The Synthesis and Thermal and Photochemical Transformations of 1,3-Dipolar Cycloadducts Derived From 1,2,3-Triazolium-N-imides.

Ciaran Byrne

DUBLIN CITY UNIVERSITY

Ollscoil Chathair Bhaile Átha Cliath

Ph.D. 1996

The Synthesis and Thermal and Photochemical Transformations of 1,3-Dipolar Cycloadducts Derived From 1,2,3-Triazolium-N-imides.

by

Ciaran Byrne

A thesis presented to Dublin City University for the degree of Doctor of Philosophy

This work has been carried out under the supervision of Dr. P. James, School of Chemical Sciences at Dublin City University.

January 1996

Declaration

I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of Ph.D. is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

Signed: Date:

TABLE OF CONTENTS

Acknowledgments

I wish to express my thanks to Dr. Paraic James for his constant interest and guidance during the execution of this work.

I would also like to thank the other members of our research group, James, Pat, Joe and Donal and all the other postgrads especially Farmer, Mark, Cormac, Shane, Jesse, Ciara, Siobhan and Orla, Karen and Miriam , and to the occupants of Loserville. Thanks also the other members of the Twighlight Zone, Dominic and John. I am also grateful to the Technical staff for their assistance and to Dr. Conor Long and the staff of the x-ray crystallography unit, Trinity College, Dublin for their work on the crystal structure determinations.

I would finally like to thank my friends and family and especially my parents, Jim and Eileen, for their continued support and encouragement, without which this work would not have been possible.

Abstract

The cycloadducts formed on addition of triazolium-1-imides to a variety of dipolarophiles were originally assigned as pyrazolotriazoles. Subsequent re-examination in the 1980's led to the discovery of a tandem cycloaddition - sigmatropic rearrangement mechanism leading to pyrrolotriazoles. These pyrrolotriazoles contain an azimine function as part of the ring system and the thermal and photochemical transformations of these compounds are of interest because of the wide structural variety found among the products.

In the current work on cycloaddition reactions leading to pyrrolotriazoles a number of side products, including triazoles and substituted anilines are identified. The acid catalyzed epimerization of the cycloadduct was also observed. A range of new cycloadducts have been synthesized.

The thermal reaction of hexahydropyrrolo[2,3-*d*]triazoles led to fragmentation to substituted triazoles. The tetrahydro-analogues, however underwent a 1,3-sigmatropic rearrangement followed by electrocyclic ring expansion to substituted 2,5-dihydro-1,2,3-triazines in high yield, and the structure was confirmed by x-ray crystallography. The importance of the unsaturation was confirmed as hexahydro derivatives were oxidized and found to produce the triazines in high yield.

The photochemical rearrangements of these species were found to depend on both the degree of unsaturation and the bridgehead substituents. For the 3a,6a-diaryl hexahydro-derivatives, irradiation led to a disrotatory ring expansion to the new 2,5,6,7-tetrahydro-1,2,3,5-tetrazocines, the structure of which was confirmed by x-ray crystallographic determination. The tetrahydro-analogues, on ring opening to 2,5-dihydro-1,2,3,5-tetrazocine underwent a transannular ring contraction followed by a 1,4-sigmatropic rearrangement to imidazo[4,5-*c*]pyrazoles. The proposed intermediacy of 2,5-dihydro-1,2,3,5-tetrazocine in the rearrangement of 3a,6a,-diaryl tetrahydropyrrolotriazoles was confirmed.

Irradiation of 3a,6a-dimethyl hexahydropyrrolo[2,3-*d*]1,2,3-triazole led to pyrrolo[3,2-*b*]indole *via* a complex series of sequential transformations. The pathway was investigated by isolation of the intermediates and was found to consist of an initial epimerization, a 1,2-phenyl migration and an eliminative rearrangement followed by 5-*exo*-trig closure to pyrrolo[3,2-*b*]indole. Two intermediates were characterized by x-ray crystallographic analyses.

Irradiation of the tetrahydro-analogues led to the formation of substituted pyrroles and azobenzene.

List of Abbreviations

AN = Acrylonitrile

BAAS = 1,2-bis(arylazo)stilbene

BPAB = 1,2-bis(phenylazo)butene

BAAC = 1,2-bis(arylazo)cyclohexene

BPAS = 1,2-bis(phenylazo)stilbene

DCM = Dichloromethane

DEAD = Diethyl Acetylene Dicarboxylate

DMF = Dimethyl Fumarate

DMAD = Dimethyl Acetylene Dicarboxylate

DMM = Dimethyl Maleate

DMSO = Dimethylsulfoxide

EA = Ethyl Acrylate

FMO = Frontier Molecular Orbital Theory.

HMO = Hückel Molecular Orbital Theory.

IR = Infra-Red

MA = Methyl Acrylate

MMA = Methyl Methacrylate

MP = Methyl Propiolate

MVK = Methyl Vinyl Ketone

NMR = Nuclear Magnetic Resonance

PIC = Phenyl Isocyanate

TLC = Thin Layer Chromatography

CHAPTER 1

Synthesis of 1,3-Dipolar Cycloadducts Derived from 1,2,3-Triazolium N-imides

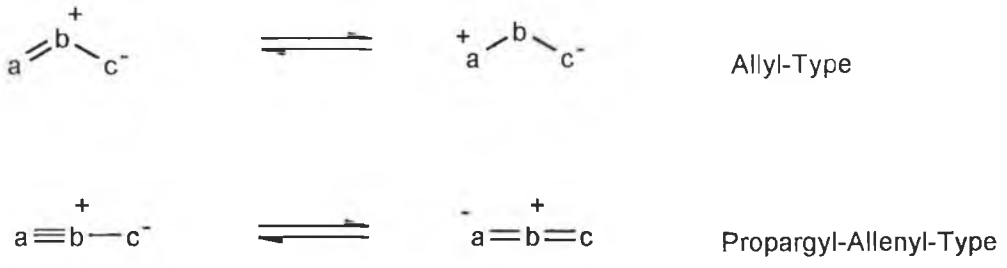
INTRODUCTION

1.1a) Introduction to 1,3-Dipolar Cycloadditions

Most of the classical methods of heterocyclic synthesis are cyclisation reactions. Cycloaddition reactions can provide routes to a wide range of heterocycles with well defined substitution patterns, in many cases with great stereochemical control. The most important types of cycloaddition are: a) 1,3-dipolar cycloadditions, b) hetero-Diels-Alder reactions, c) [2+2] cycloadditions and d) chelotropic reactions.

The concept of 1,3-dipolar cycloadditions was first suggested by Smith in 1938, even though examples were known before the turn of the century.[1,2,3] The use of these reactions was largely neglected however until the late 1950's when Huisgen was the first to recognise fully the general concept and scope of this form of cycloaddition.[4,5] Since this time many new reactions have been predicted and discovered, making this a valuable method of constructing 5-membered rings.

A 1,3-dipole a-b-c is defined as a system which contains four electrons in three parallel atomic p-orbitals, and may be represented by zwitterionic octet structures containing an allyl-anion type π-system. They contain an onium centre b, whose charge compensates the negative charge distributed in the two all octet structures over the two termini a and c (see Scheme 1.1).



Scheme 1.1 General formula for 1,3-dipoles.

Two of the four allylic π-electrons of the 1,3-dipole can be localised at the centre atom b, thereby cancelling the onium charge. Electron sextets are thus created at atoms a or c. The terminal centres can be either nucleophilic or electrophilic, and it is this ambivalence that is key to their reactivity. The 1,3-dipole may or may not contain an additional π-bond in the plane perpendicular to the allyl anion molecular orbital. The occurrence of this extra π-bond usually makes 1,3 dipoles of the propargyl-allenyl-type linear. 1,3-Dipoles of the allyl-type are bent. The centre b can be either NR or O, if we confine ourselves to second row elements, for the allyl-type and N for the propargyl-allenyl-type. Termini a and c are also somewhat restricted and again confining ourselves to second row elements C, N,and O, a total of six 1,3-dipoles of the propargyl-allenyl-type and 12 of the allyl-type are obtained. These are listed in Table 1.1. Several 1,3-dipoles containing sulphur and phosphorous are also known.

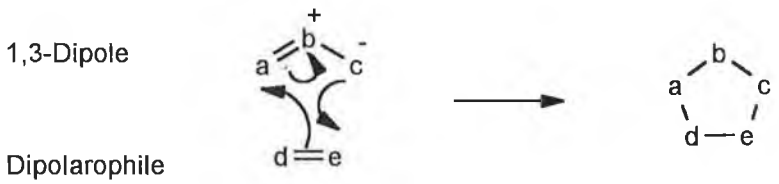
The term 1,3-dipole is often misunderstood as indicating that these compounds show high polarity. The term 1,3-dipole arose because in valence bond theory such compounds can only be described in terms of dipolar resonance contributors. They are not to be confused with zwitterions in which the positive and negative charges are localised at specific sites. In 1,3-dipoles the formal charges are interchangeable and different resonance contributors largely cancel so that such molecules generally have low dipole moments. For symmetrical 1,3-dipoles it is impossible to assign a nucleophilic or electrophilic end to the dipole. However, for unsymmetrical dipoles the contribution of some resonance structures carry different weightings in the overall description of the species, *e.g.* for azomethine imines the major resonance contributor has the negative charge on the more electronegative nitrogen terminus. The electronic asymmetry also arises naturally from a molecular orbital description.

Compounds which react with 1,3-dipoles in cycloaddition reactions are commonly called dipolarophiles. They contain unsaturated functional groups such as C≡C, C=C, C≡N, C=N, C=O, C=S, -N=N-, -N=O, -N=S= (*e.g.* in Ph-N=S=O).

Table 1.1 Classification of 1,3-Dipoles

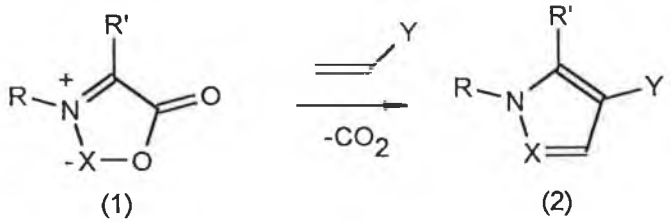
Propargyl-Allenyl Type		
Nitrilium Betaines		
$RC{\equiv}N^{+}\text{-}CR_2^{-}$	$RC^{-}{=}N^{+}{=}CR_2$	Nitrile ylides
$RC{\equiv}N^{+}\text{-}NR^{-}$	$RC^{-}{=}N^{+}{=}NR$	Nitrile imines
$RC{\equiv}N^{+}O^{-}$	$RC^{-}{=}N^{+}{=}O$	Nitrile oxides
Diazonium Betaines		
$N{\equiv}N^{+}\text{-}CR_2^{-}$	$N^{-}{=}N^{+}{=}CR_2$	Diazoalkanes
$N{\equiv}N^{+}\text{-}NR^{-}$	$N^{-}{=}N^{+}{=}NR$	Azides
$N{\equiv}N^{+}\text{-}O^{-}$	$N^{-}{=}N^{+}{=}O$	Nitrous oxide
Allyl Type		
Nitrogen Function as Middle Centre		
$R_2C{=}N^{+}(R)\text{-}C^{-}R_2$	$R_2C^{-}\text{-}N^{+}(R){=}CR_2$	Azomethine Ylides
$R_2C{=}N^{+}(R)\text{-}NR^{-}$	$R_2C^{-}\text{-}N^{+}(R){=}NR$	Azomethine Imines
$R_2C{=}N^{+}(R)\text{-}O^{-}$	$R_2C^{-}\text{-}N^{+}(R){=}O$	Nitrones
$RN{=}N^{+}(R)\text{-}NR^{-}$	$RN^{-}\text{-}N^{+}(R){=}NR$	Azimines
$RN{=}N^{+}(R)\text{-}O^{-}$	$RN^{-}\text{-}N^{+}(R){=}O$	Azoxy Compounds
$O{=}N^{+}(R)\text{-}O^{-}$	$O^{-}\text{-}N^{+}(R){=}O$	Nitro Compounds
Oxygen Atom as Middle Centre		
$R_2C{=}O^{+}\text{-}C^{-}R_2$	$R_2C^{-}\text{-}O^{+}{=}CR_2$	Carbonyl Ylides
$R^2C{=}O^{+}\text{-}N^{-}R$	$R_2C^{-}\text{-}O^{+}{=}NR$	Carbonyl Imines
$R_2C{=}O^{+}\text{-}O^{-}$	$R_2C^{-}\text{-}O^{+}{=}O$	Carbonyl Oxides
$RN{=}O^{+}\text{-}N^{-}R$	$RN^{-}\text{-}O^{+}{=}NR$	Nitrosimines
$RN{=}O^{+}\text{-}O^{-}$	$RN^{-}\text{-}O^{+}{=}O$	Nitrosoxides
$O{=}O^{+}\text{-}O^{-}$	$O^{-}\text{-}O^{+}{=}O$	Ozone

The mechanism of 1,3-dipolar cycloaddition has been systematically studied. (Scheme 1.2)[6,7]



Scheme 1.2. General mechanism for 1,3-dipolar cycloadditions.

In most cases the evidence suggests a concerted reaction in line with orbital symmetry considerations. The rates of additions are largely independent of solvent polarity. The reactions have large negative entropy values as would be expected, and only moderate enthalpy values. High stereoselectivity in addition to pairs of *cis* and *trans* substituted dipolarophiles is also observed. Sydnones and oxazolones **(1)**, which contain azomethine imine and azomethine ylide dipolar functions respectively as part of a heterocyclic ring were found to undergo cycloaddition with suitable dipolarophiles. (Scheme 1.3)



Scheme 1.3. 1,3-Dipolar cycloaddition of sydnones (X=N) (masked azomethine imine) and oxazolines (X=CR) (masked azomethine ylide).

These planar heterocycles can only be approached from above or below the reaction plane and this led to the suggestion that the dipole and dipolarophile approach each other in parallel planes, to form an array called the *two-plane orientation complex*. (See Fig. 1.1)[8]

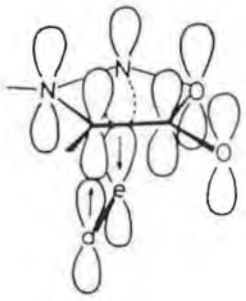


Fig.1.1 Two-Plane Orientation Complex for sydnone and a dipolarophile.

The formation of this array precedes the concerted bond making and bond breaking. The complex possesses the full allyl anion resonance of the 1,3-dipole. In the ensuing rehybridisation process the allyl anion MO's and the π MO of the dipolarophile are converted to two σ- and one n-orbital.

The terminal bonds of azomethine imine are *ca.* 2.3Å apart. The π-orbitals at the termini must bend by a slight twist about the C-N and N-N bond axes in order to make contact with the π orbitals of the dipolarophile, which themselves bend outward. Gradual rehybridization converts the two terminal *p*-orbitals of the allyl system as well as the *p*-orbitals of the dipolarophile into sp^3 orbitals, which form new σ-bonds. This is accompanied by an uplifting and pyramidalizing of the middle nitrogen; its former *p*-orbital contains the unshared pair after the process is completed.[8,9] (Figure 1.2)

(a) (b)

Fig.1.2 Front and side views [(a) and (b) respectively] of a possible transition state.

In the mostly linear dipoles of the propargyl-allenyl type, the distance between the terminal centres is greater than in 1,3-dipoles of the allyl type. Bending must occur early on in the reaction in order to allow σ-overlap of the π-orbitals of the reactants. 1,3-Dipoles of the propargyl-allenyl type in the two plane orientation complex undergo initially an in-plane bending with subsequent uplifting of the middle group b. The *two-plane orientation complex* accounts for a large entropy change but little enthalpy change in the cycloaddition process.

Until the application of FMO theory to 1,3-dipolar cycloadditions there was no satisfactory explanation for the reactivity and regioselectivity of 1,3-dipolar cycloadditions. This had led to the proposal of an alternative mechanism involving the formation of an intermediate singlet diradical which rapidly closes stereospecifically or reverts to the reactants if not suitably oriented.[10] This proved unsatisfactory and FMO theory now offers the most satisfactory picture of the process.[11]

1,3-Dipolar cycloadditions are concerted processes that proceed through unsymmetrical transition states in which the formation of one of the new σ-bonds is more advanced than the other. The reactions may be represented as going through a transition state in which the 4π-electron system of the dipole interacts with the 2π-electron system of the dipolarophile. This is a "thermally allowed" process on the basis of the Woodward-Hoffmann rules for pericyclic reactions.[12] The reaction rates are only slightly influenced by the polarity of the solvent, *i.e.* there is little change in polarity between reactants and the transition state. The lack of solvent effects and the instability of many 1,3-dipolar species impose practical limitations on the choice of conditions to bring about 1,3-dipolar cycloadditions. The reactivity of 1,3-dipoles towards different dipolarophiles often varies considerably. FMO theory provides a means of accounting for these variations and is also useful for predicting the reactivity of new dipolarophiles. Reaction occurs if there is a favourable interaction between a filled π-orbital of one of the reactants and an empty π*-orbital of the other. The orbitals must be in the correct phase to interact, the interaction must be sterically feasible and the closer in energy the orbitals are, the stronger the

interaction. The interactions are therefore dominated by the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the reactants, the so-called "frontier orbitals". It is important to note that in a number of cases the important unoccupied orbital for cycloaddition is not always the LUMO, as the LUMO may be oriented at right angles to the reaction plane. The LUMO's of linear dipoles (propargyl-allenyl type) have a node through one of the terminal atoms, and therefore cannot participate in 1,3-dipolar cycloadditions. In these cases the next lowest unoccupied orbital (NLUMO) is used.[13]

Orbital energies are determined both by the nature of the skeletal atoms in the two components and by their substituents. The dipole HOMO and LUMO energy levels and coefficients have been estimated by Houk *et al.* for a selection of common dipoles, and are shown in Table 1.2.[14,15] The rate of 1,3-dipolar addition is related to the HOMO-LUMO energy separation of the reactants. The dipole HOMO (Type I), the dipole LUMO (Type III), or both (Type II) may be involved in the dominant interaction, depending on the relative energies of the frontier orbitals.[16-18] Substituents which raise the dipole HOMO energies [electron releasing (inductive (R) and resonance (x)) and conjugating (c)] and which lower dipolarophile LUMO energies (conjugating (c)and electron withdrawing (z)) will accelerate Type I reactions, but slow down Type III reactions. Substituents which lower dipole LUMO (c,z) and raise dipolarophile HOMO energies (x,R,c) will accelerate Type III reactions. For systems of Type II, substituents which increase either frontier orbital interaction will increase the rate of reaction.

In considering this approach to reactivity the coulombic contribution to the overall energy of interaction has been neglected. Due to the excess of negative charge on the terminal atoms, there is a coulombic bias favouring reactions with electron deficient dipolarophiles. There is a tendency in FMO calculations to underestimate the reactivity for dipole HOMO controlled reactions with electron deficient dipolarophiles.[8] Another factor not dealt with in this approach is the stability of the reactants and products. The loss of aromaticity in

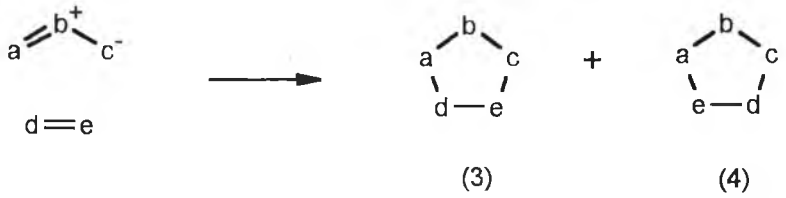
the course of the cycloaddition has a marked effect on the reaction rate. Cycloadditions with *e.g.* benzene as dipolarophile are not observed.

Table 1.2 Frontier Orbital Energies of 1,3-dipoles.

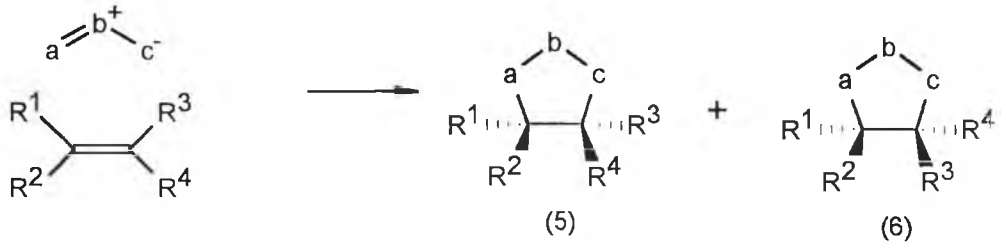
Dipole	HOMO energy (eV)	LUMO energy (eV)
$HC{\equiv}N^{+}\text{-}CH_2^{-}$	-7.7	0.9
$PhC{\equiv}N^{+}\text{-}CH_2^{-}$	-6.4	0.6
$HC{\equiv}N^{+}\text{-}NH^{-}$	-9.2	0.1
$PhC{\equiv}N^{+}\text{-}N^{-}(Ph)$	-7.5	-0.5
$HC{\equiv}N^{+}\text{-}O^{-}$	-11.0	-0.5
$PhC{\equiv}N^{+}\text{-}O^{-}$	-10.0	-1.0
$N{\equiv}N^{+}\text{-}CH_2^{-}$	-9.0	1.8
$N{\equiv}N^{+}\text{-}NH^{-}$	-11.5	0.1
$N{\equiv}N^{+}\text{-}N^{-}(Ph)$	-9.5	-0.2
$N{\equiv}N^{+}\text{-}O^{-}$	-12.9	-1.1
$CH_2{=}NH^{+}\text{-}CH_2^{-}$	-6.9	1.4
$ECH{=}N^{+}(Ar)\text{-}CH^{-}(E)$[a]	-7.7	-0.6
$CH_2{=}NH^{+}NH^{-}$	-8.6	-0.3
$PhCH{=}NH^{+}\text{-}N^{-}(Ph)$	-5.6	-1.4
$CH_2{=}NH^{+}\text{-}N^{-}(COR)$	-9.0	-0.4
$CH_2{=}NH^{+}\text{-}O^{-}$	-9.7	-0.5
$PhCH{=}NH^{+}\text{-}O^{-}$	-8.0	-0.4
$CH_2{=}O^{+}\text{-}CH_2^{-}$	-7.1	0.4
$(CN)_2C{=}O^{+}\text{-}C(CN)_2$	-9.0	-1.1
$O{=}O^{+}\text{-}O^{-}$	-13.5	-2.2

[a] $E{=}CO_2R$

Many 1,3 dipolar cycloadditions can in principle give mixtures of isomers but most such reactions show considerable selectivity, giving predominately or exclusively one isomer. The formation of possible regioisomers and stereoisomers is shown in Schemes 1.4a-b.

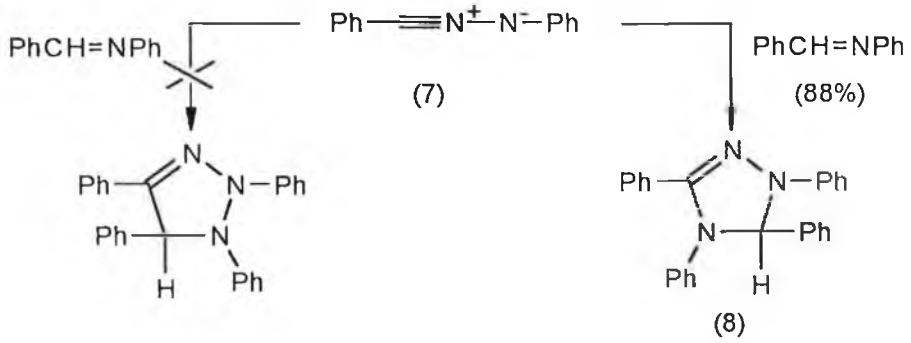


Scheme 1.4a. Formation of regioisomers on cycloaddition.



Scheme 1.4b. Formation of diastereoisomers on cycloaddition.

Regioselectivity is dominated by electronic effects with steric effects also exerting some influence. For additions to dipolarophiles containing heteroatoms, the direction of attack is dominated by the principle of maximum gain in σ-bond energy.[6] For example in the addition of diphenyl(nitrile imine) **(7)** to azomethines, a difference in σ-bond energy of the theoretical products of 24 kcal is sufficient to direct the reaction entirely toward the 1,2,4-triazolines **(8)** (Scheme 1.5). The energy of the new σ-bonds becomes only partly available in the transition state.



Scheme 1.5. Principle of maximum gain in σ-bond energy in 1,3-dipolar cycloadditions.

For alkene or alkyne dipolarophiles the gain in σ-bond energy is equal in both directions. Perturbation molecular orbital theory (PMO) predicts that the favourable direction of combination is that in which the two terminal atoms with the larger orbital coefficients interact. A list of orbital coefficients as calculated by Houk *et al.* is given in Table 1.3.[14,15]

Table 1.3. Orbital Coefficients $[(c\beta)^2/15]$ for terminal atoms[a] of some 1,3-dipoles.

Dipole	HOMO		LUMO	
HCN^+-CH_2^-	1.07	1.50	0.69	0.64
HCN^+-NH^-	0.90	1.45	0.92	0.36
HCN^+-O^-	0.81	1.24	1.18	0.17
NN^+-CH_2^-	0.85	1.57	0.56	0.66
NN^+-NH^-	0.72	1.55	0.76	0.37
NN^+-O^-	0.67	1.33	0.96	0.19
CH_2=NH^+-CH_2^-	1.28	1.28	0.73	0.73
CH_2=NH^+-NH^-	1.15	1.24	0.87	0.49
CH_2=NH^+-O^-	1.11	1.06	0.98	0.32
CH_2=O^+-CH_2^-	1.29	1.29	0.82	0.82

[a] Values are given in the same order as the atoms appear in the left hand column, *e.g.*for the HOMO of CH_2=NH^+-O^- the values are 1.11 on carbon and 1.06 on oxygen.

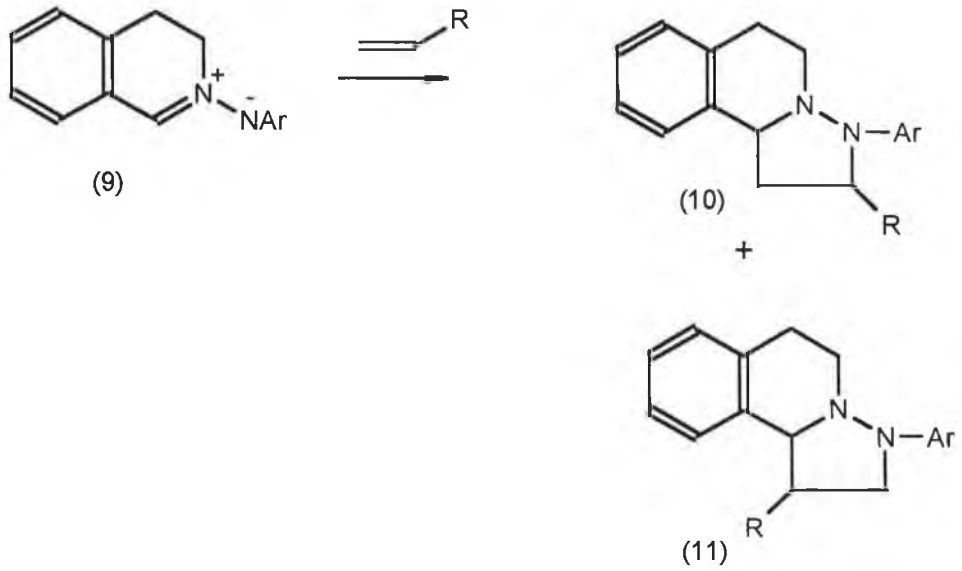
The molecular orbital coefficients of alkenes bearing neutral conjugating substituents are unequal in both the HOMO and LUMO. The larger coefficient is at the carbon remote from the substituent in both frontier orbitals. In the case of alkenes bearing an inductive electron donating substituent, the electronegativity of the carbon to which it is attached (C_α) is lowered and therefore so also is the coefficient at this point in the HOMO. The coefficient at C_α in the LUMO is increased. For mesomeric electron donating

substituents, C_α will have a reduced coefficient, while the LUMO will have a larger coefficient. For electron deficient alkenes, purely inductive electron withdrawing groups increase the coefficient on the substituent bearing carbon (C_α) in the HOMO but decrease it in the LUMO. For conjugative electron withdrawing groups, as is generally the case, the coefficient is diminished at C_α in both HOMO and LUMO. In the LUMO these trends are additive and the coefficient at C_α is much smaller than at the remote carbon (C_β). For the HOMO the trends are opposed. The coefficient has been calculated to be slightly smaller at C_α.

For polysubstituted alkenes the effects appear to be additive. The orbital coefficients for alkynes can be rationalised in much the same way. The main difference being that only one of the orthogonal π orbitals of the triple bond can conjugate with the substituent. The other is only affected inductively. For heteromultiple bonds the electron density is greater at the more electronegative end. The coefficient for the HOMO will therefore be greater at this site, while the coefficient for the LUMO is diminished.

The balance between dipole HOMO and dipole LUMO control is of great importance for the regioselectivity. The dominant frontier orbital interaction must first be identified and the orbital coefficients are then matched to indicate the direction of the addition. When the difference in frontier orbital energies for the HOMO dipole and the LUMO dipole interactions with the dipolarophile is small a mixture of products is expected. For example in the addition of azomethine imine to conjugated dipolarophiles the FMO energies are such that a mixture of the two possible regioisomers **(10)** and **(11)** is produced (See Scheme 1.6).

For addition to electron deficient alkenes, *e.g.* acrylonitrile, dipole HOMO dominates and only one regioisomer is observed **(11, R=CN)**. For addition to heteromultiple bonds the HOMO and LUMO energies approximate electron deficient alkenes.[9]

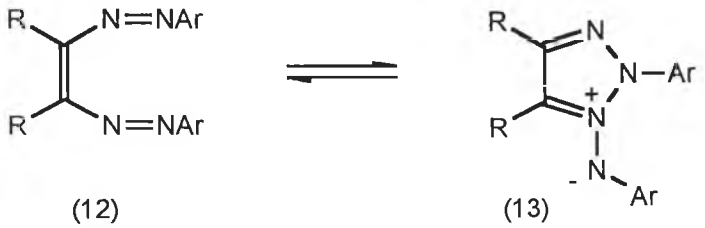


Scheme 1.6 Formation of possible regioisomers on cycloaddition of diaryl azomethine imine with a variety of dipolarophiles.

When two chiral centres, one from each reactant, are formed on cycloaddition, diastereomeric adducts are formed from two different two-plane orientation complexes. The ratio of the two diastereoisomers depends on the difference in free energy of the two transition states. Forces influencing the direction of attack include repulsive interactions due to steric hindrance and favourable π-overlap of unsaturated substituents (secondary orbital interactions). The latter is often more important and the thermodynamically less favoured product is often formed preferentially.[8] There is also some evidence to suggest that secondary orbital interactions influence the regioselectivity of the addition when the orbital coefficients on the termini of the reactants are similar. For an allyl type dipole the central lobe of the dipole LUMO can overlap with the orbitals of a conjugating substituent in the dipolarophile in a bonding fashion, giving rise to a favourable secondary interaction for the *endo* transition state. This is termed the *endo*-effect, but is only of importance for dipole LUMO controlled additions, since in the dipole HOMO there is a node or near node at the central atom and little or no interaction is expected.

1.1b) 1,3-Dipolar Cycloadditions of 1,2,3-Triazolium-1-(N-aryl)imides.

Our present work stems from the early reports of George and co-workers on the oxidation products of α-diketone-bisarylhydrazones.[19] Considerable controversy existed in the literature at the time, concerning the structure of the oxidation products of bishydrazones. In solution these *cis*-bis(areneazo)olefins **(12)** were found to undergo a remarkably facile *E*-*Z*-isomerisation followed by an electrocyclization to give the cyclic 1,2,3-triazolium imide form **(13)** (Scheme 1.7).



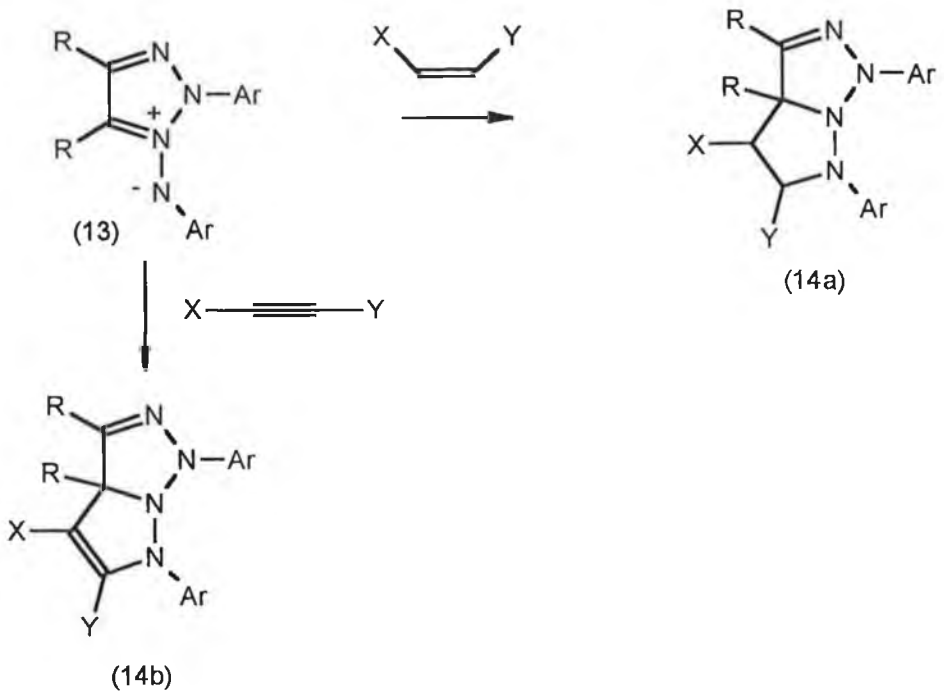
(12) (13)

Scheme 1.7 Dynamic equilibrium between *cis*-1,2-bis(arylazo)alkene and substituted 2-aryl-1,2,3-triazolium-1-arylimide.

Both the cyclic and the open chain forms have been directly detected in dynamic equilibrium by variable temperature ^{1}H nmr spectroscopy for bis(areneazo)cycloalkenes.[20,21] The dominant structural form depends on a number of factors including the aryl substituent and the size of the cycloalkyl ring.

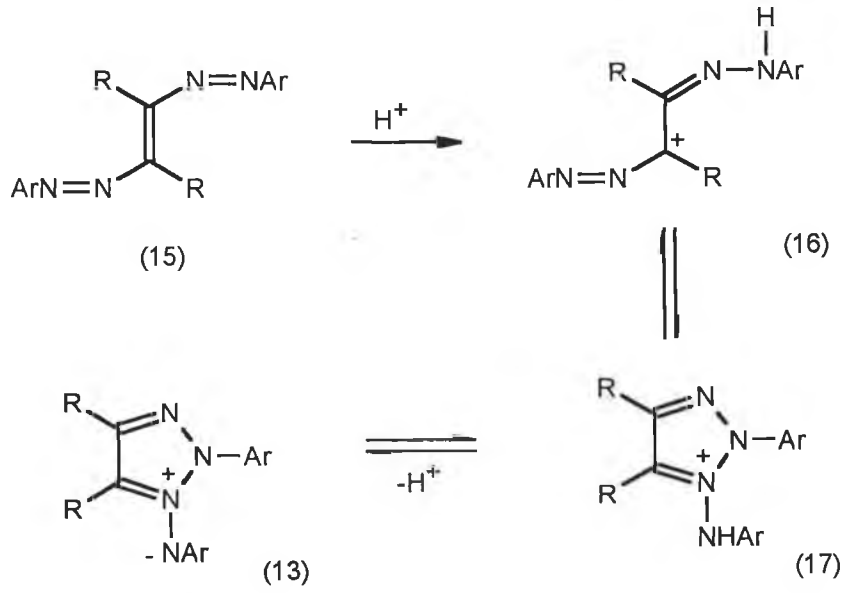
The mesoionic form **(13)** is a reactive 1,3-dipole of the azomethine imine type, and dominates the reactivity of these systems. This system extends the range of 1,3-dipole involving azole rings.[22] In 1971 George and co-workers described the first cycloadditions to be carried out with the mesoionic 1-phenylimino-2,4,5-triphenyl-1,2,3-triazole system **(13, R=Ar=Ph)**.[23] (See Scheme 1.8).

Further examples of cycloadditions subsequently appeared, all of which were generated from BPAS **(12, R=Ph)**.[24] In 1974 the first example of BPAB **(15)** undergoing cycloadditions of this type was reported.[23]



Scheme 1.8. Cycloaddition of triazolium-N-imide, as proposed by George and co-workers.[23]

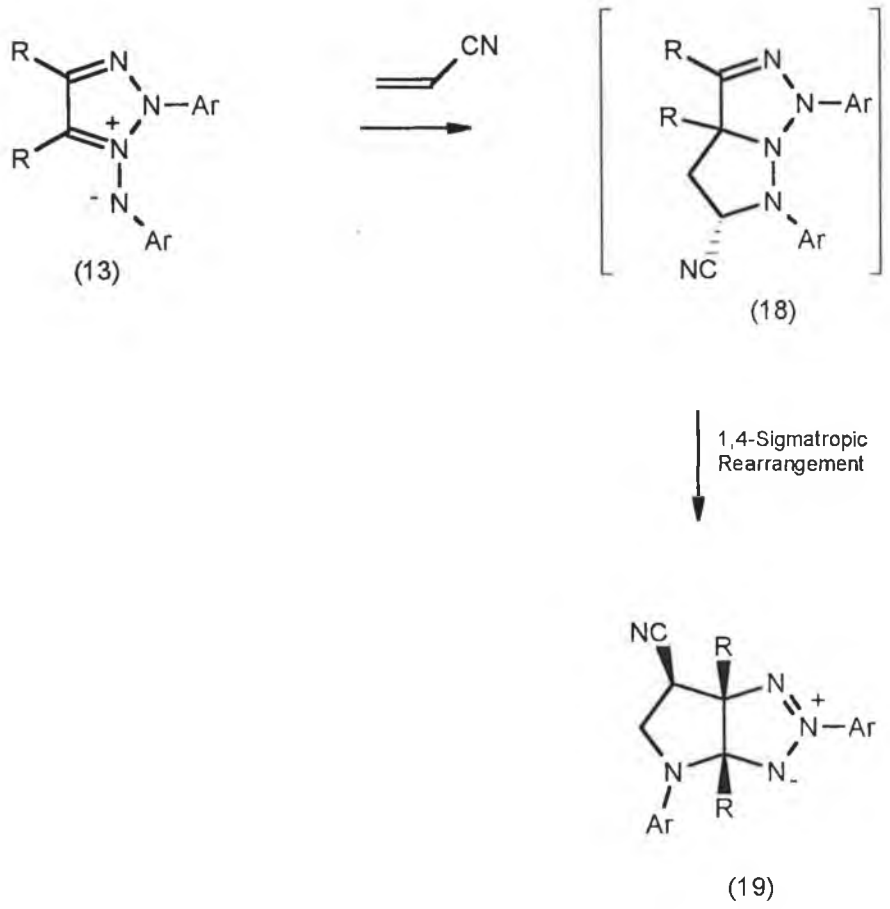
BPAB **(15)**, having a *trans* geometry across the C=C double bond, is likely to have a high activation energy towards isomerisation to the *cis* form and cycloadditions with dienophiles under mild conditions were not reported. However, under acid catalysed conditions, isomerisation to the mesoionic form **(13, R=Me)** was seen to take place and cycloadditions characteristic of this system were observed.[25] (See Scheme 1.9).



Scheme 1.9 Acid catalysed isomerization of 1,2-bis(arylazo)butene.

In 1983 Butler *et al.* examined the cycloaddition of *cis*-1,2-bis(areneazo)cyclohexene (BPAC) with acrylonitrile.[26] The product isolated was not the expected substituted pyrazolino[2,3-*c*]-1,2,3-triazole **(18)**, but rather 6-*exo*-cyano-hexahydropyrrolo[2,3-*d*]-1,2,3-triazole **(19)**. (See Scheme 1.10) ^{13}C nmr analysis of the product indicated the presence of two bridgehead carbons, characteristic of the rearranged cycloadduct. The structure was confirmed by X-ray analysis.[26]

The mechanism postulated involved the initial cycloaddition to produce the pyrazolino[2,3-*c*]triazole **(18)** as intermediate, which underwent a tandem 1,4-sigmatropic shift to produce the isolated product **(19)**. Attempts to trap the intermediate by carrying out the reaction at low temperatures failed. The driving force for the sigmatropic rearrangement appeared to be the replacement of a N-N bond with a C-N bond. A feature of the product was the azimine moiety of the ring system, having equivalent N-N bond lengths for this unit. The N-N bond lengths reported (1.299 and 1.309Å) were, as expected for the acrylonitrile cycloadduct, intermediate between an N-N single bond (1.46Å) and an N=N double bond (1.25Å).

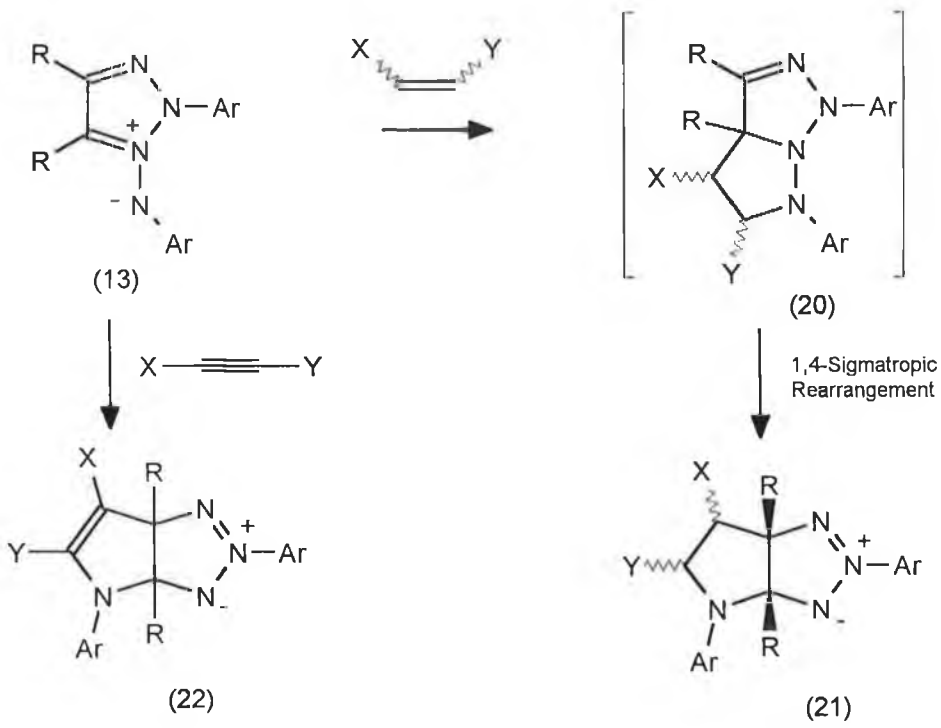


Scheme 1.10 Cycloaddition and tandem rearrangement of triazolium-N-arylimide and acrylonitrile. ($R=R=(CH_2)_4$)

Another feature of the ring system was the orientation of the cyano substituent. The nitrogen end of the dipole attacked the carbon β-to the cyano-group. The cyano group in the product has a stereospecific *exo*-orientation. An initial *endo*-addition of the dienophile with a subsequent rapid sigmatropic migration to yield the *exo*-orientation was postulated. The *endo*-orientation of the cycloaddition could be due to favourable secondary orbital interactions, or to favourable alignment of the dipoles in the transition state.

In light of this work, a re-examination of the previously reported cycloadducts of bis(areneazo)alkenes **(12)** was carried out. It was found that for all of the systems reassessed, the products showed the two saturated bridgehead carbons characteristic of

the substituted pyrrolo[2,3-*d*]triazole **(19)**.[26,27] It can be seen from Scheme 1.11 that there are four types of adduct. Type A contains methyl substituents at positions 3a and 6a and is saturated between C-5 and C-6. Type A is the dihydro-analogue of Type B which contains a double bond at between C-5 and C-6. Types C and D are the 3a, 6a-diaryl analogues of Types A and B respectively.

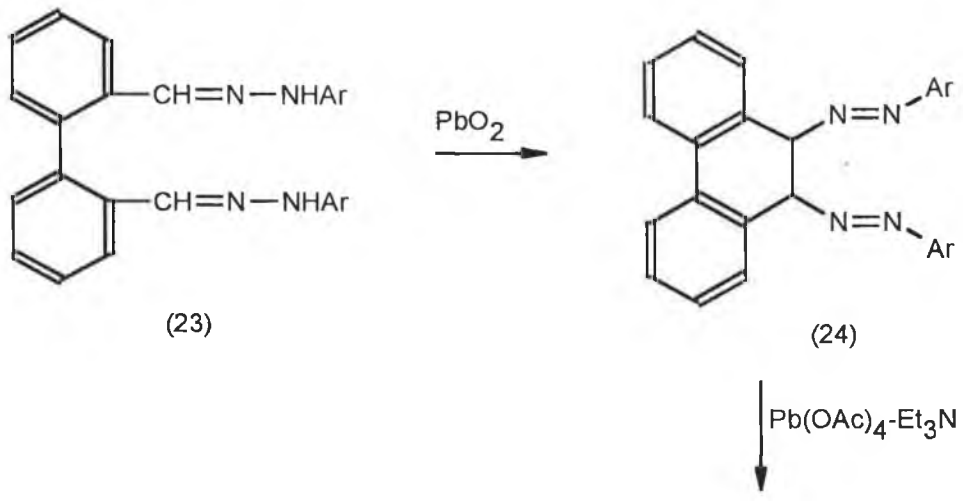


Scheme 1.11 General scope of the cycloaddition / sigmatropic rearrangement with vinylic and acetylenic dipolarophiles resulting in adducts of Type A-D. Type A **(21, R=Me)**, Type B **(22, R=Me)**, Type C **(21, R=Ar)** Type D **(22, R=Ar)**.

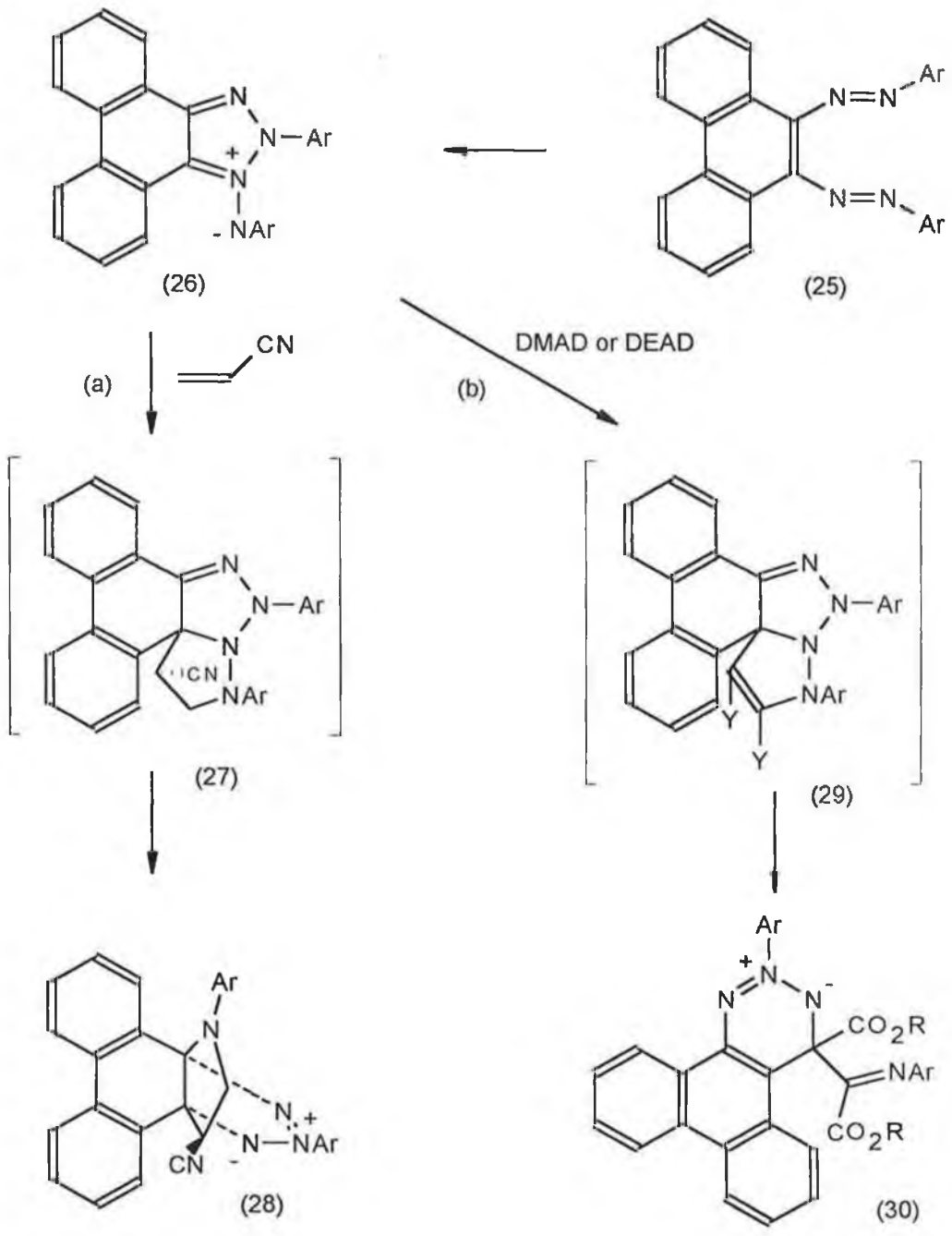
In a kinetic study it was found that the reaction rate was independent of solvent used, consistent with a concerted mechanism.[28] Hammett plots for the influence of aromatic substituents at the carbon terminus indicated a dipole HOMO controlled reaction, *i.e.* a Type I dipole.[18] Substituents at the nitrogen terminus of the dipole gave an inverted V-

shaped Hammett plot, indicating that all substituents inhibit the reaction with respect to hydrogen. Pure second order rates were observed in all cases. Arrhenius data gave a high negative entropy for the reactions which is consistent with a concerted cycloaddition process (due to the increased order in the transition state). ΔE values, calculated using HMO perturbation theory, for the gain of the transition state energy for bond formation between dipole termini a and c with the dipolarophile atoms d and e, agree with the observed regioselectivity.[28]

In 1991 Butler *et al.*, reported the cycloadditions of 1,3-dipoles derived from 2,2'-diphenyldialdehyde bisarylhydrazones **(23)**.[29] The reaction involved a similar cycloaddition and tandem 1,4-sigmatropic shift to that described in Scheme 1.11. For vinylic dipolarophiles the product isolated was the new phenanthrene azopropellanes **(28)** (Scheme 1.12a). For acetylenic dipolarophiles a further rearrangement occurred to yield the triazaphenylenes **(30)** (Scheme 1.12b), necessitated by the preservation of the aromatic phenanthrene moiety. The proposed mechanism involves a 1,2-shift in the initial adduct **(29)**.

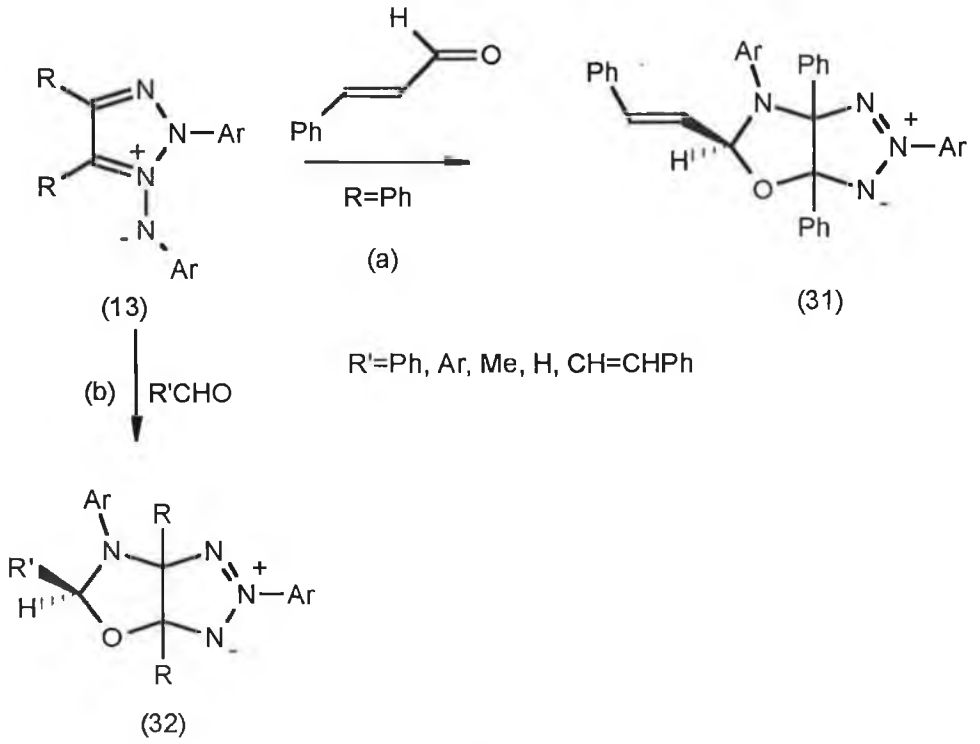


(23) (24)



Scheme 1.12 Cycloaddition of 1,3-dipoles derived from 2,2-diphenyldialdehyde bisarylhydrazones, with (a) vinylic and (b) acetylenic dipolarophiles.

The cycloaddition of **(13)** with *trans*-cinnamaldehyde did not give the expected cycloadducts *via* addition across the C=C bond. Instead it yielded oxazolo[4,5-*d*]-1,2,3-triazole derivatives **(31)** (Scheme.1.13).[30]

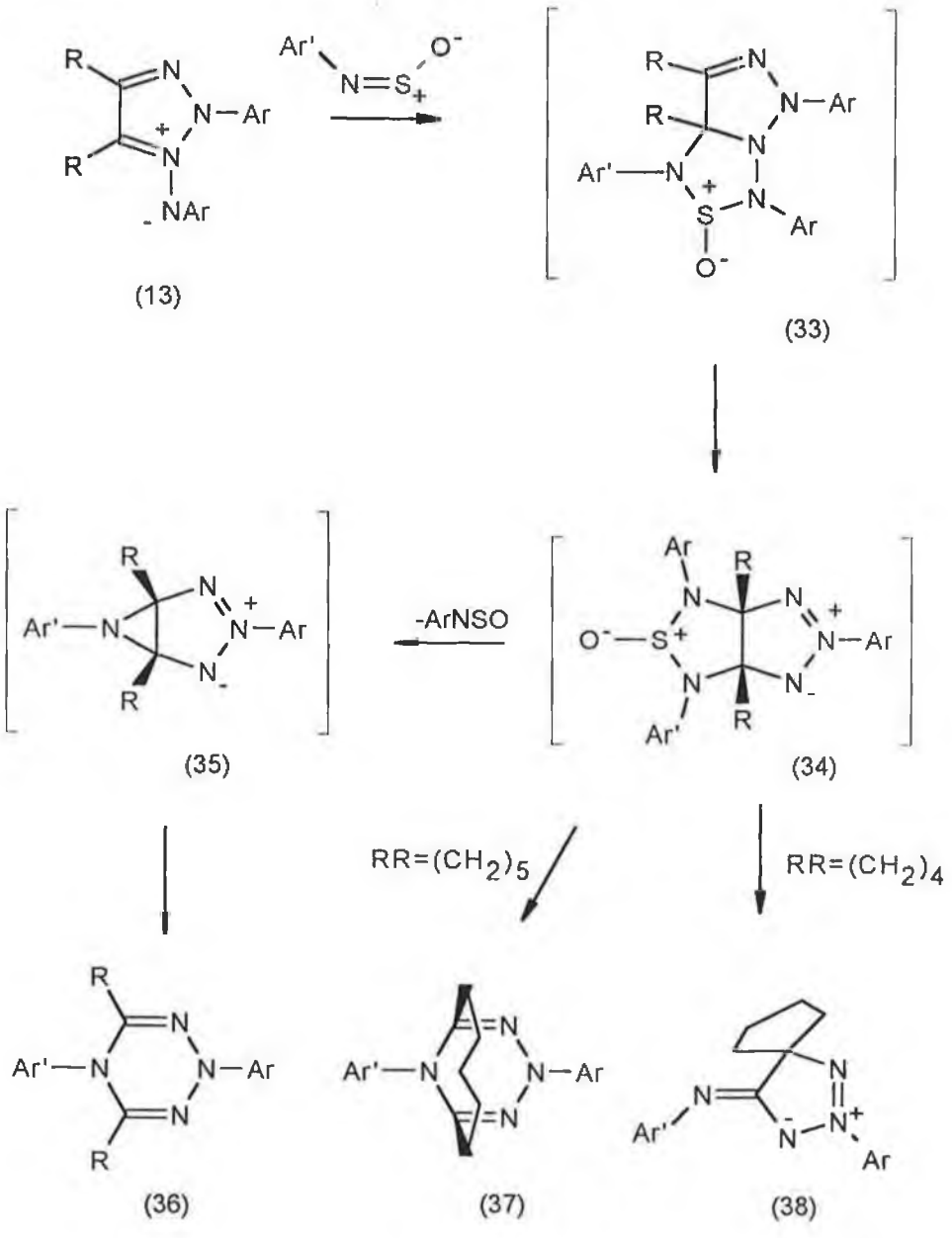


Scheme 1.13. Cycloaddition products of **(13)** with a variety of aldehydes.

Again a tandem concerted 1,3-dipolar cycloaddition and 1,4-sigmatropic shift has been proposed. Only isomers with the styrenyl group in an *exo*-orientation were isolated.[30,31] The scope of this reaction was later extended to include a variety of aldehydes to give cycloadducts **(32)**.[32] (Scheme 1.13b).

Cycloadducts formed from the treatment of **(13)** with aryl-N-sulphinylamines have been reported as intermediates in a fragmentation, ring expansion to yield 1,2,3,5-tetrazines **(36)** and **(37)** and 1,2,3-triazaspiro[4,4]nonanes **(38)**.[31,33] (Scheme.1.14).
One of the cycloadducts was isolated in 10% yield **(34, R=Ar=Ph, Ar'=*p*-Br-C_6H_4)**. A molecule of N-sulphinylamine was lost in either of two ways when the aryl substituents

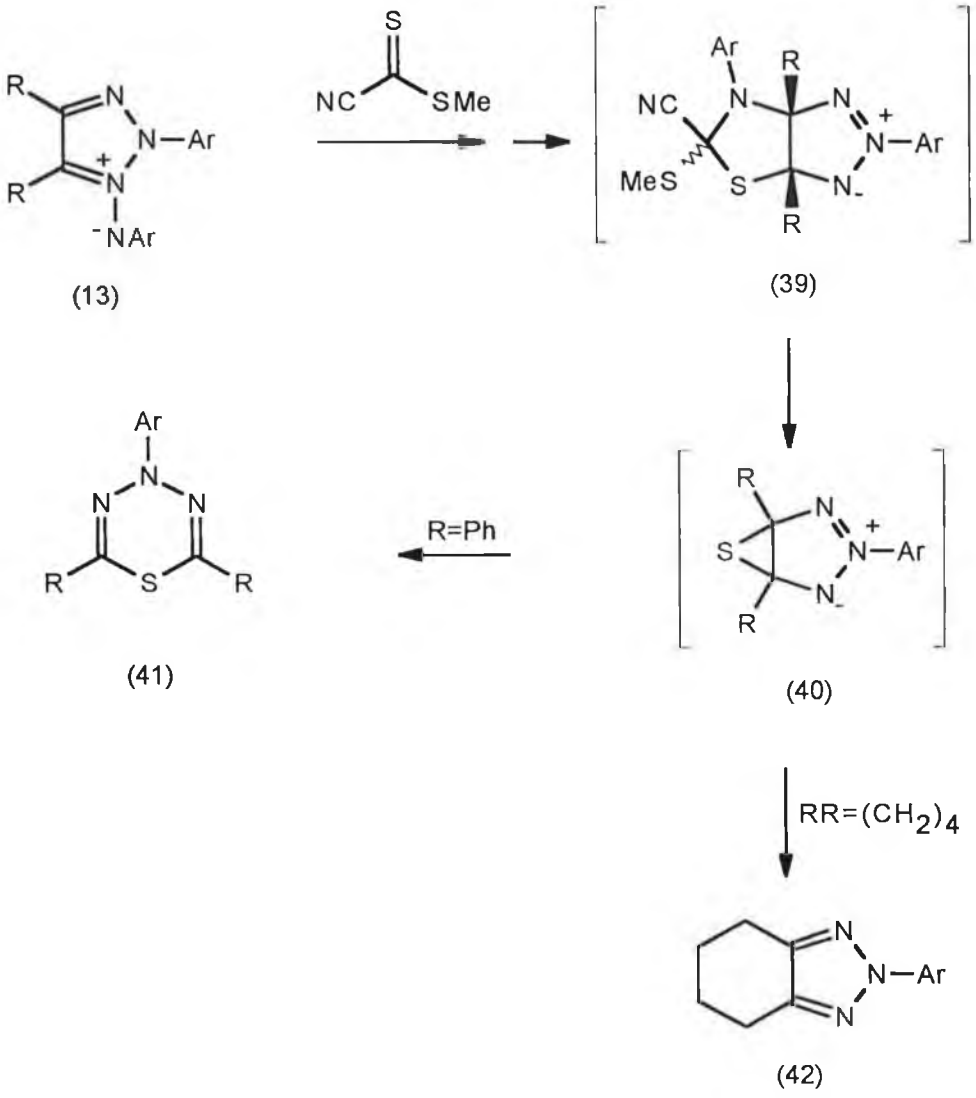
differed. Either the original sulphinylamine is regenerated or a sulphinylamine containing the N-aryl moiety of the triazolium-N-imide is generated. It was found that PhNSO was lost preferentially.



Scheme 1.14 Reaction schemes for addition of N-aryl sulphinylamines to 1,3-dipoles.

The remaining intermediate **(35)** may then undergo a disrotatory outward electrocyclic ring expansion to the substituted 2,5-dihydro-1,2,3,5-tetrazine **(36, R=Ar, R=R=$(CH_2)_n$ [n≥5])**. For derivatives of 1,2-bis(arylazo)cyclobutene **(13, RR=$(CH_2)_4$)** and smaller cycloalkenes the disrotatory outward process from the fused aziridine intermediate **(35)** was inhibited. The intermediate instead reacted *via* a ring opening and a 1,2-shift involving ring contraction of the cycloalkane ring to the substituted 4-arylimino-1,2,3-triazaspiro[4,4]non-1-ene **(38)**.

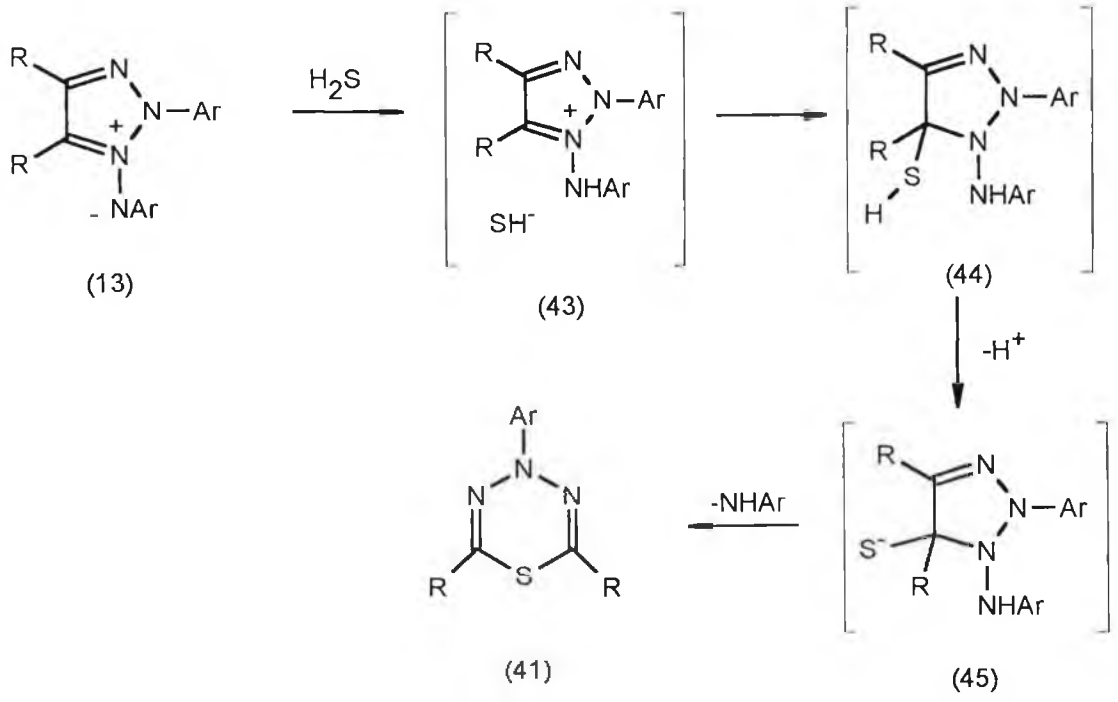
Cycloadditions of triazolium-N-imides **(13)** with methyl cyanodithioformate led to 1,3,4,5-thiatriazines **(41)**.[31,34] (Scheme 1.15).



Scheme 1.15. Cycloaddition of **(13)** with methyl cyanodithioformate.

The mechanism postulates the intermediacy of the cycloadduct **(39)**. This labile intermediate then fragmented to a fused thiirane **(40)**, which underwent a disrotatory outward electrocyclic ring expansion to the thiatriazine **(41)**. Attempts to block this ring expansion by linking the bridgehead substituents (RR=$(CH_2)_4$ resulted in 4,5,6,7-tetrahydro-2-aryl-2H-benzo[*d*]triazole **(42)**.

It was later reported that the same thiatriazine ring system **(41)** could be obtained by the attack of hydrogen sulphide on triazolium-N-imide.[35] (Scheme 1.16).



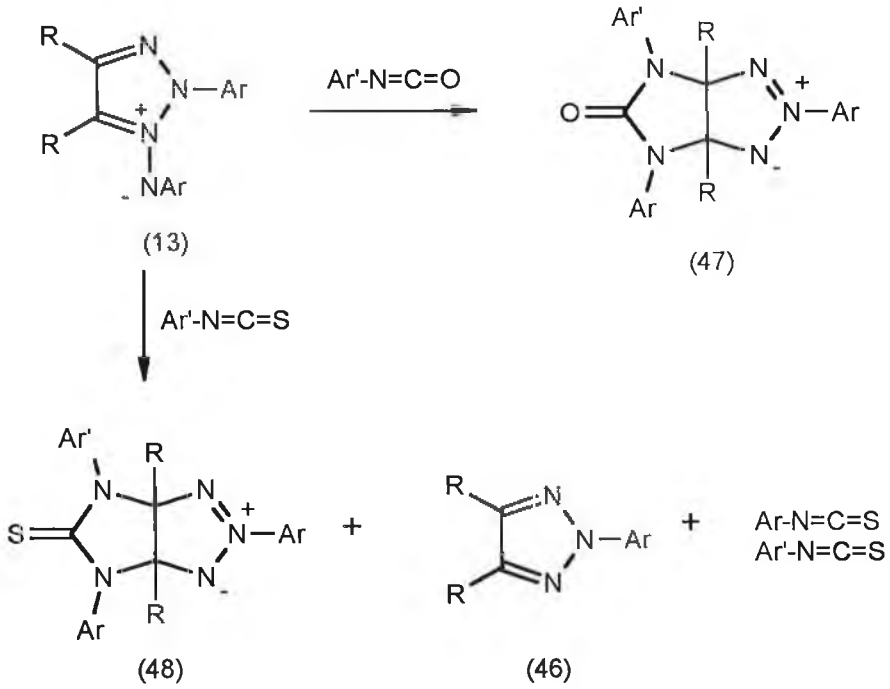
Scheme 1.16 Formation of thiatriazine by attack of **(13)** by hydrogen sulphide.

This lends support for the intermediacy of a species **(45)** in the cycloaddition-fragmentation of Scheme 1.15.[22] Treatment of these thiatriazine rings **(41)** with *m*-chloroperbenzoic acid gave the corresponding substituted-1,2,3-triazole **(46)** in high yield. (Scheme 1.17)

(41) (46)

Scheme 1.17. Ring contraction of thiatriazine **(41)** with *m*-Cl-perbenzoic acid.

Substituted imidazo[4,5-*d*]-1,2,3-triazole **(47)** and **(48)** systems have been reported using triazolium-N-imides **(13)** as 1,3-dipoles, with aryl isocyanates and isothiocyanates as dipolarophiles.[36] (Scheme 1.18).



Scheme 1.18 Reaction of **(13)** with aryl isocyanates and aryl isothiocyanates.

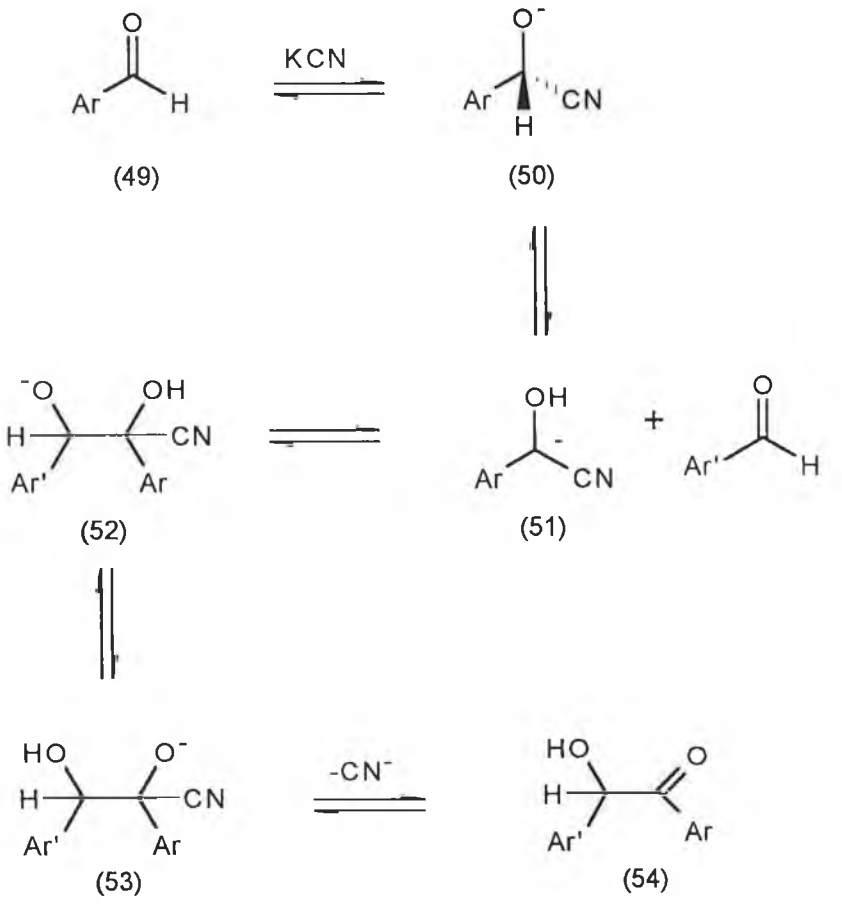
These systems were found to be stable for the all the isocyanate adducts **(47)**. Only the phenyl isothiocyanate adduct **(48, Ar'=Ph)** was isolable. For the other arylisothiocyanate adducts fragmentation occured on heating to yield substituted 1,2,3-triazoles **(46)** and two aryl isothiocyanates, the original reactant and one which had exchanged its aryl group for one on the dipole.

1.2) RESULTS AND DISCUSSION

1.2a) Synthesis of 1,2,3-Triazolium N-imides

The synthesis of the 1,2,3-triazolium-N-imide 1,3-dipoles **(13)**, involved a number of preliminary steps. First was the standard formation of the bis-aryl hydrazone of an α,β-diketone. A number of 1,2-diketones were used as precursors in this reaction, only one of which was obtained from a commercial source, *i.e.* butane-2,3-dione. The others were synthesised *via* a benzoin condensation and subsequent oxidation with c.HNO_3.[37,38]

The formation of α-hydroxyketones *via* the benzoin condensation has received much attention.[39] The original catalyst was KCN in aqueous alcohol and the mechanism of the reaction is outlined in Scheme 1.19.

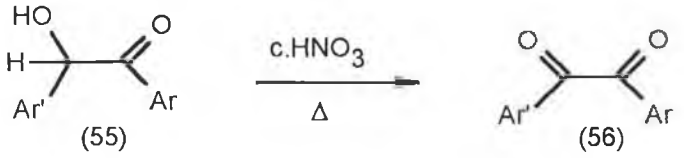


Scheme 1.19. Mechanism of Benzoin Condensation of aromatic aldehydes.

It involves the initial attack of cyanide ion to form an activated aldehyde carbanion intermediate. This activated aldehyde is termed the donor and reacts with a further molecule of aromatic aldehyde, the acceptor. Not all aromatic aldehydes act as both donor and acceptor, *e.g.* 4-(dimethylamino)benzaldehyde does not self condense, but reacts with a variety of aldehydes solely as a donor.

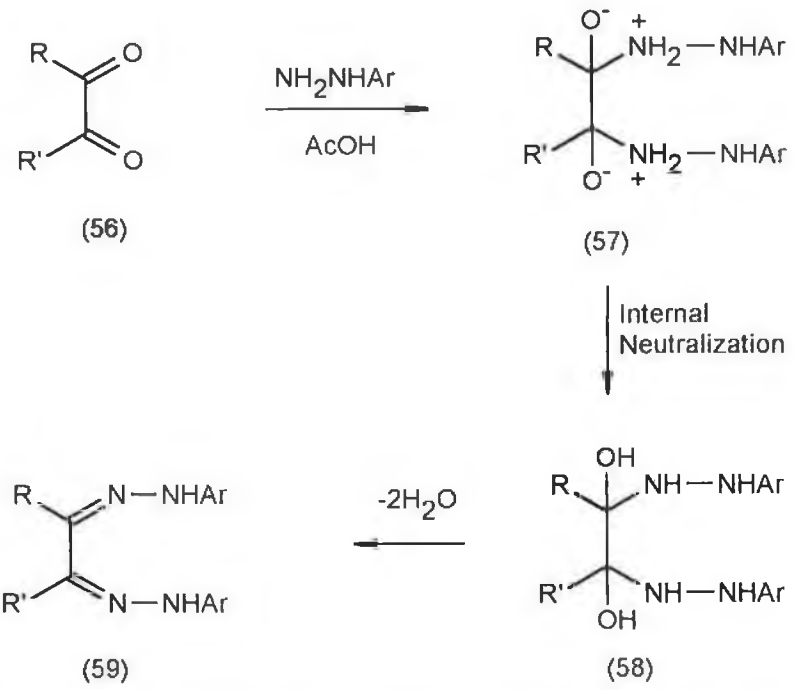
More recently the reaction has been extended to the condensation of a wide variety of aldehydes which would not normally condense under the standard conditions. Acyloins, from aliphatic aldehydes, have been prepared in high yield by thiazolium ion-catalysed condensation.[40,41] Mixed α-hydroxy ketones have been synthesised.[42] Phase transfer catalysis using benzoylated cyanohydrin allows reaction with aldehydes which would not normally self condense.[43]

For the purposes of our work, the gentle refluxing of the relevant aromatic aldehyde in aqueous ethanol, with potassium cyanide as catalyst provided high yields of the benzoin precursors. The benzoins were then oxidized to α-diketones by heating gently in c.HNO_3, until the evolution of NO_2 (in the form of nitrogen tetroxide, a brown gas) had ceased. The α-diketones synthesised in this way included benzil, 4,4'-dichlorobenzil, and 4-chloro, 4'-methoxybenzil. (Scheme 1.20). Crystallisation from a large volume of water readily provided high yields of the benzils.



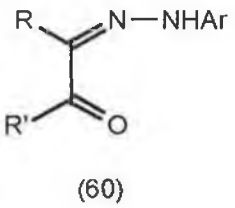
Scheme 1.20 Nitric acid oxidation of benzoin. Ar=Ph, *p*-Cl-C_6H_4, Ar'=Ph, *p*-Cl-C_6H_4, *p*-OMe-C_6H_4.

The α-diketones **(56)** were then derivatised to the bis-aryl hydrazones **(59)** using aryl hydrazine.[37] (Scheme 1.21) The conditions of this reaction varied depending on the starting dione. 2,3-Butanedione **(56, R=R'=Me)** formed both bisphenyl- and bis(4'-nitrophenyl)hydrazones in quantitative yield on stirring at room temperature in glacial acetic acid.

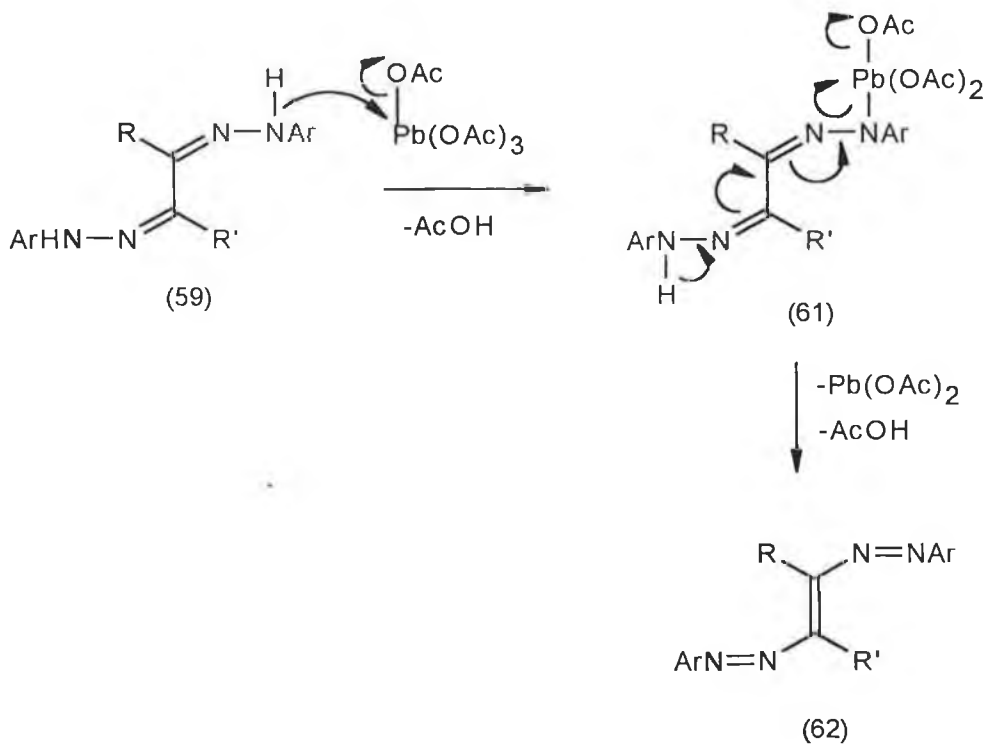


Scheme 1.21. Formation of 1,2-bis(arylhydrazone) of 1,2-diketones **(59)**.

The formation of the 1,2-bis(arylhydrazones) of aromatic diones **(59, R=R'=Ar)**, on the other hand, required refluxing glacial acetic acid to reach completion. On stirring at room temperature a yellow precipitate of benzil monohydrazone **(60)** was recovered.



The next step involved the oxidation of the bisarylhydrazones to the bisarylazo-analogues. The oxidation has previously been carried out using a number of reagents, including nickel peroxide in benzene, sodium dichromate in acetic acid, sodium in ethanol, thallium triacetate in acetic acid, lead dioxide in dichloromethane, lead tetraacetate in acetic acid or dichloromethane, and iodobenzene diacetate in acetic acid.[27,44] Herein the oxidations were carried out using excess lead tetraacetate in glacial acetic acid. In this reaction the suspension of yellow hydrazone **(59)** was transformed into the deep purple bis(phenylazo) derivative **(62)** with *trans*-geometry across the C=C bond, *via* the lead intermediate **(61)** as shown in Scheme 1.22.

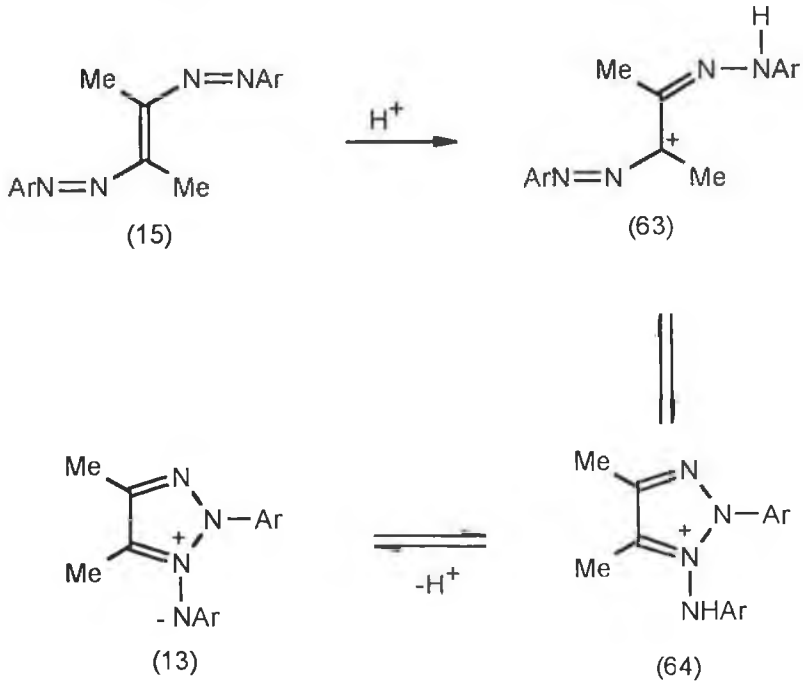


Scheme 1.22 LTA oxidation of bisarylhydrazone **(59)**

The product, obtained quantitatively, was the thermodynamically favoured *trans*-form, having the bulky azo groups away from each other. *Trans*-bisarylazo alkenes are generally highly coloured due to the extent of conjugation throughout the system. The *cis*-isomer is lighter in colour because it exists in dynamic equilibrium with the meso-ionic triazolium-N-

imide form **(13)** shown in Scheme 1.7. The aromatic N-imide **(13)** loses some of the conjugation of the open-chain form and thus its intense purple colour is dissipated.

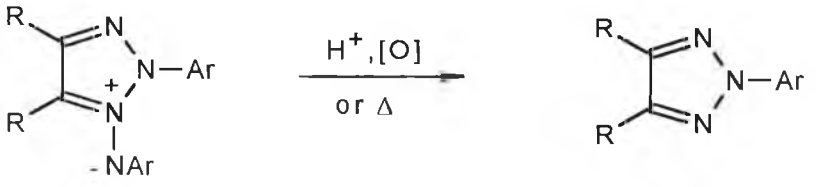
Isomerisation of BPAB **(15)** to the *cis*-form **(12)** was carried out by passing a stream of dry HCl through a solution of the *trans*-isomer in refluxing dry acetone. The solution changed colour from the deep purple to clear yellow. George *et al.* have followed this reaction using ^{1}H nmr, and found evidence for the protonated iminotriazolium derivative **(64)**.[25] The mechanism proposed was as follows.(Scheme 1.23).



Scheme 1.23 Acid catalysed isomerization of BPAB **(15)**.

George and co-workers carried out the reaction in the presence of a dipolarophile and isolated a cycloadduct, confirming the formation of the 1,3-dipolar triazolium species.[24] We have carried out this reaction in the absence of a dipolarophile and observed the formation of two products, both of which may be explained in terms of the formation of the triazolium-N-imide isomer **(13, R=Me)**. The first was 4,5-dimethyl-2-phenyl-1,2,3-triazole **(46)**. It has long been known that benzil osazones, on treatment with acid or

oxidation with certain reagents resulted in high yield conversion to 2,4,5,triphenyl-1,2,3-triazole.[45,46] Heating bis(arylazo)ethylenes in the absence of solvent at 170°C for 15 minutes led to the formation of **(46, R=Me)**.[25] The same product was obtained on photolysis but in lower yields.[47,48] The formation of triazole was explained in terms of the loss of phenyl nitrene from the mesoionic triazolium-N-imide **(13)** form. (Scheme 1.24).

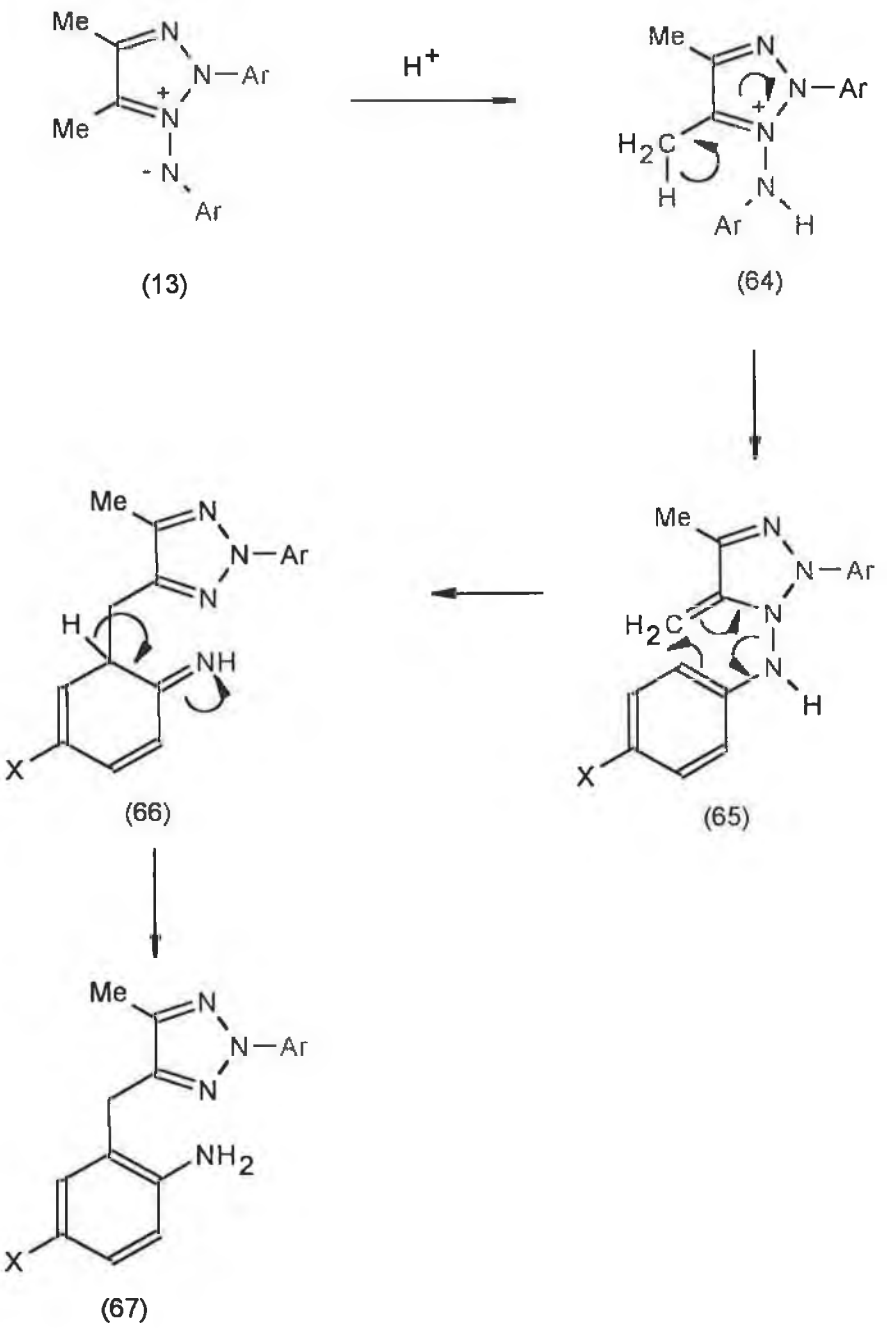


(13) (46)

Scheme 1.24 Loss of phenyl nitrene from 1,2,3-triazolium-1-(N-aryl)imides

The other and major product was the 4-(2'-amino-benzyl)-5-methyl-2-phenyl-1,2,3-triazole **(67)**. This constitutes a new chemistry for this particular series of compounds. The reaction mechanism may be explained in terms of a 3,3-sigmatropic rearrangement from the ene-hydrazine intermediate **(65)** formed from the triazolium-N-imide **(13)** (Scheme 1.25).

This is analogous to the Fischer Indole synthesis and also an *o*-benzidine rearrangement.[49,50] A similar rearrangement has been reported by Butler *et al.*, for the cycloalkenyl analogues of these compounds.[44,51] They found the rearrangement to be totally intramolecular, and also regiospecific *ortho*. A number of mechanisms were proposed but it was found that the Fischer Indole type rearrangement best explained the experimental evidence.



Scheme 1.25 Fischer-Indole-type rearrangement of **(13)**.

1.2b) Cycloaddition Reactions of 4,5-Disubstituted 2-Aryl-1,2,3-Triazolium-1-(N-aryl)imide

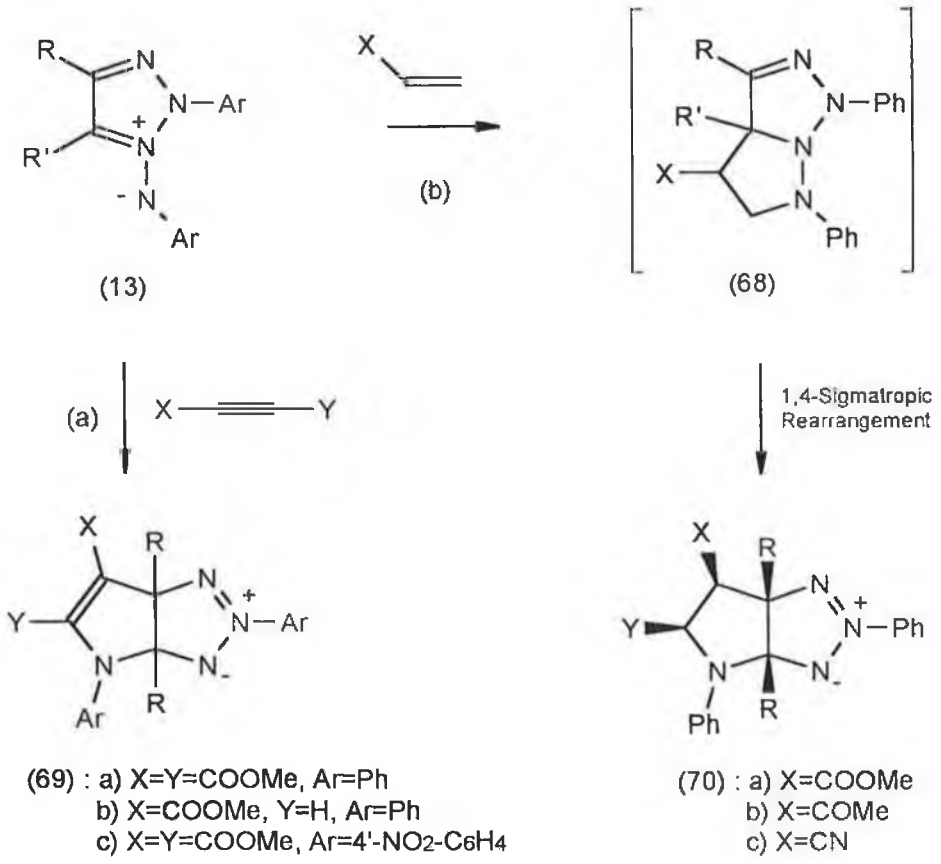
Triazolium-N-imides belong to the class called mesomeric betaines.[52] The 1,3-dipolar unit contained in the ring is of the azomethine imine type. The 1,3-dipolar cycloaddition chemistry of azomethine imines has been the subject of a large volume of work.[53] The cycloaddition chemistry of 1,2,3-triazolium 1-(N-aryl)imides **(13)** was initially studied by George and co-workers, but the products were incorrectly assigned until 1983, when Butler *et al* reported that the intially formed cycloadduct undergoes a 1,4-sigmatropic rearrangement to **(21)** or **(22)**, depending on the dipolarophile. (Scheme 1.11) The same author has subsequently published a number of papers on the cycloadditions of these compounds.[27-33] We have synthesised a variety of cycloadducts of Types A-D (See Section 1.1b), including the unpublished 3a,6a-dimethyl analogues and a variety of 3a,6a-diaryl derivatives which had not been reported previously.

1.2b.1) Cycloadditions of 4,5-Dimethyl-2-aryl-1,2,3-triazolium-1-(N-phenyl)imide.

The cycloaddition of 4,5-dimethyl-2-phenyl-1,2,3-triazolium-N-phenylimide **(13, R=Me)** with a variety of dipolarophiles has been carried out. BPAB exists in the *trans*-configuratuion and therefore does not undergo electrocyclization to the cyclic form **(13)**. On heating a solution of BPAB in dry acetone under reflux in the presence of DMAD overnight, no reaction was observed except for the formation of small quantities of 4,5-dimethyl-2-phenyl-1,2,3-triazole **(46, R=Me)**, formed on loss of phenyl nitrene as shown in Scheme 1.24.

On passing a stream of dry HCl through the same reaction mixture, a rapid colour change was observed from deep purple to clear yellow. This was attributed to the acid-catalysed formation of the triazolium N-imide **(13)** which was trapped by a dipolarophile. The product was isolated in high yield on reaction work-up and ^{13}C nmr spectroscopic analysis showed the characteristic two bridgehead carbons, attributed to the rearranged cycloadduct **(69a)** (Scheme 1.26) The mechanism of this reaction is proposed as an initial

cycloaddition between DMAD and **(13)** to yield an intermediate similar to the pyrazolo[2,3-*c*]-1,2,3-triazole **(68)** which underwent a subsequent rearangement to the isolable **(69)**.



Scheme 1.26 Mechanism of 1,3-dipolar cycloaddition and tandem rearrangement of **(13)** with (a) acetylenic and (b) vinylic dipolarophiles to form Type A **(69)** and Type B **(70)** adducts.

The mechanism is similar to that proposed by Butler *et al.*, for the 3a,6a-diaryl and bridged cyclohexyl analogues **(22, R=Ph, RR=$(CH_2)_4$)**, the identity of which were confirmed by x-ray crystallographic analyses.[26,27]

On reaction of BPAB with DMAD, the cycloadduct **(69a)** was isolated in high yield. No work up was necessary and the product was crystallised from ethanol directly on removal of the solvent. The same reaction carried out with MP required a work-up involving removal of the excess acid with sat. $NaHCO_3$ and subsequent washing with water. The water was removed by drying over anhydrous $MgSO_4$ and the residue **(69b)** recrystallised from ethanol. A similar work-up was required for the adduct formed on reaction of bis(*4'*-nitrophenylazo)butene **(13, Ar=*p*-NO_2-C_6H_4)** with DMAD to yield **(69c)**. In all cases the identity of the cycloadduct was identified using ir and nmr spectroscopy, and the ^{13}C nmr of each compound contained signals for two bridgehead carbons, characteristic of these systems.

The reaction was then extended to include vinylic dipolarophiles to form the new range of compounds **(70)**. Upon completion of the reaction , the residue was subjected to the same work-up as described above. For a number of vinylic dipolarophiles, flash column chromatography was required to separate the cycloadduct from the reaction side-products which were identified as the triazole **(46)**, and the rearranged compound **(67)**, both of which were formed, as described above (Schemes 1.24 and 1.25 respectively), in reactions competing with cycloaddition. Two orientations are possible for the substituent at C-6, an *exo* and an *endo*-orientation. The compounds have been assigned the *exo*-orientation on the basis of crystal structure analysis carried out by Butler *et al.* on the 6-cyano-3a,6a-diphenyl and bridged cyclohexyl analogues **(22, R=Ph, X=CO_2Et, Y=H; RR=$(CH_2)_4$, X=CN, Y=H)**.[26,27] In these cases the cyano group was found to be in the *exo*-orientation. The orientation was explained in terms of secondary orbital effects in the initial cycloaddition, where the cyano group interacted with π-orbitals of the dipole not directly involved in the cycloaddition, producing initially the 4-*endo*-cyano dihydropyrazolino[2,3-*c*]triazole **(20, R=Ph, $(CH_2)_4$, X=CN, Y=H)**. A 1,4-sigmatropic rearrangement then led to the isolated 6-*exo*-product **(70c)**. The cycloadducts reported herein undergo the same tandem cycloaddition and sigmatropic rearrangement and therefore should yield the *exo*-adducts **(70a-c)** (See Fig. 1.3)

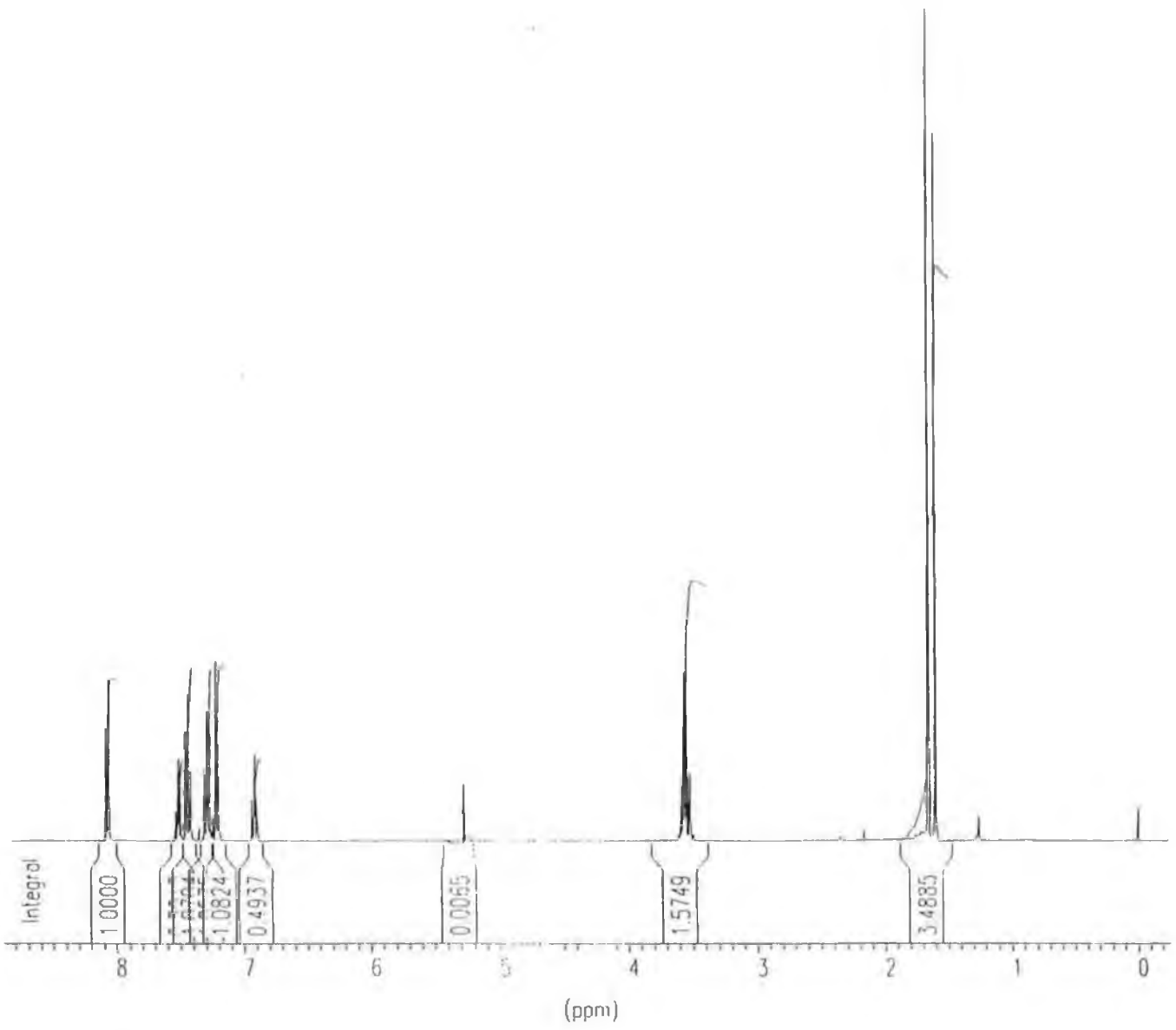


Fig. 1.3a ^{1}H nmr spectrum of **(70c)**.

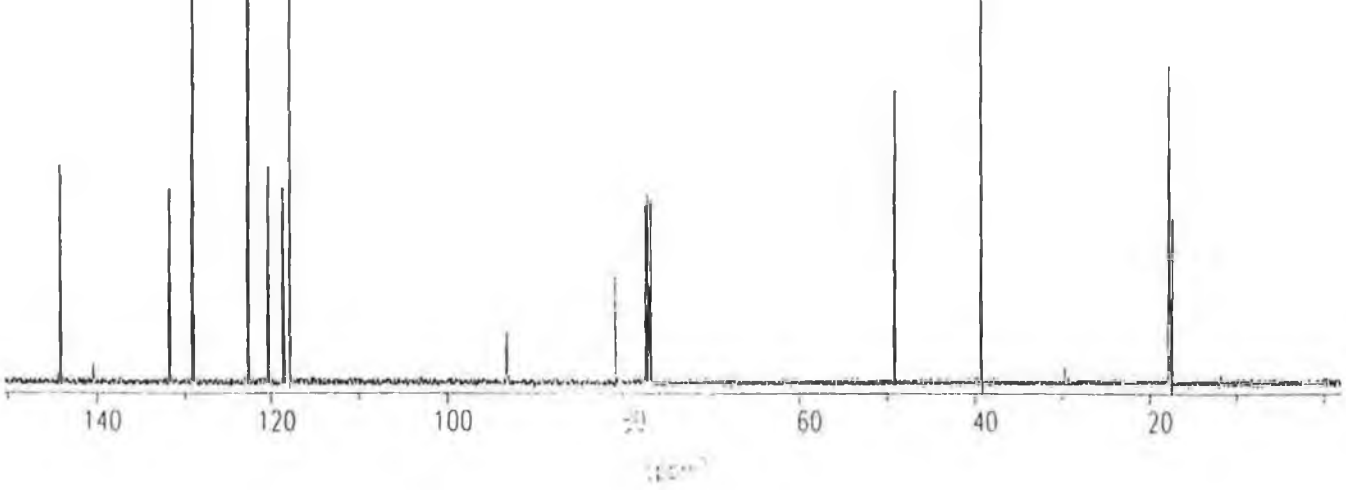
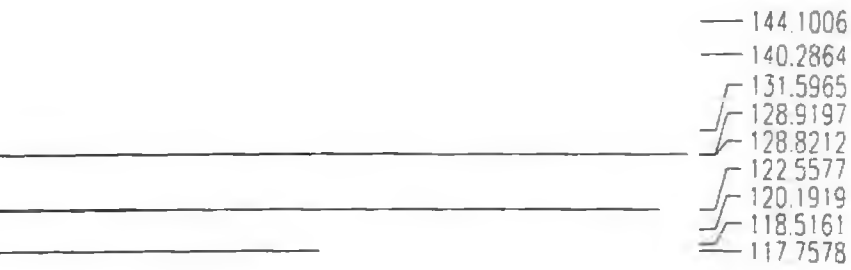


Fig. 1.3b ^{13}C nmr spectrum of **(70c)**.


144.1006
140.2864
131.5965
128.9197
128.8212
122.5577
120.1919
118.5161
117.7578


93.1590
77.0000
76.6815

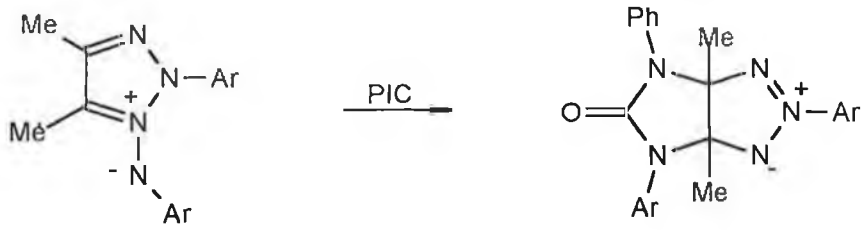

48.9662
39.1237
29.6224
17.6718
17.3458
11.8710

The fact that the addition of DMAD to the 1,3-dipole occured without significant formation of side products was an indication that the cycloaddition proceeded more rapidly than for any other dipolarophile, as was expected on the basis of the work carried out by Huisgen on azomethine imines.[6] It was shown, for a variety of azomethine imines, that the rate of addition of acetylenic dipolarophiles was greater than that for vinylic dipolarophiles and also that the greater the electron withdrawing capacity of the substituents of the dipolarophile, the greater the rate of addition. Electron withdrawing groups have the effect of reducing the LUMO energy of the dipolarophile and therefore should increase the reaction rate for HOMO-dipole controlled reactions. Butler *et al.* have determined that cycloaddition reactions of this type of compounds are dipole HOMO controlled.[28] For polysubstituted alkynes, the effect of substituents is additive, so the LUMO of DMAD being lower than that of MP interacts at a greater rate with the dipole HOMO.

In the acidic conditions of the reaction, the triazolium-N-imide underwent three competing processes, *i.e.* (i) cycloaddition with tandem sigmatropic rearrangement, (ii) Fischer indole type rearrangement to the compound **(67)** and (iii) loss of aryl nitrene leading to 4,5-dimethyl-2-aryl-1,2,3-triazole **(46, R=Me)**. The relative rates of reaction of the three processes determined the quantity of the each product formed. For DMAD the cycloaddition reaction was rapid and no rearranged product was isolated, but as the reaction rate varied with dipolarophile, so did the quantity of the side products. For acrylonitrile the yields of cycloadduct **(70c)** and substituted aniline **(67)** were 64 and 21% respectively.

The reaction of BPAB with PIC was undertaken to further evaluate whether BPAB, on cycloaddition undergoes the same tandem cycloaddition and 1,4-sigmatropic rearrangement seen for all the reactions in this series. (Scheme 1.27) If this were the case the product isolated would be the 3a,6a-dimethyl-5-oxo-2,4,6-tetraphenyl-3,3a,4,5,6,6a-hexahydroimidazo[4,5-*d*]-1,2,3-triazole **(71)**. This should possess a plane of symmetry

across the length of the molecule. It was therefore expected that the C-3a and C-6a bridgehead carbons would be magnetically equivalent.

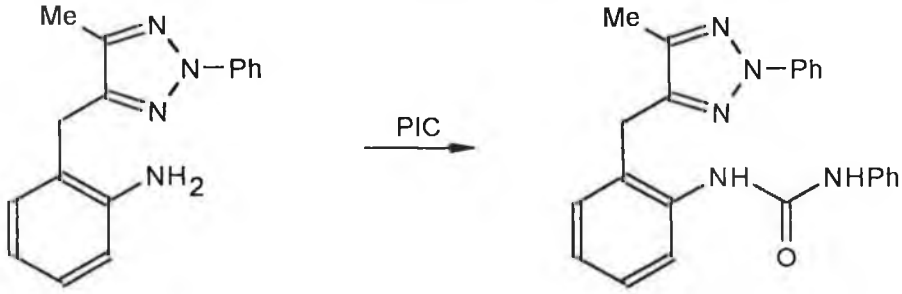


(13) (71)

Scheme 1.27 Cycloaddition of BPAB and PIC.

Examination of the ^{1}H and ^{13}C nmr spectra for this compound showed only one signal for the bridgehead carbons, the methyl substituent signals appear as one, and the number of non-equivalent signals was reduced by half compared to the unsymmetrical cycloadducts **(70)**. (Compare Figs. 1.3 and 1.4) This confirmed the 1,3-dipolar nature of the azimine moiety, both N-N bonds being of equal length. It also confirms that BPAB undergoes the same reaction sequence as other triazolium dipoles in this series, despite requiring acid catalysis to initiate the reaction.

Another product was also isolated from the reaction of BPAB with PIC. This was not the *o*-substituted aniline **(67)**, isolated as a side product in other cycloadditions in this class, but a derivative **(72)** which may arise from reaction of **(67)** with PIC. (Scheme 1.28)



(67) (72)

Scheme 1.28

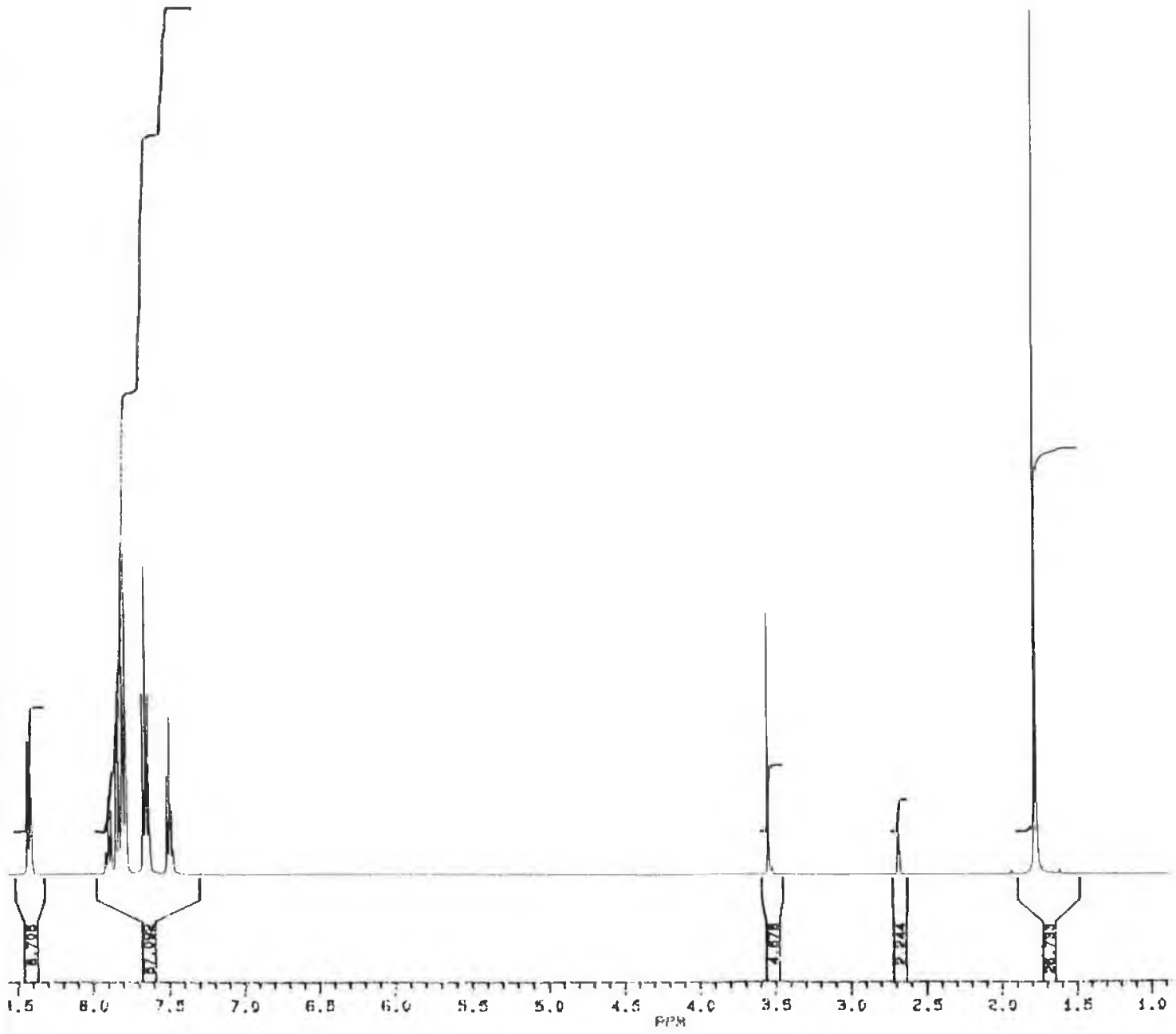


Fig 1.4a ^{1}H nmr spectrum of BPAB and PIC (71)

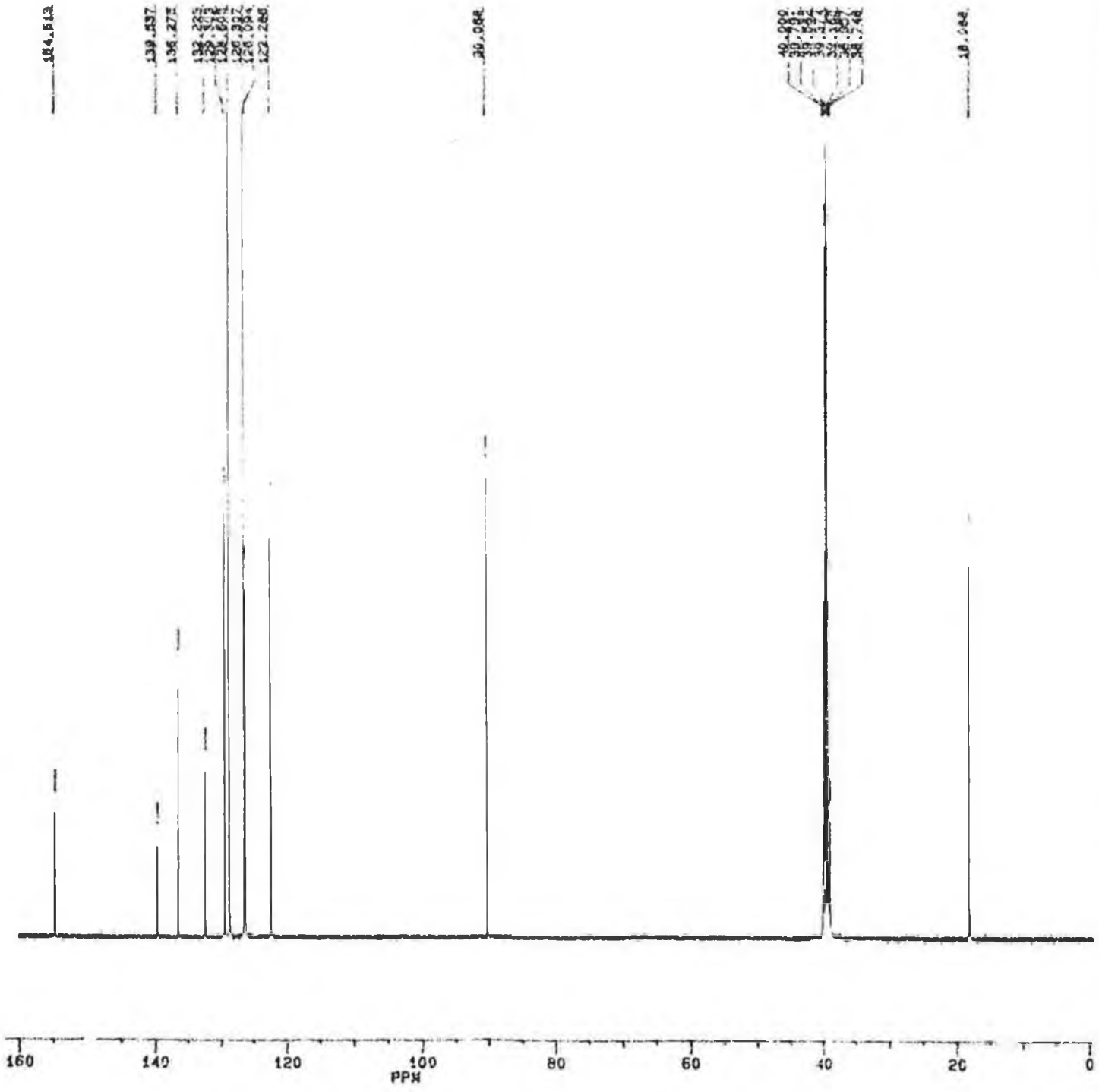
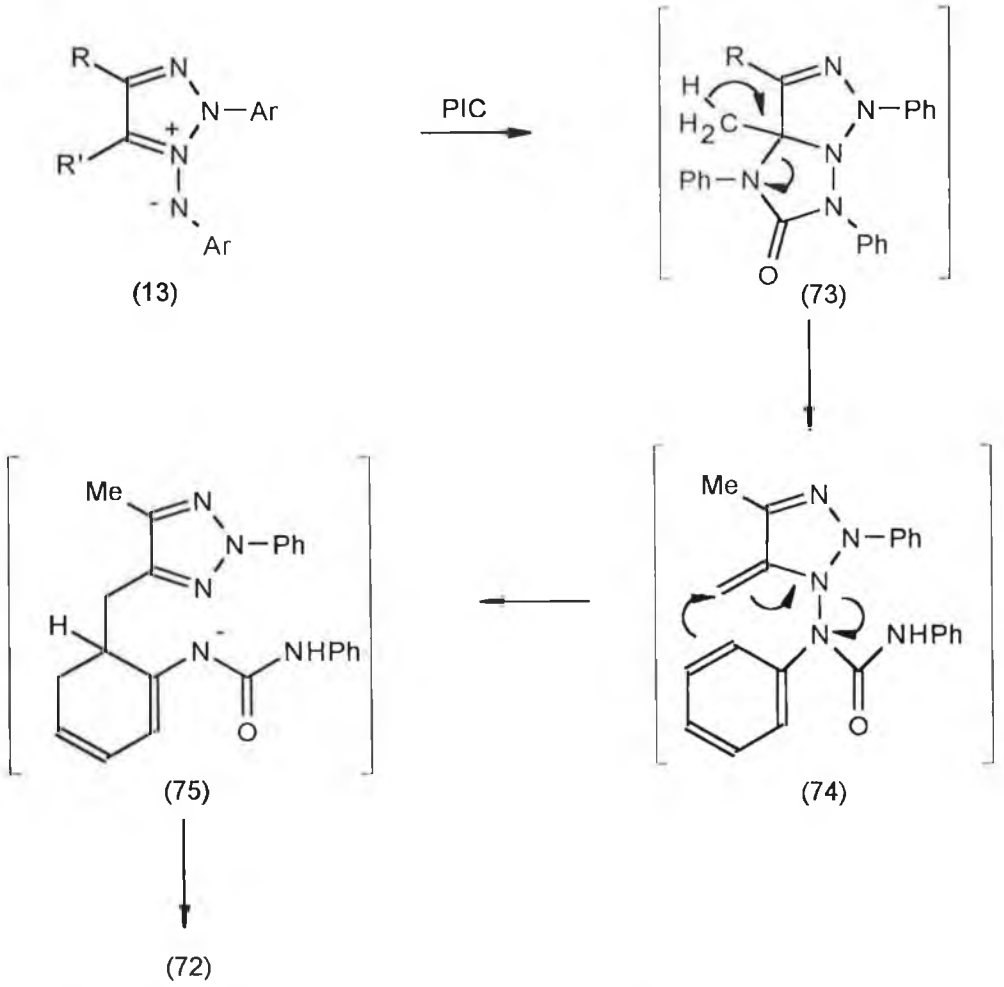


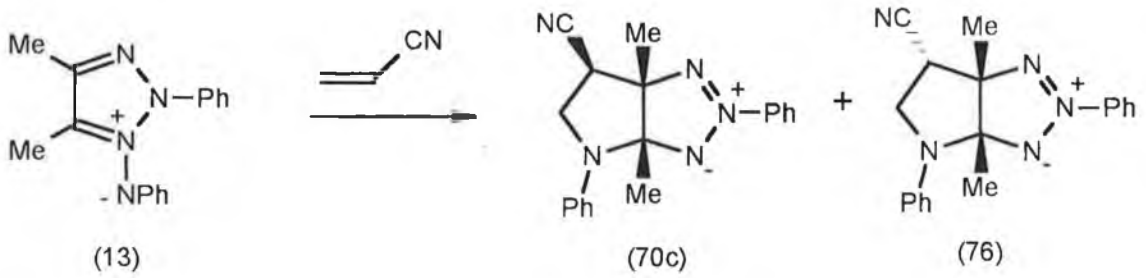
Fig. 1.4b ^{13}C nmr spectrum of BPAB and PIC (71).

The structure was elucidated using ir, nmr and mass spectroscopic techniques along with CHN analysis. The ir spectrum showed a signal at 3300 cm^{-1} indicative of the presence of NH. The characteristic carbonyl stretching frequency of ureas was seen at 1634cm^{-1}. ^{1}H nmr spectroscopy indicated the presence of one methyl and one methylene group, and also the presence of an *o*-disubstituted phenyl group. The absence of any bridgehead carbon signals in the ^{13}C nmr indicated an addition product as opposed to a cycloaddition product. The fact that **(72)** was formed from **(67)** and not from rearrangement of the cycloaddition product **(71)** (See Scheme 1.29) was confirmed by separate reaction of **(67)** with PIC, under cycloaddition reaction conditions. This addition reaction also proceeded quantitatively at room temperature. Attempted generation of **(72)** from **(71)** in refluxing toluene or acidified acetone for 3 days proved futile.



Scheme 1.29. Alternative mechanism of formation of **(72)**

An interesting product isolated on reaction of BPAB with AN was the 6-*endo*-cyano-epimer of the cycloaddition product **(76)**. (Scheme 1.30)



(13) (70c) (76)

Scheme 1.30. Epimers formed on cycloaddition with acrylonitrile.

This contrasts with the normal *exo*-orientation observed for cycloadducts in this series, as described above. (Scheme 1.26) The structure was determined by spectroscopic techniques. The major difference between the *endo*- and the *exo*-isomers **(76)** and **(70c)** respectively, in their ^{1}H nmr spectra, was the splitting pattern of the C-5 and C-6 H's. The splitting pattern for **(70c)** appeared as a complex multiplet between 3.67 and 3.75 ppm. The *endo*-isomer **(76)**, on the other hand showed a multiplet, integrating as 2H, between 3.38 and 3.47 ppm. Another signal appears between 3.77 and 3.83 ppm integrating as 1H.

One reason for the difference in the shielding of the hydrogens is that the C-6-H is now in the *exo*-position and is therefore *cis*- to the bridgehead (C-6a) methyl group. It has been observed that methyl groups cause resonances due to *cis*-vicinal protons to appear upfield of those due to the *trans*-vicinal protons.[54] The C-5-H proton for **(76)** appears 0.20 ppm upfield of the corresponding signal in **(70c)** and therefore is in good agreement with the assignment of an *endo*-configuration for **(76)**. The interaction of the nitrile π-system with that of the azimine function in the *endo*-adduct **(76)** led to an appreciable upfield shift (0.81ppm) of the nitrile carbon signal in the ^{13}C nmr spectrum.

The isolation of **(76)** from the cycloaddition reaction mixture initially seemed to indicate that the cycloaddition and sigmatropic shift may not be stereospecific as suggested by Butler *et al.*[26,27] Results obtained on the room temperature photolysis of a number of 3a,6a-diphenyl-analogues (See Section 3.2b) seemed to suggest that it may be a photochemical process, occurring in visible light. In order to investigate this, a solution of **(70c)** was stirred for 4 weeks at room temperature in visible light in the absence of acid or base. No reaction was observed. In the relatively short time span of the cycloaddition reaction (~20 minutes), a photochemical epimerization therefore appears unlikely.

It was found, however, that on irradiation using a high pressure mercury lamp with pyrex filter, the epimerization product **(76)** was observed along with a number of other photoproducts. The mechanism of this and the other photoreactions shall be discussed in Section 3.2.d. The photoinduced epimerization under pyrex filtered irradiation, although producing the same *endo*-epimer **(76)**, is thought to be formed by a different mechanism to that involved in the cycloaddition reaction mixture. The fact that this epimerization was not observed for any other 3a,6a-dimethyl analogue under either thermal or photochemical conditions indicate the strong influence of the nitrile group on this reaction. The relative pK_a's of the α-hydrogens of nitrile, ketone and ester groups have been reported and are shown in the Table 1.4.[55]

Table 1.4 Relative pK_a's of α-hydrogens of electron withdrawing groups.

Acid	Base	pK_a (relative to H_2O)
$RCOCH_2R$	$RCOCH^-(R)$	19-20
RO_2CCH_2R	$RO_2CH^-(R)$	24.5
RCH_2CN	RCH^-CN	25

The pK_a of the nitrile α-hydrogen is greater than that of either of the analogous ketone or ester. The pKa's shown here were calculated in aqueous solution. The effect of solvent

can exert considerable influence on acid and base strength by differential solvation.[56] A change from a protic to an aprotic solvent can affect the acidity or basicity since there is a difference in solvation of anions by a protic solvent (which can form hydrogen bonds) and an aprotic one. The ionic strength of the solvent also influences acidity as it has an influence on activity coefficients.[57,58]

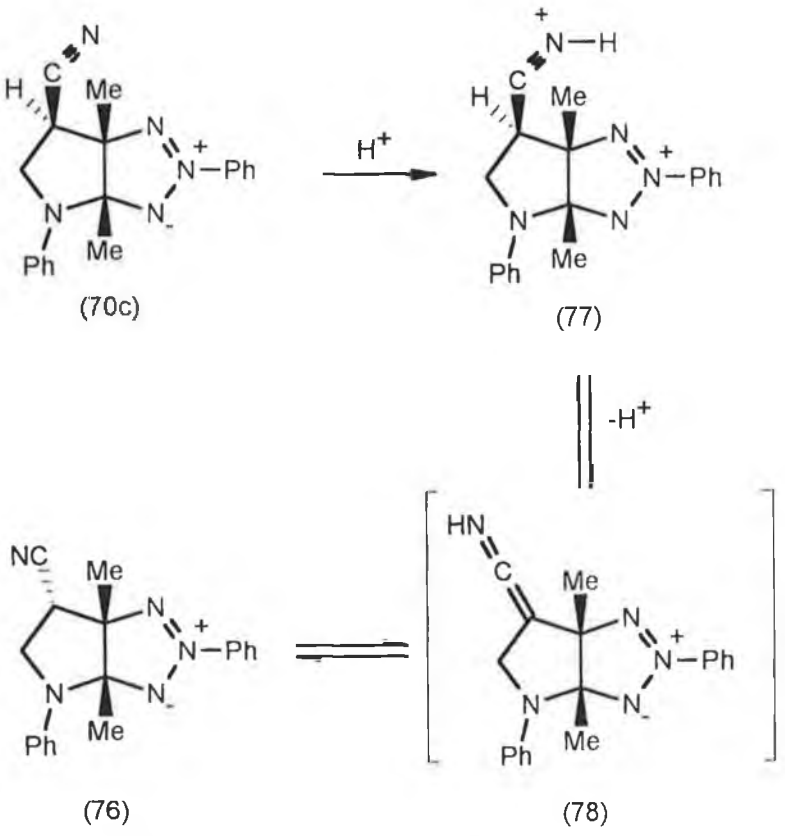
The cyano group is strongly electron attracting and alkyl cyanides condense in the presence of sodium. This is the basis of the Thorpe nitrile condensation.[59] It has also been shown that, in the presence of sodium amide in ether solution, cyanides condense with esters.[60] Methyl cyanide condenses with ethyl propionate to form propionyl methyl cyanide as follows:

$$CH_3CN + NaNH_2 \rightarrow [^-CH_2CN]Na^+ + NH_3$$

$$[^-CH_2CN]Na^+ + CH_3CH_2CO_2Et \rightarrow CH_3CH_2COCH_2CN + EtOH$$

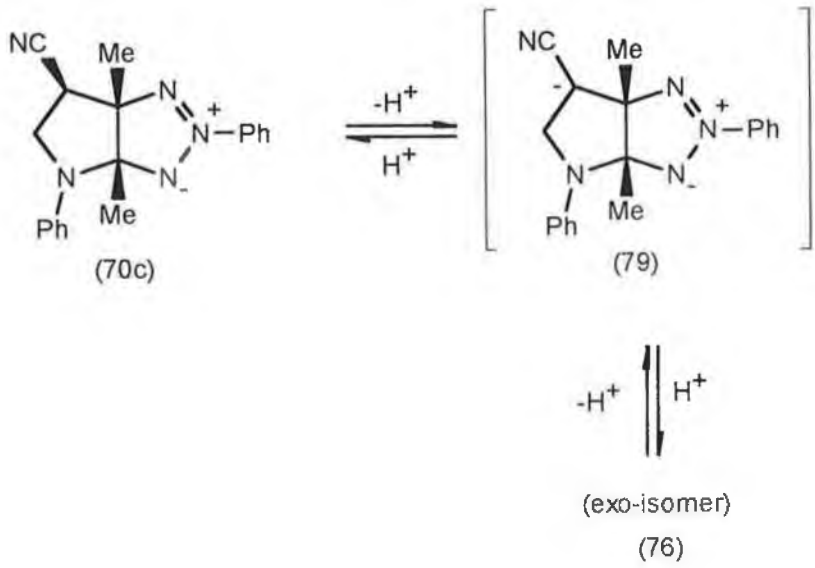
The direction of the attack indicates the greater activity of the α-hydrogen of methylcyanide with respect to the α-hydrogen of ethyl propionate.[60]

Under the acidic conditions of the reaction a possible mechanism of epimerization is *via* an achiral ketenimine intermediate. Tautomerization has regularly been used to explain observed epimerizations and racemizations.[61] The proposed mechanism of such a reaction is shown in scheme 1.31.



Scheme 1.31. Acid catalysed epimerization at C-6

It has been found more recently that racemizations about a carbon α- to a carbonyl or a conjugative electron withdrawing group occur *via* a planar (*i.e.* achiral) carbanion intermediate, formed on removal of the acidic α-hydrogen. Isotopic replacement studies have confirmed this.[62] Considerable work has been carried out on proton transfers involving cyanocarbon acids in non-aqueous solvents.[55] Experimental methods involved the comparison of rates of isotope exchange at the carbanion centre to rate of racemisation. The results have usually been explained by assuming that the carbanions are practically planar and symmetrical.[63] With this in mind the epimerization may have taken place during the basic conditions of the work up. A mechanism for base catalysed epimerization is shown in Scheme 1.32



Scheme 1.32. Base catalysed epimerization of **(70c)**.

In order to establish which of these mechanisms dominated, a sample of the *exo*-isomer **(70c)** was stirred in the dark under acidic and basic conditions. Under acidic conditions **(76)** was produced in low yield after stirring at room temperature for 4 days. Under basic conditions no reaction was observed after 10 days. It appears therefore that the epimerization proceeded as outlined in Scheme 1.31.

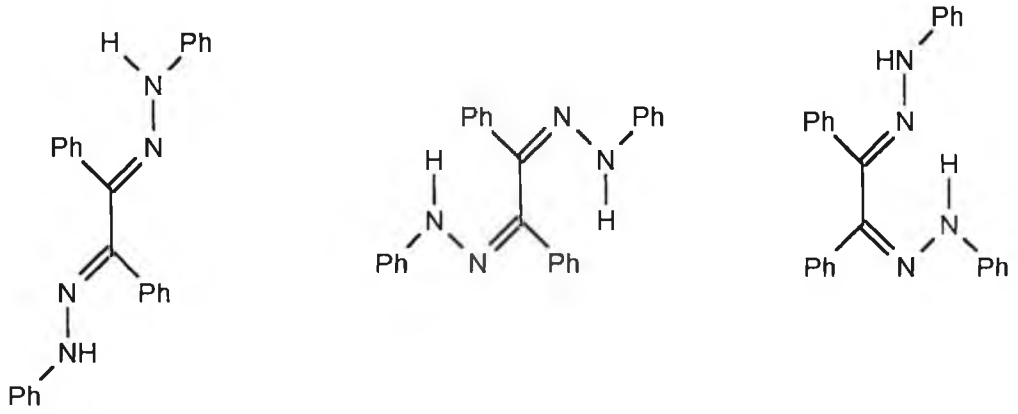
A list of the cycloadducts formed by cycloaddition with BPAB along with the physical data is given in Table 1.5

Table 1.5. Cycloaddition products from BPAB and 2,3-bis(4'-nitrophenylazo)butene

Cmpd No.	Molecular Formula	Mw.	Yield (%)	M.p (°C)	Found (Theory) C	H	N
69a	$C_{22}H_{20}N_4O_4$	406.44	82	136-138	64.87 (65.01)	5.44 (5.46)	13.65 (13.78)
69b	$C_{20}H_{20}N_4O_2$	348.40	78	117-118	68.67 (68.93)	5.89 (5.79)	15.92 (16.09)
69c	$C_{22}H_{20}N_6O_8$	496.44	69	151-153	53.13 (53.23)	3.93 (4.06)	16.80 (16.93)
70a	$C_{20}H_{22}N_4O_2$	350.42	72	87-89	68.39 (68.55)	6.34 (6.33)	16.08 (15.99)
70b	$C_{20}H_{22}N_4O$	334.42	70	100-102	71.95 (71.83)	6.67 (6.63)	16.98 (16.75)
70c	$C_{19}H_{19}N_5$	317.39	62	173-174	72.03 (71.90)	6.11 (6.03)	21.81 (22.07)
71	$C_{23}H_{21}N_5O$	383.45	55	161-162	72.25 (72.04)	5.66 (5.52)	18.53 (18.26)

1.2b.2) *Cycloadditions of 2,4,5-Triphenyl-1,2,3-triazolium-1-(N-phenyl)imide.*

The oxidation products of substituted benzil bisphenylhydrazones **(80)** have been the subject of much interest in the literature. In 1951 Spassov discovered that **(80)** has three stable isomers (*syn-*, *anti-* and *amphi-*).[64] (Scheme 1.33)



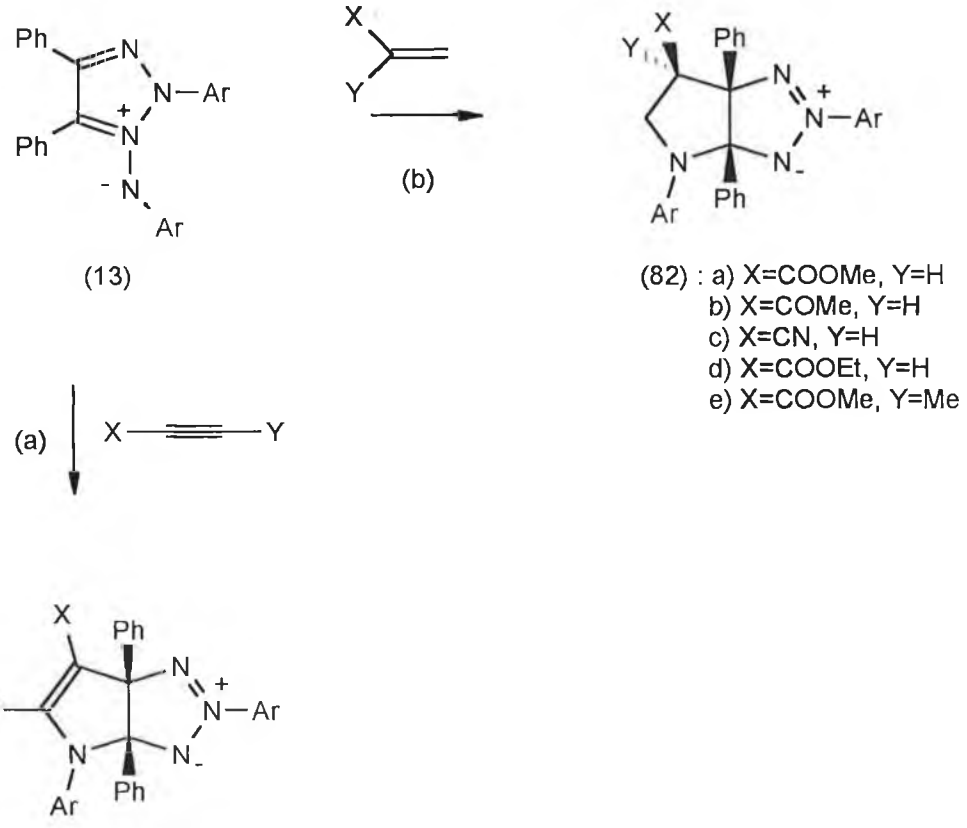
(Anti-) *(Syn-)* *(Amphi-)*

Scheme 1.33. Three stable configurations of **(80)**.

Oxidation of any of these isomers led to the same oxidation product, the *trans*-azo compound, which has been confirmed by x-ray crystallography.[65,66] In solution these *trans*-bis(areneazo)olefins were found to undergo a remarkably facile *trans-cis*-isomerisation followed by an electrocyclization to give the cyclic 1,2,3-triazolium imide form **(13, R=Ph)** (Scheme 1.7). Both the cyclic and the open chain forms have been directly detected in dynamic equilibrium by variable temperature ^{1}H n.m.r. spectroscopy for bis(areneazo)cycloalkenes.[20,21] The dominant structural form depended on a number of factors including the aryl substituent and the size of the cycloalkyl ring.

The cycloaddition of substituted alkenes to 4,5-diphenyl-1,2,3-triazolium-1-(N-phenyl) imide **(13, R=Ph)**, carried out at reflux temperature in dry acetone, proceeded in high yield to the corresponding 5,6-disubstituted-2,4-diaryl-3a,6a-diphenyl-pyrrolo[2,3-*d*]-

1,2,3-triazoles **(81)** and **(82)** (Type C and D cycloadducts respectively). (Scheme 1.34) The spectroscopic data obtained for cycloadditions with standard electron deficient alkenes was identical to that found in the literature.[26,27]

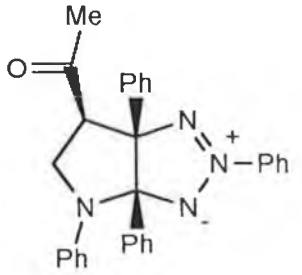


Scheme 1.34 1,3-Dipolar cycloaddition of BPAS with (a) acetylenic and (b) vinylic dipolarophiles to yield Type C and D cycloadducts **(82)** and **(81)** respectively

Compounds **(82a, f and g, X=CN, CO_2Me; Y=H, CO_2Me)** and **(81a, X=Y=CO_2Me)** have been prepared by Butler *et al.*[26,27,67] Herein the range of cycloadditions was extended to include a variety of new dipolarophiles.

The previously unreported addition of BPAS and MP, proceeded in high yield to the 5-unsubstituted cycloadduct **(81b, X=CO_2Me, Y=H)**. Characterization by spectroscopic techniques confirmed the assignment of this structure. The ^{1}H nmr signal at 8.43ppm was attributed to the C-5-H. The ^{13}C nmr showed signals at 92.8 and 105.64 ppm attributable to the bridgehead carbons C-6a and C-3a respectively, the ester carbonyl signal appeared at 165.46ppm.

The cycloaddition with MVK was previously unreported. Aldehydes are known to react in high yield with triazolium-N-imides and add preferentially across the C=O bond.[30-32] Methyl vinyl ketone however added across the C=C bond to produce the 6-methylcarbonyl-2,3a,4,6a-tetraphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-*d*]-1,2,3-triazole **(82b)**. The structure was confirmed by ir, ^{1}H nmr, ^{13}C nmr and CHN analysis. (See Figs. 1.5a, b for ^{1}H and ^{13}Cnmr spectra of **(82b)**).



(82b)

The use of vinylic dipolarophiles with *cis* and *trans* geometry formed cycloadducts regio- and stereospecifically. For example, cycloaddition with DMM formed the *cis*-cycloadduct **(82f)** whereas with DMF, the *trans*-cycloadduct **(82g)** was formed. (Scheme 1.35)

The assignments were confirmed by spectroscopic techniques including ir, ^{1}H and ^{13}C nmr and CHN analysis and also by comparison with literature spectroscopic data.[27]
Application of the Karplus equation, regarding the size of vicinal coupling constants, predicted that the coupling constants for the *cis*-isomer **(82f)** should be greater than for the *trans*-analogue **(82g)**.[68]

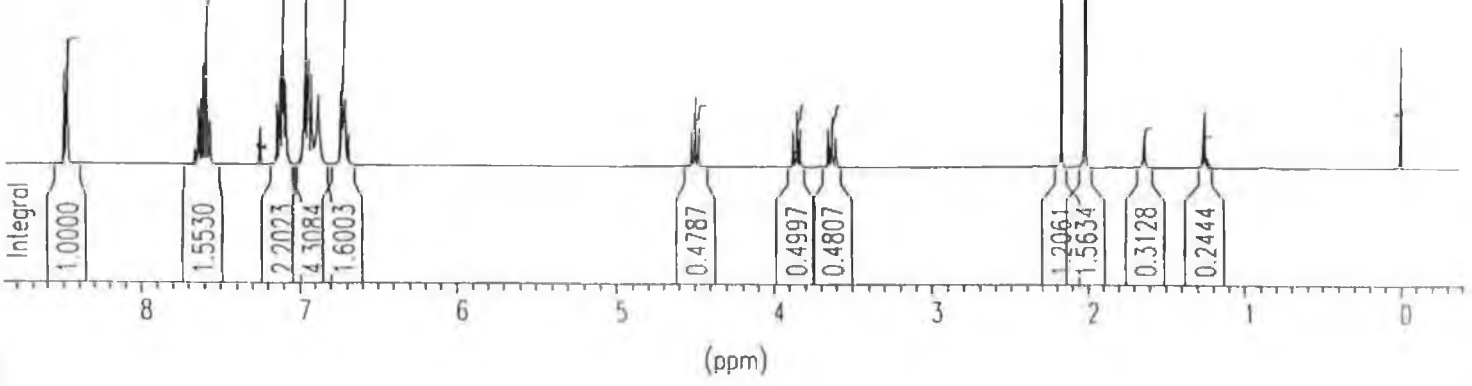


Fig. 1.5a ^{1}H nmr spectrum of **(82b)**.

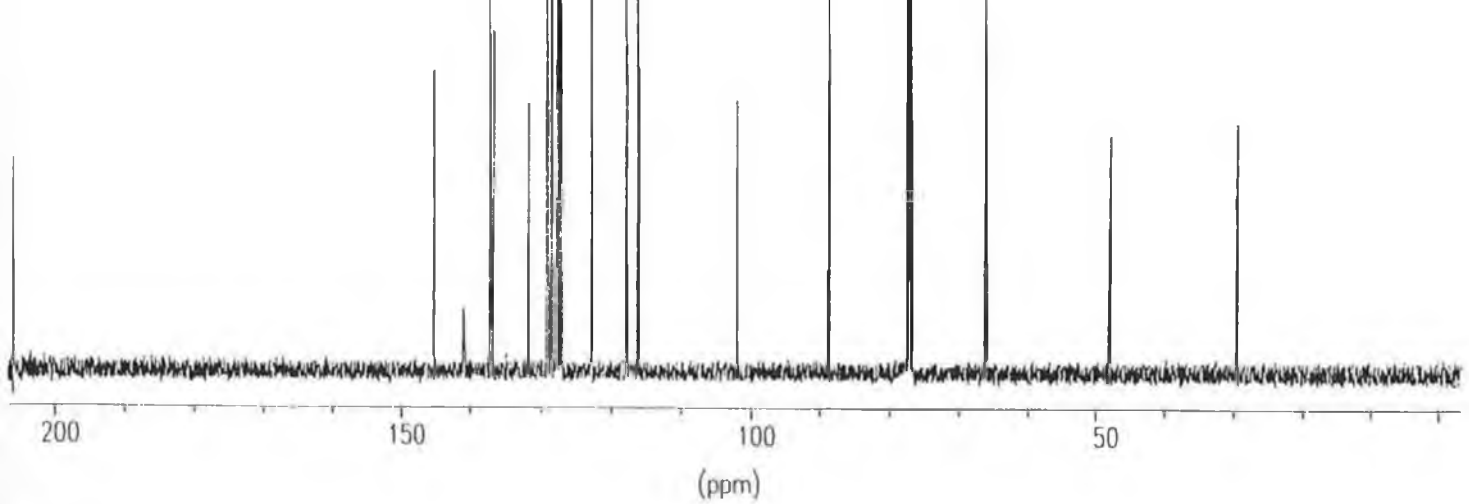
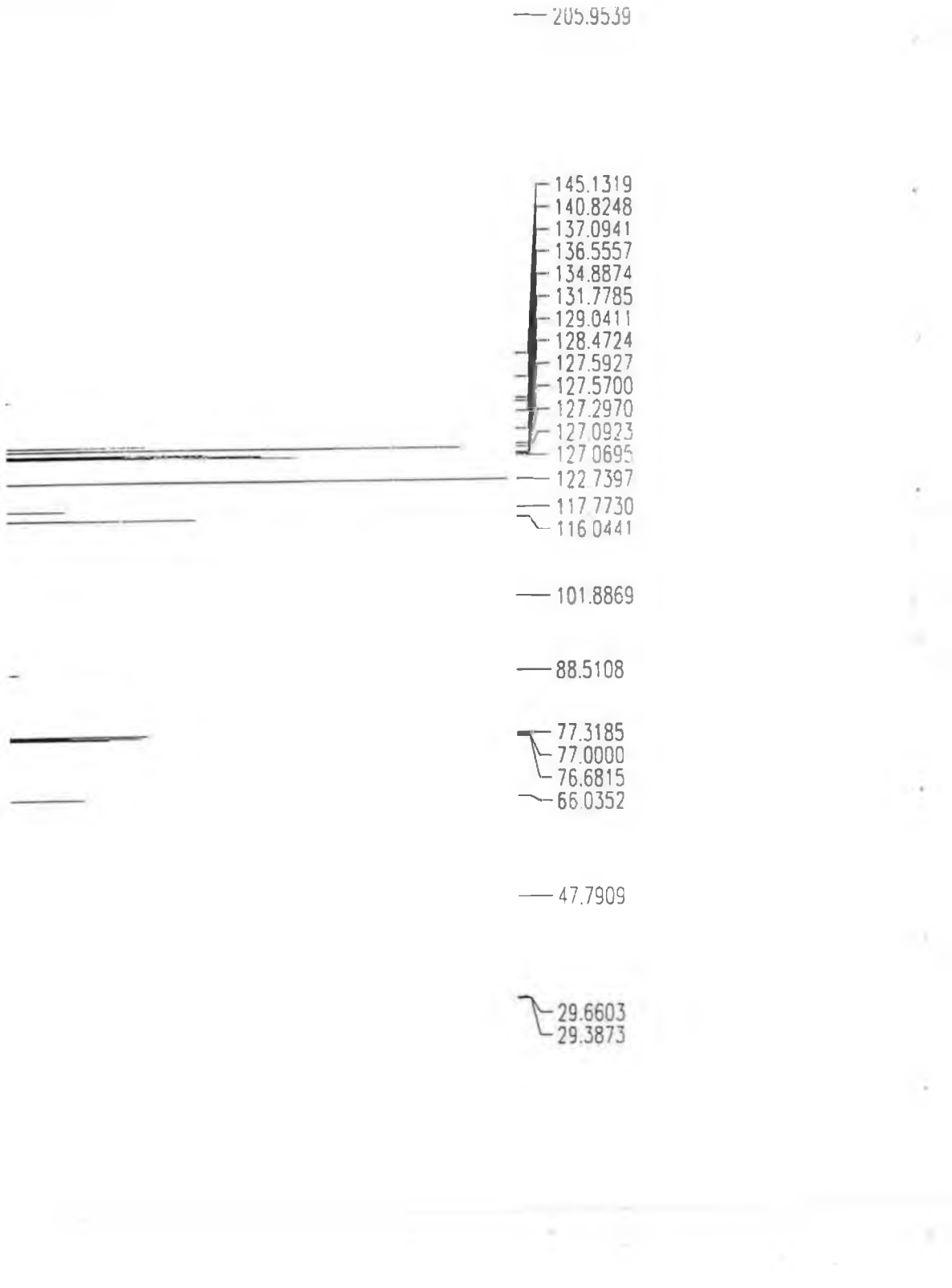
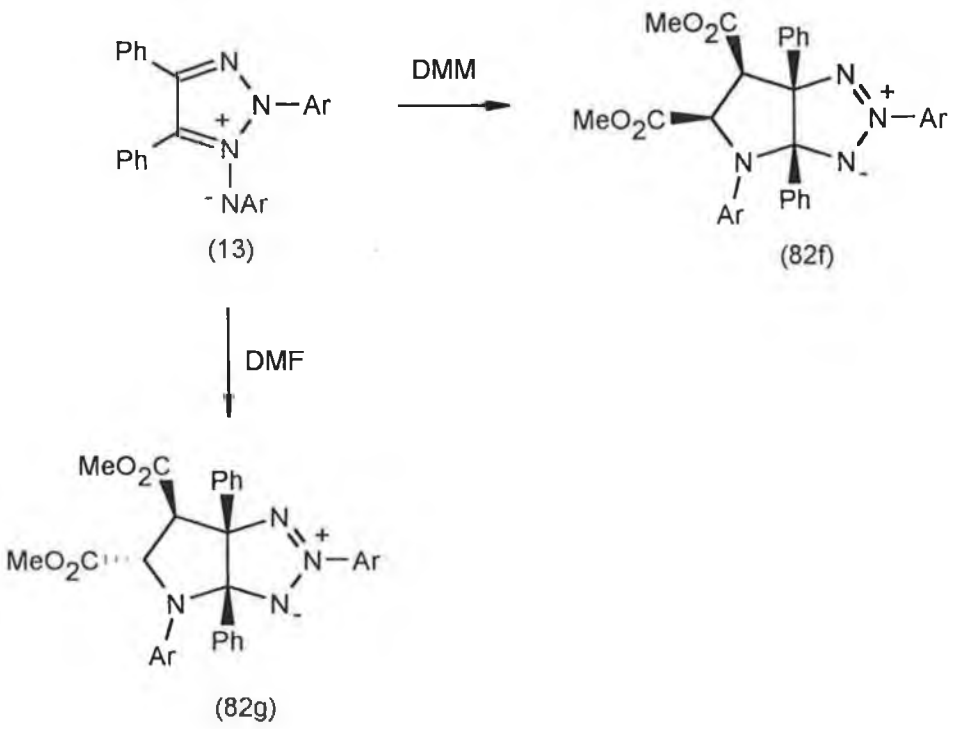


Fig. 1.5b ^{13}C nmr for **(82b)**


205.9539
145.1319
140.8248
137.0941
136.5557
134.8874
131.7785
129.0411
128.4724
127.5927
127.5700
127.2970
127.0923
127.0695
122.7397
117.7730
116.0441
101.8869
88.5108
77.3185
77.0000
76.6815
66.0352
47.7909
29.6603
29.3873



Scheme 1.35. Stereospecific formation of cycloadducts of BPAS.

For these systems the value of $J_{vicinal}$ is dependent mainly on the dihedral angle (the angle subtended by the two CH bonds when viewed in the Newman projection), according to the Karplus equation:

$$J = J^{0}\cos 2\phi \qquad [0° \leq \phi \leq 90°]$$

$$J = J^{180}\cos 2\phi \qquad [90° \leq \phi \leq 180°]$$

The dihedral angle has been estimated as ~0° for **(82f)** and ~50° for **(82g)**.[27] The coupling constants obtained experimentally were J_{cis} = 9.36Hz, J_{trans} = 3.44Hz and are in close agreement with literature values (J_{cis} = 10.4Hz, J_{trans} = 3.3Hz).[27] The vicinal coupling constant is not solely dependent on the dihedral angle and other factors including the electronegativities of the substituents, the orientation of the substituents, the hybridization

of the carbon atoms, bond angles and bond lengths all influence the vicinal coupling constant. The magnitude of these other influences is such that they may be regarded as perturbations of the Karplus rule. In this case the influence of these other factors should be equivalent for both isomers, and although an accurate value for the dihedral angle cannot be elucidated, the relative magnitude of the dihedral angles is indicative of the stereochemistry. It is found that $J_{vicinal}$ is invariably greater for the *cis*-isomer than for the *trans*-analogue.

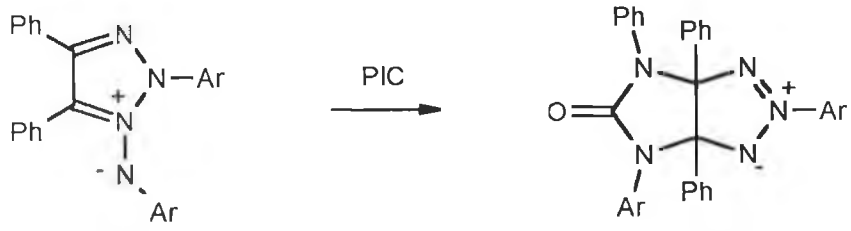
Attempts to carry out cycloadditions with conjugated (phenyl acetylene) or electron rich acetylenic dipolarophiles (propargyl alcohol and butyne-1,4-diol) proved futile. The products isolated were the starting material **(13)** and 2,4,5-triphenyl-1,2,3-triazole **(46)**, produced on elimination of phenyl nitrene from **(13)**. (Scheme 1.24) The production of triazole from the oxidation product of benzil bis-phenylhydrazones is well documented and was regarded as initial proof of the presence of the triazolium species in equilibrium with BPAS.[47]

The reason for the unreactivity of the electron rich dipolarophiles may be explained by FMO theory. Triazolium-N-imide cycloaddition is invariably a HOMO dipole / LUMO dipolarophile controlled process.[26,27] Electron rich dipolarophiles have high LUMO energies so the difference in frontier orbital energy between these dipolarophiles and **(13)** is much greater than for electron deficient dipolarophiles and reaction is therefore inhibited. The use of electron withdrawing groups on the dipole, *e.g.* the use of bis(benzoylazo)stillbene may have facilitated a Type III cycloaddition with electron rich dipolarophiles *i.e.* dipole LUMO-dipolarophile HOMO control. The frontier orbital energy separations for 1,3-dipoles with a few azomethine imines have been estimated and are shown in Table 1.6. (x = electron releasing OR, NR_2, *etc.*, c = conjugating, Ph, vinyl, *etc.*, z = electron withdrawing CO_2R, CN, *etc).*[9]

Table 1.6 Frontier orbital energy separations for azomethine imines.

ΔE (dipole HOMO-dipolarophile LUMO)(eV)					dipole LUMO-dipolarophile HOMO)(eV)			
Dipole	C=C-x	C=C-c	C=C	C=C-z	C=C-x	C=C-c	C=C	C=C-z
$H_2C{=}NH^+{-}NH^-$	11.6	9.6	10.1	8.6	7.7	8.7	10.2	11.6
$PhCH{=}N^+(R){-}N^-Ar$	8.6	6.6	7.1	5.6	6.6	7.6	9.1	9.5
$CH_2{=}N^+(R){-}N^-(COR)$	12.0	10.0	10.5	9.0	7.6	8.6	10.1	12.0

The cycloaddition of BPAS with PIC yielded an interesting adduct. Upon cycloaddition and 1,4-sigmatropic rearrangement, the substituted imidazo[4,5-*d*]-1,2,3-triazole system **(83)** was isolated (Scheme 1.36).



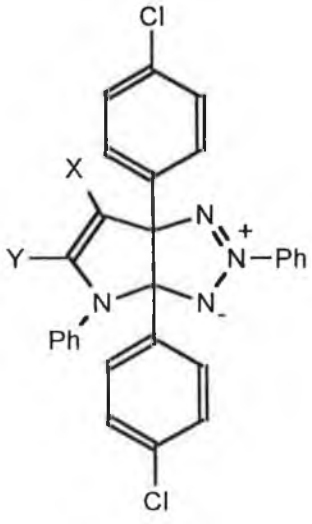
(13) (83)

Scheme 1.36 Cycloaddition of BPAS and PIC

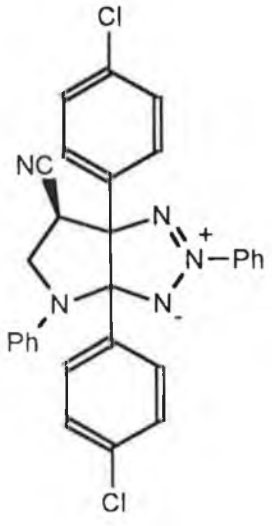
During the course of our work, these systems were reported along with analogues formed on addition of aryl isothiocyanate.[36] (see Scheme 1.18) A feature of these systems is that for equivalent aryl substituents, there is a plane of symmetry across the centre of the molecule, similar to that found for **(71)**. The number of ^{13}C nmr signals is halved and only one signal was observed for the bridgehead carbons C-3a and C-6a. The introduction of different substituents on the aryl rings removes this plane of symmetry and the full number of signals was observed.[36] This demonstrates the 1,3-dipolar character of the three contiguous nitrogen atoms on the triazole ring.

1.2b.3) Cycloadditions of 4,5-Diaryl-2-phenyl-1,2,3-triazolium-1-(N-phenyl)imides.

The cycloadditions of 4,5-bis(4'-chlorophenyl)-2-phenyl-1,2,3-triazolium-N-phenylimide **(13, R=4'-Cl-C_6H_4, Ar=Ph)** with DMAD, MP and AN led to the previously unreported cycloadducts **(84a, X=CO_2Me, Y=CO_2Me)**, **(84b, X=CO_2Me, Y=H)** and **(85)** *via* the mechanism outlined in Scheme 1.11 Characterization by spectroscopic techniques, showed the expected signals, including the two bridgehead signals in the ^{13}C nmr.



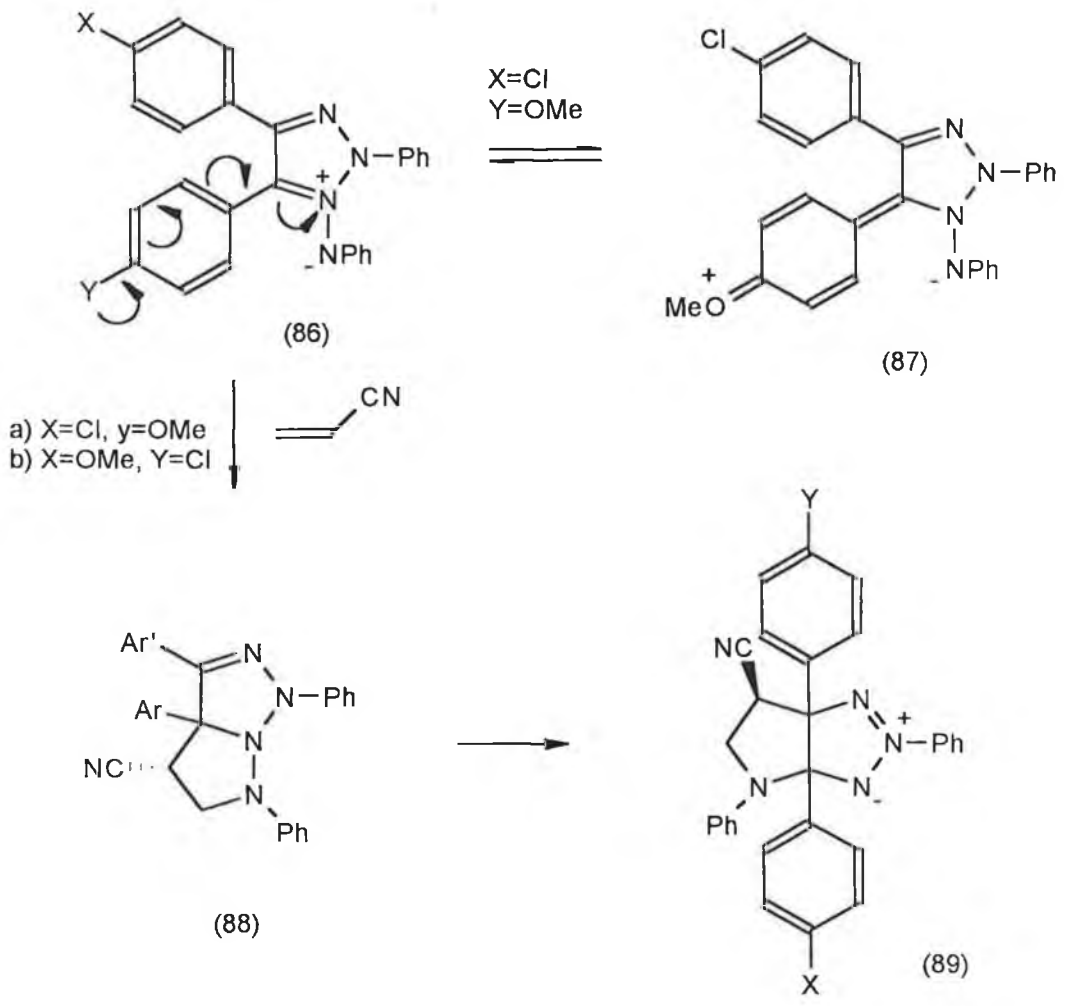
(84)



(85)

The cycloaddition of the oxidation product of bisphenylhydrazone of 1-(4'-chlorophenyl)-2-(4'-methoxyphenyl)-1,2-dione **(86)** with acrylonitrile produced, on work-up, a yellow crystalline solid. The identity of the product was determined by ir and nmr spectroscopic techniques and also by CHN analysis to be 5-cyano-3a-(4'-chlorophenyl)-6a-(4'-methoxyphenyl) 2,4-diphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-*d*]-1,2,3-triazole **(89a)**. An explanation for the formation of **(89a)** as opposed to **(89b)** can be found in the orientation of the aryl groups on **(86)**. The *p*-OMe-phenyl group at C-4 provided better resonance stabilization of the iminium charge in the triazole ring due to the contributor

(87), and thus dynamic equilibrium between the two possible triazolium isomers **(86a)** and **(86b)** should rest in favour of the former. (Scheme 1.37)



Scheme 1.37 Cycloaddition of unsymmetrically substituted triazolium imides **(85)** with AN.

On cycloaddition with **(86a)** and 1,4-sigmatropic rearrangement the *p*-OMe-phenyl group occurs at C-6a. The ^{13}C shift of C-6a in **(89a)** (at 87.81ppm) was 0.20 ppm downfield of that for the 3a,6a-bis(*p*-chlorophenyl) analogue **(85)**. The C-3a signal for **(89a)** appeared at 98.83, 0.23ppm upfield of the corresponding signal for **(85)** Also observed in very low

yield from the cycloaddition reaction was a species, the ^{13}C nmr spectrum of which produced signals at 87.27 and 99.52ppm, attributed to **(89b)**. This compound was not isolated. A list of physical data for the cycloadducts of **(13, R=Ar)** is given in Table 1.7.

Table 1.7. Physical Data for cycloadducts of **(13, R=Ar)**

Cmpd No.	Mol. formula	M.w	Yield (%)	M.P(°C)	Found (Theory) (%) C	H	N
81a	$C_{32}H_{26}N_4O_4$	530.58	88	185-187	72.62 (72.44)	5.01 (4.94)	10.43 (10.56)
81b	$C_{30}H_{24}N_4O_2$	472.55	90	164-166	75.97 (76.24)	5.20 (5.12)	11.61 (11.86)
82a	$C_{30}H_{26}N_4O_2$	474.56	86	190-191	75.78 (75.93)	5.42 (5.52)	11.69 (11.81)
82b	$C_{30}H_{26}N_4O$	458.56	81	210-203	78.69 (78.58)	6.00 (5.71)	11.30 (12.22)
82c	$C_{29}H_{23}N_5$	441.54	74	244-246	79.34 (78.89)	5.45 (5.25)	15.19 (15.86)
82d	$C_{31}H_{28}N_4O_2$	488.59	79	210-212	73.92 (76.21)	5.77 (5.78)	10.87 (11.47)
82e	$C_{31}H_{28}N_4O_2$	488.59	83	201-203	76.34 (76.21)	5.96 (5.78)	11.26 (11.47)
82f	$C_{32}H_{28}N_4O_4$	532.58	83	199-201	72.36 (72.17)	5.32 (5.30)	10.41 (10.52)
82g	$C_{32}H_{28}N_4O_4$	532.58	79	203-205	72.03 (72.17)	5.33 (5.30)	10.67 (10.52)
83	$C_{33}H_{25}N_5O$	508.59	87	231-233	78.32 (78.09	5.07 (4.96)	13.51 (13.80)

Table 1.7 Continued

84a	$C_{32}H_{24}Cl_2N_4O_4$	599.47	87	174-176	64.35	4.00	9.21
					(64.11)	(4.04)	(9.35)
84b	$C_{30}H_{22}Cl_2N_4O_2$	541.44	82	176-178	66.25	4.09	10.05
					(66.54)	(4.07)	(10.35)
85	$C_{29}H_{21}Cl_2N_5$	510.43	85	225-227	68.73	4.35	13.39
					(68.24)	(4.15)	(13.89)
89a	$C_{30}H_{24}ClN_5O$	506.01	65	220-222	70.98	4.83	13.92
					(71.21)	(4.78)	(13.84)

1.2c) Reductions of Substituted 2,3a,4,6a-tetraphenyl-3,3a,4,6a-tetrahydropyrrolo[2,3-*d*]-1,2,3-triazol-2-ium-3-ides.

In an attempt to synthesise analogues of **(81)** which contained electron donating substituents at C-5 and C-6, the reduction of the DMAD and MP adducts **(81a)** and **(81b)** was carried out.

The reduction of α,β-unsaturated esters has been carried out in good to moderate yield by K.Saoi *et al.*[69] They reported that *trans*-methyl cinnamic ester was reduced to the corresponding vinylic alcohol in 71% yield. The fully reduced alcohol was produced in 22% yield. The reducing agent used was $LiBH_4$-MeOH-Et_2O. Lithium borohydride-catalysed selective reduction of the carbonyl group of conjugated alkenones has been achieved with borane in THF at -50°C.[70]

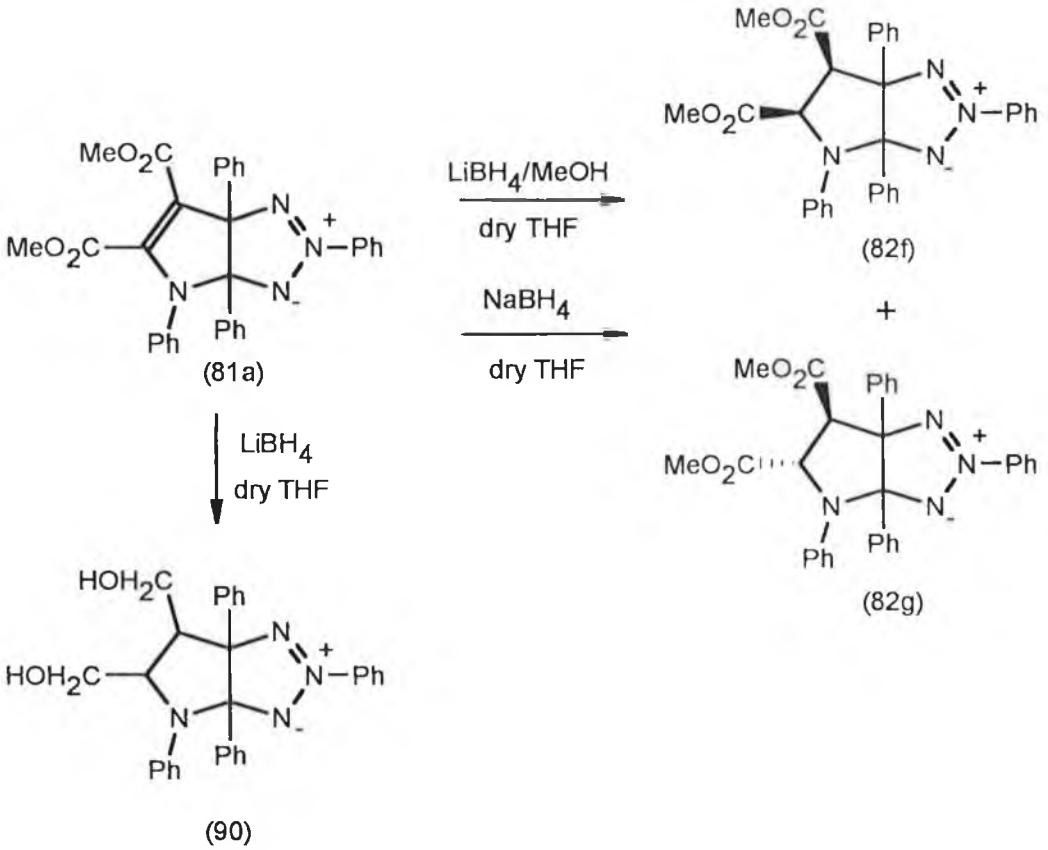
Reduction of 5,6-bis(methoxycarbonyl)-2,3a,4,6a-tetraphenyl-3,3a,4,6a-tetrahydropyrrolo[2,3-*d*]-1,2,3-triazole **(81a)** in dry Et_2O, proved difficult due to the insolubility of the starting material in the solvent. Alternate conditions were therefore required to promote reaction. $LiBH_4$/MeOH/THF is a more potent reducing agent and has the advantage that the starting material is soluble in THF.[69] Reaction of **(81a)** with this reagent in excess, produced two products, the two diastereoisomers **(82f)** and **(82g)**. The yields of the *cis*- and *trans*-isomers **(82f)** and **(82g)** were 67% and 13% respectively. (Scheme 1.38)

The structures of the products were confirmed by spectroscopic techniques and by comparison with the spectra of the same products formed by cycloaddition of BPAS to DMM and DMF.

$LiBH_4$ reductions are analogous to those of $NaBH_4$ except that lithium cation is the electrophile which is bonded to the carbonyl oxygen. $NaBH_4$ reductions require the

presence of an electrophilic catalyst such as a protic solvent in order for reactions to occur.

Reactions reported in anhydrous, alcohol free solvents generally occur during work-up with H_2O or alcohol. The reaction occurs through transfer of a hydride ion to the carbonyl carbon atom with prior or concurrent protonation of the carbonyl oxygen atom. All four hydrogens of $NaBH_4$ may be used in the reduction process. The lithium cation has been shown to be a better electrophilic catalyst than is the proton abstracted from the alcohol. This catalytic effect is no longer observed when the reduction is conducted in aqueous solution, where the lithium cation would be strongly solvated.



Scheme 1.38 Metallic hydride reductions of **(81a)**.

Reaction of the **(81a)**, in dry THF, with an excess of $NaBH_4$, resulted in the formation of the same two products **(82f)** and **(82g)**, but the yields were 39% and 51% for the *trans*- and *cis*-isomers respectively. (Scheme 1.38)

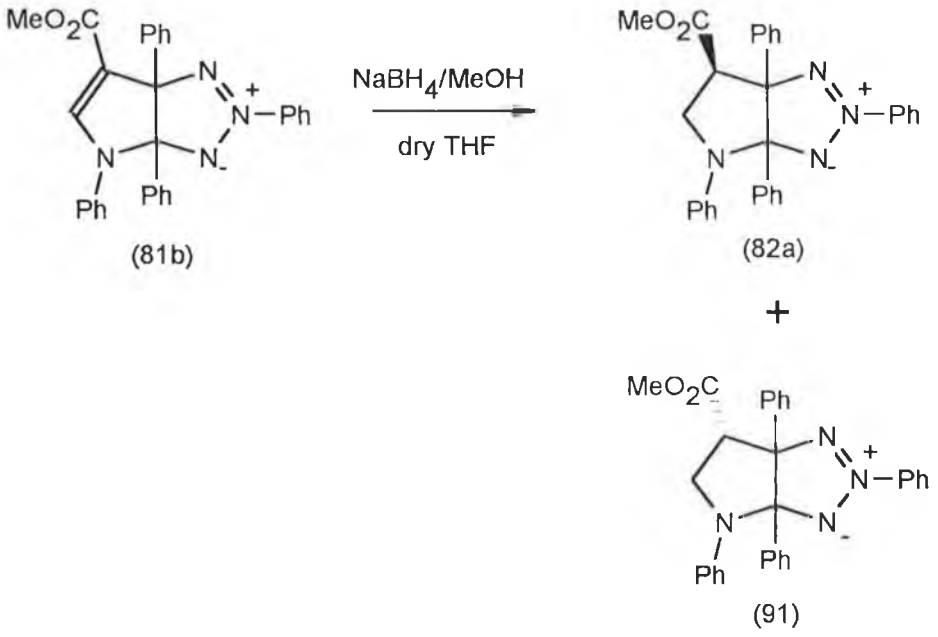
In order to reduce the ester moieties another reducing system was attempted. Reduction with an excess of $LiBH_4$ in dry THF resulted in one product. On characterisation it was found to be the fully reduced 5,6-bis(hydroxy methyl)-2,3a,4,6a-tetraphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-*d*]-1,2,3-triazole **(90)**. (Scheme 1.38)

Metallic hydrides (*e.g.* $LiAlH_4$, $NaBH_4$, $LiBH_4$) do not in general reduce C=C bonds, but can do so when the double bond is polar. They have been known to reduce double bonds in conjugation with C=O bonds as well as reducing the C=C bonds.[71] $NaBH_4$ has greater tendency than $LiAlH_4$ to effect this double bond reduction, though even with $NaBH_4$ the product of single reduction (*i.e.* of the C=O bond) is usually formed in larger amounts than the doubly reduced product. $LiAlH_4$ gives significant double bond reduction only in cinnamyl systems, *e.g.* with PhCH=CHCOOH. $LiAlH_4$ is attacked vigorously by H_2O and alcohols to give off hydrogen. Reductions using this reducing agent are therefore carried out in aprotic solvents.[72]

Reduction of **(81a)** with $LiAlH_4$ in dry THF resulted in no significant reaction. Alkyl esters in general are very slow to react with $LiAlH_4$. The reduction rate is also decreased by steric hindrance and the presence of conjugating substituents. $LiAlH_4$ reduction involves transfer of hydride to the carbonyl carbon atom which is assisted by prior or concurrent association of the carbonyl oxygen with a lithium cation, converting the carbonyl to a lithium alkoxyaluminium hydride. Each step becomes increasingly slower due to increased difficulty in removing hydride from the metal complex as the number of electronegative alkoxy substituents in the complex is increased. Alkoxy aluminium hydride derivatives have been prepared which are less reactive and therefore more selective, *e.g.* $LiAlH(OMe)_3$. Asymmetric reducing agents have been prepared by

complexing to β-amino alcohols or 1,2-diols and these have been used to form asymmetric reduction products.[72]

On examination of these results it was clear that the C=C bond was highly activated by the ester substituents and that reduction of the double bond occurred prior to reduction of the ester. A less highly activated C=C system would be required if reduction to the alcohol was to be achieved. With this in mind the mono-ester, **(81b)** was reduced using $NaBH_4$ / MeOH in dry THF. There were two products, the *exo*- and *endo*-hexahydro-analogues **(82a)** and **(91)**. The yields were 12% and 72% respectively. (Scheme 1.39) Again characterisation was achieved using spectroscopic techniques and by comparison with data obtained for the *exo*-isomer formed *via* the cycloaddition of BPAS and MA **(82a)**.



Scheme 1.39. Sodium borohydride reduction of **(81b)**

If there is a chiral centre next to the site of reduction of an sp^2 carbon, even achiral reducing agents may produce an excess of one diastereoisomer over the other, and diastereoselective reductions have even been carried out when the sp^2 carbon is part of a

carbonyl group.[60] In these cases the direction of attack is generally predicted by Cram's rule.[73]

Another factor influencing steroechemical control on the reaction is product development control, *i.e.* the more stable product will be formed in preference. For example, an equatorial substituent is more stable than an axial one, and this isomer is formed in preference unless there is severe hindrance to the approach of the reagent. The formation of pairs of epimers on reduction of the C5-C6 double bond of the cycloadducts is dictated by the substitution pattern about the site of attack and by the mechanism of attack of the reducing agent. A number of other reductions would have to be carried out before a definite trend could be identified, although it does appear that the presence of methanol in the reagent has an effect on the direction of attack. The presence of methanol led to the formation of methoxyborohydride which being bulkier than the reagent in the absence of alcohol was more influenced by steric considerations and led to the production of an excess of one epimer over the other.

1.3) CONCLUSIONS

In this section we have reported cycloaddition reactions leading to five types of adducts.

i) 3a,6a-Dimethyl hexahydropyrrolotriazoles (Type A) *e.g.* **(70)** These previously unreported cycloadducts were produced in moderate to high yield The cycloaddition was complicated by the formation of the substituted aniline **(46)** and the triazole **(67)**, formed from the triazolium N-imide 1,3-dipole. Acid catalysed epimerization of 6-*exo*-cyano-3a,6a-dimethyl-2,4-diphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-*d*]-1,2,3-triazole **(70c)** to the *endo*-epimer **(76)** was also observed.

ii) 3a,6a-Dimethyl tetrahydropyrrolotriazoles (Type B) *e.g.* **(69)** The range of cycloadducts of this type has been extended, being produced in high yield. Cycloaddition reactions leading to these systems were less complicated by the side reactions seen for Type A cycloadducts

iii) 3a,6a-Diaryl hexahydropyrrolotriazoles (Type C) *e.g.* **(82)**, **(85)** and **(89)**: A variety of new cycloadducts of this type were synthesised. For the unsymetrically substituted triazolium N-imide **(86)** cycloaddition produced one isomer predominately, due to favourable resonance stabilization of **(86a)**.

iv) 3a,6a-Diaryl tetrahydropyrrolotriazoles (Type D) *e.g.* **(81)** and **(84)**: The range of cycloadducts of this type was extended to include structural variation at C-3a, C-5 and C-6 and C-6a. The reduction of Type D cycloadducts **(81a and b)** led to diastereoisomeric Type C cycloadducts, the quantity of which depended on the reducing system used

v) Imidazotriazoles (Type E) *e.g.* **(71, 83)**: These imidazotriazoles both contain a plane of symmetry along the centre of the molecule leading to a great simplification of the nmr spectra, the number of non-equivalent signals being reduced by half compared to unsymmetrical cycloadducts such as **(70)** or **(82)**

1.4) EXPERIMENTAL

Infrared spectra were measured on a Perkin-Elmer 938G, a Nicolet 205 FT-IR, and a Perkin-Elmer 2000 FT-IR spectrophotometer. NMR spectra were recorded on a Bruker AC400, 400MHz spectrometer. U.V.spectra were recorded on a Hewlett Packard 8452A Diode Array Spectrophotometer. Microanalytical data was provided by the Chemistry Department in University College, Dublin. X-Ray crystallographic data was collected on an Enraf Nonius CAD4 single crystal diffractometer using graphite monochromated Mo-Kα radiation. The data sets were collected in the Department of Chemistry, Trinity College, Dublin by Dr. Conor Long, Sylvia Draper and Deborah Wilcox.
The synthesis and oxidation of the aryl hydrazones of 1,2-diones was carried out as described previously, as was the synthesis and oxidation of the substituted benzoins.[37]

1.4a) Synthesis of Cycloadducts of 4,5-Dimethyl-2-aryl-1,2,3-triazolium-1-(N-imide).

1.4a.1) Formation of 4,5-bis(methoxycarbonyl)-3a,6a-dimethyl-2,6-diphenyl-3, 3a, 4, 6a-tetrahydropyrrolo[2,3-d]-1,2,3-triazole ***(69a)***.

HCl (produced from c.H_2SO_4 dropping on NH_4Cl [$2NH_4Cl + H_2SO_4 \rightarrow HCl + (NH_4)_2SO_4$]), passed through a Dreschel bottle containing c.H_2SO_4, and an air trap, was passed through a refluxing solution of 2.0g (7.6 mmol) BPAB and 1.42g (10.0 mmol) DMAD in a minimum of acetone, for about 1 minute, until the solution turned from deep purple to clear yellow. The solution was allowed to reflux, upon removal of HCl generator, for a further 15 minutes. Upon allowing the solution to cool to room temperature, the acetone was removed under reduced pressure. The resultant oil was crystallised using a 1:1 mixture of pet. ether (40-60) and dichloromethane. The yellow solid was filtered off under vacuum and washed using diethyl ether. Recrystallisation from

ethanol yielded yellow crystals of **(69a)** (82%) which produced a single spot on TLC (3:1 pet. ether/ethyl acetate as eluant), m.p.136-138°C.

IR (cm^{-1})(KBr): 1737, 1691 (ester C=O), 767, 698.

CHN Analysis (found / theory) (%): M.w. 406.44; $C_{22}H_{22}N_4O_4$; C (64.87 / 65.01), H (5.44 / 5.46), N (13.65 / 13.78)

δH (CD_3CN) (ppm): 1.47 (3H, s) (CH_3), 1.81 (3H, s) (CH_3), 3.64, 3.65 (both 3H, s) (both $COOCH_3$), 7.38 (5H, m), 7.54 (2H, t), 7.61 (1H, t), 8.10 (2H, d) (all phenyl H).

δC (ppm) (CD_3CN): 17,58, 17.44 (both CH_3), 50.52, 52.48 (CO_2CH_3), 82.77 (C-6a), 100.25 (C-3a), 105.29 (C-6), 117.34, 122.32, 122.35, 126.30, 127.42, 129.08, 129.21, 131.64, 137.56, 139.32 (all phenyl C and C-5), 163.30, 164.02 (ester C=O).

U.V. spectrum (MeCN) (nm): 248, 288 (ε = 22630, 26010 l $mol^{-1}cm^{-1}$)

1.4a.2) Formation of 6-methoxycarbonyl-3a,6a-dimethyl-2,4-diphenyl-3,3a,4,6a-tetrahydropyrrolo[2,3-d]-1,2,3-triazole ***(69b).***

A stream of dry HCl was passed through a refluxing solution of 2.0g (7.6 mmol) BPAB and 1.0g (11.9 mmol) MP until the solution turned from deep purple to clear yellow. The HCl source was removed and the solution allowed to reflux for a further 15 minutes. On removal of the acetone under vacuum the resultant oil was taken up in 15cm^3 ethyl acetate and washed 3 times with 10cm^3 aliquots of saturated $NaHCO_3$ solution. The solution was then washed three times with water (10 cm^3). The ethyl acetate solution was then dried over $MgSO_4$ for ~1 hour. The $MgSO_4$ was then filtered off and the ethyl acetate removed under vacuum. The product was then crystallised using a 1:1 mixture of DCM / pet.ether (40-60). The yellow powder was recrystallised from ethanol to yield yellow crystals of **(69b)** (78%), which produced a single spot on TLC (3:1 pet.ether (40-60) / ethyl acetate as eluant), m.p.: 117-118°C.

CHN analysis (found / theory) (%): M.w. 348.40; $C_{20}H_{20}N_4O_2$; C (68.67 / 68.93), H (5.89 / 5.79), N (15.92 / 16.09)

IR (KBr) (cm^{-1}) 1689 (C=O), 763, 689.

δH ($CDCl_3$) (ppm): 1.64, 1.76 (2x3H, s) (CH_3), 3.74 (3H, s) (OCH_3), 7.73 (1H, s) (C=CH), 7.10 (1H, t), 7.33 (2H, t), 7.45 (5H, m), 8.14 (2H, d) (all phenyl CH)
δC ($CDCl_3$) (ppm): 17.92 (CH_3), 18.04 (CH_3), 50.79 (OCH_3), 83.72, (C-6a), 99.99 (C-3a), 107.45 (C-6) 119.74, 122.89, 124.05, 128.73, 129.35, 131.42, 140.55, 147.73 (all phenyl C), 140.54 (C-5), 165.82 (ester C=O)

1.4a.3) Formation of 5,6-bis(methoxycarbonyl)-3a,6a-dimethyl-2,4-bis(p-nitrophenyl)-3,3a,4,6a-tetrahydropyrrolo[2,3-d]-1,2,3-triazole ***(69c)***

A stream of dry HCl was passed through a refluxing solution of 2.0g (5.49 mmol) *trans*-1,2-bis(4'-nitrophenylazo)butene and 1.0g (7.04 mmol) DMAD, until the solution turned from very dark brown-purple to clear yellow. The source of HCl was removed and the solution refluxed for a further 15 minutes. The acetone was removed under vacuum and the residue taken up in ethyl acetate. The solution was washed with $15cm^3$ aliquots of sat. $NaHCO_3$ and then with water. The solution was dried over $MgSO_4$ which was then filtered off under vacuum. After removal of the solvent under reduced pressure the product was crystallised from ethyl acetate / pet.ether(40-60) (1:2), and recrystallised from ethanol to yield 69% (1.88g) of **(69c)**, m.p.151-153°C.
CHN Analysis (found / theory) (%): M.w.: 496.44; $C_{22}H_{20}N_6O_8$; C (53.13 / 53.23), H (3.93 / 4.06), N (16.80 / 16.93)
IR (KBr) (cm^{-1}): 1721, 1696 (C=O), 858, 748, 691 (*p*-disubstituted phenyl)
δH (DMSO-d_6) (ppm): 1.53, 1.84 (both 3H, s) (both CH_3), 3.68, 3.77 (2 x 3H, s) (OCH_3), 7.60 (2H, d), 8.32 (2H, d), 8.42 (4H, dd) (*p*-disubstituted phenyl CH)
δC (DMSO-d_6) (ppm): 17.93, 18.02 (2 x CH_3), 51.30, 53.22 (2 x OCH_3), 83.31 (C-6a), 100.14 (C-3a), 108.76 (C-6), 123.93, 124.11, 124.71, 125.02, 143.20, 144.67, 149.114, 150.07 (phenyl C), 143.13 (C-5), 162.30, 162.94 (both ester C=O).
U.V. (MeCN) (nm): 270, 364 (ε = 24176, 13085 $l\ mol^{-1}cm^{-1}$) (a shoulder was also seen on the visible side of the peak at 208nm)

1.4a.4) Formation of 6-methoxycarbonyl-3a, 6a-dimethyl-2,4-diphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-d]-1,2,3-triazole ***(70a).***

A stream of dry HCl was passed through a refluxing solution of 2.0g (7.6 mmol) BPAB and 1.0g (11.6mmol) MA in dry acetone, until the deep purple colour changed to clear yellow. The acetone was removed under vacuum. The resultant oil was taken up in 15cm^3 ethyl acetate and washed 3 times with 10cm^3 aliquots of saturated $NaHCO_3$ solution. The solution was then washed three times with water (10cm^3). The ethyl acetate solution was then dried over $MgSO_4$ for approx. 1 hour. The $MgSO_4$ was then filtered off under reduced pressure and the ethyl acetate removed under vacuum. The residue was passed through a flash chromatography column (silica gel (mesh size 0.032-0.063mm)), using (1:3) ethyl acetate / pet.ether (40-60) as eluant. The product was then crystallised using a 1:2 mixture of DCM / pet.ether (40-60). Recrystallisation from ethanol yielded 1.92 g (5.48mmol) (72%) of the yellow solid **(70a)**, m.p.: 87-89°C.

CHN Analysis (found / theory) (%): M.w.: 350.42; $C_{20}H_{22}N_4O_2$; C (68.39 / 68.55), H (6.34 / 6.33), N (16.08 / 15.99).

IR (KBr) (cm^{-1}): 1729 (CO_2CH_3), 773, 751, 716, 695, 690.

δH ($CDCl_3$) (ppm): 1.30 (3H, s) (CH_3), 1.58 (3H, s) (CH_3), 3.44 (1H, dd, *J*=7.39, 11.82) (CH), 3.57 (2H, dd, *J*=10.82, 11.82) (CH_2), 3.81 (3H, s) ($COOCH_3$), 6.84 (1H, t), 7.25 (4H, m), 7.47 (3H, m), 8.11 (2H, d) (all phenyl H).

δC ($CDCl_3$) (ppm): 15.82 (CH_3), 15.86 (CH_3), 46.66 (C-6), 51.95, 52.38 ($COOCH_3$, C-5), 81.54 (C-6a), 93.77 (C-3a), 116.35, 118.56, 122.69, 128.67, 128.76, 131.23 (phenyl CH), 140.70, 144.90 (phenyl C), 172.32 (C=O).

U.V. (MeCN) (nm): 256 (ε = 10439 l mol^{-1}cm^{-1})

1.4a.5) Formation of 6-methylcarbonyl-3a,6a-dimethyl-2,4-diphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-d]-1,2,3-triazole ***(70b).***

A stream of dry HCl was passed through a refluxing solution of 2.0g (7.6 mmol) BPAB and 1.0g (14.3 mmol) MVK in dry acetone, until the deep purple colour changed to clear

yellow. The source of HCl was then removed and the solution allowed to reflux for a further 15 minutes. The solvent was evaporated under vacuum and the residue taken up in ethyl actetate. The work-up was carried out as described in 1.4a.4 and the product was separated on a flash chromatography column (silica gel, 0.032-0.063 mm mesh size). A 3:1 mixture of pet.ether (40-60) / ethyl acetate was used as eluant. The product was recrystallised from ethanol to yield 1.78g (70%) of the yellow solid **(70b)**, m.p.:100-102°C.

CHN Analysis (found / theory) (%): M.w.: 334.42; $C_{20}H_{22}N_4O$; C (71.95 / 71.83), H (6.67 / 6.63), N (16.98 / 16.75).

IR (KBr) (cm^{-1}): 1702 ($COCH_3$), 772, 761, 725, 701, 689.

δH ($CDCl_3$) (ppm): 1.30 (3H, s) (CH_3), 1.43 (3H, s) (CH_3), 2.41 (3H, s) ($CH_3C(=O)$), 3.25 (1H, dd), 3.41 (1H, dd) (CH_2), 3.51 (1H, t) (CH) (J_{am} =9.85, J_{ax} =9.35, J_{mx} =6.89), 6.83 (1H, t), 7.18 (2H, d), 7.27 (2H, t), 7.49 (3H, m), 8.18 (2H, d) (all phenyl H).

δC ($CDCl_3$) (ppm): 15.24 (CH_3), 16.38 (CH_3), 31.25 ($CH_3(C=O)$), 44.53 (C-6), 60.99 (C-5), 80.44 (C-6a), 94.77 (C-3a), 116.57, 118.65, 122.47, 128.70, 128.72, 131.23 (all phenyl CH), 140.71, 144.93 (phenyl C), 207.49 (C=O).

U.V. (MeCN) (nm): 248 (ε = 27891 l $mol^{-1}cm^{-1}$)

1.4a.6) Formation of 6-exo-cyano-3a,6a-dimethyl-2,5-diphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-d]-1,2,3-triazole ***(70c)***.

Dry HCl (prepared as above) was passed through a refluxing solution of 2,3-butanedione bisphenylhydrazone (2.0g, 7.6 mmol) and 1.0g (18.9 mmol) AN in dry acetone, until the solution turned from deep purple to yellow. After removal of the HCl, the solution was left refluxing for about 15 minutes. The acetone was removed under vacuum The work up was carried out as described in 1.4a.4. The residue was passed through a flash chromatography column (silica gel (mesh size 0.032-0.063 mm)), using (1:3) ethyl acetate / pet.ether (40-60) as eluant. The product was then crystallised using a 1:2 mixture of DCM / pet.ether (40-60). The powder was recrystallised from ethanol to yield 1.55g

(62%) of yellow crystals of **(70c)**, which produced a single spot on TLC (3:1 pet.ether (40-60) / ethyl acetate as eluant), m.p.: 173-174°C.

CHN Analysis (found / theory) (%): M.w.: 329.40; $C_{19}H_{19}N_5$; C (72.03 / 71.90), H (6.11 / 6.03), N (21.81 / 22.07).

IR (cm^{-1}) (KBr): 2243 (-CN), 769, 760, 701, 686.

δH (DMSO-d_6) (ppm): 1.7 (3H, s), 1.8 (3H, s), 3.7 (3H, m), 7.1 (1H, t), 7.4 (5H, m), 7.6 (2H, t), 7.7 (1H, t), 8.2 (2H, d).

δC (DMSO-d_6) (ppm): 17.48, 17.72 (2x-CH_3), 39.17 (C-6), 49.04 (C-5), 80.91, 93.20 (quaternary C), 118.56 (-CN), 118.03, 120.23, 122.60, 128.85, 128.95, 131.63, (phenyl CH), 140.34, 144.14 (phenyl C).

U.V. (MeCN) (nm): 246 (ε = 19379 l $mol^{-1}cm^{-1}$) Two shoulders are seen on the visible side of the peak at 246nm.

*1.4a.7) Formation of 6-*endo*-cyano-3a,6a-dimethyl-2,5-diphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-d]-1,2,3-triazole (76).*

The product **(76)** was isolated from the above cycloaddition mixture and was eluted from the flash chromatography column with longer retention time than **(70c)**. It was crystallised from diethyl ether and was recrystallised from ethanol to yield 220mg (9%) of a yellow solid, M.P.: 174-176°C

This product is also formed on acid catalysed epimerization of the *exo*-isomer **(70c)**. (See 1.4c.7)

CHN Analysis (found / theory) (%): M.w.: 329.40; $C_{19}H_{19}N_5$; C (71.40 / 71.09), H (6.13 / 6.03), N (22.27 / 22.07).

IR (cm^{-1}) (KBr): 2247 (C≡N), 772, 753, 668.

δH (ppm) ($CDCl_3$):1.53, (3H, s) (CH_3), 1.70 (3H, s) (CH_3), 3.40 (2H, m) (CH_2), 3.80 (1H, dd) (CH) (*J*=11.32, 12.80 Hz), 6.91 (1H, t), 7.18 (2H, d), 7.28 (2H, t), 7.44 (2H, t), 7.51 (1H, t), 8.11 (2H, d) (all monosubstituted phenyl).

δC (ppm) ($CDCl_3$):18.27, 18.81 (2x CH_3), 39.80, (C-6), 50.12 (C-5), 81.07 (C-6a), 92.85 (C-3a), 117.75 (C≡N), 117.99, 120.18, 122.87, 128.79, 128.94, (all phenyl CH) 131.59, 143.82 (4-N-Ph, C-1' and 2-N-Ph, C-1').

U.V. (MeCN) (nm): 240 (ε = 18903 l $mol^{-1}cm^{-1}$). Shoulders are seen on the visible side of this peak.

1.4a.8) Formation of 3a,6a-dimethyl-2,4,6-triphenyl-5-oxo-3,3a,4,5,6,6a-hexahydroimidazo[4,5-d]-1,2,3-triazole ***(71).***

A solution of 500mg (1.89 mmol) BPAB in dry refluxing acetone and excess of PIC (3.0 mmol) was treated with dry HCl until the colour changed from deep purple to off-white. On removal of the HCl, the solution was stirred under reflux for a further 15 minutes. The solvent was then removed under vacuum and the residue taken up in ethyl acetate. The excess HCl removed by treatment with 15cm^3 aliquots of saturated $NaHCO_3$ and then water. The solution was dried over $MgSO_4$ and the solvent subsequently removed under vacuum. The residue was recrystallised from ethanol to yield 399mg (55%) of the clear white needles of **(71)**, m.p.: 161-162°C.

CHN analysis (found / theory) (%): M.w.: 383.45; $C_{23}H_{21}N_5O$; C (72.25 / 72.04), H (5.66 / 5.52), N (18.53 / 18,26).

IR (KBr) (cm^{-1}): 1702 (C=O), 856, 752, 722, 712, 681.

δH (DMSO-d_6) (ppm): 1.73 (6H, s) (C-3a and C-6a CH_3), 7.49 (2H, t), 7.64 (4H, t), 7.81 (6H, m), 7.89 (1H, t), 8.42 (2H, d) (all phenyl H).

δC (DMSO-d_6) (ppm): 18.09 (CH_3), 90.07 (C-3a, C-6a), 122.29, 126.09, 126.31, 128.61, 129.30, 132.22, 136.28, 139.54 (all phenyl C), 154.61 (C=O).

1.4b) Synthesis of 1,3-dipolar cycloadducts of 4,5-Diaryl-2-phenyl-1,2,3-triazolium-1-(N-phenyl)imide.

1.4b.1) Formation of 5,6-bis(methoxycarbonyl)-2,3a,4,6a-tetraphenyl-3,3a,4,6a-tetrahydropyrrolo[2,3-d]-1,2,3-triazole ***(81a)***.

To a solution of BPAS (1.5g, 3.9 mmol) in dry acetone (30 cm^3) was added DMAD (1g, 7.0 mmol) and the mixture stirred under reflux for 1 hour, whereupon the solution turned from brown to yellow. The acetone was then removed under reduced pressure. Recrystallisation of the residue from ethanol gave yellow crystals of **(81a)** in 88% yield.
M.p. 185-187°C (Lit. 187°C).
CHN Analysis (found / theory): M.w.: 530.58; $C_{32}H_{26}N_4O_4$; C (72.62 / 72.44), H (5.01 / 4.94), N (10.43 / 10.56)
IR (KBr) (cm^{-1}): 1748, 1689 (ester C=O), 778, 762, 746, 734, 697.
δH ($CDCl_3$) (ppm): 3.60 (3H, s), 3.83 (3H, s) (both ester CH_3), 6.99 (11H, m), 7.16 (2H, t), 7.34 (2H, d), 7.55 (2H, t), 7.62 (1H. t), 8.42 (2H, d).
δC ($CDCl_3$) (ppm): 51.53, 52.34 (both ester CH_3), 91.24 (C-6a), 104.19 (C-3a), 105.52 (C-6), 122.12, 123.72, 125.49, 126.31, 126.67, 126.72, 126.81, 127.07, 128.13, 128.32, 131.33, 134.69, 136.52, 137.60, 139.52, 154.39 (phenyl C and C-5), 162.51, 163.44 (2x ester C=O).
M S: fragments (amu) :530, 471, 412, 368, 180, 77, 51.
U.V. (MeCN) (nm): 276, 346 (ε = 89230, 12765 l $mol^{-1}cm^{-1}$)

4.1.b.2) Formation of 6-methoxycarbonyl-2,3a,4,6a-tetraphenyl-3,3a,4,6a-tetrahydropyrrolo[3,2-d]-1,2,3-triazole ***(81b)***.

To a refluxing solution of 1.5g (3.9 mmol) BPAS in dry acetone was added 1.0g (11.9 mmol) MP. The solution was stirred until the brown colour turned to clear yellow. The solvent was evaporated under vacuum and the residue recrystallised from ethanol to yield 1.60g (87%) of yellow crystals of **(81b)**, m.p.: 164-166°C.

CHN Analysis (found / theory) (%): M.w.: 472.55; $C_{30}H_{24}N_4O_2$; C (75.97 / 76.24), H (5.20 / 5.12), N (11.61 / 11.86).

IR (KBr) (cm^{-1}): 1708 (ester C=O), 772, 760, 750, 726, 698, 688.

δH ($CDCl_3$) (ppm): 3.66 (3H, s) (CO_2CH_3), 6.97 (11H, m), 7.18 (2H, t) 7.25 (2H, d), 7.54 (2H, t), 7.60 (1H, t), 8.44 (2H, d) (all phenyl H), 8.43 (1H, s) (C-5-H).

δC ($CDCl_3$) (ppm): 51.06 (ester CH_3), 92.80 (C-6a), 105.64 (C-3a), 107.28 (C-6), 118.07, 122.76, 123.13, 126.87, 127.49, 127.51, 127.61, 128.94, 129.09, 131.84, 135.76, 137.48, 139.19, 148.94 (all phenyl C and C-5), 165.46 (ester C=O).

U.V. (MeCN) (nm): 240, 298, 342 (ε = 35530, 22010, 39360 l $mol^{-1}cm^{-1}$)

1.4b.3) Formation of 3a,6a-bis(p-chlorophenyl)-5,6-bis(methoxycarbonyl)-2,4-diphenyl-3,3a,4,6a-tetrahydropyrrolo[2,3-d]-1,2,3-triazole (84a).

A solution of 1.5g (3.3 mmol) 1,2-bis(phenylazo)-1,2-bis(4'-chlorophenyl)ethylene and 1.0g (7.0 mmol) DMAD in dry acetone was allowed to reflux until the brown colour changed to clear yellow. The solvent was evaporated and the residue recrystallised from ethanol to produce 1.72g (87%) of yellow crystals of **(84a)**, m.p.: 174-176°C.

CHN analysis (found / theory) (%): M.w.: 599.47; $C_{30}H_{22}Cl_2N_4O_4$; C (64.35 / 64.11), H (4.00 / 4.04), N (9.21 / 9.35).

IR (KBr) (cm^{-1}): 1747, 1702 (C=O), 811, 774, 748, 709, 690, 688.

δH ($CDCl_3$) (ppm): 3.59 (3H, s), 3.80 (3H, s) (both $-COOCH_3$), 7.00 (9H, m), 7.17 (2H, t), 7.31 (2H, d), 7.55 (2H, t), 7.62 (1H, t), 8.39 (2H, d) (all phenyl H).

δC ($CDCl_3$) (ppm): 51.42, 53.18 (both ester CH_3), 91.50 (C-6a), 104.76 (C-3a), 105.66 (C-6), 122.94, 124.68, 126.57, 127.86, 128.00, 128.84, 128.98, 129.02, 129.22, 132.14, 133.24, 133.82, 134.10, 135.87, 137.97, 149.09, 155.40 (all phenyl C and C-5), 163.07, 164.20 (ester C=O).

U V (MeCN) (nm): 288, 365 (ε = 16950, 20140 l $mol^{-1}cm^{-1}$)

1.4b.4) Formation of 3a,6a-bis(p-chlorophenyl)-6-methoxycarbonyl-2,4-diphenyl-3,3a,4,6a-tetrahydropyrrolo[2,3-d]-1,2,3-triazole ***(84b).***

To a refluxing solution of 1.5g (3.3 mmol) 1,2-bis(phenylazo)-1,2-bis(4'-chlorophenyl)ethylene, in dry acetone, was added 1.0g (11.9 mmol) MP. The solution was stirred under reflux until the brown colour had changed to clear yellow. The solvent was removed under vacuum. Recrystallisation from ethanol yielded 1.47g (82%) of yellow crystals of **(84b)**, m.p.: 176-178°C.

CHN Analysis (found / theory) (%): M.w.: 541.44; $C_{30}H_{22}Cl_2N_4O_2$; C (66.25 / 66.54), H (4.09 / 4.07), N (10.05 / 10.35).

IR (KBr) (cm^{-1}): 1690 (ester C=O), 823, 769, 758, 745, 685.

δH ($CDCl_3$) (ppm): 3.69 (ester CH_3), 6.98 (9H, m), 7.21 (4H, m), 7.54 (2H, t), 7.61 (1H, t), 8.41 (2H, d) (all phenyl H), 8.37 (1H, s) (C=CH).

δC ($CDCl_3$) (ppm): 51.12 (ester CH_3), 92.35 (C-6a), 104.99 (C-3a), 107.04 (C-6), 118.14, 123.05, 123.19, 127.93, 128.06, 128.86, 129.00, 129.22, 132.06, 133.75, 134.33, 136.05, 138.82, 149.02 (all phenyl C and C-5)), 165.05 (ester C=O).

U.V. (MeCN) (nm): 306, 366 (ε = 20652, 1874 $l\ mol^{-1}cm^{-1}$)

1.4b.5) Formation of 6-methoxycarbonyl-2,3a,4,6a-tetraphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-d]-1,2,3-triazole ***(82a).***

A solution of 1.0g (2.6 mmol) BPAS containing an excess (1.0g, 11.6 mmol) of MA in dry acetone was refluxed for 3 hours, whereupon the colour changed from deep brown to yellow. Removal of the solvent under vacuum and recrystallisation from ethanol yielded 106 mg (86%) of the yellow compound **(82a)**, m.p.: 190-191°C.

CHN Analysis (found / theory) (%): M.w.: 474.56; $C_{30}H_{26}N_4O_2$; C (75.78 / 75.93), H (5.42 / 5.52), N (11.69 / 11.81).

IR (KBr) (cm^{-1}):1728 (ester C=O), 774, 753, 728, 719, 697, 688.

δH (CD_3CN) (ppm): 3.33 (3H, s) (ester CH_3), 4.04 (2H, m), 4.52 (1H, t, J=13.59 Hz) (5-C-H_2, 6-C-H), 6.80 (1H, t), 6.89 (2H, d), 7.10 (8H, m), 7.24 (4H, m), 7.88 (3H, m), 8.48 (2H, d) (all phenyl H).

Note: δH ($CDCl_3$): 3.38 (3H, s) (CH_3), 3.74 (1H, t, J = 9.25), 3.96 (1H, t, J = 9.25), 4.44 (1H, t, J = 9.25) (CH, and CH_2).

δC (CD_3CN) (ppm): 48.49 (C-6), 51.92 (C-5), 57.32 (ester CH_3), 89.39 (C-6a), 101.19 (C-3a), 116.12, 117.93, 122.97, 126.86, 126.94, 127.14, 127.24, 127.46, 127.62, 128.08, 128.97, 129.04, 131.67 (all phenyl CH), 136.99 (6a-C-Ph, C-1'), 137.38 (3a-C-Ph, C-1'), 140.43 (4-N-Ph, C-1'), 145.07 (2-N-Ph, C-1'), 171.05 (ester C=O).

U.V. (MeCN) (nm): 248 (ε = 15470 l $mol^{-1}cm^{-1}$). A shoulder is seen on the visible side of the peak at 248nm.

1.4b.6) Formation of 6-methylcarbonyl-2,3a,4,6a-tetraphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-d]-1,2,3-triazole (82b).

A solution of 1.0g (2.6 mmol) BPAS with an excess (1.0g, 14.4 mmol) of MVK in dry acetone was refluxed for 3 hours, whereupon the solution turned from deep brown to yellow. The solvent was removed under vacuum and the product recrystallised from ethanol to yield 966mg (81%) of the yellow product **(82b)**, m.p. 201-203°C.

CHN Analysis (found / theory) (%): M.w.: 458.56; $C_{30}H_{26}N_4O$; C (78.69 / 78.58), H (6.00 / 5.71), N (11.30 / 12.21).

IR (KBr) (cm^{-1}): 1710 (C=O), 776, 749, 720, 689.

δH ($CDCl_3$) (ppm): 2.02 (3H, s) (ketone CH_3), 3.63 (1H, dxd), 3.85 (1H, t), 4.49 (1H, t) (J_{am} = 10.09, J_{ax} = 9.85, J_{mx} = 9.35Hz) (5-C-H_2, 6-C-H), 6.71 (3H, m), 6.90 (8H, m), 7.13 (4H, m), 7.61 (3H, m), 8.49 (2H, d) (all phenyl H).

δC ($CDCl_3$) (ppm): 30.92 (ketone CH_3), 47.79 (C-6), 66.04 (C-5), 88.51 (C-6a), 101.89 (C-3a), 116.04, 117.77, 122.74, 127.07, 127.09, 127.30, 127.57, 127.59, 128.47, 129.04, 131.78 (all phenyl CH), 136.56 (6a-C-Ph, C-1'), 137.09 (3a-C-Ph, C-1'), 140.82 (4-N-Ph, C-1'), 145.13 (2-N-Ph, C-1'), 205.95 (ketone C=O).

U.V. (MeCN) (nm): 248 (ε = 19870 $lmol^{-1}cm^{-1}$). Two shoulders are seen on the visible side of the peak at 248 nm.

1.4b.7) Formation of 6-cyano-2,3a,4,6a-tetraphenyl-3,3a,4,5,6,6a-hexahydropyrrolo [2,3-d]-1,2,3-triazole ***(82c).***

A solution of 1.0g (2.6 mmol) BPAS and an excess (1.0g, 18.8 mmol) of AN in 30 cm^3 dry acetone was stirred under reflux for 3 hours, whereupon the solution turned from deep brown to yellow. Recrystallisation of the residue on removal of the solvent under vacuum resulted in 838mg (82%) of the yellow-green product **(82c)**, m.p.: 244-246°C.

CHN Analysis (found / theory) (%): M.w.: 441.54; $C_{29}H_{23}N_5$; C (79.34 / 78.89), H (5.45 / 5.25), N (15.19 / 15.86).

IR (KBr) (cm^{-1}): 2242 (CN), 774, 759, 748, 719, 695, 678, 644.

δH ($CDCl_3$) (ppm): 3.86 (1H, dd), 4.00 (1H, dd), 4.32 (1H, dd), (J_{am} = 9.45Hz, J_{ax} = 7.23Hz, J_{mx} = 5.56Hz) (5-CH_2, 6-CH), 6.78 (1H, t), 6.93 (2H, d), 7.05 (8H, m), 7.14 (2H, t), 7.22 (2H, m), 7.50 (2H, t), 7.59 (1H, t), 8.30 (2H, d).

δC ($CDCl_3$) (ppm): 41.42 (C-6), 51.42 (C-5), 88.16 (C-6a), 99.71 (C-3a), 118.49 (CN), 116.69, 119.16, 122.80, 127.48, 127.53, 127.79, 127.92, 127.97, 128.63, 129.08, 132..05 (all phenyl CH), 135.31 (6a-C-Ph, C-1'), 136.59 (3a-C-Ph, C-1'), 140.28 (4-N-Ph, C-1'), 144.07 (2-N-Ph, C-1').

U.V. (MeCN) (nm): 244 (ε = 23680 l $mol^{-1}cm^{-1}$). A shoulder is seen on the visible side of the peak at 244 nm.

1.4b.8) Formation of 6-ethoxycarbonyl-2,3a,4,6a-tetraphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3,-d]-1,2,3-triazole ***(82d).***

A solution of 1.0g (2.6 mmol) BPAS and 1.0g (10 mmol) of EA in 30 cm^3 dry acetone was stirred under reflux for 3 hours, whereupon the colour changed from brown to

yellow. The solvent was removed under vacuum and the residue recrystallised from ethanol to yield 1.05g (83%) of the yellow cycloadduct **(82d)**, m.p.: 201-203°C.

CHN Analysis (found / theory) (%): M.w.: 488.59; $C_{31}H_{28}N_4O_2$; C (76.34 / 76.21), H (5.96 / 5.78), N (11.26 / 11.47).

IR (KBr) (cm^{-1}): 1724 (ethyl ester C=O), 770, 750, 729, 718, 696, 687.

δH ($CDCl_3$) (ppm): 0.77 (3H, t) (ethyl ester CH_3), 3.70 (1H, t, J = 9.25 Hz), 3.89 (3H, m), 4.43 (1H, t, J = 9.25 Hz) (5-C-H_2, 6-C-H, ethyl ester CH_2), 6.75 (3H, m), 6.94 (8H, m), 7.14 (4H, m), 7.57 (3H, m), 8.43 (2H, d) (all phenyl H).

δC ($CDCl_3$) (ppm): 13.46 (ethyl ester CH_3), 48.46 (C-6), 57.44 (ethyl ester CH_2), 60.84 (C-5), 89.46 (C-6a), 101.21 (C-3a), 116.11, 117.87, 122.99, 126.90, 127.00, 127.09, 127.15, 127.54, 127.98, 128.93, 129.05, 131.62 (phenyl CH), 137.20 (6a-C-Ph, C-1'), 137.41 (3a-C-Ph, C-1'), 140.92 (4-N-Ph, C-1'), 145.14 (2-N-Ph, C-1'), 170.45 (C=O).

U.V. (MeCN) (nm): 248, 276 (ε = 33522, 27470 l $mol^{-1}cm^{-1}$).

1.4b.9) Formation of 6-methyl-6-methoxycarbonyl-2,3a,4,6a-tetraphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3,-d]-1,2,3-triazole ***(82e).***

A solution of 1.0g (2.6 mmol) of BPAS and an excess (1.0g, 10.0 mmol) of MMA in 30 cm^3 dry acetone was stirred under reflux for 3 hours, whereupon the solution turned from brown to yellow. The solvent was evaporated and the residue recrystallised from ethanol to yield 1.0g (79%) of the yellow cycloadduct **(82e)**, m.p.: 210-212°C.

CHN Analysis (found / theory) (%): M.w.: 488.59; $C_{31}H_{28}N_4O_2$; C (73.92 / 76.21), H (5.74 / 5.78), N (10.87 / 11.47).

IR (KBr) (cm^{-1}): 1725 (ester C=O), 774, 748, 730, 719, 693.

δH ($CDCl_3$) (ppm): 1.57 (3H, s) (CH_3), 3.23 (3H, s) (ester CH_3), 3.72 (1H, d), 4.67 (1H, d) (5-CH_2) (J_{am} = 10.34Hz), 6.73 (2H, t), 6.92 (7H, m), 7.00 (2H, d), 7.16 (4H, m), 7.57 (3H, m), 8.45 (2H, m) (all phenyl H).

δC ($CDCl_3$) (ppm): 21.36 (5-C-CH_3), 51.64 (C-6), 57.36 (ester CH_3), 61.99 (C-5), 91.03 (C-6a), 100.98 (C-3a), 115.76, 117.58, 122.97, 126.53, 126.90, 127.18, 127.37, 128.09,

128.55, 128.75, 128.97, 131.57 (all phenyl CH), 138.06 (6a-C-Ph, C-1'), 138.77 (3a-C-Ph, C-1'), 140.42 (4-N-Ph, C-1'), 145.21 (2-N-Ph, C-1'), 174.13 (ester C=O).

U.V. (MeCN) (nm): 248, 296 (ε = 23015, 17612 l $mol^{-1}cm^{-1}$).

1.4b.10) Formation of Cis-*5,6-bis(methoxycarbonyl)-2,3a,4,6a-tetraphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-*d*]-1,2,3-triazole* ***(82f).***

A solution of 1.5g (3.87 mmol) of BPAS and 1.0g (6.94 mmol) DMM in dry acetone was stirred under reflux until the deep brown colour dissipated and the solution turned yellow. The solvent was evaporated under vacuum and the residue recrystallised from ethanol to yield 1.71g (83%) of the adduct **(82f)**, m p.: 198-200°C (Lit. 200°C)[27]

CHN analysis (found / required) (%): M.w.: 532.60; $C_{32}H_{28}N_4O_4$; C (72.36 / 72.17), H (5.32 / 5.30), N (10.41 / 10.52).

IR (KBr) (cm^{-1}):1750 (C=O), 775, 755, 712, 698, 680.

δH ($CDCl_3$) (ppm): 3.39, 3.40 (2x3H, s) (2xCH_3), 4.14 (1H, d) (C-6-H), 5 50 (1H, d) (C-5-H) (J_{am} = 3.44 Hz), 6.76 (1H, m), 6 89 (2H, d), 7.04 (12H, m), 7.56 (3H, m), 8.33 (2H, d) (all phenyl H).

δC ($CDCl_3$) (ppm): 52.08, 52.45, 59.57, 63.81 (C-5, C-6, 2 x OCH_3), 88.50 (C-6a), 101.17 (C-6a), 117.17, 118.89, 123.09, 127.05, 127.10, 127.21, 127.57, 127.62, 128.38, 128.60, 128.90 (all phenyl CH), 131.57, 136.50, 140.86, 143.35 (all phenyl C), 171.14, 172.30 (both C=O).

1.4b.11) Formation of trans-*5,6-bis(methoxycarbonyl)-2,3a,4,6a-tetraphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-*d*]-1,2,3-triazole* ***(82g).***

A solution of 1.5g (3.87 mmol) of BPAS and 1.0g (6.94 mmol) DMF in dry acetone was stirred under reflux until the deep brown colour dissipated and the solution turned yellow.

The solvent was evaporated under vacuum and the residue recrystallised from ethanol to yield 1.63g (79%) of the *trans*-adduct **(82g)**, m.p.:204-206°C (Lit. 205°C)[27]

CHN analysis (found / required) (%): M.w.: 532.60; $C_{32}H_{28}N_4O_4$; C (72.03 / 72.17), H (5.33 / 5.30), N (10.41 / 10.52).

IR (KBr) (cm^{-1}):1747 (C=O), 782, 761, 750, 689, 678.

δH ($CDCl_3$) (ppm): 3.66 (3H, s) (CH_3), 3.88 (3H, s) (CH_3), 4.41 (1H, d) (C-4-H), 5.10 (1H, d) (C-5-H) (J_{am} = 9.35Hz), 6.84 (3H, m), 7.11 (12H, m), 7.45 (2H, t), 7.55 (1H, t), 8.13 (2H, d) (all phenyl H).

δC ($CDCl_3$) (ppm): 51.92, 52.43, 55.23, 62.78 (OCH_3 and C-5, C-6), 87.70 (C-6a), 101.05 (C-3a), 115.94, 118.66, 122.63, 126.24, 126.80, 127.02, 127.21, 127.38, 127.51, 127.91, 128.50, 131.35, 135.32, 137.42, 139.98, 142.27 (all phenyl C), 168.47 (C=O), 173.97 (C=O).

1.4b.12) Formation of 2,3a,4,6,6a-pentaphenyl-5-oxo-3,3a,4,5,6,6a-hexahydroimidazo[4,5-d]-1,2,3-triazole ***(83)***.

A solution of 500mg (1.29 mmol) BPAS in dry acetone was treated with an excess of PIC (3.0 mmol) and stirred under reflux until the colour changed from deep brown to off-white. The solvent was removed under vacuum and the residue recrystallised from ethanol to yield **(83)** in 87% yield (570mg), m.p.: 231-233°C (Lit.: 232-233°C)[36]

CHN analysis (found / required) (%): M.w.: 507.59; $C_{33}H_{25}N_5O$; C (78.32 / 78.09), H (5.07 / 4.96), N (13.51 / 13.80).

IR (KBr) (cm^{-1}): 1712 (C=O), 759, 750, 689.

δH (DMSO-d_6) (ppm): 6.80 (6H, m), 7.15 (6H, m), 7.28 (4H, m), 7.81 (7H, m), 8.51 (2H, d) (all phenyl H).

δC (DMSO-d_6) (ppm): 95.96 (C-3a, C-6a), 122.59, 124.28, 124.88, 127.34, 127.59, 128.01, 128.23, 129.69 (all phenyl CH), 132.89, 134.28, 136.99, 139.47 (all phenyl C), 155.36 (C=O).

M.S. fragments (amu): 507, 388, 313, 180, 119, 91, 77, 51.

1.4b.13) Formation of 3a,6a-bis(4'-chlorophenyl)-6-cyano-2,4-diphenyl-3,3a,4a,5,6,6a-hexahydropyrrolo[2,3-d]-1,2,3-triazole ***(85)***.

A solution of 1.0g (2.2mmol) 1,2-bis(phenylazo)1,2-bis(4'-chlorophenyl)ethene with an excess (1.0g, 18.8mmol) of AN in 30cm^3 dry acetone was stirred under reflux for 3 hours. The brown solution turns yellow. The solvent was evaporated off under vacuum, and the residue recrystallised from ethanol. The cycloadduct **(85)** was obtained in 85% yield (955 mg), m.p.: 225-227°C.

CHN Analysis (found / theory) (%): M.w.: 510.43; $C_{29}H_{21}Cl_2N_5$; C (68.73 / 68.24), H (4.35 / 4.15), N (13.39 / 13.89).

IR (KBr) (cm^{-1}): 2241 (CN), 876, 857, 826, 813, 768, 755, 707, 695, 682, 652.

δH ($CDCl_3$) (ppm): 3.85 (1H, dd), 3.95 (1H, dd), 4.31 (1H, dd) (J_{am} = 9.35, J_{ax} = 7.38, J_{mx} = 5.42) (5-CH_2, 6-CH), 6.82 (1H, t), 6.91 (2H, d), 7.10 (10H, m), 7.51 (2H, t), 7.60 (1H, t), 8.26 (2H, d) (all phenyl H).

δC ($CDCl_3$) (ppm): 41.24 (C-6), 51.64 (C-5), 87.60 (C-6a), 99.03 (C-3a), 118.30 (CN), 116.90, 119.67, 122.70, 127.94, 128.41, 128.73, 128.86, 129.14, 129.21, 132.29 (all phenyl CH), 133.67 (6a-C-Ph, C-1'), 134.16, 134.25 (6a-C-Ph, C-4', 3a-C-Ph, C-4'), 135.09 (3a-C-Ph, C-1'), 139.97 (4-N-Ph, C-1'), 143.61 (2-N-Ph, C-1').

1.4b.14) Formation of 3a-(4'-chlorophenyl)-6a-(4'-methoxyphenyl)-6-cyano-2,4-diphenyl-3,3a,4a,5,6,6a-hexahydropyrrolo[2,3-d]-1,2,3-triazole ***(89a)***.

A solution of 1.5g (3.3 mmol) of **(86a)** and 1.0g (18.8 mmol) AN in dry acetone was stirred under reflux until the deep brown colour dissipated and the solution turned yellow. The solvent was evaporated under vacuum and the residue recrystallised from ethanol to yield 1.12g (67%) of the yellow solid **(89a)**, m.p: 220-222°C.

CHN Analysis (found / theory) (%): M.w.: 506.01; $C_{30}H_{24}ClN_5O$: C (70.98 / 71.21), H (4.83 / 4.78), N (13.89 / 13.84).

IR (cm^{-1}) (KBr): 2242 (C≡N), 826, 813, 772, 755, 738, 696, 685.

δH (ppm) ($CDCl_3$): 3.72 (3H, s) (CH_3), 3.90 (2H, m) (5-CH_2), 4.30 (1H, m) (6-CH), 6.65 (2H, d), 6.81 (1H, t), 6.94 (2H, m), 7.14 (8H, m), 7.51 (2H, t), 7.59 (1H, t), 8.25 (2H, d). (all phenyl H).

δC (ppm) ($CDCl_3$): 41.01 (OCH_3), 51.76 (C-6), 55.11 (C-5), 87.81 (C-6a), 98.83 (C-3a),113.10, 116.76, 118.74, 119.43, 122.75, 126.87, 128.24, 128.69, 128.71, 129.03, 129.30, 132.13, 133.94, 135.54, 143.76, 159.08.

1.4c) Isolation and Characterization of Cycloaddition Reaction Side Products

1.4c.1) Formation of 5-methyl-2-phenyl-4-(2'-aminobenzyl)-1,2,3-triazole (67).

To a solution of 500 mg (1.89 mmol) BPAB in refluxing acetone was passed a stream of dry HCl. The solution turned from a deep purple to clear yellow, whereupon the source of HCl was removed. The solution was allowed to stir for a further 10 minutes. The solvent was removed under vacuum and the excess acid removed by successive washing with saturated $NaHCO_3$ and H_2O, using ethyl acetate as solvent. The solution was dried over $MgSO_4$ and the solvent then evaporated under reduced pressure. The residue was recrystallised from ethanol to yield 345mg (69%) of the product **(67)**, m.p.111-112°C.

CHN analysis (Found / Theory) (%): M.w.: 264.35; $C_{16}H_{16}N_4$; C (72.40 / 72.70), H (6.08 / 6.10), N (21.06 / 21.20).

IR (KBr) (cm^{-1}): 3340, 3430 (NH_2), 1640 (C=N), 775, 755, 740, 720, 699, 670, 655 (mono- and *o*-di-substituted phenyl)

δH ($CDCl_3$) (ppm): 2.32 (3H, s) (CH_3), 3.96 (2H, s) (CH_2), 6.69 (1H, d), 6.74 (1H, t), 7.11 (1H, t), 7.16 (1H, d), 7.30 (1H, t), 7.45 (2H, t), 7.99 (2H, d) (all phenyl CH).

δC ($CDCl_3$) (ppm): 10.23 (CH_2), 28.21 (CH_3), 116.23, 118.07, 118.4, 126.63, 127.99, 129.13, 130.05 (all phenyl CH), 122.50 (benzyl C-1'), 133.64 (benzyl C-2'), 143.87 (2-N-Ph, C-1'), 145.28, 145.43 (C-4, C-5)

M.S fragments (amu): 265, 264, 263, 248, 222, 195, 171, 159, 132, 131, 117, 104, 91, 77, 64, 51.

U.V. (MeCN) (nm): 276 ($\varepsilon = 85150\ l\ mol^{-1}cm^{-1}$)

1.4c.2) Formation of 5-methyl-2-phenyl-4-(2'-N-phenylureido)benzyl-1,2,3-triazole (72).

To a solution of 500mg 5-methyl-2-phenyl-4-(2'-aminobenzyl)-1,2,3-triazole **(67)** in dry acetone was added an excess of PIC. The mixture was stirred for 10 minutes whereupon a white solid precipitated out of solution. The solid was filtered under vacuum and recrystallised from ethanol to yield **(72)** almost quantitatively (95%), m.p.: 224-225°C.

CHN analysis (found / required): M.w.: 383.45; $C_{23}H_{21}N_5O$; C (72.08 / 72.04), H (5.50 / 5.52), N (18.11 / 18.26).

IR (KBr) (cm^{-1}): 3300 (NH), 1634 (C=O), 753, 723, 688, 659 (mono- and *o*-di-substituted phenyl)

δH (DMSO-d_6): 2.21 (3H, s) (CH_3), 4.08 (2H, s), 6.82 (1H, t), 6.91 (1H, t), 6.97 (1H, d), 7.12 (4H, m), 7.30 (4H, m), 7.53 (1H, d), 7.74 (2H, d) (all phenyl H), 8.01 (1H, s) (NH), 8.87 (1H, s) (NH).

δC (DMSO-d_6) (ppm): 9.74 (CH_3), 26.38 (CH_2), 117.59, 118.06, 118.17, 121.69, 123.81, 123.83, 126.81, 126.91, 128.79, 129.28, 129.48, 130.0 (all phenyl C), 136,89, 139.08, 139.88, 143.91, 145.72 (C-4, C-5, 2-C-Ph, C-1', benzyl-C-2', ureido-phenyl,C-1'), 152.95 (C=O).

M S fragments (amu):384, 383, 364, 290, 264, 248, 220, 195, 172, 157, 132, 119, 103, 93, 91, 77, 64, 51.

U.V. (MeCN) (nm): 258 (ε = 34500 l $mol^{-1}cm^{-1}$)

1.4c.3) Formation of 2,4,5-triphenyl-1,2,3-triazole ***(46, R=Ph).***

This compound was produced in a number of reactions as outlined in Section 1.2. It was prepared separately for comparison as follows. 500 mg (1.29 mmol) of BPAS was heated to 175-180°C in an oil bath. The product was flash chromatographed over silica gel (0.032-0.063 mm mesh size), using pet.ether (60-80) as eluant. The product **(46, R=Ph)** was isolated in 83% yield (318mg), m.p.: 119-121°C (Lit:122°C)[46]

CHN Analysis (found / theory) (%): M.w.: 297.36; $C_{20}H_{15}N_3$; C (80.97 / 80.78), H (5.11 / 5.08), N (14.41 / 14.13).

IR (cm^{-1}) (KBr):782, 775, 736, 689, 655, 617.

δH (ppm) ($CDCl_3$): 7.36 (12H, m), 7.47 (2H, t), 7.63 (4H, m), 8.16 (2H, d) (all phenyl H).

δC (ppm) ($CDCl_3$): 118.70, 127.34, 128.41, 128.58, 128.61, 129.23, 130.71, 139.66, 145.91.

1.4c.4) Formation of 4,5-dimethyl-2-phenyl-1,2,3-triazole (46, R=Me).

500mg (1.88 mmol) of BPAB was heated to 150°C for 1 hour on an oil bath. The product was seperated on a flash chromatography column (silica gel 0.032-0.063mm mesh size) using pet.ether (60-80) as eluant. The product **(46, R=Me)** was isolated in 54% yield (174 mg), m.p.: 33-35°C (Lit: 34-35°C)[77]

M.w.: 173.22; $C_{10}H_{11}N_3$

IR (cm^{-1}) (KBr): 756, 690, 652 (all monosubstituted phenyl).

δH (ppm) ($CDCl_3$): 1.85 (3H, s) (CH_3), 6.80 (1H, t), 6.96 (2H, t), 7.50 (2H, d) (monosubstituted phenyl H).

δC (ppm) ($CDCl_3$): 9.91 (CH_3), 117.95, 126.36, 129.09, 139.76, 143.65.

1.4c.5) Formation of 4,5-bis(4'-chlorophenyl)-2-phenyl-1,2,3-triazole (46, R=Ar)

500 mg (1.09 mmol) of 1,2-bis(4'-chlorophenyl)-1,2-bis(phenylazo)ethylene was heated to 210°C for 1 hour. The product **(46, R=4'-Cl-C_6H_4)** was separated as above to yield 232mg (58%) of the product. M.w.: 366.25; $C_{20}H_{13}Cl_2N_3$; C (65.36 / 65.59), H (4.03 / 3.58), N (11.18 / 11.47).

IR (cm^{-1}) (KBr):1497, 1459, 1375, 1267, 974, 776, 756, 740, 700, 668, 612

δH (ppm) ($CDCl_3$): 7.39 (5H, d), 7.53 (6H, m), 8.15 (2H, d) (phenyl H).

δC (ppm) ($CDCl_3$): 118.74, 127.67, 128.97, 129.30, 129.64, 134.83, 139.47, 144.81.

1.4c.6) *Visible Photolysis of (70c).*

A solution of 200mg (0.61mmol) **(70c)** in dichloromethane was stirred in sunlight at ambient temperature for 4 weeks. No reaction was observed.

1.4c.7) *Acid Catalysed Epimerization of (70c).*

To a solution of 200mg (0.61mmol) **(70c)** in dry acetone passed a stream of dry HCl. The solution was stirred at room temperature in the absence of light for 4 days. The product was separated from the starting material on passing the residue through a flash chromatography column. (silica gel, 0.032-0.063 mesh size 3:1 pet.ether (40-60) / ethyl acetate as eluant). The product was crystallised from diethyl ether / pet.ether (40-60) to yield 20mg (0.06mmol) (11%) of the yellow solid **(76)**, M.p.: 174-176°C

For spectroscopic details see 1.4a.4.

1.4c.8) *Base Catalysed Epimerization of (70c).*

A solution of 200mg (0.61mmol) of **(70c)** was stirred at ambient temperature in 10cm^3 acetone containing 2cm^3 sat. $NaHCO_3$ for 10 days. No reaction was observed.

1.4d) Metallic Hydride Reductions

1.4d.1) Lithium Borohydride Reduction of ***(81a)***.

To a solution of 500mg (0.94 mmol) **(81a)** in dry THF was added an excess of $LiBH_4$ (formed *in situ* by reacting equal amounts of LiCl and $NaBH_4$). The solution was stirred overnight, using a $CaCl_2$ air trap to prevent the introduction of atmospheric moisture. The reaction was quenched using water and the residue on removal of the solvent under vacuum was separated on a flash chromatography column (silica gel, 0.032-0.063 mm mesh size). The orange product **(90)** which ran slower than the starting material was isolated on recrystallisation from ethanol in 83% yield (372 mg), m.p.: 193-194°C.

CHN analysis (found / required) (%): M.w.: 476.58; $C_{30}H_{28}N_4O_2$; C (75.35 / 75.61), H (5.79 / 5.92), N (11.95 / 11.76).

IR (KBr) (cm^{-1}): 3450 (OH), 775, 755, 738, 726, 689.

δH ($CDCl_3$) (ppm): 3.68 (1H, t), 3.93 (3H, m), 4.36 (1H, t), 4.59 (2H, m), 4.89 (1H, t) (C-5-H, C-6-H, 5-C-CH_2OH, 6-C-CH_2OH), 6.65 (1H, t), 6.95 (14H, m), 7.51 (3H, m), 8.31 (2H, d) (all phenyl H).

δC ($CDCl_3$) (ppm): 49.07, 60.11, 60.25, 61.02 (C-4, CH_3,C-5, CH_3,C-4, C-5), 87.86 (C-6a), 100.57 (C-3a), 116.08, 117.37, 122.51, 126.20, 126.93, 127.06, 127.38, 127.55, 127.61, 128.30, 128.82, 131.43, 135.94, 136.86, 140.47, 142.40 (all phenyl C).

1.4d.2) Lithium Borohydride / MeOH Reduction of ***(81a)***.

To a solution of of 500 mg (0.94 mmol) **(81a)** in dry THF was added a four-fold excess of $LiBH_4$ / MeOH. The solution was stirred at room temperature overnight, in a flask fitted with a drying tube. The reaction was quenched with water and the solvent removed under vacuum. The residue which contained two products was separated on a flash chromatography column (silica gel 0.032-0.063 mm mesh size) with 3:1 pet.ether (40-60) / ethyl acetate as eluant. Recrystallisation was from ethanol. The main product, the *cis*-isomer **(82f)**, was isolated in 67% yield (255mg), **(82g)** was isolated in 13% yield.

(82f): M.p.:198-200°C. Spectroscopic data was identical to that obtained for the product formed on cycloaddition of BPAS and DMM. (1.4b.10)

(82g): M.p.: 203-205°C. Spectroscopic data was identical to that for the product formed on cycloaddition of BPAS and DMF. (See 1.4b.11)

1.4d.3) *Sodium Borohydride Reduction of* ***(81a).***

The above reduction was repeated using 500mg (0.94mmol) **(81a)** and a four-fold excess of $NaBH_4$ in dry THF. On allowing to stir for 2 days, the ratio of the products was 39% : 51% **(82f)** / **(82g)**. The products were separated by flash chromatography as above, and recrystallisation was from ethanol.

(82f): M.p.:198-200°C. Spectroscopic data was identical to that obtained for the product formed on cycloaddition of BPAS and DMM. (See 1.4b.10)

(82g): M.p.: 202-204°C. Spectroscopic data was identical to that for the product formed on cycloaddition of BPAS and DMF. (See 1.4b.11)

1.4d.4) *Sodium Borohydride / Methanol Reduction of* ***(81b).***

To a solution of 500 mg (1.06 mmol) of **(81b)** in 30 cm^3 dry THF was added a 2-fold excess of $NaBH_4$ / MeOH and stirred in the absence of atmospheric moisture for 2 days. On quenching the reaction with water and removal of the solvent under vacuum, the residue was passed through a flash chromatography column (silica gel, 0.032-0.063mm mesh size) with 3:1 pet.ether (40-60) / ethyl acetate as eluant. On recrystallisation from ethanol, the two main products, the *endo*- and *exo*-hexahydro-isomers **(91)** and **(82a)** were isolated in 75% (377mg) and 10% (50mg) yields respectively.

(91): M.p.: 192-193°C. CHN analysis (found / theory) (%): M.w. 474.56; $C_{30}H_{26}N_4O_2$; C (75.78 / 75.93), H (5.42 / 5.52), N (11.69 / 11.81).

IR (KBr) (cm^{-1}): 1730 (C=O), 775, 755, 748, 727, 696, 688.

δH ($CDCl_3$) (ppm): 3.60 (3H, s) (CH_3), 3.91 (1H, t, J = 9.35Hz), 4.36 (2H, m), 6.72 (1H, t), 7.02 (12H, m), 7.45 (2H, t), 7.50 (1H, t), 8.22 (2H, d).

δC ($CDCl_3$) (ppm): 49.84, 50.16, 52.04 (OCH_3, C-5, C-6), 89.09 (C-6a), 100.26 (C-3a), 116.09, 117.99, 122.97, 123.07, 126.78, 126.92, 127.14, 127.51, 127.82, 128.38, 128.86, 131.60 (all phenyl CH), 136.86, 137.84, 140.52, 144.13 (all phenyl C), 170.33 (C=O).

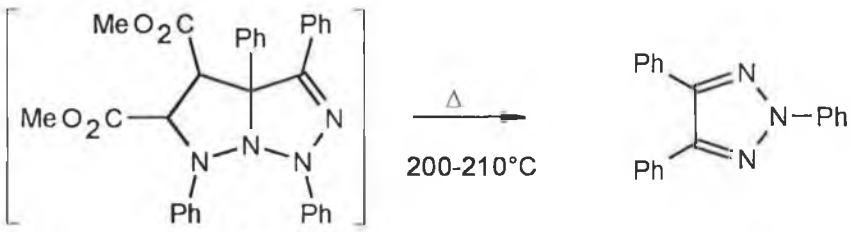
(81a): M.p.: 190-191°C. The spectral and physical data was identical to that obtained for the product formed on reaction of BPAS with MA. (See 1.4b.5)

CHAPTER 2

Thermal Transformations of 1,3-Dipolar Cycloadducts Derived from 1,2,3-Triazolium-N-imides

2.1) INTRODUCTION

There have been a number of reports on the thermal transformations of systems of the type described in Chapter 1. In 1972 George and co-workers investigated the products formed on pyrolysis of **(92)**, which have since been reassigned as **(82f)** and **(82g)**.[24,26,27] (See Section 1.1b) The product, isolated in high yield in both cases, was the triazole **(46, R=Ph)**. See Scheme 2.1.



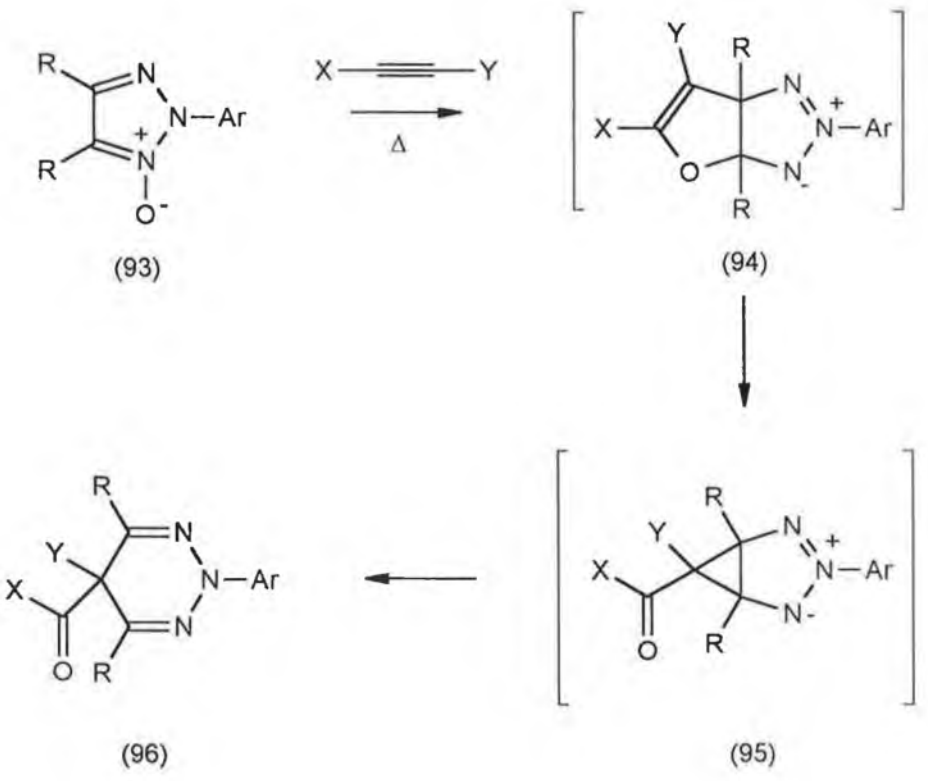
(92) (46)

Scheme 2.1 Thermolysis of **(92)**.

A similar fragmentation has been observed on cycloaddition of BPAS and aryl isothiocyanates.[36] (See Scheme 1.18) The cycloaddition product was isolated for **(48a)** In all other cases the initially formed cycloadduct fragmented on heating to yield substituted 1,2,3-triazoles **(46, R=Ph, RR=$(CH_2)_4$)** and two aryl isothiocyanates, the original dipolarophile and one which had exchanged its aryl group for one on the dipole, thus proving the intermediacy of the cycloadduct.
The analogous aryl isocyanate cycloadducts **(47)** were found to be stable on heating.

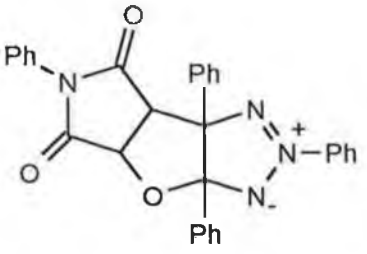
In 1987 Butler *et al.* reported that on reaction of triazolium-N-oxide **(93)** with acetylenic dipolarophiles in refluxing toluene, the unexpected 1,2,3-triazines **(96)** were isolated in high yields.[74] (Scheme 2.2) The structure was confirmed by spectroscopic and x-ray crystallographic analysis.

The mechanism proposed the intermediacy of the cycloaddition product, the tetrahydrofuro[2,3-*d*]-1,2,3-triazole **(94)**, which underwent 1,3-sigmatropic



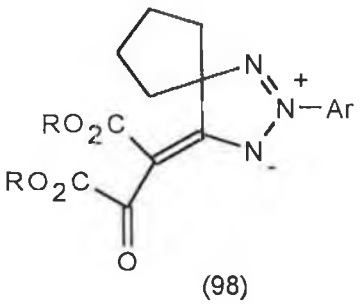
Scheme 2.2 Thermal rearrangement of tetrahydrofurotriazoles **(93)**

rearrangement to the fused cyclopropane structure **(95)**. This subsequently underwent a disrotatory electrocyclic ring expansion to the observed triazine **(96)**. Proof for the intermediacy of **(94)** was supported by the isolation of the stable adduct **(97)** formed on addition of **(93)** and N-phenylmaleimide.[75] The stability of this adduct suggested the importance of the unsaturation between C-5 and C-6 in the thermal rearrangement.



(97)

An attempt to block the outward ring expansion by linking the bridgehead substituents **(93, RR=$(CH_2)_n$)** resulted in the spiro product **(98)**.



(98)

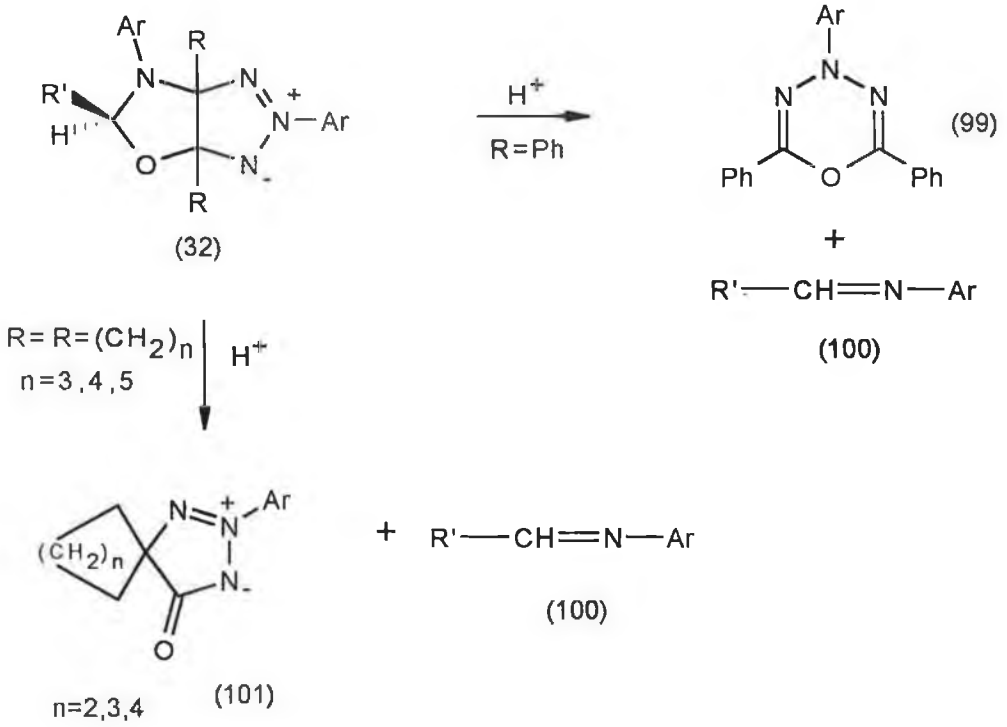
This was rationalised in terms of a 1,2-shift in the fused cyclopropane intermediate **(95)**. This type of 1,2-shift has been reported for strained cyclopropane systems.[31]

A similar rearrangement was observed on cycloaddition of acetylenic dipolarophiles with **(26)**. The isolated product was identified as **(30)**, and confirmed by x-ray crystal structure analysis. Two mechanisms were proposed, the more likely of which involved a 1,2-shift in the initial cycloadduct **(29)**.[29] (See Scheme 1.12)

As shown in Section 1.1b, the reaction of triazolium-N-imides **(13)** with a number of heteromultiple bond dipolarophiles led to fragmentation-ring expansion reactions. Reaction of BAAS and bis(arylazo)cycloalkanes with N-aryl sulphinilamines led *via* the cycloadduct **(34)** to 1,2,3,5-tetrazines **(36)**.[31,33] (Scheme 1.14) For reaction with BAAC **(13, RR=$(CH_2)_4$)** the isolated product was the bridged cyclohexyl tetrazine **(37)**. For smaller cycloalkane rings a 1,2-shift similar to that shown in Scheme 2.2 was observed to produce **(38)**.

Reaction of BPAS and bis(arlyazo)cycloalkanes with methyl cyanodithioforamte resulted in the thiatriazine **(41)**.[31,34] (Scheme 1.15) Linking of the bridgehead positions led in this case to the formation of the triazole **(42)** on elimination of sulphur from the intermediate.

On heating the cycloadduct formed on cycloaddition of BPAS or bis(arlyazo)cycloalkanes with a variety of ketones in ethanol or acetic acid solution, a similar ring expansion has been observed.[30-32] (Scheme 2.3).



Scheme 2.3 Thermolysis of **(32)**.

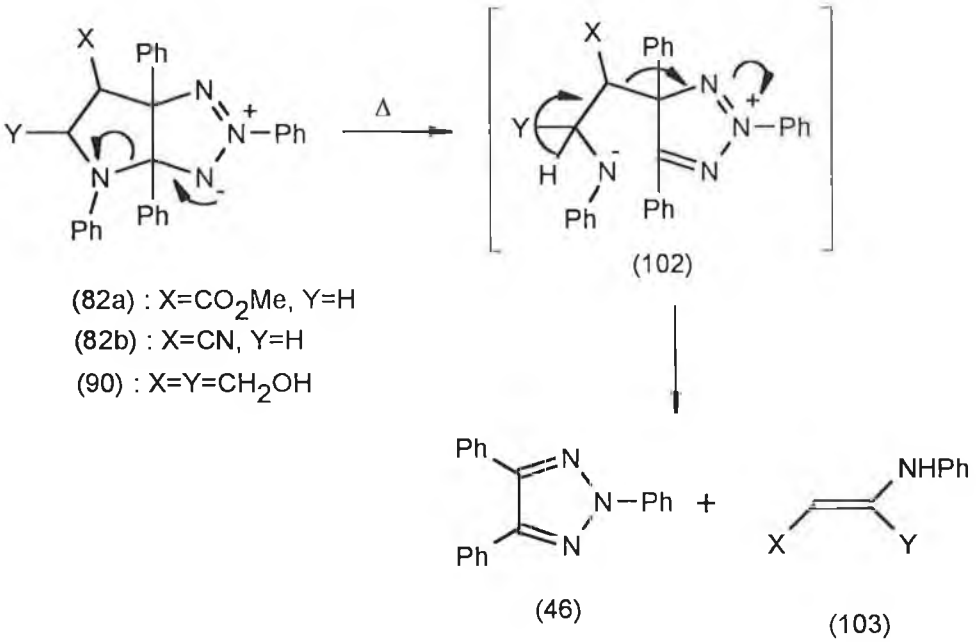
An attempt to block the ring expansion by linking the bridgehead substituents resulted in the triazaspirononane **(101)** *via* a 1,2-shift similar to that shown in Scheme 2.2.

2.2) RESULTS AND DISCUSSION

2.2a) Thermal Transformations of Substituted Hexahydropyrrolo[2,3-*d*]-1,2,3-triazoles

The thermal rearrangements of a number of substituted hexahydropyrrolo[2,3-*d*]-1,2,3-triazoles have been examined.

Thermolysis of **(82a and b)** in toluene for 40 hours resulted in high yields of 2,4,5-triphenyl-1,2,3-triazole. (Scheme 2.4) The driving force for this reaction is the generation of the aromatic triazole **(46)**. The reaction was analogous to that reported by George and co-workers, noting that the reaction proceeded from **(82)** and not the incorrectly assigned imidazotriazole **(92)**.[24]

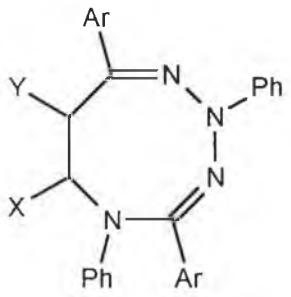


Scheme 2.4. Thermal decomposition of **(82a,b) and (90)**

The mechanism of the decomposition involves initial cleavage of the C3a-N4 bond to yield the intermediate **(102)**, which further fragments to the aromatic 1,2,3-triazole **(46)**. The other decomposition product, the enamine **(103)** was not isolated. George and co-workers have reported a dipolar species as the other decomposition product

but were unable to trap this species, stating that it may undergo further decomposition to intractable products.[24]

On allowing the thermolysis of **(82a)** and **(82b)** to proceed in sunlight for 3 days a large number of products were observed. These were rationalised in terms of decomposition products formed on thermolysis of a tetrazocine **(104)** formed on photochemical excitation of **(82a)** in direct sunlight. This reaction shall be discussed in detail in Section 3.2b. The decomposition products were not isolated. Thermolysis of 5,6-bis(hydroxymethyl)-2,3-diphenylhexahydropyrrolotriazole **(90)** in sunlight for 4 days produced **(46)** in low yield. No other decomposition products were observed as **(90)** has been shown not to undergo photochemical ring expansion to the tetrazocine **(104)**. (See Section 3.2b)



(104)

Thermolysis of the 3a,6a-dimethyl analogues **(70a and b)** and **(71)** under the same conditions for 40 hours resulted in no reaction. The difference in reactivity is clearly related to the bridgehead substituents, with the aryl substituents weakening the C3a-N4 bond. The influence of substitution pattern on bond strength has been well documented. The influence of increased substitution has the effect of making the bond more susceptible to homolysis or heterolysis by stabilization of the radicals or ions produced.[76] In the present case the C3a-N4 bond is weakened by the phenyl groups, the bond dissociation energy is decreased and a lower activation energy to bond fission is required. A list of bond dissociation energies for the C-C bond of a variety of substituted alkanes is given in Table 2.1.

A summary of the thermolysis products formed is given in Table 2.2

Table 2.1 Bond Dissociation energies (kcal / mol) of C-C bond of substituted alkanes.

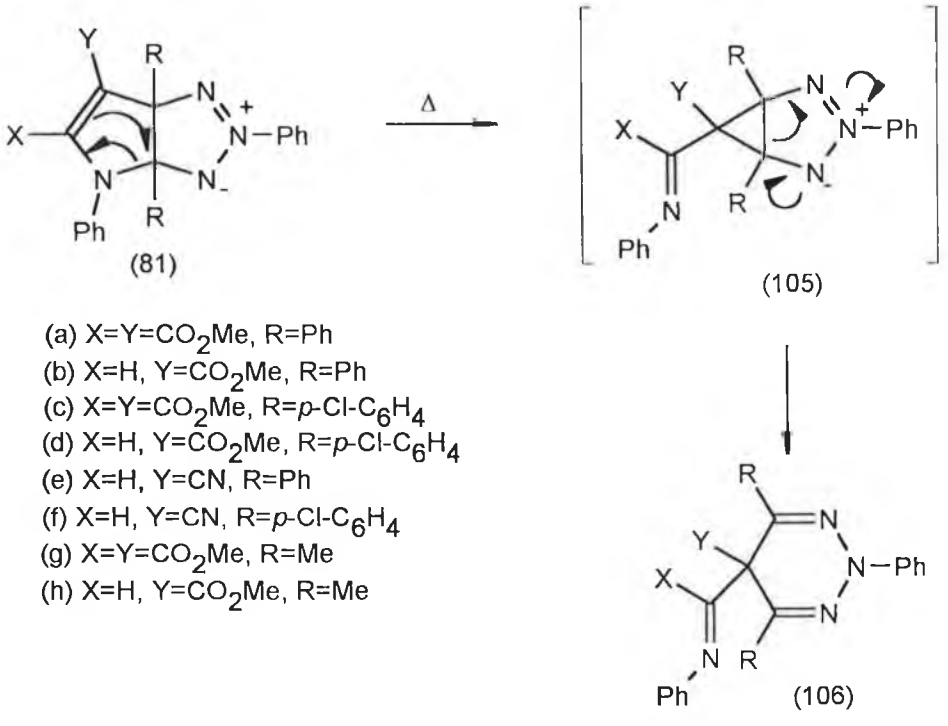
$H_3C\text{-}CH_3$	88
$H_5C_2\text{-}CH_3$	85
$(CH_3)_2C\text{-}CH_3$	83
$PhCH_2\text{-}CH_3$	70
$H_5C_2\text{-}C_2H_5$	82
$(CH_3)_2CH\text{-}CH(CH_3)_2$	78

Table 2.2 Summary of thermolysis reactions of substituted hexahydropyrrolo [2,3-*d*]-1,2,3-triazoles

Compound	Reaction Time (Hours)	Product	Melting Point (°C)	Yield (%)
82a	40	1.51a	119-121	87
82b	30	1.51a	120-122	83
91	100	1.51a	119-121	10
70a	40	No Reaction	-----	0
70c	48	No Reaction	-----	0
71	40	No Reaction	-----	0

2.2b) Thermal Transformations of Substituted Tetrahydropyrrolo[2,3-*d*]-1,2,3-triazoles.

In order to investigate whether a thermal rearrangement of the type seen for **(94)** would occur for the tetrahydropyrrolotriazole analogues, compound **(81a)** was stirred under reflux in toluene solution. The reaction was followed by TLC. On completion, the product was separated by flash chromatography, to yield an orange powder. The product was characterised by CHN analysis, and ir and nmr spectroscopic techniques and determined to be the 5,5-disubstituted 1,2,3-triazine **(106a)**, *i.e.* the 5-formimidoyl analogue of **(96)**. The process was repeated for **(81b, R-Ph)**, **(84a and b, R=*p*-Cl-C_6H_4)** and **(69a and b, R=Me)** to produce compounds **(106 b-d, g and h)**. (Scheme 2.5)



Scheme 2.5 Thermal rearrangement of tetrahydropyrrolo[2,3-*d*]triazoles **(81)**.

The ^{1}H and ^{13}C nmr spectra for **(106d)** are shown in Fig.2.1. Of note in the ^{1}H nmr spectrum of **(106d)** is the peak at 8.42 ppm, attributed to the imino hydrogen **(106d, X=H)**.

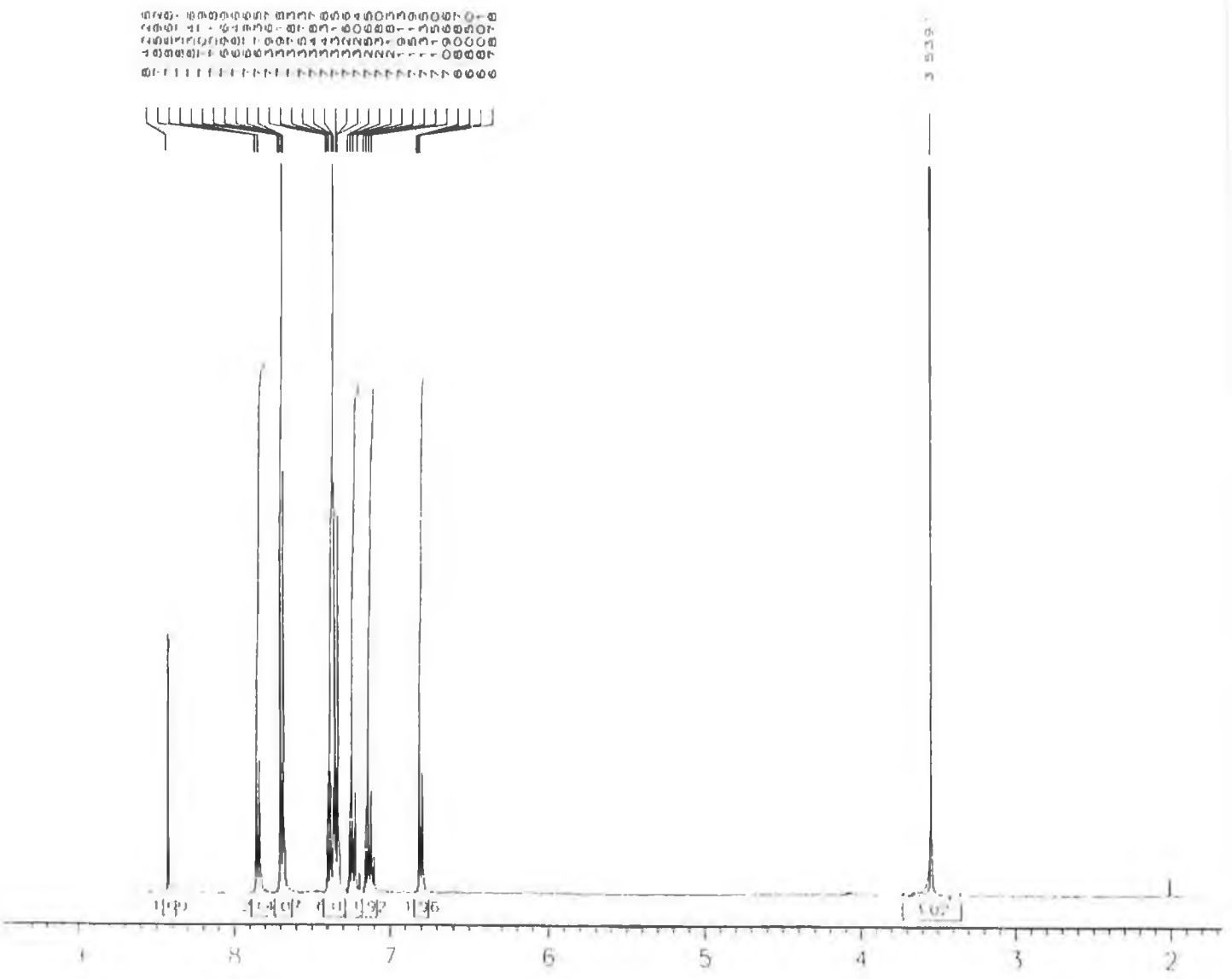


Fig. 2.1a. ^{1}H nmr spectrum of **(106d)**.

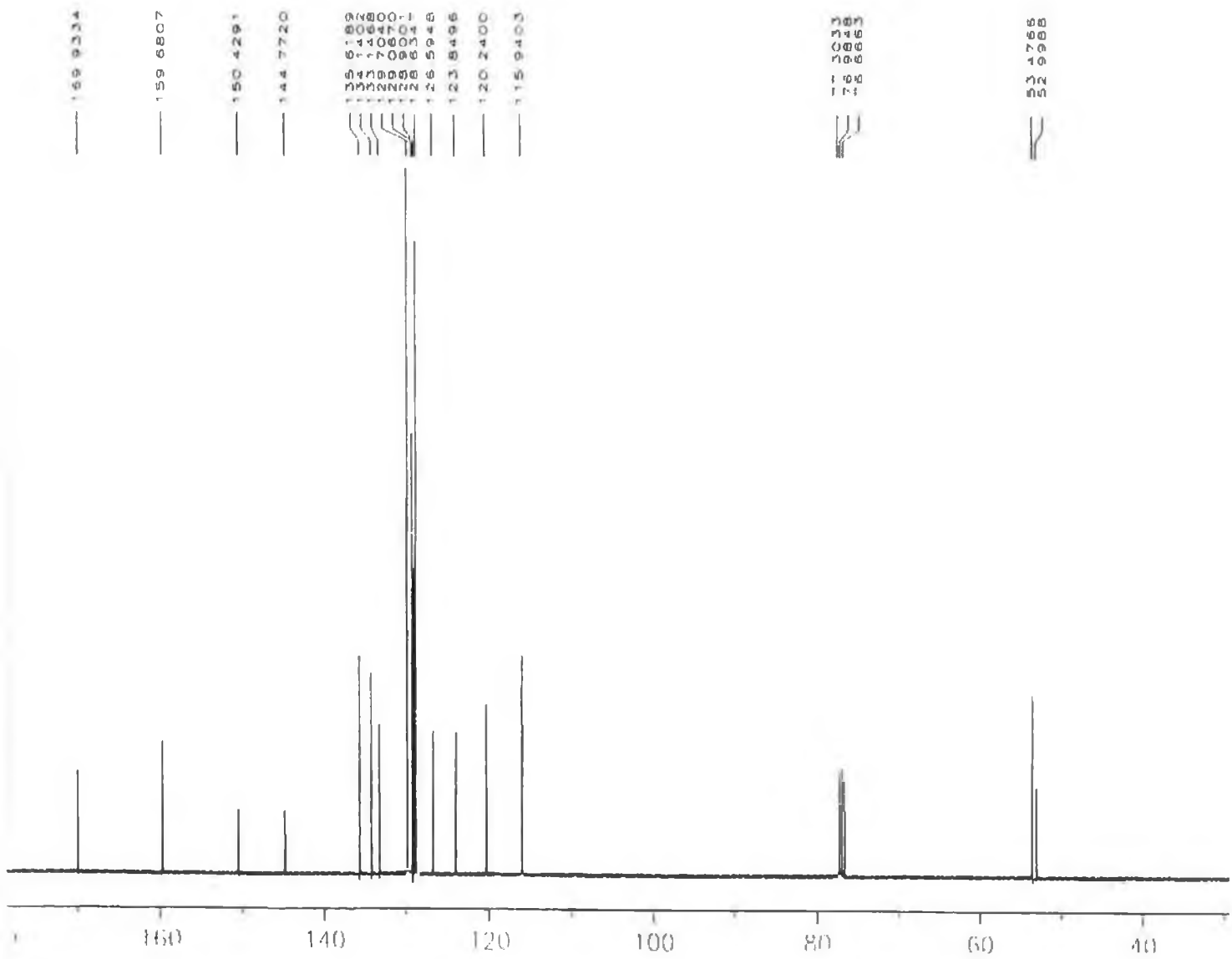
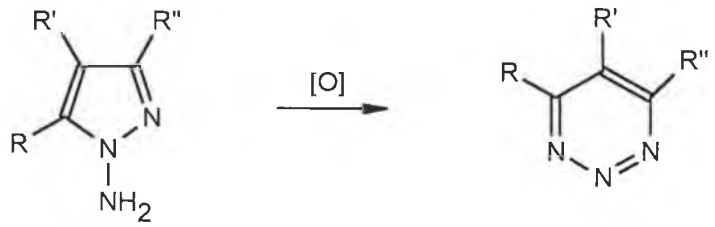


Fig. 2.1b. ^{13}C nmr spectrum of **(106d)**

Among the high nitrogen systems, 1,2,3-triazines are relatively rare and are by far the least studied of the triazine class. High nitrogen systems have been defined as compounds containing three directly bonded nitrogen atoms.[77] The parent compound of the 1,2,3-triazine series **(108)** was prepared for the first time at the end of 1981 by the nickel peroxide oxidation of N-aminopyrazole **(107)**, in low yield.[78] Lead tetraacetate has since been used successfully as oxidizing agent.[79] (Scheme 2.6)



(107) (108)

Scheme 2.6 Oxidative rearrangement of N-aminopyrazoles to 1,2,3-triazines.

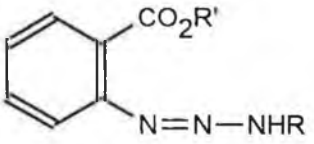
Substituted monocyclic 1,2,3-triazines have been synthesised by rearrangement of substituted cyclopropenyl azides **(109)**.[80] (Scheme 2.7)

(109) (108)

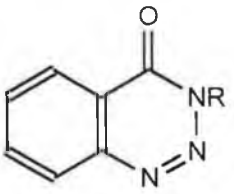
Scheme 2.7 Formation of substituted 1,2,3-triazines by rearrangement of cyclopropenylazides.

Most of the known compounds of the 1,2,3-triazine class are fused benzo-derivatives. They are generally synthesised by LTA or nickel peroxide oxidation of N-aminoindazoles, although the oxidation of hydrazones of *o*-aminophenyl alkyl and aryl ketones also provides an efficient route to these compounds.[81] Benzotriazin-4-ones, -thiones and imines are well known and synthetic entry into these systems has been achieved by diazotisation of anthranilamides or cyclisation of *o*-triazenobenzoate esters **(110)**.[82] The increased interest in the chemistry of 1,2,3-triazines is as a result of the wide range of biological activity associated with many derivatives of 1,2,3-benzotriazin-4-(3H)-one **(111)** and especially phosphoric acid and thiophosphoric acid

derivatives, which are used as plant protection agents.[83] 1-*t*-Butyl-3-ethyl-2-methylhexahydro-1,2,3-triazine has been used as a corrosion inhibitor for steel.[83] New reactions which give high yields of monocyclic 1,2,3-triazine derivatives are of particular interest.



(110)



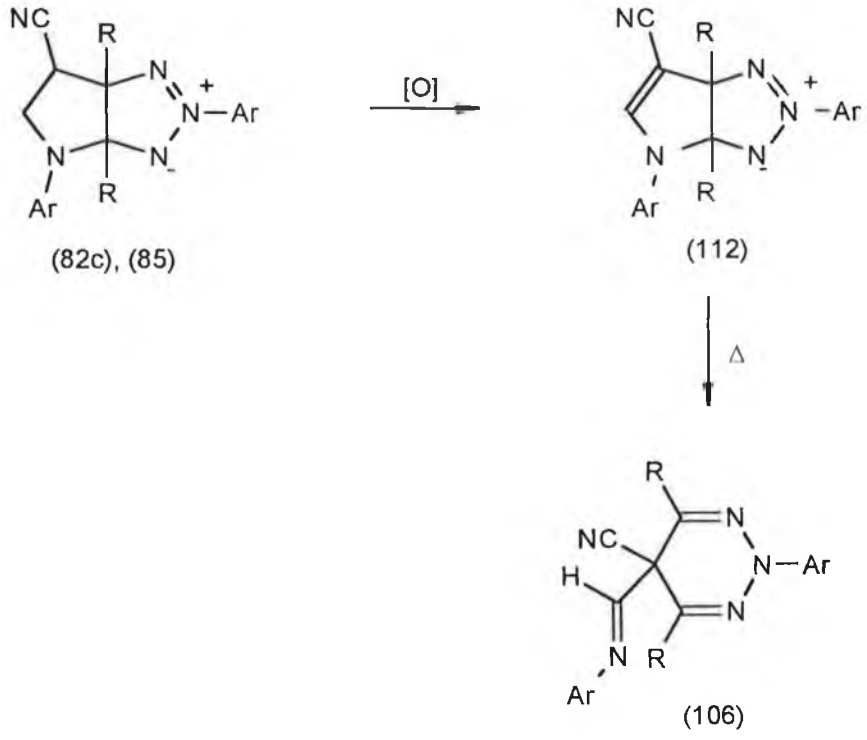
(111)

The mechanism proposed for the thermal rearrangement reported here may be rationalised in terms of an initial 1,3-sigmatropic rearrangement of the fused pyrrolidine ring to give the strained fused cyclopropane intermediate **(105)**. This then relieved the considerable ring strain by a disrotatory outward ring expansion to the triazine **(106)**. (Scheme 2.5)

The reaction was then extended to include a variety of substituents at the bridgehead positions C-3a and C-6a and also at C-5 and C-6. Variation of the bridgehead substituents had little effect on the reaction pathway, although yields for the 3a,6a-dimethyl analogues were lower, possibly for the same reasons as outlined in Section 2.2a. The lack of an electron withdrawing group at C-5 had no effect on the reaction. An attempt to synthesise cycloadducts with electron donating groups at C-5 and C-6, in order to study the effect on the rearrangement, failed as outlined in Section 1.2c.

The unsaturation between C-5 and C-6 appears essential for the sigmatropic rearrangement. This is supported by the fact that the hexahydro-analogues do not undergo this rearrangement (see Section 2.2a), but when oxidized using MnO_2 in refluxing toluene the rearranged product **(106)** was isolated in high yield. The only site available for oxidation on the hexahydro analogues was between C-5 and C-6. On oxidation, the facile sequential transformation to the triazine proceeded readily.

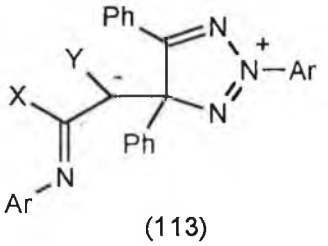
Oxidation of 6-cyano-2,3a,4,6a-tetraphenyl- and 3a,6a-bis(4'-chlorophenyl)-2,4-diphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-*d*]-1,2,3-triazoles **(82c)** and **(85)** with MnO_2 in refluxing toluene, using a Dean and Stark apparatus to remove any water generated in the reaction, produced good yields of 5-(cyanoformimidoyl)-4,6-diaryl-2-phenyl-2,5-dihydro-1,2,3-triazines **(106e and f)**. (See Scheme 2.8) On oxidation of **(82c)** at room temperature in dry DCM, **(112)** was isolated as a mixture including the starting material. The same reaction carried out at 0°C produced no reaction. Attempts to purify **(112)** led to rearrangement to **(106e)** in high yield. Oxidation of **(82a)** at room temperature using the same conditions led to the formation of **(81b)** in high yield. The structure was confirmed by spectroscopic techniques and also by comparison with the spectra obtained for the product formed on cycloaddition of BPAS and MP.



Scheme 2.8 Oxidative rearrangement of hexahydropyrrolo-[2,3-*d*]triazoles

During the course of this work, the identical reaction was reported by Butler *et.al.*[67] They reported a mechanism similar to that described here and that described earlier for the furo-analogues.[22,74,75] A mechanism involving the zwitterionic intermediate **(113)** was discounted for a number of reasons, *i.e.* the reactions occur in non-polar

hydrocarbon solvents and extensive attempts to trap the zwitterionic intermediate proved futile.



(113)

A list of the triazines **(106)** produced along with the relevant physical data is presented in Table 2.3. Among these, **(106b and 106d-h)** constitute previously unreported triazines in this series.

Table 2.3. Physical Data for 1,2,3-Triazines **(106)**

Cmpd No.	Mol. Formula	M.W	Yield (%)	M.P. (°C)	Found (Theory) (%) C	H	N
106a	$C_{32}H_{26}N_4O_4$	530.58	83	152-154	72.50	5.00	10.33
					(72.45)	(4.91)	(10.54)
106b	$C_{30}H_{24}N_4O_2$	472.19	78	142-144	76.36	5.16	11.74
					(76.24)	(5.12)	(11.86)
106c	$C_{32}H_{24}Cl_2N_4O_4$	599.47	77	183-185	64.23	3.99	9.56
					(64.11)	(4.04)	(9.35)
106d	$C_{30}H_{22}Cl_2N_4O_2$	541.44	85	170-171	66.69	4.07	10.33
					(66.55)	(4.10)	(10.35)
106e	$C_{29}H_{21}N_5$	439.52	69	142-144	79.35	4.93	15.97
					(79.25)	(4.82)	(15.93)
106f	$C_{29}H_{19}Cl_2N_5$	508.41	64	166-168	68.65	4.03	13.72
					(68.51)	(3.77)	(13.95)
106g	$C_{22}H_{22}N_4O_4$	406.44	54	80-82	65.26	5.58	13.52
					(65.01)	(5.46)	(13.78)
106h	$C_{20}H_{20}N_4O_2$	348.44	57		68.72	5.91	16.23
					(68.95)	(5.79)	(16.08)

We have obtained a crystal structure of one of the products and have confirmed the structure as **(106d)**. This is the nitrogen analogue of the triazine **(96)**, a crystal structure determiation of which was reported by Butler *et al* [74,75]. Crystals of 4,6-bis(4'-chlorophenyl)-5-methoxycarbonyl-2-phenyl-5-(N-phenylformimidoyl)-2,5-dihydro-1,2,3-triazine **(106d)** were grown from a saturated solution in n-hexane / diethyl ether (3:1), and the structure is shown in Fig.2.2. Of interest in the structure of the dihydrotriazine ring is the planar symmetrical nature of the atoms comprising the C-N-N-N-C system in which the N(1)-N(2)-N(3) and the C-N-N bond angles of 124.9° and 119.8° respectively, contrast with the buckled saturated region with almost normal C-C bond lengths and tetrahedral bond angles.

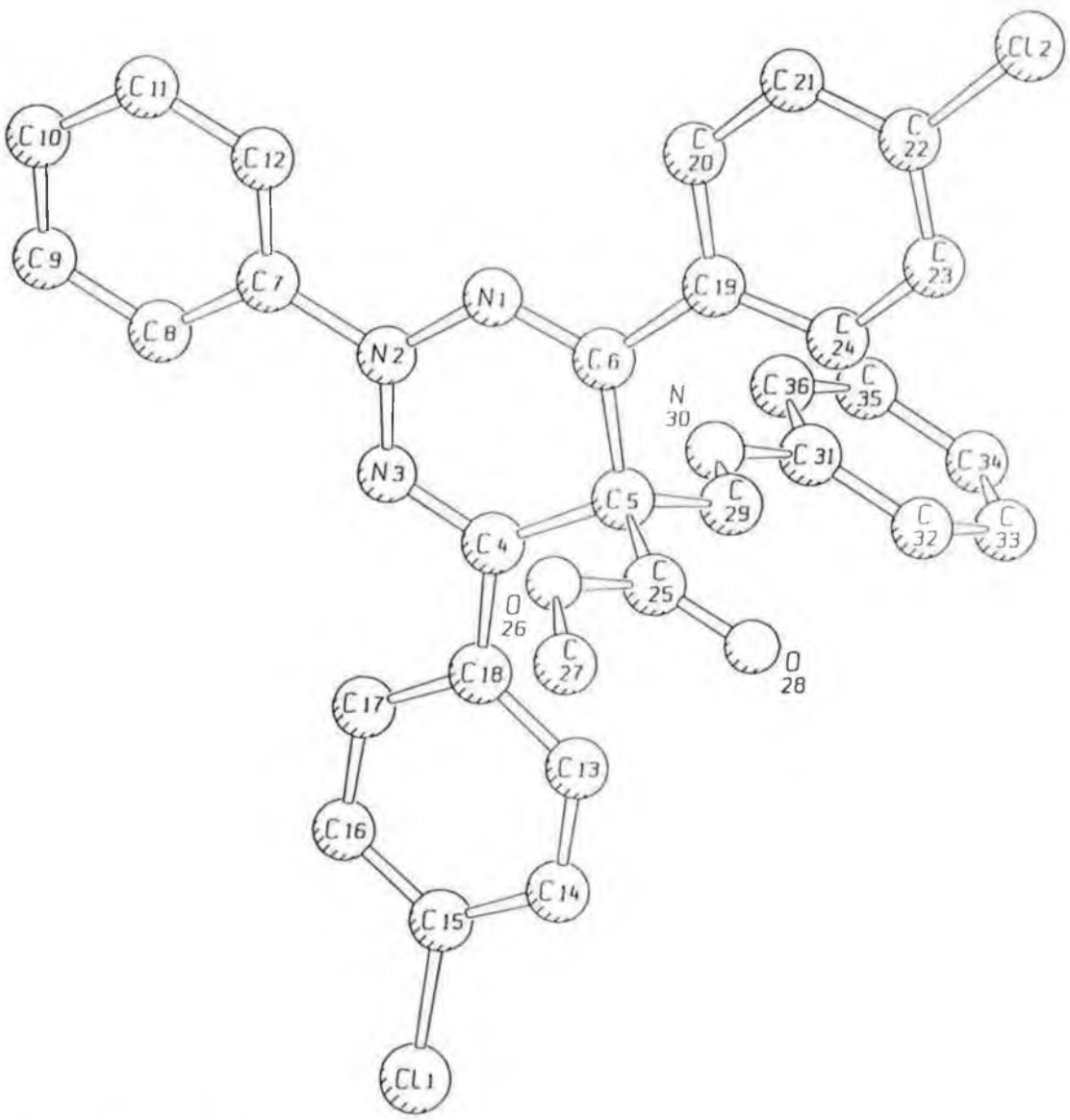


Fig. 2.2 Crystal Structure of **(106d)**

2.3) CONCLUSIONS

The thermal reactions of pyrrolotriazoles vary with substitution pattern. The reactions all involve initial cleavage of the C3a-N4 bond. Thermolysis of substituted 3a,6a-hexahydropyrrolo[2,3-*d*]triazoles leads, *via* C3a-N4 cleavage and subsequent fragmentation, to the aromatic triazole **(46)**. (Scheme 2.4) The 3a,6a-dimethyl hexahydropyrrolotriazole analogues **(69)** do not react under these conditions.

On thermolysis, tetrahydropyrrolo[2,3-*d*]triazoles undergo an initial sigmatropic rearrangement to a fused cyclopropane structure, followed by an electrocyclic ring expansion to monocyclic 1,2,3-triazines **(106)**. Alteration of substitution pattern appeared to have no effect on the reaction pathway.

The importance of the C5-C6 double bond in the rearrangement of tetrahydropyrrolotriazoles was confirmed as oxidation of hexahydropyrrolotriazoles **(82c)** and **(85)** led to the corresponding triazines in high yield *via* the tetrahydropyrrolotriazole intermediate **(112)**.

Table 2.4 Summary of Thermal Transformations of Pyrrolo[2,3-*d*]triazoles.

Bridgehead Substsituents	C5-C6 Saturation	Product
Ph	Saturated	1,2,3-Triazole **(46)**
Me	Saturated	No Reaction
Ph	Unsaturated	1,2,3-Triazine**(106a-f)**
Me	Unsaturated	1,2,3-Triazine **(106g,h)**

2.4) EXPERIMENTAL

2.4a) Thermolysis of Substituted Hexahydropyrrolo[2,3-*d*]-1,2,3,-triazoles.

2.4a.1) *Thermolysis of (82a).*

A solution of 500mg (1.13 mmol) of **(82a)** in toluene was refluxed for 40 hours. The product was separated from the remaining starting material by flash chromatography (silica gel 0.032-0.063mm mesh size) using 3:1 pet.ether (40-60) / ethyl acetate as eluant. The product **(46)** was crystallised from pet.ether (60-80) in 87% yield. M.p: 119-121°C (Lit.122°C).[46] The ir spectrum was identical to that obtained in 1.4c.3.

2.4a.2) *Thermolysis of (82b).*

A solution of 500mg (1.05 mmol) of **(82b)** in toluene was refluxed for 30 hours. The product was separated from the remaining starting material by flash chromatography (silica gel 0.032-0.063mm mesh size) using 3:1 pet.ether (40-60) / ethyl acetate as eluant. The product **(46)** was crystallised from pet.ether (60-80) in 83% yield. M.p: 120-122°C (Lit. 122°C).[46] The ir spectrum was identical to that obtained in 1.4c.3.

2.4a.3) *Thermolysis of (91).*

A solution of 500mg (1.05 mmol) of **(91)** in toluene was refluxed for 100 hours. The product was separated from the remaining starting material by flash chromatography (silica gel 0.032-0.063mm mesh size) using 3:1 pet.ether (40-60) / ethyl acetate as eluant. The product **(46)** was crystallised from pet.ether (60-80) in 10% yield. M.p: 119-121°C (Lit. 122°C).[46] The ir spectrum was identical to that obtained in 1.4c.3.

2.4a.4) *Thermolysis of (70b).*

A solution of 500mg (1.50 mmol) of **(70b)** in toluene was refluxed in toluene for 40 hours. No reaction was observed.

2.4a.5) *Thermolysis of (70c).*

A solution of 500mg (1.58 mmol) of **(70c)** in toluene was refluxed in toluene for 48 hours. No reaction was observed.

2.4a.6) *Thermolysis of (71).*

A solution of 500mg (1.30 mmol) of **(71)** in toluene was refluxed in toluene for 40 hours. No reaction was observed.

2.4b) Thermal Transformations of Tetrahydropyrrolo[2,3-*d*]-1,2,3-triazoles.

2.4b.1) Thermal rearrangement of (81a).

A solution of 1.5g (2.84 mmol) **(81a)** in toluene was stirred under reflux for 10 hours, cooled and the solvent removed under vacuum. The residue was passed through a flash chromatography column of silica gel (0.032-0.063 mm mesh size) and eluted with 3:1 pet.ether / ethyl acetate to give 1.25g (83%) of the orange product **(106a)** on recrystallisation from 1/1 diethyl ether / pet.ether (40-60). M.p.152-154°C (Lit. 151-152°C).[67]

CHN Analysis (found / theory) (%): M.w.: 530.58; $C_{32}H_{26}N_4O_4$; C (72.50 / 72.45), H (5.00 / 4.91), N (10.33 / 10.54).

IR (KBr) (cm^{-1}): 1749, 1730 (both CO_2CH_3), 1662 (C=N), 778, 756, 693.

δH ($CDCl_3$) (ppm): 2.91, 3.76 (both 3H, s) (both CO_2CH_3), 6.49 (2H, d), 7.14 (4H, m), 7.40 (8H, m), 7.88 (6H, m) (all phenyl H).

δC ($CDCl_3$) (ppm): 51.61, 53.46 (both CO_2CH_3), 58.71 (C-5), 116.36, 117.73, 123.73, 124.98, 127.99, 128.59, 128.79, 129.41, 130.44 (all phenyl CH), 134.78 (4-C-Ph, C-1'), 136.18 (C-4), 145.73 (2-N-Ph, C-1'), 148.68 (iminyl N-Ph, C-1'), 156.89 (ester CO), 160.24 (ester CO), 168.99 (C=N).

2.4b.2) *Thermal rearrangement of (81b).*

A solution of 1.5g (3.18 mmol) of **(81b)** in toluene was stirred under reflux for 10 hours. The toluene was removed under vacuum and the product separated through a flash chromatography column (silica gel, 0.032-0.063 mm mesh size) with 3:1 pet.ether (40-60) / ethyl acetate as eluant The product was recrystallised from 1/1

diethyl ether / pet.ether (40-60) to yield 1.17g (78%) of the bright yellow / green product **(106b)**, m.p 142-144°C.

CHN Analysis: $C_{30}H_{24}N_4O_2$; M.w.: 472.19; C (76.36 / 76.24), H (5.16 / 5.12), N (11.74 / 11.86).

IR (KBr) (cm^{-1}): 1727 (C=O), 1638 (C=N), 774, 759, 748, 693, 637.

δH ($CDCl_3$) (ppm): 3.57 (3H, s) (ester CH_3), 6.78 (2H, d), 7.15 (2H, t), 7.23 (2H, t), 7.40 (8H , m), 7.78 (4H, m), 7.91 (2H, d) (all phenyl H), 8.47 (1H, s) (HC=N).

δC ($CDCl_3$) (ppm): 53.27 (ester C=O), 53.46 (C-5), 116.00, 120.26, 123.53, 126.22, 128.38, 128.85, 128.93 (all phenyl CH), 134.83 (4-C-Ph, C-1'), 135.23 (C-4), 145.17 (2-N-Ph, C-1'), 150.93 (iminyl N-Ph, C-1'), 160.46 (C=N), 170.17 (ester C=O).

2.4b.3) *Thermal Rearrangement of* ***(84a).***

A solution of 1.5g (2.50 mmol) of **(84a)** in toluene was stirred under reflux for 10 hours. The toluene was removed under vacuum and the product separated on a flash chromatography column (silica gel, 0.032-0.063 mm mesh size) with 3:1 pet.ether / ethyl acetate as eluant. The product **(106c)** was recrystallised from 1:1 diethyl ether / pet. ether (40-60) to yield 1.16g (77%), m.p. 183-185°C.

CHN Analysis (found / theory) (%): M.w.: 599.47; $C_{32}H_{24}Cl_2N_4O_4$; C (64.23 / 64.11), H (3.99 / 4.04), N (9.56 / 9.35).

IR (KBr) (cm^{-1}):1747, 1728 (both ester C=O), 1652 (C=N), 834, 755, 751, 728, 694.

δH ($CDCl_3$) (ppm): 2.95 (3H, s) (ester CH_3), 3.76 (3H, s) (ester CH_3), 6.49 (2H, d), 7.09 (1H, t), 7.14 (1H, t), 7.24 (2H, t), 7.34 (4H. d), 7.39 (2H, t), 7.80 (4H, d), 7.86 (2H, d) (phenyl H).

δC ($CDCl_3$) (ppm): 51.80, 53.61 (both ester CH_3), 57.95 (C-5), 116.26, 117.89, 124.04, 125.45, 128.15, 128.77, 128.96, 131.65 (all phenyl CH) ,133.1 8 (4-C-Ph, C-4'), 134.82 (4-C-Ph, C-1'), 135.67 (C-4), 145.28 (2-N-Ph, C-1'), 148.57 (iminyl N-Ph, C-1'), 156.69 (ester C=O), 160.70 (ester C=O), 168.75 (C=N).

2.4b.4) *Thermal Rearrangement of* ***(84b)***.

A solution of 1.5g (2.77 mmol) of **(84b)** in toluene was stirred under reflux for 10 hours. The toluene was removed under vacuum and the product separated on a column using the same system as above. Recrystallisation of the product from diethyl ether / pet. ether (40-60) (1:1) yielded 1.28g (85%) of the orange-green crystals of **(106d)**, m.p.170-171°C. Crystals were carefully grown from the same solvent mixture. X-ray crystal structure analysis was performed at room temperature on an Enraf Nonius CAD4 single crystal diffractometer using graphite monochromated Mo-Kα radiation.

CHN Analysis (found / theory) (%) M.w. 541.44; $C_{30}H_{22}Cl_2N_4O_2$; C (66.69 / 66.55), H (4.07 / 4.10), N (10.33 / 10.35).

IR (KBr) (cm^{-1}): 1727 (ester C=O), 1627 (C=N), 829, 769, 745, 688 (mono- and *p*-disubstituted phenyl).

δH ($CDCl_3$) (ppm): 3.54 (3H, s) (ester CH_3), 6.80 (2H, d), 7.13 (2H, dd), 7.24 (2H, t), 7.34 (4H, d), 7.38 (2H, t), 7.69 (4H, d), 7.85 (2H, d) (mono-or *p*-disubstituted phenyl), 8.42 (1H, s) (HC=N).

δC ($CDCl_3$) (ppm): 53.00 (C-5), 53.48 (ester CH_3), 115.94, 120.24, 123.85, 126.59, 128.63, 128.90, 129.07, 129.70 (all phenyl CH), 133.15 (4-C-Ph, C-4'), 134.14 (4-C-Ph, C-1'), 135.62 (C-4), 144.77 (2-N-Ph, C-1'), 150.43 (iminyl N-Ph, C-1'), 159.68 (HC=N), 169.93 (ester CO).

Crystal Data for ***(106d)***: $C_{30}H_{22}Cl_2N_4O_2$; M.w. = 541.42, F(000) = 2240, monoclinic, a = 20.48(2)Å, b = 10.972(5)Å, c = 23.06(2)Å, α = 90°, β = 96.55(8)°, γ = 90°, V = 5147(7)Å^3, space group C2c, Z = 8, D_c =1.397g/cm^3, μ = 0.289mm^{-1}. The experimental data were collected at room temperature on an Enraf Nonius CAD4 automatic diffractometer, using graphite-monochromated Mo-Kα radiation (λ = 0.71069Å). The structure was solved by direct methods (SHELXS 86).[84] The structure was refined by full matrix least squares on F^2 to a final R value of 0.0524 (wR^2 = 0.1282) (SHELXL 93).[85]

Table 2.5. Atomic coordinates ($x10^4$) **(106d)**.

	X	Y	Z
Cl(2)	5634(1)	756(1)	3694(1)
Cl(1)	3561(1)	12553(1)	2819(1)
O(26)	3375(1)	6050(2)	3210(1)
O(28)	4210(1)	6286(2)	2681(1)
N(1)	4070(1)	5539(2)	4606(1)
N(2)	3752(1)	6541(2)	4756(1)
N(3)	3744(1)	7614(2)	4474(1)
N(30)	5422(1)	7443(2)	4093(1)
C(4)	4018(1)	7704(3)	3999(1)
C(5)	4372(1)	6646(3)	3731(1)
C(6)	4369(1)	5547(3)	4143(1)
C(7)	3446(1)	6489(3)	5283(1)
C(8)	3164(2)	7525(3)	5488(1)
C(9)	2868(2)	7465(3)	5998(1)
C(10)	2853(2)	6397(3)	6300(1)
C(11)	3130(2)	5365(3)	6091(1)
C(12)	3430(2)	5398(3)	5582(1)
C(13)	4123(2)	9127(3)	3155(1)
C(14)	4007(2)	10235(3)	2881(2)
C(15)	3715(2)	11139(3)	3165(2)
C(16)	3544(2)	10976(3)	3715(2)
C(17)	3658(2)	9860(3)	3982(1)
C(18)	3948(1)	8906(3)	3710(1)
C(19)	4705(1)	4401(3)	4018(1)
C(20)	4728(2)	3451(3)	4428(1)
C(21)	5016(2)	2351(3)	4331(1)
C(22)	5280(2)	2176(3)	3814(2)
C(23)	5284(2)	3074(3)	3409(1)
C(24)	4998(2)	4187(3)	3510(1)
C(25)	3995(1)	6302(3)	3140(1)

Table 2.5 continued.

C(27)	2943(2)	5760(4)	2690(1)
C(29)	5077(1)	7037(3)	3670(1)
C(31)	6075(1)	7862(3)	4063(1)
C(32)	6371(2)	7947(3)	3556(2)
C(33)	7002(2)	8403(4)	3572(2)
C(34)	7336(2)	8792(3)	4079(2)
C(35)	7050(2)	8712(4)	4585(2)
C(36)	6420(2)	8256(3)	4576(2)

Table 2.6. Interatomic distances (Å) for **(106d)**.

	Bond length (Å)		Bond length (Å)
Cl(2)-C(22)	1.755(3)	C(9)-C(10)	1.366(5)
Cl(1)-C(15)	1.758(3)	C(10)-C(11)	1.378(5)
O(26)-C(27)	1.327(4)	C(11)-C(12)	1.384(4)
O(28)-C(25)	1.442(4)	C(13)-C(14)	1.378(5)
N(1)-C(6)	1.192(3)	C(13)-C(18)	1.389(4)
N(1)-N(2)	1.289(3)	C(14)-C(15)	1.363(5)
N(2)-N(3)	1.343(3)	C(15)-C(16)	1.365(4)
N(2)-C(7)	1.431(3)	C(16)-C(17)	1.379(4)
N(3)-C(4)	1.291(3)	C(17)-C(18)	1.388(4)
N(30)-C(29)	1.222(4)	C(19)-C(24)	1.395(4)
N(30)-C(31)	1.424(4)	C(19)-C(20)	1.404(4)
C(4)-C(18)	1.477(4)	C(20)-C(21)	1.374(4)
C(4)-C(5)	1.536(4)	C(21)-C(22)	1.377(4)
C(5)-C(29)	1.527(4)	C(22)-C(23)	1.358(5)
C(5)-C(6)	1.536(4)	C(23)-C(24)	1.386(4)
C(5)-C(25)	1.536(4)	C(31)-C(36)	1.376(4)
C(6)-C(19)	1.478(4)	C(31)-C(32)	1.380(4)
C(7)-C(12)	1.384(4)	C(32)-C(33)	1.382(5)
C(7)-C(8)	1.382(4)	C(33)-C(34)	1.355(5)
C(8)-C(9)	1.383(4)	C(34)-C(35)	1.367(5)
		C(35)-C(36)	1.380(5)

Table 2.7 Bond angles for **(106d)**.

Angle	Degrees	Angle	Degrees
C(25)-O(26)-C(27)	116.6(2)	C(14)-C(15)-Cl(1)	119.3(3)
C(6)-N(1)-N(2)	119.8(2)	C(16)-C(15)-Cl(1)	119.1(3)
N(1)-N(2)-N(3)	124.9(2)	C(15)-C(16)-C(17)	118.9(3)
N(1)-N(2)-N(7)	117.2(2)	C(16)-C(17)-C(18)	121.8(3)
N(3)-N(2)-N(7)	117.6(2)	C(17)-C(18)-C(13)	117.0(3)
C(4)-N(3)-N(2)	119.7(2)	C(17)-C(18)-C(4)	119.6(3)
C(29)-N(30)-C(31)	122.6(3)	C(13)-C(18)-C(4)	123.3(3)
N(3)-C(4)-C(18)	114.9(3)	C(24)-C(19)-C(20)	117.1(3)
N(3)-C(4)-C(5)	123.7(3)	C(24)-C(19)-C(6)	124.2(3)
C(18)-C(4)-C(5)	121.4(2)	C(20)-C(19)-C(6)	118.7(2)
C(29)-C(5)-C(4)	108.6(2)	C(21)-C(20)-C(19)	121.7(3)
C(29)-C(5)-C(6)	110.4(2)	C(20)-C(21)-C(22)	118.8(3)
C(4)-C(5)-C(6)	108.0(2)	C(23)-C(22)-C(21)	121.9(3)
C(29)-C(5)-C(25)	111.9(2)	C(23)-C(22)-Cl(2)	120.0(3)
C(4)-C(5)-C(25)	109.2(2)	C(21)-C(22)-Cl(2)	118.1(3)
C(6)-C(5)-C(25)	108.6(2)	C(22)-C(23)-C(24)	119.2(3)
N(1)-C(6)-C(19)	115.6(2)	C(23)-C(24)-C(19)	121.3(3)
N(1)-C(6)-C(5)	123.6(2)	O(28)-C(25)-O(26)	124.2(3)
C(19)-C(6)-C(5)	120.8(2)	O(28)-C(25)-C(5)	126.3(3)
C(12)-C(7)-C(8)	120.4(3)	O(26)-C(25)-C(5)	109.5(2)
C(12)-C(7)-N(2)	119.7(3)	N(30)-C(29)-C(5)	119.7(3)
C(8)-C(7)-N(2)	119.9(3)	C(36)-C(31)-C(32)	118.3(3)
C(9)-C(8)-C(7)	119.5(3)	C(36)-C(31)-N(30)	116.9(3)
C(10)-C(9)-C(8)	120.8(3)	C(32)-C(31)-N(30)	124.7(3)
C(9)-C(10)-C(11)	119.4(3)	C(33)-C(32)-C(31)	120.1(3)
C(10C(11-C(12)	121.0(3)	C(34)-C(33)-C(32)	121.0(4)
C(7)-C(12)-C(11)	118.8(3)	C(33)-C(34)-C(35)	119.6(4)
C(14)-C(13)-C(18)	121.8(3)	C(34)-C(35)-C(36)	120.0(4)
C(15)-C(14)-C(13)	118.9(3)	C(31)-C(36)-C(35)	121.0(3)
C(14)-C(15)-C(16)	121.6(3)		

2.4b.5) *Oxidative Rearrangement of* ***(81c).***

A solution of 1.5g (3.40 mmol) of **(81c)** in 30cm^3 of toluene, containing an excess of manganese dioxide was refluxed for 5 hours. On completion, the solution was allowed to cool and the insoluble salts filtered off under vacuum. The toluene was then removed under reduced pressure and the residue was separated on a flash chromatographic column using silica gel. The compound was recrystallised from diethyl ether / pet. ether (40-60) and yielded a brightly fluorescent green-yellow compound **(106e)** in 69% yield (1.03g), m.p. 142-144°C. (Lit. 146-147°C)[67]

CHN Analysis: (found / theory) (%): M.w.: 439.52; $C_{29}H_{21}N_5$; C (79.35 / 79.25), H (4.93 / 4.82), N (15.97 / 15.93).

IR (KBr) (cm^{-1}): 2240 (CN), 1638 (C=N), 844, 824, 764, 752, 740, 691, 631.

δH ($CDCl_3$) (ppm): 6.54 (2H, d), 6.78 (2H, m), 6.88 (2H, t), 7.04 (8H, m), 7.45 (2H, d), 7.55 (4H, m)

δC ($CDCl_3$) (ppm): 43.29 (C-5), 114.85 (CN), 115.92, 120.55, 124.37, 127.35, 128.48, 129.08, 129.15, 129.27, 130.45 (all phenyl CH), 130.36 (4-C-Ph, C-1'), 132.99 (C-4), 144.40 (2-N-Ph, C-1'), 149.07 (iminyl N-Ph, C-1'), 154.01 (C=N).

2.4b.6) *Oxidative Rearrangement of* ***(85).***

To a solution of 1.5g (2.95 mmol) of **(85)** in toluene was added an excess of activated manganese dioxide. The solution was refluxed using a Dean and Stark apparatus for 5 hours. The manganese dioxide was removed by gravity filtration and the toluene removed under vacuum. The product was separated on a flash chromatography column using the same system as above. The product was recrystallised from 1:1 diethyl ether / pet.ether (40-60) to yield 956mg (64%) of a fluorescent orange yellow compound **(106f)** m.p. 166-168°C.

CHN analysis (found / theory) (%): M.w. 508.41; $C_{29}H_{19}Cl_2N_5$; C (68.65 / 68.51), H (4.03 / 3.77), N (13.72 / 13.95).

IR (KBr) (cm^{-1}): 2239 (CN), 1633 (HC=N), 861, 840, 818, 770, 753, 695, 693.

δH ($CDCl_3$) (ppm): 7.06 (2H, d), 7.24 (1H, t), 7.30 (1H, t), 7.39 (2H, t), 7.48 (6H, m), 7.87 (2H, d), 7.96 (4H, d) (all phenyl H), 7.81 (1H, s) (HC=N).

δC ($CDCl_3$) (ppm): 43.00 (C-5), 114.61 (CN), 115.91, 120.66, 124.71, 127.82, 128.82, 128.18, 129.43, 130.22 (all phenyl CH), 131.35 (4-C-Ph, C-1'), 136.84 (C-4), 144.10 (2-N-Ph, C-1'), 148.56 (iminyl N-phenyl, C-1), 153.24 (C=N). (Peak overlap prevented observation of other peaks).

2.4b.7) *Thermal Rearrangement of (69a).*

A solution of 1.5g (3.69 mmol) of **(69a)** in toluene was refluxed for 10 hours. The toluene was then removed under vacuum and the residue separated using the same chromatography system as above (Section 2.4b.1). The product proved difficult to crystallise but an orange solid of **(106g)** was formed from pet. ether (60-80) in 54% yield (810mg), m.p. 80-82°C.

CHN Analysis (Found / Theory) (%): M.w.: 406.44; $C_{22}H_{22}N_4O_4$; C (65.26 / 65.01), H (5.58 / 5.46), (13.52 / 13.78).

IR (KBr) (cm^{-1}): 1736 (ester C=O), 1643 (C=N), 868, 843, 761, 746, 695, 658

δH ($CDCl_3$) (ppm): 2.37 (6H, s) (2 x CH_3), 3.52 (3H, s) (ester CH_3), 3.80 (3H, s) (ester CH_3), 6.81 (2H, d), 7.10 (2H, m), 7.34 (4H, m), 7.76 (2H, d) (all phenyl H)

δC ($CDCl_3$) (ppm): 19.94 (2 x CH_3), 51.91 (ester CH_3), 53.00 (ester CH_3), 56.87 (C-5), 115.17, 118.19, 124.47, 125.29, 128.47, 128.61 (all phenyl CH), 134.04 (C-4), 145.20 (2-N-Ph, C-1'), 148.53 (iminyl N-Ph, C-1'), 158.28 (C=N), 163.34 (ester C=O), 167.22 (ester C=O).

2.4b.8) *Thermal Rearrangement of (69b).*

A solution of 1.5g (4.31 mmol) **(69b)** in toluene was refluxed for 10 hours. The toluene was then removed under vacuum and the residue passed through the same chromatography system as above. The product proved difficult to crystallise but on precipitation from pet. ether (60-80) in 57% (855mg) a yellow low melting solid **(106h)** was formed.

CHN Analysis (found / theory) (%): M.w.: 348.4; $C_{20}H_{20}N_4O_2$; C (68.72 / 68.95), H (5.91 / 5.79), N (16.23 / 16.08).

IR (KBr) (cm^{-1}): 1730 (ester C=O), 1645 (C=N), 892, 855, 824, 789, 755, 691, 672.

δH ($CDCl_3$) (ppm): 2.18 (6H s) (CH_3), 3.81 (3H, s) (ester CH_3), 7.05 (3H, m), 7.28 (5H, m), 7.70 (2H, d) (all phenyl H), 8.09 (1H, s) (HC=N).

δC ($CDCl_3$) (ppm): 20.16 (2 x CH_3), 53.04 (ester CH_3), 54.47 (C-5), 115.18, 120.46, 122.44, 126.52, 128.61, 129.01 (all phenyl CH), 134.23 (C-4), 145.38, 2-N-Ph, C-1'), 150.45 (iminyl N-Ph, C-1'), 157.77 (C=N), 168.51 (ester CO).

2.4c) Oxidation reactions

2.4c.1) Oxidation of 6-cyano-2,3a,4,6a-tetraphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-d]-1,2,3-triazole ***(82c)***.

To a solution of 1.0g (2.3 mmol) of the hexahydro-analogue in dry dichloromethane, stirred at room temperature, was added an excess of activated MnO_2 (1.1M equiv.). The reaction was followed by TLC (3:1 pet.ether(40-60) / ethyl acetate as eluant). After about 2 hours, the dichloromethane was removed under vacuum to yield a yellow powder **(112)**. Crude yield 748mg (74%). Attempts to purify **(112)** further led to the formation of the rearrangement product **(106e)**. M.w.: 439.52; $C_{29}H_{21}N_5$.

IR (KBr) (cm^{-1}): 2198 (-CN).

δH ($CDCl_3$) (ppm): 7.11 (16H, m), 7.56 (2H, t), 7.63 (1H, t), 8.43 (2H, d) (all phenyl H), (8.05 1H, s) (C=CH).

δC ($CDCl_3$) (ppm): 86.40 (C-6a), 93.51 (C-3a), 105.26 (C-6), 117.33 (CN), 118.18, 122.90, 123.31, 127.29, 127.70, 127.73, 127.79, 127.86, 127.95, 129.00, 129.14, 132.08, 134.89, 135.37, 138.69, 149.83.

2.4c.2) *Oxidation of (82b).*

To a solution of 500mg (1.05 mmol) of **(82b)** in dry DCM was added an excess of activated MnO_2. The mixture was stirred vigorously at room temperature for 2 hours. The MnO_2 was removed by vacuum filtration and the residue recrystallised from ethanol to yield 428mg (86%) of **(81b)**, m.p:141-143°C.

The ir, ^1H and ^{13}C nmr spectra were identical to those obtained for the product on cycloaddition of BPAS and MP (Section 1.4b.2).

CHAPTER 3

Photochemical Transformations of 1,3-Dipolar Cycloadducts Derived from 1,2,3-Triazolium N-imides

3.1) INTRODUCTION

3.1a) Principles of Photochemistry[86-88]

The field of photochemistry covers all processes which involve chemical change brought about by the action of visible or ultraviolet radiation, and these processes generally involve the direct participation of an electronically excited state of the molecule. Many everyday processes involve photochemical reactions, such as those of photosynthesis and vision, and this reflects that the major source of energy on the earth is the sun's radiation. Recently this has assumed a new prominence as an intensive search is made for ways of harnessing solar energy. Photographic processes, which have been in use for over a century, also employ visible radiation to produce chemical change in a system. Organic photochemistry, in which visible or ultraviolet radiation is used to bring about chemical reactions in organic molecules, has become a major field of study. The qualitative study of such reactions began long ago, and a more detailed study of simple gas phase processes followed, but it is only since about 1950 that intensive and systematic study of liquid and solid phase photochemical processes has emerged.

Photochemical reactions have made considerable impact in synthetic chemistry as they allow access to compounds which are difficult if not impossible to make thermally. Other reactions can be carried out more readily at reduced cost. The reason for the slow development of photochemistry as a synthetic technique was a lack of suitable u.v sources and adequate analytical techniques. Recent advances in these areas have allowed rapid development in the field of organic photochemistry. Thermal and photochemical reactions are simply different aspects of chemistry and the same basic theoretical considerations and descriptive models can be used in both areas. One of the major causes of difference between thermal and photochemistry lies in the electronic distributiuon in the ground and excited electronic states of a molecule. The second major difference involves thermodynamical considerations as to the feasibility of reaction. An electronically excited state of a molecule has a higher internal energy than the ground state and can give rise to

high energy products such as radicals, biradicals or strained ring compounds, which are not readily formed from the ground state

Electromagnetic radiation is regarded as having a dual nature. It propagates through space in wave form, obeying the relationship

$$c = \upsilon\lambda$$

where c = speed of electromagnetic radiation, υ = the frequency of the radiation, λ = the wavelength of the electromagnetic radiation. At the same time, absorption or emission of radiation by matter occurs only in discrete quanta (photons) and is governed by the relationship:

$$E = h\upsilon = hc / \lambda$$

where E is the energy absorbed or emitted, h = Planck's constant ($\sim 6.63 \times 10^{-34}$ Js).

When a photon passes close to a molecule there is an interaction between the electric field associated with the molecule and that associated with the radiation. This perturbation may result in no permanent change in the molecule but it is possible for a reaction to occur in which the photon is absorbed by the molecule. The photon ceases to exist and its energy is transferred to the molecule whose electronic structure changes. This change is visualised in simple molecular orbital terms as a change in the occupation pattern of a set of orbitals which is the same set as in the ground state. This is the "one electron approximation". The energy levels for a molecule are quantized, *i.e.* the energy required to raise an electron from one level to a higher one is a fixed quantity and the energy difference between levels given by ΔE. It is therefore possible, by knowing ΔE for particular orbitals to predict the frequency of light required to bring about that transition. For example, the π–π^* transition in buta-1,3-diene requires 254nm radiation for excitation. The energy of the incident photon will not often match exactly the energy

difference between the lowest vibrational levels of the ground and excited states of the absorbing molecule so that in most cases the state initially produced is an upper vibrational / rotational state of the excited electronic state.

Absorption by a molecule of radiation in u.v. (200-400 nm) or visible (400-800 nm) region of the spectrum can result in an excited state so high that the energy absorbed is comparable to the bond dissociation energies associated with organic molecules. Absorption at 250nm (480kJmol^{-1}) has an associated energy greater than the bond dissociation energy of a C-C σ-bond (D~347kJmol^{-1}). It is absorption of light in this region of the electromagnetic spectrum that is of primary concern to organic chemists.

The electrons in a ground state molecule have all their electrons spin paired. The total spin angular momentum (S) is therefore zero and the spin multiplicity, *i.e* the number of states expected in the presence of an applied magnetic field, given by 2S+1 is one. The ground state is therefore referred to as a singlet state and denoted 'S_0'. On excitation, two different possible electronically excited states may arise, one which preserves the spin orientation of the excited electron and one in which the spin is inverted. In the former case the spins are still opposed, and this is therefore a singlet excited state, denoted 'S_1' for the lowest excited singlet state. Inverting the spin orientation results in a spin angular momentum of 1. The multiplicity is 3 and this is termed a triplet state, denoted 'T_1' for the lowest excited triplet configuration.

In the electron excitation process there is a preference for preservation of spin, so S_0-S_1 transitions are allowed and appear as large peaks in the absorption spectrum of a molecule. S_0-T_1 transitions are 'spin forbidden' and are much weaker than the spin allowed processes. The energy of the triplet state is generally lower than that of the singlet state and is a consequence of Hund's Rule of maximum multiplicity. There is a repulsion energy associated with electrons of parallel spin and this depends on the extent of spatial overlap between the orbitals involved. This repulsion energy determines the energy difference

between the singlet and triplet states A consequence of this is the triplet states are longer lived than singlet states

The rate constants for the initial photochemical reactions involving the excited state are high (~10^6-10^9 s^{-1}). The reason for this is that the excited state is short lived, decaying to the ground state very rapidly, and an efficient photochemical reaction must compete successfully with these rapid photophysical processes Activation energies for excited state reactions are therefore generally small. The decay processes may be radiative (fluorescence, emission from an excited singlet state or phosphorescence, emission from a triplet excited state which involves spin inversion) or non-radiative (internal conversion between states of the same multiplicity or intersystem crossing between states of different multiplicity). Decay from higher to lower vibrational states involes collisions with solvent molecules and is called vibrational relaxation or vibrational cascade A general outline of these processes is given in the Jablonski diagram (Fig 3 1)

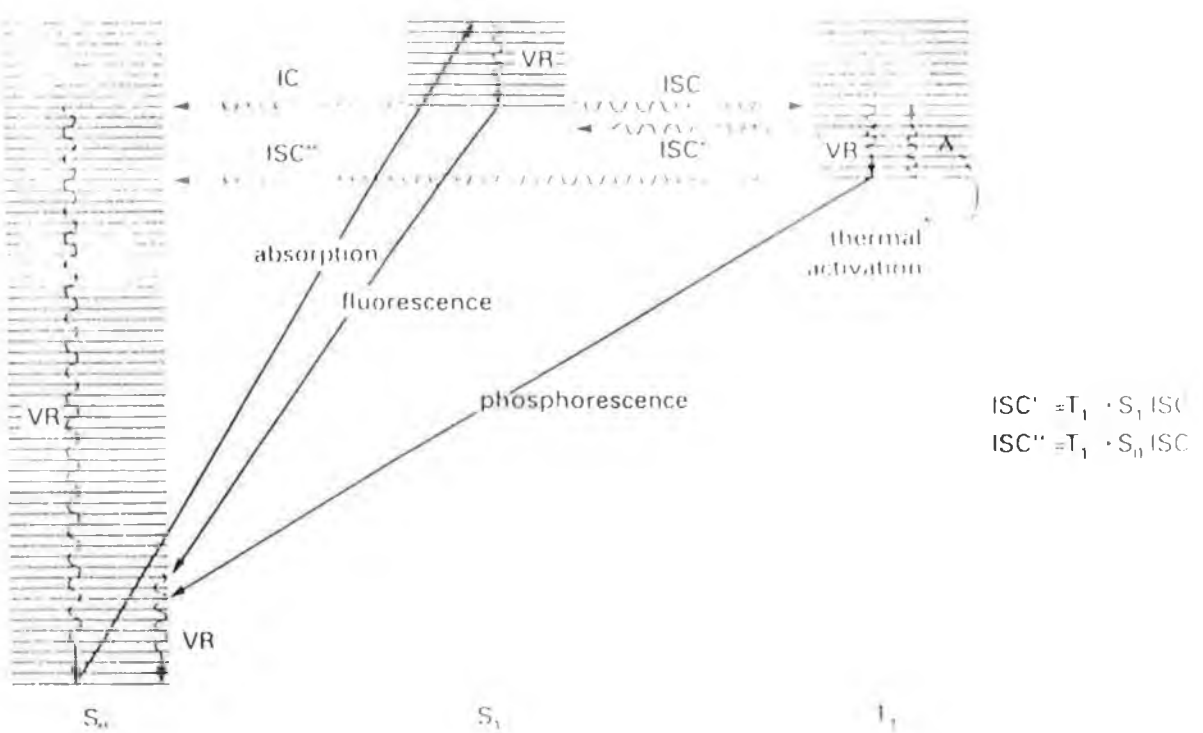


Fig 3.1 A Jablonski diagram

Although both excited singlet and triplet states can undergo chemical reactions, they are much more common for triplet states because they are longer lived. A list of possible primary photochemical pathways is given in Table 3.1.[89]

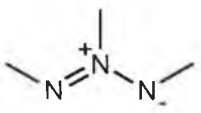
Table 3.1. Primary photochemical reactions of an excited molecule A-B-C.

(A-B-C-)*→A-B·+ C·	Simple cleavage into radicals
(A-B-C)*→E+F	Decomposition into molecules
(A-B-C)*→A-C-B	Intramolecular rearrangement
(A-B-C)*→A-B-C'	Photoisomerization
(A-B-C)*+RH→A-B-C-H+R·	Hydrogen-atom extraction
(A-B-C)*→$(ABC)_2$	Photodimerization
(A-B-C)*+A→ABC+A*	Photosensitization

3.1b) The Photochemical Rearrangements of Azimines

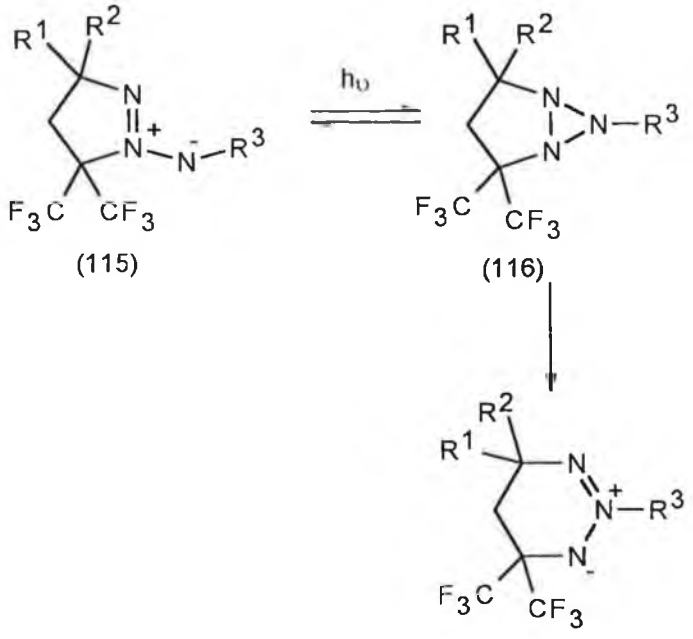
The photochemical activity of 1,3-dipoles has been known for some time and the change in colour on exposure of nitrones to direct sunlight was considered a property of these materials.[90] The photochemistry of 1,3-dipoles has been reviewed extensively.[88,91 92] The systems which have received the most attention are of the allyl type containing nitrogen as the centre atom. In this section the photochemistry of azimines is examined.

Azimines possess the three-nitrogen 4π dipolar system **(114)**. The azimine system is relatively not well known with studies on its synthesis and properties not appearing until 1970. Azimines are classified into cyclic, semicyclic and open chain systems and most of the known azimines are relatively stable and easily isolated. The synthetic approaches to these systems have been outlined.[93]



(114)

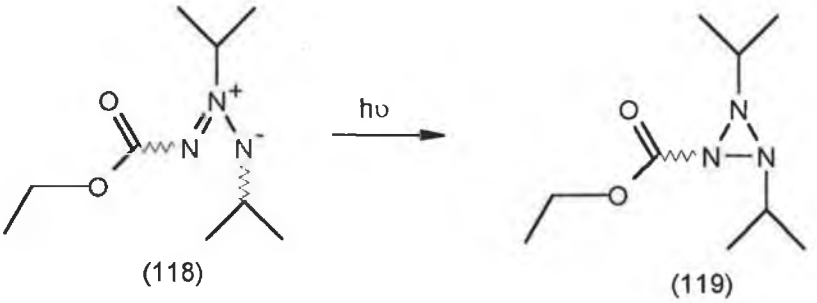
The nitrogen homocycles, triaziridines **(116)** have been postulated as intermediates in the photoisomerization of azimines **(115)**.[94]



(115) (116) (117)

Scheme 3.1

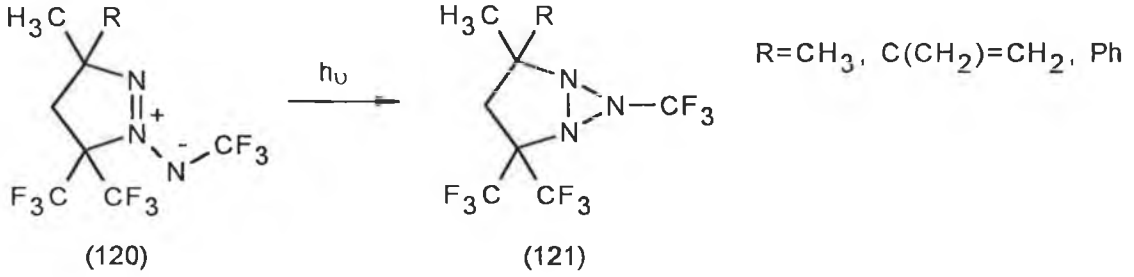
In 1980 Drieding *et al.* isolated the first authentic triaziridine **(119)** in low yield by u.v photolysis of the azimine **(118)**.[95] (Scheme 3.1)



Scheme 3.2

The structure of **(119)** was confirmed by spectroscopic techniques. The two isopropyl methine protons became ^{1}H nmr equivalent, and shifted to high field, an effect seen in hetero 3-membered rings. On standing at room temperature however the triaziridine reconverted to the azimine.[96,97]

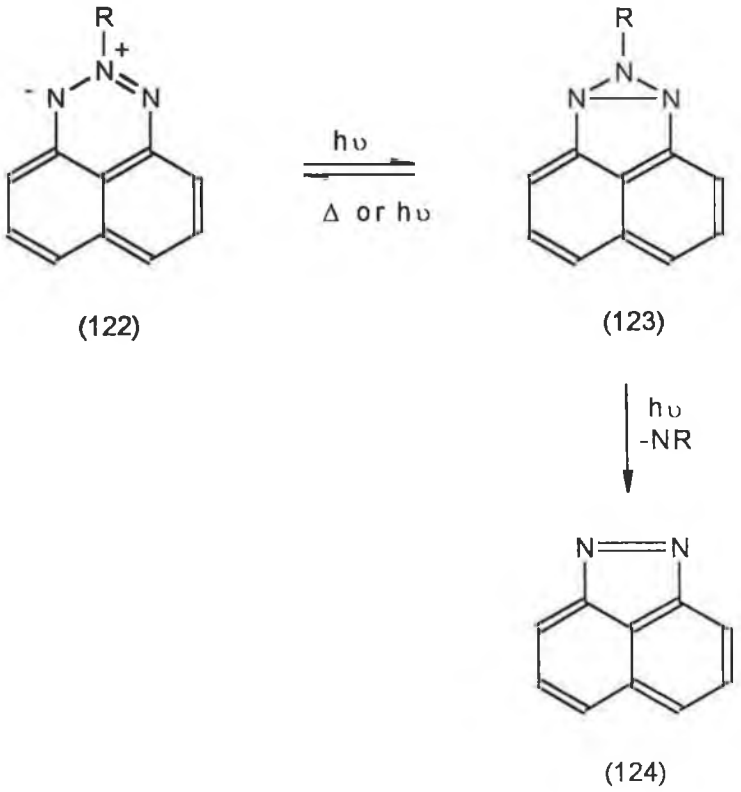
Kaupp *et al.* reported the synthesis of triaziridines **(121)** that are stable to at least 80°C by exploiting the stabilizing effect of perfluoroalkyl groups.[98] (Scheme 3.2)



Scheme 3.3

The blue azimine **(122)**, of interest as an inhibitor in the photooxidation of polymers and as a trapping reagent for the detection of free radicals, proved to be stable on long and

short wavelength irradiation.[99] However, multiple excitation with excimer laser pulses led to a disappearance of the blue colour and the product was assigned the isomeric structure **(123)**. Further irradiation of **(123)** using a low pressure lamp led to the reformation of **(122)**, along with a number of others, the major by-product being **(124)**, formed by loss of methyl nitrene. (Scheme 3.4)

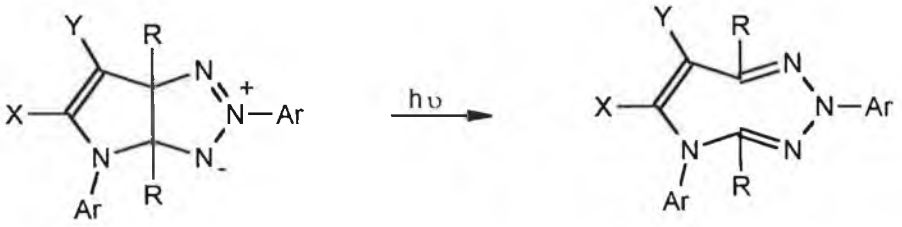


(122) (123) (124)

Scheme 3.4

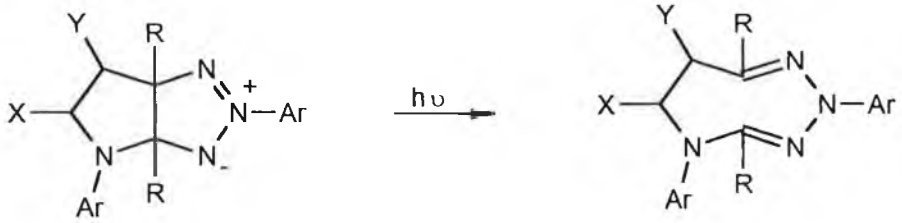
3.2) Results and Discussion

Compounds **(21)** and **(22)** contain an azimine function which was thought should lead to a number of rearrangements in which the formal charges would be dissipated. Of great interest was the possibility that the C3a-C6a bond would be cleaved to produce the novel substituted-1,2,3,5-tetrazocines **(125)** and **(126)**. (Schemes 3.5a and b)



(21) (125)

Scheme 3.5a

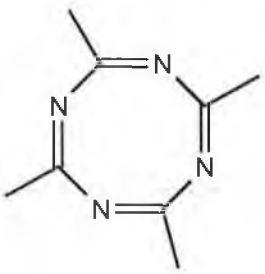


(22) (126)

Scheme 3.5b

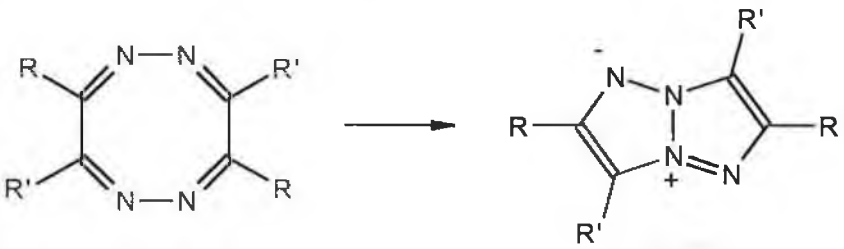
This would constitute a new entry into the tetrazocine ring system. Being a 10π-electron 8-membered ring it was thought that **(125)** might benefit from some aromatic stabilization and therefore be stable enough to isolate. The 10π-electron cyclooctatetraenedianion is known to be aromatic.[100]

Of the tetrazocine series, 1,3,5,7-tetrazocines **(127)** have been the most extensively studied, mainly with regard to their use as gun and rocket propellants.[101,102]



(127)

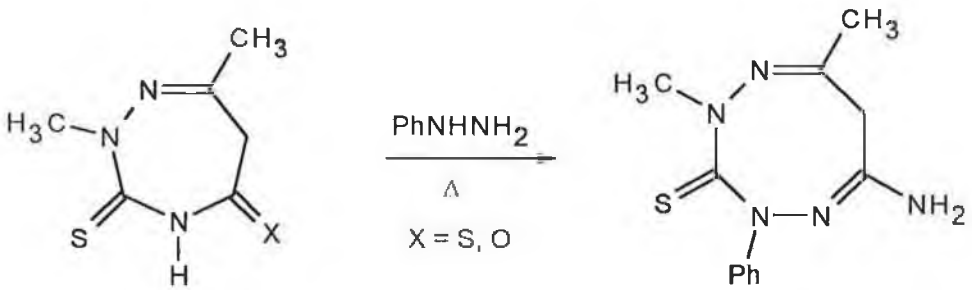
The 1,2,5,6-tetrazocines **(128)**, described regularly in early literature, have been shown in fact to be tetrazapentalenes **(129)**.[103-105] (Scheme 3.6)



(128) (129)

Scheme 3.6

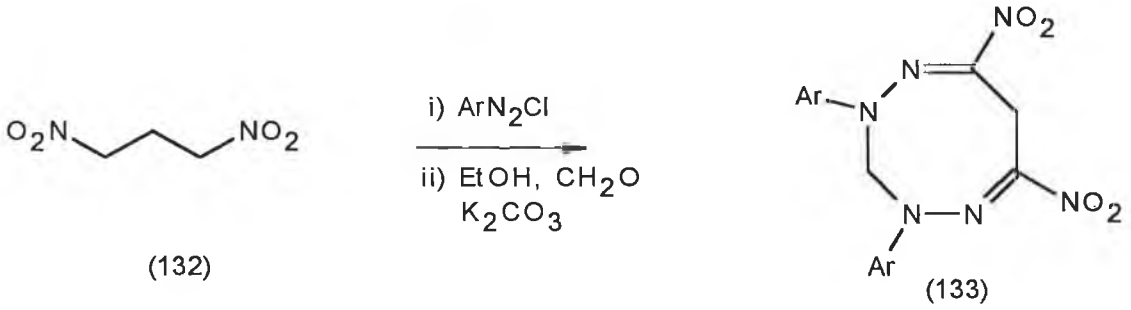
Reports on other tetrazocines (*i.e.* 1,2,3,4-tetrazocine[106], 1,2,4,6-tetrazocine[106] and 1,2,4,5-tetrazocine[107,108]) have been rare. (Schemes 3.7 and 3.8)



(130) (131)

Scheme 3.7. Formation of 2,8-dimethyl-3-thioxo-4-phenyl-6-amino-2,3,4,7-tetrahydro-1,2,4,5-tetrazocine **(131)**.[107]

The mechanism of this reaction involved initial attack at C-5 followed by transannular attack at C-3. Cleavage of the C3-N4 bond with elimination of water or H_2S led to **(131)**. The use of hydrazine or methyl hydrazine led to the formation of pyrazoles by preferential transannular attack at C-7 followed by ring cleavage.[107]



(132) (133)

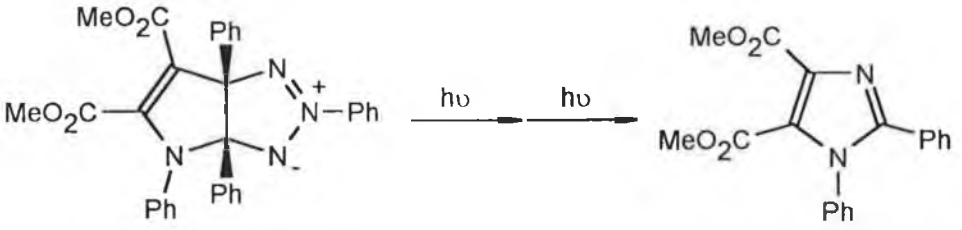
Scheme 3.8 Formation of 2,4-diphenyl-6,8-dinitro-2,3,4,7-tetrahydro-1,2,4,5-tetrazocine **(133)**.[108]

Compound **(133)** was also formed on condensation of $ArNHN{=}CHNO_2$ **(134)** with formaldehyde in the presence of piperazine in ethanol. This led to the formation of $(ArHNN{=}CNO_2)_2CH_2$ **(135)**. This was then reacted further with formaldehyde in ethanolic solution containing potassium carbonate to form **(133)**.[108]

As described in Section 2.2, the desired ring opening does not occur thermally. Reactions that are forbidden thermally are allowed photochemically according to the Woodward-Hoffmann rules for pericyclic reactions.[12] According to these rules thermal electrocyclic reactions are symmetry allowed when the total number of (4n+2) suprafacial and 4n antarafacial components is odd. The π-systems of **(21)** and **(22)** contain 4n electrons. Disrotatory electrocyclic ring expansion is therefore thermally forbidden and requires irradiation for disrotation. It was therefore thought that photolysis of **(21)** and **(22)** would lead to the novel tetrazocines **(125)** and **(126)**.

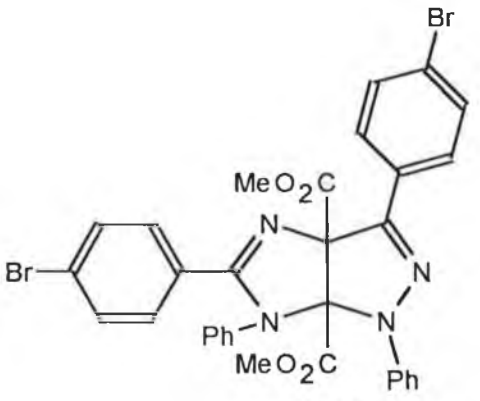
3.2a) Photorearrangement of Substituted 3a,6a-diaryl-2,4-diphenyl-3,3a,4,6a-tetrahydropyrrolo[2,3-*d*]-1,2,3-triazoles.

The photolysis of **(81a)** was carried out using a medium pressure mercury lamp with a pyrex filter. The reaction proceeded in high yield to a white powder which crystallised from *n*-hexane to clear white plates. CHN analysis revealed that the molecule was still intact. ^{13}C nmr spectroscopic analysis revealed two bridgehead carbon signals at 98.11 and 98.16ppm. In an attempt to further elucidate its structure the photoproduct was subjected to secondary photolysis, using the same photochemical conditions. The product isolated in moderate yield was the imidazole **(136)**, produced by the photofragmentation of the primary photoproduct. This led to the proposal of a bicyclic ring structure, one ring of which contained the imidazole moiety.



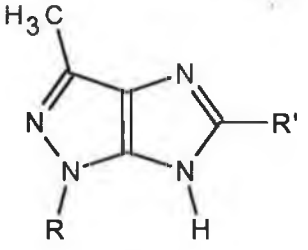
(81a) (136)

During the course of our work, Butler *et. al* reported the same electrocyclic rearrangement.[109] They carried out crystal structure analysis on the 2,4-bis(4'-bromophenyl)-5,6-bis(methoxycarbonyl)-analogue and found it to be the imidazo[4,5-*c*]pyrazole **(137)**.



(137)

There has been a growing interest in the imidazo[4,5-*c*]pyrazole ring system in recent years mainly due to photographic and pharmacalogical applications of its products, *e.g.* imidazopyrazoles **(138)** are strong central nervous system depressants with activity as anticonvulsants, sedatives, analgesics, and antipyretics.[110-113]



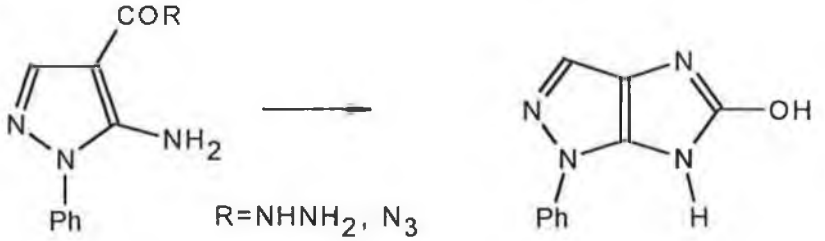
R=C_{1-4}alkyl, halophenyl

R'=C_{1-4}alkyl, Ph

(138)

Nevertheless these ring systems are still relatively rare and there are only a small number of reported synthetic approaches. These are as follows:

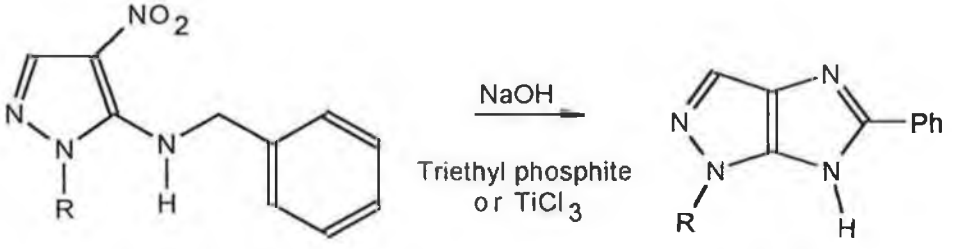
a) the Curtius rearrangement followed by cyclisation of 5-amino-4-pyrazolecarbonylazides:[114]



(139) (140)

Scheme 3.9

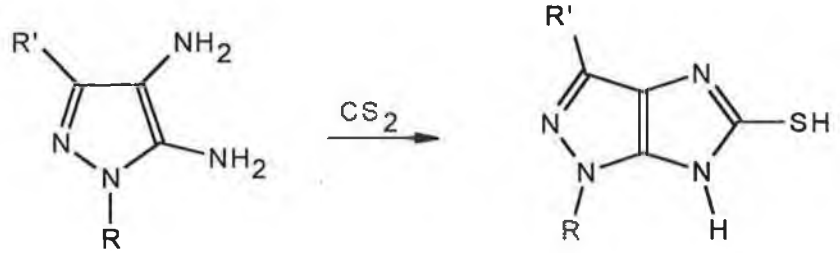
b) the cyclisation of 4-nitro-5-benzylamino-pyrazoles:[115]



(141) (142)

Scheme 3.10

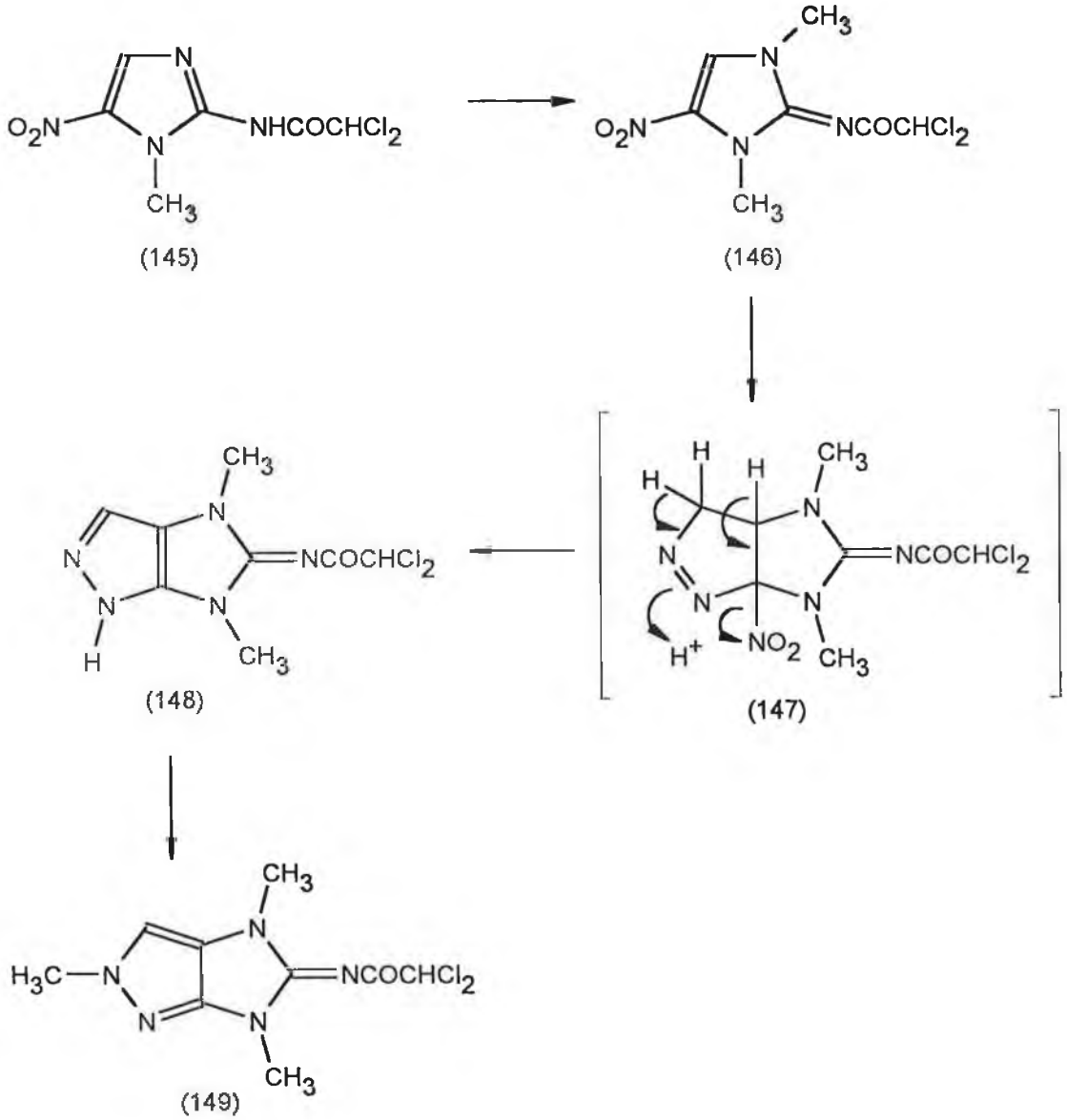
c) the reaction of 4,5-diamino-pyrazoles with carbon disulfide:[116]



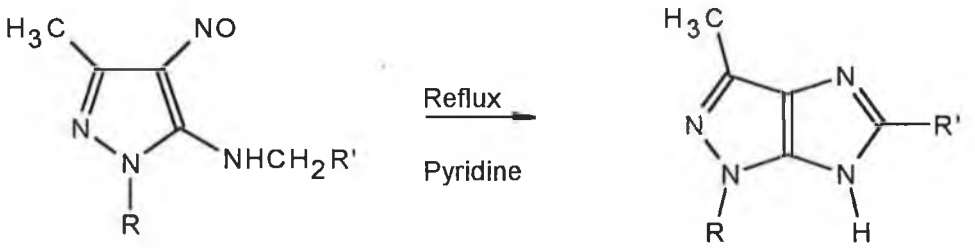
(143) (144)

Scheme 3.11

d) the cycloaddition of diazomethane to the C=C double bond of 5-nitroimidazoles:[117,118]



and e) the cyclisation of 4-nitroso-5-alkylamino-pyrazoles formed from the sequential acylation, reduction, and nitrosation of 5-aminopyrazoles:[119,120]



(150) (151)

Scheme 3.13

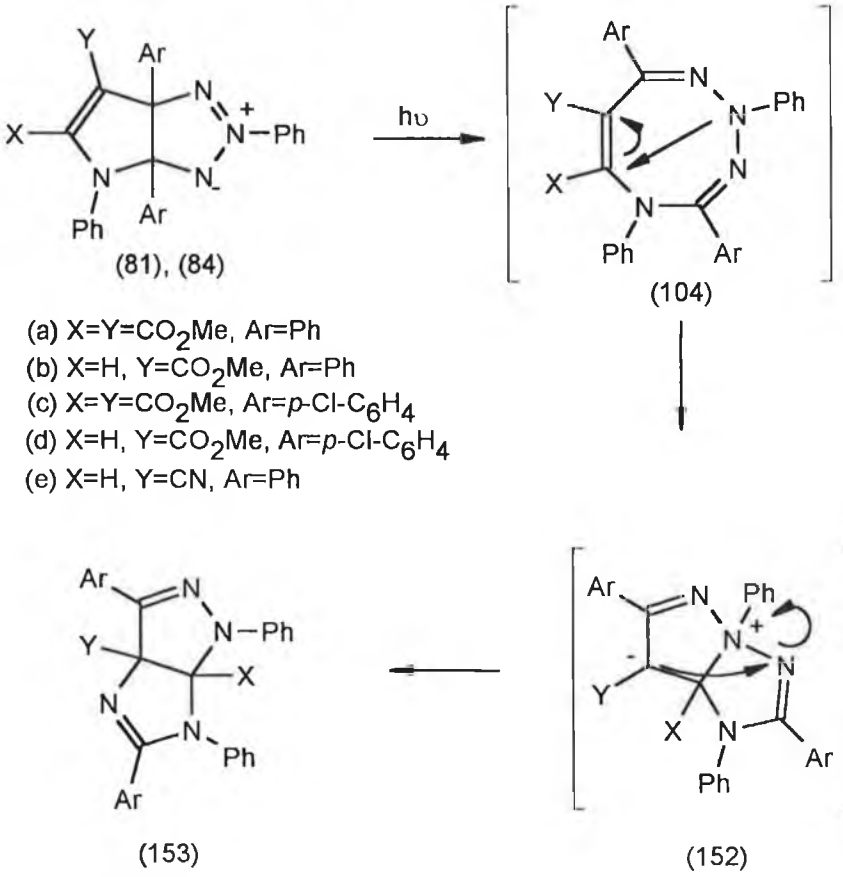
With the exception of route (d) all these routes depend on the availability of substituted 5-amino-pyrazole derivatives from which the imidazole ring is constructed.

The rearrangement observed on photolysis of compounds **(81)** constitutes a new route to imidazopyrazoles, proceeding in high yield from readily available precursors. The synthesis of the starting azapentalenes from 1,2-diketones and aryl hydrazones has been outlined in Section 1.2a. (Schemes 1.21, 1.22 and 1.34)

The mechanism proposed by Butler *et. al.* for this complex rearrangement involved an initial disrotatory outward electrocyclic ring expansion to the 10π-tetrazocine **(104)**.[109] This was then followed by a transannular ring contraction to the intermediate **(152)** and a 1,4-sigmatropic rearrangement involving N-N bond cleavage and C-N bond formation to yield the stable products **(153)**. (Scheme 3.14)

The instability of 8-membered heterocycles and their transannular ring contraction to azapentalenes is well documented. Gluz *et.al.* have calculated that unlike the aromatic cyclooctatetraene dianion its neutral heteroaromatic analogues should be assigned to the class of antiaromatic compounds.[121] HMO calculations indicate substantial resonance

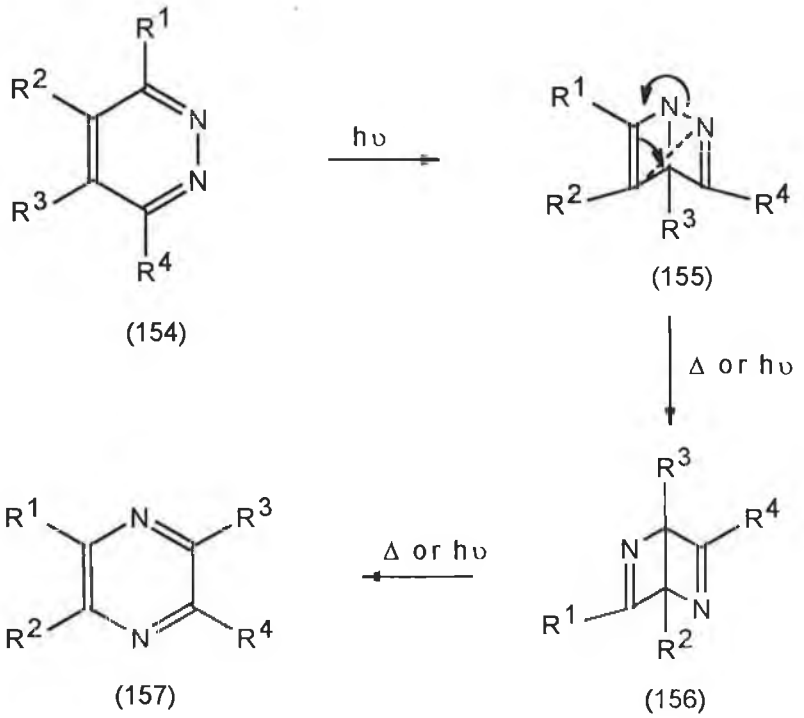
stabilization for the aromatic 10π-electron tetraazapentalene system **(127)** and significantly greater stability compared to the 1,2,5,6-tetrazocine **(126)**.[122] (See Scheme 3.6) The valence tautomeric relationships of polyazocines and polyazapentalenes have been summarized by Elguero *et. al.*[123]



Scheme 3.14. Mechanism of formation of imidazo[4,5-*c*]pyrazole **(153)** on pyrex filtered irradiation of substituted 3a,6a-tetrahydropyrrolo[2,3-*d*]triazole **(81), (84)**.

The 1,4-sigmatropic rearrangement of **(152)** to **(153)** is a thermally allowed suprafacial process. It involves 6 electrons, two of which come from the negative charge of the zwitterionic intermediate **(152)**. The migration dissipates the formal charges of **(152)** and is also favourable as it involves the breaking of a N-N bond and the formation of a C-N bond. This process is related to the photoisomerization of 3,6-difluoropyridazines **(154)**, where the rearrangement of **(155)** to **(156)** is an example of conversion of one type of valence isomer into another of the same type. (Scheme 3.15) The main driving force was

the removal of the relatively weak N-N bond. This process led to a 1,3-shift in an aromatic ring and has been suggested as a possible alternative to schemes involving the intermediacy of prismane derivatives when specific 1,3-shifts are observed.[124,125]



Scheme 3.15

The imidazo[4,5-*c*]pyrazoles reported by Butler *et al.* were derived from cycloadducts of 1,2-bis(arylazo)stillbenes with DMAD and DEAD.[109] We have extended the scope of the photorearrangement of **(81)** with the formation of imidazo[4,5-*c*]pyrazoles including structural variety at the bridgehead carbons (C3a and C6a) of both the reactant and the product **(153)**.[126] The presence of *p*-Cl-phenyl groups at C-3a and C-6a did not inhibit the reaction. The formation of **(153e)** proved somewhat troublesome as the starting tetrahydropyrrolotriazole **(112)** formed on oxidation of **(82c)** rearranged in solution at room temperature to the corresponding triazine **(106c)**, and therefore could not be isolated pure. (Scheme 2.8) Photolysis of a crude sample of **(112)** led to a complex

mixture of photoproducts, including products from the photolysis of **(82a)**, present as an impurity.

Separation of the desired photoproduct **(153e)** was achieved by flash chromatography and the off-white powder was recrystallised from *n*-hexane in 67% yield. A list of the imidazopyrazoles formed is given in Table 3.2

Table 3.2 Substituted tetrahydroimidazo[4,5-*c*]pyrazoles **(153)**.

	Mol. Formula	Mol. Weight	Yield (%)	M.P (°C)	Found (Theory) (%) C	H	N
153a	$C_{32}H_{26}N_4O_4$	530.58	89	152-154	72.62 (72.45)	4.89 (4.90)	10.46 (10.57)
153b	$C_{30}H_{24}N_4O_2$	472.55	83	176-178	75.97 (76.24)	5.20 (5.12)	11.61 (11.86)
153c	$C_{32}H_{24}Cl_2N_4O_4$	599.47	87	196-198	64.23 (64.11)	4.05 (4.01)	9.21 (9.35)
153d	$C_{30}H_{22}Cl_2N_4O_2$	541.44	82	218-220	66.25 (66.54)	4.09 (4.07)	10.05 (10.35)
153e	$C_{29}H_{21}N_5$	439.52	67	132-134	78.97 (79.27)	4.77 (4.78)	16.12 (15.95)

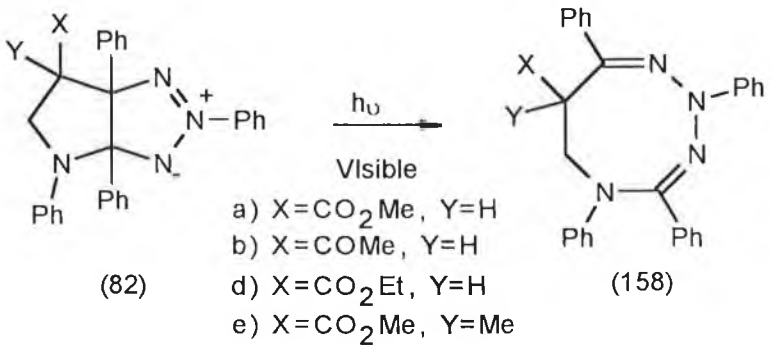
The intermediate tetrazocine ring **(104)** proposedly undergoes transannular ring contraction *via* nucleophilic attack of the N-2 lone pair on the electron deficient C-6. It can be seen from Table 3.2 that transannular ring contraction occurs also for tetrazocine intermediates which do not contain electron withdrawing substituents at C-6 (*i.e.* **(104b)** and **(104d)** for both of which X=H). The absence of the electron withdrawing group at C-6 did not hinder ring contraction and produced imidazopyrazoles unsubstituted at C-3a **(153b)** and **(153d)**. In light of this, an attempt was made to reduce the ester substituents

to alcohols which might prevent this ring contraction. Details of the attempted reductions are given in Section 1.2c. As described we were unable to carry out the selective reduction of the ester moiety, the C=C bond of both the α,β-unsaturated ester **(81b)** and the diester **(81a)** being reduced first. (Schemes 1.38 and 1.39)

3.2b) Photorearrangements of Substituted 2,3a,4,6a-tetraphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-*d*]-1,2,3-triazoles

The photolysis of the 3a,6a-diphenyl hexahydro-pyrrolo[2,3-*d*]triazoles **(82)** was examined. The absence of unsaturation between C-5 and C-6 would hopefully prevent transannular ring contraction and lead to isolation of the tetrazocine **(158)**. Irradiation of **(82a)** in visible light for 4 weeks led to nearly quantitative production of orange / green crystals. The reaction was also carried out using a xenon arc lamp at wavelengths greater than 385nm, with shorter reaction times but in slightly lower yields. Photolysis of compounds **(82)** in the visible region is an inefficient process as only the tail of longest wavelength peak in the uv spectrum is being irradiated. This was necessary as photolysis of **(82)** using a pyrex filter led to a large number of photoproducts, presumbly formed on fragmentation of the primary photoproduct.

On completion of the reaction, the product structure was determined by ir and ^{1}H and ^{13}C nmr spectroscopy. CHN analysis revealed that the molecule had remained intact. Analysis of the ^{13}C nmr spectrum of the product revealed the conversion of the two sp^3 bridgehead carbons characteristic of the starting tetraazapentalene **(82a)** into sp^2 hybridized carbons at 143.18 (C-8) and 168.81 (C-4). This led us to propose the ring opened 8-membered ring structure **(158)**. (Scheme 3.16) Orange / green crystals of **(158d)** were grown form 3:1 *n*-hexane / diethyl ether and the proposed structure was confirmed by x-ray crystallographic analysis.[126] (See Figure 3.2).



(82) (158)

Scheme 3.16

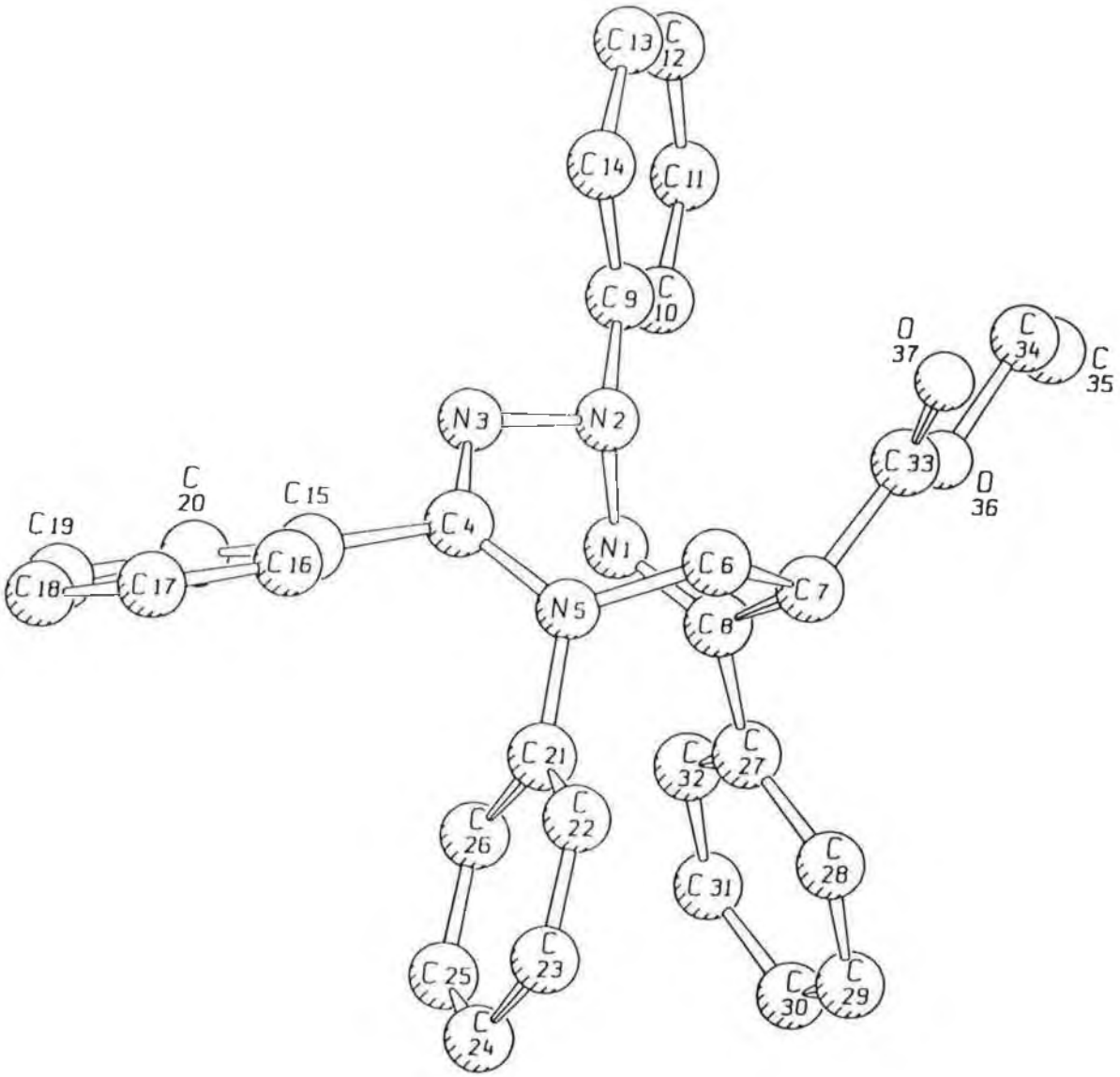


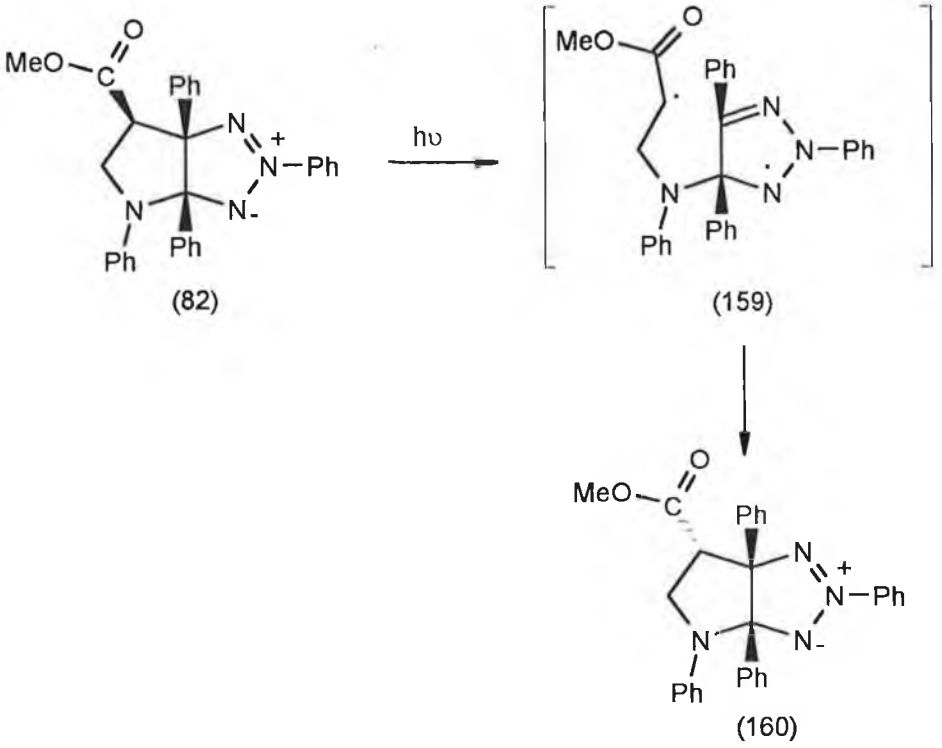
Fig.3.2. X-Ray Crystal Structure of **(158d)**

Of interest in the crystal structure is the twisted boat configuration seen for eight-membered rings with two strong torsional constraints (*i.e.* two endocyclic *cis*-double bonds). From this it is clear that the geometry is favoured for attack of N-2 on an electron deficient C-6 as would be the case for the dihydrotetrazocines **(106)**. Of greater importance however was the orientation of the ester group at C-7. From simple molecular modelling it was expected that disrotatory electrocyclic ring opening would lead to retention of the *cis*- relative stereochemistry of the C-7 ester group and the C-8 phenyl group. In order to determine whether the *trans*-geometry was induced prior or subsequent to rearrangement a re-examination of the phototransformation was undertaken.

On monitoring the photolysis of **(82a)** by TLC, using 3:1 pet.ether (40-60) / ethyl acetate as eluant, an intermediate was observed, which dissipated as the tetrazocine **(158a)** was formed. The intermediate was isolated by separation on a flash chromatography column using the same eluant system as for TLC. Spectroscopic analysis showed the intermediate to be very similar to the **(82a)**. The main difference was to be seen in the ^{1}H nmr spectra, where the chemical shift and the coupling constants of the C-5 and C-6 hydrogens differed to that of **(82a)**. The starting material showed three distinct triplets at 3.74, 3.96 and 4.44 ppm for 6-C-H and 5-C-H_2 respectively. For the photoproduct the signals appeared as a triplet for the 6-C-H at 3.89 ppm and a multiplet between 4.29 and 4.40. The ^{13}C signals for C-5 and C-6 also varied. For **(82a)** C-6 appears at 48.48 ppm and C-5 at 57.32, for the corresponding photoproduct the signals appeared at 49.84 and 50.16 ppm. The two characteristic bridgehead signals were still present. This led us to suggest that the initial step in the photochemical electrocyclic ring opening was an *exo-endo*-epimerization leading to **(160)**. (Scheme 3.17)

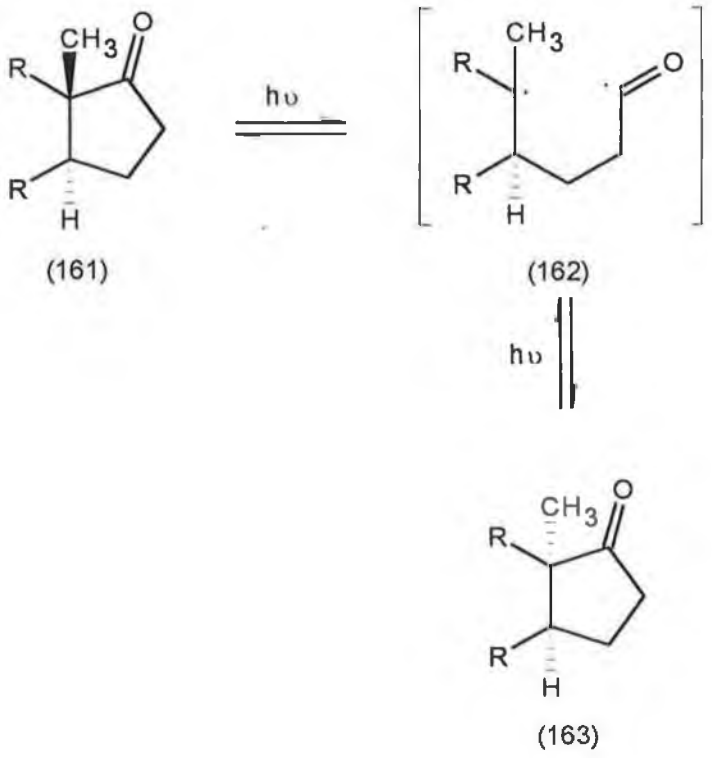
The possiblity that the epimerization was thermally induced was discounted as a control sample of **(82b)** stirred at room temperature in the dark for 6 weeks remained unchanged. In Chapter 1 (Section 1.2b) the 6-*exo*-cyano-3a,6a-dimethyl analogue **(70c)** underwent acid catalysed epimerization to the *endo*-analogue **(76)**. (Scheme 1.31) The mechanism

of that epimerization relied on the presence of a hydrogen α- to the electron withdrawing group. The fact that the epimerization occurred for **(82d)**, which has no α-hydrogen indicates that acid or base catalysed epimerization is not important in this case.



Scheme 3.17

The mechanism of this reaction may be explained in terms of eccitation of the azimine chromopohore leading to the formation of the biradical **(159)**. The resultant radical pair **(159)** is held within a solvent cage and may recombine to reform the starting material **(82a)** or may form the *endo*-isomer **(160)** *via* attack on the planar heterocyclic radical centre from the opposite direction. Photochemical racemization on the basis of α-cleavage of carbonyl groups is well documented.[127] The formation of a 1:2.6 ratio of *cis*- to *trans*-2,3-dimethylcyclohexanones from irradiation of either isomer provided evidence for the formation and recombination of an acyl-alkyl diradical intermediate.[128] 17-Keto steroids **(161)** and **(163)** are epimerized, in low quantum yield, by photoinduced cleavage and recombination.[86] (Scheme 3.18)



Scheme 3.18

8-Methyl-hydrindanones **(164)** and 9-methyl-1-decalones **(165)** exhibit *cis-trans* isomerisation *via* cage recombination of intermediate biradicals. Results suggest that these transformations occur almost exclusively *via* singlet excited states. (Scheme 3.19)[128]

Scheme 3.19a

(166) (167)

Scheme 3.19b

Examination of the u.v spectra for the *exo*- and *endo*- epimers **(82a)** and **(160)** reveals a difference in peak distribution. (See Appendix A) The spectrum of the *exo*-epimer **(82a)** contains a peak at 248nm (ε = 15470 l $mol^{-1}cm^{-1}$) as the lowest energy transition. The u.v spectrum of a 10^{-4}M solution of **(82a)** revealed a shoulder on the visible side of this peak, but with a low extinction coefficient. In the spectrum of the *endo*-epimer **(160)** the lowest energy transition can be seen at 294nm (ε = 22140 l $mol^{-1}cm^{-1}$). The difference in the spectra can be rationalised in terms of an interaction between the π-system of the electron withdrawing substituent in the *endo*-position with the azimine π-system. This interaction is not possible when the C-6-substituent is in the *exo*-configuration.

Steric considerations may also play a major part in the ring opening process. As can be seen from Fig. 3.2, an *equatorial*-configuration of the C-7 ester substituent would place it in the region of the C-8 and N-5 phenyl groups, and ring opening from **(82a)**, bringing these bulky substituents closer together would be thermodynamically unfavoured, compared to ring opening from **(160)**.

An attempt to extend this photochemically induced electrocyclic ring opening to compounds with electron donating groups at C-5 and C-6 failed. On stirring 5,6-bis(hydroxymethyl)-2,3a,4,6a-tetraphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-*d*]-1,2,3-triazole **(90)** for 6 weeks in sunlight, no reaction was observed. The reason for this may be explained in terms of the orientation of the C-6 substituent. An *endo*-orientation of the C-6 substituent appears to be a prerequisite for ring opening as mentioned above. The products formed on reduction of **(81a and b)** were found invariably to contain the C-6

substituent in the *exo*-orientation. (See Schemes 1.37 and 1.38) For ring opening to occur epimerisation about this bond was required. Epimerization due to α-cleavage could not occur in the case of **(90)**.

The photorearrangement of 3a,6a-diphenyl hexahydropyrrolotriazoles **(82)** was attempted for a number of different ring substituents, *i.e.* X=CO_2Me, COMe, CO_2Et, CN; Y=H, Me **(82a-e)** and the physical data for these compounds is given in Table 3.4.

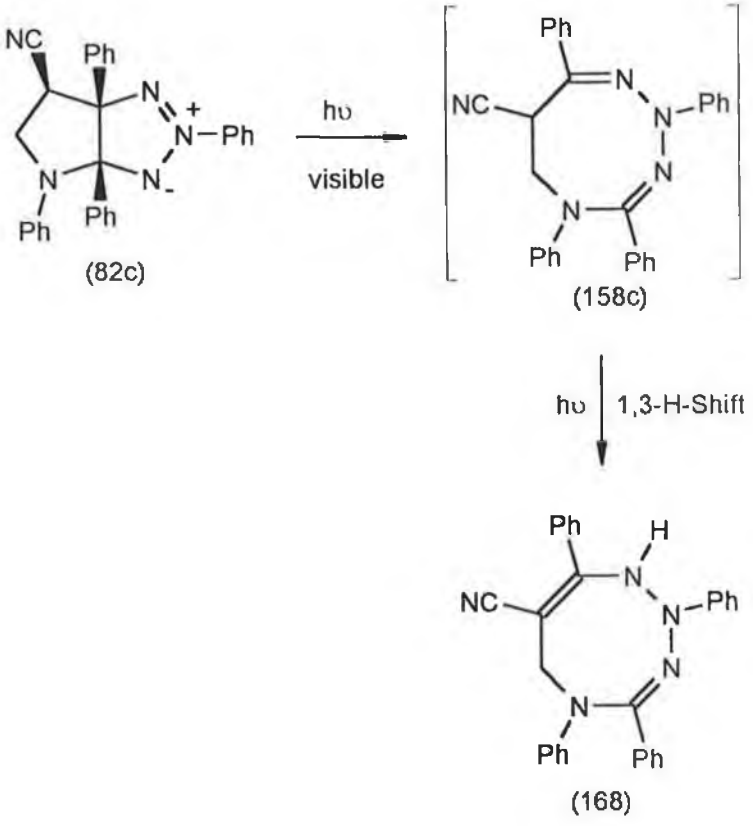
Table 3.4 Substituted tetrahydro-1,2,3,5-tetrazocines.

	Mol. Formula	Mol. Weight	Yield (%)	M.P. (T / °C)	Found (Theory) (%) C	H	N
158a	$C_{30}H_{26}N_4O_2$	474.56	82	114-115	76.20	5.63	11.52
					(75.95)	(5.74)	(11.81)
158b	$C_{31}H_{28}N_4O_2$	488.59	86	101-103	75.98	5.83	11.36
					(76.23)	(5.74)	(11.48)
158c	$C_{31}H_{28}N_4O_2$	488.59	79	138-140	76.34	5.96	11.26
					(76.23)	(5.74)	(11.48)
158d	$C_{30}H_{26}N_4O$	458.56	65	168-169	78.69	5.90	11.98
					(78.60)	(5.63)	(12.23)
168	$C_{29}H_{23}N_5$	441.54	68	164-166	78.60	5.23	15.44
					(78.90)	(5.22)	(15.87)

For all substituents except X=CN, Y=H **(82c)**, the reaction proceeded in high yield to the corresponding 2,5,6,7-tetrahydro-1,2,3,5-tetrazocine **(158a-d)** On photolysis of **(82c)** the expected tetrazocine was not isolated, but rather the 1,2,5,6-tetrahydro-1,2,3,5-tetrazocine **(168)**, resulting from a 1,3-H sigmatropic shift, was formed in 68% yield. The mechanism of this reaction is outlined in Scheme (3.20) and involves initial disrotatory

electrocyclic ring opening to **(158c)**, which then undergoes a 1,3-H sigmatropic rearrangement to the isolable **(168)**.[126] The ^{1}H and ^{13}C nmr of **(168)** are given in Fig. 3.3.

A sigmatropic rearrangement is defined as migration in an uncatalysed intramolecular process, of a σ-bond, adjacent to one or more π-systems, to a new position in a molecule, with the π-systems becoming reorganized in the process.[9] The migration is dictated by orbital symmetry considerations but is also subject to geometrical constraints. Hydrogen migration occurs *via* a cyclic transition state in which the bonding hydrogen orbital must overlap simultaneously with orbitals on both the terminal atoms.



Scheme 3.20

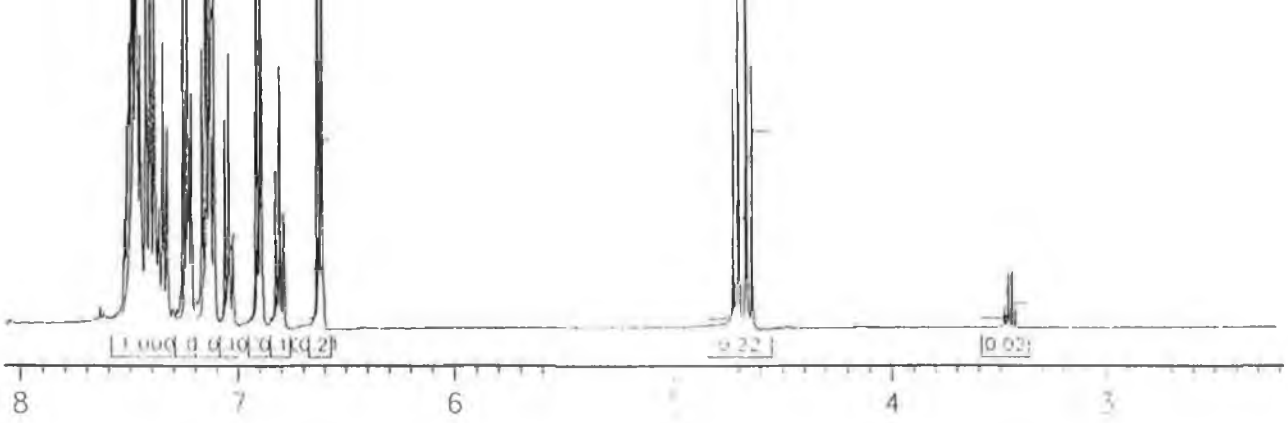
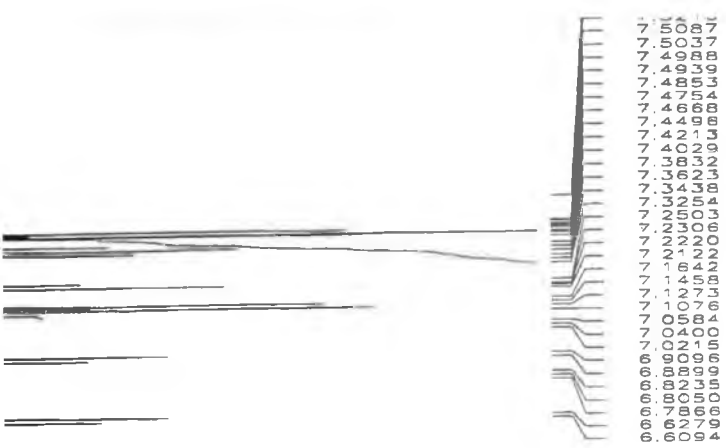


Fig. 3.3a. ^{1}H nmr spectrum of **(168)**.


7.50837
7.50037
7.49888
7.49239
7.48853
7.47754
7.46668
7.44998
7.42213
7.40229
7.38832
7.36623
7.34388
7.32554
7.25003
7.23006
7.22220
7.21222
7.16422
7.14583
7.12753
7.10776
7.05584
7.04000
7.02155
6.90996
6.88899
6.82355
6.80550
6.78666
6.62779
6.60094


4.7212
4.69554
4.65597
4.63339


3.47739
3.45866
3.43882
3.42210

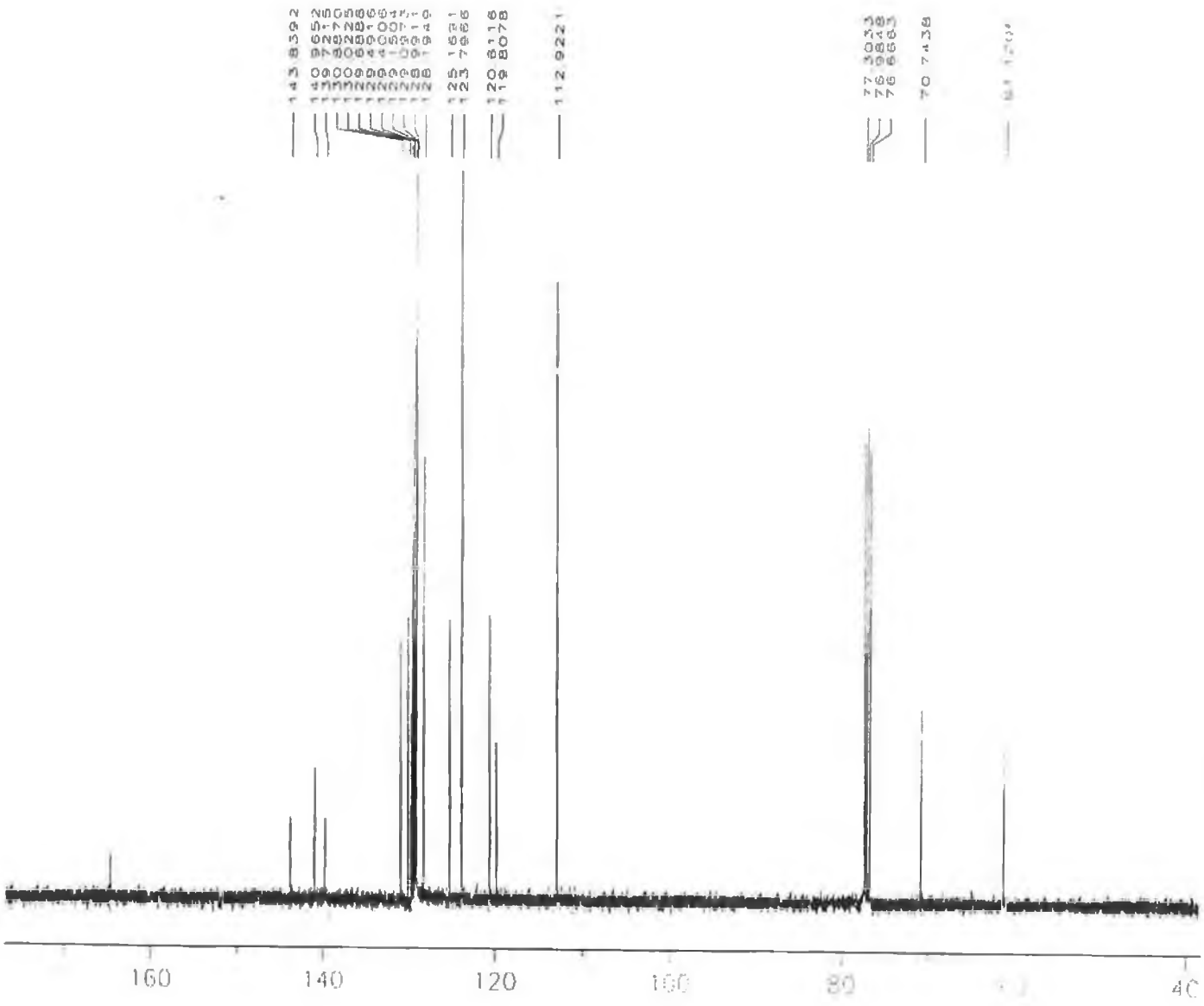
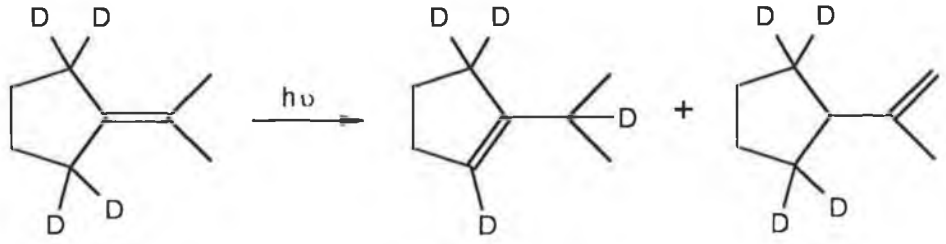


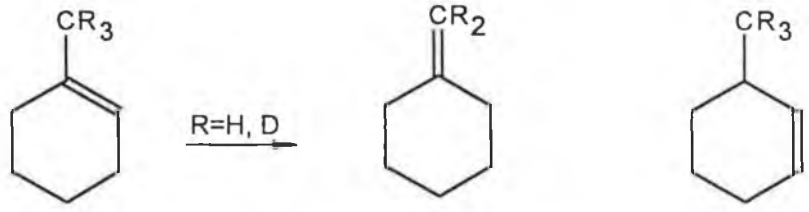
Fig. 3.3b. ^{13}C nmr spectrum of **(168)**

For 1,3-H migration involving 4n electrons, the thermally allowed transition occurs antarafacially. The transition state involved in this migration would be extremely strained and thermal 1,3-sigmatropic migrations of hydrogen are unknown.[129] On the other hand photochemical 1,3-migration occurs suprafacially and a few such migrations have been observed.[130] (Schemes 3.21 and 3.22)



(169) (170) (171)

Scheme 3.21



(172) (173) (174)

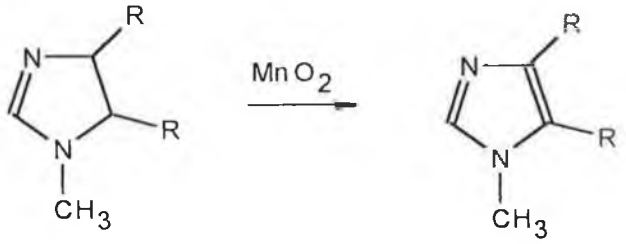
Scheme 3.22

In view of these reports, it seems likely that the 1,3-H shift observed in this reaction occurred photochemically on formation of the initial ring-opened structure **(158c)**. The fact that this 1,3-H-shift was only observed for the cyano derivative **(158c)** may be attributed to the lability of the cyanocarbon acid C-H bond (7-C-H). The nitrile α-CH bond appears to be more labile than the α-CH bond of the ester and ketone analogues **(158a-d)**.

3.2c) Investigation of Intermediacy of (104) in Photorearrangement of (81).

On isolation of the tetrahydrotetrazocine **(158)**, it was a matter of some interest to prove the intermediacy of the 2,4-dihydrotetrazocine **(104)** proposed by Butler *et al.* in the formation of the imidazo[4,5-*c*]pyrazoles **(153)**.[109] (Scheme 3.70) As the only significant difference between **(104)** and tetrahydro-tetrazocines **(158)** was the unsaturation between C-6 and C-7, it seemed plausible that oxidation of **(158)** should lead to **(104)**. Following on the Butler postulate, this should cyclise spontaneously to the analogous imidazopyrazole **(153)**.

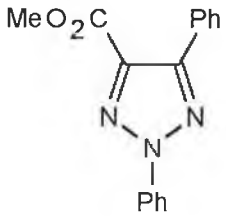
Mangenese dioxide was chosen as oxidizing agent for this reaction due to the successful use of this reagent in the oxidation of **(82a)** and **(82c)** to their tetrahydro-analogues **(81b)** and **(112)** respectively. (See Scheme 2.8) The oxidizing power of MnO_2 is optimal when it is slightly impure, the impurities most likely being cationic. Active forms of the reagent can be generated by particular methods of synthesis and these will accomplish oxidations which are not possible using 'inactive' oxides. 4-8% water of hydration seems to be required for activation of MnO_2. The oxidation medium is generally inert and success depends on the preferential diffusion of the alcohol to the aqueous oxidation phase and reactions occur on the metal oxide surface. Manganese dioxide has generally been used to oxidise alcohols to carbonyl compounds but has been known to oxidize heterocycles, *e.g.* imidazoles have been synthesised from imidazolines.[131] (Scheme 3.23)



(175) (176)

Scheme 3.23. Manganese dioxide oxidation of imidazoline **(175)**

On oxidation of 7-methoxycarbonyl-2,4,5,8-tetraphenyl-2,5,6,7-tetrahydro-1,2,3,5-tetrazocine **(158a)** with MnO_2 in dichloromethane at room temperature, two products were isolated. The main product was identified, on the basis of ir and nmr spectroscopic analysis and by CHN analysis, as 4-methoxycarbonyl-2,5-diphenyl-1,2,3-triazole **(177)**.



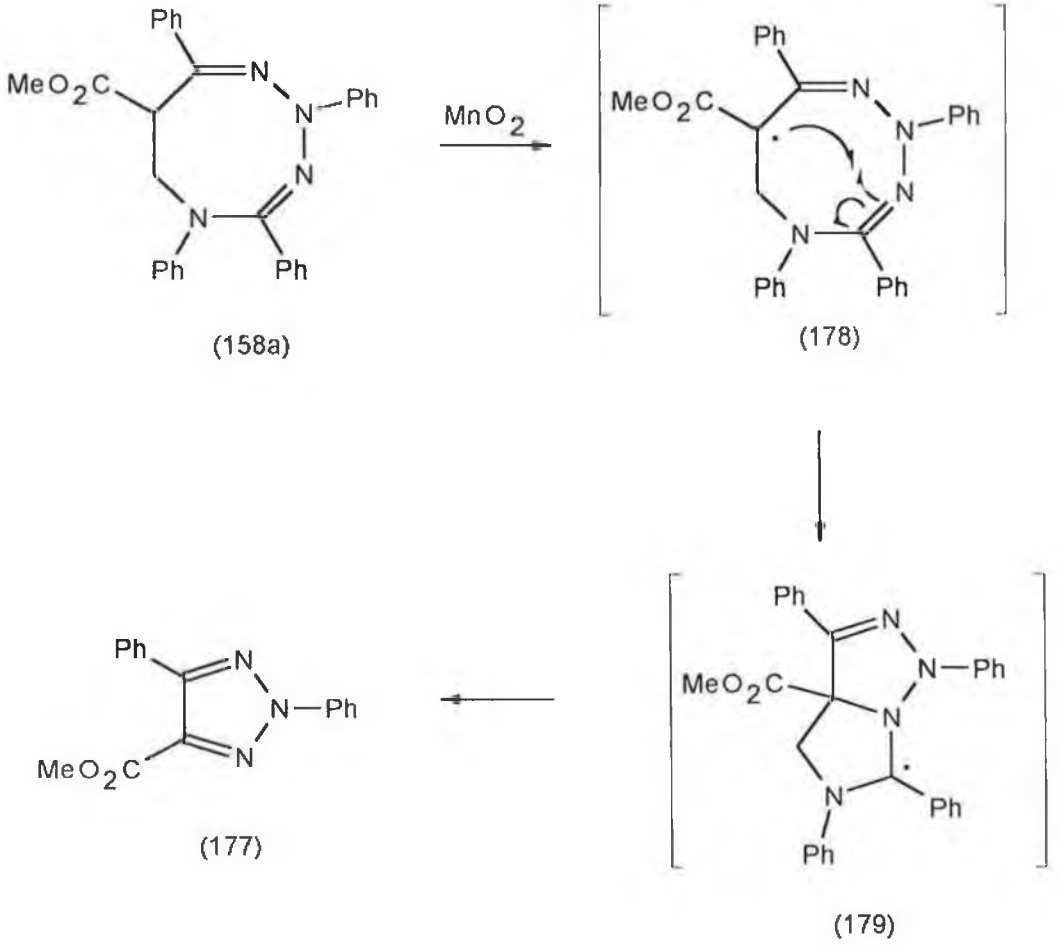
(177)

A 1-phenyl structure was discounted as 4-methoxycarbonyl-1,5-diphenyl-1,2,3-triazole has been reported and the melting point (135°C) was significantly larger than that obtained for **(177)** (83-84°C).[132] It has been well documented that the melting points of 1-substituted 1,2,3-triazoles are appreciably greater than those of the 2-substituted analogues. A list of comparative melting points is given in Table 3.5.[77]

Table 3.5 Comparison of melting points of 1- and 2-substituted 1,2,3-triazoles (A) and (B)

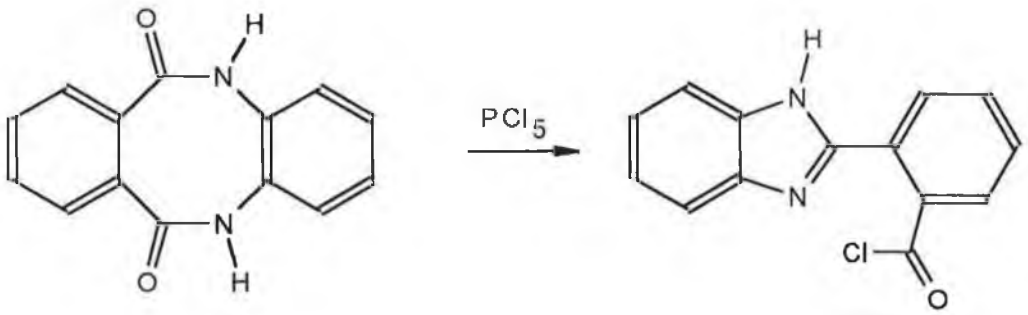
R_1 / R_2	R_4	R_5	M.P (°C) (A)	M.P. (°C) (B)
CH_3	H	H	b.p. 102-103	b.p. 223-225
CH_3CHO	H	H	60-62	33-36
Ph	H	NH_2	110	70
Ph	Me	Me	85-86	34-35
Ph	Ph	Ph	228-229	122

The mechanism of formation of (177) is tentatively proposed as follows. Manganese dioxide oxidation proceeds *via* a radical mechanism. If this is the case the initially formed radical would be more stabilized at C-7 **(178)**. This reactive centre could then attack transannularly at N-3 to form the bicyclic intermediate **(179)**, which oxidatively disproportionates to the observed aromatic triazole **(178)** (Scheme 3.24).



Scheme 3.24

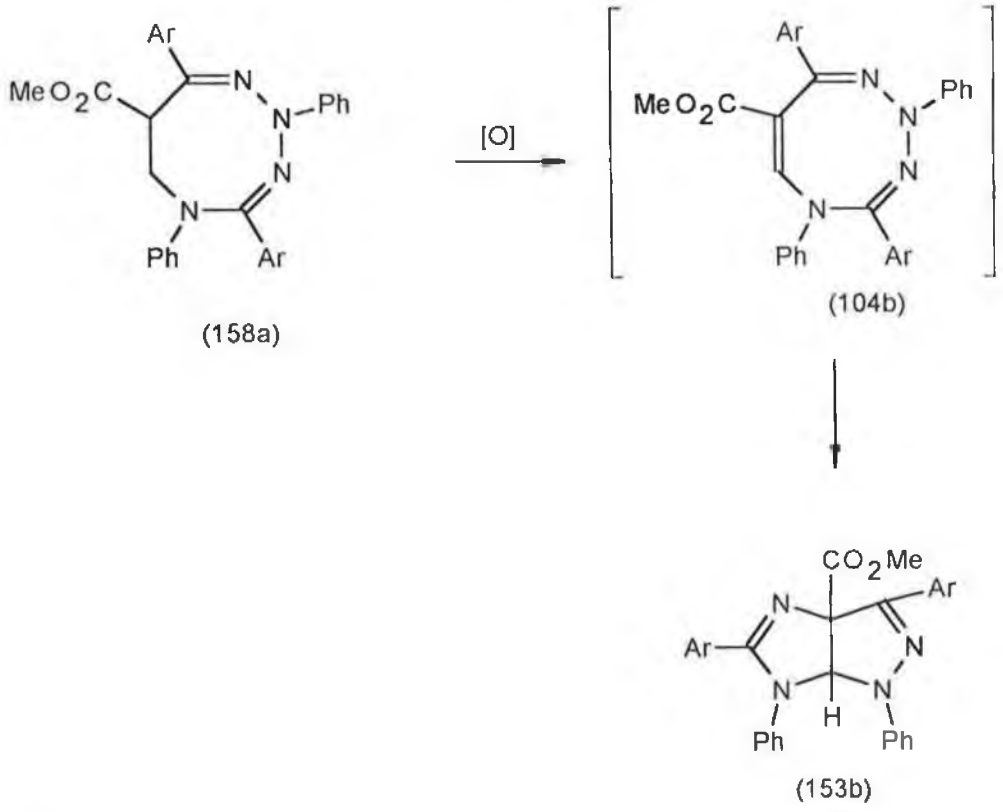
Oxidative degradation of the diazocine **(180)** to the 5-membered aromatic heterocycle **(181)** has been reported.[133] (Scheme 3.25) Ring contraction also occured on heating or treatment with base.



(180) (181)

Scheme 3.25

The other product isolated from the oxidation of **(158a)** with MnO_2 was an off-white powder isolated in 10% yield. This was identified from spectroscopic analysis as 6a-methoxycarbonyl-1,3,5,6-tetraphenyl-1,3a,6,6a-tetrahydroimidazo[4,5-*c*]pyrazole **(153b)**. The spectra obtained were identical to those obtained on photolysis of **(81c)**. The mechanism of formation of this product is outlined in Scheme 3.26.



(158a) (104b) (153b)

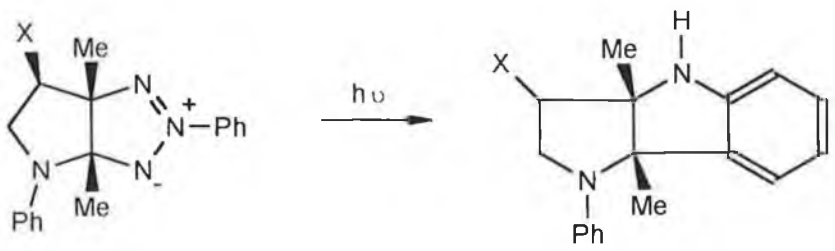
Scheme 3.26

The C6-C7 bond is oxidized by the activated MnO_2 leading to the 2,5-dihydrotetrazocine **(102b)**, which undergoes the same transannular ring contraction and 1,4-sigmatropic rearrangement outlined in the phototransformation of tetrahydropyrrolo[2,3-*d*]-1,2,3-triazoles **(81)** to imidazo[4,5-*c*]pyrazoles **(153)** (Scheme 3.14). The fact that imidazo[4,5-*c*]pyrazole **(153b)** can be synthesised *via* the oxidation of tetrahydrotetrazocine **(158a)** strongly supports the intermediacy of 2,5-dihydro-1,2,3,5-tetrazocine **(104)** in the photorearrangement of substituted tetrahydropyrrolo[2,3-*d*]-1,2,3-triazoles **(81)**.

3.2d) Photochemical Transformations of Substituted 3a,6a-Dimethyl-3,3a,4,5,6,6a-Hexahydropyrrolo[2,3-*d*]-1,2,3-triazoles.

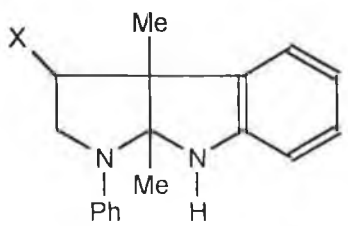
In Sections 3.2a-c the photorearrangements of 3a,6a-diaryl pyrrolo[2,3-*d*]triazoles were investigated. It was found that the photochemistry of these systems was dominated by the initial cleavage of the C3a-C6a bond. In the following sections the photochemical transformations of the 3a,6a-dimethyl analogues are investigated.

Substituted 3a,6a-dimethyl hexahydropyrrolo[2,3-*d*]-1,2,3-triazole **(70b, X=COMe)**, when irradiated using a medium pressure mercury lamp with pyrex filter, yielded the stable hexahydropyrrolo[3,2-*b*]indole **(182b)**. This structure was assigned on the basis of CHN analysis, confirming loss of molecular nitrogen and spectroscopic techniques. ^{1}H nmr and ir spectroscopy indicated the presence of an *o*-disubstituted phenyl ring. ^{13}C nmr spectroscopy revealed two quaternary carbons appearing at 75.34 and 76.81 ppm, the chemical shift proximity of which led us to propose the pyrrolo[3,2-*b*]indole structure as opposed to the more common pyrrolo[2,3-*b*]indole **(183)**. (Scheme 3.27)



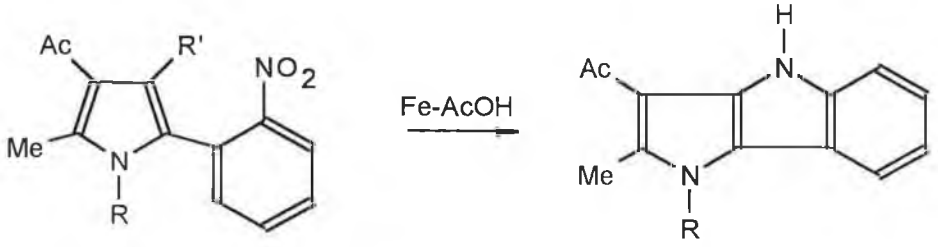
(70) (182)

Scheme 3.27



(183)

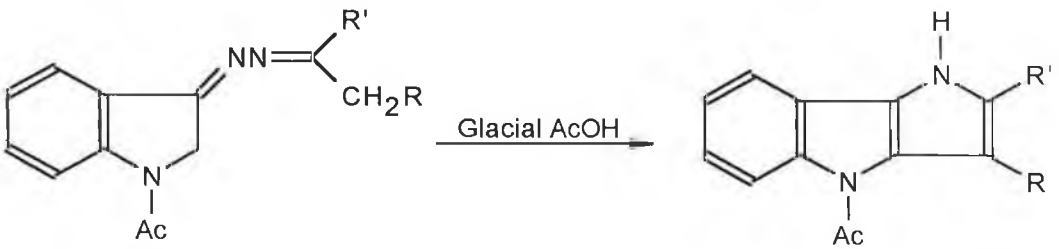
This constitutes a new entry into these sparsely reported benzodiazapentalenes. Aiello *et al.* have synthesised these systems as part of their study on polycondensed nitrogen heterocycles as potentially active pharmaceutical agents.[134,135] The reported synthetic route involved an intramolecular acid catalysed nucleophilic attack on pyrrole by the 2-aminophenyl group formed on iron-acetic acid reduction of **(184)**. (See Scheme 3.28)



(184) (185)

Scheme 3.28 (R'=NO_2, Br, Cl, I; R=H, Ph)

Another route to these fused ring systems has been reported by Grinev *et al.*[136] This method involved the reaction of N-acetylindoxyl hydrazone with a suitable ketone. Subsequent reaction in glacial acetic acid led to high yields of **(187)**. (See Scheme 3.29)

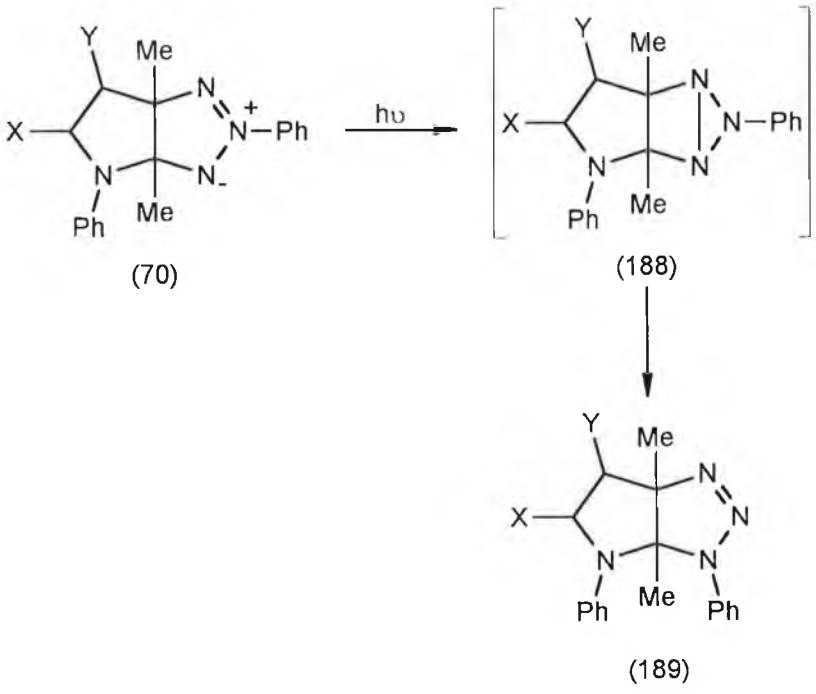


(186) (187)

Scheme 3.29.

In the current case the mechanism may be explained in terms of a series of photoinduced sequential transformations. In order to elucidate the mechanism of this eliminative rearrangement, an attempt was made to isolate and characterise the intermediates formed at each step.

On irradiation of 6-*exo*-cyano-3a,6a-dimethyl-2,4-diphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-*d*]triazole **(70c)**, the main product isolated was a white powder, formed in moderate yield. CHN analysis of this compound showed that the molecule was still intact, but had undergone a rearrangement resulting in colour loss. The ^{1}H nmr spectrum revealed an unusual splitting pattern for the CH-CH_2 system, *i.e* a doublet at 3.37 ppm, a doublet of doublets at 3.45 ppm and a doublet at 3.60 ppm, which is somewhat simplified compared to the spectrum of the starting material **(70c)**. This pattern may be explained in terms of the Karplus equation, where the dihedral angle between the Hm and Hx hydrogens approaches 90° and therefore J_{mx} approaches zero.[68] (See Fig. 3.4a) The ^{13}C nmr spectrum indicated the presence of two sp^3 bridgehead carbons. (Fig. 3.4b) A COLOC nmr experiment carried out on the product formed on irradiation of **(70c)** indicated that the C3a-C6a bond was still intact, and that C-3a and C-6a were still the bridgehead carbons (See Appendix B) This led to the proposal of the 1-substituted fused 1,2,3-triazole **(189)** as the initial intermediate in the sequential transformation. (Scheme 3.30)



Scheme 3.30

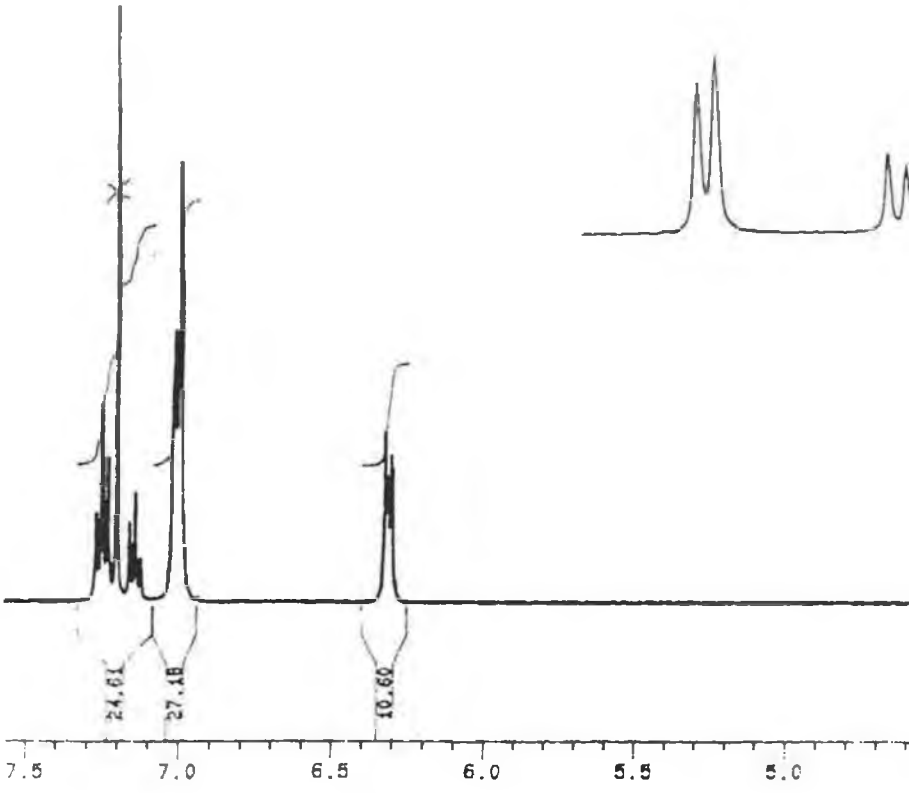
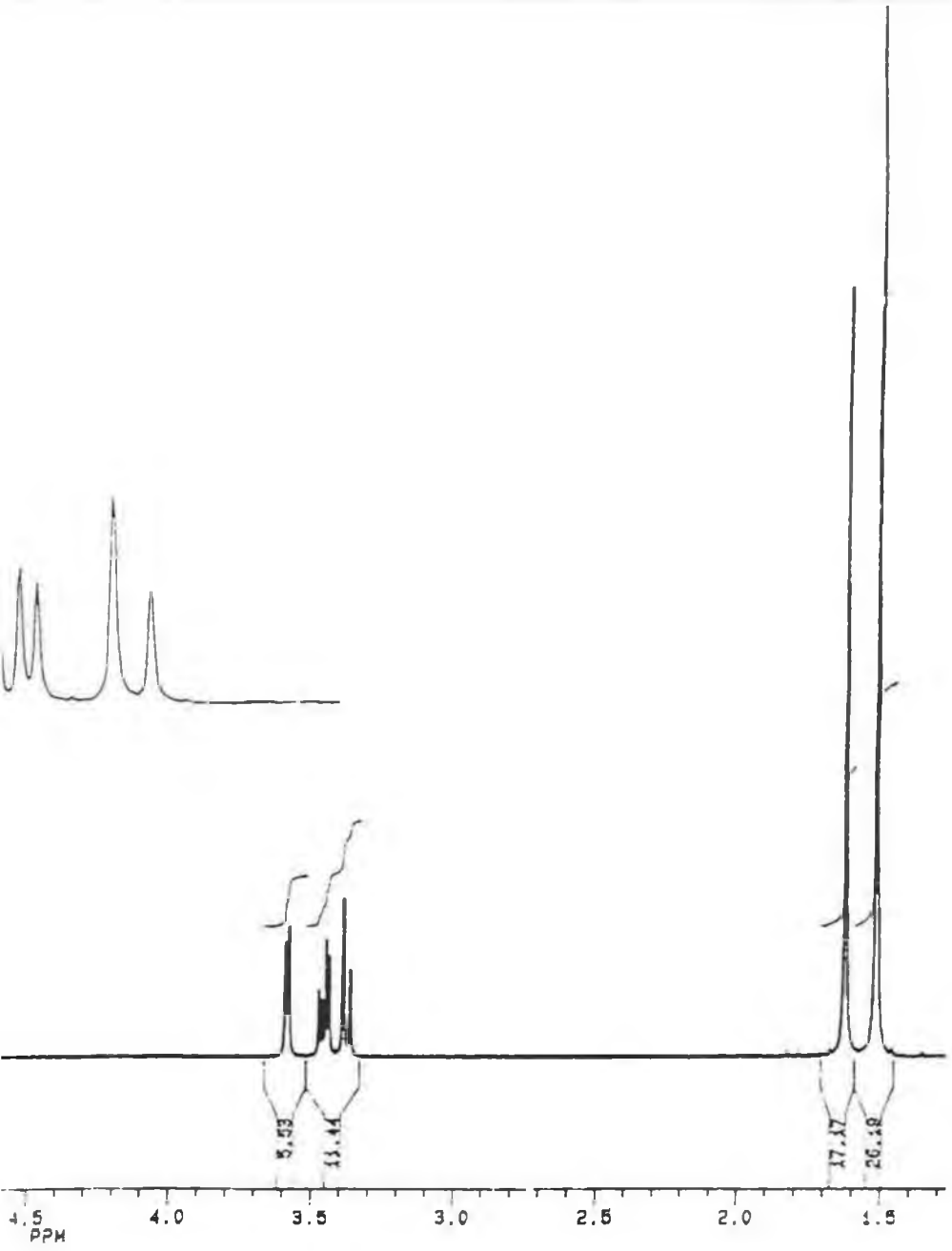
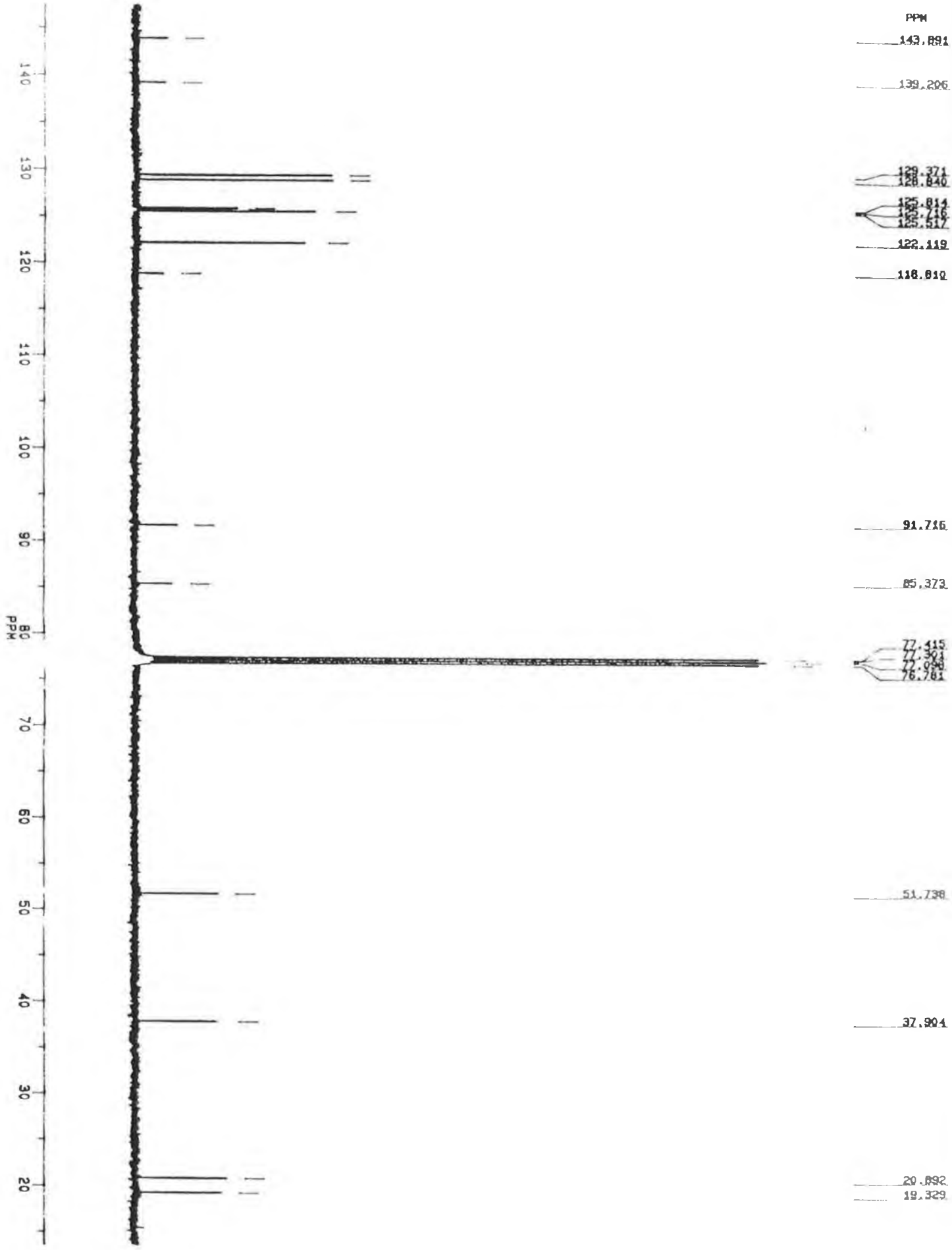


Fig 3 4a ^{1}H nmr spectrum of **(189c)**

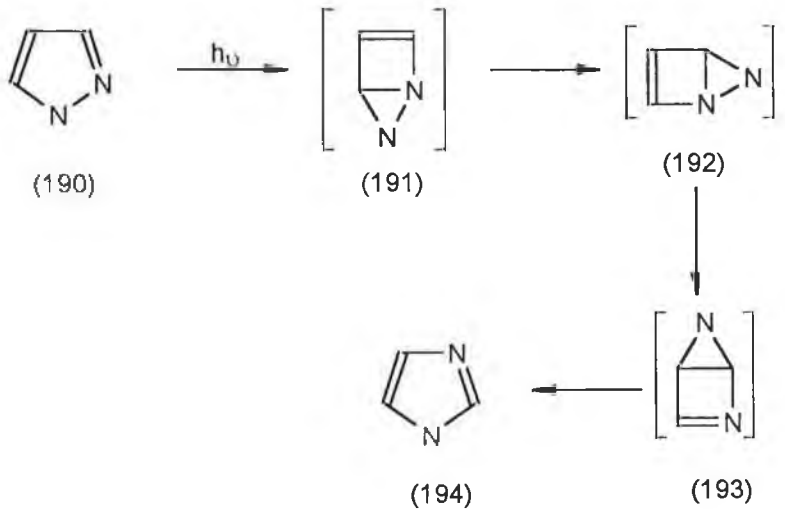

5.53
11.44
17.17
26.18
4.5
PPM
4.0
3.5
3.0
2.5
2.0
1.5


PPM
143.891
139.206
129.371
128.840
125.814
125.716
125.517
122.119
118.810
91.716
85.373
77.415
77.301
77.094
76.781
51.738
37.904
20.892
19.329
140
130
120
110
100
90
80
PPM
70
60
50
40
30
20

Ring systems of this type have been widely studied with regard to the elimination of molecular nitrogen and the isolation of such a system under photolytic conditions is rare.[137-139] The mechanism of the current rearrangement, a net 1,2-phenyl shift, may be explained in terms of the initial formation of a tricyclic fused triaziridine **(188)**.

Precedence for formation of a triaziridine intermediate has been found in that irradiation of **(122)** led to the triaziridine **(123)**.[99] (Scheme 3.4) On further irradiation this triaziridine **(123)** either underwent photoisomerization back to the azimine or lost methyl nitrene to form the major by-product **(124)**, depending on the wavelength of irradiation. Heating the triaziridine led to reformation of the azimine. A discussion on the photorearrangements of azimines is given in Section 3.1b.

The triaziridine intermediate **(188)** appears to undergo a tandem ring opening and 1,3-sigmatropic rearrangement to **(189)**. (Scheme 3.30) This rearrangement was favoured as it relieved the considerable ring strain of the intermediate **(188)**. This rearrangement is analogous to the "walk mechanism" observed in the phototranspositions of 5-membered heteroaromatic rings.[88] (Scheme 3.31)



Scheme 3.31 Phototransposition of pyrazole **(190)** to imidazole **(194)**.

In the present case such a shift requires the breaking of the one of the C-N bonds exocyclic to the triaziridine intermediate **(188)**. The presence of the pyrrolidine nitrogen lone pair appears to facilitate opening in the observed direction, *i.e.* breaking of the N3-C3a bond, even though this direction appears to be sterically less favoured.

In order to confirm the assigned structure, colourless crystals of **(189b)** were grown from a 6:1 mixture of *n*-hexane / ethyl acetate and subjected to x-ray crystallographic analysis (Fig. 3.5).

A noteworthy feature of the crystal structure (Fig.3.5) is the *endo*-conformation of the ketone group, *trans* to the 3a-C-CH_3 group. While all the systems under discussion are racemic, the relative stereochemistries of the substituents of the starting materials have been determined previously.[26,27] The starting tetraazapentalene has been determined to contain the C-6 substituent in the *exo*-orientation on the basis of x-ray crystallographic assignments for diaryl and bridged cyclohexyl analogues.

The conformation of **(189)** may be explained in terms of an *exo-endo* epimerization about the α-carbon of the ketone. In order to determine whether the epimerization took place prior or subsequent to rearrangement, the photoprocess was re-examined. On irradiation of **(70c)** a small amount of the *endo*-epimer **(76)** was isolated. Assignment of this structure was based on spectroscopic analysis and also by comparison with spectroscopic data obtained for the *endo*-epimer formed on acid catalysed epimerization of **(70c)**. (See Scheme 1.30). It was also shown that the epimerization was not induced by visible light (Section 1.2b.1). Under the conditions of the photolysis carried out here, acid or base catalysed epimerization may be discounted.

The photoepimerization may be related to that observed for the 3a,6a-diphenyl analogues as outlined in Section 3.2b. (See Scheme 3.17) The reaction was rationalised in terms of initial cleavage of the C6-C6a bond. The resultant biradical **(195)** is held within a solvent cage and radical recombination follows to either reform the *exo*-epimer **(70c)** or

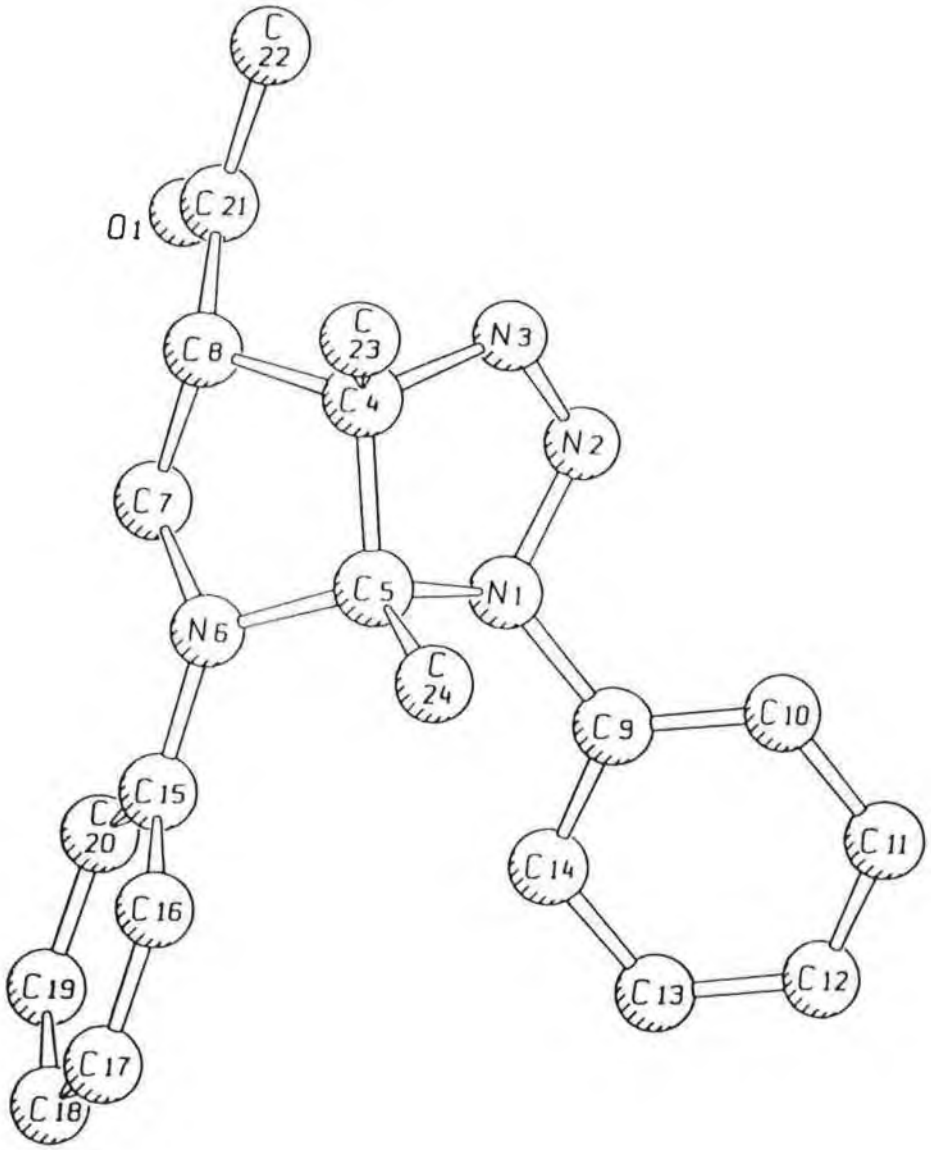
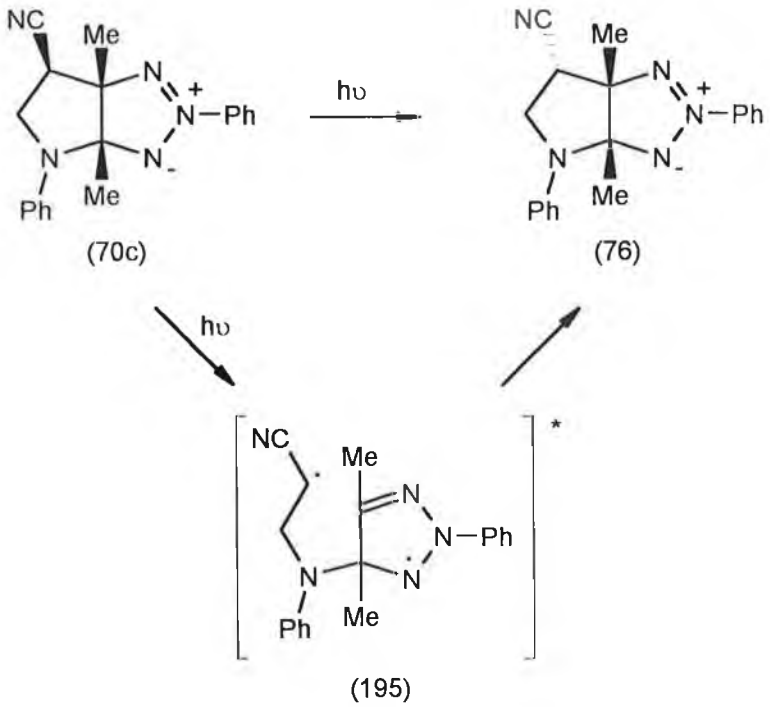


Fig. 3.5 Crystal Structure of **(189b)**

form the *endo*-conformer **(76)**, depending on the direction of closure of the diradical.[127] (Scheme 3.32) The formation of **(189)** from **(70)** may be viewed in terms of an initial epimerization to a form such as **(76)** followed by a net 1,2-phenyl shift as shown in Scheme 3.30.

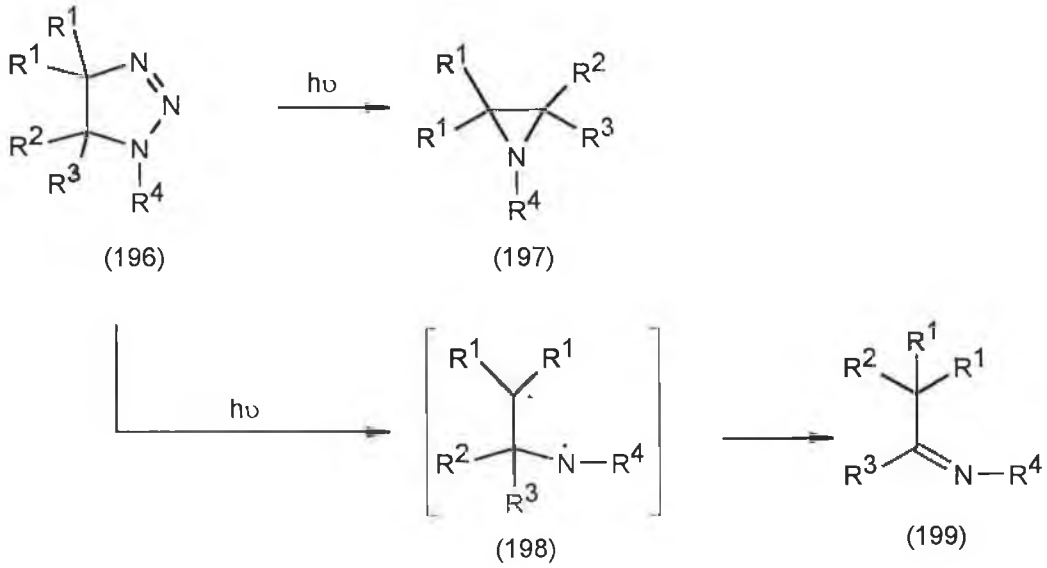
The reason for the rearrangement occurring solely from the *endo*-epimer may be related to favourable interaction of the C-6 substituent and azimine π-systems, not possible for the *exo*-analogues. The *endo*-epimer of the ketone derivative **(70b)** was not observed, presumably rearranging efficiently, once formed, to the 1-substituted fused triazoline **(189b)**.



Scheme 3.32

Compound **(189)** is a fused 1-substituted-1,2,3-triazoline. The photochemical elimination of nitrogen from such systems is a general reaction and usually leads to the formation of fused aziridines which are either isolated or undergo further rearrangement to the observed photoproducts. The elimination of nitrogen from suitable triazolines provides an

excellent synthetic entry to aziridines. The photochemically induced decomposition provides good yields of aziridines with little imine formation (a complication which plagues the thermally induced decomposition.[140,141] (Scheme 3.33)

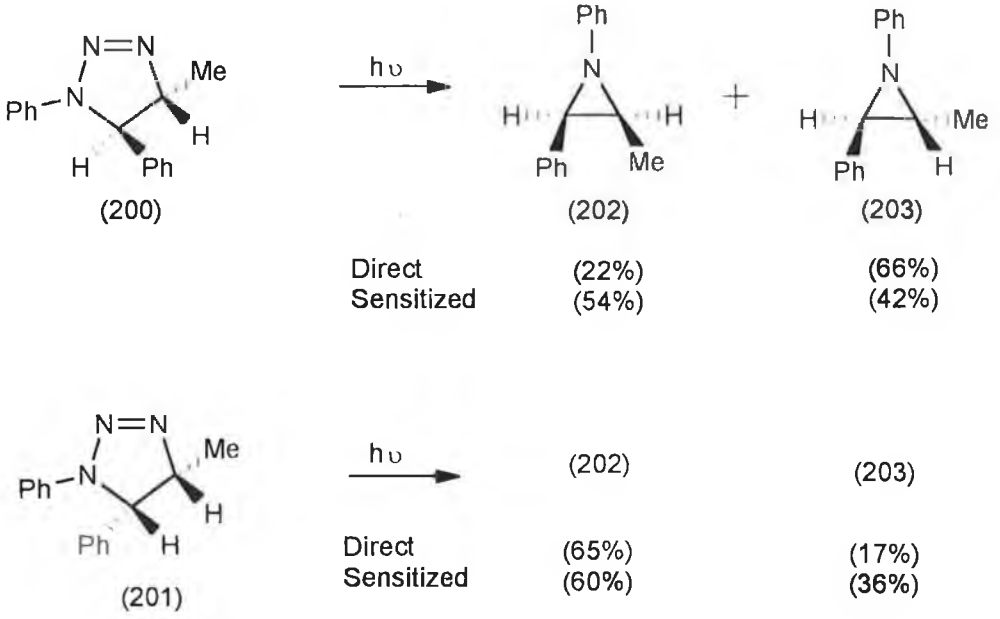


(196) (197) (198) (199)

Scheme 3.33

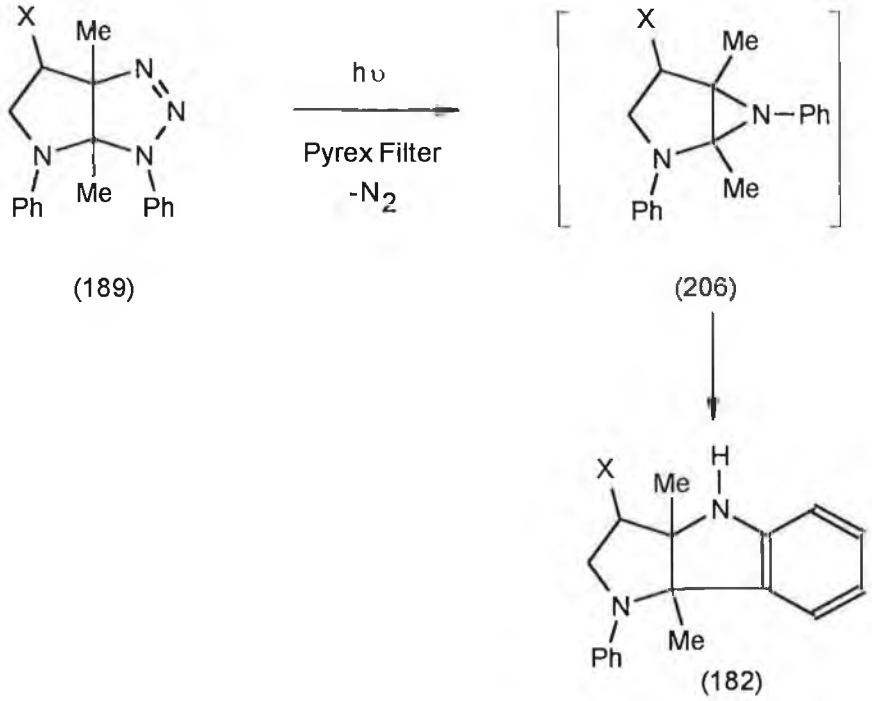
This photoelimination is practically independent of the nature of the substituents of the triazoline and is little affected by solvent effects.[142] The stereochemistry of the aziridines **(202)** and **(203)** formed on irradiation of **(200)** and **(201)** depends on whether singlet or triplet biradical intermediates are produced.

Direct irradiation leads to singlet biradicals which ring close with good retention of configuration. On sensitized decomposition (*e.g.* with benzophenone) triplet states were produced. Due to spin restrictions, ring closure is slowed, giving the intermediate a longer lifetime. As a result there is a possibility of rotation about single bonds, with consequent equilibration between the two biradical intermediates **(204)** and **(205)**.[143]



Scheme 3.34

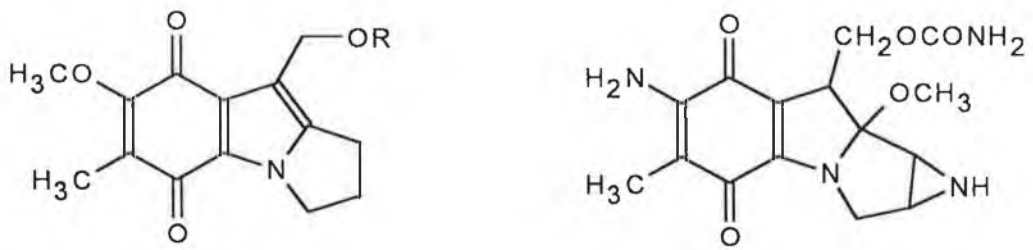
Further irradiation of **(189b)** led to the formation of a white powder whose spectroscopic data was identical to that obtained for **(182b)** formed in low yield on photolysis of the starting cycloadduct **(70b)** CHN analysis confirmed the loss of nitrogen. ^{1}H nmr and ir spectra of this stable product indicated the presence of an *o*-disubstituted phenyl ring. Analysis of the ^{13}C nmr spectrum revealed the presence of the two quaternary bridgehead carbons at 75.34 and 76.81 ppm. The pyrroloindole **(182b)** was formed on intramolecular cyclization subsequent to nitrogen elimination from **(189b)**. (Scheme 3.35)



(189) (206) (182)

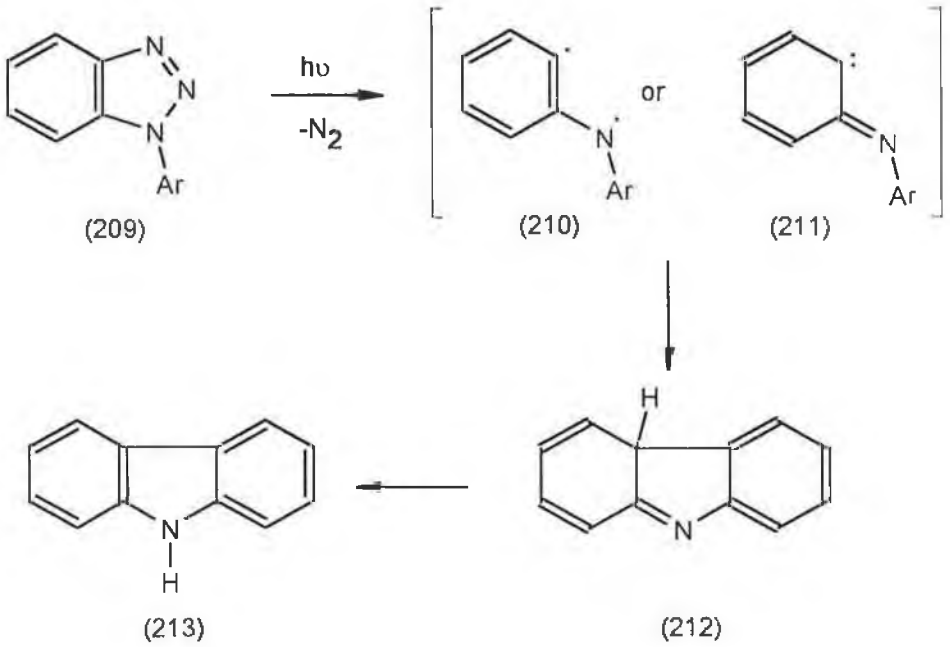
Scheme 3.35

It has been well documented that substituted N-aryl-1,2,3-triazoles, on elimination of nitrogen, react intramolecularly with the aryl group to form a variety of polycyclic cyclisation products. This appears to be an efficient conversion, occurring at room temperature, leading to regiospecific products. This photoelimination-electrocyclization has been used in the synthesis of highly substituted indoles in a route to mitosene **(207)**, a Gram positive antibiotic and analogue of mitomycin **(208)**, a chemotherapeutic agent.[144]



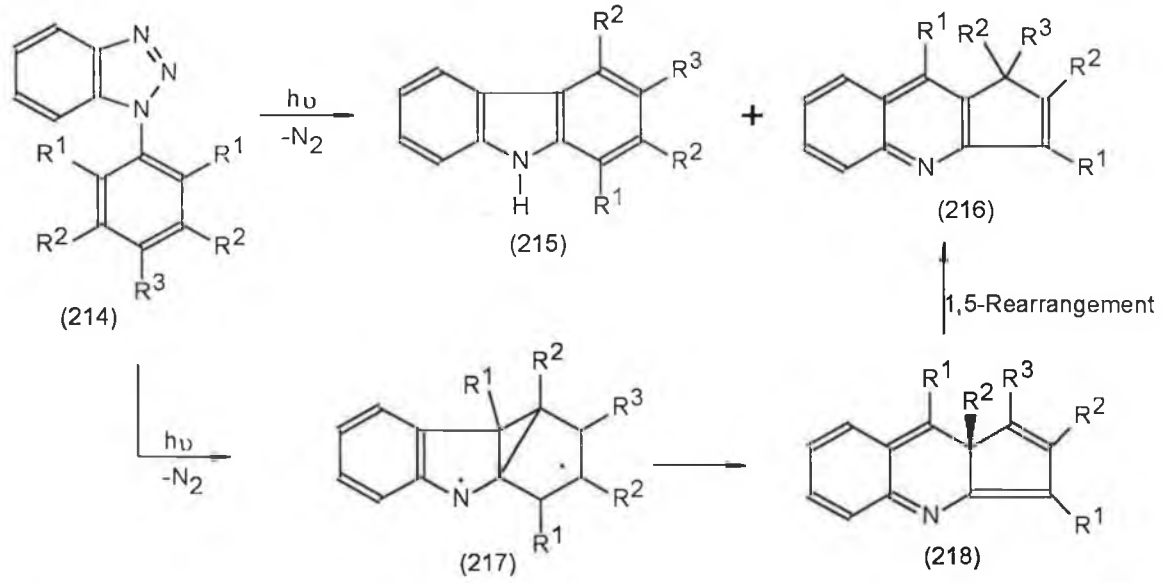
(207) (208)

The well known Graebe-Ullmann photosynthesis of carbazoles **(213)**, by extrusion of nitrogen from N-aryl benzotriazoles **(209)**, is believed to involve cyclization of the diradical **(210)** or the iminocarbene **(211)** to the 4aH-carbazole **(212)**, followed by an aromatizing hydrogen shift.[145] (Scheme 3.36)

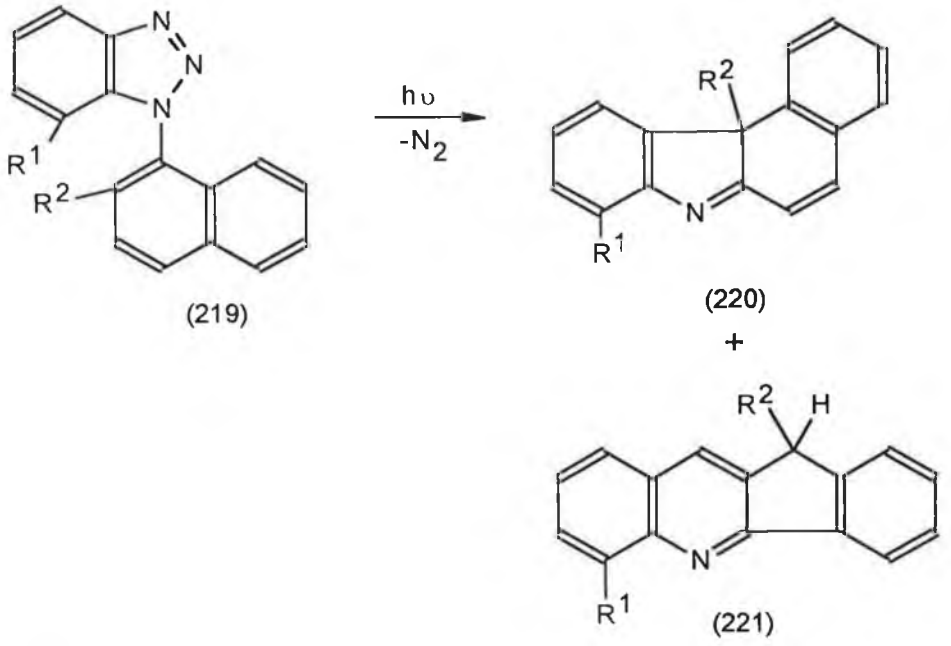


Scheme 3.36

A variety of other polycyclic heterocycles have been synthesised by this route, including a number of interesting compounds formed on aza-di-π-methane rearrangement of the initially formed carbazole, *e.g.* cyclopentaquinolines **(216)** and indenequinolines **(221)** have been formed.[146-150] (See Schemes 3.37 and 3.38)



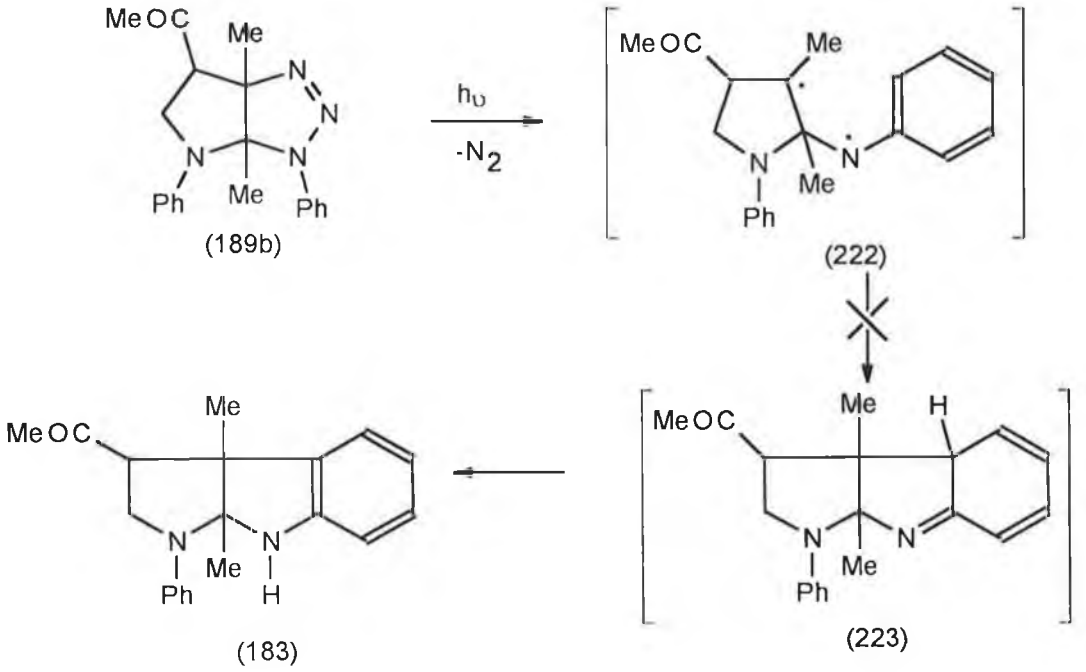
Scheme 3.37



Scheme 3.38

The similarity in chemical shifts of the quaternary carbons in the ^{13}C nmr spectrum of the product isolated on irradiation of **(189b)** indicated it to be the hexahydropyrrolo[3,2-*b*]indole **(182)** and not the more common hexahydropyrrolo[2,3-*b*]indole **(183)** expected, given the position of the triazoline N-phenyl group in **(189)**. The elimination of molecular

nitrogen from **(189b)** would be expected to result in a biradical such as **(222)**. Following the mechanism of the cyclizations outlined in Schemes 3.36-3.38 ring closure to **(183)** would be expected. (Scheme 3.39)



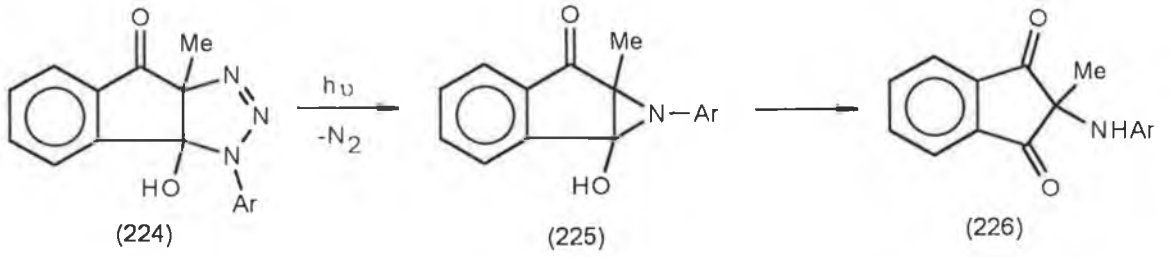
Scheme 3.39

The eliminative rearrangement of **(189)** differs from the above cases (Schemes 3.36-3.38) in that the rearrangement proceeds from the fused aziridine intermediate **(206)**. The orientation of the rings in the isolated tricyclic product **(182)** requires the intermediacy of **(206)** as the anilino nitrogen has migrated from the C-2 to the C-3 position of the pyrrolidine ring. Once formed the fused aziridine **(206)** may ring open to form either pyrrolo[2,3-*b*]indole **(183)** or in the opposite direction to produce the observed pyrrolo[3,2-*b*]indole **(182)**. Ring opening in the observed direction may have been facilitated by the pyrrolidine nitrogen lone pair.

Fused triazolines are well known to lead, on elimination of molecular nitrogen to fused aziridines, which subsequently ring open to form the observed photoproduct. The

direction of the ring opening depends on the stability of the product as well as steric and electronic effects.

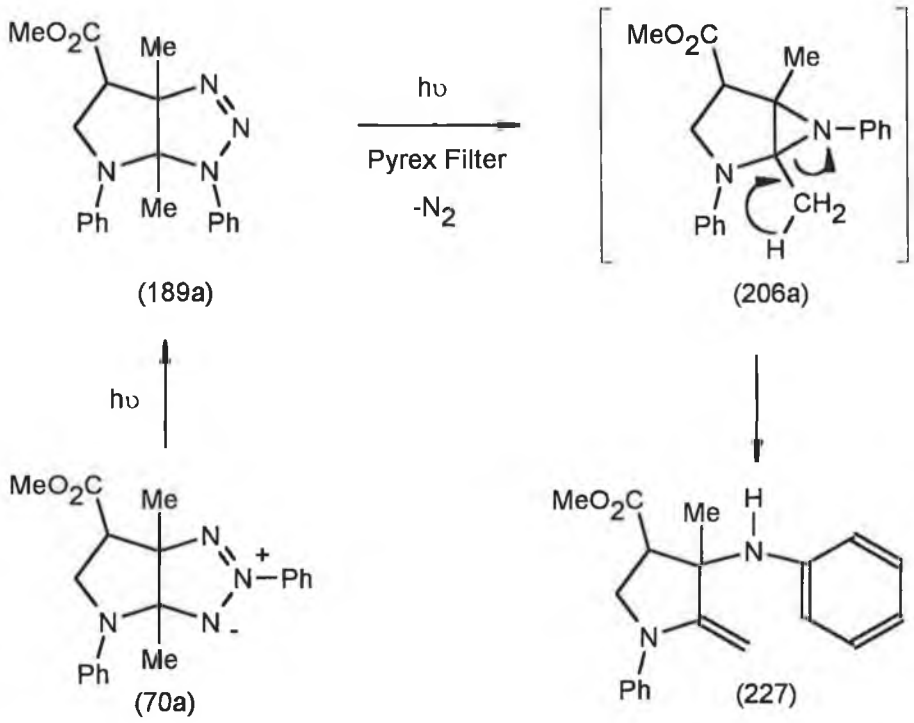
For example **(224)** on irradiation underwent elimination of nitrogen to yield **(226)** in virtually quantitative yield. The position of the anilino groups indicates the intermediacy of the fused aziridine **(225)**.[151] (Scheme 3.40)



(224) (225) (226)

Scheme 3.40

On pyrex filtered irradiation of 6-methoxycarbonyl 3a,6a-dimethyl-2,4-diphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-*d*]-1,2,3-triazole **(70a)**, two photoproducts were isolated. The minor product was identified as the tricyclic eliminative rearrangement product, the methoxycarbonyl analogue **(182a)**. The major product was not the hexahydropyrrolo[3,2-*d*]-1,2,3-triazole **(189a)**. CHN analysis confirmed the loss of nitrogen, but the fused aziridine structure **(206a)** expected as intermediate in the formation of the tricycle was discounted due to the presence of only one methyl group (3.70 ppm) in the ^{1}H nmr. Also evident was the presence of an exocyclic double bond in place of one of the methyl groups, as indicated by two doublets at 4.22 and 4.46 ppm (J = 0.98Hz). ^{13}C nmr confirmed the presence of the exocyclic double bond and indicated it, by reference to standard ^{13}C nmr spectral data, to be located at C-2 of the pyrrolidine ring.[152] Colourless crystals of the photoproduct were grown from a 6:1 mixture of *n*-hexane / ethyl acetate and the structure was confirmed by x-ray crystallographic analysis to be **(227)**. (See Fig. 3.6) The mechanism of formation of **(227)** is outlined in Scheme 3.41.



Scheme 3.41

Of note in the structure of **(227)** is the relative orientations of the C-3 methyl and the C-4 methxoycarbonyl substituents. (Fig 3.6) As seen in Figure 3.5, these groups were in a *trans*-configuration in **(189b)**. In **(227)** they appear in a *cis*-orientation. This alteration in relative stereochemistry is not satisfactorily explained by the proposed mechanism. An epimerization in **(227)** may explain the relative stereochemistries. An alteration in the stereochemistry of the 3a-C-methyl group appears less likely. An alternative pathway to **(227)** which does not proceed *via* **(189a)** and does not involve an alteration in relative stereochemistries from that of the starting material may also be possible and is supported by the fact that **(189a)** was not isolated. However the eliminative photorearrangement of 1-substituted triazolines, with methyl groups in either the C-4 or C-5 position of the triazole ring, to yield ring structures with exocyclic double bonds, has been documented. For compound **(228)** photoelimination of nitrogen led to the formation of the dienone **(229)** as the major photoproduct.[153] (Scheme 3.42) The mechanism is explained in terms of H-atom transfer from the C-4 methyl substituent to give **(229)**.

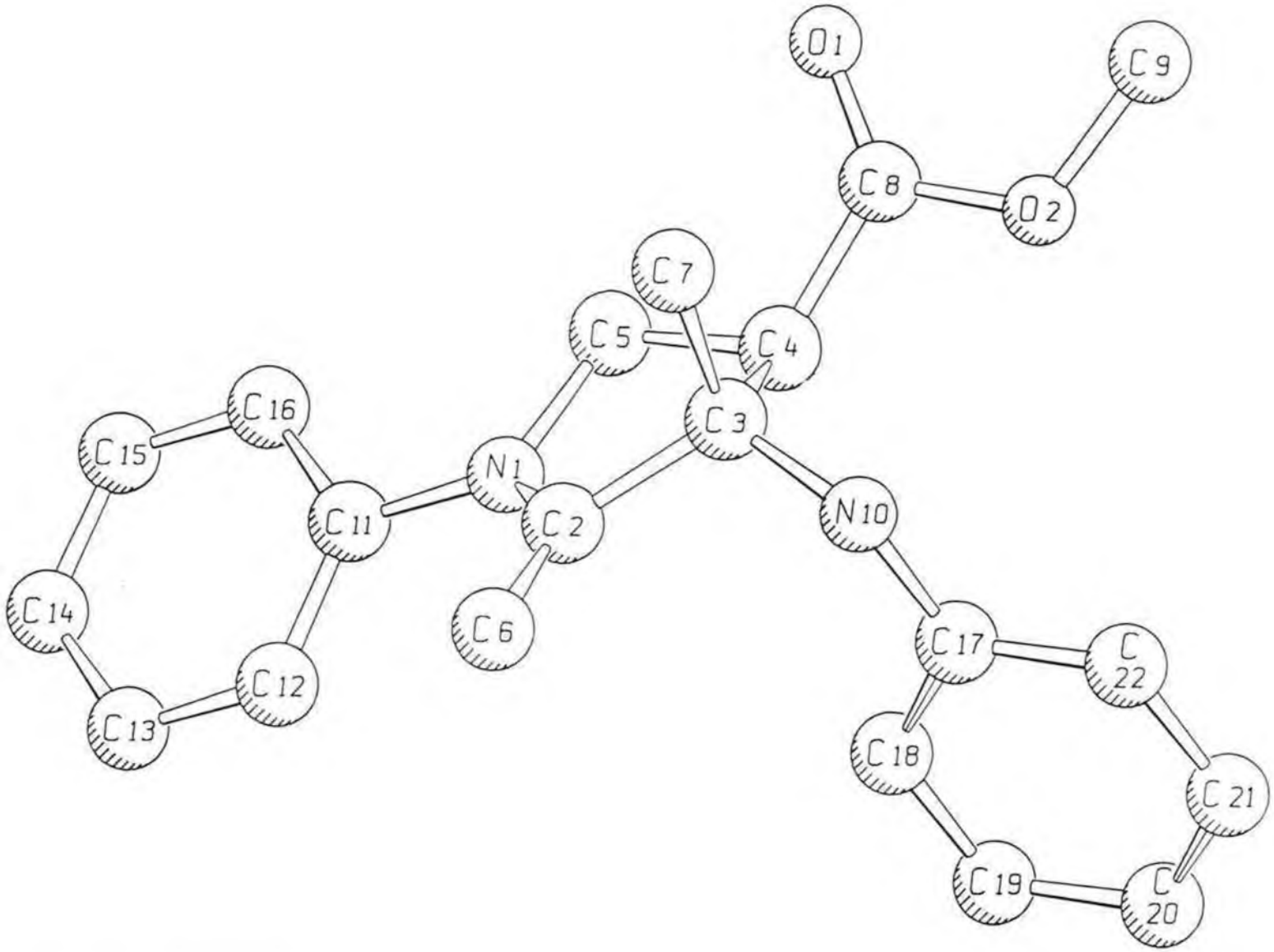
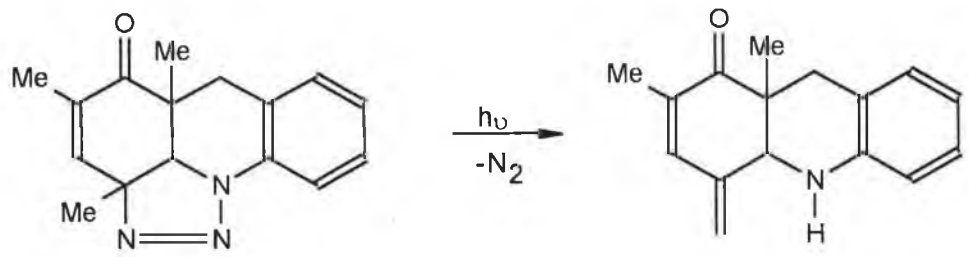


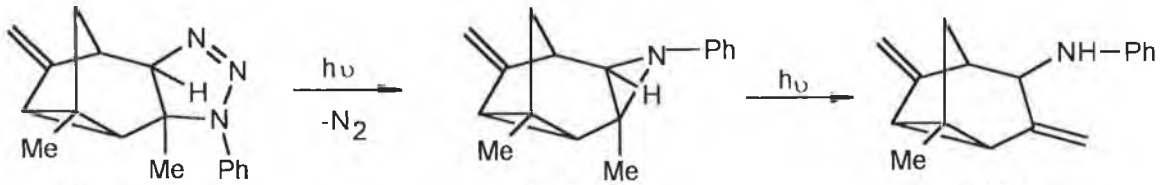
Fig. 3.6 X-Ray Crystal Structure of **(227)**



(228) (229)

Scheme 3.42

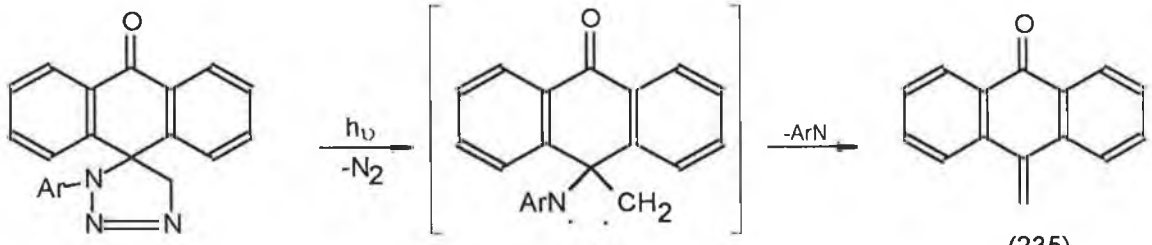
The eliminative rearrangement of the fused triazoline **(230)** leads to the isolable fused aziridine **(231)**.[154] (Scheme 3.43) On further irradiation **(231)** rearranges to form the exocyclic double bond structure **(232)**.



(230) (231) (232)

Scheme 3.43

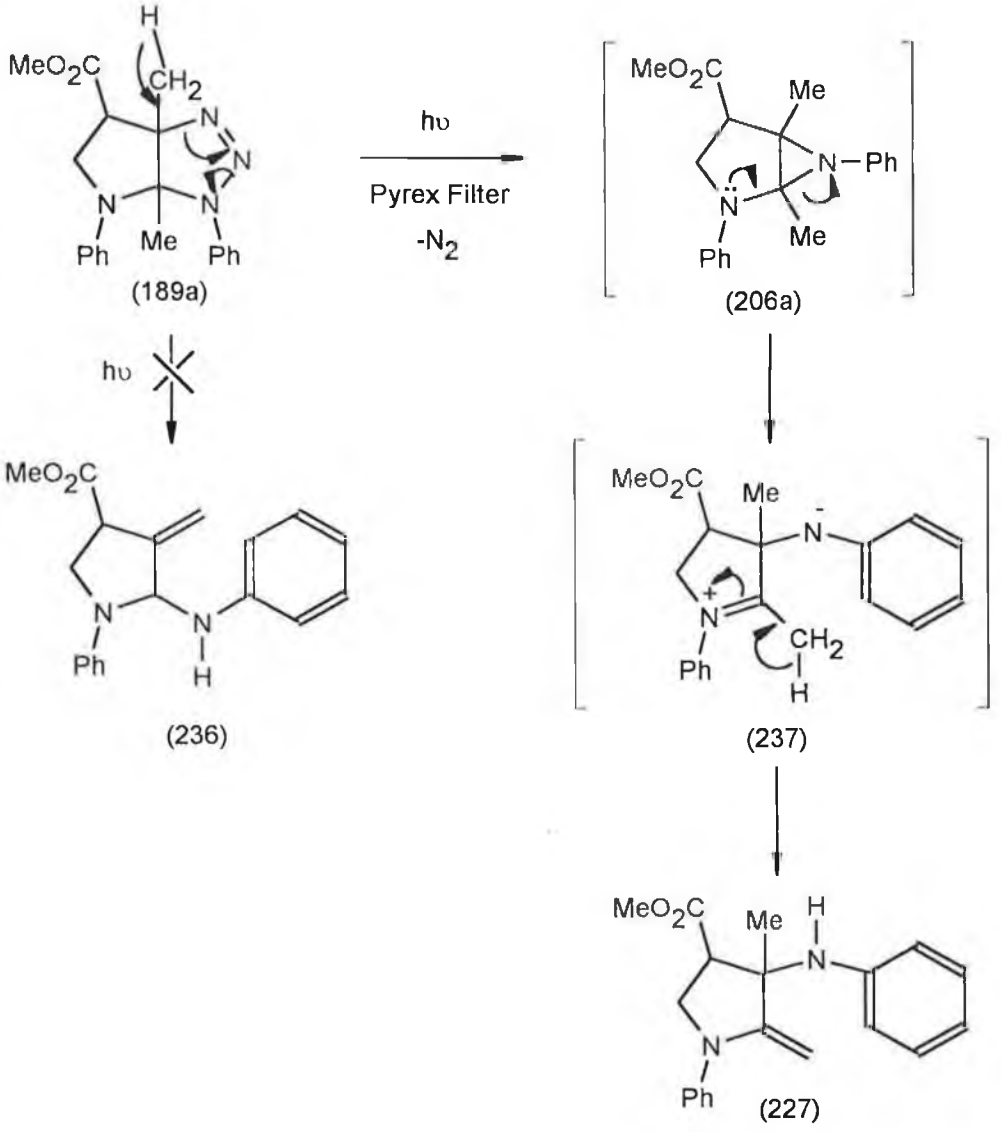
A related reaction is the irradiation of the spiroanthronetriazoline **(233)** in benzene under nitrogen which gave 10-methyleneanthrone **(235)** by photochemical deamination of the biradical intermediate **(234)**.[155] (See Scheme 3.44)



(233) (234) (235)

Scheme 3.44

In the current case of the transformation of **(70a)** to **(227)**, despite the presence of the methyl at C-4, preferential H-atom transfer occurs from the methyl at C-5, indicating the importance of the intermediate fused aziridine **(206a)** in this eliminative rearrangement. The direction of opening of **(206a)** may be facilitated by the presence of the pyrrolidine nitrogen lone pair. (Scheme 3.45)

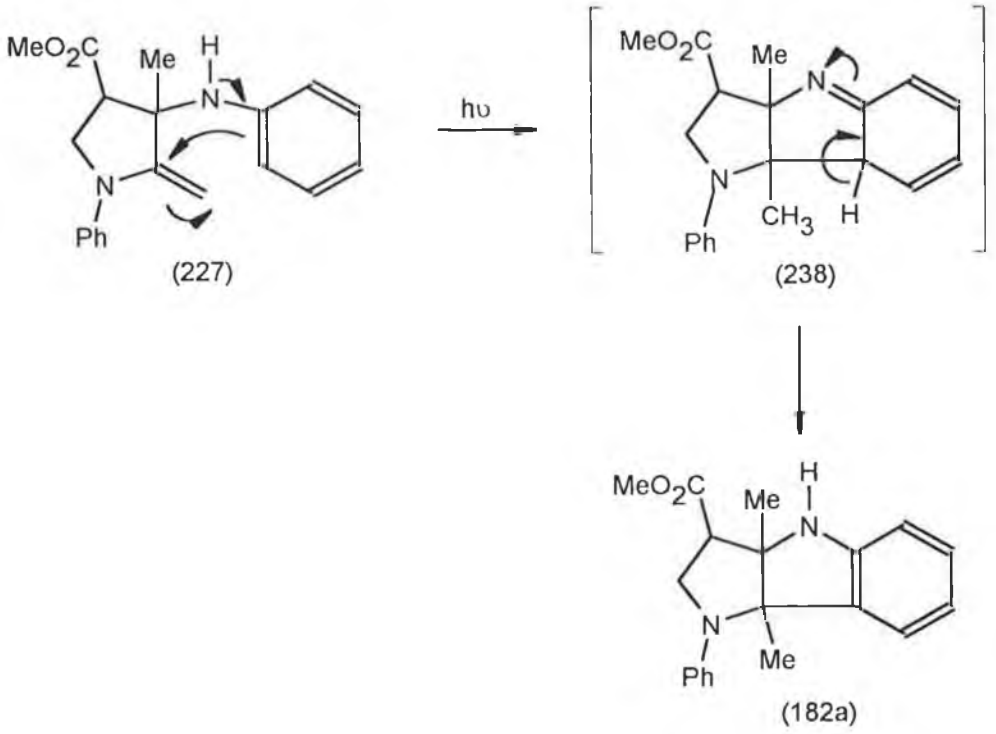


Scheme 3.45

The photorearrangement of **(227)** in $CDCl_3$ was monitored by ^1H nmr on exposure to sunlight. (See Fig. 3.7) After a few hours the characteristic splitting pattern of the

exocyclic double bond was shifted upfield and transformed to a singlet at 1.58ppm, integrating as 3H. (Fig. 3.7b) The reaction reached completion after 8 hours. (Fig. 3.7c)

The phototransformation was also carried out using pyrex filtered irradiation but while the reaction proceeded more rapidly, it was not as clean and was not as amenable to monitoring by nmr spectroscopy. Examination of the aromatic region indicated the presence of an *o*-disubstituted phenyl ring. The ^{13}C nmr revealed two methyl signals at 16.36 and 20.43ppm and two bridgehead carbon signals at 74.21 and 74.74 ppm, the chemical shift proximity of which led us to propose the tricyclic structure **(182a)**. The mechanism is explained in terms of 5-*exo*-trig ring closure.[156] (Scheme 3.46)



Scheme 3.46

As mentioned previously, the eliminative intramolecular cyclization of N-aryl-1,2,3-triazoles leading to polycyclic structures has been well documented.[146-150] (Schemes 3.36-3.38) In these cases the mechanism has been explained in terms of a diradical or imino carbene intermediate. The formation of pyrrolo[3,2-*b*]indole **(182)** by 5-*exo*-trig closure constitues a new pathway to this benzodiazapentalene system.

a) ^1H nmr spectrum of **(227)**

b) Reaction mixture
after 3 hours

c) Reaction mixture on
completion of reaction
(8 hours)

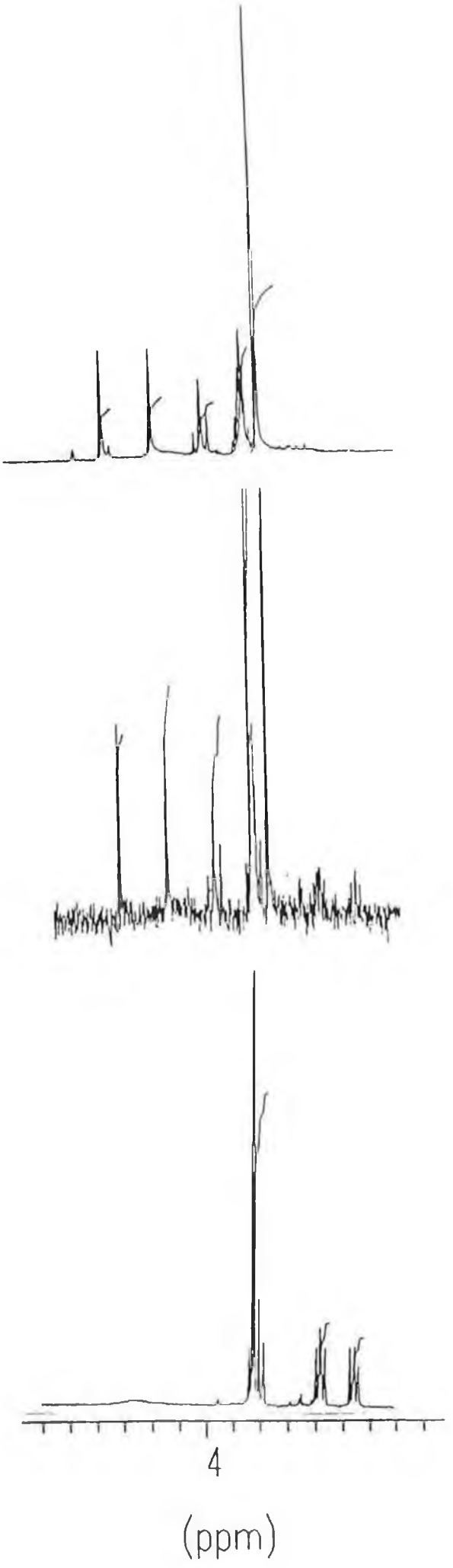
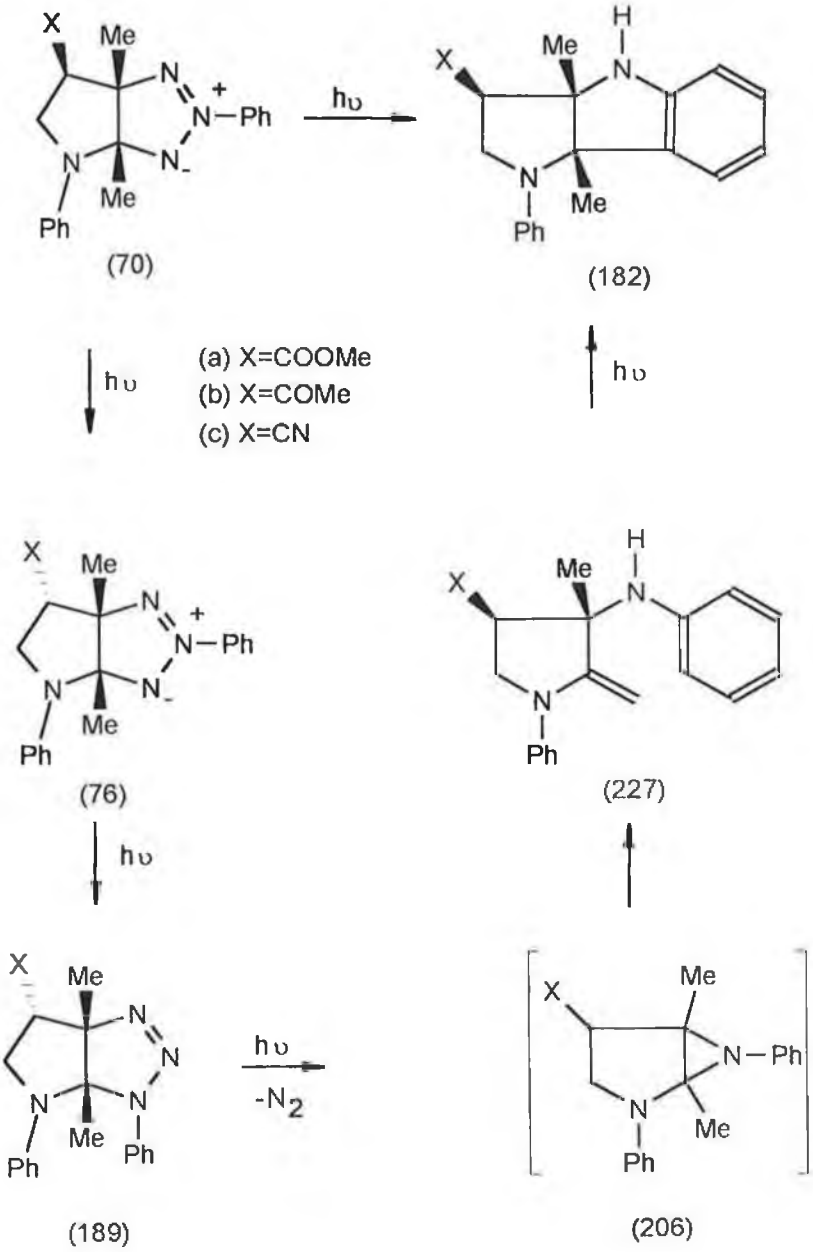


Fig 3 7 ^1H nmr monitoring of photochemical transformation of **(227)** - **(182a)**

The stereochemistry of **(182)** cannot be deduced accurately spectroscopically but it follows from Scheme 3.46 that 5-*exo*-trig closure from **(227)** would result in **(182)** containing the C-3, C-3a and C-8b substituents with the same relative stereochemistry. On the basis of the above experimental evidence the mechanism of formation of **(182)** on irradiation of **(70)** is proposed as outlined in Scheme 3.47 and involves a complex series of sequential transformations.



Scheme 3.47

The alteration in stereochemistry between **(189)** and **(229)** may be explained in terms of an epimerization, shown previously (Schemes 3.17 and 3.32) to be an important process under the reaction conditions.

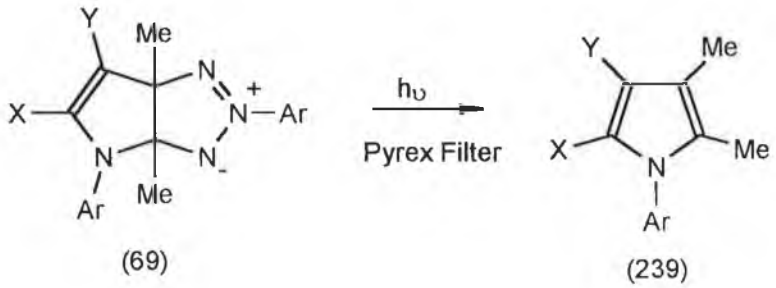
Physical data for the products and intermediates formed in this series of transformations is given in Table 3.5.

Table 3.5. Physical Data of Photoproducts.

	Mol Formula	Mol. Weight	Yield (%)	M.P (°C)	Found (Theory) (%) C	H	N
182a	$C_{20}H_{22}N_2O_2$	322.41	57	164-166	74.04 (74.51)	6.88 (6.88)	8.81 (8.69)
182b	$C_{20}H_{22}N_2O$	306.41	70	152-154	78.22 (78.40)	7.08 (7.24)	9.14 (9.14)
189b	$C_{20}H_{22}N_4O$	334.42	45	108-110	71.78 (71.83)	6.63 (6.25)	16.61 (16.75)
189c	$C_{19}H_{19}N_5$	317.39	51	136-138	71.60 (71.90)	6.03 (6.03)	22.00 (22.07)
227	$C_{20}H_{22}N_2O_2$	322.41	57	114-116	74.44 (74.51)	6.94 (6.88)	8.39 (8.69)

3.2e) Photochemical Transformations of Substituted 3a,6a-Dimethyl-3,3a,4,6a-Tetrahydropyrrolo[2,3-*d*]-1,2,3-triazoles.

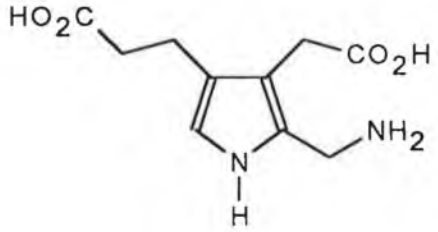
Further to the study of these bicyclic azimines, the 3a,6a-tetrahydro-analogues **(69)** were photolysed. On irradiation, in acetonitrile solution, using a medium pressure mercury lamp with pyrex filter, two products were isolated. The main product was a white powder identified by spectroscopic techniques as the substituted pyrrole **(239)**.



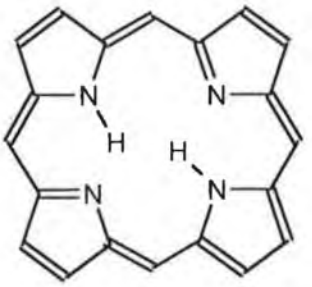
(69) (239)

Scheme 3.48

Apart from interest in the aromatic nature of the pyrrole system, it is of importance due to its incorporation in a wide variety of natural products. Perhaps the most important naturally occurring monopyrrole is porphobilinogen **(240)**, a biological precursor of chlorophylls, vitamin B_{12} and porphyrins. The porphyrin ring system **(241)** is a macrocycle in which four pyrrole units are linked by single-carbon bridges through the 2- and 5-positions. They occur naturally as metal complexes, the most important being haemin, the oxygen carrying component of haemoglobin. Chlorophyll is a closely related structure, a dihydroporphyrin, called a chlorin. Bile pigments, are oxidative degradation products of heme, one of which, bilirubin, is responsible for the yellow skin colouration in jaundice. Another related system is the corrin ring system, the most important member of which is vitamin B_{12}. The applications of naturally occurring and synthetic pyrrole derivatives have been outlined.[157]

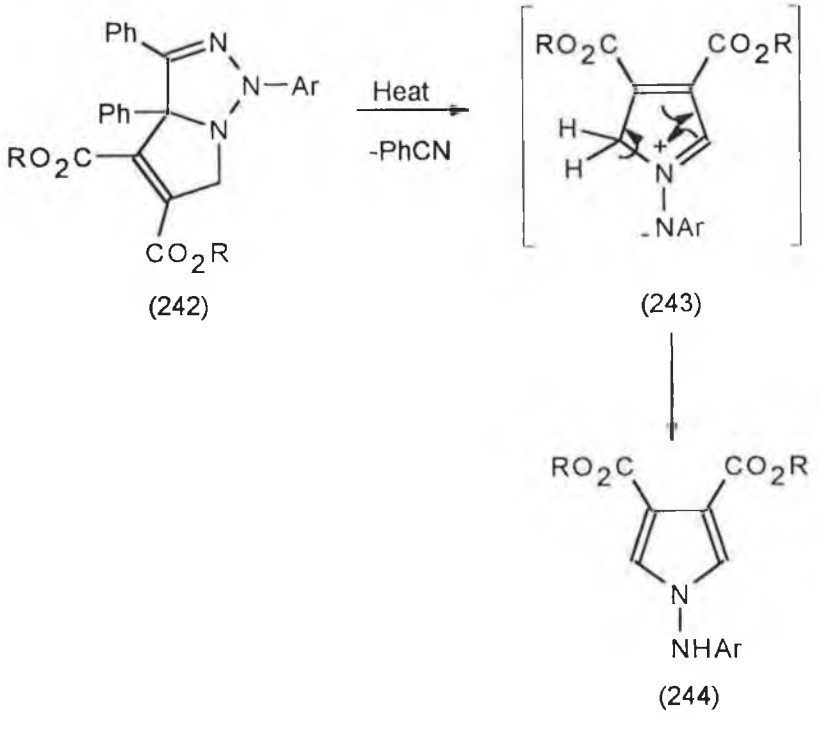


(240)



(241)

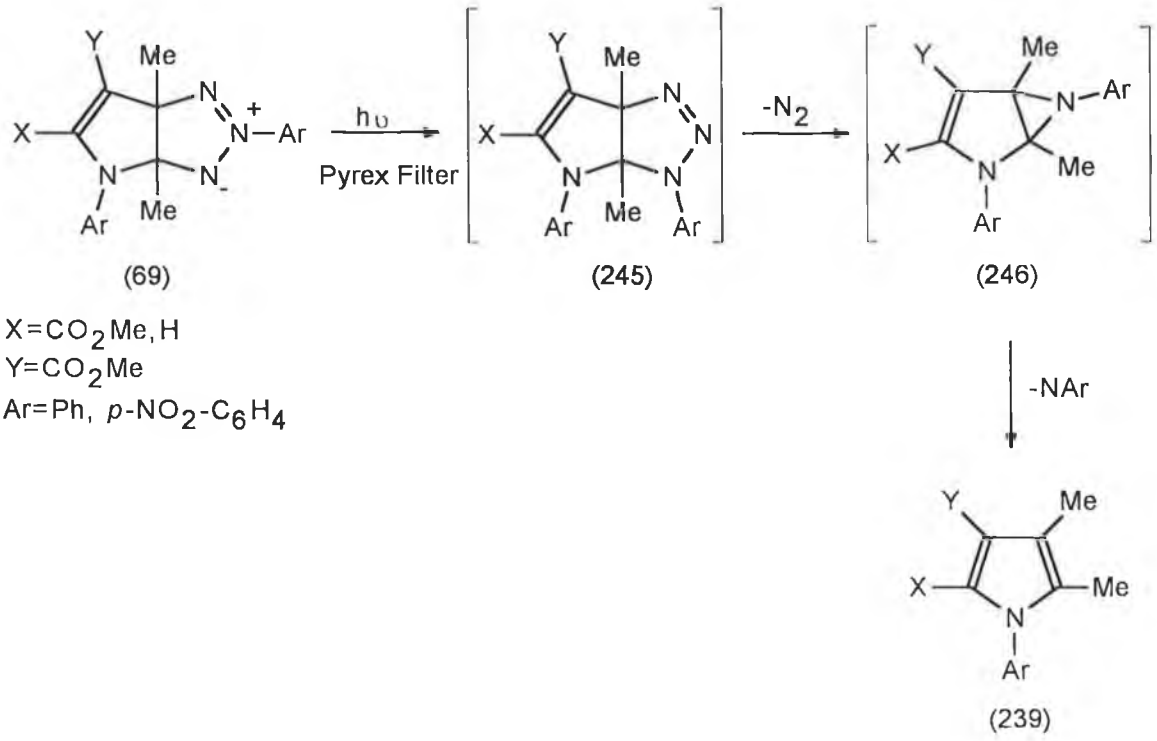
The most widely used syntheses of the pyrrole system involve cyclization reactions. The current route constitues a new pathway to pyrroles from readily available precursors *i.e.*, butane-2,3-dione, aryl hydrazine and a suitable dipolarophile. A thermal degradative formation of N-aminopyrrole has been reported by Butler *et al.* from **(242)**, formed on cycloaddition of 1,2,3-triazolium N-methylide and acetylenic dipolarophiles, DMAD or DEAD.[158] The mechanism involved extrusion of benzonitrile followed by a 1,3-H migration in **(243)** to give the 1-amino pyrroles **(244)**. (Scheme 3.49)



(242) (243) (244)

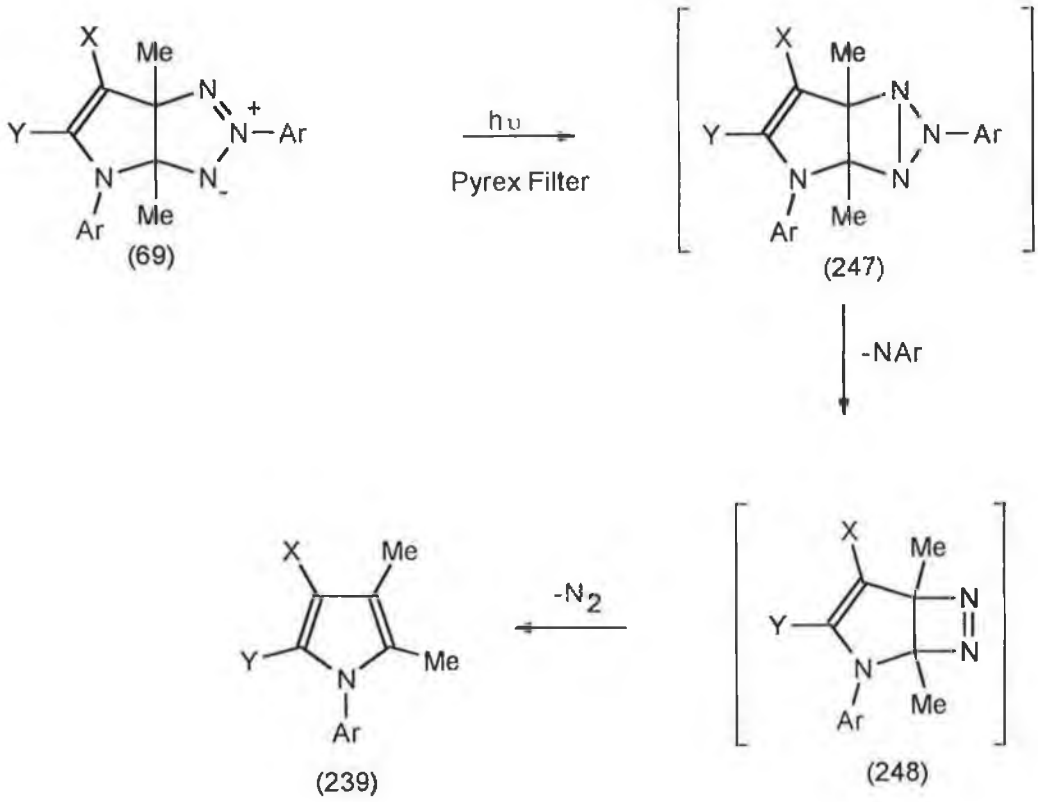
Scheme 3.49

The formation of **(239)** may be explained in terms of a mechanism similar to that proposed for the hexahydro-analogues **(70a-c)**. Initial photorearrangement to **(245)**. Loss of nitrogen and subsequent loss of aryl nitrene from the fused aziridine intermediate **(246)** yielded the substituted pyrrole **(239)**. (Scheme 3.50) The driving force for the elimination of aryl nitrene was the formation of the aromatic five-membered ring.



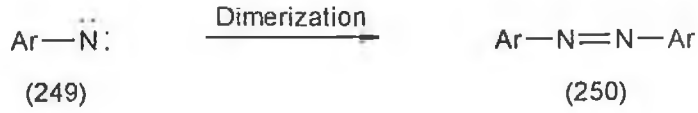
Scheme 3.50

An alternative mechanism involving the initial formation of the triaziridine **(247)**, subsequent loss of aryl nitrene, followed by loss of nitrogen from the resulting bicycle **(248)** cannot be discounted. (Scheme 3.51). Literature precedence exists for this second mechanism. On photolysis of the azimine **(122)**, the major by-product was **(123)**, formed on loss of methyl nitrene.[99] (See Scheme 3.4) In the present case the formation of such an intermediate, a fused four-membered ring **(248)** would be expected to be unstable and loss of molecular nitrogen to yield the aromatic heterocycle should occur readily.



Scheme 3.51

The other photoproduct isolated was azoarene **(250)**, formed on dimerization of the aryl nitrene **(249)** eliminated during the reaction process. (Scheme 3.52) This reaction is known to involve the triplet excited state of the nitrene.[86]



Scheme 3.52.

A list of the pyrroles formed along with the relevant physical data is given in Table 3.7

Table 3.7. Physical data for substituted pyrroles **(239)** .

	Mol. Formula	Mol. Weight	Yield (%)	M.P. (°C)	Found (Theory)(%) C	H	N
239a	$C_{16}H_{11}NO_4$	287.32	62	91-93	67.08	6.05	4.60
					(66.89)	(5.96)	(4.88)
239b	$C_{14}H_{15}NO_2$	229.28	65	75-77	73.49	6.62	6.01
					(73.34)	(6.59)	(6.11)
239c	$C_{16}H_{16}N_2O_6$	332.31	52	103-105	57.97	4.79	8.60
					(57.83)	(4.85)	(8.43)

3.3) CONCLUSIONS

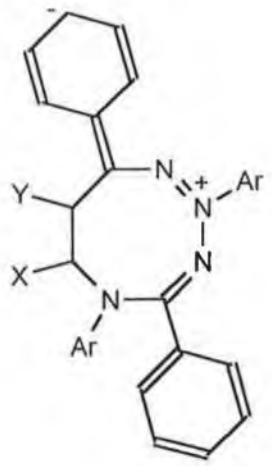
Just as with the thermal reactions, the photochemical rearrangements of the pyrrolo[2,3-*d*]triazole systems under investigation vary greatly with substitution pattern. It is therefore possible by variation of the substitution pattern of these compounds, to access a wide variety of novel heterocycles from simple, readily accessible precursors.

For systems containing aryl groups at the bridgehead positions (C-3a and C-6a), the initial reaction involved cleavage of the C3a-C6a bond. For hexahydropyrrolotriazoles **(82)** this led to the formation of the novel 1,2,3,5-tetrazocines **(158)**. For the tetrahydro-analogues **(81)** a further transannular ring contraction was observed which led *via* a 1,4-sigmatropic rearrangement to the imidazo[4,5-*c*]pyrazole system **(153)**.

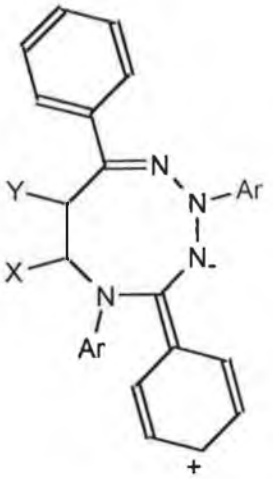
For systems containing methyl at the bridgehead position a much more complex sequence of transformations was observed. The initial reaction involved cleavage of the N1-N2 and N3-C3a bonds with formation of new N-N and C-N bonds to form the 1-substituted fused 1,2,3-triazoline **(189)**. On irradiation of **(189)** nitrogen loss was observed, leading to a methylidine pyrrolidine **(229)** which on further irradiation underwent 5-*exo*-trig closure to the tricyclic system **(182)**. For systems containing a double bond between C5 and C6 **(69)**, a similar reaction is observed, except that on loss of nitrogen, aryl nitrene was also lost leading to the formation of the aromatic pyrroles **(239),** along with azoarene **(250)**, formed on dimerization of aryl nitrene **(249)**.

For hexahydropyrrlo[2,3-*d*]triazoles, **(69)** and **(81)** rearrangement appears to be preceeded by epimerization about the C-6 position

The reason for the appreciable difference in reactivity between the aryl and methyl bridgehead substituted analogues is unclear, but may be related to resonance stablization of species such as **(251)** and **(252)** which lead to a weakening of the C3a-C6a bond, and thus favour the symmetry allowed photochemically induced disrotatory ring opening.



(251)



(252)

This resonance stabilization is not available for the 3a,6a-dimethylpyrrolo[2,3-*d*]triazoles **(69)** and **(70)** and therefore reaction is concentrated about the azimine moiety of the pyrrolotriazole system.

The reactions are summarized in Table 3.8 in terms of substituent and degree of saturation.

Table 3.8

Bridgehead Substituents	C5-C6 Saturation	Product
Ph	Saturated	1,2,3,5-Tetrazocine **(158)**
Ph	Unsaturated	Imidazo[4,5-*c*]pyrazole **(153)**
Me	Saturated	Sequential transformation to pyrrolo[3,2-*b*]indole **(182)**
Me	Unsaturated	Pyrrole **(239)**

3.4) EXPERIMENTAL

3.4a) Photorearrangements of Substituted 3a,6a-Diphenyl-3,3a,4,6a-tetrahydropyrrolo[2,3-*d*]-1,2,3-triazoles.

3.4a.1) Photorearrangement of 5,6-bis(methoxycarbonyl)-2,3a,4,6a-tetrahydropyrrolo[2,3-d]-1,2,3-triazole ***(81a)*** .

A solution of 500mg (0.94 mmol) **(81a)** in 300 cm^3 dry dichloromethane was flushed with gaseous nitrogen for 15 minutes and then irradiated, with continuous bubbling of nitrogen, for 3 hours using a medium pressure mercury lamp with pyrex filter. The solvent was removed under vacuum and the residue recrystallised from *n*-hexane to yield clear crystals of *3a,6a-bis(methoxycarbonyl)-1,3,5,6-tetraphenyl-1,3a,6,6a-tetrahydroimidazo[4,5-c]pyrazole* ***(153a)***, in 89% yield, m.p.: 152-154°C (Lit. 153-154°C).

CHN Analysis (found / theory) (%): M.w.: 530.58; $C_{32}H_{26}N_4O_4$; C (72.62 / 72.45), H (4.89 / 4.90), N (10.46 / 10.57).

IR (KBr) (cm^{-1}): 1760 (ester C=O), 1741 (ester C=O), 1619 (C=N), 807, 761, 700.

δH (DMSO-d_6) (ppm): 3.58 (3H, s) (ester CH_3), 3.73 (3H, s) (ester CH_3), 6.69 (2H, d), 6.87 (1H, t), 7.10 (2H, t), 7.38 (13H, m), 8.19 (2H, d) (all phenyl H).

δC (DMSO-d_6) (ppm): 53.34 (ester CH_3), 53.57 (ester CH_3), 97.28, 97.34 (C-3a, C-6a), 116.28, 122.99, 127.06, 128.26, 128.56, 128.68, 128.76, 129.12, 130.37, 131.28 all aromatic CH), 129.42 (3-C-Ph, C-1'), 130.91 (5-C-Ph, C-1'), 137.84 (C-3), 142.47 (6-N-Ph, C-1'), 147.67 (1-N-Ph, C-1'), 165.04 (C-5), 166.81 (ester C=O), 168.04 (ester C=O).

3.4a.2) Photorearrangement of ***(81b)***.

Irradiation was carried out as for (3.4a.1) except using 500mg (1.06 mmol) **(81b)**. On removal of the solvent under reduced pressure, the photoproduct was crystallised using diethyl ether. Recrystallisation from n-hexane yielded 83% of *3a-methoxycarbonyl-1,3,5,6-tetraphenyl-1,3a,6,6a-tetrahydroimidazo[4,5-c]pyrazole* ***(153b)***, m.p. 176-178°C.

CHN Analysis (found / theory) (%): M.w.: 472.55; $C_{30}H_{24}N_4O_2$; C (75.97 / 76.24), H (5.20 / 5.12), N (11.61 / 11.86).

IR (KBr) (cm^{-1}): 1759 (ester C=O), 1609 (C=N), 797, 778, 768, 749, 778, 768, 749, 704, 690, 654.

δH ($CDCl_3$) (ppm): 3.74 (3H, s) (ester CH_3), 6.32 (1H, s) (6a-C-H), 6.84 (1H, t), 6.94 (2H, d), 7.13 (6H, m), 7.24 (4H, m), 7.35 (1H, t), 7.40 (2H, t), 7.48 (2H, d), 8.17 (2H, d) (all phenyl H).

δC ($CDCl_3$) (ppm): 89.81 (C-3a), 90.82 (C-6a), 115.10, 120.81, 127.24, 127.87, 128.09, 128.44, 128.78, 129.10, 129.32, 129.44, 129.51, 129.58 (all phenyl CH), 130.32 (3-C-Ph, C-1'), 130.60 (5-C-Ph, C-1'), 140.79 (C-3), 143.83, (6-N-Ph, C-1'), 148.90 (1-N-Ph, C-1'), 165.01 (C-5), 170.12 (ester C=O).

3.4a.3) Photorearrangement of 3a,6a-bis(4'-chlorophenyl)-5,6-bis(methoxycarbonyl)-2,4-diphenyl-3,3a,4,6a-tetrahydropyrrolo[2,3-d]triazole ***(84a).***

Irradiation was carried out as for (3.4a.1) except using 500mg (0.834 mmol) **(84a)**. Recrystallisation from n-hexane yielded clear white crystals of *3,5-bis(4'-chlorophenyl)-3a,6a-bis(methoxycarbonyl)-1,6-diphenyl-1,3a,6,6a-tetrahydroimidazo[4,5-c]pyrazole* ***(153c)*** in 87% yield, m.p.: 196-198°C.

CHN Analysis (found / theory) (%): M.w.: 599.47; $C_{32}H_{24}Cl_2N_4O_4$; C (64.23 / 64.11), H (4.05 / 4.01), N (9.21 / 9.35).

IR (KBr) (cm^{-1}): 1766 (ester C=O), 1739 (ester C=O), 845, 797, 790, 755, 747, 723, 699, 665.

δH ($CDCl_3$) (ppm): 3.51 (3H, s) (ester CH_3), 3.72 (3H, s) (ester CH_3), 6.64 (2H, d), 6.82 (1H, t), 6.99 (2H, t), 7.16 (6H, m), 7.44 (5H, m), 8.11 (2H, d) (all phenyl H).

δC ($CDCl_3$) (ppm): 53.16 (ester CH_3), 53.26 (ester CH_3), 97.34 (C-3a), 97.92 (C-6a), 116.73, 122.73, 127.36, 128.26, 128.45, 128.62, 128.68, 128.78, 129.19, 130.89, 131.61 (all phenyl C), 135.03 (3-C-Ar, C-4'), 136.80 (5-C-Ar, C-4'), 137.85 (C-3), 142.78 (6-C-Ph, C-1'), 147.15, 1-C-Ph, C-1'), 165.02 (C-5), 167.10 (ester C=O), 168.25 (ester C=O).

*3.4a.4) Photorearrangement of **(84b)**.*

As for 3.4a.1 except using 500mg (0.92 mmol) **(84b)**. On recrystallisation from n-hexane clear white crystals of *3,5-bis(4'-chlorophenyl)-3a-methoxycarbonyl-1,6-diphenyl-1,3a,5,6a-tetrahydroimidazo[4,5-c]pyrazole **(153d)*** in 82% yield, m.p.: 218-220°C.

CHN Analysis (found / theory) (%): M.w. 541.44; $C_{30}H_{22}Cl_2N_4O_2$; C (66.25 / 66.54), H (4.09 / 4.07), N (10.05 / 10.35).

IR (KBr) (cm^{-1}): 1755 (ester C=O), 1609 (C=N), 832, 824, 796, 764, 749, 741, 733, 713, 702, 692, 670.

δH ($CDCl_3$) (ppm): 3.73 (3H, s) (ester CH_3), 6.32 (1H, s) (6a-C-H), 6.89 (3H, m), 7.12 (6H, m), 7.24 (3H, m), 7.35 (2H, d), 7.42 (2H, d), 8.09 (2H, d) (all phenyl H).

δC ($CDCl_3$) (ppm): 53.03 (ester CH_3), 89.31 (C-3a), 90.45 (C-6a), 114.80, 120.77, 127.32, 127.94, 128.09, 128.14, 128.39, 128.54, 128.77, 129.15, 129.31, 130.54 (all phenyl C), 134.68 (3-C-Ph, C-4'), 136.33 (5-C-Ph, C-4'), 140.27 (C-3), 143.08 (6-N-Ph, C-1'), 147.30 (1-N-Ph, C-1'), 163.82 (C-5), 169.39 (ester C=O).

*3.4a.5) Photorearrangement of 6-cyano-2,3a,4,6a-tetraphenyl-3,3a,4,6a-tetrahydropyrrolo[2,3-d]-triazole **(110)**.*

The crude product of the oxidation of 500mg of the hexahydro-analougue **(82a)** (See 2.3c.1) of was dissolved in 300cm^3 of dry dichloromethane, degassed using gaseous nitrogen and irradiated similarly to the above reactions. The solvent was removed under vacuum on completion of the reaction, and the residue passed through a flash chromatography column containing silica gel (0.032-0.063mm mesh size), using *n*-hexane / ethyl acetate (1:1) as eluant. The photoproduct **(153e)** was isolated in 67% yield after recrystallisation from *n*-hexane, m.p. 132-134°C.

CHN Analysis (found / theory) (%): M.w.: 439.52, $C_{29}H_{21}N_5$; C (78.97 / 79.27), H (4.77 / 4.88), N (16.12 / 15.95).

IR (KBr) (cm^{-1}): 2226 (CN), 824, 754, 732, 686.

δH ($CDCl_3$) (ppm): 6.32 (1H, s), 6.92 (1H, t), 7.19 (2H, m), 7.42 (13H, m), 7.74 (2H, d), 8.06 (2H, m), (all phenyl H).

δC ($CDCl_3$) (ppm): 91.08, 91.76 (C-3a, C-6a), 114.18 (CN), 115.12, 119.72, 125.31, 126.78, 126.84, 127.25, 128.09, 128.18, 128.78, 128.90, 128.92, 129.00, 129.20, 129.22, 129.44, 129.49, 129.64, 129.71, 130.12, 133.51, 138.74.

3.4b) Photorearrangements of substituted 3a,6a-diaryl-hexahydropyrrolo[2,3-*d*]-1,2,3-triazoles.

All photochemical reactions in this section were carried out using sunlight as irradiation source. They may also be carried out using a xenon arc lamp at $\lambda > 385$nm., in which case the reaction time is reduced. There was a problem with the second source however in that the lamp overheated after about 1-2 hours irradiation, and had to be switched off, so reaction times of 48 hours actually involved considerably more laboratory time There was little overall gain in time. Reactions carried out using this second source did not proceed as cleanly.

*3.4b.1) Photorearrangement of 6-methoxycarbonyl-2,3a,4,6a-tetraphenyl-3.3a,4.5.6,6a-. hexahydropyrrolo[2,3-*d*]-1,2,3-triazole **(82a)**.*

200mg (0.422 mmol) of **(82a)** was dissolved in 15cm^3 of dry dichloromethane, and allowed to stir in sunlight at ambient temperature for 4 weeks. After this time the solvent was removed under vacuum and the residue was crystallised from diethyl ether / *n*-hexane to give orange / green crystals of *7-methoxycarbonyl-2,4,5,8-tetraphenyl-2,5,6,7-tetrahydro-1,2,3,5-tetrazocine **(158a)***, (164mg, 82%), m.p. 114-115°C.

CHN Analysis (found / theory) (%): M.w.: 474.56; $C_{30}H_{26}N_4O_2$; C (76.20 / 75.95), H (5.63 / 5.49), N (11.52 / 11.81).

IR (KBr) (cm^{-1}): 1739 (ester C=O), 760, 750, 730, 692.

δH ($CDCl_3$) (ppm): 3.40 (3H, s) (ester CH_3), 4.38 (2H, m), 4.66 (1H, dd) (J = 8 86, 12.02), 6.72 (3H, m), 6.94 (2H, t), 7.00 (1H, m), 7.24 (12H, m), 7.68 (2H, d) (all phenyl H).

δC ($CDCl_3$) (ppm): 48.24 (CH_3), 49.18 (CH), 52.24 (ester CH_3), 116.86, 122.17, 122.54, 127.46, 128.03, 128.08, 128.28, 129.04, 129.28, 129.81, 130.57 (all phenyl CH), 134.87 (8-C-Ph, C-1'), 136.05 (4-C-Ph, C-1'), 143.21 (C-8), 150.00 (5-N-Ph, C-1'), 154.46 (2-N-Ph, C-1'), 169.32 (C-4), 175.99 (ester C=O).

3.4b.2) Photorearrangement of (82b).

A solution of 500mg (1.09 mmol) **(82b)** in dry dichloromethane was stirred in sunlight for 4 weeks at ambient temperature. After this time, the solvent was removed under vacuum and the product, *7-methylcarbonyl-2,4,5,8-tetraphenyl-2,5,6,7-tetrahydro-1,2,3,5-tetrazocine **(158b)***, was recrystallised from diethyl ether / pet.ether (40-60) (1:1) in 65% yield (325mg), m.p.: 168-169°C.

CHN Analysis (found / theory) (%): M.w.: 458.56; $C_{30}H_{26}N_4O$; C (78.69 / 78.60), H (5.90 / 5.63), N (11.98 / 12.23).

IR (KBr) (cm^{-1}): 1713 (ketone C=O), 1612 (C=N), 758, 734, 693.

δH ($CDCl_3$) (ppm): 1.98 (3H, s), (ketone CH_3), 4.31 (1H, t) (C-7, CH), 4.51 (1H, dd) (C-6, CH_2), 4.63 (1H, dd) (C-6, CH_2) (*Jam* = 15.26, *Jax* = 8.86, *Jmx* = 8.86) 7.79 (3H, m), 7.04 (3H, m), 7.30 (12H, m), 7.68 (2H, d) (all phenyl H).

δC ($CDCl_3$) (ppm): 29.29 (ketone CH_3), 47.88 (C-6), 58.47 (C-7), 117.25, 122.52, 122.77, 127.62, 128.04, 128.36, 128.52, 129.08, 129.39, 129.81, 130.83 (all phenyl CH), 134.83 (8-C-Ph, C-1'), 136.38 (4-C-Ph, C-1'), 143.40 (C-8), 150.67 (5-C-Ph, C-1'), 154.54 (2-C-Ph, C-1'), 175.62 (C-4), 200.70 (ketone C=O).

*3.4b.3) Photorearrangement of 6-ethoxycarbonyl-2,3a,4,6a-tetraphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-d]-1,2,3-triazole **(82d)**.*

As for 3.4b.1 except using 200mg (0.41 mmol) of **(82d)**. On recrystallisation from diethyl ether / *n*-hexane (1:1), 172mg (86%) of a yellow compound, *7-ethoxycarbonyl-2,4,5,8-tetraphenyl-2,5,6,7-tetrahydro-1,2,3,5-tetrazocine **(158d)***, m.p.: 101-103°C, was obtained.

CHN Analysis (found / theory) (%): M.w.: 488.59; $C_{31}H_{28}N_4O_2$; C (75.98 / 76.23), H (5.83 / 5.74), N (11.36 / 11.48).

IR (KBr) (cm^{-1}): 1730 (ester C=O), 1621 (C=N), 804, 775, 758, 750, 729, 693, 655

δH ($CDCl_3$) (ppm): 0.59 (3H, t) (ethyl ester CH_3), 3.36 (1H, m), 3.52 (1H, m) (ethyl ester CH_3), 3.96 (2H, m) (C-6, CH_2), 4.21 (1H, dxd) (C-7, CH) (*J* = 8.86, 14.77), 6.30 (3H, m), 6.52 (1H, t), 6.57 (1H, t), 6.81 (12H, m), 7.25 (2H, d) (all phenyl H).

δC ($CDCl_3$) (ppm): 13.72 (ethyl ester CH_3), 48.08 (C-6, CH_3), 49,55 (C-7, CH), 61.60 (ethyl ester CH_3), 116.95, 122.15, 122.52, 127.46, 127.98, 128.06, 128.20, 129.04, 129.26, 129.79, 130.43 (all phenyl CH), 134.88 (8-C-Ph, C-1'), 136.34 (4-C-Ph, C-1'), 143.18 (C-8), 150.15 (5-N-Ph, C-1'), 154.40 (2-N-Ph, C-1'), 168.81 (C-4), 176.05 (ester C=O).

Crystal Data for (7-ethoxycarbonyl-2,4,5,8-tetraphenyl-2,5,6,7-tetrahydro-1,2,3,5-tetrazocine) ***(158d)***-($C_{31}H_{28}N_4O_2$); M_r = 488.57, F(000) = 1032, triclinic: *a* = 10.191(2)Å, *b* = 12.600(3)Å, *c* = 21.568(4)Å, α = 91.370(12)°, β = 100.128(10)°, γ = 104.299(10)°, *V* = 2633.6(9)Å^3, space group P-1, *Z* = 4, *Dc* = 1.232g/cm^3, μ = 0.079mm^{-1}. The experimental data was collected at room temperature on an Enraf Nonius CAD4 automatic diffractometer, using graphite-monochromated MoKα radiation (λ = 0.71069Å). The structure was solved by direct methods (SHELXS 86).[84] The structure was refined by full matrix least squares on F^2 to a final R value of 0.083 (wR^2 = 0.1635) (SHELXL 93).[85] The asymmetric unit consists of two molecules exhibiting a close contact (2.457(12)Å) between O-37 and H-24. This introduces some disorder to the atomic positions of C-24A and C-25A, and presumably results in a slight increase in the residual R factors. The hydrogen atoms were located at their calculated positions. The estimated standard deviations for the geometrical parameters involving non-hydrogen atoms lie within the following ranges: bond lengths, 0.008-0.02 Å, bond angles 0.5-1.3°.

Table 3.9 Atomic coordinates (Åx10^4) **(158d)**

	X	Y	Z		X	Y	Z
N-1	1035(7)	1763(5)	3077(3)	N-1A	-4026(7)	7908(5)	2171(3)
N-2	488(7)	2730(5)	3006(3)	N-2A	-5146(7)	8350(5)	2324(3)
N-3	897(7)	3260(5)	2464(3)	N-3A	-4947(7)	8528(5)	2992(3)
N-5	-684(7)	1716(5)	1844(3)	N-5A	-5593(7)	6573(5)	3051(3)
O-36	-1232(7)	1198(4)	3929(3)	O-36A	-6147(6)	6601(4)	815(2)
O-37	-2803(7)	1890(5)	3321(3)	O-37A	-8004(7)	6528(6)	1236(3)
C-4	379(9)	2653(6)	1948(4)	C-4A	-5098(8)	7653(6)	3301(3)
C-6	-1758(9)	1514(6)	2231(4)	C-6A	-6615(9)	6337(6)	2463(3)
C-7	-1458(9)	901(6)	2836(4)	C-7A	-1958(9)	6230(6)	1883(3)
C-8	42(9)	889(6)	2998(4)	C-8A	-4468(8)	6895(6)	1961(3)
C-9	992(9)	3464(6)	3564(4)	C-9A	-5218(8)	9324(6)	2018(3)
C-10	1677(10)	3196(7)	4114(4)	C-10A	-5120(9)	9336(6)	1380(4)
C-11	2017(10)	3897(8)	4653(4)	C-11A	-5356(9)	10226(8)	1056(4)
C-12	1655(11)	4861(8)	4642(5)	C-12A	-5661(10)	11099(8)	1339(4)
C-13	979(10)	5153(6)	4089(5)	C-13A	-5715(11)	11070(7)	1966(5)
C-14	647(9)	4469(6)	3544(4)	C-14A	-5528(9)	10197(6)	2307(4)
C-15	968(10)	3053(6)	1379(4)	C-15A	-4830(9)	7833(6)	4004(3)
C-16	122(11)	3132(6)	809(4)	C-16A	-3968(10)	8787(7)	4305(4)
C-17	684(12)	3508(7)	294(4)	C-17A	-3855(10)	8997(8)	4944(4)
C-18	2084(13)	3776(6)	344(5)	C-18A	-4548(10)	8248(8)	5293(4)
C-19	2943(11)	3723(6)	906(5)	C-19A	-5371(10)	7280(7)	5003(4)
C-20	2391(9)	3359(6)	1427(4)	C-20A	-5515(9)	7069(6)	4358(3)
C-21	-679(10)	816(6)	1418(4)	C-21A	-4879(10)	5775(6)	3242(4)
C-22	-1778(10)	364(7)	946(4)	C-22A	-3473(11)	6106(7)	3466(4)
C-23	-1703(14)	-467(8)	533(5)	C-23A	-2750(12)	5330(10)	3626(4)
C-24	-541(16)	-848(7)	587(6)	C-24A	-3432(17)	4252(11)	3551(5)
C-25	552(13)	-386(7)	1058(5)	C-25A	-4792(17)	3909(9)	3332(5)

Table 3.9 continued

C-26	512(11)	442(6)	1481(5)	C-26A	-5549(11)	4669(7)	3181(4)
C-27	443(9)	-165(6)	3096(3)	C-27A	-3411(8)	6364(6)	1791(4)
C-28	-452(10)	-1181(7)	2900(4)	C-28A	-3423(10)	5290(7)	1917(4)
C-29	0(13)	-2127(7)	2996(4)	C-29A	-2344(11)	4854(7)	21810(5)
C-30	1308(12)	-2084(7)	3291(4)	C-30A	-1267(10)	5485(8)	1568(4)
C-31	2213(10)	-1070(8)	3495(4)	C-31A	-1264(10)	6536(8)	1424(4)
C-32	1765(11)	-131(7)	3398(4)	C-32A	-2317(9)	6986(7)	1541(4)
C-33	-1932(11)	1412(6)	3373(4)	C-33A	-6824(12)	6486(7)	1293(5)
C-34	-1497(12)	1710(8)	4487(4)	C-34A	-6903(14)	6820(8)	208(4)
C-35	-598(12)	1425(10)	5050(5)	C-35A	-5918(15)	6975(11)	-220(5)

Table 3.10 Bond Lengths for **(158d)** (Å).

N1-C8	1.282(8)	N1A-C8A	1.285(8)
N1-N2	1.461(8)	N1A-N2A	1.471(8)
N2-C9	1.435(9)	N2AC9A	1.418(9)
N2-N3	1.436(7)	N2A-N3A	1.424(7)
N3-C4	1.285(9)	N3A-C4A	1.293(8)
N5-C4	1.374(9)	N5A-C4A	1.387(8)
N5-C21	1.445(9)	N5A-C21A	1.409(10)
N5-C6	1.469(8)	N5A-C6A	1.462(9)
O36-C33	1.350(11)	O36A-C33A	1.332(9)
O36-C34	1.451(8)	O36A-C34A	1.464(13)
O37-C33	1.181(11)	O37A-C33A	1.201(12)
C4-C15	1.504(10)	C4A-C15A	1.492(10)
C6-C7	1.554(11)	C6A-C7A	1.539(8)
C7-C8	1.510(11)	C7A-C33A	1.504(13)
C7-C33	1.520(10)	C7A-C8A	1.520(10)
C8-C27	1.492(10)	C8A-C27A	1.493(10)
C9-C10	1.359(11)	C9A-C14A	1.382(9)
C9-C14	1.395(10)	C9A-C10A	1.398(9)
C10-C11	1.381(10)	C10A-C11A	1.383(11)
C11-C12	1.353(11)	C11A-C12A	1.371(11)
C12-C13	1.373(12)	C12A-C13A	1.365(11)
C13-C14	1.379(10)	C13A-C14A	1.370(10)
C14-C16	1.390(12)	C14A-C16A	1.370(10)
C15-C20	1.390(11)	C15A-C20A	1.376(9)
C16-C17	1.381(10)	C16A-C17A	1.375(10)
C17-C18	1.365(14)	C17-C18A	1.361(10)
C18-C19	1.377(13)	C18A-C19A	1.362(11)
C19-C20	1.383(10)	C19A-C20A	1.384(10)
C21-C22	1.365(12)	C21A-C22A	1.382(12)

Table 3.10 continued

C21-C26	1.393(12)	C21A-C26A	1.383(10)
C22-C23	1.384(12)	C22A-C23A	1.378(12)
C23-C24	1.370(2)	C23A-C24A	1.356(14)
C24-C25	1.360(2)	C24A-C25A	1.340(2)
C25-C26	1.382(11)	C25A-C26A	1.381(14)
C27-C32	1.378(10)	C27A-C32A	1.384(10)
C27-C28	1.382(10)	C27A-C28A	1.398(9)
C28-C29	1.387(10)	C28A-C29A	1.396(12)
C29-C30	1.358(12)	C29A-C30A	1.379(11)
C30-C31	1.387(11)	C30A-C31A	1.367(11)
C31-C32	1.376(11)	C31A-C32A	1.388(11)
C34-C35	1.492(13)	C34A-C35A	1.462(13)

Table 3.11 Bond angles for **(158d)** (°).

C8-N1-N2	110.1(7)	C8A-N1A-N2A	111.5(6)
C9-N2-N3	110.8(5)	C9A-N2A-N3A	111.7(5)
C9-N2-N1	110.4(6)	C9A-N2A-N1A	111.8(5)
N3-N2-N1	108.3(5)	N3A-N2A-N1A	108.5(6)
C4-N3-N2	112.4(6)	C4A-N3A-N2A	115.6(6)
C4-N5-C21	121.2(6)	C4A-N5A-C21A	121.0(7)
C4-N5-C6	121.4(6)	C4A-N5A-C6A	118.5(7)
C21-N5-C6	116.7(6)	C21A-N5A-C6A	118.1(7)
C33-O36C34	115.4(7)	C33A-O36A-C34A	116.5(8)
N3-C4-N5	128.3(7)	N3A-C4A-N5A	127.1(7)
N3-C4-C15	115.6(7)	N3A-C4A-C15A	116.0(6)
N5-C4-C15	116.0(7)	N5A-C4A-C15A	116.6(6)
N5-C6-C7	115.8(7)	N5A-C6A-C7A	112.2(6)
C8-C7-C33	112.5(7)	C33A-C7A-C8A	111.2(7)
C8-C7-C6	111.5(6)	C33A-C7A-C6A	111.2(7)
C33-C7-C6	109.2(7)	C8A-C7A-C6A	113.9(6)
N1-C8-C27	116.2(8)	N1A-C8A-C27A	115.9(7)
N1-C8-C7	123.2(7)	N1A-C8A-C7A	124.6(7)
C27-C8-C7	120.7(7)	C27A-C8A-C7A	119.5(6)
C10-C9-C14	119.3(8)	C14A-C9A-C10A	119.5(7)
C10-C9-N2	123.7(7)	C14A-C9A-N2A	122.3(6)
C14-C9-N2	116.8(8)	C10A-C9A-N2A	117.8(7)
C9-C10-C11	121.0(9)	C11A-C10A-C9A	118.3(7)
C12-C11-C10	120.1(9)	C12A-C11A-C10A	122.7(8)
C11-C12-C13	119.7(9)	C13A-C12A-C11A	117.3(9)
C12-C13-C14	120.9(8)	C12A-C13A-C14A	122.6(9)
C13-C14-C9	119.0(8)	C13A-C14A-C9A	119.5(8)
C16-C15-C20	119.4(8)	C16A-C15A-C20A	118.6(7)
C16-C15-C4	121.6(8)	C16A-C15A-C4A	120.9(7)

Table 3.11 continued.

C20-C15-C4	119.1(9)	C20A-C15A-C4A	120.3(7)
C1-C16-C15	120.6(9)	C15A-C16A-C17A	120.3(8)
C18-C17-C16	119.3(11)	C18A-C17A-C16A	121.0(9)
C17-C18-C19	121.1(10)	C17A-C18A-C19A	119.3(8)
C18-C19-C20	120.0(9)	C18A-C19A-C20A	120.2(8)
C19-C20-C15	119.6(9)	C15A-C20A-C19A	120.5(8)
C22-C21-C26	120.0(9)	C22A-C21A-C26A	119.8(9)
C22-C21-N5	121.8(9)	C22A-C21A-N5A	118.9(8)
C26-C21-N5	118.1(9)	C26A-C21A-N5A	121.2(9)
C21-C22-C23	119.7(10)	C23A-C22A-C21A	119.6(9)
C24-C23-C22	121.2(13)	C24A-C23A-C22A	119.2(12)
C25-C24-C23	118.5(11)	C25A-C24A-C23A	122.4(13)
C24-C25-C26	121.9(12)	C24A-C25A-C26A	119.7(12)
C25-C26-C21	118.7(11)	C25A-C26A-C21A	119.3(10)
C32-C27-C28	118.0(8)	C28A-C27A-C32A	118.5(7)
C32-C27-C8	118.9(8)	C28A-C27A-C8A	121.9(6)
C28-C27-C8	123.1(9)	C32A-C27A-C8A	119.4(7)
C27-C28-C29	120.0(10)	C27A-C28A-C29A	120.3(8)
C30-C29-C28	121.5(10)	C30A-C29A-C28A	120.2(8)
C29-C30-C31	119.1(9)	C31A-C30A-C29A	120.0(8)
C32-C31-C30	119.4(10)	C30A-C31A-C32A	120.2(8)
C31-C32-C27	122.0(9)	C31A-C32A-C27A	120.6(8)
O37-C33-O36	124.8(8)	O37A-C33A-O36A	122.8(11)
O37-C33-C7	126.1(10)	O37A-C33A-O36A	125.6(11)
O36-C33-C7	109.0(9)	O36A-C33A-C7A	111.5(8)
O36-C34-C35	108.0(8)	C35A-C34A-O36A	105.6(11)

3.4b.4) Photorearrangement of 6-methyl-6-methoxycarbonyl-2,3a,4,6a-tetraphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-d]-1,2,3-triazole (82e).

A solution of 500mg (1.02mmol) of **(82e)** was stirred at room temperature in sunlight for 4 weeks. The solvent was removed under vacuum and the residue passed through a flash chromatographic column using silica gel (0.032-0.063mm mesh size) with 3:1 *n*-hexane / ethyl acetate as eluant. The main product was recrystallised from diethyl ether / pet. ether (40-60) (1:1) to produce 395 mg (79%) of *6-methyl-7-methoxycarbonyl-2,4,5,8-tetraphenyl-2,5,6,7-tetrahydro-1,2,3,5-tetrazocine* ***(158e)***, m.p :138-140°C.

CHN Analysis (found / theory) (%): M.w.: 488.59; $C_{31}H_{28}N_4O_2$; C (76.34 / 76.23), H (5.96 / 5.74), N (11.26 / 11.48).

IR (KBr) (cm^{-1}): 1718 (ester C=O), 774, 762, 748, 736, 699, 678.

δH ($CDCl_3$) (ppm):1.36 (3H, s) (CH_3), 3.39 (ester CH_3), 4.44 (1H, d), 4.71 (1H, d) (*Jam*=15.75 Hz) (6-C-H_2), 6.78 (2H, d), 6.93 (2H, t), 7.05 (1H, t), 7.26 (13H, m), 7.59 (2H,d) (all phenyl H).

δC ($CDCl_3$) (ppm): 27.20 (CH_3), 52.10 (C-6), 55.75 (ester CH_3), 56.41 (C-7), 117.45, 122.45, 122.73, 127.67, 128.02, 128.12, 128.25, 128.88, 129.22, 129.39 (all phenyl CH), 134.80 (8-C-Ph, C-1'), 135.60 (4-C-Ph, C-1'), 143.59 (C-8), 149.68 (5-N-Ph, C-1'), 153.87 (2-N-Ph, C-1'), 172.88 (C-4), 182.80 (ester C=O).

3.4b.5) Photorearrangement of 6-cyano-2,3a,4,6a-tetraphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-d]-1,2,3-triazole (82c).

A solution of 500mg (1.13 mmol) of **(82c)** in 100cm^3 of dry dichloromethane was stirred at room temperature in sunlight for 4 weeks. On completion of the reaction the solvent was removed under vacuum and the residue passed through a flash chromatographic column (silica gel of 0.032-0.063mm mesh size) using a 3:1 mixture of *n*-hexane / ethyl acetate as eluant. The main product was recrystallised from diethyl ether / *n*-hexane to yield 340 mg (68%) of *7-cyano-2,4,5,8-tetraphenyl-1,2,5,6-tetrahydro-1,2,3,5-tetrazocine* ***(168)***, m.p :164-166°C.

CHN Analysis (found / theory) (%): M.w.: 441.54: $C_{29}H_{23}N_5$; C (78.97 / 79.27), H (4.77 / 4.88), N (16.12 / 15.95).

IR (KBr) (cm^{-1}): 3317 (NH), 2249 (CN), 783, 776, 761, 732, 711, 695, 675, 664.

δH ($CDCl_3$) (ppm): 4.71 (2H, dd, *J*=10.34, 24.61 Hz), 6.65 (2H, d), 6.84 (1H, t), 6.93 (2H, d), 7.07 (1H, t), 7.19 (4H, dd), 7.26 (2H, t), 7.37 (1H, t), 7.43 (2H, t), 7.52 (6H, m) (phenyl H and NH).

δC ($CDCl_3$) (ppm): 61.12 (C-6), 70.74 (C-7), 119.81 (CN), 112.92, 120.61, 123.80, 125.17, 128.19, 128.99, 129.10, 129.15, 129.40, 129.49, 129.69, 130.02, 130.89 (phenyl C), 139.72 (5-N-Ph, C-1'), 140.97 (C-7), 143.84 (2-N-Ph, C-1'), 164.59 (C-4).

3.4b.6) Formation of endo-*6-methoxycarbonyl-2,3a,4,6a-tetraphenyl-3,3a,4,5,6,6a-hexahydropyrrolo-[2,3-*d*]-1,2,3,-triazole* ***(160)***.

A solution of 200mg of the **(82a)** in dry dichloromethane was stirred at ambient temperature in direct sunlight. The reaction was followed by thin layer chromatography using 3:1 pet.ether (40-60) / ethyl acetate as eluant. The reaction initially produced a compound running slightly slower than the starting material, which over the course of time, disappeared to produce **(158a)**. The dichloromethane was removed under vacuum and the primary product was isolated from the residue by flash chromatographic separation, using the same solvent system as for TLC (silica gel 0.032-0.063 mm mesh size). The yellow / green product was crystallised from 4:1 pet.ether (40-60) / ethyl acetate and recrystallised from ethanol to yield 115 mg of the *endo*-isomer **(160)** (91% yield), m.p.: 192-193°C.

CHN Analysis (found / theory) (%): M.w.: 474.56; $C_{30}H_{26}N_4O_2$; C (75.78 / 75.95), H (5.42 / 5.49), N (11.69 / 11.81).

IR (cm^{-1}) (KBr): 1732 (ester C=O), 775, 761, 752, 737, 714, 688.

δH (ppm) ($CDCl_3$): 3.63 (3H, s) (CH_3), 3.89 (1H, t) (6-CH), 4.35 (2H, m) (5-CH_2) 6.72 (1H, t), 6.86 (2H, d), 6 90 (3H, m), 7.01 (7H, m), 7.10 (2H, t), 7.46 (2H, t), 7.54 (1H, t), 8.23 (2H, d) (all phenyl H).

δC (ppm) ($CDCl_3$): 49.84, 50.16, 52.04 (C-5, C-6, OCH_3), 89.09 (C-6a), 100.26 (C-3a), 116.09, 117.99, 122.97, 126.78, 126,92, 127.14, 127.51, 127.82, 128.38, 128.56, 131.60, 136.86, 137.84, 140.52, 144.13, 170.33.

3.4c) Isolation of Secondary Reaction Products.

3.4c.1) Photofragmentation of (153a).

A solution of 500mg (0.94mmol) of **(153a)** in dry dichloromethane was degassed under nitrogen and irradiated, with stirring, for 2 hours, using a medium pressure mercury lamp with pyrex filter. Upon completion, the solvent was evaporated under vacuum and the residue passed through a flash chromatography column (silica gel 0.032-0.063 mm mesh size) with 3:1 *n*-hexane / ethyl acetate as eluant. The product **(136)**, a white powder, was isolated in 65 % yield (205mg) on recrystallisation from *n*-hexane / diethyl ether. M.p.: 162-163°C

CHN analysis (found / required) (%): M.w: 336.35; $C_{19}H_{16}N_2O_4$; C(67.59 / 67.85), H (4.83 / 4.79), N (8.46 / 8.33).

IR (KBr) (cm^{-1}): 1724 (C=O), 765, 698.

δH ($CDCl_3$) (ppm): 3.71 (3H, s) (CH_3), 4.08 (3H, s) (CH_3), 7.53 (6H, m), 7.63 (2H, d), 8.01 (2H, d) (all phenyl H).

δC ($CDCl_3$) (ppm): 53.14 (CH_3), 53.93 (CH_3), 115.24, 118.45, 128.62, 128.65, 128.70, 129.15, 130.36, 130.90, 137.78, 16.54 (C=O), 165.20 (C=O).

3.4c.2) Oxidation of (158a).

To a solution of 500mg (1.05mmol) of **(158a)** in 30cm^3 dichloromethane was added a 1.1M excess of MnO_2. The solution was stirred vigorously for 30 minutes. The MnO_2 was then removed by gravity filtration and the solvent removed under vacuum. The product was then separated through a flash chromatography column (silica gel, mesh size 0.032-0.063mm) with 3:1 *n*-hexane / ethyl acetate as eluant. The main product 4-

methoxycarbonyl-2,5-diphenyl-1,2,3-triazole **(177)** was obtained and recrystallised from diethyl ether / *n*-hexane in 73% yield (214mg), m.p.: 83-84°C.

CHN analysis (found / required) (%): M.w.: 279.30; $C_{16}H_{13}N_3O_2$; C (68.60 / 68.81), H (4.62 / 4.66), N (14.95 / 15.04).

IR (KBr) (cm^{-1}): 1729 (C=O), 822, 758, 688, 666.

δH ($CDCl_3$) (ppm): 3.96 (3H, s) (CH_3), 7.40 (1H, t), 7.50 (5H, m), 7.92 (2H, m), 8.20 (2H, m) (all phenyl H)

δC ($CDCl_3$) (ppm): 52.44 (CH_3), 119.51, 128.21, 128.62, 129.25, 129.33, 129.43 (all phenyl CH), 129.14 (C-4-Ph, C-1'), 136.65, 139.11, 150.70 (C-4, C-5, 2-N-Ph, C-1'), 161.67 (C=O).

Also isolated from the reaction in 10% yield was an off-white powder of **(153b)**, m.p. 175-178°C. The ir, ^1H and ^{13}C nmr spectra were identical to those obtined on photorearrangement of **(81b)**.

3.4d) Photochemical Transformations of Substituted 3a,6a-dimethyl-2,4-diphenyl-hexahydropyrrolo[2,3-*d*]triazoles.

All photochemical reactions in the following sections were carried out using a medium pressure mercury lamp, with a pyrex filter. The samples were made up in either acetonitrile or dichloromethane.

3.4d.1) Formation of 3a,6a-dimethyl-4-methylcarbonyl-1,6-diphenyl-1,3a,4,5,6,6a-tetrahydropyrrolo[3,2-d]-1,2,3-triazole ***(189b)***.

A solution of 500mg (1.50 mmol) of **(70b)**, in 300cm^3 dry dichloromethane, was deoxygenated by bubbling gaseous nitrogen through the stirring solution for 15 minutes. The solution was then irradiated, with continued bubbling of nitrogen, for 45 minutes. The solvent was removed under reduced pressure and the residue passed through a flash chromatography column (silica gel, 0.032-0.063 mm mesh size), using a Charles Austin air pump and a 3:1 mixture of *n*-hexane / ethyl acetate as eluant. The product **(189b)** was isolated in 45% yield (225 mg) and was recrystallised from *n*-hexane / ethyl acetate (6:1) to yield clear white crystals, m.p.108-110°C.

CHN Analysis (found / theory) (%): M.w.: 334.42 ; $C_{20}H_{22}N_4O$; C (71.78 / 71.83), H (6.63 / 6.25), N (16.61 / 16.75).

IR (KBr) (cm^{-1}): 1703 (ketone CH_3), 811, 787, 771, 758, 717, 702, 697.

δH ($CDCl_3$) (ppm):1.50 (3H, s) (CH_3), 1.68 (3H, s) (CH_3), 2.43 (3H, s) (ketone CH_3), 3.12 (1H, dd), 3.28 (1H, dd), 3.65 (1H, dd) (4-C-H, 5-C-H_2), (*Jam* =11.32, *Jax* =9.85, *Jmx*=6.40 Hz) 6.43 (2H, d), 7.04 (5H, m), 7.15 (1H, t), 7.29 (2H, t) (phenyl H).

δC ($CDCl_3$) (ppm): 20.93 (CH_3), 21.12 (CH_3), 30.86 (ketone CH_3), 49.95 (C-5), 59.83 (C-4), 87.58 (C-3a), 91.79 (C-6a), 122.02, 124.33, 124.49, 125.23, 128.57, 129.07 (all phenyl CH), 139.79 (6-N-Ph, C-1'), 144.87 (1-N-Ph, C-1'), 204.98 (ketone C=O).

U.V. (MeCN) (nm): 254 (ε = 21720 l mol^{-1}cm^{-1}). A shoulder is seen on the visible side of the peak at 254nm.

Crystal Data for ***(189b)***: $C_{20}H_{22}N_4O$, M_w: 334.42, F(000) = 712, monoclinic, *a* = 8.4031(9)Å, *b* = 12.9267(7)Å, *c* = 16.484(2)Å, α = 90°, β = 96.289(5)°, γ = 90°, *V* = 1779.8(3)Å^3, space group P_21/n, *Z* = 4, D_c = 1.248g/cm^3, μ = 0.080mm^{-1}. The structure was solved by direct methods (SHELXS 86).[84] The structure was refined by

full matrix least squares on F^2 to a final R value of 0.0415 (wR^2=0.0982) (SHELXL 93).[85]

Table 3.12 Atomic Co-ordinates for **(189b)** (Åx10^4)

	X	Y	Z
O-1	2384(2)	7146(1)	5352(1)
N-1	782(2)	9106(1)	3257(1)
N-2	597(2)	8072(1)	3101(1)
N-3	1870(2)	7575(1)	3213(1)
N-6	3058(2)	9877(1)	4154(1)
C-4	3239(2)	8272(1)	3479(1)
C-5	2541(2)	9387(1)	3373(1)
C-7	2963(2)	9094(1)	4785(1)
C-8	3675(2)	8149(1)	4420(1)
C-9	-485(2)	9729(1)	2863(1)
C-10	-1340(2)	9396(2)	2141(1)
C-11	-2608(2)	9981(2)	1783(1)
C-12	-3018(2)	10897(2)	2129(1)
C-13	-2161(2)	11233(2)	2838(1)
C-14	-896(2)	10650(1)	3212(1)
C-15	2714(2)	10916(1)	4345(1)
C-16	3294(2)	11735(1)	3907(1)
C-17	2979(2)	12745(2)	4112(1)
C-18	2129(2)	12967(2)	4753(1)
C-19	1613(2)	12171(2)	5208(1)
C-20	1898(2)	11157(2)	5007(1)
C-21	3186(2)	7136(1)	4788(1)
C-22	3795(2)	6144(2)	4476(1)
C-23	4637(2)	8027(2)	3005(1)
C-24	2950(2)	9980(2)	2633(1)

Table 3.13 Bond Lengths for **(189b)** (Å).

O1-C21	1.207(2)	C8-C21	1.518(3)
N1-N2	1.376(2)	C9-C14	1.382(3)
N1-C9	1.433(2)	C9-C10	1.389(3)
N1-C5	1.514(2)	C10-C11	1.385(3)
N2-N3	1.251(2)	C11-C12	1 374(3)
N3-C4	1.483(2)	C12-C13	1.374(3)
N6-C15	1.417(2)	C13-C14	1.391(3)
N6-C5	1.458(2)	C15-C20	1.386(2)
N6-C7	1.459(2)	C15-C16	1.397(2)
C4-C23	1.514(3)	C16-C17	1.382(3)
C4-C5	1.559(2)	C17-C18	1 370(3)
C4-C8	1.562(2)	C18-C19	1.371(3)
C5-C24	1.511(2)	C19-C20	1,380(3)
C7-C8	1.513(2)	C21-C22	1.494(3)

Table 3.14 Bond Angles for **(189b)** (°)

N2-N1-C9	113.68(13)	C7-C8-C4	104.64(13)
N2-N1-C5	110.33(13)	C21-C8-C4	116.10(2)
C9-N1-C5	126.08(13)	C14-C9-C10	119.60(2)
N3-N2-N1	113.33(14)	C14-C9-N1	120.20(2)
N2-N3-C4	110.84(14)	C10-C9-N1	120.20(2)
C15-N6-C5	124.02(13)	C11-C10-C9	119.90(2)
C15-N6-C7	118.09(13)	C12-C11-C10	120.60(2)
C5-N6-C7	107.09(12)	C11-C12-C13	119.60(2)
N3-C4-C23	109.70(2)	C12-C13-C14	120.7(2)
N3-C4-C5	105.05(13)	C9-C14-C13	119.70(2)
C23-C4-C5	116.00(2)	C20-C15-C16	117.80(2)
N3-C4-C8	108.74(14)	C20-C15-N6	121.20(2)
C23-C4-C8	112.40(2)	C16-C15-N6	120.80(2)
C5-C4-C8	104.45(13)	C17-C16-C15	120.20(2)
N6-C5-C24	114.80(14)	C18-C17-C16	121.10(2)
N6-C5-N1	114.10(12)	C17-C18-C19	119.10(2)
C24-C5-N1	109.01(13)	C18-C19-C20	120.60(2)
N6-C5-C4	103.29(12)	C19-C20-C15	121.00(2)
C24-C5-C4	116.35(14)	O1-C21-C22	121.00(2)
N1-C5-C4	98.21(12)	O1-C21-C8	119.80(2)
N6-C7-C8	102.82(13)	C22-C21-C8	119.10(2)
C7-C8-C21	113.70(2)		

3.4d.2) Formation of 3a,8b-dimethyl-3-methylcarbonyl-1-phenyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole ***(182b).***

(182b) was isolated in 25% yield (115 mg) from reaction 3.4d.1, on flash chromatography of the reaction mixture. The compound was recrystallised from 4:1 *n*-hexane / ethyl acetate to yield clear colourless crystals. M.p.: 152-154°C.

CHN Analysis (found / theory) (%): M.w.: 306.41; $C_{20}H_{22}N_2O$; C (78.22 / 78.40), H (7.08 / 7.24), N (9.14 / 9.14).

IR (KBr) (cm^{-1}): 3409 (NH), 1710 (ketone C=O), 788, 754, 741, 693.

δH ($CDCl_3$) (ppm): 1.38 (3H, s), 1.71 (3H, s) (3a-C-CH_3, 8b-C-CH_3), 2.28 (3H, s) (ketone CH_3), 3.19 (1H ,dd, J = 7.87, 10.83 Hz), 3.66 (2H, m) (2-C-H, 3-C-H_2), 4.14 (1H, s) (NH), 6.55 (2H, m), 6.75 (1H, t), 6.90 (2H, d), 6.98 (1H, t), 7.05 (1H, d), 7.16 (2H, t) (mono- and o-disubstituted phenyl H).

δC ($CDCl_3$) (ppm): 21.08, 21.12 (3a-C-CH_3, 8b-C-CH_3), 30.69 (ketone CH_3), 50.63 (C-3), 56.78 (C-2), 75.34, 76.81 (C-3a, C-8b), 109.52, 116.76, 116.95, 118.52, 126.07, 128.52, 128.87 (phenyl CH), 128.68 (C-8a), 145.44 (1-N-Ph, C-1'), 150.20 (C-4a), 207.49 (ketone C=O).

U.V. (MeCN) (nm): 254, 302 (ε = 18335, 6905 l $mol^{-1}cm^{-1}$)

3.4d.3) Formation of 4-cyano-3a,6a-dimethyl-1,6-diphenyl-1,3a,4,5,6,6a-hexahydropyrrolo[3,2-d]-1,2,3-triazole ***(189c).***

A solution of 500mg (158mmol) of **(70c)** in 300cm^3 dry dichloromethane was purged of oxygen using gaseous nitrogen for 15 minutes. The solution was then irradiated using a medium pressure mercury lamp with pyrex filter for 45 minutes at room temperature. The solvent was removed under vacuum and the residue passed through a flash chromatography column packed with silica gel (0.032-0.063mm mesh size). A 3:1 *n*-hexane / ethyl acetate mixture was used as eluant. The main product, **(189c)** was isolated in 51% yield (255 mg), after recrystallisation from 6:1 *n*-hexane / ethyl acetate, m.p.: 136-138°C.

CHN Analysis (found / theory) (%): M.w: 317.39 $C_{19}H_{19}N_5$; C (71.60 / 71.90), H (6.03 / 6.03), N (22.00 / 22.07).

IR (KBr) (cm^{-1}): 2244 (CN), 810, 774, 764, 754, 698.

δH ($CDCl_3$) (ppm): 1.58 (3a-C-CH_3), 1.68 (6a-C-CH_3), 3.37 (1H, d), 3.45 (1H, dd), 3.60 (1H, d) (5-C-H_2), (4-C-H), (*Jam* = 9.88, *Jax* = 4.54, *Jmx* = 0 Hz) 6.34 (2H, m), 7.04 (5H, m), 7.19 (1H, t), 7.28 (2H, t) (all Phenyl H).

δC ($CDCl_3$) (ppm): 19.32 (3a-C-CH_3), 20.89 (6a-C-CH_3), 37.90 (C-4), 51.74 (C-5), 85.37 (C-3a), 85.92 (C-6a), 118.81 (CN), 122.52, 125.52, 125.72, 125.81, 128.84, 128.37 (all phenyl CH), 139.21 (6-N-Ph, C-1'), 143.89 (1-N-Ph, C-1').

U.V. (MeCN) (nm): 234, 254(s), 275(s) (ε = 14567, 13670, 11240 $lmol^{-1}\,cm^{-1}$)

3.4d.4) Formation of 4-carboxymethyl-3-N'-anilino-3-methyl-4,5-dihydro-3-H-2-methylidenepyrrolidine (227).

A solution of 500mg (1.42 mmol) of **(70a)** in 300cm^3 was deoxygenated for 15 minutes using gaseous nitrogen. The solution was then irradiated using a high pressure mercury lamp with pyrex filter for 45 minutes, with continued bubbling of nitrogen, at ambient temperature. The solvent was then removed under vacuum and the residue passed through a flash chromatographic column packed with silica gel (0.032-0.063 mm mesh size), using 3:1 *n*-hexane-ethyl acetate as eluant. The product was isolated crude in 57% yield (262mg). Recrystallisation from diethyl ether / *n*-hexane (1:3) yielded clear white crystals of **(227)**, m.p.164-166°C.

CHN Analysis (found / theory) (%): 322.41; $C_{20}H_{22}N_2O_2$; C (74.44 / 74.51), H (6.94 / 6.88), N (8.39 / 8.69).

IR (KBr) (cm^{-1}): 3379 (NH), 1734 (ester C=O), 787, 748, 694.

δH ($CDCl_3$) (ppm): 1.38 (3H, s) (3-C-CH_3), 3.70 (3H, s) (ester CH_3), 3.78 (2H, m), 3.97 (1H, t, *J* = 12.31 Hz) (C-5-H_2, C-4-H), 4.22 (1H, d, *J* = 0.98 Hz) (4-C-H), 4.46 (1H, d, *J* = 0.98 Hz) (vinyl CH_2), 6.78 (3H, m), 7.03 (1H, t), 7.36 (4H, m) (all phenyl H).

δC ($CDCl_3$) (ppm):26.76 (3-C-CH_3), 42.97 (ester CH_3), 49.33 (C-5), 51.87 (C-4), 64.40 (C-3), 77.54 (vinyl CH_2), 116.03, 118.52, 119.83, 122.07, 128.97, 129.03 (all phenyl CH), 143.77 (anilino-N-Ph, C-1'), 144.52 (1-N-Ph, C-1'), 150.90 (C-2), 171.40 (ester CH_3).

U.V. (MeCN) (nm): 246, 290 (24738, 16746 l $mol^{-1}cm^{-1}$)

Crystal data for (227): $C_{20}H_{22}N_2O_2$: M_w: 322.41, F(000) = 688, monoclinic, a = 8.366(4) Å, b = 25.268(5)Å, c = 8.523(5)Å, $\alpha = 90°$, $\beta = 107.83(3)°$, $\gamma = 90°$, V = 1715.1(14)Å^3, space group P_21/c, $Z = 4$, $D_c = 1.249 g/cm^3$, $\mu = 0.081 mm^{-1}$. The structure was solved by direct methods.[84] The structure was refined by full matrix least squares on F^2 to a final R value of 0.0468 ($wR^2 = 0.1196$).[85]

Table 3.15 Atomic co-ordinates ($x10^{-4}$) for **(227)**

	X	Y	Z
O-1	2065(3)	2896(1)	8691(3)
O-2	2939(2)	3119(1)	6564(3)
N-1	-2244(3)	3776(1)	6562(2)
N-10	-349(3)	3305(1)	3611(3)
C-2	-2460(3)	3542(1)	5025(3)
C-3	-821(3)	3259(1)	5109(3)
C-4	458(3)	3509(1)	6665(3)
C-5	-614(3)	3647(1)	7741(3)
C-6	-3806(4)	3512(1)	3713(4)
C-7	-1081(4)	2669(1)	5359(4)
C-8	1891(3)	3147(1)	7461(4)
C-9	4343(5)	2760(1)	7124(6)
C-11	-3486(3)	4020(1)	7109(3)
C-12	-4779(3)	4315(1)	6068(4)
C-13	-5942(4)	4561(1)	6668(4)
C-14	-5841(4)	4525(1)	8306(4)
C-15	-4554(4)	42349(1)	9348(4)
C-16	-3383(4)	3990(1)	8773(3)
C-17	224(3)	3775(1)	3095(3)
C-18	-357(4)	4269(1)	3352(4)
C-19	229(4)	4715(1)	2761(4)
C-20	1380(4)	4678(2)	1905(4)
C-21	1949(4)	4187(2)	1648(4)
C-22	1379(3)	3743(1)	2232(3)

Table 3.16 Bond Lengths (Å) for **(227)**.

O1-C8	1.196(3)	C4-C5	1.507(4)
O2-C8	1.330(3)	C11-C12	1.388(4)
O2-C9	1.444(4)	C11-C16	1.396(4)
N1-C2	1.398(3)	C12-C13	1.378(4)
N1-C11	1.405(3)	C13-C14	1.375(5)
N1-C5	1.461(3)	C14-C15	1.373(5)
N10-C17	1.402(3)	C15-C16	1.375(4)
N10-C3	1.452(3)	C17-C18	1.380(4)
C2-C6	1.342(4)	C17-C22	1.385(4)
C2-C3	1.529(4)	C18-C19	1.386(4)
C3-C7	1.531(4)	C19-C20	1.378(5)
C3-C4	1.560(4)	C20-C21	1.369(5)
C4-C8	1.496(4)	C21-C22	1.371(4)

Table 3.17 Bond angles (°) for **(227)**.

C8-O2-C9	117.1(3)	O1-C8-C4	126.0(2)
C2-N1-C11	126.9(2)	O2-C8-C4	110.4(2)
C2-N1-C5	112.1(2)	C12-C11-C16	118.2(3)
C11-N1-C5	119.9(2)	C12-C11-N1	122.3(2)
C17-N10-C3	123.6(2)	C16-C11-N1	119.5(2)
C6-C2-N1	130.4(3)	C13-C12-C11	120.4(3)
C6-C2-C3	122.1(2)	C14-C13-C12	121.1(3)
N1-C2-C3	107.3(2)	C15-C14-C13	118.9(3)
N10-C3-C2	113.7(2)	C14-C15-C16	120.9(3)
N10-C3-C7	106.7(2)	C15-C16-C11	120.6(3)
C2-C3-C7	107.4(2)	C18-C17-C22	118.3(3)
N10-C3-C4	114.5(2)	C18-C17-N10	123.1(2)
C2-C3-C4	102.9(2)	C22-C17-N10	118.5(3)
C7-C3-C4	111.5(2)	C17-C18-C19	119.8(3)
C8-C4-C5	114.1(2)	C20-C19-C18	121.3(4)
C8-C4-C3	112.6(2)	C21-C20-C19	118.7(3)
C5-C4-C3	103.3(2)	C22-C21-C20	120.4(3)
N1-C5-C4	103.7(2)	C21-C22-C17	121.4(3)
O1-C8-O2	123.5(3)		

3.4d.5) Formation of 3a,8b-dimethyl-3-methoxycarbonyl-1-phenyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,2-b]indole ***(182a)***.

This product was isolated in low yield from reaction 3.4d.4, on flash chromatography of the reaction mixture. The solvent was removed under reduced pressure and the residue recrystallised from 1:1 diethyl ether / *n*-hexane to yield clear white crystals of **(182a)**, m.p. 114-116°C.

(182a) was formed in higher yields on allowing 100mg (0.31 mmol) **(227)** to stir in sunlight for 48 hours in 50cm^3 dry CH_2Cl_2 solution. The solvent was evaporated and the product recrystallised from 1:1 diethyl ether / *n*-hexane to yield 78mg (78%) of

clear white crystals, m p 114-116°C. This reaction was also carried out in an nmr tube, with $CDCl_3$ as solvent in nearly quantitative.

CHN Analysis (found / theory) (%): M.w.: 322.41; $C_{20}H_{22}N_2O_2$; C (74.04 / 74.51), H (6.88 / 6.88), N (8.81 / 8.69).

IR (KBr) (cm^{-1}): 3359 (NH), 1738 (ester C=O), 755, 696, 674, 658, 609.

δH ($CDCl_3$) (ppm): 1.23, 1.58 (3a-C-CH_3, 8b-C-CH_3), 3.29 (1H, dd), 3.46 (1H, dd), 3.79 (1H, dd) (*Jam* = 18.70, *Jax* = 9.85, *Jmx* = 7.88 Hz), (C-2-H_2, C-3-H) 3.80 (3H, s) (ester CH_3), 6.69 (1H, d), 6.75 (1H, t), 6.79 (1H, t), 7.05 (2H, d), 7.10 (1H, t), 7.27 (2H, t), 7.51 (1H, d) (phenyl H).

δC ($CDCl_3$) (ppm): 16.36 (CH_3), 20.43 (CH_3), 48.98 (C-3), 49.87 (ester CH_3), 51.93 (C-2), 74.21, 74.74 (C-3a, C-8b), 111.04, 115.23, 119.68, 122.79, 125.27, 128.58, 128.81 (all phenyl CH), 135.09 (C-8a), 145.62 (4-N-Ph, C-1'), 146.76 (C-4a), 172.22 (ester C=O).

3.4d.6) *Photochemical formation of 6-endo-cyano-3a,6a-dimethyl-2,4-diphenyl-3,3a,4,5,6,6a-hexahydropyrrolo[2,3-d]-1,2,3-triazole (76).*

(76) was isolated in low yield from the reaction mixtue produced in 3.4d.3. by flash column chromatography as described, having a longer elution time than the starting material **(70c)**. On removal of solvent under reduced pressure the residue was recrystallised from ethanol to yield yellow crystals of **(76)**. M.p: 174-176°C

Characterization was carried out by comparison of ir and nmr spectra obtained for the product isolated on acid catalysed epimerization of **(70c)**. For spectroscopic detail see 1.4a.4.

3.4e) Photochemical Transformations of Substituted 3a,6a-dimethyl-tetrahydropyrrolo[2,3-*d*]-1,2,3-triazoles.

3.4e.1) *Photochemical transformation of 3a,6a-dimethyl-5,6-bis(methoxycarbonyl)-2,4-diphenyl-3,3a,4,6a-tetrahydropyrrolo[2,3-d]-1,2,3-triazole* ***(69a)***.

A solution of 0.5g (1.59 mmol) of **(69a)** in 300cm^3 acetonitrile was placed in an immersion well and degassed for 15 minutes with gaseous nitrogen. The solution was then irradiated, with stirring, for 24 hours. The acetonitrile was removed under vacuum and the residue passed through a flash chromatography column, packed with silica gel (0.032-0.063 mm mesh size), using a Charles Austin air pump. Two products were isolated from the reaction mixture after columning. The major product was *2,3-dimethyl-4,5-bis(methoxycarbonyl)-1-phenyl pyrrole* ***(239a)***, which was isolated in 62% (282mg) yield, m.p. 91-93°C.

CHN Analysis (found / theory) (%): M.w.: 287.32, $C_{16}H_{17}NO_4$; C (67.08 / 66.89), H (6.05 / 5.96), N (4.60 / 4.88).

IR (KBr) (cm^{-1}): 1728, 1706 (ester C=O), 786, 775, 744, 723, 699, 622.

δH ($CDCl_3$) (ppm): 1.90 (3H, s) (CH_3), 2.11 (3H, s) (CH_3), 3.59 (3H, s) (ester CH_3), 3.85 (3H, s) (ester C=O), 7.16 (2H, s), 7.42 (3H, s) (both phenyl H).

δC ($CDCl_3$) (ppm): 10.17 (CH_3), 10.77 (CH_3), 51.91 (ester CH_3), 52.12 (ester CH_3), 116.64 (C-3), 121.14 (C-2), 123.17 (C-4), 127.91, 128.83, 129.22 (all phenyl H), 132.58 (C-5), 138.59 (1-N-Ph, C-1'), 161.25 (ester C=O), 166.85 (ester C=O).

M.S. (fragments, amu): 287, 255, 226, 197, 169, 154, 118, 77, 65, 51.

The other photoproduct isolated in 30 % yield was azobenzene **(250)** and was characterised by comparison with reference spectra [159], and also by analysis of the ^{1}H and ^{13}C nmr spectra.

IR (KBr) (cm^{-1}): 770, 868 (monosubstituted phenyl)

δH (CD_3CN) (ppm): 7.58 (3H, m), 7.92 (2H, d) (both monosubstituted phenyl H).

δC (CD_3CN) (ppm): 122.36 (C-3'), 129.31 (C-2'), 131.38 (C-4'), 151.74 (C-1').

(Lit. ($CDCl_3$): 122.7, 128.8, 130.7, 152.5 ppm).

3.4e.2) Photofragmentation of 3a,6a-dimethyl-6-methoxycarbonyl-2-4-diphenyl-2,3a,4,6a-tetrahydropyrrolo[2,3-d]-1,2,3-triazole (69b).

A solution of 0.5g (1.94 mmol) of **(69b)** in 300ml acetonitrile was placed in an immersion well and degassed for 15 mins. with gaseous nitrogen. The solution was then irradiated, with stirring, for 24 hours. The acetonitrile was removed under vacuum and the residue passed through a flash chromatography column, packed with silica gel (0.032-0.063 mm mesh size), using a Charles Austin air pump. After columning the main product isolated was *2,3-dimethyl-4-methoxycarbonyl-1-phenylpyrrole (239b)*. Azobenzene **(250)** was also isolated.

Yield: 289mg (65%), m.p.: 75-77°C.

CHN Analysis (found / theory) (%): M.w.: 229.28; $C_{14}H_{15}NO_2$; C (73.49 / 73.34), H (6.62 / 6.59), N (6.01 / 6.11).

IR (KBr) (cm^{-1}): 1714 (ester C=O), 776, 753, 697.

δH ($CDCl_3$) (ppm): 2.07 (3H, s) (CH_3), 2.28 (CH_3), 3.80 (3H, s) (ester CH_3), 7.26 (2H, d), 7.38 (1H, t), 7.45 (2H, t) (all monosubstituted phenyl H), 7.35 (1H, s) (pyrrole C-4 aromatic H).

δC ($CDCl_3$) (ppm): 10.33 (CH_3), 10.60 (CH_3), 50.64 (ester CH_3), 114.27 (C-3), 117.69 (C-2), 125.79, 127.64, 129.18 (all phenyl CH), 126.16 (C-5), 126.98 (C-4), 139.46 (1-N-Ph, C-1'), 165.85 (ester C=O).

3.4e.3) Photofragmentation of 3a,6a-dimethyl-5,6-bis(methoxycarbonyl)-2,4-bis(4'-nitrophenyl)3,3a,4,6a-tetrahydropyrrolo[2,3-d]-1,2,3-triazole (69c).

A solution of 0.5g (1.38mmol) of **(69c)** in 300ml acetonitrile was placed in an immersion well and degassed for 15 mins. with gaseous nitrogen. The solution was then irradiated, with stirring, for 24 hours. The acetonitrile was removed under vacuum and the residue passed through a flash chromatography column, packed with silica gel (0.032-0.063 mm mesh size), using a Charles Austin air pump. The main photoproduct isolated was *2,3-dimethyl-4,5-bis(methoxycarbonyl)-1-(4'-nitrophenyl)-pyrrole (239c)* in 52% yield (240mg), m.p.103-105°C.

CHN Analysis (found / theory) (%): M.w.: 332.31; $C_{16}H_{16}N_2O_6$; C (57.97 / 57.83), H (4.79 / 4.85), N (8.60 / 8.43).

IR (KBr) (cm^{-1}): 1706 (ester C=O), 1522, 1350 (NO_2), 801, 733.

δH ($CDCl_3$) (ppm): 1.89 (3H, s) (CH_3), 2.09 (3H, s) (CH_3), 3.56 (3H, s) (ester CH_3), 3.83 (3H, s) (ester CH_3), 7.40 (2H, d), 8.39 (2H, d).

δC ($CDCl_3$) (ppm): 9.69 (CH_3), 10.58 (CH_3), 51.76 (ester CH_3), 52.09 (ester CH_3), 117.27 (C-3), 121.73 (C-2), 122.99 (C-4), 124.37, 128.85 (both phenyl CH), 132.50 (C-5), 144.03 (1-N-Ph, C-1'), 147.45 (1-N-Ph, C-4'), 160.39 (ester C=O), 166.34 (ester C=O).

References

1. L.I.Smith, *Chem.Rev.*, 1938, **23**, 193.
2. E.Buchner, *Berichte*, 1890, **23**, 701.
3. A.Michael, *J.Prakt.Chem.*, 1893, **48** (2), 94.
4. R.Huisgen, *Naturwiss.Rundschau*, 1961, **14**, 63.
5. R.Huisgen, *Proc.Chem.Soc.*, 1961, 357.
6. R.Huisgen, *Angew.Chem, Int.Ed. Engl.*, 1963, **2** (11), 565 and 633.
7. R.Huisgen, *J.Org.Chem.*, 1976, **41**, 403.
8. R.Huisgen, '*1,3-Dipolar Cycloadditions-Introduction, Survey and Mechanism,*' in "*1,3-Dipolar Cycloaddition Chemistry, Vol.1,*" Ed. A.Padwa, Wiley Interscience, New York, 1984.
9. T.L.Gilchrist and R.C.Storr, "*Organic Reactions and Orbital Symmetry,*" Cambridge University Press, Cambridge, 1979.
10. R.A.Firestone, *J.Org.Chem.*, 1968, **33**, 2285.
11. R.Huisgen, *J.Org.Chem.*, 1968, **33**, 2291.
12. R.B.Woodward, R.Hoffmann, *Angew.Chem.Int.Ed.Engl.*, 1969, **8**,781.
13. I.Fleming, "*Frontier Orbitals and Organic Chemical Reactions*", Wiley Interscience, Chichester, 1990.
14. K.N.Houk, J.Sims, R.E.Duke, R.W.Strozier, J.K.George, *J.Am.Chem.Soc.*, 1973, **95**, 7287.
15. K.N.Houk, J.Sims, C.R.Watts, L.J Luskus, *J.Am.Chem.Soc.*, 1973, **95**, 7301
16. R.Sustmann, *Tet.Lett.*, 1971, 2717.
17. R.Sustmann, H.Trill, *Angew.Chem.Int.Ed.Engl.*, 1972, **11**, 838.
18. R.Sustmann, *Pure.Appl.Chem.*, 1974, **40**, 569.
19. I.Bhatnagar, M.V.George, *J.Org.Chem.*, 1967, **32**, 2252.
20. R.N.Butler, J.P.James, *J.Chem.Soc.,Chem.Commun.*,1983, 627.
21. R.N.Butler, A.M.Gillan, S.Collier, J.P.James, *J.Chem.Research (S)*, 1987, 332.
22. R.N.Butler and D.F.O'Shea, *Heterocycles*, 1994, **37**, 571
23. C.S.Angadiyavar, K.B.Sukumaran and M.V.George, *Tet.Lett.*, 1971, 633.
24. K.B.Sukumaran, C.S.Angadiyavar, M.V.George, *Tetrahedron*, 1972, **28**, 3987.
25. K.B.Sukumaran, S.Satish, M.V George, *Tetrahedron*, 1974, **30**, 445.

26. R.N.Butler, D.Cunningham, J.P.James, P.McArdle, *J.Chem.Soc., Chem.Commun.*, 1983, 762.
27. R.N.Butler, A.M.Evans, A.M.Gillan, J.P.James, E.M.McNeela, D.Cunningham, P.McArdle, *J.Chem.Soc.,Perkin Trans.1*,1990, 2537.
28. R.N.Butler, F.A.Lysaght and L.A.Burke, *J.Chem.Soc., Perkin Trans. 2*, 1992, 1103.
29. R.N.Butler, F.A.Lysaght, D.Cunningham, P.McArdle, C.S.Pyne, *Chem. and Ind.London*, 1991, **15**, 549.
30. R.N.Butler, A.M.Evans, P.McArdle, D.Cunningham, *J.Chem.Soc., Chem.Commun.*, 1987, 1090.
31. R.N.Butler, A,M.Evans, E.McNeela, G.A.O'Halloran, P.D.O'Shea, D.Cunningham, P.McArdle, *J.Chem.Soc., Perkin Trans.1*, 1990, 2527.
32. R.N.Butler, D.F.O'Shea, *J.Chem.Soc., Perkin Trans.1*, 1994, 2797.
33. R.N.Butler, D.Cunningham, P.McArdle, and G.A.O'Halloran, *J.Chem.Soc., Chem.Commun.*, 1988, 232.
34. R.N.Butler, P.D.O'Shea, D.Cunningham, P.McArdle, *J.Chem.Soc., Perkin Trans.1*, 1989, 371.
35. R.N.Butler, D.F.O'Shea, *J.Chem.Research (S)*, 1994, 350.
36. R.N.Butler, D.M.Colleran, *J.Chem.Soc., Perkin Trans.1.*, 1992, 2159.
37. "*Vogel's Textbook of Practical Organic Chemistry*", 5th Ed., B P.Furniss, A.J.Hannaford, P.W.G.Smith, A.R.Tatchell, Longman Scientific and Technical, U.K., 1989.
38. J.P.Kuebrich, R.L.Schowen, M-S.Wang, M.E.Lupes, *J.Am.Chem.Soc.*, 1971, **93**, 1214.
39. T.Laird, in "*Comprehensive Organic Chemistry*," Vol.1, 1979, p.1142 .
40. T.Mastsumoto, M.Ohishi, S.Inoue, *J.Org.Chem.*, 1985, **50**, 603.
41. H.Stetter, H.Kuhlmann, *Org.Synth.VII*, 1990, 95.
42. H.Stetter, G.Dambkes, *Synthesis*, 1977, 403.
43. M.D.Rozwadowska, *Tetrahedron*, 1985, **41**, 3135.
44. J.P James PhD. Thesis, U.C.G, 1983.45

45. H.Ingle, H.H.Mann, *J.Chem.Soc.*, 1895, **67**, 606.

46. H.Blitz, R.Weiss, *Ber.*, 1902, 3519.

47. C.S.Angadiyavar and M.V.George, *J.Org.Chem.*, 1971, **36**, 1589.

48. C.Winter, *Tet. Lett.*, 1970, 2275.

49. B.Robinson, *Chem.Rev.*, 1963, **63**, 373.

50. R.Robinson, G.M.Robinson, *J.Chem.Soc.*, 1918, **113**, 639.

51. R.N.Butler, A.M.Gillan, J.P.James, A.M.Evans, *J.Chem.Soc., Perkin Trans.1*, 989, 159.

52. C.A.Ramsden, *Tetrahedron*, 1977, **33**, 3203.

53. R.Grashey, *'Azomethine Imines'* in *"1,3-Dipolar Cycloaddition Chemistry Vol.1"*, A.Padwa, Ed., Wiley-Interscience, New York, 1984.

54. L.M.Jackman, S.Sternell, in *"Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,"* 2nd Ed., Permagon PressLtd., England, 1978, pp.234.

55. F.Hibbert *'Acidity and Proton Transfer of Cyanocarbon Acids'*, in *"The Chemistry of Triple Bonded Functional Groups"*, Ed. S.Patai, Z.Rapoport, Wiley-Interscience, New York, 1983, pp 699-736.

56. L.M.Ephstein, A.V.Iogansen, *Russ.Chem.Rev.*, 1990, **59**, 134.

57. J.T.Edward, *J.Chem.Education*,1982, **59**, 354.

58. L.M.Schwartz, *J.Chem.Education*, 1981, **58**, 778.

59 H.Baron, F.G.P.Remfry, J.F.Thorpe, *J.Chem.Soc.*, 1904, **85**, 1726.

60. E.L.Eliel, S.H.Wilen, *'Stereochemistry of.Organic Compounds,'* Wiley Interscience, New York, 1994.

61. A.K.Mills, A.E.Wilder, *Helv.Chim.Acta*, 1960, **234**, 1915.

62. R.D.Gutherie, E.C.Nicholas, *J.Am.Chem.Soc.*, 1981, **103**, 4637.

63 D.J.Cram, L.Gossar, *J.Am.Chem.Soc.*, 1964, **86**, 5457.

64. A.V.Spassov, *Bulgaraska Akad.Nauk., Odtel.Geol.Geograf.Khim.Nuak. Izvest Khim.Inst.*, 1951, **1**, 217 and 245. A.V.Spassov, D.Elenkovard and St.Robev, *Bulgaraska Akad.Nauk., Odtel.Geol.Geograf.Khim.Nuak.Izvest Khim.Inst.*, 1951, **1**, 229 (*Chem.Abstr.*, 1953, **47**, 2153e).

65. R.B.Woodward and C.Winter, *Tet.Lett.*, 1969, 2697.

66. J.P.Chesick, *Acta Cryst.*, 1973, **B29**, 2309.

67. R.N.Butler, D.M.Colleran, F.A.Lysaght, D.F.O'Shea, *J.Chem.Res. (S)*, 1993, 78.

68. M.Karplus, *J.Chem.Phys.*, 1959, **30**, 11.

69. K.Saoi, A.Okawa, *J.Org.Chem*, 1986, **51**, 4000.

70. A.Arase, M.Hoshi, T.Yamaki, H.Nakanishi., *J.Chem.Soc., Chem.Commun.*, 1994, 855.

71. H.C.Brown, H.M.Hess, *J.Org.Chem.*, 1969, **34**, 2206.

72. H.O.House, "*Modern Synthetic Reactions,*" 2nd Ed. R.Breslow, Benjamin / Cummings, Massachusetts, U.S.A, 1972.

73. D.J.Cram, F.A.A.Elhafez, *J.Am.Chem.Soc.*, 1952, **74**, 5828.

74. R.N.Butler, D.Cunningham, E.G.Marren, P.McArdle, *J.Chem.Soc, Chem.Commun.*, 1987, 706

75. R.N.Butler, D.Cunningham, E.G.Marren, P.McArdle, *J.Chem.Soc., Perkin Trans.1*, 1990, 3321.

76. F.A.Carey, R.J.Sundberg, *"Advanced Organic Chemistry, Part 1 Structure and Mechanism,"* 3rd Ed., Plenum Press, New York, 1990.

77. F.R.Benson, "*The High Nitrogen Compounds*," Wiley, New York, 1984.

78. A.Ohsawa, H.Arai, H.Ohnishi, H.Igeta, *J.Chem.Soc., Chem.Commun.*, 1981, 1174.

79. H.Neuhoeffer, H.-D.Vötter, H.Ohl, C.Kruger, K.Angermund, *Liebigs Ann. Chem.*, 1985, 1732.

80. E.A.Chandross, G.Smolinsky, Tet.Lett., 1960, 19.

81. S.Bradbury, M.Keating, C.W.Rees, R.C.Storr, *J.Chem.Soc., Chem.Commun.*, 1971, 827

82. B.Adger, S.Bradbury, M.Keating, C.W.Rees, R.C.Storr, M.T.Williams, *J.Chem.Soc., Perkin Trans.1*, 1975, 31.

83. H.Neuhoffer in "*Comprehensive Heterocyclic Chemistry*," vol. eds. A.J.Boulton, A.McKillop, series eds. A.R.Katritsky, C.W.Rees, Permagon Press, Oxford, 1984, Vol 3, pp. 369-384

84. G.M.Sheldrick, SHELXS 86, Program for Crystal Structure Solution, University of Göttingham, 1986.

85. G.M.Sheldrick, SHELXL 93, Program for Crystal Structure Determination, University of Cambridge, 1992.

86. A.Gilbert, J.Baggott, "*Essentials of Molecular Photochemistry*," Blackwell Scientific Publications, Oxford, 1991.

87. J.A.Barltrop, J.D.Coyle, "*Principles of Photochemistry*," Wiley-Interscience, Chichester, 1978.

88. O.Buchardt, "*The Photochemistry of Heterocyclic Compounds*," Wiley-Interscience, New York, 1976.

89. J.March, "*Advanced Organic Chemistry, Reactions, Mechanisms and Structures*," 4th Ed., Wiley-Interscience, New York, 1992.

90. A.Albini, M.Alpegiani, *Chem.Rev.*, 1984, **84**, 43.

91. G.G.Spence, E.C.Taylor, O.Buchardt, *Chem.Rev.*, 1970, **70**, 231.

92. J.Streith, *Pure Appl.Chem.*, 1977, **49**, 309.

93. R.C.Storr, '*Azimines, Azoxy Compounds, and Nitro Compounds*' in "*1,3-Dipolar Cycloaddition Chemistry, Vol. 2*," Ed. A.Padwa, Wiley Interscience, New York, 1984.

94. K.Burger, O.Dengler, A.Gieren, V.Lamm, *Chem.-Ztg.*, 1982, **106**, 408.

95. C.Leuenberger, L Hoesch, A.S.Drieding, *J.Chem.Soc.Chem.Commun.*, 1980, 1197.

96. L.Hoesch, C.Leuenberger, H.Hilpert, A.S.Drieding, *Helv.Chim.Acta*, 1982, **65**, 2682.

97. L.Hoesch, C.Leuenberger, A.S.Drieding, *Helv.Chim.Acta*, 1985, **68**, 1691.

98. G.Kaupp, O.Dengler, K.Burger, S.Rottegger, *Angew.Chem.Int.Ed.Engl.*, 1985, **24**, 341.

99. G.Kaupp, J.A.Döhle, *Angew.Chem.Int.Ed.Engl.*, 1986, **25**, 828.

100. P.J.Garrett in "*Aromaticity*," Wiley-Interscience, New York, 1986.

101. J.Elguero in "*Comprehensive Heterocyclic Chemistry*" series eds. A.R.Katritsky and C.W.Rees, pp 167-303, *cf.* p.272.

102. S.Ehrenberg, R.Gompper, K.Polborn, H.Wagner, *Angew.Chem.Int.Ed.Engl.*, 1991, **30,** 344

103. R.Pfleger, E.Garthe, K.Rauer, *Chem.Ber.*, 1963, 1827

104. R.Metze, *Angew.Chem.*, 1956, 580

105. R.A.Carboni, J.C.Kauer, J.E.Castle, H.E.Simmons, *J.Am.Chem.Soc.*, 1967, **89**, 2618.

106. T.S.Pivina, M.S.Molchanova, V.A.Shlyapochnikov, D.V.Sukhacev, H.Xiao, L.D.Lu, X.D.Gong, Proc.Int.Pyrotech.Semin. 1992, 18th, 685. (*Chem. Abstr.*, 1993, **119**, 11597b)

107. A.Hasanaoui, J.P.Lavergne, P.Viallefont, *Recl.Trav.Chim.Pays Bas.*, 1978, **97** (78), 204

108. W.E.Hahn, H.Zawadzka, *Rocniki Chem.*, 1964, **38** (4), 557. (*Chem.Abstr.*, 1964, **61**, 10686a).

109. R.N.Butler, D.M.Colleran, D.F.O'Shea, D.Cunningham, P.McArdle, A.M.Gillan, *J.Chem.Soc., Perkin Trans.1*, 1993, 2757

110. F.Ishii, JP 02 195 34 1990. (*Chem.Abstr.*, 1991, **114**, 153878q)

111. F.Ishii, JP 02 195 348 1990. (*Chem.Abstr.*, 1991, **115**, 102716y)

112. C.B.Vincentini, A.C.Veronese, M.Guarneri, Eur.Pat.Appl.EP., 190 457, 1986. (*Chem.Abstr.*, 1986, **105**, 226578t)

113. T.Sato, T.Kawagishi, JP 0 125 765, 1989. (*Chem.Abstr.*, 1989, **111**, 57732e)

114. A.Dornow, E.Hinz, *Chem.Ber.*, 1958, **91**, 1834

115. M.Lange, R.Quell, H.Lettau, H.Schubert, *Z.Chem.*, 1977, **17**, 94

116. I.I.Grandberg, G.V.Klyuchko, *Zh.Obshch.Khim.*, 1962, **32**, 1898 (*Chem.Abstr.*, 1963, **58**, 4537f)

117. V.Sudarsanam, K.Nagarajan, K.Rama Rao, S.J.Shenoy, *Tet.Lett.*, 1980, **21**, 4757

118. K.Nagarajan, V.Sundarsanam, S.J.Shenoy, K.Rama Rao, *Indian.J.Chem., Sect.B*, 1982, **21B**, 997.

119. C.B.Vincentini, A.C.Veronese, P.Giori, M.Guarneri, *Tet.Lett.*, 1988, 6171

120. C.B.Vincentini, A.C.Veronese, P.Giori, B.Lumachi, M.Guarneri, *Tetrahedron*, 1990, **46**, 5777

121. E.B.Gluz, K.E. Kletsky, R.M.Minayev, *Revue Roumanie De Chimie*, 1991, **36**, 333.

122. Y.T.Chia, H.E.Simmons, *J.Am.Chem.Soc.*, 1967, **89**, 2638

123. J.Elguero, R.M.Claramunt, A.J.Summers, *Adv.Heterocycl.Chem.*, 1978, **22**, 183.

124. R.D.Chambers, J.A.H.MacBride, J.R.Malakiewicz, K.C.Srivastava, *J.Chem.Soc., Perkin Trans.1*, 1975, 396

125. R.D.Chambers, J.R.Maslakiewicz and K.C.Srivastava, *J.Chem.Soc., Perkin Trans.1*, 1975, 1130.

126. C.Byrne, S.Draper, J.P.James, C.Long, *J.Chem.Res., (S)*, 1995, 438, *J.Chem.Res., (M)*, 2501.

127. E.N.Step, A.L.Buchachenko, N.J.Turro, *J.Org.Chem.*, 1992, **57**, 7018.

128. N.C.Yang, R.H.-K.Chen, *J.Am.Chem.Soc.*, 1971, **93**, 530

129. C.W.Spangler, *Chem.Rev.*, 1976, **76**, 187-217.

130. P.J.Kropp, H.G.Fravel Jr., T.R.Fields, *J.Am.Chem.Soc.*, 1976, **98**, 840.

131. P.K.Martin, H.R.Matthews, H.Rapaport, G.Thyagarajan, *J.Org.Chem.*, 1968, **33**, 3758.

132. F.Texier, R.Carrié, *Bull.Soc.Chim.Fr.*, 1971, 3642.

133. W.W.Paudler, A.G.Zeiler, *J.Org.Chem.*, 1969, **34**, 2138

134. E.Aiello, G.Datallo, G.Cirrincione, *J.Chem.Soc., Perkin Trans.1*, 1981, 1.

135. E.Aiello, G.Datollo, G.Cirrincione, A.M.Almerico, *J.Heterocycl.Chem.*, 1984, **21(3)**, 721.

136. A.N.Grinev, S.Y.Ryabova, *Khim., Geterotsikl.Soedin.* 1982, **(2)** 201. (*Chem.Abstr.*, 1982, **96**, 181173j).

137. M.P.Servé, W.A.Feld, P.G.Seybold, R.N.Steppel, *J.Heterocyclic Chem.*, 1975, **12**, 811.

138. J.Van Thielen, T.Van Thien, F.C.De Schryver, *Tet.Lett.*, 1977, 3031.

139. A.Albini, G.F.Bettinetti, G.Minoli, S.Pietra, *J.Chem.Soc., Perkin Trans. 1*, 1980, 2904.

140. P.Scheiner, *J.Am.Chem.Soc.*, 1968, **90**, 988.

141. P.Scheiner, *J.Org.Chem.*, 1965, **30**, 7.

142. P.Scheiner, *Tetrahedron*, 1968, **24**, 2757.

143. P.Scheiner, *J.Am.Chem.Soc.*, 1966, **88**, 4759.

144. P.A.Wender, C.B.Cooper, *Tet.Lett.*, 1987, 6125

145. J.J.Kulagowski, C.J.Moody, C.W.Rees, *J.Chem.Soc., Chem.Commun.*, 1982, 548.

146. J.J.Kulagowski, C.J.Moody, C.W.Rees, *J.Chem.Soc., Perkin Trans.1*, 1985, 2725.

147. J.J.Kulagowski, C.J.Moody, C.W.Rees, *J.Chem.Soc., Perkin Trans.1*, 1985, 2733.

148. G.Mitchell, C.W.Rees, *J.Chem.Soc., Perkin Trans.1*, 1987, 403.

149. J.J.Kulagowski, G.Mitchell, C.J.Moody, C.W.Rees, *J.Chem.Soc., Chem.Commun.*, 1985, 651

150. J.J.Kulagowski, G.Mitchell, C.J.Moody, C.W.Rees, *J.Chem.Soc., Chem.Commun.*, 1985, 652.

151. L.Benati, P.C.Montavecchi, P.Spagnolo, E.Foresti, *J.Chem.Soc., Perkin.Trans.1*, 1992, 2845.

152. Pretsch, Clerc, Seibl, Simon, *"Tables of Spectral Data for Structure Determination of Organic Compounds,"* 2nd Ed., Springer-Verlag, 1989.

153. A.G.Schultz, S.O.Myong, *J.Org.Chem.*, 1983, **48**, 2432.

154. N.Kanomata, *Bull.Chem.Soc., Jpn.*, 1987, **60**, 683.

155. K.Hirakawa, T.Ito, Y.Okubo, S.Nakazawa, *J.Org.Chem.*, 1980, **45**, 1668.

156. J.E.Baldwin, *J.Chem.Soc., Chem.Commun.*, 1976, 734.

157. R.J.Sundberg, *'Pyrrole and their Benzo Derivatives (iii) Synthesis and Applications,'* in *"Comprehensive Heterocyclic Chemistry: Part 3,"* Ed. A.R.Katritsky and C.W.Rees, pp. 370-376.

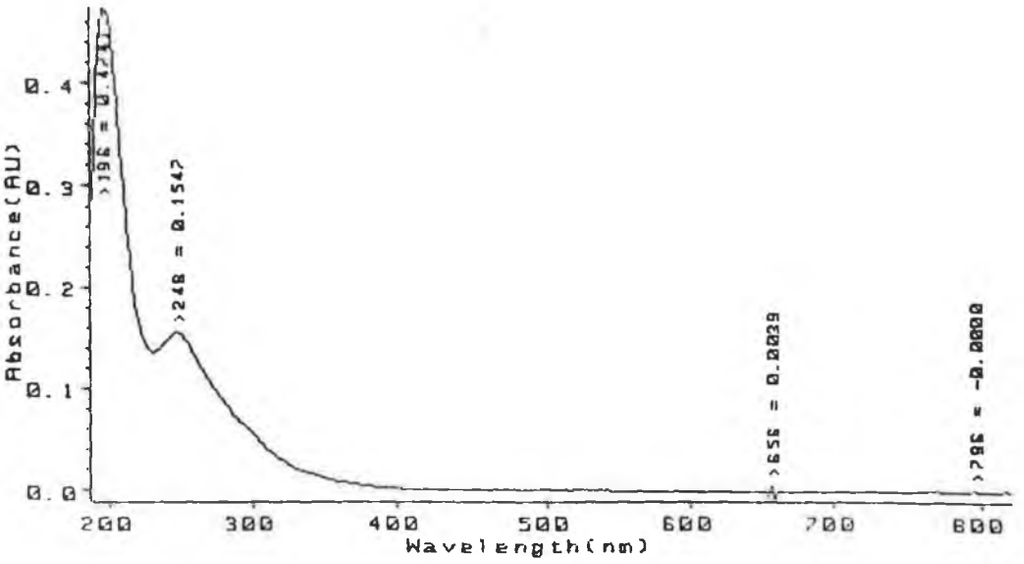
158. R.N.Butler, P.D.McDonald, P.McArdle, D.Cunningham, *J.Chem.Soc., Perkin Trans. 1*, 1994, 1053

159. C.J.Pouchert *"The Aldrich Library of Infra Red Spectra Data,"* 3rd Ed, Aldrich Chemical Co. Inc., Wisconsin, 1981.

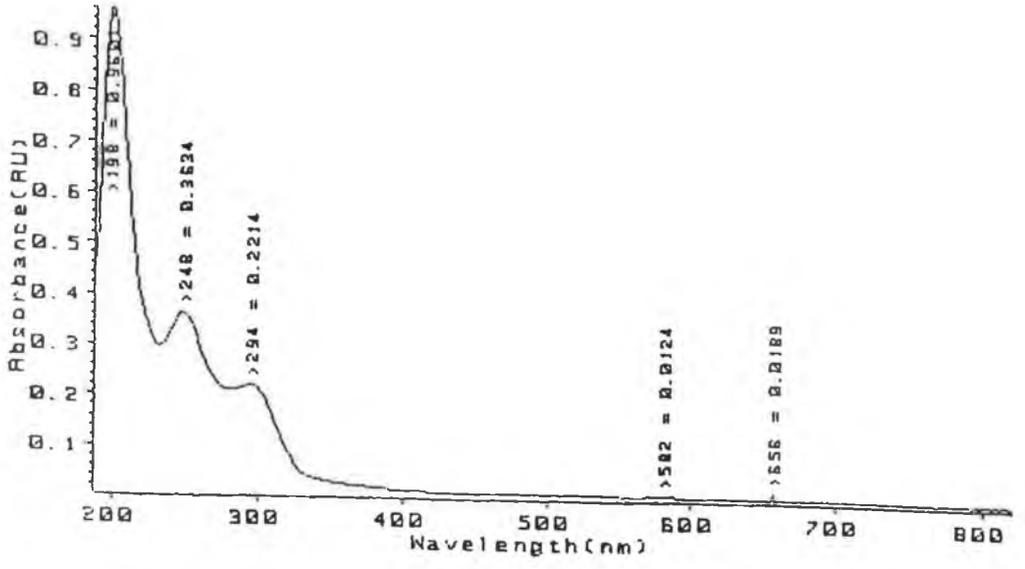
Appendix

Appendix A: U.V Spectra of a) **(82a)**, and b) **(160)**.

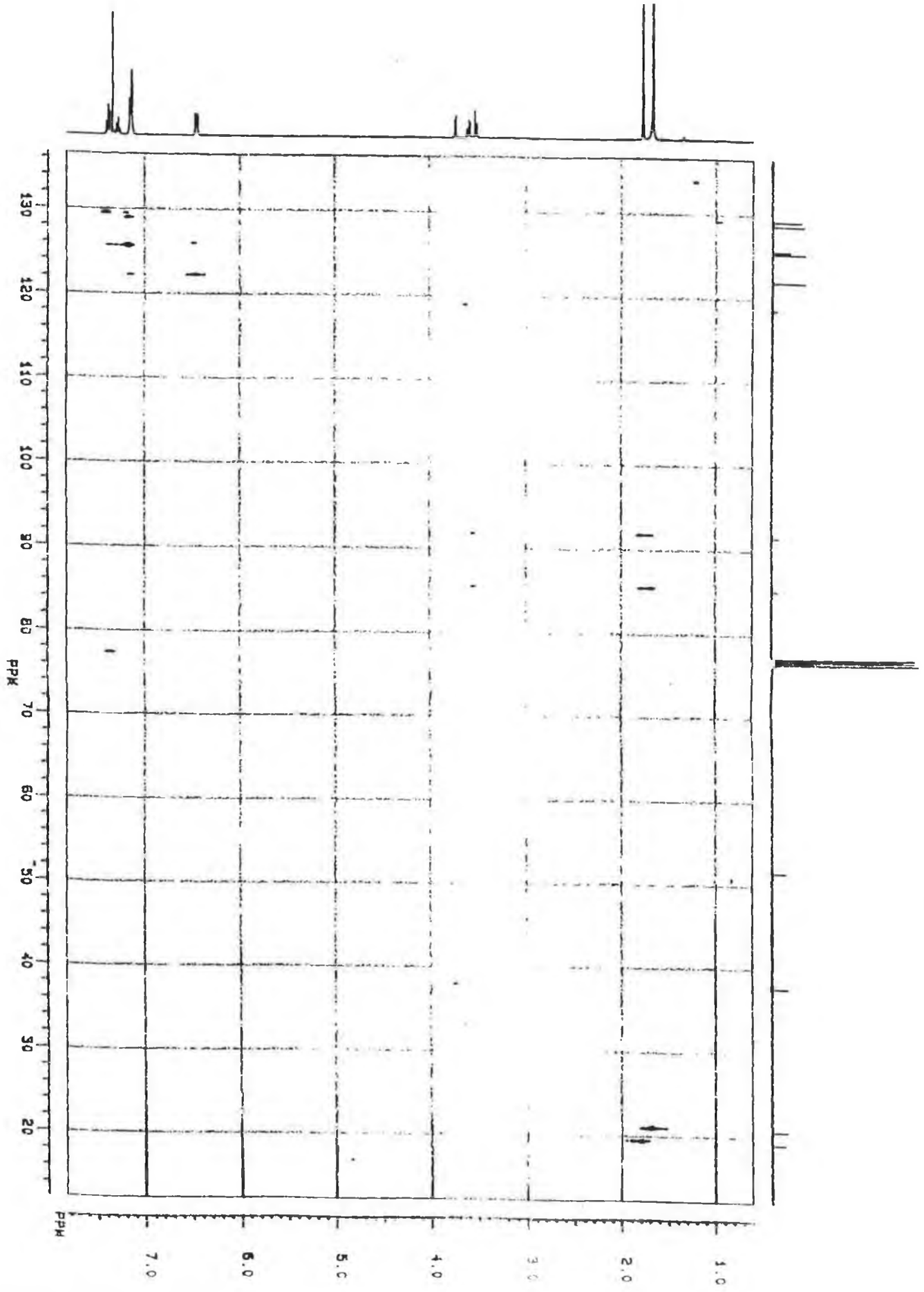
(a)



(b)



Appendix B: COLOC nmr spectrum of **(189c)**.



ɔendix C: Observed and Calculated Structure factors for **(106d)**.

h	k	l	10Fo	10Fc	10s
0	0	0	1787	1942	15
0	0	0	2998	3104	21
0	0	0	711	704	6
0	0	0	685	669	6
0	0	0	77	113	31
0	0	0	412	421	8
0	0	0	936	947	8
0	0	0	235	230	14
0	0	0	168	148	21
0	0	0	277	278	15
0	0	0	91	55	49
0	0	0	161	176	26
0	0	0	573	705	5
0	0	0	617	610	6
0	0	0	1999	1984	20
0	0	0	315	337	7
0	0	0	396	361	7
0	0	0	688	705	7
0	0	0	201	177	14
0	0	0	416	396	10
0	0	0	235	225	15
0	0	0	94	131	45
0	0	0	169	174	22
0	0	0	51	26	51
0	0	0	2349	2464	20
0	0	0	318	321	5
0	0	0	0	22	1
0	0	0	1449	1505	14
0	0	0	1535	1551	15
0	0	0	174	182	13
0	0	0	759	779	7
0	0	0	125	119	22
0	0	0	113	144	33
0	0	0	209	196	17
0	0	0	106	58	34
0	0	0	148	141	28
0	0	0	615	587	5
0	0	0	1240	1217	12
0	0	0	553	537	6
0	0	0	0	1	1
0	0	0	416	371	8
0	0	0	166	142	16
0	0	0	246	253	13
0	0	0	76	53	75
0	0	0	71	58	70
0	0	0	68	58	68
0	0	0	186	203	22
0	0	0	0	50	1
0	0	0	181	186	11
0	0	0	553	540	6
0	0	0	391	388	7
0	0	0	1202	1211	11
0	0	0	711	698	7
0	0	0	174	180	14
0	0	0	317	336	11
0	0	0	140	153	23
0	0	0	0	33	1
0	0	0	224	187	16
0	0	0	187	164	20
0	0	0	324	296	15
0	0	0	47	10	47
0	0	0	558	570	7
0	0	0	70	71	37
0	0	0	573	556	7
0	0	0	416	442	9
0	0	0	254	260	13
0	0	0	102	89	34
0	0	0	232	234	15
0	0	0	196	201	18
0	0	0	128	119	31
0	0	0	69	3	69
0	0	0	1776	1772	17
0	0	0	503	489	8
0	0	0	335	333	9
0	0	0	0	36	1
0	0	0	154	151	19
0	0	0	195	182	16
0	0	0	153	174	22
0	0	0	333	293	12
0	0	0	0	24	1
0	0	0	52	79	52
0	0	0	160	153	25
0	0	0	692	672	8
0	0	0	0	21	1
0	0	0	810	810	8
0	0	0	265	282	13
0	0	0	251	235	14
0	0	0	62	53	61
0	0	0	94	19	42
0	0	0	0	38	1
17	7	0	165	138	22
19	7	0	78	45	78
0	8	0	532	524	9
2	8	0	733	732	9
4	8	0	647	649	9
6	8	0	249	266	14
8	8	0	522	538	10
10	8	0	0	38	1
12	8	0	149	138	22
14	8	0	0	10	1
16	8	0	143	153	25
18	8	0	0	72	1
1	9	0	658	659	9
3	9	0	100	108	39
5	9	0	288	284	13
7	9	0	96	110	38
9	9	0	373	377	12
11	9	0	0	12	1
13	9	0	170	159	21
15	9	0	71	123	71
17	9	0	0	21	1
0	10	0	559	554	10
2	10	0	41	42	40
4	10	0	130	77	26
6	10	0	72	93	72
8	10	0	217	200	17
10	10	0	193	200	21
12	10	0	170	169	23
14	10	0	47	55	47
1	11	0	207	232	19
3	11	0	239	244	16
5	11	0	231	252	18
7	11	0	96	109	45
9	11	0	183	196	22
11	11	0	141	74	27
13	11	0	178	143	25
0	12	0	221	240	19
2	12	0	61	57	61
4	12	0	88	69	55
6	12	0	36	71	36
8	12	0	121	114	36
1	13	0	128	114	34
-23	1	1	115	82	37
-21	1	1	0	4	1
-19	1	1	150	115	23
-17	1	1	319	330	13
-15	1	1	108	135	29
-13	1	1	359	352	9
-11	1	1	1073	1066	10
-9	1	1	1421	1405	13
-7	1	1	1103	1134	10
-5	1	1	1488	1480	14
-3	1	1	1232	1255	13
-1	1	1	778	879	8
1	1	1	1194	1123	11
3	1	1	810	858	8
5	1	1	1361	1281	13
7	1	1	1589	1591	16
9	1	1	465	436	7
11	1	1	666	709	7
13	1	1	68	108	67
15	1	1	368	365	11
17	1	1	226	230	16
19	1	1	486	494	11
21	1	1	105	68	35
23	1	1	94	54	46
-22	2	1	139	166	29
-20	2	1	103	81	37
-18	2	1	306	315	13
-16	2	1	200	186	17
-14	2	1	365	368	10
-12	2	1	944	942	7
-10	2	1	741	742	7
-8	2	1	533	527	6
-6	2	1	163	158	11
-4	2	1	879	898	9
-2	2	1	1291	1303	13
0	2	1	980	1056	10
2	2	1	2982	3029	22
4	2	1	3161	3246	25
6	2	1	1253	1302	12
8	2	1	1172	1157	11
10	2	1	379	353	8
12	2	1	141	105	17
14	2	1	340	332	11
16	2	1	367	360	11
18	2	1	0	3	1
20	2	1	93	44	44
22	2	1	116	57	35
-23	3	1	203	164	20
-21	3	1	233	258	18
-19	3	1	0	49	1
-17	3	1	339	285	11
-15	3	1	219	222	16
-13	3	1	515	514	9
-11	3	1	1062	1006	9
-9	3	1	362	397	8
-7	3	1	0	60	1
-5	3	1	83	26	24
-3	3	1	3321	3399	27
-1	3	1	322	313	7
1	3	1	319	324	7
3	3	1	361	358	6
5	3	1	340	340	7
7	3	1	81	40	25
9	3	1	420	414	8
11	3	1	830	821	7
13	3	1	172	175	16
15	3	1	221	220	16
17	3	1	647	632	10
19	3	1	74	22	73
21	3	1	304	296	15
23	3	1	83	23	82
-22	4	1	154	155	25
-20	4	1	89	134	61
-18	4	1	118	60	28
-16	4	1	74	7	74
-14	4	1	225	227	15
-12	4	1	748	765	8
-10	4	1	149	178	17
-8	4	1	463	465	8
-6	4	1	584	590	6
-4	4	1	505	481	6
-2	4	1	67	70	34
0	4	1	1181	1149	8
2	4	1	1009	1012	9
4	4	1	1168	1081	10
6	4	1	420	417	7
8	4	1	449	454	8
10	4	1	619	593	8
12	4	1	120	66	24
14	4	1	561	576	9
16	4	1	0	73	1
18	4	1	0	79	1
20	4	1	53	23	52
22	4	1	129	84	31
-21	5	1	138	106	29
-19	5	1	99	38	41
-17	5	1	156	172	23
-15	5	1	253	257	14
-13	5	1	349	342	11
-11	5	1	44	24	43
-9	5	1	828	818	7
-7	5	1	220	213	11
-5	5	1	284	255	9
-3	5	1	345	365	8
-1	5	1	2025	1992	21
1	5	1	294	270	8
3	5	1	528	548	7
5	5	1	255	247	10
7	5	1	0	30	1
9	5	1	234	216	12
11	5	1	75	70	51
13	5	1	409	417	11
15	5	1	209	214	17
17	5	1	269	256	14
19	5	1	63	9	62
21	5	1	98	84	40
-20	6	1	108	67	39
-18	6	1	228	244	18
-16	6	1	181	164	20
-14	6	1	102	65	35
-12	6	1	232	202	15
-10	6	1	571	583	9
-8	6	1	0	23	1
-6	6	1	0	15	1
-4	6	1	673	688	7
-2	6	1	283	257	9
0	6	1	428	423	5
2	6	1	113	92	20
4	6	1	1201	1199	11
6	6	1	482	494	8
8	6	1	403	407	9
10	6	1	195	175	15
12	6	1	159	162	22
14	6	1	87	61	49
16	6	1	84	43	52
18	6	1	0	79	1
20	6	1	116	105	35
-19	7	1	0	19	1
-17	7	1	87	4	52
-15	7	1	646	674	10
-13	7	1	450	457	11
-11	7	1	111	146	34
-9	7	1	269	270	14
-7	7	1	311	320	11
-5	7	1	68	7	67
-3	7	1	355	353	10
-1	7	1	0	6	1
1	7	1	123	148	23
3	7	1	301	302	11
5	7	1	194	185	15
7	7	1	644	616	9
9	7	1	113	120	31
11	7	1	729	706	9
13	7	1	101	103	38
15	7	1	570	574	11
17	7	1	0	42	1
19	7	1	42	103	41
-18	8	1	60	21	59
-16	8	1	92	78	48
-14	8	1	96	87	41
-12	8	1	117	124	30
-10	8	1	372	386	12
-8	8	1	339	360	13
-6	8	1	444	455	11
-4	8	1	537	529	9
-2	8	1	460	477	10
0	8	1	133	134	16
2	8	1	754	740	9
4	8	1	138	125	25
6	8	1	343	350	12
8	8	1	82	90	60
10	8	1	0	63	1
12	8	1	0	5	1
14	8	1	175	172	21
16	8	1	0	6	1
18	8	1	0	79	1
-17	9	1	169	172	26
-15	9	1	21	24	20
-13	9	1	126	104	31
-11	9	1	99	86	38
-9	9	1	248	216	14
-7	9	1	182	196	19
-5	9	1	438	420	11
-3	9	1	594	588	10
-1	9	1	198	190	18
1	9	1	346	343	12
3	9	1	447	434	11
5	9	1	716	700	9
7	9	1	524	510	10
9	9	1	74	47	73
11	9	1	236	194	15
13	9	1	0	65	1
15	9	1	0	13	1
17	9	1	149	148	27
-14	10	1	146	173	29
-12	10	1	133	141	30
-10	10	1	328	325	14
-8	10	1	267	275	15
-6	10	1	70	83	70
-4	10	1	26	90	26
-2	10	1	111	139	34
0	10	1	133	159	19
2	10	1	134	160	26
4	10	1	147	132	23
6	10	1	331	343	13
8	10	1	118	82	33
10	10	1	110	78	35
12	10	1	0	20	1
14	10	1	99	109	46
-13	11	1	94	16	47
-11	11	1	216	188	19
-9	11	1	211	185	19
-7	11	1	102	5	40
-5	11	1	0	28	1
-3	11	1	91	54	47
-1	11	1	425	441	12
1	11	1	0	23	1
3	11	1	229	239	17
5	11	1	86	42	62
7	11	1	309	301	15
9	11	1	92	115	58
11	11	1	84	64	75
-8	12	1	0	53	1
-6	12	1	0	5	1
-4	12	1	178	180	23
-2	12	1	107	149	40
0	12	1	34	16	33
2	12	1	147	95	24
4	12	1	77	46	77
6	12	1	246	236	17
8	12	1	305	299	16
-1	13	1	87	107	66
1	13	1	0	49	1
-24	0	2	122	91	35
-22	0	2	20	20	20
-20	0	2	252	226	15
-18	0	2	43	35	43
-16	0	2	156	141	20
-14	0	2	81	116	41
-12	0	2	370	349	9
-10	0	2	297	249	8
-8	0	2	274	262	8
-6	0	2	2922	3087	26
-4	0	2	2054	2101	22
-2	0	2	979	977	10
0	0	2	18	585	18
2	0	2	1124	1099	11
4	0	2	898	800	9
6	0	2	4177	4313	27
8	0	2	416	396	6
10	0	2	337	322	8
12	0	2	584	584	8
14	0	2	782	768	8
16	0	2	174	187	19
18	0	2	330	296	12
20	0	2	47	9	47
22	0	2	29	19	28
-23	1	2	59	73	59
-21	1	2	157	152	24
-19	1	2	198	189	18
-17	1	2	57	32	56
-15	1	2	317	295	11
-13	1	2	376	389	9
-11	1	2	588	602	7
-9	1	2	508	508	6
-7	1	2	956	950	8
-5	1	2	1130	1154	12
-3	1	2	947	975	9
-1	1	2	862	898	9
1	1	2	708	730	7
3	1	2	678	723	6
5	1	2	3451	3630	26
7	1	2	404	388	6
9	1	2	200	199	11
11	1	2	548	559	8
13	1	2	144	138	19
15	1	2	87	99	42
17	1	2	0	86	1
19	1	2	268	277	15
21	1	2	135	125	28
23	1	2	0	41	1
-24	2	2	158	153	27
-22	2	2	177	121	20
-20	2	2	0	22	1
-18	2	2	436	455	11
-16	2	2	179	166	19
-14	2	2	652	649	8
-12	2	2	683	686	8
-10	2	2	153	113	15
-8	2	2	280	286	8
-6	2	2	984	1029	9
-4	2	2	378	383	6
-2	2	2	775	723	8
0	2	2	691	658	7
2	2	2	1098	1088	11
4	2	2	773	823	7
6	2	2	491	466	6
8	2	2	236	208	9
10	2	2	1828	1867	18
12	2	2	381	395	9
14	2	2	106	147	31
16	2	2	292	299	13
18	2	2	91	61	42
20	2	2	155	136	23
22	2	2	172	138	21
-23	3	2	48	15	47
-21	3	2	104	114	41
-19	3	2	160	163	23
-17	3	2	290	299	14
-15	3	2	186	126	17
-13	3	2	371	379	10
-11	3	2	527	505	8
-9	3	2	120	115	19
-7	3	2	589	611	6
-5	3	2	340	342	7
-3	3	2	328	310	7
-1	3	2	446	463	6
1	3	2	2260	2185	21

l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
2	89	54	21	7	7	2	703	698	9	-7	1	3	1453	1520	14	-15	5	3	465	458	10	5	9	3	365	361	12
2	1058	1004	10	9	7	2	212	226	16	-5	1	3	333	363	6	-13	5	3	100	87	36	7	9	3	188	175	19
2	596	606	6	11	7	2	382	390	11	-3	1	3	1173	1231	12	-11	5	3	269	268	12	9	9	3	85	20	47
2	112	147	21	13	7	2	424	428	12	-1	1	3	185	161	6	-9	5	3	137	131	19	11	9	3	606	583	11
2	390	395	9	15	7	2	93	43	45	1	1	3	1137	1144	10	-7	5	3	605	630	7	13	9	3	89	64	54
2	179	161	16	17	7	2	0	63	1	3	1	3	1817	1870	19	-5	5	3	1219	1118	11	15	9	3	123	122	34
2	223	219	16	19	7	2	149	127	25	5	1	3	4567	4738	26	-3	5	3	695	663	6	17	9	3	57	5	57
2	0	48	1	-18	8	2	186	146	21	7	1	3	578	599	6	-1	5	3	177	155	12	-14	10	3	52	47	51
2	0	28	1	-16	8	2	251	261	17	9	1	3	1270	1304	12	1	5	3	1010	997	9	-12	10	3	144	129	28
2	0	99	1	-14	8	2	231	198	16	11	1	3	705	728	7	3	5	3	84	102	27	-10	10	3	125	155	32
2	71	16	71	-12	8	2	312	270	13	13	1	3	579	584	8	5	5	3	1526	1532	14	-8	10	3	43	36	43
2	0	95	1	-10	8	2	282	260	13	15	1	3	126	47	24	7	5	3	254	267	10	-6	10	3	401	399	12
2	196	211	19	-8	8	2	68	87	68	17	1	3	413	405	11	9	5	3	102	130	28	-4	10	3	592	603	11
2	301	300	13	-6	8	2	504	512	10	19	1	3	77	37	59	11	5	3	134	116	23	-2	10	3	257	263	14
2	391	388	11	-4	8	2	810	817	9	21	1	3	228	234	17	13	5	3	325	322	12	0	10	3	441	449	19
2	388	387	11	-2	8	2	520	505	9	23	1	3	0	68	1	15	5	3	0	18	1	2	10	3	227	228	17
2	312	298	11	0	8	2	324	314	10	-24	2	3	0	49	1	17	5	3	386	376	12	4	10	3	151	148	25
2	690	677	8	2	8	2	734	727	9	-22	2	3	127	52	29	19	5	3	146	148	28	6	10	3	500	516	11
2	1167	1122	10	4	8	2	422	423	11	-20	2	3	47	50	47	21	5	3	0	90	1	8	10	3	260	276	17
2	844	782	6	6	8	2	677	672	9	-18	2	3	82	121	61	-20	6	3	29	8	29	10	10	3	114	88	36
2	340	293	7	8	8	2	303	317	13	-16	2	3	488	495	10	-18	6	3	163	143	22	12	10	3	21	7	20
2	169	140	11	10	8	2	161	180	21	-14	2	3	283	270	12	-16	6	3	0	51	1	14	10	3	95	44	49
2	510	480	4	12	8	2	46	96	45	-12	2	3	332	325	10	-14	6	3	56	28	56	-13	11	3	0	93	1
2	1120	1119	10	14	8	2	0	44	1	-10	2	3	417	396	8	-12	6	3	310	301	12	-11	11	3	236	219	19
2	432	434	7	16	8	2	99	86	42	-8	2	3	285	274	8	-10	6	3	0	58	1	-9	11	3	206	217	20
2	326	336	8	18	8	2	48	36	47	-6	2	3	105	70	18	-8	6	3	423	402	9	-7	11	3	163	163	24
2	85	50	27	-17	9	2	0	59	1	-4	2	3	1162	1199	11	-6	6	3	463	432	8	-5	11	3	155	157	25
2	607	603	8	-15	9	2	226	202	18	-2	2	3	1593	1664	15	-4	6	3	548	527	8	-3	11	3	80	70	73
2	837	830	8	-13	9	2	179	183	21	0	2	3	2138	2133	16	-2	6	3	31	3	30	-1	11	3	219	193	17
2	81	132	62	-11	9	2	132	107	28	2	2	3	1351	1417	14	0	6	3	478	489	5	1	11	3	97	31	39
2	123	68	26	-9	9	2	80	1	57	4	2	3	946	1011	9	2	6	3	753	748	7	3	11	3	193	205	20
2	131	107	27	-7	9	2	0	40	1	6	2	3	542	519	6	4	6	3	789	767	7	5	11	3	374	384	13
2	35	8	34	-5	9	2	214	218	17	8	2	3	734	707	6	6	6	3	262	244	11	7	11	3	154	137	25
2	0	5	1	-3	9	2	366	361	12	10	2	3	797	808	7	8	6	3	70	123	70	9	11	3	143	116	26
2	127	66	30	-1	9	2	599	588	10	12	2	3	113	91	23	10	6	3	136	111	22	11	11	3	0	4	1
2	0	68	1	1	9	2	272	268	15	14	2	3	152	155	21	12	6	3	106	61	33	-8	12	3	206	208	21
2	83	58	56	3	9	2	657	649	10	16	2	3	585	574	10	14	6	3	409	409	11	-6	12	3	30	7	29
2	133	140	26	5	9	2	341	366	13	18	2	3	225	209	17	16	6	3	99	60	40	-4	12	3	0	78	1
2	89	22	41	7	9	2	119	106	31	20	2	3	39	8	39	18	6	3	124	37	31	-2	12	3	107	104	39
2	540	517	9	9	9	2	135	102	24	22	2	3	158	147	25	20	6	3	0	4	1	0	12	3	117	149	47
2	176	194	15	11	9	2	38	15	38	-23	3	3	93	112	62	-19	7	3	30	46	29	2	12	3	268	270	16
2	987	949	8	13	9	2	250	284	17	-21	3	3	45	94	44	-17	7	3	364	382	13	4	12	3	0	18	1
2	443	445	8	15	9	2	62	17	62	-19	3	3	63	68	62	-15	7	3	162	176	23	6	12	3	0	69	1
2	299	313	8	17	9	2	22	89	21	-17	3	3	431	411	11	-13	7	3	173	151	20	8	12	3	81	105	80
2	416	415	7	-14	10	2	0	15	1	-15	3	3	133	153	24	-11	7	3	349	355	12	-24	0	4	228	243	20
2	70	9	35	-12	10	2	108	38	34	-13	3	3	465	475	9	-9	7	3	720	722	9	-22	0	4	93	80	46
2	191	181	12	-10	10	2	168	173	22	-11	3	3	76	102	40	-7	7	3	188	183	17	-20	0	4	87	40	40
2	926	938	8	-8	10	2	0	12	1	-9	3	3	302	335	9	-5	7	3	293	305	11	-18	0	4	0	27	1
2	100	77	22	-6	10	2	50	31	49	-7	3	3	481	421	6	-3	7	3	173	150	16	-16	0	4	238	208	13
2	277	277	11	-4	10	2	386	384	12	-5	3	3	656	673	6	-1	7	3	0	110	1	-14	0	4	407	427	9
2	149	159	20	-2	10	2	191	156	18	-3	3	3	1619	1700	16	1	7	3	121	73	21	-12	0	4	891	891	7
2	182	176	19	0	10	2	390	380	8	-1	3	3	487	474	6	3	7	3	376	348	9	-10	0	4	660	647	7
2	75	93	75	2	10	2	137	143	27	1	3	3	3412	3478	27	5	7	3	181	168	17	-8	0	4	421	439	6
2	0	12	1	4	10	2	361	368	13	3	3	3	0	101	1	7	7	3	680	677	9	-6	0	4	824	892	8
2	256	283	18	6	10	2	0	27	1	5	3	3	711	731	6	9	7	3	496	490	10	-4	0	4	82	25	22
2	0	12	1	8	10	2	111	46	36	7	3	3	728	755	6	11	7	3	487	451	10	-2	0	4	4462	4859	21
2	192	189	21	10	10	2	52	7	52	9	3	3	989	1006	8	13	7	3	536	536	11	0	0	4	3884	4148	20
2	139	118	27	12	10	2	91	28	48	11	3	3	1005	1032	8	15	7	3	287	308	15	2	0	4	485	470	5
2	273	268	14	14	10	2	95	160	51	13	3	3	135	160	23	17	7	3	134	133	29	4	0	4	4122	4304	25
2	0	70	1	-13	11	2	89	113	69	15	3	3	115	98	31	19	7	3	125	101	33	6	0	4	280	304	8
2	314	308	12	-11	11	2	0	68	1	17	3	3	216	244	17	-18	8	3	224	236	20	8	0	4	593	678	6
2	901	890	8	-9	11	2	58	51	57	19	3	3	185	179	20	-16	8	3	119	148	34	10	0	4	596	571	7
2	371	361	10	-7	11	2	0	17	1	21	3	3	238	244	18	-14	8	3	165	143	23	12	0	4	203	186	13
2	1399	1357	13	-5	11	2	100	81	43	23	3	3	61	19	61	-12	8	3	61	24	61	14	0	4	483	491	9
2	163	168	15	-3	11	2	82	88	60	-22	4	3	63	22	62	-10	8	3	59	6	58	16	0	4	278	261	13
2	582	546	7	-1	11	2	0	13	1	-20	4	3	0	60	1	-8	8	3	222	210	15	18	0	4	867	844	9
2	684	667	7	1	11	2	39	48	38	-18	4	3	62	19	61	-6	8	3	131	136	25	20	0	4	0	12	1
2	36	72	36	3	11	2	94	105	46	-16	4	3	55	31	55	-4	8	3	314	300	12	22	0	4	264	277	17
2	1577	1565	14	5	11	2	97	99	45	-14	4	3	326	306	11	-2	8	3	179	159	17	-23	1	4	0	17	1
2	252	218	11	7	11	2	88	73	61	-12	4	3	92	72	32	0	8	3	368	358	7	-21	1	4	121	137	34
2	433	420	9	9	11	2	304	276	15	-10	4	3	102	119	25	2	8	3	109	118	33	-19	1	4	0	68	1
2	253	251	13	11	11	2	140	173	30	-8	4	3	145	136	16	4	8	3	740	733	9	-17	1	4	62	105	62
2	156	161	22	-8	12	2	152	151	28	-6	4	3	1924	1895	20	6	8	3	893	918	9	-15	1	4	102	151	35
2	725	711	9	-6	12	2	109	123	43	-4	4	3	2096	2097	20	8	8	3	442	427	11	-13	1	4	276	286	11
2	0	19	1	-4	12	2	103	110	41	-2	4	3	255	248	8	10	8	3	434	425	11	-11	1	4	293	276	9
2	402	366	13	-2	12	2	148	97	26	0	4	3	90	121	14	12	8	3	242	243	16	-9	1	4	242	263	9
2	51	47	51	0	12	2	93	66	29	2	4	3	781	804	6	14	8	3	122	164	33	-7	1	4	1069	1113	9
2	84	35	57	2	12	2	0	27	1	4	4	3	409	374	7	16	8	3	0	19	1	-5	1	4	125	130	14
2	52	28	52	4	12	2	147	182	28	6	4	3	204	211	11	18	8	3	100	134	46	-3	1	4	237	226	7
2	0	62	1	6	12	2	109	110	43	8	4	3	812	809	7	-17	9	3	121	127	34	-1	1	4	1061	1111	10
2	234	213	15	8	12	2	0	84	1	10	4	3	502	500	8	-15	9	3	123	126	34	1	1	4	1103	1116	10
2	84	110	56	-1	13	2	106	65	45	12	4	3	97	26	32	-13	9	3	159	124	24	3	1	4	1981	1953	20
2	49	22	49	-23	1	3	167	146	25	14	4	3	75	35	74	-11	9	3	142	118	24	5	1	4	2837	2875	28
2	349	374	11	-21	1	3	451	466	12	16	4	3	91	25	42	-9	9	3	167	179	22	7	1	4	203	190	10
2	51	72	50	-19	1	3	187	208	20	18	4	3	60	98	60	-7	9	3	0	45	1	9	1	4	209	233	11
2	668	655	8	-17	1	3	298	279	13	20	4	3	88	64	51	-5	9	3	220	237	17	11	1	4	945	958	8
2	128	143	20	-15	1	3	208	217	15	22	4	3	0	16	1	-3	9	3	510	506	10	13	1	4	138	135	20
2	423	416	9	-13	1	3	149	139	18	-21	5	3	222	177	17	-1	9	3	78	36	78	15	1	4	188	194	18
2	317	310	10	-11	1	3	980	981	9	-19	5	3	143	174	28	1	9	3	674	651	10	17	1	4	196	192	18
2	415	389	9	-9	1	3	606	602	6	-17	5	3	204	173	17	3	9	3	248	248	16	19	1	4	71	28	70

h	k	l	10Fo	10Fc	10s
15	5	4	195	176	21
17	5	4	119	116	35
19	5	4	185	176	23
21	5	4	176	121	21
-20	6	4	84	15	54
-18	6	4	44	31	44
-16	6	4	401	385	11
-14	6	4	571	570	9
-12	6	4	493	508	8
-10	6	4	999	1011	9
-8	6	4	511	505	6
-6	6	4	353	382	7
-4	6	4	1209	1221	12
-2	6	4	822	874	8
0	6	4	69	82	27
2	6	4	39	66	38
4	6	4	1141	1207	10
6	6	4	1049	1030	9
8	6	4	284	283	8
10	6	4	1079	1087	8
12	6	4	328	354	10
14	6	4	372	372	11
16	6	4	526	545	10
18	6	4	194	208	19
20	6	4	154	173	25
-19	7	4	144	134	28
-17	7	4	214	162	18
-15	7	4	75	105	75
-13	7	4	46	86	46
-11	7	4	0	98	1
-9	7	4	303	295	12
-7	7	4	427	417	9
-5	7	4	638	611	8
-3	7	4	1127	1058	9
-1	7	4	459	427	7
1	7	4	638	615	6
3	7	4	1236	1180	12
5	7	4	849	869	8
7	7	4	105	109	18
9	7	4	315	313	7
11	7	4	448	433	6
13	7	4	263	268	9
15	7	4	613	614	7
17	7	4	176	175	15
19	7	4	105	38	29
-18	8	4	197	208	18
-16	8	4	269	298	15
-14	8	4	171	167	21
-12	8	4	105	107	41
-10	8	4	103	48	40
-8	8	4	137	176	30
-6	8	4	196	177	19
-4	8	4	0	42	1
-2	8	4	424	426	10
0	8	4	159	180	18
2	8	4	355	387	9
4	8	4	532	517	7
6	8	4	809	705	6
8	8	4	187	185	11
10	8	4	46	65	45
12	8	4	35	57	34
14	8	4	977	956	8
16	8	4	568	556	6
18	8	4	613	591	7
-17	9	4	658	654	7
-15	9	4	239	234	12
-13	9	4	195	195	15
-11	9	4	130	90	26
-9	9	4	160	165	21
-7	9	4	0	11	1
-5	9	4	29	4	28
-3	9	4	127	42	31
-1	9	4	125	153	34
1	9	4	110	74	34
3	9	4	329	342	13
5	9	4	136	131	25
7	9	4	107	77	32
9	9	4	147	140	21
11	9	4	247	214	11
13	9	4	993	985	8
15	9	4	476	473	8
-14	10	4	69	72	41
-12	10	4	897	847	8
-10	10	4	422	442	7
-8	10	4	317	348	8
-6	10	4	122	112	20
-4	10	4	240	241	11
-2	10	4	419	423	9
0	10	4	62	17	61
2	10	4	579	591	10
4	10	4	643	663	10
6	10	4	235	252	17
8	10	4	583	599	11
10	10	4	49	94	49
12	10	4	29	54	29
14	10	4	0	107	1
-11	11	4	145	81	27
-9	11	4	58	7	58
-7	11	4	173	206	24
-5	11	4	48	149	48
-3	11	4	0	27	1
-1	11	4	120	50	29
1	11	4	87	125	51
3	11	4	158	147	23
5	11	4	194	224	21
7	11	4	107	101	40
9	11	4	59	126	58
11	11	4	88	57	62
-8	12	4	234	186	18
-6	12	4	137	154	30
-4	12	4	0	55	1
-2	12	4	134	101	30
0	12	4	115	63	35
2	12	4	145	152	28
4	12	4	161	119	23
6	12	4	259	258	17
8	12	4	350	336	15
-23	1	5	316	274	15
-21	1	5	193	168	20
-19	1	5	244	249	15
-17	1	5	235	223	16
-15	1	5	383	384	10
-13	1	5	1027	1015	8
-11	1	5	694	693	7
-9	1	5	381	413	7
-7	1	5	1185	1174	10
-5	1	5	1245	1284	12
-3	1	5	234	267	8
-1	1	5	521	574	5
1	1	5	320	355	6
3	1	5	406	367	6
5	1	5	427	396	6
7	1	5	839	868	7
9	1	5	292	244	9
11	1	5	466	445	8
13	1	5	335	327	10
15	1	5	116	102	28
17	1	5	201	211	18
19	1	5	132	170	28
21	1	5	237	266	18
23	1	5	108	26	36
-24	2	5	178	202	24
-22	2	5	331	316	14
-20	2	5	133	87	28
-18	2	5	88	52	46
-16	2	5	51	4	50
-14	2	5	250	233	13
-12	2	5	451	427	8
-10	2	5	1156	1164	10
-8	2	5	46	35	45
-6	2	5	319	308	7
-4	2	5	197	225	9
-2	2	5	1670	1785	16
0	2	5	276	301	5
2	2	5	1318	1304	13
4	2	5	886	880	8
6	2	5	1141	1096	10
8	2	5	515	549	7
10	2	5	1386	1413	13
12	2	5	268	261	12
14	2	5	0	20	1
16	2	5	0	19	1
18	2	5	196	201	19
20	2	5	74	56	74
22	2	5	121	70	32
-23	3	5	98	95	49
-21	3	5	386	368	13
-19	3	5	358	356	13
-17	3	5	248	254	14
-15	3	5	81	103	64
-13	3	5	304	314	11
-11	3	5	152	149	17
-9	3	5	425	447	8
-7	3	5	162	175	13
-5	3	5	1502	1472	14
-3	3	5	275	261	8
-1	3	5	338	335	7
1	3	5	2428	2540	24
3	3	5	419	384	6
5	3	5	328	358	7
7	3	5	649	631	7
9	3	5	474	457	8
11	3	5	119	97	24
13	3	5	896	900	8
15	3	5	1530	1540	14
17	3	5	80	37	69
19	3	5	260	274	16
21	3	5	119	117	32
-22	4	5	141	105	29
-20	4	5	0	24	1
-18	4	5	0	51	1
-16	4	5	75	55	74
-14	4	5	98	17	35
-12	4	5	444	441	9
-10	4	5	695	716	8
-8	4	5	573	598	7
-6	4	5	269	247	9
-4	4	5	37	4	36
-2	4	5	135	108	14
0	4	5	133	111	10
2	4	5	762	709	6
4	4	5	360	377	8
6	4	5	0	27	1
8	4	5	217	236	12
10	4	5	585	566	8
12	4	5	117	103	25
14	4	5	193	187	18
16	4	5	152	151	22
18	4	5	119	69	30
20	4	5	205	197	20
22	4	5	78	58	78
-21	5	5	47	62	46
-19	5	5	192	132	18
-17	5	5	238	243	16
-15	5	5	116	107	31
-13	5	5	503	483	10
-11	5	5	278	274	12
-9	5	5	133	140	20
-7	5	5	812	813	7
-5	5	5	867	840	7
-3	5	5	1457	1402	14
-1	5	5	1640	1542	16
1	5	5	643	619	7
3	5	5	209	193	11
5	5	5	360	356	8
7	5	5	383	391	9
9	5	5	254	256	12
11	5	5	485	484	10
13	5	5	0	74	1
15	5	5	244	242	15
17	5	5	115	52	31
19	5	5	91	94	53
21	5	5	166	182	27
-20	6	5	181	166	21
-18	6	5	143	124	26
-16	6	5	108	136	36
-14	6	5	194	177	17
-12	6	5	127	23	26
-10	6	5	308	299	12
-8	6	5	0	40	1
-6	6	5	450	424	9
-4	6	5	457	461	8
-2	6	5	389	347	9
0	6	5	243	246	8
2	6	5	511	529	8
4	6	5	305	280	10
6	6	5	651	654	8
8	6	5	0	58	1
10	6	5	257	256	13
12	6	5	85	73	54
14	6	5	110	121	34
16	6	5	0	74	1
18	6	5	89	112	58
20	6	5	91	83	63
-19	7	5	144	109	26
-17	7	5	69	131	69
-15	7	5	393	400	12
-13	7	5	81	58	62
-11	7	5	99	136	40
-9	7	5	247	255	15
-7	7	5	466	442	9
-5	7	5	315	287	11
-3	7	5	201	200	14
-1	7	5	48	15	47
1	7	5	0	15	1
3	7	5	234	244	13
5	7	5	429	409	9
7	7	5	0	48	1
9	7	5	218	214	16
11	7	5	413	424	11
13	7	5	126	106	27
15	7	5	34	40	33
17	7	5	124	39	30
19	7	5	0	33	1
-18	8	5	99	71	42
-16	8	5	136	111	29
-14	8	5	110	45	36
-12	8	5	74	75	74
-10	8	5	173	171	20
-8	8	5	95	96	42
-6	8	5	269	271	14
-4	8	5	87	74	43
-2	8	5	196	196	17
0	8	5	167	163	18
2	8	5	57	89	56
4	8	5	303	269	13
6	8	5	755	740	9
8	8	5	150	153	24
10	8	5	231	231	16
12	8	5	83	130	72
14	8	5	105	44	39
16	8	5	168	165	25
18	8	5	130	97	31
-17	9	5	48	43	48
-15	9	5	198	162	19
-13	9	5	200	236	19
-11	9	5	107	80	35
-9	9	5	385	387	12
-7	9	5	147	121	23
-5	9	5	540	537	10
-3	9	5	146	50	23
-1	9	5	95	71	38
1	9	5	709	706	9
3	9	5	93	53	42
5	9	5	277	259	14
7	9	5	32	24	31
9	9	5	220	205	17
11	9	5	151	145	26
13	9	5	103	105	41
15	9	5	194	207	20
-14	10	5	0	58	1
-12	10	5	118	101	33
-10	10	5	159	163	24
-8	10	5	146	117	25
-6	10	5	0	23	1
-4	10	5	81	160	73
-2	10	5	128	126	28
0	10	5	110	61	22
2	10	5	233	240	16
4	10	5	117	128	31
6	10	5	326	297	13
8	10	5	310	307	15
10	10	5	171	203	24
12	10	5	263	248	17
14	10	5	136	144	32
-11	11	5	243	248	18
-9	11	5	0	6	1
-7	11	5	67	106	66
-5	11	5	114	151	33
-3	11	5	124	107	30
-1	11	5	186	196	20
1	11	5	0	6	1
3	11	5	59	39	59
5	11	5	204	223	21
7	11	5	82	78	81
9	11	5	161	121	24
11	11	5	255	253	18
-8	12	5	0	9	1
-6	12	5	0	101	1
-4	12	5	72	140	72
-2	12	5	72	72	71
0	12	5	18	12	18
2	12	5	132	119	30
4	12	5	94	113	54
6	12	5	253	238	18
-24	0	6	257	240	18
-22	0	6	203	218	21
-20	0	6	0	71	1
-18	0	6	273	271	13
-16	0	6	561	554	9
-14	0	6	38	39	37
-12	0	6	294	268	10
-10	0	6	775	737	7
-8	0	6	298	274	8
-6	0	6	1169	1156	11
-4	0	6	852	876	7
-2	0	6	2750	2931	25
0	0	6	1417	1382	14
2	0	6	2633	2707	26
4	0	6	1815	1845	18

h	k	l	10Fo	10Fc	10s
6	2	6	213	189	10
6	4	6	933	880	8
6	4	6	494	490	8
6	4	6	430	433	9
6	4	6	116	78	26
6	4	6	225	225	16
6	4	6	0	16	1
6	4	6	0	53	1
6	4	6	0	115	1
6	4	6	73	133	72
6	5	6	0	18	1
6	5	6	42	67	41
6	5	6	81	121	58
6	5	6	119	102	26
6	5	6	514	507	8
6	5	6	833	821	7
6	5	6	363	365	8
6	5	6	761	728	6
6	5	6	910	956	8
6	5	6	810	835	8
6	5	6	438	425	5
6	5	6	1210	1196	12
6	5	6	576	612	5
6	5	6	907	939	8
6	5	6	1392	1372	14
6	5	6	541	556	7
6	5	6	643	641	8
6	5	6	96	93	33
6	5	6	440	463	11
6	5	6	174	202	21
6	5	6	373	377	13
6	5	6	191	178	22
6	6	6	281	296	16
6	6	6	243	262	16
6	6	6	307	265	13
6	6	6	558	559	10
6	6	6	76	43	54
6	6	6	542	545	8
6	6	6	1323	1310	12
6	6	6	1030	1039	9
6	6	6	722	718	6
6	6	6	699	700	5
6	6	6	0	63	1
6	6	6	490	476	4
6	6	6	886	907	8
6	6	6	675	700	6
6	6	6	991	983	9
6	6	6	1425	1475	14
6	6	6	1599	1608	15
6	6	6	199	206	15
6	6	6	29	19	28
6	6	6	237	239	16
6	6	6	73	121	73
6	6	6	100	97	39
6	6	6	71	8	70
6	7	6	121	132	35
6	7	6	86	25	61
6	7	6	162	178	22
6	7	6	0	30	1
6	7	6	156	142	20
6	7	6	103	117	31
6	7	6	336	332	10
6	7	6	189	178	13
6	7	6	0	25	1
6	7	6	243	239	9
6	7	6	437	441	6
6	7	6	1017	998	9
6	7	6	35	36	35
6	7	6	455	428	6
6	7	6	336	306	8
6	7	6	281	275	9
6	7	6	203	185	13
6	7	6	184	202	16
6	8	6	107	106	33
6	8	6	506	512	11
6	8	6	189	217	19
6	8	6	161	158	24
6	8	6	0	38	1
6	8	6	114	145	38
6	8	6	239	224	16
6	8	6	401	412	12
6	8	6	202	190	18
6	8	6	44	52	44
6	8	6	84	4	37
6	8	6	469	507	8
6	8	6	310	322	9
6	8	6	1190	1202	10
6	8	6	718	680	6
6	8	6	439	436	7
6	8	6	2410	2340	16
6	4	6	642	580	6
6	4	6	1450	1414	13
6	4	6	127	99	16
6	4	6	809	827	7
6	4	6	443	443	9
6	4	6	418	403	10
6	4	6	39	41	38
6	4	6	120	144	29
6	4	6	157	98	24
6	4	6	160	167	24
6	5	6	165	131	24
6	5	6	0	20	1
6	5	6	186	170	19
6	5	6	47	91	47
6	5	6	325	332	12
6	5	6	272	279	13
6	5	6	375	377	10
6	5	6	0	48	1
6	5	6	237	222	11
6	5	6	371	388	8
6	5	6	491	464	7
6	5	6	1124	1069	10
6	5	6	172	173	14
6	5	6	790	757	7
6	5	6	311	327	10
6	5	6	115	135	26
6	5	6	288	295	13
6	5	6	39	16	38
6	5	6	137	116	24
6	5	6	333	339	14
6	5	6	191	185	21
6	5	6	43	23	43
6	6	6	30	21	29
6	6	6	0	42	1
6	6	6	344	341	13
6	6	6	129	112	28
6	6	6	497	497	10
6	6	6	226	208	14
6	6	6	285	266	11
6	6	6	247	242	12
6	6	6	148	172	17
6	6	6	998	1007	8
6	6	6	698	644	5
6	6	6	881	866	7
6	6	6	390	373	9
6	6	6	57	58	57
6	6	6	367	385	10
6	6	6	143	144	24
6	6	6	1202	1215	10
6	6	6	161	149	22
6	6	6	165	156	22
6	6	6	0	38	1
6	6	6	149	114	26
6	7	6	73	113	72
6	7	6	53	102	53
6	7	6	105	92	37
6	7	6	201	219	18
6	7	6	251	233	14
6	7	6	144	162	23
6	7	6	166	174	18
6	7	6	338	317	11
6	7	6	271	261	12
6	7	6	239	206	12
6	7	6	217	207	14
6	7	6	718	716	8
6	7	6	567	571	9
6	7	6	260	265	14
6	7	6	274	286	14
6	7	6	394	396	12
6	7	6	219	231	17
6	7	6	143	152	29
6	7	6	58	99	58
6	7	6	159	166	26
6	8	6	0	2	1
6	8	6	29	67	28
6	8	6	0	82	1
6	8	6	210	231	17
6	8	6	347	359	12
6	8	6	105	109	35
6	8	6	475	444	10
6	8	6	370	359	11
6	8	6	40	21	40
6	8	6	370	371	21
6	8	6	217	225	16
6	8	6	129	155	28
6	8	6	371	352	12
6	8	6	474	452	11
6	8	6	258	241	15
6	8	6	231	241	17
6	8	6	145	180	30
16	8	6	130	72	29
-17	9	6	43	93	43
-15	9	6	97	104	43
-13	9	6	169	139	22
-11	9	6	188	217	21
-9	9	6	0	24	1
-7	9	6	215	224	16
-5	9	6	132	167	27
-3	9	6	75	91	74
-1	9	6	446	453	11
1	9	6	182	144	18
3	9	6	129	140	26
5	9	6	72	74	72
7	9	6	154	171	22
9	9	6	133	121	28
11	9	6	339	311	13
13	9	6	139	123	28
15	9	6	170	113	23
-14	10	6	169	209	27
-12	10	6	122	72	33
-10	10	6	378	371	13
-8	10	6	0	38	1
-6	10	6	367	361	13
-4	10	6	46	91	45
-2	10	6	85	45	42
0	10	6	482	485	8
2	10	6	450	464	11
4	10	6	0	4	1
6	10	6	135	56	27
8	10	6	20	70	19
10	10	6	0	15	1
12	10	6	0	36	1
14	10	6	0	26	1
-11	11	6	0	48	1
-9	11	6	93	117	51
-7	11	6	152	160	24
-5	11	6	108	8	36
-3	11	6	52	40	52
-1	11	6	108	151	37
1	11	6	74	40	73
3	11	6	207	195	19
5	11	6	313	307	15
7	11	6	0	66	1
9	11	6	415	412	14
11	11	6	138	97	32
-8	12	6	0	70	1
-6	12	6	122	138	35
-4	12	6	92	63	50
-2	12	6	131	130	30
0	12	6	28	8	27
2	12	6	36	45	36
4	12	6	73	38	73
6	12	6	86	119	85
-23	1	7	92	146	57
-21	1	7	210	210	19
-19	1	7	0	17	1
-17	1	7	0	3	1
-15	1	7	189	196	17
-13	1	7	266	280	12
-11	1	7	334	301	9
-9	1	7	684	732	7
-7	1	7	118	127	16
-5	1	7	507	481	6
-3	1	7	1997	2013	20
-1	1	7	695	713	6
1	1	7	228	263	8
3	1	7	344	303	7
5	1	7	345	295	7
7	1	7	605	568	7
9	1	7	1001	1015	8
11	1	7	558	555	8
13	1	7	169	153	18
15	1	7	250	244	15
17	1	7	372	371	11
19	1	7	157	156	24
21	1	7	126	113	32
-22	2	7	297	292	17
-20	2	7	108	91	36
-18	2	7	345	350	13
-16	2	7	269	288	15
-14	2	7	614	605	9
-12	2	7	255	246	12
-10	2	7	100	124	24
-8	2	7	280	293	9
-6	2	7	0	41	1
-4	2	7	318	305	7
-2	2	7	422	399	6
0	2	7	543	533	8
2	2	7	976	1033	8
4	2	7	1590	1628	16
6	2	7	131	114	16
8	2	7	1494	1460	14
10	2	7	986	1005	8
12	2	7	52	40	51
14	2	7	643	671	9
16	2	7	0	7	1
18	2	7	101	87	40
20	2	7	161	194	26
22	2	7	101	8	42
-23	3	7	30	12	30
-21	3	7	165	176	24
-19	3	7	285	276	14
-17	3	7	180	170	19
-15	3	7	17	66	16
-13	3	7	178	184	18
-11	3	7	408	422	9
-9	3	7	104	43	20
-7	3	7	162	188	14
-5	3	7	915	943	7
-3	3	7	177	173	11
-1	3	7	1195	1244	11
1	3	7	819	779	6
3	3	7	0	63	1
5	3	7	468	526	7
7	3	7	719	684	7
9	3	7	862	851	7
11	3	7	839	848	8
13	3	7	0	58	1
15	3	7	668	694	10
17	3	7	0	2	1
19	3	7	485	447	12
21	3	7	101	132	46
-22	4	7	0	63	1
-20	4	7	0	63	1
-18	4	7	265	249	15
-16	4	7	275	256	14
-14	4	7	557	559	10
-12	4	7	489	484	9
-10	4	7	446	423	9
-8	4	7	209	198	12
-6	4	7	1160	1146	9
-4	4	7	633	602	7
-2	4	7	1402	1369	14
0	4	7	611	566	4
2	4	7	1138	1100	10
4	4	7	376	349	8
6	4	7	248	231	11
8	4	7	362	357	9
10	4	7	47	55	46
12	4	7	365	342	11
14	4	7	114	124	35
16	4	7	369	354	13
18	4	7	298	288	14
20	4	7	210	229	21
-21	5	7	103	115	44
-19	5	7	60	70	59
-17	5	7	163	180	21
-15	5	7	0	78	1
-13	5	7	308	318	13
-11	5	7	0	90	1
-9	5	7	325	316	10
-7	5	7	346	353	9
-5	5	7	103	116	23
-3	5	7	165	191	13
-1	5	7	603	534	7
1	5	7	316	321	9
3	5	7	811	799	7
5	5	7	0	98	1
7	5	7	70	71	51
9	5	7	110	114	28
11	5	7	327	318	12
13	5	7	127	121	27
15	5	7	46	23	45
17	5	7	111	113	36
19	5	7	356	370	15
-20	6	7	284	278	16
-18	6	7	220	207	17
-16	6	7	148	183	25
-14	6	7	92	124	44
-12	6	7	91	130	45
-10	6	7	314	300	11
-8	6	7	184	187	17
-6	6	7	93	79	31
-4	6	7	74	37	42
-2	6	7	120	69	21
0	6	7	271	270	8
2	6	7	125	67	20
4	6	7	21	10	21
6	6	7	450	456	9
8	6	7	257	275	14
10	6	7	523	518	10
12	6	7	111	125	35
14	6	7	37	41	37
16	6	7	138	113	28
18	6	7	119	115	33
-19	7	7	253	223	17
-17	7	7	83	79	70
-15	7	7	0	4	1
-13	7	7	480	478	11
-11	7	7	121	93	29
-9	7	7	391	389	11
-7	7	7	121	118	27
-5	7	7	335	325	11
-3	7	7	208	209	15
-1	7	7	262	253	12
1	7	7	268	268	12
3	7	7	71	93	70
5	7	7	136	90	22
7	7	7	175	186	20
9	7	7	97	8	39
11	7	7	304	292	14
13	7	7	68	15	68
15	7	7	119	164	32
17	7	7	75	71	75
-18	8	7	362	349	14
-16	8	7	147	122	25
-14	8	7	229	184	17
-12	8	7	253	238	15
-10	8	7	123	87	27
-8	8	7	221	243	17
-6	8	7	448	437	11
-4	8	7	219	227	17
-2	8	7	0	66	1
0	8	7	144	106	16
2	8	7	126	141	26
4	8	7	246	273	16
6	8	7	328	355	13
8	8	7	51	86	50
10	8	7	42	95	41
12	8	7	43	34	43
14	8	7	0	28	1
16	8	7	30	95	29
-17	9	7	0	84	1
-15	9	7	122	100	34
-13	9	7	149	140	26
-11	9	7	51	84	51
-9	9	7	103	32	33
-7	9	7	84	81	46
-5	9	7	433	413	11
-3	9	7	110	18	31
-1	9	7	330	315	12
1	9	7	47	23	46
3	9	7	250	238	14
5	9	7	227	212	15
7	9	7	46	22	45
9	9	7	641	657	11
11	9	7	122	78	30
13	9	7	244	222	17
15	9	7	215	214	19
-14	10	7	124	173	34
-12	10	7	299	312	15
-10	10	7	173	178	23
-8	10	7	121	130	31
-6	10	7	247	258	16
-4	10	7	189	175	18
-2	10	7	65	45	65
0	10	7	367	375	9
2	10	7	0	104	1
4	10	7	135	165	28
6	10	7	179	182	22
8	10	7	60	65	59
10	10	7	46	9	45
12	10	7	223	173	19
-11	11	7	43	66	42
-9	11	7	100	53	45
-7	11	7	94	142	55
-5	11	7	224	251	19
-3	11	7	274	306	15
-1	11	7	0	92	1
1	11	7	276	282	15
3	11	7	154	125	25
5	11	7	268	271	16
7	11	7	220	220	20
9	11	7	400	417	14
-6	12	7	48	54	47
-4	12	7	125	126	31
-2	12	7	124	81	32
0	12	7	133	121	19
2	12	7	158	127	24
4	12	7	0	37	1
10	6	7	523	518	10
12	6	7	111	125	35
14	6	7	37	41	37
16	6	7	138	113	28
18	6	7	119	115	33
-19	7	7	253	223	17
-17	7	7	83	79	70
-15	7	7	0	4	1
-13	7	7	480	478	11
-11	7	7	121	93	29
-9	7	7	391	389	11
-7	7	7	121	118	27
-5	7	7	335	325	11
-3	7	7	208	209	15
-1	7	7	262	253	12
1	7	7	268	268	12
3	7	7	71	93	70
5	7	7	136	90	22
7	7	7	175	186	20
9	7	7	97	8	39
11	7	7	304	292	14
13	7	7	68	15	68
15	7	7	119	164	32
17	7	7	75	71	75
-18	8	7	362	349	14
-16	8	7	147	122	25
-14	8	7	229	184	17
-12	8	7	253	238	15
-10	8	7	123	87	27
-8	8	7	221	243	17
-6	8	7	448	437	11
-4	8	7	219	227	17
-2	8	7	0	66	1
0	8	7	144	106	16
2	8	7	126	141	26
4	8	7	246	273	16
6	8	7	328	355	13
8	8	7	51	86	50
10	8	7	42	95	41
12	8	7	43	34	43
14	8	7	0	28	1
16	8	7	30	95	29
-17	9	7	0	84	1
-15	9	7	122	100	34
-13	9	7	149	140	26
-11	9	7	51	84	51
-9	9	7	103	32	33
-7	9	7	84	81	46
-5	9	7	433	413	11
-3	9	7	110	18	31
-1	9	7	330	315	12
1	9	7	47	23	46
3	9	7	250	238	14
5	9	7	227	212	15
7	9	7	46	22	45
9	9	7	641	657	11
11	9	7	122	78	30
13	9	7	244	222	17
15	9	7	215	214	19
-14	10	7	124	173	34
-12	10	7	299	312	15
-10	10	7	173	178	23
-8	10	7	121	130	31
-6	10	7	247	258	16
-4	10	7	189	175	18
-2	10	7	65	45	65
0	10	7	367	375	9
2	10	7	0	104	1
4	10	7	135	165	28
6	10	7	179	182	22
8	10	7	60	65	59
10	10	7	46	9	45
12	10	7	223	173	19
-11	11	7	43	66	42
-9	11	7	100	53	45
-7	11	7	94	142	55
-5	11	7	224	251	19
-3	11	7	274	306	15
-1	11	7	0	92	1
1	11	7	276	282	15
3	11	7	154	125	25
5	11	7	268	271	16
7	11	7	220	220	20
9	11	7	400	417	14
-6	12	7	48	54	47
-4	12	7	125	126	31
-2	12	7	124	81	32
0	12	7	133	121	19
2	12	7	158	127	24
4	12	7	0	37	1

l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
7	81	178	80	17	3	8	163	117	21	-8	8	8	188	212	17	-8	2	9	203	215	11	-2	6	9	133	144	20
8	382	361	14	19	3	8	92	41	46	-6	8	8	361	393	12	-6	2	9	1305	1303	11	0	6	9	677	658	5
8	135	103	26	21	3	8	30	45	30	-4	8	8	144	107	23	-4	2	9	92	14	18	2	6	9	131	146	22
8	231	220	16	-22	4	8	161	156	27	-2	8	8	465	449	10	-2	2	9	1191	1225	10	4	6	9	707	715	8
8	518	518	10	-20	4	8	160	163	24	0	8	8	505	491	7	0	2	9	292	299	12	6	6	9	95	99	33
8	493	486	9	-18	4	8	291	295	15	2	8	8	88	30	46	2	2	9	415	431	7	8	6	9	218	207	16
8	266	261	11	-16	4	8	345	353	12	4	8	8	293	294	13	4	2	9	296	260	9	10	6	9	189	194	19
8	279	285	10	-14	4	8	535	530	10	6	8	8	582	578	10	6	2	9	573	596	7	12	6	9	107	135	35
8	1741	1731	16	-12	4	8	225	196	14	8	8	8	93	73	40	8	2	9	782	764	7	14	6	9	390	406	13
8	857	845	7	-10	4	8	357	338	10	10	8	8	208	228	17	10	2	9	290	316	11	16	6	9	352	360	14
8	1291	1382	13	-8	4	8	356	376	9	12	8	8	0	50	1	12	2	9	43	48	43	18	6	9	73	82	73
8	1603	1588	15	-6	4	8	1465	1458	13	14	8	8	76	72	76	14	2	9	0	20	1	-19	7	9	30	2	30
8	620	662	5	-4	4	8	364	353	8	16	8	8	120	122	36	16	2	9	277	273	14	-17	7	9	261	265	16
8	1996	2045	19	-2	4	8	606	581	7	-15	9	8	154	171	26	18	2	9	0	11	1	-15	7	9	52	17	51
8	482	520	6	0	4	8	500	475	8	-13	9	8	20	5	20	20	2	9	208	195	19	-13	7	9	327	358	13
8	730	748	6	2	4	8	395	374	8	-11	9	8	48	83	47	-23	3	9	0	31	1	-11	7	9	320	347	13
8	151	150	15	4	4	8	190	182	12	-9	9	8	0	24	1	-21	3	9	41	34	40	-9	7	9	507	509	11
8	178	189	14	6	4	8	822	835	7	-7	9	8	0	121	1	-19	3	9	240	261	17	-7	7	9	305	339	13
8	786	804	8	8	4	8	581	616	8	-5	9	8	209	231	17	-17	3	9	769	774	10	-5	7	9	474	460	10
8	481	494	10	10	4	8	223	199	14	-3	9	8	223	228	16	-15	3	9	330	321	12	-3	7	9	185	139	16
8	999	974	9	12	4	8	220	219	16	-1	9	8	125	109	27	-13	3	9	357	349	11	-1	7	9	0	30	1
8	76	87	76	14	4	8	111	93	32	1	9	8	100	111	38	-11	3	9	172	161	16	1	7	9	874	862	8
8	0	19	1	16	4	8	224	233	16	3	9	8	282	269	13	-9	3	9	282	284	10	3	7	9	88	54	42
8	0	62	1	18	4	8	53	29	52	5	9	8	114	48	30	-7	3	9	345	365	8	5	7	9	500	526	10
8	302	334	16	20	4	8	146	175	29	7	9	8	378	374	12	-5	3	9	32	9	31	7	7	9	122	142	29
8	96	24	45	-21	5	8	103	115	45	9	9	8	103	81	39	-3	3	9	415	423	7	9	7	9	285	290	14
8	385	347	12	-19	5	8	92	124	52	11	9	8	154	134	24	-1	3	9	1129	1191	10	11	7	9	192	199	19
8	0	42	1	-17	5	8	393	371	12	13	9	8	55	4	54	1	3	9	162	164	13	13	7	9	194	199	19
8	118	87	27	-15	5	8	108	67	31	15	9	8	143	117	29	3	3	9	341	362	8	15	7	9	177	166	22
8	232	244	13	-13	5	8	48	32	48	-14	10	8	110	103	40	5	3	9	592	556	7	17	7	9	161	114	26
8	492	469	8	-11	5	8	180	202	18	-12	10	8	69	14	69	7	3	9	25	24	24	-18	8	9	0	6	1
8	384	435	8	-9	5	8	295	313	11	-10	10	8	0	10	1	9	3	9	484	523	9	-16	8	9	194	181	22
8	661	626	6	-7	5	8	356	378	10	-8	10	8	360	363	13	11	3	9	198	210	17	-14	8	9	205	206	19
8	296	274	7	-5	5	8	309	289	9	-6	10	8	75	31	74	13	3	9	1420	1429	13	-12	8	9	196	240	19
8	546	536	6	-3	5	8	37	24	36	-4	10	8	206	209	18	15	3	9	613	649	10	-10	8	9	0	48	1
8	386	409	6	-1	5	8	725	751	7	-2	10	8	306	265	13	17	3	9	116	110	36	-8	8	9	126	110	25
8	1049	1111	9	1	5	8	66	14	66	0	10	8	201	180	20	19	3	9	149	127	26	-6	8	9	25	37	24
8	330	358	7	3	5	8	0	15	1	2	10	8	91	23	43	21	3	9	0	14	1	-4	8	9	128	135	25
8	1348	1304	12	5	5	8	0	30	1	4	10	8	170	198	22	-22	4	9	0	17	1	-2	8	9	82	61	51
8	136	97	15	7	5	8	294	280	11	6	10	8	196	134	19	-20	4	9	203	196	19	0	8	9	314	319	9
8	930	935	8	9	5	8	181	193	16	8	10	8	0	6	1	-18	4	9	241	252	16	2	8	9	171	116	19
8	0	13	1	11	5	8	191	193	18	10	10	8	140	164	29	-16	4	9	439	454	11	4	8	9	242	251	15
8	157	158	19	13	5	8	289	316	13	12	10	8	133	155	34	-14	4	9	151	149	23	6	8	9	341	320	12
8	365	378	12	15	5	8	50	35	49	-11	11	8	134	138	31	-12	4	9	353	333	11	8	8	9	296	294	13
8	49	69	49	17	5	8	270	259	16	-9	11	8	148	116	28	-10	4	9	471	463	9	10	8	9	81	23	69
8	52	76	52	19	5	8	295	303	16	-7	11	8	82	66	72	-8	4	9	402	406	9	12	8	9	0	27	1
8	69	44	69	-20	6	8	87	79	61	-5	11	8	81	138	81	-6	4	9	216	252	11	14	8	9	71	58	71
8	343	338	14	-18	6	8	193	223	20	-3	11	8	138	132	27	-4	4	9	323	334	9	16	8	9	118	136	35
8	340	348	13	-16	6	8	268	267	15	-1	11	8	83	137	76	-2	4	9	0	14	1	-15	9	9	149	171	28
8	84	130	52	-14	6	8	118	112	28	1	11	8	0	61	1	0	4	9	432	444	5	-13	9	9	54	9	53
8	854	827	9	-12	6	8	88	77	44	3	11	8	91	95	54	2	4	9	469	423	8	-11	9	9	93	92	46
8	369	373	11	-10	6	8	60	95	59	5	11	8	112	30	36	4	4	9	497	474	8	-9	9	9	0	104	1
8	364	372	10	-8	6	8	295	281	12	7	11	8	0	3	1	6	4	9	14	103	14	-7	9	9	159	178	23
8	477	456	8	-6	6	8	60	70	59	9	11	8	161	165	27	8	4	9	502	499	9	-5	9	9	379	429	12
8	272	277	9	-4	6	8	219	211	12	-6	12	8	0	35	1	10	4	9	0	55	1	-3	9	9	169	191	20
8	539	558	6	-2	6	8	274	244	11	-4	12	8	90	46	53	12	4	9	61	10	61	-1	9	9	405	413	11
8	941	946	8	0	6	8	73	70	28	-2	12	8	160	190	25	14	4	9	151	105	23	1	9	9	93	37	36
8	424	441	6	2	6	8	379	390	9	0	12	8	90	111	33	16	4	9	51	85	50	3	9	9	95	92	40
8	346	354	5	4	6	8	259	239	12	2	12	8	213	168	19	18	4	9	295	306	15	5	9	9	72	112	72
8	307	328	7	6	6	8	312	302	12	4	12	8	176	198	26	20	4	9	143	127	28	7	9	9	124	107	28
8	985	960	9	8	6	8	103	8	32	-23	1	9	216	205	20	-21	5	9	0	41	1	9	9	9	213	194	17
8	895	869	8	10	6	8	242	240	15	-21	1	9	110	72	36	-19	5	9	90	48	49	11	9	9	177	201	21
8	480	479	8	12	6	8	142	161	24	-19	1	9	276	283	15	-17	5	9	180	193	23	13	9	9	212	184	20
8	328	309	10	14	6	8	0	74	1	-17	1	9	0	73	1	-15	5	9	206	201	18	-14	10	9	0	27	1
8	64	64	63	16	6	8	20	42	19	-15	1	9	634	646	9	-13	5	9	195	218	18	-12	10	9	30	52	29
8	338	358	13	18	6	8	72	57	72	-13	1	9	148	163	20	-11	5	9	220	191	14	-10	10	9	79	62	78
8	0	52	1	-19	7	8	76	59	76	-11	1	9	427	401	9	-9	5	9	922	940	8	-8	10	9	303	312	15
8	89	109	53	-17	7	8	190	163	20	-9	1	9	1469	1512	13	-7	5	9	413	409	9	-6	10	9	102	146	44
8	177	183	21	-15	7	8	93	92	48	-7	1	9	673	680	6	-5	5	9	155	176	16	-4	10	9	51	57	50
8	113	120	42	-13	7	8	0	98	1	-5	1	9	1269	1255	12	-3	5	9	411	409	8	-2	10	9	120	128	31
8	0	51	1	-11	7	8	0	38	1	-3	1	9	266	260	8	-1	5	9	185	160	12	0	10	9	196	186	12
8	138	44	27	-9	7	8	289	276	13	-1	1	9	197	207	9	1	5	9	1285	1246	11	2	10	9	186	213	20
8	184	147	19	-7	7	8	256	265	14	1	1	9	427	446	6	3	5	9	996	973	8	4	10	9	39	107	39
8	424	414	11	-5	7	8	362	361	11	3	1	9	613	642	6	5	5	9	902	884	8	6	10	9	269	261	16
8	352	344	12	-3	7	8	0	75	1	5	1	9	1271	1303	12	7	5	9	343	344	10	8	10	9	197	160	20
8	77	14	53	-1	7	8	542	530	9	7	1	9	437	421	8	9	5	9	115	151	29	10	10	9	93	69	48
8	169	147	16	1	7	8	136	135	23	9	1	9	145	155	17	11	5	9	183	191	19	12	10	9	0	4	1
8	28	50	28	3	7	8	293	249	12	11	1	9	127	140	24	13	5	9	285	284	13	-11	11	9	61	39	61
8	135	126	16	5	7	8	220	212	16	13	1	9	123	122	27	15	5	9	562	556	11	-9	11	9	298	312	16
8	366	386	8	7	7	8	428	442	11	15	1	9	618	631	10	17	5	9	384	391	14	-7	11	9	21	27	20
8	193	216	10	9	7	8	673	669	10	17	1	9	0	17	1	19	5	9	180	142	21	-5	11	9	242	255	17
8	213	213	9	11	7	8	776	777	10	19	1	9	0	45	1	-20	6	9	90	111	64	-3	11	9	79	78	78
8	395	366	7	13	7	8	260	241	16	21	1	9	0	31	1	-18	6	9	67	73	67	-1	11	9	40	19	40
8	288	271	8	15	7	8	187	207	21	-22	2	9	93	125	51	-16	6	9	75	45	74	1	11	9	150	194	26
8	47	37	47	17	7	8	119	107	36	-20	2	9	234	209	17	-14	6	9	126	107	26	3	11	9	110	150	40
8	480	467	8	-18	8	8	0	2	1	-18	2	9	314	310	13	-12	6	9	222	201	16	5	11	9	271	274	16
8	0	69	1	-16	8	8	465	446	12	-16	2	9	117	143	34	-10	6	9	489	480	10	7	11	9	47	56	47
8	265	274	13	-14	8	8	193	156	18	-14	2	9	168	181	19	-8	6	9	440	438	10	9	11	9	101	42	47
8	704	714	9	-12	8	8	111	67	34	-12	2	9	269	251	12	-6	6	9	437	443	9	-6	12	9	0	24	1
8	551	563	11	-10	8	8	283	295	14	-10	2	9	183	175	13	-4	6	9	229	227	13	-4	12	9	30	32	30

l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
9	64	90	64	17	3	10	399	406	13	-4	8	10	170	182	20	14	2	11	44	19	44	-13	7	11	229	201	17
9	171	173	16	19	3	10	103	59	41	-2	8	10	356	354	12	16	2	11	265	270	16	-11	7	11	642	645	10
9	0	42	1	-22	4	10	94	22	50	0	8	10	342	318	10	18	2	11	149	214	30	-9	7	11	113	72	30
9	268	250	18	-20	4	10	188	205	21	2	8	10	284	292	14	20	2	11	112	76	37	-7	7	11	265	287	14
10	133	93	30	-18	4	10	445	453	12	4	8	10	423	410	11	-21	3	11	91	94	65	-5	7	11	465	462	10
10	271	291	16	-16	4	10	191	162	18	6	8	10	0	49	1	-19	3	11	113	62	33	-3	7	11	289	299	13
10	0	33	1	-14	4	10	371	360	12	8	8	10	19	22	18	-17	3	11	90	43	47	-1	7	11	103	117	33
10	396	389	11	-12	4	10	561	545	9	10	8	10	77	16	77	-15	3	11	523	531	11	1	7	11	41	49	41
10	540	568	9	-10	4	10	103	96	29	12	8	10	304	309	15	-13	3	11	325	317	12	3	7	11	149	170	24
10	324	298	10	-8	4	10	50	84	49	14	8	10	148	131	27	-11	3	11	508	489	9	5	7	11	217	248	16
10	202	158	12	-6	4	10	389	388	8	-15	9	10	112	94	39	-9	3	11	296	292	11	7	7	11	204	184	17
10	310	254	9	-4	4	10	392	360	8	-13	9	10	125	126	32	-7	3	11	97	95	26	9	7	11	145	135	25
10	2155	2155	22	-2	4	10	946	931	7	-11	9	10	74	33	74	-5	3	11	190	185	12	11	7	11	145	107	25
10	0	113	1	0	4	10	824	795	11	-9	9	10	95	2	42	-3	3	11	159	142	13	13	7	11	0	42	1
10	110	67	16	2	4	10	443	452	8	-7	9	10	240	252	16	-1	3	11	404	422	8	15	7	11	182	184	23
10	379	349	7	4	4	10	532	505	8	-5	9	10	0	17	1	1	3	11	489	509	7	-16	8	11	96	68	50
10	395	404	7	6	4	10	52	80	51	-3	9	10	265	301	14	3	3	11	509	539	8	-14	8	11	97	98	44
10	655	619	6	8	4	10	592	612	9	-1	9	10	191	204	18	5	3	11	481	478	8	-12	8	11	92	96	47
10	0	104	1	10	4	10	37	20	36	1	9	10	228	222	16	7	3	11	728	701	8	-10	8	11	38	62	37
10	341	348	10	12	4	10	17	41	17	3	9	10	0	73	1	9	3	11	197	189	15	-8	8	11	0	42	1
10	590	582	8	14	4	10	26	5	26	5	9	10	65	4	65	11	3	11	124	145	28	-6	8	11	152	199	22
10	216	215	16	16	4	10	254	261	16	7	9	10	0	6	1	13	3	11	280	287	13	-4	8	11	171	160	19
10	427	430	11	18	4	10	149	180	27	9	9	10	181	193	21	15	3	11	385	380	12	-2	8	11	361	409	12
10	304	335	14	20	4	10	146	131	29	11	9	10	0	20	1	17	3	11	258	212	16	0	8	11	216	217	11
10	225	223	18	-21	5	10	147	151	28	13	9	10	102	107	46	19	3	11	63	26	62	2	8	11	351	350	12
10	262	233	16	-19	5	10	188	186	22	-12	10	10	21	115	21	-22	4	11	0	4	1	4	8	11	269	264	14
10	220	198	19	-17	5	10	206	220	18	-10	10	10	80	87	79	-20	4	11	62	102	61	6	8	11	90	70	41
10	244	215	17	-15	5	10	309	292	13	-8	10	10	92	39	45	-18	4	11	107	59	33	8	8	11	89	93	47
10	0	10	1	-13	5	10	364	339	12	-6	10	10	135	203	28	-16	4	11	64	85	64	10	8	11	0	69	1
10	472	448	11	-11	5	10	112	113	31	-4	10	10	151	140	23	-14	4	11	806	771	9	12	8	11	50	73	49
10	147	171	25	-9	5	10	567	583	9	-2	10	10	325	320	13	-12	4	11	1149	1158	9	14	8	11	134	10	28
10	772	787	8	-7	5	10	387	381	10	0	10	10	0	21	1	-10	4	11	359	372	11	-15	9	11	0	17	1
10	365	363	9	-5	5	10	269	259	11	2	10	10	48	33	47	-8	4	11	113	79	24	-13	9	11	144	97	25
10	923	925	8	-3	5	10	445	427	9	4	10	10	174	178	21	-6	4	11	387	368	9	-11	9	11	35	43	34
10	453	433	7	-1	5	10	92	111	29	6	10	10	124	148	30	-4	4	11	414	405	8	-9	9	11	68	87	67
10	1195	1188	11	1	5	10	435	393	9	8	10	10	205	196	20	-2	4	11	337	320	9	-7	9	11	54	62	54
10	733	745	6	3	5	10	77	65	43	10	10	10	94	121	52	0	4	11	108	84	21	-5	9	11	132	150	27
10	384	361	7	5	5	10	568	571	9	-9	11	10	189	196	21	2	4	11	104	139	24	-3	9	11	0	60	1
10	436	434	7	7	5	10	28	12	27	-7	11	10	111	167	40	4	4	11	188	164	14	-1	9	11	91	104	45
10	629	634	6	9	5	10	396	386	11	-5	11	10	74	28	74	6	4	11	97	101	30	1	9	11	81	88	49
10	477	473	7	11	5	10	184	159	19	-3	11	10	0	27	1	8	4	11	154	153	20	3	9	11	210	192	17
10	193	190	12	13	5	10	78	57	64	-1	11	10	0	36	1	10	4	11	390	385	11	5	9	11	79	15	63
10	184	174	15	15	5	10	195	228	20	1	11	10	89	88	55	12	4	11	288	310	13	7	9	11	130	69	29
10	94	80	34	17	5	10	233	244	19	3	11	10	0	2	1	14	4	11	81	91	51	9	9	11	137	92	26
10	163	179	21	19	5	10	64	33	64	5	11	10	278	264	17	16	4	11	94	73	44	11	9	11	69	5	69
10	120	140	31	-20	6	10	142	122	30	7	11	10	160	120	24	18	4	11	265	281	17	13	9	11	179	133	23
10	297	274	14	-18	6	10	517	512	12	-4	12	10	147	140	28	-21	5	11	91	62	51	-12	10	11	228	210	18
10	0	11	1	-16	6	10	286	285	15	-2	12	10	0	40	1	-19	5	11	109	121	37	-10	10	11	161	168	25
10	0	22	1	-14	6	10	194	151	17	0	12	10	89	138	62	-17	5	11	0	106	1	-8	10	11	76	43	75
10	89	32	55	-12	6	10	214	212	16	2	12	10	156	162	27	-15	5	11	453	466	11	-6	10	11	129	115	31
10	360	350	14	-10	6	10	196	203	18	-23	1	11	148	125	29	-13	5	11	660	655	10	-4	10	11	201	198	19
10	410	406	12	-8	6	10	164	162	20	-21	1	11	143	129	27	-11	5	11	915	918	9	-2	10	11	102	133	41
10	502	506	11	-6	6	10	310	312	12	-19	1	11	331	335	13	-9	5	11	102	85	34	0	10	11	334	305	12
10	370	362	11	-4	6	10	639	655	8	-17	1	11	241	253	16	-7	5	11	522	539	9	2	10	11	0	24	1
10	434	417	9	-2	6	10	0	42	1	-15	1	11	754	759	9	-5	5	11	545	548	9	4	10	11	77	63	77
10	243	239	12	0	6	10	277	257	8	-13	1	11	186	184	16	-3	5	11	238	238	12	6	10	11	148	175	25
10	215	231	11	2	6	10	60	12	60	-11	1	11	613	606	8	-1	5	11	491	463	8	8	10	11	0	67	1
10	515	492	7	4	6	10	869	860	8	-9	1	11	116	118	21	1	5	11	410	398	9	10	10	11	220	184	19
10	388	358	7	6	6	10	306	283	12	-7	1	11	124	89	16	3	5	11	0	52	1	-9	11	11	0	21	1
10	655	684	6	8	6	10	229	234	16	-5	1	11	927	961	7	5	5	11	76	98	52	-7	11	11	229	239	19
10	225	208	6	10	6	10	564	558	10	-3	1	11	1443	1415	13	7	5	11	287	280	13	-5	11	11	151	192	28
10	638	648	6	12	6	10	236	241	15	-1	1	11	124	106	15	9	5	11	154	132	21	-3	11	11	167	166	24
10	527	489	7	14	6	10	177	212	21	1	1	11	203	167	11	11	5	11	0	3	1	-1	11	11	41	22	41
10	579	567	7	16	6	10	490	474	12	3	1	11	409	406	8	13	5	11	46	4	45	1	11	11	69	27	68
10	506	519	8	18	6	10	216	196	20	5	1	11	1121	1089	10	15	5	11	124	87	28	3	11	11	0	9	1
10	234	244	14	-19	7	10	301	290	16	7	1	11	41	58	40	17	5	11	55	93	54	5	11	11	104	139	42
10	643	652	9	-17	7	10	174	154	24	9	1	11	716	731	8	19	5	11	203	227	23	7	11	11	171	156	25
10	238	260	16	-15	7	10	301	305	15	11	1	11	355	348	11	-20	6	11	218	192	20	-22	0	12	97	4	48
10	316	333	13	-13	7	10	163	172	23	13	1	11	104	129	37	-18	6	11	155	131	25	-20	0	12	130	139	30
10	0	64	1	-11	7	10	652	637	10	15	1	11	409	404	12	-16	6	11	324	343	14	-18	0	12	192	204	20
10	215	233	19	-9	7	10	502	470	10	17	1	11	239	211	16	-14	6	11	257	265	16	-16	0	12	173	145	20
10	62	13	61	-7	7	10	248	279	15	19	1	11	182	165	21	-12	6	11	241	243	15	-14	0	12	540	527	10
10	182	175	20	-5	7	10	287	289	13	-22	2	11	110	114	39	-10	6	11	144	103	23	-12	0	12	252	241	12
10	331	309	13	-3	7	10	124	78	25	-20	2	11	339	334	13	-8	6	11	0	14	1	-10	0	12	43	17	42
10	121	80	29	-1	7	10	354	370	11	-18	2	11	383	379	12	-6	6	11	517	526	10	-8	0	12	150	119	15
10	273	259	12	1	7	10	147	115	21	-16	2	11	779	789	10	-4	6	11	16	14	15	-6	0	12	723	676	7
10	47	35	46	3	7	10	279	249	13	-14	2	11	0	26	1	-2	6	11	382	397	10	-4	0	12	1328	1276	12
10	0	1	1	5	7	10	258	258	14	-12	2	11	267	278	12	0	6	11	147	148	29	-2	0	12	622	567	7
10	364	348	8	7	7	10	39	24	39	-10	2	11	43	85	42	2	6	11	80	74	51	0	0	12	1790	1788	17
10	127	115	17	9	7	10	240	274	17	-8	2	11	0	32	1	4	6	11	111	122	29	2	0	12	303	305	9
10	525	469	7	11	7	10	394	397	12	-6	2	11	308	267	9	6	6	11	247	249	14	4	0	12	711	714	7
10	0	26	1	13	7	10	20	28	19	-4	2	11	295	336	8	8	6	11	176	172	19	6	0	12	247	256	11
10	169	132	13	15	7	10	0	26	1	-2	2	11	695	706	6	10	6	11	189	171	19	8	0	12	167	116	16
10	1488	1403	14	17	7	10	68	138	67	0	2	11	405	423	5	12	6	11	82	61	54	10	0	12	171	153	17
10	591	577	7	-16	8	10	75	58	75	2	2	11	453	467	8	14	6	11	239	258	18	12	0	12	100	110	35
10	301	301	10	-14	8	10	20	45	20	4	2	11	502	501	8	16	6	11	29	6	29	14	0	12	465	454	11
10	102	54	27	-12	8	10	316	316	14	6	2	11	220	192	12	18	6	11	142	165	29	16	0	12	0	23	1
10	164	157	19	-10	8	10	181	165	19	8	2	11	496	508	9	-19	7	11	159	214	27	18	0	12	0	22	1
10	418	412	11	-8	8	10	351	354	13	10	2	11	0	38	1	-17	7	11	369	370	14	20	0	12	130	135	31
10	354	379	13	-6	8	10	87	3	45	12	2	11	0	44	1	-15	7	11	368	366	13	-21	1	12	0	5	1

l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
12	163	179	22	-5	5	12	524	547	9	-5	11	12	148	76	25	-17	5	13	137	122	27	8	10	13	0	36	1
12	310	297	12	-3	5	12	504	517	9	-3	11	12	302	354	16	-15	5	13	211	195	17	-7	11	13	0	79	1
12	109	144	38	-1	5	12	485	496	9	-1	11	12	0	22	1	-13	5	13	322	317	12	-5	11	13	0	9	1
12	310	317	12	1	5	12	405	405	9	1	11	12	244	212	18	-11	5	13	58	26	58	-3	11	13	205	212	21
12	63	42	62	3	5	12	97	106	31	3	11	12	37	59	36	-9	5	13	622	631	9	-1	11	13	302	296	15
12	66	76	66	5	5	12	168	155	18	5	11	12	52	25	52	-7	5	13	66	68	65	1	11	13	64	57	63
12	238	234	10	7	5	12	0	35	1	-21	1	13	174	191	22	-5	5	13	339	355	11	3	11	13	0	29	1
12	344	352	8	9	5	12	229	228	16	-19	1	13	20	52	19	-3	5	13	199	195	14	-22	0	14	0	51	1
12	86	58	24	11	5	12	145	165	24	-17	1	13	182	187	20	-1	5	13	930	921	8	-20	0	14	281	251	15
12	478	492	7	13	5	12	0	87	1	-15	1	13	413	426	11	1	5	13	308	306	11	-18	0	14	361	347	13
12	798	810	7	15	5	12	171	170	22	-13	1	13	73	89	73	3	5	13	498	455	9	-16	0	14	793	836	10
12	269	286	10	17	5	12	250	240	17	-11	1	13	86	51	39	5	5	13	184	180	17	-14	0	14	495	488	10
12	127	104	19	-18	6	12	176	200	23	-9	1	13	93	118	30	7	5	13	0	17	1	-12	0	14	326	321	11
12	153	163	18	-16	6	12	317	268	14	-7	1	13	58	39	58	9	5	13	493	495	11	-10	0	14	767	767	8
12	688	681	8	-14	6	12	294	325	15	-5	1	13	581	576	7	11	5	13	0	17	1	-8	0	14	193	205	14
12	175	149	18	-12	6	12	187	172	18	-3	1	13	174	151	12	13	5	13	264	247	15	-6	0	14	751	766	8
12	302	322	13	-10	6	12	418	420	11	-1	1	13	1450	1472	14	15	5	13	136	59	26	-4	0	14	440	427	8
12	170	136	20	-8	6	12	24	23	24	1	1	13	127	138	18	17	5	13	0	14	1	-2	0	14	694	691	7
12	286	313	15	-6	6	12	307	301	12	3	1	13	592	596	8	-18	6	13	128	117	30	0	0	14	582	558	8
12	36	46	36	-4	6	12	813	835	8	5	1	13	53	17	53	-16	6	13	0	13	1	2	0	14	278	262	11
12	158	160	24	-2	6	12	129	132	23	7	1	13	0	98	1	-14	6	13	398	390	13	4	0	14	763	723	8
12	129	92	28	0	6	12	115	114	18	9	1	13	264	287	13	-12	6	13	205	195	17	6	0	14	320	313	10
12	274	289	15	2	6	12	205	197	16	11	1	13	0	2	1	-10	6	13	928	913	9	8	0	14	111	154	29
12	317	307	13	4	6	12	60	64	60	13	1	13	74	14	74	-8	6	13	488	500	10	10	0	14	180	168	19
12	472	477	10	6	6	12	242	254	15	15	1	13	125	132	29	-6	6	13	131	130	24	12	0	14	365	363	12
12	559	562	9	8	6	12	0	60	1	17	1	13	94	91	45	-4	6	13	0	42	1	14	0	14	543	545	11
12	69	34	62	10	6	12	489	500	11	19	1	13	0	84	1	-2	6	13	652	650	9	16	0	14	53	16	52
12	793	833	8	12	6	12	201	149	17	-22	2	13	101	20	45	0	6	13	525	525	13	18	0	14	101	35	40
12	630	628	7	14	6	12	297	268	15	-20	2	13	50	24	50	2	6	13	0	5	1	-21	1	14	0	45	1
12	196	148	11	16	6	12	0	28	1	-18	2	13	132	143	28	4	6	13	104	71	36	-19	1	14	80	50	67
12	377	358	8	-17	7	12	256	213	17	-16	2	13	200	218	17	6	6	13	137	93	24	-17	1	14	33	48	32
12	227	239	7	-15	7	12	248	250	17	-14	2	13	105	93	37	8	6	13	154	180	23	-15	1	14	413	422	11
12	933	938	8	-13	7	12	93	114	46	-12	2	13	375	365	11	10	6	13	195	215	19	-13	1	14	189	188	16
12	304	277	10	-11	7	12	390	359	12	-10	2	13	356	360	10	12	6	13	78	24	78	-11	1	14	100	120	31
12	902	880	8	-9	7	12	0	72	1	-8	2	13	531	555	8	14	6	13	143	151	27	-9	1	14	205	175	13
12	233	192	13	-7	7	12	121	105	27	-6	2	13	56	46	56	16	6	13	157	122	24	-7	1	14	48	22	47
12	591	592	9	-5	7	12	93	59	38	-4	2	13	1035	1016	8	-17	7	13	177	194	23	-5	1	14	48	44	48
12	298	307	13	-3	7	12	262	254	14	-2	2	13	312	318	9	-15	7	13	0	59	1	-3	1	14	298	273	9
12	288	303	14	-1	7	12	221	247	15	0	2	13	150	110	11	-13	7	13	299	299	15	-1	1	14	221	174	11
12	133	110	27	1	7	12	293	315	13	2	2	13	636	621	8	-11	7	13	0	55	1	1	1	14	766	771	8
12	102	65	40	3	7	12	219	176	15	4	2	13	153	132	17	-9	7	13	95	94	39	3	1	14	310	332	11
12	84	116	62	5	7	12	163	159	20	6	2	13	780	777	8	-7	7	13	150	128	20	5	1	14	354	376	10
12	101	18	44	7	7	12	423	443	11	8	2	13	126	126	25	-5	7	13	162	186	20	7	1	14	359	342	10
12	0	9	1	9	7	12	630	624	10	10	2	13	97	112	38	-3	7	13	25	81	24	9	1	14	209	236	16
12	268	265	14	11	7	12	277	310	15	12	2	13	163	153	21	-1	7	13	476	448	10	11	1	14	348	347	12
12	460	459	11	13	7	12	128	94	28	14	2	13	0	69	1	1	7	13	255	241	15	13	1	14	69	48	69
12	162	164	21	15	7	12	90	9	53	16	2	13	59	7	59	3	7	13	94	56	38	15	1	14	236	229	17
12	440	440	10	-16	8	12	74	62	73	18	2	13	55	118	54	5	7	13	355	356	12	17	1	14	136	60	25
12	117	92	23	-14	8	12	0	20	1	-21	3	13	147	172	29	7	7	13	42	7	41	19	1	14	101	65	44
12	96	98	28	-12	8	12	327	353	14	-19	3	13	145	101	24	9	7	13	458	454	12	-20	2	14	99	161	47
12	99	124	24	-10	8	12	165	182	22	-17	3	13	51	29	50	11	7	13	0	22	1	-18	2	14	305	287	14
12	421	425	8	-8	8	12	355	365	12	-15	3	13	331	361	13	13	7	13	116	116	35	-16	2	14	184	202	19
12	123	101	17	-6	8	12	296	297	13	-13	3	13	951	951	9	15	7	13	37	61	37	-14	2	14	561	558	10
12	237	222	11	-4	8	12	0	24	1	-11	3	13	225	226	15	-16	8	13	0	15	1	-12	2	14	314	313	12
12	0	61	1	-2	8	12	36	30	35	-9	3	13	478	471	9	-14	8	13	97	125	47	-10	2	14	306	321	11
12	238	253	12	0	8	12	30	8	29	-7	3	13	595	574	8	-12	8	13	0	115	1	-8	2	14	52	61	51
12	407	397	10	2	8	12	389	386	11	-5	3	13	163	136	15	-10	8	13	211	244	18	-6	2	14	94	92	29
12	43	60	43	4	8	12	257	280	15	-3	3	13	99	82	24	-8	8	13	119	96	30	-4	2	14	602	629	8
12	147	159	24	6	8	12	127	135	28	-1	3	13	135	132	16	-6	8	13	249	232	15	-2	2	14	368	392	9
12	145	127	22	8	8	12	0	75	1	1	3	13	455	459	8	-4	8	13	187	211	19	0	2	14	337	340	8
12	0	59	1	10	8	12	28	64	28	3	3	13	15	102	14	-2	8	13	455	467	11	2	2	14	434	406	9
12	196	205	21	12	8	12	51	65	50	5	3	13	78	98	44	0	8	13	191	199	12	4	2	14	246	250	13
12	149	145	27	14	8	12	119	78	34	7	3	13	120	131	25	2	8	13	121	93	29	6	2	14	863	861	8
12	0	51	1	-15	9	12	150	184	30	9	3	13	77	56	60	4	8	13	37	122	37	8	2	14	368	377	11
12	242	219	16	-13	9	12	21	4	20	11	3	13	0	14	1	6	8	13	103	103	36	10	2	14	30	89	30
12	84	1	47	-11	9	12	206	187	20	13	3	13	32	16	32	8	8	13	0	22	1	12	2	14	141	146	25
12	419	441	12	-9	9	12	40	3	39	15	3	13	273	284	16	10	8	13	88	115	52	14	2	14	0	51	1
12	232	231	16	-7	9	12	43	69	43	17	3	13	328	355	15	12	8	13	42	33	41	16	2	14	0	38	1
12	171	157	18	-5	9	12	57	71	57	19	3	13	53	5	52	-13	9	13	0	105	1	18	2	14	122	147	35
12	264	251	12	-3	9	12	190	208	19	-20	4	13	70	13	69	-11	9	13	0	26	1	-21	3	14	30	46	30
12	143	146	17	-1	9	12	46	15	46	-18	4	13	244	285	16	-9	9	13	282	294	15	-19	3	14	41	51	40
12	498	504	8	1	9	12	112	31	30	-16	4	13	0	26	1	-7	9	13	393	380	13	-17	3	14	0	49	1
12	308	300	10	3	9	12	121	78	29	-14	4	13	123	114	27	-5	9	13	73	98	72	-15	3	14	249	251	15
12	0	10	1	5	9	12	76	17	75	-12	4	13	847	857	9	-3	9	13	74	26	74	-13	3	14	267	229	14
12	819	815	8	7	9	12	116	104	35	-10	4	13	377	375	11	-1	9	13	380	389	12	-11	3	14	332	349	12
12	115	100	24	9	9	12	61	75	61	-8	4	13	230	235	14	1	9	13	109	120	34	-9	3	14	0	45	1
12	556	579	9	11	9	12	167	126	23	-6	4	13	58	78	58	3	9	13	0	39	1	-7	3	14	805	853	8
12	255	241	14	-12	10	12	256	240	17	-4	4	13	0	5	1	5	9	13	251	288	17	-5	3	14	43	29	43
12	330	345	13	-10	10	12	121	34	32	-2	4	13	0	8	1	7	9	13	176	178	23	-3	3	14	240	240	12
12	269	276	14	-8	10	12	188	184	21	0	4	13	396	382	6	9	9	13	62	20	62	-1	3	14	220	215	12
12	208	214	17	-6	10	12	99	4	38	2	4	13	0	14	1	11	9	13	159	86	24	1	3	14	124	97	22
12	106	59	38	-4	10	12	239	225	17	4	4	13	213	207	14	-10	10	13	331	324	15	3	3	14	258	249	12
12	155	110	24	-2	10	12	74	77	74	6	4	13	352	344	11	-8	10	13	264	254	17	5	3	14	240	230	13
12	115	127	37	0	10	12	219	205	12	8	4	13	63	17	63	-6	10	13	98	89	45	7	3	14	410	392	10
12	39	12	39	2	10	12	320	335	14	10	4	13	66	44	65	-4	10	13	86	162	61	9	3	14	332	346	12
12	162	151	22	4	10	12	171	125	22	12	4	13	0	10	1	-2	10	13	95	53	44	11	3	14	31	33	31
12	222	214	17	6	10	12	124	129	34	14	4	13	251	216	15	0	10	13	200	200	14	13	3	14	50	20	49
12	101	80	42	8	10	12	151	163	26	16	4	13	0	27	1	2	10	13	141	94	26	15	3	14	63	65	62
12	0	8	1	10	10	12	43	63	43	18	4	13	248	264	18	4	10	13	109	100	37	17	3	14	164	128	25
12	108	110	28	-7	11	12	174	191	24	-19	5	13	0	86	1	6	10	13	187	152	21	-20	4	14	0	20	1

l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
14	0	43	1	-7	9	14	122	88	30	-6	4	15	297	270	12	-4	10	15	0	7	1	-6	4	16	786	812	9
14	164	182	22	-5	9	14	106	34	37	-4	4	15	130	150	23	-2	10	15	21	15	20	-4	4	16	409	409	10
14	508	491	11	-3	9	14	122	37	29	-2	4	15	0	9	1	0	10	15	68	42	67	-2	4	16	74	81	73
14	282	310	14	-1	9	14	166	173	22	0	4	15	201	184	11	2	10	15	96	50	53	0	4	16	787	788	6
14	493	490	10	1	9	14	44	99	43	2	4	15	123	61	26	4	10	15	206	193	21	2	4	16	253	225	14
14	805	813	9	3	9	14	200	201	20	4	4	15	261	258	14	6	10	15	0	22	1	4	4	16	614	628	9
14	194	172	15	5	9	14	166	161	24	6	4	15	410	436	11	-20	0	16	113	90	38	6	4	16	115	78	27
14	733	736	8	7	9	14	133	152	30	8	4	15	281	290	13	-18	0	16	353	344	13	8	4	16	83	37	47
14	56	85	56	9	9	14	130	157	31	10	4	15	377	389	12	-16	0	16	0	14	1	10	4	16	341	351	13
14	404	385	14	11	9	14	108	14	40	12	4	15	125	105	28	-14	0	16	100	113	34	12	4	16	186	150	20
14	254	241	12	-10	10	14	190	146	21	14	4	15	130	150	30	-12	0	16	410	420	11	14	4	16	87	51	56
14	337	328	11	-8	10	14	21	68	20	16	4	15	63	51	63	-10	0	16	118	64	25	16	4	16	139	191	31
14	579	580	9	-6	10	14	0	18	1	-19	5	15	123	124	34	-8	0	16	189	189	14	-17	5	16	91	8	49
14	95	52	39	-4	10	14	145	109	25	-17	5	15	105	81	35	-6	0	16	42	20	41	-15	5	16	269	242	16
14	217	192	17	-2	10	14	119	148	32	-15	5	15	0	74	1	-4	0	16	265	251	11	-13	5	16	19	39	19
14	80	47	58	0	10	14	106	38	24	-13	5	15	114	70	32	-2	0	16	256	253	11	-11	5	16	194	160	17
14	0	44	1	2	10	14	251	287	18	-11	5	15	363	336	12	0	0	16	208	216	15	-9	5	16	206	177	17
14	0	2	1	4	10	14	21	3	20	-9	5	15	1044	1027	9	2	0	16	614	596	8	-7	5	16	86	75	50
14	84	15	73	6	10	14	228	219	19	-7	5	15	848	862	9	4	0	16	518	501	9	-5	5	16	826	820	9
14	261	219	16	8	10	14	0	31	1	-5	5	15	191	183	17	6	0	16	144	114	21	-3	5	16	30	51	29
14	45	20	45	-5	11	14	48	41	48	-3	5	15	151	156	22	8	0	16	340	325	12	-1	5	16	817	834	9
14	323	344	14	-3	11	14	118	55	33	-1	5	15	83	94	44	10	0	16	0	75	1	1	5	16	55	78	54
14	107	79	31	-1	11	14	0	2	1	1	5	15	129	131	26	12	0	16	171	190	21	3	5	16	35	65	35
14	186	172	18	1	11	14	0	3	1	3	5	15	500	482	10	14	0	16	175	172	22	5	5	16	62	55	61
14	463	446	11	-21	1	15	111	78	36	5	5	15	212	215	17	16	0	16	300	291	15	7	5	16	0	18	1
14	116	77	26	-19	1	15	272	265	15	7	5	15	142	119	25	18	0	16	169	148	25	9	5	16	133	130	26
14	206	186	15	-17	1	15	235	238	17	9	5	15	19	16	18	-21	1	16	101	7	40	11	5	16	81	26	65
14	201	199	15	-15	1	15	305	313	13	11	5	15	132	11	26	-19	1	16	183	188	22	13	5	16	128	98	29
14	0	37	1	-13	1	15	195	221	18	13	5	15	0	9	1	-17	1	16	187	222	20	15	5	16	0	71	1
14	561	564	9	-11	1	15	92	69	35	15	5	15	105	101	40	-15	1	16	427	452	12	-16	6	16	194	192	21
14	81	13	51	-9	1	15	58	102	58	-18	6	15	193	156	21	-13	1	16	368	364	11	-14	6	16	0	35	1
14	105	86	31	-7	1	15	406	402	9	-16	6	15	101	118	44	-11	1	16	126	124	27	-12	6	16	160	170	23
14	219	191	15	-5	1	15	96	52	25	-14	6	15	119	114	32	-9	1	16	184	187	17	-10	6	16	0	10	1
14	0	57	1	-3	1	15	235	271	12	-12	6	15	175	163	20	-7	1	16	243	250	13	-8	6	16	0	79	1
14	109	22	30	-1	1	15	100	56	21	-10	6	15	0	31	1	-5	1	16	227	205	12	-6	6	16	107	107	32
14	65	64	65	1	1	15	357	324	10	-8	6	15	104	111	33	-3	1	16	338	354	10	-4	6	16	603	586	10
14	0	16	1	3	1	15	438	440	9	-6	6	15	164	188	21	-1	1	16	532	560	8	-2	6	16	226	280	16
14	86	43	67	5	1	15	517	521	9	-4	6	15	259	251	14	1	1	16	410	380	9	0	6	16	80	35	30
14	116	103	33	7	1	15	337	339	11	-2	6	15	343	333	12	3	1	16	331	312	11	2	6	16	237	211	15
14	314	313	15	9	1	15	0	28	1	0	6	15	74	70	37	5	1	16	234	251	15	4	6	16	117	109	28
14	425	429	12	11	1	15	92	88	38	2	6	15	139	99	23	7	1	16	93	55	39	6	6	16	95	90	41
14	0	33	1	13	1	15	458	490	11	4	6	15	76	116	75	9	1	16	25	52	24	8	6	16	19	69	19
14	789	772	10	15	1	15	271	269	16	6	6	15	120	43	28	11	1	16	191	191	18	10	6	16	118	40	32
14	519	520	10	17	1	15	0	65	1	8	6	15	94	40	38	13	1	16	223	216	17	12	6	16	0	2	1
14	890	866	9	-20	2	15	120	97	35	10	6	15	85	83	55	15	1	16	35	85	35	14	6	16	0	40	1
14	0	42	1	-18	2	15	0	18	1	12	6	15	145	97	24	17	1	16	156	143	25	-15	7	16	0	2	1
14	162	146	20	-16	2	15	78	80	64	14	6	15	79	86	78	-20	2	16	235	205	17	-13	7	16	193	161	20
14	266	236	9	-14	2	15	146	140	22	-17	7	15	0	54	1	-18	2	16	99	18	41	-11	7	16	118	111	33
14	57	45	56	-12	2	15	192	202	17	-15	7	15	0	7	1	-16	2	16	311	320	13	-9	7	16	70	6	69
14	348	343	12	-10	2	15	83	89	42	-13	7	15	227	215	18	-14	2	16	52	25	52	-7	7	16	213	226	16
14	200	174	17	-8	2	15	232	225	13	-11	7	15	167	188	22	-12	2	16	165	119	18	-5	7	16	95	66	34
14	67	86	66	-6	2	15	312	307	10	-9	7	15	66	4	65	-10	2	16	426	418	11	-3	7	16	83	77	47
14	43	5	42	-4	2	15	363	377	10	-7	7	15	152	136	21	-8	2	16	104	105	27	-1	7	16	345	343	13
14	111	66	35	-2	2	15	669	671	8	-5	7	15	0	1	1	-6	2	16	174	148	15	1	7	16	588	576	10
14	267	249	16	0	2	15	366	357	6	-3	7	15	152	115	21	-4	2	16	499	500	9	3	7	16	379	418	13
14	65	75	64	2	2	15	778	764	8	-1	7	15	327	328	12	-2	2	16	260	249	11	5	7	16	139	105	25
14	64	30	64	4	2	15	217	212	14	1	7	15	165	149	21	0	2	16	396	396	9	7	7	16	264	272	16
14	74	117	74	6	2	15	246	245	13	3	7	15	388	408	12	2	2	16	339	327	11	9	7	16	78	103	78
14	99	114	43	8	2	15	38	20	37	5	7	15	146	115	24	4	2	16	617	618	9	11	7	16	185	222	23
14	387	379	12	10	2	15	264	223	13	7	7	15	262	243	15	6	2	16	184	182	18	13	7	16	68	74	68
14	212	198	17	12	2	15	145	163	22	9	7	15	0	38	1	8	2	16	99	50	34	-14	8	16	218	193	19
14	161	135	20	14	2	15	110	40	32	11	7	15	172	175	24	10	2	16	305	344	13	-12	8	16	162	139	24
14	255	252	14	16	2	15	35	26	35	13	7	15	82	37	64	12	2	16	144	108	25	-10	8	16	269	255	16
14	132	143	25	18	2	15	37	79	37	-14	8	15	0	26	1	14	2	16	0	56	1	-8	8	16	0	55	1
14	79	117	60	-19	3	15	311	316	15	-12	8	15	105	58	36	16	2	16	168	133	23	-6	8	16	116	158	32
14	143	118	22	-17	3	15	79	97	78	-10	8	15	85	63	56	-19	3	16	0	26	1	-4	8	16	0	13	1
14	0	5	1	-15	3	15	395	395	12	-8	8	15	297	312	14	-17	3	16	98	81	39	-2	8	16	0	3	1
14	64	55	63	-13	3	15	173	170	19	-6	8	15	195	200	18	-15	3	16	72	112	71	0	8	16	78	78	78
14	123	119	27	-11	3	15	715	724	9	-4	8	15	183	171	19	-13	3	16	61	59	61	2	8	16	127	194	34
14	39	70	39	-9	3	15	69	53	68	-2	8	15	73	121	73	-11	3	16	335	328	12	4	8	16	117	121	31
14	53	16	53	-7	3	15	171	186	18	0	8	15	338	326	9	-9	3	16	111	81	28	6	8	16	111	139	38
14	0	23	1	-5	3	15	560	582	9	2	8	15	177	161	20	-7	3	16	781	776	9	8	8	16	216	225	19
14	119	19	31	-3	3	15	293	297	11	4	8	15	61	21	61	-5	3	16	108	66	28	10	8	16	183	248	25
14	113	95	35	-1	3	15	81	91	38	6	8	15	333	364	14	-3	3	16	299	290	11	-11	9	16	71	103	71
14	174	170	22	1	3	15	110	143	27	8	8	15	115	112	33	-1	3	16	0	1	1	-9	9	16	174	168	23
14	101	107	41	3	3	15	358	351	10	10	8	15	113	106	38	1	3	16	233	235	14	-7	9	16	273	261	16
14	47	33	47	5	3	15	203	228	16	12	8	15	122	87	35	3	3	16	240	215	14	-5	9	16	251	226	17
14	165	153	21	7	3	15	213	228	17	-11	9	15	0	48	1	5	3	16	142	143	23	-3	9	16	40	76	40
14	255	234	14	9	3	15	193	177	16	-9	9	15	284	273	15	7	3	16	185	187	18	-1	9	16	128	126	29
14	19	50	18	11	3	15	417	417	11	-7	9	15	194	207	21	9	3	16	60	21	60	1	9	16	0	6	1
14	55	43	54	13	3	15	138	115	24	-5	9	15	329	339	15	11	3	16	0	19	1	3	9	16	65	69	64
14	208	202	17	15	3	15	353	347	14	-3	9	15	392	393	12	13	3	16	0	35	1	5	9	16	120	37	30
14	0	137	1	17	3	15	52	5	52	-1	9	15	49	42	48	15	3	16	80	113	79	7	9	16	0	29	1
14	199	177	18	-20	4	15	125	89	33	1	9	15	45	43	44	17	3	16	0	48	1	-8	10	16	69	72	68
14	85	80	55	-18	4	15	46	68	45	3	9	15	29	27	28	-18	4	16	0	2	1	-6	10	16	111	29	33
14	74	3	74	-16	4	15	160	131	22	5	9	15	164	148	25	-16	4	16	348	356	14	-4	10	16	122	137	31
14	56	9	56	-14	4	15	305	307	13	7	9	15	93	39	45	-14	4	16	211	221	18	-2	10	16	0	81	1
14	166	149	24	-12	4	15	0	120	1	9	9	15	52	71	52	-12	4	16	216	211	16	0	10	16	247	232	12
14	106	69	41	-10	4	15	523	539	10	-8	10	15	60	43	60	-10	4	16	424	430	11	2	10	16	0	14	1
14	131	48	27	-8	4	15	844	865	9	-6	10	15	82	49	65	-8	4	16	77	45	77	4	10	16	208	235	21

l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
17	66	30	66	-14	6	17	74	10	74	-18	2	18	120	102	32	-1	7	18	64	74	64	10	4	19	149	128	25
17	91	25	45	-12	6	17	20	2	19	-16	2	18	20	21	20	1	7	18	34	119	33	12	4	19	127	98	31
17	0	87	1	-10	6	17	89	15	41	-14	2	18	0	78	1	3	7	18	90	13	47	-15	5	19	0	2	1
17	52	9	51	-8	6	17	191	184	17	-12	2	18	136	60	22	5	7	18	290	277	15	-13	5	19	208	172	19
17	83	31	44	-6	6	17	103	79	34	-10	2	18	78	37	53	7	7	18	133	113	30	-11	5	19	134	138	31
17	54	30	53	-4	6	17	568	560	10	-8	2	18	49	22	49	9	7	18	0	54	1	-9	5	19	240	236	15
17	150	142	20	-2	6	17	397	415	11	-6	2	18	113	121	28	11	7	18	78	125	78	-7	5	19	0	9	1
17	213	222	13	0	6	17	309	297	9	-4	2	18	192	194	16	-12	8	18	89	97	63	-5	5	19	614	624	10
17	371	355	10	2	6	17	0	2	1	-2	2	18	466	471	10	-10	8	18	183	149	20	-3	5	19	49	22	49
17	306	310	11	4	6	17	237	204	15	0	2	18	197	168	11	-8	8	18	113	25	34	-1	5	19	741	745	10
17	596	600	9	6	6	17	81	96	65	2	2	18	131	162	26	-6	8	18	195	210	21	1	5	19	0	34	1
17	228	234	15	8	6	17	139	195	29	4	2	18	368	353	12	-4	8	18	40	16	40	3	5	19	73	88	73
17	309	305	13	10	6	17	0	99	1	6	2	18	284	272	13	-2	8	18	212	214	18	5	5	19	131	83	27
17	297	264	13	12	6	17	0	33	1	8	2	18	112	33	29	0	8	18	201	217	14	7	5	19	127	104	30
17	125	133	27	-15	7	17	37	55	37	10	2	18	94	80	44	2	8	18	140	131	30	9	5	19	120	132	32
17	33	36	32	-13	7	17	47	15	46	12	2	18	0	16	1	4	8	18	263	285	16	11	5	19	119	82	34
17	86	12	56	-11	7	17	76	37	75	14	2	18	162	151	25	6	8	18	124	129	32	-14	6	19	144	204	29
17	120	56	33	-9	7	17	0	45	1	16	2	18	75	98	75	8	8	18	107	86	44	-12	6	19	203	192	19
17	0	33	1	-7	7	17	72	98	72	-19	3	18	43	69	43	-9	9	18	84	69	54	-10	6	19	45	53	44
17	37	88	37	-5	7	17	205	193	16	-17	3	18	166	166	23	-7	9	18	43	16	42	-8	6	19	110	148	35
17	50	44	50	-3	7	17	450	455	11	-15	3	18	0	13	1	-5	9	18	155	125	25	-6	6	19	108	45	32
17	221	240	18	-1	7	17	214	198	17	-13	3	18	166	156	22	-3	9	18	107	100	39	-4	6	19	127	89	26
17	46	6	46	1	7	17	38	17	38	-11	3	18	168	177	21	-1	9	18	0	47	1	-2	6	19	131	66	26
17	110	44	29	3	7	17	227	205	17	-9	3	18	130	138	26	1	9	18	121	60	31	0	6	19	16	16	16
17	0	32	1	5	7	17	119	81	30	-7	3	18	88	95	44	3	9	18	0	48	1	2	6	19	321	323	14
17	0	60	1	7	7	17	119	138	35	-5	3	18	284	255	13	5	9	18	174	187	24	4	6	19	0	16	1
17	172	161	16	9	7	17	36	42	35	-3	3	18	475	481	10	-19	1	19	57	11	57	6	6	19	49	93	49
17	73	100	55	11	7	17	0	19	1	-1	3	18	178	181	17	-17	1	19	124	71	28	8	6	19	180	202	22
17	273	300	12	-12	8	17	223	178	18	1	3	18	168	149	20	-15	1	19	203	189	18	10	6	19	0	5	1
17	607	620	6	-10	8	17	59	37	58	3	3	18	0	20	1	-13	1	19	79	3	54	-13	7	19	218	199	18
17	351	338	11	-8	8	17	91	38	42	5	3	18	406	404	11	-11	1	19	108	123	31	-11	7	19	0	73	1
17	181	198	19	-6	8	17	77	48	77	7	3	18	274	294	13	-9	1	19	203	203	16	-9	7	19	0	77	1
17	241	248	14	-4	8	17	120	129	29	9	3	18	113	115	34	-7	1	19	322	332	12	-7	7	19	0	61	1
17	97	39	34	-2	8	17	59	80	59	11	3	18	59	104	59	-5	1	19	120	135	25	-5	7	19	82	21	58
17	426	431	11	0	8	17	117	137	22	13	3	18	231	222	18	-3	1	19	463	456	10	-3	7	19	103	129	38
17	143	172	26	2	8	17	211	223	19	15	3	18	91	0	49	-1	1	19	158	172	20	-1	7	19	0	30	1
17	156	126	24	4	8	17	0	63	1	-18	4	18	0	8	1	1	1	19	648	652	9	1	7	19	80	8	66
17	201	177	20	6	8	17	0	27	1	-16	4	18	0	27	1	3	1	19	259	275	15	3	7	19	0	41	1
17	80	46	71	8	8	17	149	176	28	-14	4	18	0	53	1	5	1	19	0	15	1	5	7	19	0	23	1
17	239	233	17	10	8	17	75	85	75	-12	4	18	61	64	60	7	1	19	186	196	20	7	7	19	94	128	51
17	563	599	11	-9	9	17	74	113	73	-10	4	18	0	28	1	9	1	19	0	31	1	9	7	19	0	39	1
17	569	569	11	-7	9	17	0	93	1	-8	4	18	229	243	17	11	1	19	364	367	13	-10	8	19	115	63	33
17	418	450	11	-5	9	17	131	167	29	-6	4	18	651	657	10	13	1	19	124	112	32	-8	8	19	182	224	23
17	680	682	9	-3	9	17	240	270	17	-4	4	18	733	729	9	15	1	19	91	63	57	-6	8	19	29	80	29
17	134	85	23	-1	9	17	87	62	54	-2	4	18	951	952	9	-18	2	19	126	69	30	-4	8	19	304	290	14
17	329	328	11	1	9	17	59	76	58	0	4	18	708	708	7	-16	2	19	169	168	22	-2	8	19	112	46	31
17	553	562	9	3	9	17	236	232	18	2	4	18	441	457	11	-14	2	19	187	187	19	0	8	19	197	201	14
17	237	227	14	5	9	17	21	53	21	4	4	18	315	307	13	-12	2	19	215	228	17	2	8	19	78	73	77
17	74	22	74	7	9	17	0	14	1	6	4	18	276	259	14	-10	2	19	0	95	1	4	8	19	265	250	17
17	0	88	1	-4	10	17	122	53	33	8	4	18	155	138	23	-8	2	19	153	200	20	6	8	19	238	239	18
17	139	168	25	-2	10	17	276	238	16	10	4	18	0	2	1	-6	2	19	56	62	55	-5	9	19	0	83	1
17	47	86	47	0	10	17	0	15	1	12	4	18	0	26	1	-4	2	19	194	189	15	-3	9	19	48	20	47
17	130	121	25	2	10	17	43	12	43	14	4	18	185	188	23	-2	2	19	422	418	10	-1	9	19	179	197	22
17	229	204	16	-20	0	18	191	189	22	-17	5	18	68	71	67	0	2	19	413	438	10	1	9	19	96	115	49
17	40	48	40	-18	0	18	325	319	14	-15	5	18	0	95	1	2	2	19	502	492	10	3	9	19	48	20	48
17	220	159	18	-16	0	18	232	221	16	-13	5	18	96	32	40	4	2	19	155	128	22	-18	0	20	216	217	19
17	85	28	63	-14	0	18	316	319	13	-11	5	18	237	234	16	6	2	19	243	248	16	-16	0	20	58	1	58
17	103	85	38	-12	0	18	76	28	56	-9	5	18	42	19	42	8	2	19	0	59	1	-14	0	20	558	587	11
17	81	60	70	-10	0	18	166	173	18	-7	5	18	92	66	35	10	2	19	159	119	23	-12	0	20	430	441	11
17	310	311	13	-8	0	18	89	6	36	-5	5	18	295	304	13	12	2	19	100	99	44	-10	0	20	664	743	10
17	685	681	10	-6	0	18	474	459	10	-3	5	18	31	52	31	14	2	19	88	111	58	-8	0	20	446	436	11
17	728	721	9	-4	0	18	349	332	10	-1	5	18	241	214	14	-17	3	19	149	118	25	-6	0	20	118	149	27
17	201	168	17	-2	0	18	180	203	16	1	5	18	248	238	15	-15	3	19	86	1	50	-4	0	20	53	6	52
17	595	610	9	0	0	18	89	57	42	3	5	18	94	93	42	-13	3	19	116	142	31	-2	0	20	134	167	22
17	305	292	12	2	0	18	687	731	9	5	5	18	0	22	1	-11	3	19	50	82	50	0	0	20	200	156	17
17	166	163	14	4	0	18	269	278	14	7	5	18	134	126	28	-9	3	19	297	275	13	2	0	20	67	73	66
17	0	27	1	6	0	18	373	372	12	9	5	18	28	40	28	-7	3	19	350	372	12	4	0	20	413	400	11
17	251	258	15	8	0	18	153	142	22	11	5	18	184	200	23	-5	3	19	446	475	11	6	0	20	153	145	23
17	79	63	58	10	0	18	89	27	44	13	5	18	98	74	43	-3	3	19	665	640	9	8	0	20	96	25	41
17	0	32	1	12	0	18	0	20	1	-16	6	18	0	37	1	-1	3	19	869	881	9	10	0	20	20	19	19
17	0	2	1	14	0	18	0	24	1	-14	6	18	164	165	24	1	3	19	18	63	17	12	0	20	0	15	1
17	40	82	40	16	0	18	61	107	60	-12	6	18	0	2	1	3	3	19	308	318	13	14	0	20	114	125	37
17	63	86	62	-19	1	18	0	53	1	-10	6	18	68	78	68	5	3	19	314	303	13	-17	1	20	0	8	1
17	123	141	32	-17	1	18	89	48	51	-8	6	18	64	66	64	7	3	19	350	349	13	-15	1	20	138	105	26
17	155	145	24	-15	1	18	176	213	20	-6	6	18	248	217	15	9	3	19	345	348	13	-13	1	20	128	103	25
17	48	82	48	-13	1	18	117	143	28	-4	6	18	569	587	11	11	3	19	158	165	24	-11	1	20	288	281	13
17	268	300	15	-11	1	18	141	172	22	-2	6	18	480	431	11	13	3	19	73	83	72	-9	1	20	291	282	13
17	589	577	10	-9	1	18	329	323	12	0	6	18	88	104	28	-16	4	19	51	57	51	-7	1	20	54	2	54
17	79	102	67	-7	1	18	82	2	43	2	6	18	264	276	15	-14	4	19	64	27	64	-5	1	20	80	29	44
17	804	806	9	-5	1	18	254	252	13	4	6	18	0	81	1	-12	4	19	106	79	35	-3	1	20	77	74	53
17	537	516	10	-3	1	18	95	57	28	6	6	18	199	204	19	-10	4	19	202	181	18	-1	1	20	316	304	12
17	474	455	10	-1	1	18	107	56	26	8	6	18	228	233	18	-8	4	19	221	216	16	1	1	20	443	429	11
17	112	74	31	1	1	18	33	23	33	10	6	18	0	23	1	-6	4	19	260	272	15	3	1	20	633	620	10
17	189	162	18	3	1	18	211	211	17	12	6	18	142	119	27	-4	4	19	251	271	15	5	1	20	175	165	19
17	142	156	24	5	1	18	95	48	39	-13	7	18	60	104	59	-2	4	19	353	329	12	7	1	20	50	92	50
17	369	364	13	7	1	18	176	205	20	-11	7	18	41	87	41	0	4	19	305	304	9	9	1	20	255	215	15
17	269	287	15	9	1	18	70	44	69	-9	7	18	45	91	45	2	4	19	331	331	13	11	1	20	29	32	28
17	53	5	53	11	1	18	185	223	21	-7	7	18	177	166	19	4	4	19	473	474	11	13	1	20	0	65	1
17	124	80	30	13	1	18	73	15	72	-5	7	18	0	15	1	6	4	19	87	61	46	-18	2	20	0	45	1
17	0	40	1	15	1	18	0	9	1	-3	7	18	591	593	11	8	4	19	131	150	27	-16	2	20	0	26	1

l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
20	133	174	27	-17	1	21	0	24	1	-4	8	21	37	45	37	0	6	22	440	442	9	-13	1	24	77	44	77
20	141	225	26	-15	1	21	72	7	71	-2	8	21	103	81	40	2	6	22	59	77	58	-11	1	24	190	181	19
20	160	158	20	-13	1	21	20	96	19	0	8	21	79	63	46	4	6	22	366	371	14	-9	1	24	0	41	1
20	118	66	27	-11	1	21	108	115	35	2	8	21	199	187	21	6	6	22	0	88	1	-7	1	24	70	131	69
20	340	351	12	-9	1	21	335	362	12	-16	0	22	52	2	52	-7	7	22	191	161	21	-5	1	24	63	26	62
20	261	268	14	-7	1	21	303	301	13	-14	0	22	208	231	18	-5	7	22	90	95	48	-3	1	24	52	44	52
20	367	353	11	-5	1	21	55	82	54	-12	0	22	161	167	22	-3	7	22	118	71	32	-1	1	24	154	154	22
20	117	121	20	-3	1	21	273	262	13	-10	0	22	311	340	13	-1	7	22	141	143	26	1	1	24	173	155	22
20	597	595	10	-1	1	21	495	466	10	-8	0	22	165	181	22	1	7	22	128	109	33	3	1	24	0	84	1
20	99	39	33	1	1	21	343	351	13	-6	0	22	170	198	20	3	7	22	230	226	20	5	1	24	206	168	19
20	137	181	27	3	1	21	320	294	13	-4	0	22	0	16	1	-15	1	23	0	8	1	7	1	24	260	274	18
20	246	246	16	5	1	21	292	286	14	-2	0	22	0	40	1	-13	1	23	78	30	78	9	1	24	97	116	54
20	138	90	27	7	1	21	98	82	45	0	0	22	900	887	10	-11	1	23	166	167	22	-12	2	24	175	154	21
20	112	21	36	9	1	21	291	298	15	2	0	22	167	157	23	-9	1	23	382	393	13	-10	2	24	106	104	40
20	48	73	48	11	1	21	229	238	18	4	0	22	452	442	12	-7	1	23	0	41	1	-8	2	24	0	54	1
20	93	99	49	13	1	21	110	10	35	6	0	22	420	398	12	-5	1	23	402	404	12	-6	2	24	20	104	20
20	21	39	20	-16	2	21	176	171	23	8	0	22	146	161	27	-3	1	23	0	15	1	-4	2	24	184	161	19
20	0	38	1	-14	2	21	77	101	76	10	0	22	161	118	24	-1	1	23	399	406	12	-2	2	24	28	40	28
20	78	16	54	-12	2	21	186	180	19	12	0	22	167	177	25	1	1	23	169	158	22	0	2	24	63	4	62
20	121	132	27	-10	2	21	254	248	15	-15	1	22	73	7	73	3	1	23	159	166	25	2	2	24	45	47	45
20	139	186	26	-8	2	21	383	395	12	-13	1	22	247	234	16	5	1	23	0	41	1	4	2	24	71	104	71
20	0	13	1	-6	2	21	19	72	18	-11	1	22	372	398	13	7	1	23	65	66	65	6	2	24	380	362	14
20	307	287	13	-4	2	21	41	73	41	-9	1	22	89	45	44	9	1	23	137	121	28	8	2	24	81	58	80
20	276	261	13	-2	2	21	427	429	11	-7	1	22	186	231	18	-14	2	23	100	3	39	-11	3	24	97	93	45
20	381	380	12	0	2	21	634	638	7	-5	1	22	88	77	36	-12	2	23	222	241	18	-9	3	24	0	8	1
20	130	174	29	2	2	21	278	279	14	-3	1	22	26	48	26	-10	2	23	0	53	1	-7	3	24	85	27	52
20	104	99	38	4	2	21	0	8	1	-1	1	22	0	25	1	-8	2	23	85	74	49	-5	3	24	84	124	56
20	39	15	38	6	2	21	34	78	33	1	1	22	78	90	77	-6	2	23	137	90	23	-3	3	24	149	111	23
20	0	24	1	8	2	21	116	79	34	3	1	22	191	206	20	-4	2	23	44	43	43	-1	3	24	0	1	1
20	0	15	1	10	2	21	21	84	20	5	1	22	0	15	1	-2	2	23	87	110	42	1	3	24	123	103	32
20	103	112	48	12	2	21	109	84	39	7	1	22	90	114	57	0	2	23	97	10	39	3	3	24	21	36	20
20	77	94	77	-15	3	21	138	126	27	9	1	22	0	78	1	2	2	23	192	157	20	5	3	24	228	216	19
20	36	3	35	-13	3	21	170	158	19	11	1	22	77	109	76	4	2	23	180	181	23	7	3	24	61	84	60
20	0	78	1	-11	3	21	190	210	18	-16	2	22	53	34	53	6	2	23	79	125	79	-10	4	24	140	130	26
20	34	73	33	-9	3	21	67	66	67	-14	2	22	81	137	74	8	2	23	56	26	55	-8	4	24	168	177	23
20	91	117	45	-7	3	21	83	78	48	-12	2	22	158	126	22	10	2	23	0	26	1	-6	4	24	219	157	17
20	492	479	11	-5	3	21	101	14	31	-10	2	22	77	17	55	-13	3	23	172	169	24	-4	4	24	46	29	46
20	311	304	13	-3	3	21	37	71	37	-8	2	22	118	72	27	-11	3	23	150	141	26	-2	4	24	170	151	21
20	226	223	15	-1	3	21	56	95	56	-6	2	22	0	8	1	-9	3	23	102	144	37	0	4	24	105	71	25
20	696	691	7	1	3	21	364	379	12	-4	2	22	0	6	1	-7	3	23	227	273	17	2	4	24	162	152	25
20	500	499	11	3	3	21	461	416	11	-2	2	22	116	93	27	-5	3	23	59	144	59	4	4	24	63	95	63
20	586	585	11	5	3	21	410	408	13	0	2	22	117	109	32	-3	3	23	535	522	11	6	4	24	84	35	83
20	139	154	29	7	3	21	93	9	46	2	2	22	223	172	16	-1	3	23	343	304	13	-9	5	24	0	2	1
20	45	4	44	9	3	21	205	167	20	4	2	22	214	211	17	1	3	23	112	88	34	-7	5	24	80	24	79
20	0	2	1	11	3	21	173	207	24	6	2	22	120	142	34	3	3	23	106	75	40	-5	5	24	0	25	1
20	43	80	42	-14	4	21	110	91	34	8	2	22	182	138	20	5	3	23	260	240	16	-3	5	24	0	27	1
20	119	105	33	-12	4	21	0	9	1	10	2	22	47	91	47	7	3	23	175	193	23	-1	5	24	186	196	20
20	0	10	1	-10	4	21	191	195	19	-15	3	22	158	143	26	9	3	23	94	55	47	1	5	24	182	218	24
20	174	135	19	-8	4	21	245	233	16	-13	3	22	127	137	29	-12	4	23	181	181	23	3	5	24	0	6	1
20	234	222	16	-6	4	21	111	96	28	-11	3	22	205	231	19	-10	4	23	30	22	29	-6	6	24	187	187	22
20	0	13	1	-4	4	21	116	51	29	-9	3	22	40	29	39	-8	4	23	101	80	38	-4	6	24	213	194	18
20	442	439	11	-2	4	21	162	155	20	-7	3	22	109	102	34	-6	4	23	0	76	1	-2	6	24	0	35	1
20	95	55	39	0	4	21	274	257	18	-5	3	22	129	97	25	-4	4	23	0	42	1	0	6	24	85	24	57
20	274	282	14	2	4	21	84	110	65	-3	3	22	252	250	15	-2	4	23	132	159	28	-11	1	25	30	73	30
20	266	215	15	4	4	21	52	106	51	-1	3	22	51	64	50	0	4	23	106	91	24	-9	1	25	131	111	28
20	73	3	72	6	4	21	72	8	72	1	3	22	271	297	16	2	4	23	95	83	49	-7	1	25	0	29	1
20	56	98	55	8	4	21	130	78	28	3	3	22	150	136	25	4	4	23	0	10	1	-5	1	25	129	127	26
20	232	245	17	10	4	21	0	12	1	5	3	22	212	200	18	6	4	23	160	138	24	-3	1	25	46	108	45
20	88	110	54	-13	5	21	0	113	1	7	3	22	106	133	39	8	4	23	0	46	1	-1	1	25	230	214	17
20	119	74	34	-11	5	21	120	146	32	9	3	22	21	65	20	-11	5	23	75	7	74	1	1	25	130	73	29
20	208	195	21	-9	5	21	40	67	40	11	3	22	150	142	27	-9	5	23	218	177	17	3	1	25	216	225	19
20	163	160	24	-7	5	21	136	170	27	-14	4	22	284	245	15	-7	5	23	176	170	21	5	1	25	151	180	26
20	146	174	26	-5	5	21	44	84	43	-12	4	22	146	144	24	-5	5	23	192	182	19	7	1	25	280	292	17
20	181	158	19	-3	5	21	39	30	39	-10	4	22	91	69	46	-3	5	23	82	44	60	-10	2	25	172	169	21
20	59	26	59	-1	5	21	360	358	13	-8	4	22	172	148	19	-1	5	23	50	60	50	-8	2	25	115	84	33
20	206	187	16	1	5	21	370	365	13	-6	4	22	0	2	1	1	5	23	55	7	54	-6	2	25	0	15	1
20	0	22	1	3	5	21	0	65	1	-4	4	22	119	97	30	3	5	23	174	162	24	-4	2	25	175	163	20
20	87	57	32	5	5	21	495	479	12	-2	4	22	153	129	21	5	5	23	52	86	52	-2	2	25	41	111	41
20	116	97	35	7	5	21	115	49	34	0	4	22	120	123	39	7	5	23	92	58	53	0	2	25	102	35	33
20	67	13	66	9	5	21	0	20	1	2	4	22	82	110	81	-8	6	23	170	153	23	2	2	25	100	103	46
20	159	104	23	-12	6	21	207	201	20	4	4	22	129	136	31	-6	6	23	314	312	15	4	2	25	329	299	14
20	70	87	69	-10	6	21	105	48	38	6	4	22	229	230	17	-4	6	23	87	36	50	6	2	25	333	327	16
20	178	151	22	-8	6	21	145	122	24	8	4	22	94	53	44	-2	6	23	111	141	35	-9	3	25	21	56	21
20	142	131	28	-6	6	21	81	21	58	10	4	22	65	139	64	0	6	23	358	364	10	-7	3	25	226	186	17
20	86	106	56	-4	6	21	108	20	30	-13	5	22	133	112	28	2	6	23	100	42	45	-5	3	25	0	89	1
20	55	75	54	-2	6	21	85	62	51	-11	5	22	0	19	1	4	6	23	408	400	14	-3	3	25	100	91	39
20	68	4	67	0	6	21	303	309	10	-9	5	22	0	5	1	-3	7	23	87	100	55	-1	3	25	172	146	21
20	0	31	1	2	6	21	67	10	67	-7	5	22	0	9	1	-1	7	23	108	71	36	1	3	25	296	246	15
20	218	227	18	4	6	21	132	100	31	-5	5	22	73	89	72	-14	0	24	0	96	1	3	3	25	0	33	1
20	276	262	16	6	6	21	0	79	1	-3	5	22	192	174	18	-12	0	24	125	13	25	5	3	25	255	260	18
20	99	56	41	8	6	21	139	136	31	-1	5	22	150	141	24	-10	0	24	149	116	23	-8	4	25	144	150	25
20	55	127	55	-9	7	21	111	92	38	1	5	22	149	122	24	-8	0	24	81	64	53	-6	4	25	115	34	31
20	43	63	42	-7	7	21	76	14	75	3	5	22	299	278	15	-6	0	24	424	428	12	-4	4	25	201	175	18
20	111	112	37	-5	7	21	112	69	36	5	5	22	102	13	44	-4	0	24	101	136	36	-2	4	25	56	10	55
20	52	8	51	-3	7	21	159	155	24	7	5	22	0	59	1	-2	0	24	272	287	15	0	4	25	166	153	16
20	63	82	63	-1	7	21	108	55	36	-10	6	22	205	184	18	0	0	24	206	208	19	2	4	25	43	115	42
20	101	55	37	1	7	21	363	382	14	-8	6	22	213	202	20	2	0	24	142	147	27	4	4	25	126	13	32
20	39	57	39	3	7	21	67	77	66	-6	6	22	0	33	1	4	0	24	46	85	45	-5	5	25	0	55	1
20	145	141	28	5	7	21	123	127	35	-4	6	22	58	8	58	6	0	24	0	1	1	-3	5	25	68	9	67
20	137	84	30	-6	8	21	0	15	1	-2	6	22	105	13	34	8	0	24	460	445	13	-1	5	25	86	60	54

l	10Fo	10Fc	10s
25	65	143	65
26	0	59	1
26	152	209	24
26	73	87	73
26	105	75	35
26	142	146	26
26	331	339	15
26	0	75	1

h	k	l	10Fo	10Fc	10s
4	0	26	68	75	67
-9	1	26	0	18	1
-7	1	26	112	137	36
-5	1	26	147	139	26
-3	1	26	101	90	38
-1	1	26	145	145	24
1	1	26	0	46	1
3	1	26	68	107	67

h	k	l	10Fo	10Fc	10s
-8	2	26	123	91	32
-6	2	26	122	29	28
-4	2	26	0	8	1
-2	2	26	52	74	51
0	2	26	177	183	15
2	2	26	60	56	60
4	2	26	0	31	1
-7	3	26	91	47	48

h	k	l	10Fo	10Fc	10s
-5	3	26	0	61	1
-3	3	26	43	1	42
-1	3	26	200	180	19
1	3	26	120	7	33
-4	4	26	94	55	43
-2	4	26	94	85	46
-5	1	27	180	142	22
-3	1	27	99	37	42

h	k	l	10Fo	10Fc	10s
-1	1	27	175	177	23
1	1	27	0	61	1
-4	2	27	61	33	61
-2	2	27	53	38	53

pendix D: Observed and Calculated Structure factors for **(158d)**.

h	k	l	10Fo	10Fc	10s
0	0	2	28	37	27
0	0	4	1259	1301	3
0	0	6	811	827	3
0	0	8	114	119	5
0	0	10	159	154	4
0	0	12	45	31	19
0	0	14	187	186	6
0	0	16	98	99	12
0	0	18	63	20	18
0	0	20	77	28	34
0	0	22	116	67	10
0	0	24	104	124	12
0	0	26	42	41	41
0	0	28	66	70	66
0	0	30	243	251	3
0	0	32	368	347	2
0	0	34	577	587	2
0	0	36	144	126	4
0	0	38	1332	1343	4
0	0	40	411	419	1
0	0	42	131	130	1
0	0	44	439	469	4
0	0	46	648	663	2
0	0	48	849	858	3
0	0	50	21	41	20
0	0	52	164	161	4
0	0	54	36	3	36
0	0	56	147	135	7
0	0	58	30	13	30
0	0	60	176	181	7
0	0	62	34	3	33
0	0	64	70	107	70
0	0	66	90	67	57
0	0	68	82	93	12
0	0	70	195	209	4
0	0	72	152	150	4
0	0	74	462	473	2
0	0	76	346	353	2
0	0	78	2494	2170	-11
0	0	80	622	630	2
0	0	82	229	230	1
0	0	84	859	895	2
0	0	86	1220	1249	4
0	0	88	403	419	2
0	0	90	246	237	3
0	0	92	26	24	25
0	0	94	33	37	32
0	0	96	36	24	36
0	0	98	66	149	65
0	0	100	41	8	40
0	0	102	86	72	22
0	0	104	156	153	8
0	0	106	204	203	6
0	0	108	19	51	19
0	0	110	192	185	4
0	0	112	236	231	3
0	0	114	52	85	51
0	0	116	392	396	2
0	0	118	569	582	2
0	0	120	76	16	14
0	0	122	560	566	2
0	0	124	174	182	2
0	0	126	219	210	2
0	0	128	191	194	2
0	0	130	0	11	1
0	0	132	149	134	6
0	0	134	89	54	10
0	0	136	70	18	69
0	0	138	112	111	10
0	0	140	103	100	11
0	0	142	68	73	19
0	0	144	0	84	1
0	0	146	51	28	50
0	0	148	46	20	27
0	0	150	51	52	17
0	0	152	28	71	28
0	0	154	632	619	3
0	0	156	151	153	4
0	0	158	850	831	2
0	0	160	382	384	1
0	0	162	908	917	5
0	0	164	91	101	4
0	0	166	263	259	2
0	0	168	16	0	15
0	0	170	60	15	2
0	0	172	82	84	11
0	0	174	61	61	17
0	0	176	115	112	10
0	0	178	46	22	46
0	0	180	94	71	13
1	0	0	159	165	7
1	0	2	135	137	9
1	0	4	0	79	1
1	0	6	359	357	3
1	0	8	108	114	7
1	0	10	47	13	47
1	0	12	49	4	49
1	0	14	349	353	1
1	0	16	208	198	2
1	0	18	401	405	1
1	0	20	466	477	2
1	0	22	25	32	25
1	0	24	69	70	7
1	0	26	102	93	8
1	0	28	74	40	27
1	0	30	73	12	73
1	0	32	130	153	9
1	0	34	95	76	12
1	0	36	77	32	76
1	0	38	57	40	22
1	0	40	255	266	5
1	0	42	92	59	18
1	0	44	187	183	5
1	0	46	242	238	4
1	0	48	314	304	3
1	0	50	458	463	2
1	0	52	208	211	3
1	0	54	89	39	4
1	0	56	584	577	3
1	0	58	123	125	3
1	0	60	196	195	3
1	0	62	51	57	51
1	0	64	43	58	43
1	0	66	92	40	16
1	0	68	101	38	11
1	0	70	23	42	23
1	0	72	35	43	34
1	0	74	104	35	12
1	0	76	260	281	5
1	0	78	175	187	7
1	0	80	215	227	5
1	0	82	32	43	32
1	0	84	62	47	14
1	0	86	24	45	24
1	0	88	370	364	3
1	0	90	52	51	51
1	0	92	240	243	2
1	0	94	116	2	31
1	0	96	111	31	33
1	0	98	181	181	4
1	0	100	46	138	45
1	0	102	22	37	21
1	0	104	51	111	51
1	0	106	0	58	1
1	0	108	95	45	57
1	0	110	150	139	8
1	0	112	52	65	52
1	0	114	45	49	45
1	0	116	206	230	6
1	0	118	56	50	56
1	0	120	102	92	11
1	0	122	174	166	4
1	0	124	187	191	3
1	0	126	38	29	38
1	0	128	47	28	46
1	0	130	99	104	19
1	0	132	112	103	6
1	0	134	80	39	13
1	0	136	107	108	10
1	0	138	82	85	14
1	0	140	165	166	8
1	0	142	109	55	15
1	0	144	187	188	7
1	0	146	210	203	6
1	0	148	119	108	10
1	0	150	20	4	19
1	0	152	67	10	67
1	0	154	63	68	62
1	0	156	102	16	16
1	0	158	84	76	17
1	0	160	99	15	19
1	0	162	13	51	12
1	0	164	59	60	59
1	0	166	110	107	10
1	0	168	72	43	71
1	0	170	140	12	8
1	0	172	93	96	14
1	0	174	207	200	6
1	0	176	280	300	5
1	0	178	123	141	10
2	0	0	150	144	6
2	0	2	58	57	57
2	0	4	130	43	43
2	0	6	48	23	24
2	0	8	79	37	11
2	0	10	47	40	24
2	0	12	78	70	32
2	0	14	76	40	75
2	0	16	195	192	7
2	0	18	71	69	18
2	0	20	101	34	15
2	0	22	153	180	9
2	0	24	195	199	7
2	0	26	207	215	7
2	0	28	59	110	58
2	0	30	72	61	24
2	0	32	54	2	53
2	0	34	146	154	5
2	0	36	99	73	11
2	0	38	34	39	34
2	0	40	63	26	62
2	0	42	123	56	10
2	0	44	47	23	11
2	0	46	86	58	48
2	0	48	45	14	18
2	0	50	71	13	25
2	0	52	69	80	15
2	0	54	25	2	24
2	0	56	49	57	48
2	0	58	67	29	54
2	0	60	62	69	21
2	0	62	118	1	10
2	0	64	69	87	69
2	0	66	106	118	12
2	0	68	77	47	15
2	0	70	58	67	57
2	0	72	0	68	1
2	0	74	137	139	9
2	0	76	127	129	9
2	0	78	84	12	19
2	0	80	200	207	6
2	0	82	55	44	54
2	0	84	265	266	5
2	0	86	178	193	7
2	0	88	59	39	58
2	0	90	54	58	23
2	0	92	91	28	19
2	0	94	169	171	7
2	0	96	208	205	6
2	0	98	107	116	11
2	0	100	142	145	8
2	0	102	70	66	16
2	0	104	153	23	-4
2	0	106	160	141	7
2	0	108	84	27	22
2	0	110	16	72	16
2	0	112	120	132	8
2	0	114	244	246	4
2	0	116	0	50	1
2	0	118	7	33	6
2	0	120	23	48	22
2	0	122	68	30	68
2	0	124	82	56	24
2	0	126	137	112	7
2	0	128	121	121	8
2	0	130	20	20	20
2	0	132	112	117	8
2	0	134	36	37	36
2	0	136	88	19	21
2	0	138	110	68	10
2	0	140	53	38	52
2	0	142	84	21	55
2	0	144	33	45	33
2	0	146	93	12	11
2	0	148	68	76	22
2	0	150	266	261	3
2	0	152	176	177	4
2	0	154	87	79	8
2	0	156	84	78	62
2	0	158	142	147	8
2	0	160	74	38	74
2	0	162	137	119	7
2	0	164	316	316	3
2	0	166	24	39	24
2	0	168	80	65	8
2	0	170	205	202	3
2	0	172	407	390	2
2	0	174	420	416	2
2	0	176	129	55	7
2	0	178	127	88	7
-6	-5	1	[illegible]	[illegible]	35
-5	-5	1	184	[illegible]	6
-4	-5	1	76	[illegible]	10
-3	-5	1	29	[illegible]	29
-2	-5	1	324	328	2
-1	-5	1	209	[illegible]	3
0	-5	1	125	[illegible]	4
1	-5	1	333	[illegible]	2
2	-5	1	335	328	2
-9	-4	1	34	[illegible]	33
-8	-4	1	264	252	5
-7	-4	1	81	104	80
-6	-4	1	130	129	8
-5	-4	1	179	186	5
-4	-4	1	137	138	5
-3	-4	1	152	156	4
-2	-4	1	640	627	3
-1	-4	1	286	287	2
0	-4	1	63	37	16
1	-4	1	236	226	2
2	-4	1	75	20	8
-9	-3	1	68	26	68
-8	-3	1	108	49	10
-7	-3	1	189	195	6
-6	-3	1	126	112	7
-5	-3	1	283	281	3
-4	-3	1	49	2	48
-3	-3	1	29	27	29
-2	-3	1	45	45	45
-1	-3	1	965	994	4
0	-3	1	1568	1651	5
1	-3	1	706	728	3
2	-3	1	107	117	5
-9	-2	1	58	110	57
-8	-2	1	145	145	8
-7	-2	1	174	203	6
-6	-2	1	62	30	61
-5	-2	1	389	361	2
-4	-2	1	385	385	2
-3	-2	1	93	96	5
-2	-2	1	540	540	2
-1	-2	1	781	818	3
0	-2	1	688	718	3
1	-2	1	210	216	1
2	-2	1	445	452	2
-10	-1	1	85	76	85
-9	-1	1	69	10	38
-8	-1	1	292	274	4
-7	-1	1	80	90	13
-6	-1	1	171	172	5
-5	-1	1	244	223	3
-4	-1	1	109	113	5
-3	-1	1	278	287	2
-2	-1	1	671	695	3
-1	-1	1	1039	1067	4
0	-1	1	138	152	1
1	-1	1	1821	1628	8
2	-1	1	1125	1135	5
-10	0	1	64	43	64
-9	0	1	88	30	57
-8	0	1	154	156	7
-7	0	1	84	30	19
-6	0	1	140	147	6
-5	0	1	634	635	3
-4	0	1	31	38	31
-3	0	1	1257	1263	4
-2	0	1	193	201	2
-1	0	1	183	185	1
1	0	1	124	142	1
2	0	1	247	236	2
-10	1	1	90	83	13
-9	1	1	178	184	7
-8	1	1	98	92	12
-7	1	1	78	36	59
-6	1	1	0	5	1
-5	1	1	228	210	3
-4	1	1	239	234	3
-3	1	1	521	515	2
-2	1	1	686	683	3
-1	1	1	1569	1391	7
0	1	1	105	115	1
1	1	1	1278	1355	4
2	1	1	616	635	3
-10	2	1	34	11	33
-9	2	1	218	220	6
-8	2	1	238	248	5
-7	2	1	139	135	7
-6	2	1	158	161	5
-5	2	1	318	311	2
-4	2	1	347	[illegible]	[illegible]
-3	2	1	[illegible]	[illegible]	35
-2	2	1	[illegible]	373	[illegible]
-1	2	1	64	25	[illegible]
0	2	1	389	407	2
1	2	1	255	262	2
2	2	1	781	802	[illegible]
3	2	1	463	453	2
-10	3	1	24	33	23
-9	3	1	128	133	9
-8	3	1	90	144	70
-7	3	1	108	117	9
-6	3	1	192	174	4
-5	3	1	114	93	6
-4	3	1	223	239	3
-3	3	1	376	359	2
-2	3	1	288	295	2
-1	3	1	1234	1263	5
0	3	1	1403	1472	5
1	3	1	604	608	3
2	3	1	381	384	2
3	3	1	58	39	57
-10	4	1	0	92	1
-9	4	1	237	239	5
-8	4	1	130	123	9
-7	4	1	265	256	4
-6	4	1	129	142	7
-5	4	1	455	471	2
-4	4	1	60	28	9
-3	4	1	521	515	2
-2	4	1	301	309	2
-1	4	1	426	441	2
0	4	1	199	209	3
1	4	1	42	33	13
2	4	1	788	791	3
3	4	1	382	377	2
-10	5	1	72	131	71
-9	5	1	57	6	21
-8	5	1	60	65	20
-7	5	1	39	99	38
-6	5	1	88	75	10
-5	5	1	300	301	3
-4	5	1	321	327	2
-3	5	1	285	282	2
-2	5	1	213	213	3
-1	5	1	299	309	2
0	5	1	151	150	4
1	5	1	243	244	3
2	5	1	253	247	3
3	5	1	333	332	3
-9	6	1	39	6	39
-8	6	1	105	103	11
-7	6	1	150	151	7
-6	6	1	93	85	10
-5	6	1	170	172	5
-4	6	1	65	118	64
-3	6	1	455	442	2
-2	6	1	168	164	4
-1	6	1	59	55	11
0	6	1	460	446	2
1	6	1	232	232	3
2	6	1	114	116	7
3	6	1	49	56	48
-10	7	1	25	7	24
-9	7	1	115	112	10
-8	7	1	188	204	7
-7	7	1	188	189	6
-6	7	1	214	227	5
-5	7	1	129	114	7
-4	7	1	195	175	5
-3	7	1	66	18	66
-2	7	1	44	35	44
-1	7	1	266	270	3
0	7	1	319	330	3
1	7	1	64	68	63
2	7	1	32	38	32
3	7	1	90	87	11
-9	8	1	75	64	74
-8	8	1	126	126	9
-7	8	1	179	162	7
-6	8	1	89	7	65
-5	8	1	28	47	27
-4	8	1	65	18	54
-3	8	1	63	78	63
-2	8	1	317	321	3
-1	8	1	38	23	31
0	8	1	342	348	3
1	8	1	154	146	6
2	8	1	49	98	48
3	8	1	41	4	41
-9	9	1	[illegible]	[illegible]	68

.	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
1	72	84	17	-1	-7	2	181	181	4	-8	1	2	85	59	72	-1	7	2	517	507	2	0	-9	3	226	231	5
1	104	94	12	0	-7	2	188	186	4	-7	1	2	112	100	9	0	7	2	121	122	6	1	-9	3	186	167	6
1	70	60	70	1	-7	2	153	147	5	-6	1	2	315	309	3	1	7	2	139	138	6	2	-9	3	117	107	9
1	89	92	56	2	-7	2	41	23	41	-5	1	2	49	66	49	2	7	2	147	149	6	-6	-8	3	101	64	15
1	224	221	5	-8	-6	2	71	74	17	-4	1	2	988	988	5	3	7	2	48	17	48	-5	-8	3	91	19	13
1	152	153	7	-7	-6	2	46	65	28	-3	1	2	331	342	2	-9	8	2	53	86	52	-4	-8	3	185	183	6
1	51	21	23	-6	-6	2	276	289	5	-2	1	2	460	445	2	-8	8	2	102	119	12	-3	-8	3	339	336	4
1	28	99	27	-5	-6	2	64	68	17	-1	1	2	306	303	1	-7	8	2	60	70	60	-2	-8	3	258	252	4
1	44	33	44	-4	-6	2	97	74	9	0	1	2	41	59	27	-6	8	2	189	202	6	-1	-8	3	50	67	50
1	59	34	18	-3	-6	2	310	302	3	1	1	2	115	121	3	-5	8	2	212	202	5	0	-8	3	149	154	6
1	89	40	54	-2	-6	2	29	38	29	2	1	2	845	853	4	-4	8	2	80	59	79	1	-8	3	41	7	40
1	160	156	7	-1	-6	2	33	47	32	-10	2	2	46	23	11	-3	8	2	66	16	66	2	-8	3	63	18	63
1	83	48	32	0	-6	2	102	84	6	-9	2	2	54	73	54	-2	8	2	118	118	8	-7	-7	3	24	19	24
1	76	4	76	1	-6	2	622	598	3	-8	2	2	82	22	28	-1	8	2	83	90	11	-6	-7	3	88	91	52
1	77	149	76	2	-6	2	213	203	3	-7	2	2	133	142	7	0	8	2	53	45	52	-5	-7	3	146	140	7
1	74	61	74	-8	-5	2	66	42	18	-6	2	2	256	240	3	1	8	2	86	71	16	-4	-7	3	0	96	1
1	80	74	15	-7	-5	2	31	110	31	-5	2	2	177	168	4	2	8	2	77	8	77	-3	-7	3	84	24	49
1	93	11	23	-6	-5	2	61	71	18	-4	2	2	61	2	9	3	8	2	133	149	8	-2	-7	3	78	60	50
1	282	272	4	-5	-5	2	200	190	5	-3	2	2	386	396	2	-9	9	2	119	105	10	-1	-7	3	289	283	3
1	90	92	22	-4	-5	2	77	22	46	-2	2	2	710	708	3	-8	9	2	80	3	27	0	-7	3	147	137	5
1	73	13	73	-3	-5	2	272	267	3	-1	2	2	726	736	3	-7	9	2	222	212	6	1	-7	3	21	44	20
1	139	134	8	-2	-5	2	518	528	2	0	2	2	543	567	2	-6	9	2	97	87	13	2	-7	3	108	120	7
1	11	29	10	-1	-5	2	433	437	2	1	2	2	731	757	3	-5	9	2	66	45	19	-8	-6	3	89	25	19
1	77	54	14	0	-5	2	38	23	37	2	2	2	206	217	3	-4	9	2	262	263	5	-7	-6	3	61	133	61
1	24	4	24	1	-5	2	47	69	12	3	2	2	397	385	2	-3	9	2	48	59	48	-6	-6	3	31	46	30
1	27	1	26	2	-5	2	81	73	7	-10	3	2	158	165	8	-2	9	2	65	30	64	-5	-6	3	192	189	6
1	170	187	8	-9	-4	2	78	72	26	-9	3	2	91	117	62	-1	9	2	65	78	64	-4	-6	3	67	38	14
1	258	263	5	-8	-4	2	160	157	7	-8	3	2	142	147	8	0	9	2	56	100	56	-3	-6	3	154	150	5
1	249	240	6	-7	-4	2	53	75	52	-7	3	2	87	76	11	1	9	2	89	39	54	-2	-6	3	23	21	23
1	134	127	9	-6	-4	2	102	87	12	-6	3	2	661	652	3	2	9	2	21	56	21	-1	-6	3	23	93	22
1	262	268	5	-5	-4	2	145	148	6	-5	3	2	83	88	8	3	9	2	131	133	9	0	-6	3	50	33	50
1	45	48	44	-4	-4	2	45	47	45	-4	3	2	223	229	3	-8	10	2	0	36	1	1	-6	3	219	223	3
1	102	95	11	-3	-4	2	153	151	4	-3	3	2	65	64	38	-7	10	2	46	93	45	2	-6	3	67	51	10
1	91	31	18	-2	-4	2	32	34	32	-2	3	2	215	209	3	-6	10	2	31	106	31	-8	-5	3	34	83	33
1	81	40	30	-1	-4	2	683	694	3	-1	3	2	709	721	3	-5	10	2	186	187	7	-7	-5	3	89	167	66
1	101	74	13	0	-4	2	24	10	19	0	3	2	683	709	3	-4	10	2	48	48	32	-6	-5	3	125	120	8
1	0	89	1	1	-4	2	272	267	2	1	3	2	500	513	2	-3	10	2	112	123	11	-5	-5	3	142	62	4
1	93	104	59	2	-4	2	50	33	11	2	3	2	335	331	2	-2	10	2	155	153	7	-4	-5	3	214	201	4
1	57	36	56	-9	-3	2	96	119	58	3	3	2	423	405	2	-1	10	2	59	63	59	-3	-5	3	64	28	23
1	123	123	10	-8	-3	2	123	134	9	-10	4	2	125	89	8	0	10	2	124	131	9	-2	-5	3	75	93	8
1	23	93	23	-7	-3	2	107	111	10	-9	4	2	50	65	49	1	10	2	137	130	8	-1	-5	3	224	234	3
1	132	78	8	-6	-3	2	82	78	11	-8	4	2	51	115	50	2	10	2	102	107	11	0	-5	3	199	199	3
1	24	4	24	-5	-3	2	178	170	4	-7	4	2	172	167	6	3	10	2	55	20	21	1	-5	3	78	105	7
1	145	32	7	-4	-3	2	596	582	2	-6	4	2	373	378	3	-8	11	2	136	130	10	2	-5	3	414	399	2
1	0	31	1	-3	-3	2	101	120	5	-5	4	2	342	350	2	-7	11	2	130	131	10	-9	-4	3	55	30	54
1	95	87	66	-2	-3	2	438	467	2	-4	4	2	329	328	2	-6	11	2	73	63	43	-8	-4	3	108	115	10
1	89	29	22	-1	-3	2	518	529	2	-3	4	2	676	667	3	-5	11	2	45	97	45	-7	-4	3	128	140	8
2	65	80	65	0	-3	2	171	164	3	-2	4	2	319	326	2	-4	11	2	38	30	38	-6	-4	3	57	100	56
2	81	35	31	1	-3	2	110	116	5	-1	4	2	1149	1175	4	-3	11	2	289	306	5	-5	-4	3	56	19	55
2	74	38	16	2	-3	2	574	579	2	0	4	2	87	58	6	-2	11	2	122	12	9	-4	-4	3	80	1	13
2	80	117	79	-9	-2	2	25	77	25	1	4	2	353	361	2	-1	11	2	22	138	22	-3	-4	3	407	395	2
2	33	37	33	-8	-2	2	66	70	18	2	4	2	64	76	46	0	11	2	194	190	6	-2	-4	3	115	120	5
2	56	88	23	-7	-2	2	180	195	6	3	4	2	293	295	3	1	11	2	81	107	15	-1	-4	3	123	132	4
2	33	3	32	-6	-2	2	159	152	6	-10	5	2	136	155	9	2	11	2	34	11	34	0	-4	3	286	291	2
2	81	85	14	-5	-2	2	275	255	3	-9	5	2	107	135	12	3	11	2	96	98	13	1	-4	3	41	33	41
2	91	96	12	-4	-2	2	389	384	2	-8	5	2	91	192	73	-6	12	2	128	56	8	2	-4	3	47	27	46
2	32	63	32	-3	-2	2	75	91	7	-7	5	2	20	99	19	-5	12	2	116	142	11	-9	-3	3	53	57	53
2	63	44	62	-2	-2	2	162	162	3	-6	5	2	180	178	5	-4	12	2	127	139	10	-8	-3	3	135	151	8
2	44	7	43	-1	-2	2	116	112	4	-5	5	2	17	54	17	-3	12	2	89	92	14	-7	-3	3	83	96	62
2	162	158	8	0	-2	2	522	525	2	-4	5	2	402	400	2	-2	12	2	74	141	73	-6	-3	3	98	88	10
2	74	84	16	1	-2	2	817	844	3	-3	5	2	200	196	3	-1	12	2	47	44	46	-5	-3	3	177	174	4
2	73	7	36	2	-2	2	175	156	3	-2	5	2	53	72	53	0	12	2	63	19	62	-4	-3	3	260	253	3
2	102	114	12	-10	-1	2	107	16	12	-1	5	2	220	218	3	1	12	2	53	87	26	-3	-3	3	29	58	29
2	138	153	9	-9	-1	2	120	111	9	0	5	2	418	424	2	-4	13	2	65	30	65	-2	-3	3	33	25	32
2	163	172	7	-8	-1	2	85	51	85	1	5	2	142	126	4	-3	13	2	0	28	1	-1	-3	3	12	13	12
2	209	209	6	-7	-1	2	152	164	7	2	5	2	40	59	39	-2	13	2	85	21	67	0	-3	3	112	105	5
2	254	263	5	-6	-1	2	331	329	3	3	5	2	190	185	4	1-13		3	96	100	20	1	-3	3	162	167	3
2	82	14	68	-5	-1	2	61	86	23	-10	6	2	76	67	76	2-13		3	59	8	23	2	-3	3	325	338	2
2	109	133	10	-4	-1	2	181	176	3	-9	6	2	68	63	47	-2-12		3	55	58	25	-9	-2	3	27	28	27
2	84	41	58	-3	-1	2	1465	1513	6	-8	6	2	80	52	79	0-12		3	65	16	18	-8	-2	3	84	23	63
2	73	45	15	-2	-1	2	503	521	2	-7	6	2	204	196	5	1-12		3	84	93	58	-7	-2	3	83	92	60
2	111	106	10	-1	-1	2	532	568	2	-6	6	2	26	2	26	2-12		3	52	74	51	-6	-2	3	71	58	12
2	20	52	19	0	-1	2	415	415	2	-5	6	2	473	469	3	-3-11		3	106	87	11	-5	-2	3	76	2	13
2	99	112	10	1	-1	2	414	421	2	-4	6	2	255	251	3	-2-11		3	62	4	61	-4	-2	3	67	16	39
2	73	1	31	2	-1	2	398	377	2	-3	6	2	92	92	8	-1-11		3	279	284	5	-3	-2	3	210	196	3
2	41	51	41	-10	0	2	34	5	34	-2	6	2	52	43	51	0-11		3	74	22	38	-2	-2	3	107	123	5
2	99	3	14	-9	0	2	40	11	40	-1	6	2	138	145	5	1-11		3	177	179	7	-1	-2	3	141	145	3
2	118	142	9	-8	0	2	102	56	15	0	6	2	113	110	6	2-11		3	73	160	72	0	-2	3	281	308	2
2	105	103	10	-7	0	2	113	102	9	1	6	2	194	214	4	-4-10		3	34	64	33	1	-2	3	60	66	13
2	109	87	9	-6	0	2	116	124	7	2	6	2	58	67	14	-3-10		3	166	178	7	2	-2	3	149	161	4
2	123	125	8	-5	0	2	259	262	3	3	6	2	214	204	4	-2-10		3	50	49	49	-10	-1	3	111	121	12
2	138	136	6	-4	0	2	162	166	3	-10	7	2	51	53	29	-1-10		3	382	386	4	-9	-1	3	157	180	7
2	73	5	22	-3	0	2	234	255	2	-9	7	2	196	194	6	0-10		3	76	67	15	-8	-1	3	186	172	6
2	63	31	39	-2	0	2	1958	1789	9	-8	7	2	103	89	12	1-10		3	92	92	13	-7	-1	3	64	40	16
2	76	54	29	-1	0	2	231	239	1	-7	7	2	144	165	8	2-10		3	51	16	50	-6	-1	3	57	51	56
2	119	61	8	0	0	2	1382	1241	6	-6	7	2	48	56	25	-5	-9	3	86	101	13	-5	-1	3	175	174	4
2	86	71	55	1	0	2	38	55	38	-5	7	2	39	25	38	-4	-9	3	92	108	12	-4	-1	3	209	209	3
2	84	31	57	2	0	2	338	323	2	-4	7	2	31	88	30	-3	-9	3	27	50	26	-3	-1	3	472	480	2
2	244	247	4	-10	1	2	79	39	79	-3	7	2	237	224	4	-2	-9	3	113	127	10	-2	-1	3	1502	1555	5
2	89	90	10	-9	1	2	191	192	7	-2	7	2	113	114	7	-1	-9	3	86	39	53	-1	-1	3	593	616	3

l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
3	111	107	2	-5	6	3	366	368	3	-2-11	4		81	124	81	-4	-2	4	44	40	43	-8	5	4	73	88	72
3	555	571	2	-4	6	3	155	160	5	-1-11	4		150	135	7	-3	-2	4	472	465	2	-7	5	4	65	28	46
3	78	73	7	-3	6	3	49	26	48	0-11	4		117	138	10	-2	-2	4	968	984	4	-6	5	4	267	245	4
3	76	66	76	-2	6	3	196	196	4	1-11	4		207	202	6	-1	-2	4	889	930	4	-5	5	4	93	99	8
3	138	136	8	-1	6	3	344	348	2	2-11	4		86	82	70	0	-2	4	1253	1302	5	-4	5	4	164	173	4
3	81	100	80	0	6	3	311	305	2	-4-10	4		86	49	58	1	-2	4	244	244	2	-3	5	4	307	297	2
3	67	84	66	1	6	3	208	200	4	-3-10	4		56	35	56	2	-2	4	556	551	2	-2	5	4	139	154	4
3	362	343	3	2	6	3	126	102	6	-2-10	4		63	40	62	-10	-1	4	88	43	24	-1	5	4	425	430	2
3	166	176	4	3	6	3	0	109	1	-1-10	4		89	39	53	-9	-1	4	134	125	8	0	5	4	15	13	15
3	126	128	4	-10	7	3	85	1	21	0-10	4		201	206	6	-8	-1	4	70	68	70	1	5	4	255	250	3
3	72	76	8	-9	7	3	72	85	17	1-10	4		139	153	9	-7	-1	4	56	31	55	2	5	4	465	444	2
3	79	71	6	-8	7	3	161	161	8	2-10	4		210	205	6	-6	-1	4	207	194	4	3	5	4	162	165	5
3	733	770	3	-7	7	3	168	162	7	-5	-9	4	82	10	57	-5	-1	4	174	171	4	-10	6	4	54	119	53
3	39	61	32	-6	7	3	78	103	78	-4	-9	4	163	171	7	-4	-1	4	49	53	49	-9	6	4	99	26	14
3	31	69	31	-5	7	3	89	5	17	-3	-9	4	307	308	4	-3	-1	4	347	349	2	-8	6	4	74	12	73
3	23	12	22	-4	7	3	309	324	3	-2	-9	4	221	213	5	-2	-1	4	20	54	19	-7	6	4	102	23	12
3	98	56	17	-3	7	3	89	86	9	-1	-9	4	71	84	16	-1	-1	4	587	590	3	-6	6	4	133	137	7
3	50	40	49	-2	7	3	145	137	6	0	-9	4	207	208	5	0	-1	4	351	362	1	-5	6	4	169	164	5
3	74	26	74	-1	7	3	193	202	4	1	-9	4	28	25	27	1	-1	4	279	287	2	-4	6	4	181	165	4
3	104	104	9	0	7	3	80	128	50	2	-9	4	163	156	6	2	-1	4	77	90	7	-3	6	4	356	351	3
3	223	205	4	1	7	3	106	94	8	-6	-8	4	65	64	18	-10	0	4	113	5	9	-2	6	4	515	505	2
3	382	373	2	2	7	3	244	241	4	-5	-8	4	75	49	75	-9	0	4	29	28	29	-1	6	4	382	376	2
3	292	287	2	3	7	3	75	0	74	-4	-8	4	106	97	10	-8	0	4	121	115	9	0	6	4	66	60	56
3	82	62	8	-9	8	3	71	57	70	-3	-8	4	88	63	12	-7	0	4	67	29	66	1	6	4	290	284	3
3	774	785	4	-8	8	3	168	181	7	-2	-8	4	67	86	16	-6	0	4	137	117	6	2	6	4	271	272	3
3	87	82	3	-7	8	3	177	176	7	-1	-8	4	47	103	46	-5	0	4	239	232	3	3	6	4	192	195	5
3	390	403	1	-6	8	3	198	190	6	0	-8	4	77	23	19	-4	0	4	221	231	3	-10	7	4	77	51	77
3	1938	1785	10	-5	8	3	76	95	15	1	-8	4	32	13	31	-3	0	4	512	513	2	-9	7	4	203	205	6
3	1110	1129	4	-4	8	3	19	32	18	2	-8	4	57	34	16	-2	0	4	580	575	2	-8	7	4	129	64	7
3	64	75	20	-3	8	3	123	99	8	-7	-7	4	24	85	24	-1	0	4	71	4	5	-7	7	4	126	15	8
3	193	212	7	-2	8	3	182	183	5	-6	-7	4	39	57	39	0	0	4	770	774	3	-6	7	4	62	29	61
3	319	315	4	-1	8	3	278	265	4	-5	-7	4	150	140	7	1	0	4	764	751	4	-5	7	4	104	92	10
3	66	81	15	0	8	3	33	0	32	-4	-7	4	189	192	6	2	0	4	341	343	2	-4	7	4	131	125	7
3	155	167	5	1	8	3	58	1	58	-3	-7	4	77	118	77	-10	1	4	62	38	20	-3	7	4	78	76	51
3	403	408	2	2	8	3	53	42	53	-2	-7	4	421	419	3	-9	1	4	180	193	7	-2	7	4	35	55	34
3	665	639	3	3	8	3	87	17	53	-1	-7	4	18	61	17	-8	1	4	163	170	7	-1	7	4	163	155	5
3	414	415	2	-9	9	3	116	118	10	0	-7	4	184	174	4	-7	1	4	148	146	6	0	7	4	87	83	9
3	392	392	2	-8	9	3	65	37	65	1	-7	4	214	203	4	-6	1	4	394	371	3	1	7	4	45	47	44
3	76	54	6	-7	9	3	83	127	82	2	-7	4	188	170	4	-5	1	4	177	174	4	2	7	4	84	64	19
3	186	186	2	-6	9	3	90	70	64	-8	-6	4	110	25	10	-4	1	4	55	1	54	3	7	4	40	18	40
3	448	442	2	-5	9	3	0	85	1	-7	-6	4	33	32	32	-3	1	4	12	49	12	-9	8	4	36	11	35
3	727	747	3	-4	9	3	69	82	69	-6	-6	4	58	25	57	-2	1	4	374	368	2	-8	8	4	59	5	59
3	49	23	48	-3	9	3	106	106	10	-5	-6	4	213	214	5	-1	1	4	44	4	36	-7	8	4	83	26	82
3	82	112	81	-2	9	3	90	70	12	-4	-6	4	181	181	5	0	1	4	272	275	2	-6	8	4	31	30	30
3	54	9	53	-1	9	3	203	198	5	-3	-6	4	145	140	6	1	1	4	454	476	2	-5	8	4	28	63	27
3	106	66	10	0	9	3	152	159	7	-2	-6	4	54	82	54	2	1	4	219	219	2	-4	8	4	54	11	53
3	46	121	46	1	9	3	88	7	19	-1	-6	4	268	284	3	-10	2	4	92	44	18	-3	8	4	143	148	7
3	65	64	27	2	9	3	173	174	7	0	-6	4	60	7	59	-9	2	4	136	163	9	-2	8	4	45	87	45
3	680	669	3	3	9	3	45	6	44	1	-6	4	474	449	2	-8	2	4	36	24	36	-1	8	4	199	195	5
3	298	292	2	-8	10	3	94	104	14	2	-6	4	166	160	4	-7	2	4	57	89	56	0	8	4	140	137	7
3	47	10	47	-7	10	3	80	5	32	-8	-5	4	41	15	41	-6	2	4	49	60	49	1	8	4	28	95	27
3	198	203	3	-6	10	3	101	115	12	-7	-5	4	86	14	20	-5	2	4	104	82	6	2	8	4	0	66	1
3	440	449	2	-5	10	3	189	185	7	-6	-5	4	125	142	9	-4	2	4	276	266	2	3	8	4	176	181	6
3	207	212	3	-4	10	3	11	33	11	-5	-5	4	104	101	9	-3	2	4	215	208	3	-9	9	4	80	29	15
3	71	78	7	-3	10	3	81	73	80	-4	-5	4	35	10	35	-2	2	4	305	307	2	-8	9	4	23	25	23
3	118	124	4	-2	10	3	86	125	75	-3	-5	4	72	10	44	-1	2	4	568	589	3	-7	9	4	140	145	9
3	188	189	3	-1	10	3	177	169	7	-2	-5	4	422	420	2	0	2	4	175	153	3	-6	9	4	97	80	12
4	16	37	16	0	10	3	74	30	32	-1	-5	4	91	96	6	1	2	4	30	67	29	-5	9	4	92	44	55
4	108	126	11	1	10	3	66	34	65	0	-5	4	173	167	3	2	2	4	185	188	3	-4	9	4	61	47	20
4	72	34	37	2	10	3	56	73	55	1	-5	4	164	146	3	3	2	4	96	100	6	-3	9	4	263	267	4
4	80	55	13	3	10	3	145	127	8	2	-5	4	469	464	2	-10	3	4	105	121	12	-2	9	4	121	121	9
4	159	177	6	-7	11	3	59	49	23	-9	-4	4	124	132	10	-9	3	4	54	15	53	-1	9	4	107	89	10
4	171	161	4	-6	11	3	138	136	9	-8	-4	4	40	33	39	-8	3	4	187	178	6	0	9	4	57	75	57
4	60	64	21	-5	11	3	107	107	12	-7	-4	4	21	69	21	-7	3	4	189	168	6	1	9	4	80	89	14
4	297	294	2	-4	11	3	50	85	49	-6	-4	4	40	62	40	-6	3	4	330	319	3	2	9	4	89	101	53
4	56	14	10	-3	11	3	215	214	6	-5	-4	4	113	116	8	-5	3	4	143	135	5	3	9	4	119	1	7
4	511	518	2	-2	11	3	62	108	62	-4	-4	4	30	15	29	-4	3	4	90	79	6	-8	10	4	107	25	12
4	241	254	2	-1	11	3	31	53	31	-3	-4	4	151	156	4	-3	3	4	45	3	44	-7	10	4	76	64	76
4	72	45	8	0	11	3	60	20	59	-2	-4	4	160	164	3	-2	3	4	153	157	3	-6	10	4	50	90	49
4	163	149	3	1	11	3	110	112	10	-1	-4	4	201	194	3	-1	3	4	67	71	8	-5	10	4	97	96	13
4	47	59	16	2	11	3	89	100	58	0	-4	4	33	20	32	0	3	4	471	468	2	-4	10	4	79	53	16
5	41	87	41	3	11	3	58	72	23	1	-4	4	313	309	2	1	3	4	183	174	3	-3	10	4	107	69	13
5	77	4	32	-6	12	3	45	47	44	2	-4	4	429	402	2	2	3	4	72	72	7	-2	10	4	21	59	20
5	55	101	55	-5	12	3	82	25	32	-9	-3	4	112	91	10	3	3	4	185	181	3	-1	10	4	47	15	47
5	28	107	27	-4	12	3	33	19	33	-8	-3	4	112	113	10	-10	4	4	53	49	52	0	10	4	250	252	5
5	54	6	54	-3	12	3	77	0	36	-7	-3	4	150	160	7	-9	4	4	92	91	13	1	10	4	66	22	66
5	14	3	14	-2	12	3	121	134	10	-6	-3	4	69	29	69	-8	4	4	90	113	60	2	10	4	65	69	64
5	192	178	4	-1	12	3	82	36	81	-5	-3	4	56	27	49	-7	4	4	296	301	4	3	10	4	72	64	16
5	486	461	2	0	12	3	68	55	67	-4	-3	4	70	73	9	-6	4	4	88	102	10	-7	11	4	48	31	48
5	79	73	7	1	12	3	40	43	39	-3	-3	4	207	198	3	-5	4	4	233	237	3	-6	11	4	102	101	13
5	205	201	3	-4	13	3	128	2	9	-2	-3	4	299	304	2	-4	4	4	548	534	2	-5	11	4	56	33	55
5	753	742	3	-3	13	3	35	36	34	-1	-3	4	488	505	2	-3	4	4	456	452	2	-4	11	4	59	27	59
5	153	151	4	-2	13	3	74	61	74	0	-3	4	368	368	2	-2	4	4	355	349	2	-3	11	4	49	53	30
5	430	415	2	1-13		4	35	58	35	1	-3	4	150	164	4	-1	4	4	215	235	3	-2	11	4	197	192	7
5	120	121	6	2-13		4	56	5	7	2	-3	4	360	349	2	0	4	4	24	40	24	-1	11	4	243	255	5
6	73	65	17	-1-12		4	41	38	40	-9	-2	4	62	4	61	1	4	4	21	53	20	0	11	4	137	8	6
6	123	136	10	0-12		4	114	22	11	-8	-2	4	212	211	6	2	4	4	337	342	2	1	11	4	80	23	14
6	52	123	52	1-12		4	91	142	25	-7	-2	4	184	176	6	3	4	4	78	91	9	2	11	4	118	125	10
6	85	11	61	2-12		4	126	73	9	-6	-2	4	248	252	4	-10	5	4	63	67	62	-6	12	4	39	48	39
6	3	126	146	8	-3-11	4	73	39	32	-5	-2	4	266	265	3	-9	5	4	50	125	49	-5	12	4	31	36	30

h	k	l	10Fo	10Fc	10s
4	3	5	53	64	52
4	4	5	74	59	74
4	5	5	83	100	15
4	6	5	41	18	41
4	7	5	63	74	20
4	8	5	77	36	15
4	9	5	78	28	78
5	0	5	89	24	54
5	1	5	59	33	59
5	2	5	34	55	33
5	3	5	127	137	9
5	4	5	110	34	11
5	5	5	24	51	24
5	6	5	74	84	17
5	7	5	80	66	26
5	8	5	81	8	23
5	9	5	86	69	68
5	10	5	102	37	14
5	11	5	63	88	63
5	12	5	226	210	5
5	13	5	105	98	11
5	14	5	170	178	7
5	15	5	0	57	1
5	16	5	94	95	12
5	17	5	145	142	8
5	18	5	147	149	8
5	19	5	64	80	64
5	20	5	58	22	57
5	21	5	84	14	68
5	22	5	128	137	9
5	23	5	46	37	26
5	24	5	40	104	39
5	25	5	156	141	7
5	26	5	97	110	12
5	27	5	104	2	12
5	28	5	117	105	9
5	29	5	179	187	6
5	30	5	72	19	29
5	31	5	216	211	5
5	32	5	53	10	53
5	33	5	19	58	18
5	34	5	65	51	15
5	35	5	145	162	8
5	36	5	102	95	11
5	37	5	206	195	6
5	38	5	207	209	5
5	39	5	55	27	54
5	40	5	31	45	31
5	41	5	55	23	15
5	42	5	46	48	46
5	43	5	260	265	3
5	44	5	0	24	1
5	45	5	78	39	77
5	46	5	23	13	23
5	47	5	51	14	7
5	48	5	46	6	45
5	49	5	75	42	22
5	50	5	45	46	44
5	51	5	46	28	45
5	52	5	87	83	9
6	53	5	204	205	3
6	54	5	106	110	6
6	55	5	341	335	3
5	56	5	79	27	28
5	57	5	0	42	1
5	58	5	117	47	10
5	59	5	139	142	7
5	60	5	41	37	41
5	61	5	38	1	38
5	62	5	252	235	3
5	63	5	224	222	3
5	64	5	154	165	4
5	65	5	291	280	2
5	66	5	795	785	3
-4	0	5	43	35	42
-4	1	5	76	88	76
-4	2	5	142	137	8
-4	3	5	60	66	17
-4	4	5	128	48	5
-4	5	5	220	211	4
-4	6	5	181	165	4
-4	7	5	280	278	2
-4	8	5	532	527	2
-4	9	5	130	128	4
-4	10	5	37	19	36
-4	11	5	229	242	3
-3	12	5	164	152	7
-3	13	5	22	41	22
-3	14	5	86	69	24
-3	15	5	102	9	10

h	k	l	10Fo	10Fc	10s
-5	-3	5	67	58	66
-4	-3	5	44	55	43
-3	-3	5	192	203	3
-2	-3	5	644	643	3
-1	-3	5	212	220	3
0	-3	5	466	470	2
1	-3	5	259	263	2
2	-3	5	207	208	3
-9	-2	5	149	143	8
-8	-2	5	22	15	21
-7	-2	5	73	11	33
-6	-2	5	123	117	7
-5	-2	5	348	361	3
-4	-2	5	83	76	7
-3	-2	5	251	270	2
-2	-2	5	39	38	38
-1	-2	5	12	95	11
0	-2	5	749	770	3
1	-2	5	337	341	2
2	-2	5	296	282	2
-10	-1	5	35	12	34
-9	-1	5	56	45	56
-8	-1	5	0	0	1
-7	-1	5	53	71	20
-6	-1	5	36	73	36
-5	-1	5	279	291	3
-4	-1	5	343	338	2
-3	-1	5	586	591	2
-2	-1	5	349	345	2
-1	-1	5	1446	1472	5
0	-1	5	536	541	2
1	-1	5	623	630	3
2	-1	5	298	295	2
-10	0	5	64	57	63
-9	0	5	84	96	14
-8	0	5	139	146	8
-7	0	5	52	32	20
-6	0	5	343	342	3
-5	0	5	96	36	7
-4	0	5	145	142	4
-3	0	5	207	213	3
-2	0	5	973	992	4
-1	0	5	200	199	2
0	0	5	691	691	3
1	0	5	750	742	3
2	0	5	114	120	4
-10	1	5	41	14	41
-9	1	5	113	114	10
-8	1	5	77	52	32
-7	1	5	57	79	57
-6	1	5	260	267	4
-5	1	5	86	67	8
-4	1	5	241	219	3
-3	1	5	144	145	4
-2	1	5	225	237	3
-1	1	5	1492	1538	5
0	1	5	766	784	3
1	1	5	17	43	17
2	1	5	540	549	2
-10	2	5	137	140	9
-9	2	5	62	38	62
-8	2	5	167	162	7
-7	2	5	280	271	4
-6	2	5	223	212	4
-5	2	5	291	282	3
-4	2	5	68	46	12
-3	2	5	73	10	10
-2	2	5	273	274	2
-1	2	5	312	317	2
0	2	5	526	539	2
1	2	5	402	413	2
2	2	5	45	55	11
3	2	5	361	355	2
-10	3	5	23	47	23
-9	3	5	138	31	6
-8	3	5	14	11	14
-7	3	5	38	12	38
-6	3	5	118	116	7
-5	3	5	323	308	3
-4	3	5	157	153	4
-3	3	5	308	299	2
-2	3	5	359	363	2
-1	3	5	53	13	52
0	3	5	213	211	3
1	3	5	194	193	3
2	3	5	325	321	2
3	3	5	93	22	7
-10	4	5	75	32	74
-9	4	5	113	37	11
-8	4	5	62	81	62

h	k	l	10Fo	10Fc	10s
-7	4	5	43	8	43
-6	4	5	36	45	35
-5	4	5	195	187	4
-4	4	5	401	391	2
-3	4	5	78	79	7
-2	4	5	136	137	4
-1	4	5	78	65	7
0	4	5	51	59	11
1	4	5	237	228	3
2	4	5	177	174	4
3	4	5	0	62	1
-10	5	5	24	19	23
-9	5	5	39	44	38
-8	5	5	174	161	7
-7	5	5	34	28	34
-6	5	5	125	116	7
-5	5	5	397	406	3
-4	5	5	16	57	16
-3	5	5	357	336	2
-2	5	5	34	89	34
-1	5	5	454	444	2
0	5	5	117	119	5
1	5	5	133	148	5
2	5	5	124	124	6
3	5	5	181	173	5
-10	6	5	42	39	41
-9	6	5	107	29	12
-8	6	5	93	136	58
-7	6	5	47	42	28
-6	6	5	66	5	66
-5	6	5	166	154	5
-4	6	5	164	165	5
-3	6	5	433	431	2
-2	6	5	68	45	51
-1	6	5	420	416	2
0	6	5	149	141	5
1	6	5	39	26	38
2	6	5	155	148	6
3	6	5	135	131	7
-10	7	5	0	67	1
-9	7	5	77	60	16
-8	7	5	80	88	15
-7	7	5	95	103	59
-6	7	5	44	4	44
-5	7	5	60	64	59
-4	7	5	81	64	49
-3	7	5	66	69	66
-2	7	5	366	353	3
-1	7	5	200	189	4
0	7	5	40	17	40
1	7	5	91	39	12
2	7	5	78	72	57
3	7	5	46	52	45
-9	8	5	105	110	12
-8	8	5	129	126	9
-7	8	5	127	58	9
-6	8	5	132	131	9
-5	8	5	139	151	8
-4	8	5	90	63	54
-3	8	5	80	120	70
-2	8	5	121	126	8
-1	8	5	76	72	75
0	8	5	33	42	33
1	8	5	160	162	6
2	8	5	109	121	10
3	8	5	86	61	52
-9	9	5	88	60	58
-8	9	5	23	62	23
-7	9	5	77	31	37
-6	9	5	60	65	22
-5	9	5	78	128	77
-4	9	5	161	170	7
-3	9	5	90	59	57
-2	9	5	43	15	37
-1	9	5	122	127	9
0	9	5	114	106	10
1	9	5	21	69	21
2	9	5	69	70	69
3	9	5	51	102	50
-8	10	5	66	40	20
-7	10	5	93	57	13
-6	10	5	87	20	80
-5	10	5	292	290	5
-4	10	5	137	140	9
-3	10	5	32	50	32
-2	10	5	118	119	10
-1	10	5	80	79	80
0	10	5	9	8	8
1	10	5	266	269	5
2	10	5	134	122	8

h	k	l	10Fo	10Fc	10s
3	10	5	122	110	9
-6	11	5	33	31	33
-5	11	5	69	44	3
-4	11	5	130	67	8
-3	11	5	55	36	23
-2	11	5	84	73	29
-1	11	5	115	121	10
0	11	5	81	85	14
1	11	5	0	51	1
2	11	5	120	115	9
-6	12	5	42	24	42
-5	12	5	87	18	75
-4	12	5	92	80	59
-3	12	5	187	183	7
-2	12	5	111	2	11
-1	12	5	98	87	12
0	12	5	21	28	21
-11	12	6	112	15	12
0	12	6	83	90	15
1	12	6	53	33	53
2	12	6	66	80	19
-11	11	6	71	56	17
-11	10	6	58	94	58
-11	9	6	199	200	6
-11	8	6	116	16	9
-11	7	6	115	116	10
-11	6	6	22	21	22
-10	5	6	99	71	17
-10	4	6	0	8	1
-10	3	6	55	3	54
-10	2	6	82	114	81
-10	1	6	215	207	6
-10	0	6	93	75	20
-10	1	6	64	20	63
-9	-9	6	68	14	67
-9	-8	6	60	32	60
-9	-7	6	60	57	20
-9	-6	6	121	121	9
-9	-5	6	111	96	10
-9	-4	6	158	164	7
-9	-3	6	139	141	8
-9	-2	6	30	19	30
-8	-8	6	59	100	58
-8	-5	6	161	167	7
-8	-4	6	129	36	7
-8	-3	6	118	141	9
-8	-2	6	53	52	52
-8	-1	6	75	12	67
-8	0	6	35	43	34
-8	1	6	155	154	6
-8	2	6	169	173	6
-7	-7	6	49	7	48
-7	-6	6	119	45	8
-7	-5	6	84	18	61
-7	-4	6	36	11	35
-7	-3	6	18	30	18
-7	-2	6	112	113	8
-7	-1	6	145	145	6
-7	0	6	79	66	10
-7	1	6	140	124	6
-7	2	6	150	154	6
-6	-6	6	92	33	17
-6	-5	6	81	8	67
-6	-4	6	222	227	6
-6	-3	6	36	9	35
-6	-2	6	81	2	19
-6	-1	6	182	192	5
-6	0	6	320	311	3
-6	1	6	254	239	3
-6	2	6	262	257	3
-6	3	6	513	497	2
-6	4	6	300	286	3
-5	-5	6	41	13	41
-5	-4	6	39	7	38
-5	-3	6	124	126	9
-5	-2	6	141	143	7
-5	-1	6	306	313	3
-5	0	6	113	99	6
-5	1	6	102	109	6
-5	2	6	63	96	63
-5	3	6	311	296	2
-5	4	6	240	230	3
-5	5	6	231	227	3
-4	-4	6	63	67	19
-4	-3	6	46	31	46
-4	-2	6	190	186	6
-4	-1	6	97	109	11
-4	0	6	80	86	55
-4	1	6	172	188	5
-4	2	6	148	130	4

h	k	l	10Fo	10Fc	10s
-2	-4	6	44	4	43
-1	-4	6	369	355	2
0	-4	6	20	15	20
1	-4	6	59	11	15
2	-4	6	241	233	3
-9	-3	6	59	92	58
-8	-3	6	78	82	73
-7	-3	6	174	161	6
-6	-3	6	75	35	69
-5	-3	6	147	147	6
-4	-3	6	62	81	23
-3	-3	6	312	297	2
-2	-3	6	241	229	2
-1	-3	6	372	375	2
0	-3	6	345	349	2
1	-3	6	155	144	3
2	-3	6	22	0	21
-9	-2	6	94	119	57
-8	-2	6	111	129	10
-7	-2	6	86	116	65
-6	-2	6	180	187	5
-5	-2	6	284	273	3
-4	-2	6	60	70	59
-3	-2	6	567	570	2
-2	-2	6	138	144	4
-1	-2	6	55	73	21
0	-2	6	328	343	2
1	-2	6	490	490	2
2	-2	6	41	1	41
-10	-1	6	74	9	37
-9	-1	6	122	117	9
-8	-1	6	39	38	16
-7	-1	6	74	59	33
-6	-1	6	134	125	7
-5	-1	6	142	129	5
-4	-1	6	217	232	3
-3	-1	6	161	155	3
-2	-1	6	400	392	2
-1	-1	6	981	1013	4
0	-1	6	372	383	2
1	-1	6	382	380	2
2	-1	6	439	440	2
-10	0	6	64	60	64
-9	0	6	78	85	78
-8	0	6	66	43	60
-7	0	6	283	286	4
-6	0	6	123	110	7
-5	0	6	268	262	3
-4	0	6	442	445	2
-3	0	6	185	178	3
-2	0	6	317	324	2
-1	0	6	618	618	3
0	0	6	1293	1317	6
1	0	6	545	546	2
2	0	6	171	176	3
-10	1	6	102	108	12
-9	1	6	50	36	49
-8	1	6	137	122	8
-7	1	6	107	43	10
-6	1	6	50	64	50
-5	1	6	254	255	3
-4	1	6	306	305	2
-3	1	6	43	64	42
-2	1	6	521	534	2
-1	1	6	547	539	2
0	1	6	510	526	2
1	1	6	189	188	3
2	1	6	303	294	2
-10	2	6	67	7	67
-9	2	6	74	91	73
-8	2	6	62	61	61
-7	2	6	64	83	63
-6	2	6	151	147	6
-5	2	6	202	209	4
-4	2	6	460	462	2
-3	2	6	119	109	5
-2	2	6	29	29	28
-1	2	6	345	353	2
0	2	6	327	328	2
1	2	6	455	456	2
2	2	6	90	96	6
3	2	6	281	279	3
-10	3	6	71	103	70
-9	3	6	89	107	14
-8	3	6	51	46	50
-7	3	6	130	137	8
-6	3	6	44	40	43
-5	3	6	193	179	4
-4	3	6	160	166	4
-3	3	6	222	207	3

h	k	l	10Fo	10Fc	10s
6	142	138	4		
6	309	305	2		
6	242	239	2		
6	263	258	2		
6	162	173	4		
6	126	129	5		
6	67	10	67		
6	161	175	8		
6	59	84	58		
6	51	57	51		
6	223	226	4		
6	130	144	6		
6	171	158	4		
6	160	155	4		
6	178	187	3		
6	504	492	2		
6	95	91	6		
6	304	292	2		
6	84	86	8		
6	369	367	3		
6	94	79	13		
6	199	196	6		
6	63	79	63		
6	82	48	23		
6	59	64	17		
6	35	19	35		
6	267	260	3		
6	170	181	4		
6	259	256	3		
6	370	374	2		
6	480	469	2		
6	353	338	3		
6	64	51	27		
6	33	63	32		
6	59	30	59		
6	0	52	1		
6	85	83	14		
6	58	43	57		
6	143	140	7		
6	261	264	4		
6	80	52	50		
6	249	243	3		
6	196	208	4		
6	151	140	5		
6	54	28	54		
6	237	243	4		
6	159	153	6		
6	109	121	9		
6	54	43	26		
6	33	43	32		
6	110	72	11		
6	30	60	29		
6	80	78	79		
6	67	30	16		
6	195	205	5		
6	74	127	74		
6	211	194	4		
6	72	16	52		
6	101	96	9		
6	95	109	10		
6	56	74	56		
6	86	3	57		
6	79	8	78		
6	80	80	15		
6	42	52	41		
6	83	99	83		
6	351	359	4		
6	31	41	30		
6	52	39	21		
6	76	61	76		
6	10	44	10		
6	109	50	9		
6	76	72	75		
6	76	36	31		
6	0	122	1		
6	53	8	26		
6	0	26	1		
6	45	51	44		
6	146	136	8		
6	0	66	1		
6	308	308	4		
6	157	155	7		
6	91	19	17		
6	54	0	54		
6	198	203	6		
6	183	172	6		
6	299	297	4		
6	91	82	12		
6	76	82	76		
6	33	64	33		
-6	10	6	34	10	34
-5	10	6	173	171	7
-4	10	6	86	64	14
-3	10	6	202	191	6
-2	10	6	251	254	5
-1	10	6	161	148	7
0	10	6	204	208	6
1	10	6	51	60	50
2	10	6	114	124	10
3	10	6	84	91	67
-7	11	6	54	22	54
-6	11	6	94	33	23
-5	11	6	33	55	32
-4	11	6	151	166	8
-3	11	6	64	63	64
-2	11	6	60	86	60
-1	11	6	69	58	68
0	11	6	151	154	8
1	11	6	96	6	16
2	11	6	104	19	15
-6	12	6	116	21	12
-5	12	6	45	35	44
-4	12	6	86	107	69
-3	12	6	89	49	65
-2	12	6	76	24	37
-1	12	6	24	1	24
0	12	6	35	55	34
-1	-12	7	49	37	49
0	-12	7	59	45	59
1	-12	7	83	57	78
2	-12	7	75	29	36
-3	-11	7	132	31	6
-2	-11	7	46	6	31
-1	-11	7	57	11	57
0	-11	7	115	60	11
1	-11	7	53	71	24
2	-11	7	126	54	6
-4	-10	7	45	68	35
-3	-10	7	81	84	80
-2	-10	7	23	96	22
-1	-10	7	19	8	19
0	-10	7	259	252	5
1	-10	7	71	83	71
2	-10	7	68	99	68
-5	-9	7	54	17	53
-4	-9	7	119	146	10
-3	-9	7	84	97	14
-2	-9	7	105	40	12
-1	-9	7	81	53	80
0	-9	7	94	73	11
1	-9	7	50	18	49
2	-9	7	0	20	1
-6	-8	7	20	2	20
-5	-8	7	76	31	24
-4	-8	7	114	125	10
-3	-8	7	52	47	23
-2	-8	7	175	173	6
-1	-8	7	49	47	22
0	-8	7	72	37	72
1	-8	7	163	158	6
2	-8	7	61	34	60
-7	-7	7	49	20	48
-6	-7	7	107	99	10
-5	-7	7	69	96	69
-4	-7	7	98	6	14
-3	-7	7	69	47	39
-2	-7	7	60	99	60
-1	-7	7	49	129	49
0	-7	7	54	23	54
1	-7	7	175	171	5
2	-7	7	140	132	6
-7	-6	7	23	110	23
-6	-6	7	115	35	10
-5	-6	7	169	164	6
-4	-6	7	56	47	55
-3	-6	7	73	62	26
-2	-6	7	123	107	6
-1	-6	7	54	62	14
0	-6	7	90	91	8
1	-6	7	34	21	34
2	-6	7	182	169	4
-8	-5	7	42	33	41
-7	-5	7	84	54	12
-6	-5	7	162	132	7
-5	-5	7	80	46	54
-4	-5	7	46	54	45
-3	-5	7	339	335	3
-2	-5	7	272	276	3
-1	-5	7	330	328	2
0	-5	7	575	559	2
1	-5	7	62	27	61
2	-5	7	217	199	3
-9	-4	7	60	32	60
-8	-4	7	77	75	76
-7	-4	7	140	147	8
-6	-4	7	35	34	35
-5	-4	7	19	25	19
-4	-4	7	0	0	1
-3	-4	7	478	462	2
-2	-4	7	104	94	6
-1	-4	7	268	264	2
0	-4	7	538	533	2
1	-4	7	26	9	26
2	-4	7	84	91	7
-9	-3	7	24	33	24
-8	-3	7	77	66	14
-7	-3	7	36	53	36
-6	-3	7	62	18	62
-5	-3	7	192	209	5
-4	-3	7	483	469	2
-3	-3	7	247	252	3
-2	-3	7	105	102	5
-1	-3	7	181	179	3
0	-3	7	167	174	3
1	-3	7	222	217	3
2	-3	7	741	712	3
-9	-2	7	70	27	46
-8	-2	7	179	180	7
-7	-2	7	113	99	9
-6	-2	7	64	68	15
-5	-2	7	413	427	3
-4	-2	7	186	183	3
-3	-2	7	138	131	4
-2	-2	7	545	548	2
-1	-2	7	216	245	2
0	-2	7	210	224	2
1	-2	7	87	86	6
2	-2	7	407	416	2
-10	-1	7	80	76	15
-9	-1	7	124	120	9
-8	-1	7	68	28	53
-7	-1	7	90	95	12
-6	-1	7	143	118	6
-5	-1	7	292	295	3
-4	-1	7	334	308	2
-3	-1	7	536	528	2
-2	-1	7	27	18	26
-1	-1	7	64	81	37
0	-1	7	221	226	2
1	-1	7	52	12	1
2	-1	7	521	495	2
-10	0	7	59	21	59
-9	0	7	64	115	64
-8	0	7	173	176	7
-7	0	7	62	73	62
-6	0	7	62	57	14
-5	0	7	53	67	52
-4	0	7	197	188	3
-3	0	7	31	37	31
-2	0	7	587	596	3
-1	0	7	341	351	2
0	0	7	120	135	5
1	0	7	800	802	4
2	0	7	166	155	3
-10	1	7	64	39	63
-9	1	7	108	112	11
-8	1	7	51	18	25
-7	1	7	53	14	20
-6	1	7	153	147	6
-5	1	7	333	336	3
-4	1	7	61	58	60
-3	1	7	315	331	2
-2	1	7	727	734	3
-1	1	7	353	352	2
0	1	7	83	97	6
1	1	7	476	470	2
2	1	7	44	45	44
-10	2	7	63	24	62
-9	2	7	234	232	5
-8	2	7	66	66	65
-7	2	7	163	171	6
-6	2	7	119	97	7
-5	2	7	277	271	3
-4	2	7	102	106	6
-3	2	7	347	347	2
-2	2	7	177	165	3
-1	2	7	468	488	2
0	2	7	264	273	2
1	2	7	45	55	11
2	2	7	74	71	8
3	2	7	114	105	6
-10	3	7	65	40	19
-9	3	7	116	109	10
-8	3	7	89	81	13
-7	3	7	78	54	13
-6	3	7	138	113	6
-5	3	7	73	79	51
-4	3	7	65	9	46
-3	3	7	211	211	3
-2	3	7	251	254	2
-1	3	7	196	190	3
0	3	7	284	300	2
1	3	7	141	144	4
2	3	7	27	40	26
3	3	7	152	148	5
-10	4	7	58	64	23
-9	4	7	84	76	26
-8	4	7	30	38	29
-7	4	7	31	27	30
-6	4	7	18	94	18
-5	4	7	229	206	4
-4	4	7	227	217	3
-3	4	7	226	228	3
-2	4	7	140	133	4
-1	4	7	142	141	4
0	4	7	427	419	2
1	4	7	67	10	51
2	4	7	54	45	53
3	4	7	58	29	52
-10	5	7	42	106	41
-9	5	7	72	65	71
-8	5	7	84	77	14
-7	5	7	124	153	9
-6	5	7	199	211	5
-5	5	7	45	17	6
-4	5	7	66	15	22
-3	5	7	215	215	3
-2	5	7	51	34	50
-1	5	7	16	50	16
0	5	7	217	223	3
1	5	7	97	52	7
2	5	7	134	124	6
3	5	7	66	34	33
-10	6	7	49	63	48
-9	6	7	33	52	32
-8	6	7	43	71	43
-7	6	7	0	3	1
-6	6	7	145	136	7
-5	6	7	56	32	55
-4	6	7	64	25	31
-3	6	7	104	46	8
-2	6	7	107	100	7
-1	6	7	421	419	3
0	6	7	18	2	17
1	6	7	155	152	6
2	6	7	72	20	71
3	6	7	83	25	56
-10	7	7	82	11	31
-9	7	7	33	38	33
-8	7	7	22	36	22
-7	7	7	92	75	59
-6	7	7	57	58	21
-5	7	7	70	91	69
-4	7	7	237	233	4
-3	7	7	80	70	18
-2	7	7	99	109	9
-1	7	7	60	2	15
0	7	7	81	84	11
1	7	7	171	165	6
2	7	7	111	118	9
3	7	7	56	74	56
-9	8	7	168	169	8
-8	8	7	51	78	51
-7	8	7	109	61	13
-6	8	7	75	60	16
-5	8	7	180	178	7
-4	8	7	139	141	8
-3	8	7	224	226	5
-2	8	7	301	304	4
-1	8	7	62	57	61
0	8	7	63	66	63
1	8	7	260	260	4
2	8	7	160	161	7
3	8	7	116	127	10
-9	9	7	43	42	42
-8	9	7	70	87	69
-7	9	7	175	176	7
-6	9	7	85	126	84
-5	9	7	43	6	42
-4	9	7	36	29	36
-3	9	7	143	138	8
-2	9	7	87	15	58
-1	9	7	88	102	59
0	9	7	23	2	22
1	9	7	72	105	72
2	9	7	45	14	44
3	9	7	41	60	40
-8	10	7	77	15	76
-7	10	7	9	3	9
-6	10	7	68	77	68
-5	10	7	277	275	5
-4	10	7	31	79	30
-3	10	7	180	194	7
-2	10	7	199	195	6
-1	10	7	342	341	4
0	10	7	273	280	5
1	10	7	89	77	12
2	10	7	98	21	16
3	10	7	60	50	60
-7	11	7	106	59	17
-6	11	7	154	157	9
-5	11	7	201	205	7
-4	11	7	159	144	8
-3	11	7	131	124	9
-2	11	7	146	150	8
-1	11	7	66	98	65
0	11	7	58	12	57
1	11	7	80	77	80
-5	12	7	42	13	42
-4	12	7	143	69	7
-3	12	7	42	149	41
-2	12	7	164	146	8
-1	12	7	127	49	9
-1	-12	8	96	3	15
0	-12	8	44	30	43
1	-12	8	48	35	48
2	-12	8	145	88	7
-3	-11	8	25	68	24
-2	-11	8	97	111	12
-1	-11	8	116	135	10
0	-11	8	69	57	69
1	-11	8	83	10	60
2	-11	8	79	73	15
-4	-10	8	91	41	61
-3	-10	8	47	38	46
-2	-10	8	156	163	8
-1	-10	8	167	169	7
0	-10	8	49	77	49
1	-10	8	53	26	53
2	-10	8	82	81	29
-5	-9	8	59	74	59
-4	-9	8	46	40	46
-3	-9	8	55	15	54
-2	-9	8	217	219	5
-1	-9	8	126	94	9
0	-9	8	6	19	5
1	-9	8	137	135	8
2	-9	8	21	13	20
-6	-8	8	80	17	27
-5	-8	8	74	69	14
-4	-8	8	69	54	16
-3	-8	8	74	66	73
-2	-8	8	154	164	7
-1	-8	8	28	33	28
0	-8	8	138	128	7
1	-8	8	152	146	6
2	-8	8	34	9	34
-7	-7	8	91	73	13
-6	-7	8	77	134	76
-5	-7	8	88	126	14
-4	-7	8	63	124	62
-3	-7	8	53	23	53
-2	-7	8	73	62	13
-1	-7	8	129	120	7
0	-7	8	158	153	6
1	-7	8	64	35	64
2	-7	8	0	90	1
-7	-6	8	41	93	40
-6	-6	8	22	38	22
-5	-6	8	125	67	7
-4	-6	8	129	119	8
-3	-6	8	174	175	5
-2	-6	8	309	294	3
-1	-6	8	291	286	3
0	-6	8	99	50	7
1	-6	8	194	185	4
2	-6	8	162	157	5
-8	-5	8	64	30	63
-7	-5	8	45	37	45
-6	-5	8	223	238	5

l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
8	67	127	66	-2	2	8	458	441	2	-7	9	8	116	3	11	-5	-5	9	108	104	10	-1	2	9	33	17	33
8	153	148	6	-1	2	8	366	364	2	-6	9	8	41	21	41	-4	-5	9	43	3	43	0	2	9	138	129	4
8	273	279	3	0	2	8	79	8	7	-5	9	8	89	67	79	-3	-5	9	176	184	5	1	2	9	72	71	8
8	179	183	4	1	2	8	57	23	56	-4	9	8	266	268	5	-2	-5	9	97	80	9	2	2	9	220	226	3
8	53	39	52	2	2	8	440	427	2	-3	9	8	266	270	5	-1	-5	9	67	65	11	3	2	9	112	122	7
8	17	46	16	3	2	8	334	324	3	-2	9	8	112	122	10	0	-5	9	350	363	3	-10	3	9	118	35	10
8	289	272	3	-10	3	8	131	136	9	-1	9	8	83	31	13	1	-5	9	314	307	3	-9	3	9	88	109	67
8	79	54	13	-9	3	8	84	106	83	0	9	8	246	242	5	2	-5	9	142	143	5	-8	3	9	145	131	8
8	121	94	9	-8	3	8	131	4	8	1	9	8	203	186	6	-8	-4	9	47	48	46	-7	3	9	66	10	66
8	79	29	78	-7	3	8	83	18	20	2	9	8	72	46	72	-7	-4	9	23	38	22	-6	3	9	241	242	4
8	21	13	20	-6	3	8	64	32	63	3	9	8	75	32	30	-6	-4	9	243	247	5	-5	3	9	251	239	4
8	108	72	9	-5	3	8	83	14	13	-8	10	8	60	95	59	-5	-4	9	166	166	6	-4	3	9	167	159	4
8	265	252	3	-4	3	8	293	288	3	-7	10	8	75	84	49	-4	-4	9	378	361	3	-3	3	9	204	214	3
8	124	119	6	-3	3	8	101	111	6	-6	10	8	69	10	47	-3	-4	9	91	86	8	-2	3	9	341	340	2
8	309	305	2	-2	3	8	111	112	5	-5	10	8	90	42	19	-2	-4	9	84	93	8	-1	3	9	78	59	9
8	61	42	60	-1	3	8	176	174	3	-4	10	8	169	172	7	-1	-4	9	114	75	4	0	3	9	96	101	6
8	128	121	5	0	3	8	471	479	2	-3	10	8	212	215	6	0	-4	9	39	71	39	1	3	9	146	145	5
8	241	238	3	1	3	8	307	303	2	-2	10	8	73	13	36	1	-4	9	121	118	5	2	3	9	230	215	3
8	36	9	19	2	3	8	171	164	4	-1	10	8	105	66	12	2	-4	9	630	615	3	3	3	9	73	57	12
8	126	134	10	3	3	8	188	184	4	0	10	8	96	59	16	-9	-3	9	156	147	8	-10	4	9	54	68	53
8	82	16	65	-10	4	8	112	113	12	1	10	8	84	38	58	-8	-3	9	262	252	5	-9	4	9	97	14	16
8	27	3	27	-9	4	8	32	33	32	2	10	8	34	49	34	-7	-3	9	176	172	6	-8	4	9	203	212	6
8	38	71	37	-8	4	8	90	17	60	-7	11	8	74	36	73	-6	-3	9	53	52	53	-7	4	9	41	29	13
8	209	212	4	-7	4	8	220	223	5	-6	11	8	154	80	6	-5	-3	9	203	198	5	-6	4	9	27	14	26
8	167	166	4	-6	4	8	170	169	6	-5	11	8	78	71	16	-4	-3	9	205	187	4	-5	4	9	233	232	4
8	114	120	6	-5	4	8	53	18	52	-4	11	8	221	226	6	-3	-3	9	58	33	27	-4	4	9	241	222	4
8	74	36	11	-4	4	8	230	234	4	-3	11	8	140	147	9	-2	-3	9	586	583	3	-3	4	9	50	58	15
8	436	423	2	-3	4	8	325	319	3	-2	11	8	58	19	21	-1	-3	9	405	399	2	-2	4	9	180	164	4
8	320	323	2	-2	4	8	77	5	10	-1	11	8	191	209	7	0	-3	9	198	197	3	-1	4	9	75	65	9
8	326	310	2	-1	4	8	602	595	3	0	11	8	24	36	24	1	-3	9	226	229	3	0	4	9	15	41	15
8	445	444	2	0	4	8	476	460	2	1	11	8	130	65	8	2	-3	9	40	20	39	1	4	9	276	281	3
8	91	61	57	1	4	8	380	373	2	-5	12	8	78	13	77	-9	-2	9	37	3	24	2	4	9	157	149	5
8	38	6	38	2	4	8	59	98	58	-4	12	8	73	77	73	-8	-2	9	77	25	26	3	4	9	93	96	10
8	135	128	8	3	4	8	216	223	4	-3	12	8	73	47	40	-7	-2	9	59	115	59	-10	5	9	49	62	48
8	101	94	10	-10	5	8	24	62	24	-2	12	8	25	35	24	-6	-2	9	441	431	3	-9	5	9	46	88	45
8	31	60	30	-9	5	8	157	157	8	0	-12	9	92	57	19	-5	-2	9	86	96	10	-8	5	9	69	119	68
8	33	5	33	-8	5	8	86	16	62	1	-12	9	73	33	73	-4	-2	9	186	191	4	-7	5	9	272	271	5
8	501	490	2	-7	5	8	73	51	73	2	-12	9	54	3	54	-3	-2	9	42	11	15	-6	5	9	76	56	75
8	453	457	2	-6	5	8	79	111	78	-2	-11	9	77	33	76	-2	-2	9	203	213	3	-5	5	9	187	192	5
8	106	94	5	-5	5	8	83	106	52	-1	-11	9	89	8	18	-1	-2	9	71	8	8	-4	5	9	264	266	4
8	233	223	2	-4	5	8	72	106	71	0	-11	9	33	55	33	0	-2	9	397	387	2	-3	5	9	413	415	3
8	633	614	3	-3	5	8	147	166	5	1	-11	9	98	108	12	1	-2	9	185	182	3	-2	5	9	17	38	17
8	171	177	3	-2	5	8	67	3	21	2	-11	9	68	34	17	2	-2	9	88	81	6	-1	5	9	17	53	17
8	60	1	60	-1	5	8	62	40	25	-4	-10	9	60	68	60	-9	-1	9	59	66	20	0	5	9	515	508	2
8	40	44	40	0	5	8	137	140	5	-3	-10	9	98	21	14	-8	-1	9	62	71	61	1	5	9	83	69	10
8	147	160	8	1	5	8	211	215	4	-2	-10	9	164	155	7	-7	-1	9	29	63	28	2	5	9	159	152	6
8	29	78	28	2	5	8	59	69	58	-1	-10	9	64	16	63	-6	-1	9	300	301	4	3	5	9	60	47	17
8	73	65	13	3	5	8	128	131	7	0	-10	9	170	165	7	-5	-1	9	184	181	5	-10	6	9	74	1	73
8	103	20	7	-10	6	8	120	83	10	1	-10	9	0	61	1	-4	-1	9	334	317	3	-9	6	9	67	75	19
8	152	148	4	-9	6	8	52	91	51	2	-10	9	115	122	10	-3	-1	9	500	484	2	-8	6	9	203	201	6
8	360	356	2	-8	6	8	197	191	7	-5	-9	9	84	31	84	-2	-1	9	110	115	5	-7	6	9	141	136	9
8	344	341	2	-7	6	8	93	129	56	-4	-9	9	66	68	17	-1	-1	9	226	221	3	-6	6	9	279	291	4
8	595	601	2	-6	6	8	20	41	19	-3	-9	9	62	64	18	0	-1	9	169	178	3	-5	6	9	72	51	14
8	85	89	6	-5	6	8	76	28	71	-2	-9	9	88	99	58	1	-1	9	889	901	4	-4	6	9	150	146	6
8	450	458	2	-4	6	8	202	197	5	-1	-9	9	109	102	10	2	-1	9	303	280	2	-3	6	9	132	131	7
8	319	308	2	-3	6	8	53	77	53	0	-9	9	108	41	12	-10	0	9	88	45	60	-2	6	9	216	215	4
8	54	32	54	-2	6	8	124	116	7	1	-9	9	51	20	51	-9	0	9	123	114	9	-1	6	9	77	19	47
8	60	80	60	-1	6	8	47	70	46	2	-9	9	96	98	12	-8	0	9	355	355	4	0	6	9	86	66	10
8	126	38	7	0	6	8	85	35	13	-6	-8	9	94	137	57	-7	0	9	133	134	8	1	6	9	19	17	19
8	20	114	19	1	6	8	108	98	8	-5	-8	9	87	32	17	-6	0	9	121	128	8	2	6	9	127	1	6
8	55	36	55	2	6	8	48	121	48	-4	-8	9	50	54	49	-5	0	9	43	37	42	3	6	9	92	80	17
8	328	314	3	3	6	8	152	137	7	-3	-8	9	80	116	80	-4	0	9	199	189	3	-9	7	9	58	108	58
8	36	40	21	-9	7	8	180	172	7	-2	-8	9	29	44	29	-3	0	9	624	620	3	-8	7	9	77	68	16
8	438	436	2	-8	7	8	146	127	8	-1	-8	9	73	12	73	-2	0	9	175	170	3	-7	7	9	100	108	12
8	776	789	3	-7	7	8	206	207	6	0	-8	9	155	149	7	-1	0	9	414	411	2	-6	7	9	108	78	11
8	24	12	23	-6	7	8	65	27	64	1	-8	9	191	183	6	0	0	9	444	462	2	-5	7	9	244	252	5
8	453	456	2	-5	7	8	71	26	15	2	-8	9	236	238	5	1	0	9	766	769	4	-4	7	9	66	16	16
8	146	165	3	-4	7	8	86	67	12	-7	-7	9	60	27	60	2	0	9	234	222	3	-3	7	9	86	5	19
8	279	278	2	-3	7	8	38	13	38	-6	-7	9	94	89	12	-10	1	9	81	7	80	-2	7	9	236	227	4
8	24	94	24	-2	7	8	165	169	6	-5	-7	9	100	24	13	-9	1	9	39	13	39	-1	7	9	255	260	4
8	75	24	74	-1	7	8	147	158	6	-4	-7	9	43	88	42	-8	1	9	155	153	7	0	7	9	52	8	52
8	107	79	11	0	7	8	128	113	7	-3	-7	9	79	76	78	-7	1	9	160	152	7	1	7	9	156	149	7
8	224	217	5	1	7	8	80	115	79	-2	-7	9	130	138	8	-6	1	9	65	58	64	2	7	9	21	15	21
8	62	59	15	2	7	8	176	159	6	-1	-7	9	31	14	31	-5	1	9	65	33	65	3	7	9	232	223	5
8	123	136	6	3	7	8	143	127	7	0	-7	9	175	153	5	-4	1	9	97	108	7	-9	8	9	84	61	15
8	133	123	5	-9	8	8	7	11	6	1	-7	9	73	79	68	-3	1	9	511	492	2	-8	8	9	203	202	6
8	203	209	3	-8	8	8	103	47	15	2	-7	9	110	114	9	-2	1	9	1011	988	5	-7	8	9	123	144	10
8	270	266	2	-7	8	8	226	217	6	-7	-6	9	161	164	7	-1	1	9	14	7	14	-6	8	9	105	46	13
8	724	730	3	-6	8	8	195	185	6	-6	-6	9	64	35	63	0	1	9	200	201	3	-5	8	9	23	44	22
8	80	83	6	-5	8	8	67	84	18	-5	-6	9	192	185	6	1	1	9	569	567	2	-4	8	9	85	89	14
8	309	304	2	-4	8	8	83	23	69	-4	-6	9	210	210	5	2	1	9	134	112	4	-3	8	9	130	123	9
8	58	8	58	-3	8	8	86	140	72	-3	-6	9	39	45	38	-10	2	9	93	129	58	-2	8	9	121	23	8
8	38	50	38	-2	8	8	139	151	8	-2	-6	9	187	189	5	-9	2	9	0	105	1	-1	8	9	104	98	10
8	81	73	26	-1	8	8	184	170	6	-1	-6	9	373	372	3	-8	2	9	85	23	74	0	8	9	51	82	50
8	204	207	6	0	8	8	68	71	50	0	-6	9	335	326	3	-7	2	9	226	204	5	1	8	9	105	113	10
8	200	200	6	1	8	8	91	8	16	1	-6	9	77	41	10	-6	2	9	134	140	7	2	8	9	83	93	70
8	41	64	40	2	8	8	43	65	43	2	-6	9	45	119	44	-5	2	9	65	42	65	3	8	9	44	59	34
8	64	15	63	3	8	8	85	94	68	-8	-5	9	59	52	59	-4	2	9	162	158	4	-8	9	9	122	122	11
8	271	263	3	-9	9	8	35	4	34	-7	-5	9	69	6	39	-3	2	9	134	146	5	-7	9	9	121	125	10
8	394	387	2	-8	9	8	79	25	78	-6	-5	9	211	203	6	-2	2	9	350	349	2	-6	9	9	197	188	6

10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
58	119	57	-7	-4	10	263	282	5	-5	3	10	36	82	36	-5	10	10	86	61	27	1	-3	11	161	161	4
83	135	83	-6	-4	10	172	167	6	-4	3	10	35	2	10	-4	10	10	203	215	6	2	-3	11	53	65	52
21	97	21	-5	-4	10	40	19	40	-3	3	10	477	481	2	-3	10	10	88	36	22	-9	-2	11	77	66	16
64	47	63	-4	-4	10	144	148	6	-2	3	10	571	553	2	-2	10	10	76	82	75	-8	-2	11	23	13	22
53	24	52	-3	-4	10	105	109	8	-1	3	10	75	57	8	-1	10	10	89	16	22	-7	-2	11	170	179	7
58	52	20	-2	-4	10	256	249	3	0	3	10	254	248	3	0	10	10	74	69	74	-6	-2	11	73	121	73
60	52	59	-1	-4	10	229	221	3	1	3	10	204	194	4	1	10	10	65	49	18	-5	-2	11	87	66	11
52	7	52	0	-4	10	186	184	4	2	3	10	36	68	36	-6	11	10	120	66	10	-4	-2	11	93	94	9
34	46	33	1	-4	10	291	287	3	3	3	10	165	177	6	-5	11	10	130	151	10	-3	-2	11	60	44	59
86	18	29	2	-4	10	197	200	4	-10	4	10	73	83	73	-4	11	10	177	152	7	-2	-2	11	402	387	2
104	51	16	-9	-3	10	35	75	34	-9	4	10	56	89	56	-3	11	10	110	124	12	-1	-2	11	61	41	61
106	104	11	-8	-3	10	23	75	22	-8	4	10	129	33	7	-2	11	10	113	106	11	0	-2	11	311	317	2
80	67	15	-7	-3	10	332	333	4	-7	4	10	82	27	25	-1	11	10	137	137	9	1	-2	11	53	61	13
229	224	6	-6	-3	10	79	64	64	-6	4	10	183	188	6	0	11	10	0	14	1	2	-2	11	67	29	50
87	30	23	-5	-3	10	293	291	4	-5	4	10	70	77	14	-1	-11	11	54	17	54	-9	-1	11	53	63	53
188	199	7	-4	-3	10	79	12	15	-4	4	10	56	41	56	0	-11	11	89	107	14	-8	-1	11	61	82	20
93	117	13	-3	-3	10	174	154	4	-3	4	10	112	111	7	1	-11	11	44	21	34	-7	-1	11	194	175	6
146	163	8	-2	-3	10	476	471	2	-2	4	10	345	342	3	2	-11	11	42	66	41	-6	-1	11	63	84	62
63	50	62	-1	-3	10	109	100	6	-1	4	10	45	37	44	-3	-10	11	173	173	7	-5	-1	11	147	136	6
54	32	54	0	-3	10	112	104	5	0	4	10	67	78	11	-2	-10	11	167	163	7	-4	-1	11	119	117	7
59	50	23	1	-3	10	649	634	3	1	4	10	241	242	4	-1	-10	11	93	130	56	-3	-1	11	45	1	44
156	161	9	2	-3	10	171	178	4	2	4	10	48	40	19	0	-10	11	125	120	9	-2	-1	11	126	128	5
100	20	17	-9	-2	10	145	140	8	3	4	10	52	89	52	1	-10	11	193	205	6	-1	-1	11	60	16	59
85	54	84	-8	-2	10	83	102	14	-10	5	10	43	97	42	2	-10	11	56	31	56	0	-1	11	268	249	3
123	139	10	-7	-2	10	177	178	6	-9	5	10	61	121	61	-4	-9	11	86	83	60	1	-1	11	152	149	4
66	57	19	-6	-2	10	71	71	15	-8	5	10	116	35	10	-3	-9	11	65	58	17	2	-1	11	35	39	34
70	68	17	-5	-2	10	88	99	10	-7	5	10	225	224	6	-2	-9	11	106	101	10	-9	0	11	38	12	21
78	85	78	-4	-2	10	183	181	4	-6	5	10	84	30	24	-1	-9	11	203	188	6	-8	0	11	38	19	38
114	113	11	-3	-2	10	55	18	38	-5	5	10	38	21	37	0	-9	11	79	63	78	-7	0	11	215	205	6
49	9	49	-2	-2	10	678	666	3	-4	5	10	113	103	8	1	-9	11	188	188	7	-6	0	11	90	57	11
74	36	74	-1	-2	10	52	24	51	-3	5	10	78	65	61	2	-9	11	141	144	9	-5	0	11	321	322	3
125	119	10	0	-2	10	228	231	3	-2	5	10	59	37	14	-5	-8	11	53	10	53	-4	0	11	107	108	7
136	47	5	1	-2	10	281	267	3	-1	5	10	69	45	21	-4	-8	11	90	66	12	-3	0	11	351	338	3
82	61	26	2	-2	10	196	194	4	0	5	10	70	2	70	-3	-8	11	22	92	22	-2	0	11	409	405	2
118	96	9	-9	-1	10	78	36	32	1	5	10	229	232	4	-2	-8	11	43	8	43	-1	0	11	259	252	3
92	82	12	-8	-1	10	22	61	22	2	5	10	100	19	10	-1	-8	11	42	12	42	0	0	11	470	456	2
34	47	33	-7	-1	10	194	202	6	3	5	10	145	148	7	0	-8	11	78	126	77	1	0	11	97	110	7
33	125	33	-6	-1	10	89	119	61	-9	6	10	78	48	78	1	-8	11	46	61	46	2	0	11	354	356	3
114	140	10	-5	-1	10	60	27	3	-8	6	10	250	272	6	2	-8	11	85	105	13	-10	1	11	42	13	15
62	19	18	-4	-1	10	253	251	3	-7	6	10	212	212	6	-6	-7	11	83	15	22	-9	1	11	66	28	65
62	64	19	-3	-1	10	425	428	2	-6	6	10	181	204	7	-5	-7	11	85	22	19	-8	1	11	117	132	11
127	133	9	-2	-1	10	296	289	2	-5	6	10	40	17	14	-4	-7	11	71	74	16	-7	1	11	253	259	5
43	127	42	-1	-1	10	201	207	3	-4	6	10	85	77	53	-3	-7	11	16	22	16	-6	1	11	97	97	10
130	59	7	0	-1	10	162	147	3	-3	6	10	109	50	10	-2	-7	11	105	85	10	-5	1	11	71	85	29
51	39	51	1	-1	10	376	375	2	-2	6	10	72	85	72	-1	-7	11	60	45	17	-4	1	11	363	376	3
116	116	10	2	-1	10	286	275	3	-1	6	10	15	16	14	0	-7	11	186	193	6	-3	1	11	218	214	3
31	100	30	-10	0	10	65	55	65	0	6	10	85	74	11	1	-7	11	77	101	76	-2	1	11	347	338	2
57	56	56	-8	0	10	183	197	7	1	6	10	114	112	8	2	-7	11	115	71	7	-1	1	11	173	163	4
316	328	4	-7	0	10	289	288	4	2	6	10	74	9	74	-7	-6	11	101	96	12	0	1	11	414	397	2
37	11	37	-6	0	10	124	99	8	3	6	10	94	24	16	-6	-6	11	121	126	9	1	1	11	183	174	4
104	31	13	-5	0	10	199	209	4	-9	7	10	76	34	75	-5	-6	11	79	66	78	2	1	11	144	149	5
53	51	52	-4	0	10	219	217	4	-8	7	10	34	31	34	-4	-6	11	66	73	66	-10	2	11	57	63	24
81	4	24	-3	0	10	261	251	3	-7	7	10	210	221	6	-3	-6	11	67	29	66	-9	2	11	66	41	65
75	97	75	-2	0	10	1058	1051	5	-6	7	10	170	182	7	-2	-6	11	137	135	7	-8	2	11	87	41	72
151	146	7	-1	0	10	144	152	4	-5	7	10	246	246	5	-1	-6	11	62	65	15	-7	2	11	285	292	4
36	76	35	0	0	10	273	263	2	-4	7	10	89	90	54	0	-6	11	57	124	56	-6	2	11	28	28	28
88	94	12	1	0	10	516	500	2	-3	7	10	48	33	48	1	-6	11	88	86	11	-5	2	11	31	30	30
171	170	6	2	0	10	341	328	3	-2	7	10	78	26	23	2	-6	11	84	82	11	-4	2	11	110	101	7
123	138	9	-10	1	10	77	11	77	-1	7	10	20	45	20	-8	-5	11	85	103	71	-3	2	11	173	183	4
24	54	23	-9	1	10	92	140	65	0	7	10	29	6	28	-7	-5	11	88	94	60	-2	2	11	338	334	2
22	57	22	-8	1	10	281	278	4	1	7	10	280	277	4	-6	-5	11	119	118	9	-1	2	11	295	267	3
37	74	37	-7	1	10	205	201	6	2	7	10	210	221	5	-5	-5	11	62	26	18	0	2	11	160	162	4
108	87	10	-6	1	10	165	160	6	3	7	10	45	36	44	-4	-5	11	69	54	15	1	2	11	81	20	10
40	68	40	-5	1	10	299	294	3	-9	8	10	78	54	77	-3	-5	11	76	72	12	2	2	11	254	241	4
117	125	8	-4	1	10	60	15	28	-8	8	10	78	18	37	-2	-5	11	95	92	9	3	2	11	176	179	5
61	19	61	-3	1	10	110	107	6	-7	8	10	108	125	12	-1	-5	11	250	240	4	-10	3	11	84	97	15
61	67	61	-2	1	10	210	212	3	-6	8	10	238	241	6	0	-5	11	115	92	7	-9	3	11	136	138	9
93	70	10	-1	1	10	95	87	6	-5	8	10	56	80	56	1	-5	11	15	23	14	-8	3	11	138	86	7
72	66	71	0	1	10	494	476	2	-4	8	10	75	90	75	2	-5	11	67	79	34	-7	3	11	92	19	20
70	71	16	1	1	10	235	245	3	-3	8	10	167	159	7	-8	-4	11	59	67	58	-6	3	11	81	56	80
86	130	60	2	1	10	284	273	3	-2	8	10	205	204	6	-7	-4	11	45	35	45	-5	3	11	105	77	9
77	18	28	-10	2	10	34	4	34	-1	8	10	21	86	20	-6	-4	11	124	110	9	-4	3	11	327	318	3
160	158	6	-9	2	10	39	17	39	0	8	10	21	104	21	-5	-4	11	111	101	10	-3	3	11	30	2	29
33	80	33	-8	2	10	232	229	5	1	8	10	80	71	14	-4	-4	11	248	225	4	-2	3	11	475	467	2
121	9	5	-7	2	10	264	267	5	2	8	10	55	67	55	-3	-4	11	67	95	66	-1	3	11	248	242	3
41	116	41	-6	2	10	63	20	52	3	8	10	74	84	74	-2	-4	11	167	178	5	0	3	11	25	53	24
250	250	4	-5	2	10	94	97	9	-8	9	10	68	10	57	-1	-4	11	99	89	7	1	3	11	220	206	4
69	59	13	-4	2	10	475	462	2	-7	9	10	175	176	7	0	-4	11	98	3	7	2	3	11	188	185	5
54	24	23	-3	2	10	74	43	14	-6	9	10	85	56	26	1	-4	11	53	24	52	3	3	11	71	41	28
23	103	23	-2	2	10	63	30	51	-5	9	10	83	30	56	2	-4	11	421	416	3	-10	4	11	61	54	22
66	89	65	-1	2	10	80	75	7	-4	9	10	58	37	57	-9	-3	11	65	118	65	-9	4	11	84	142	83
191	187	6	0	2	10	42	83	42	-3	9	10	125	127	9	-8	-3	11	93	149	57	-8	4	11	83	57	15
71	83	70	1	2	10	499	489	2	-2	9	10	35	35	34	-7	-3	11	193	196	7	-7	4	11	91	90	21
38	41	37	2	2	10	63	23	62	-1	9	10	112	1	11	-6	-3	11	98	118	11	-6	4	11	127	33	7
121	116	6	3	2	10	187	179	5	0	9	10	102	48	12	-5	-3	11	76	128	76	-5	4	11	53	68	21
86	60	8	-10	3	10	70	68	18	1	9	10	76	31	25	-4	-3	11	258	251	4	-4	4	11	252	252	4
239	241	3	-9	3	10	254	255	5	2	9	10	85	3	22	-3	-3	11	71	18	46	-3	4	11	143	136	6
172	183	5	-8	3	10	154	164	8	3	9	10	91	86	13	-2	-3	11	71	36	46	-2	4	11	110	5	5
188	198	4	-7	3	10	350	349	4	-7	10	10	49	67	48	-1	-3	11	193	190	4	-1	4	11	118	128	7
58	36	58	-6	3	10	168	181	6	-6	10	10	71	17	70	0	-3	11	123	102	6	0	4	11	81	9	13

l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
11	273	270	4	-3	-9	12	78	37	71	-8	0	12	133	138	9	-7	7	12	186	186	7	2	-5	13	105	76	9
11	46	36	23	-2	-9	12	195	187	6	-7	0	12	152	162	7	-6	7	12	26	48	26	-8	-4	13	92	84	61
11	185	196	6	-1	-9	12	187	190	6	-6	0	12	45	2	44	-5	7	12	122	125	10	-7	-4	13	114	114	10
11	98	87	12	0	-9	12	51	54	25	-5	0	12	128	122	7	-4	7	12	21	18	20	-6	-4	13	22	64	22
11	22	60	22	1	-9	12	63	43	62	-4	0	12	76	95	52	-3	7	12	120	128	9	-5	-4	13	67	48	66
11	305	294	4	2	-9	12	0	107	1	-3	0	12	25	15	24	-2	7	12	85	28	57	-4	-4	13	175	167	6
11	172	179	7	-5	-8	12	76	24	76	-2	0	12	59	66	12	-1	7	12	21	60	20	-3	-4	13	39	26	38
11	52	26	22	-4	-8	12	57	8	56	-1	0	12	312	309	3	0	7	12	43	50	42	-2	-4	13	46	14	46
11	222	219	4	-3	-8	12	37	47	36	0	0	12	56	6	34	1	7	12	44	12	43	-1	-4	13	75	68	11
11	319	314	3	-2	-8	12	38	81	37	1	0	12	49	26	49	2	7	12	39	20	39	0	-4	13	154	140	6
11	72	76	12	-1	-8	12	102	118	11	2	0	12	238	241	4	3	7	12	23	15	23	1	-4	13	131	109	6
11	90	81	10	0	-8	12	110	24	10	-9	1	12	33	89	33	-8	8	12	73	6	48	2	-4	13	164	162	6
11	73	75	72	1	-8	12	216	209	6	-8	1	12	259	267	5	-7	8	12	93	124	71	-8	-3	13	72	25	71
11	61	40	41	2	-8	12	172	163	7	-7	1	12	36	58	36	-6	8	12	109	109	11	-7	-3	13	107	91	10
11	91	105	11	-6	-7	12	100	41	14	-6	1	12	147	136	7	-5	8	12	101	76	12	-6	-3	13	78	59	77
11	70	47	32	-5	-7	12	33	32	32	-5	1	12	73	58	28	-4	8	12	140	147	9	-5	-3	13	44	30	28
11	53	65	53	-4	-7	12	118	2	8	-4	1	12	150	152	6	-3	8	12	65	11	64	-4	-3	13	274	270	4
11	72	41	71	-3	-7	12	228	235	5	-3	1	12	209	206	4	-2	8	12	99	108	11	-3	-3	13	141	145	6
11	132	77	7	-2	-7	12	73	35	72	-2	1	12	565	569	2	-1	8	12	22	77	21	-2	-3	13	126	112	6
11	264	259	5	-1	-7	12	78	75	13	-1	1	12	211	197	4	0	8	12	50	53	49	-1	-3	13	143	145	6
11	83	22	24	0	-7	12	111	109	9	0	1	12	240	243	3	1	8	12	32	40	32	0	-3	13	43	49	21
11	85	76	13	1	-7	12	45	21	45	1	1	12	81	68	11	2	8	12	62	65	62	1	-3	13	37	52	36
11	153	146	7	2	-7	12	101	104	11	2	1	12	280	284	3	3	8	12	60	39	59	2	-3	13	27	21	26
11	143	137	7	-7	-6	12	55	38	54	-9	2	12	144	138	9	-7	9	12	123	124	10	-8	-2	13	23	37	23
11	72	49	33	-6	-6	12	114	25	8	-8	2	12	103	85	11	-6	9	12	117	23	10	-7	-2	13	50	100	49
11	48	50	48	-5	-6	12	179	193	6	-7	2	12	64	62	19	-5	9	12	61	47	60	-6	-2	13	79	26	78
11	84	66	12	-4	-6	12	99	106	11	-6	2	12	211	208	5	-4	9	12	96	44	15	-5	-2	13	20	53	20
11	210	214	6	-3	-6	12	142	143	7	-5	2	12	54	64	19	-3	9	12	71	13	32	-4	-2	13	74	34	74
11	150	143	7	-2	-6	12	69	47	69	-4	2	12	232	230	4	-2	9	12	75	1	33	-3	-2	13	21	39	21
11	94	84	13	-1	-6	12	60	74	17	-3	2	12	242	236	3	-1	9	12	46	43	10	-2	-2	13	87	87	9
11	23	10	23	0	-6	12	285	271	4	-2	2	12	143	139	5	0	9	12	84	19	22	-1	-2	13	47	5	46
11	63	45	62	1	-6	12	208	202	5	-1	2	12	129	105	6	1	9	12	21	14	20	0	-2	13	72	58	18
11	22	30	22	2	-6	12	49	39	48	0	2	12	66	54	11	2	9	12	79	29	14	1	-2	13	61	94	14
11	78	59	77	-7	-5	12	67	26	66	1	2	12	383	385	3	-6	10	12	103	7	15	2	-2	13	59	48	54
11	82	98	81	-6	-5	12	82	92	13	2	2	12	62	59	62	-5	10	12	68	8	67	-9	-1	13	122	72	10
11	62	69	18	-5	-5	12	74	112	74	3	2	12	44	64	44	-4	10	12	106	53	15	-8	-1	13	108	64	12
11	45	72	44	-4	-5	12	106	97	10	-9	3	12	99	44	16	-3	10	12	71	86	70	-7	-1	13	95	51	17
11	84	49	21	-3	-5	12	151	136	6	-8	3	12	86	90	64	-2	10	12	120	117	10	-6	-1	13	52	1	22
11	215	216	5	-2	-5	12	63	61	14	-7	3	12	72	1	16	-1	10	12	63	49	4	-5	-1	13	122	124	8
11	134	138	8	-1	-5	12	68	20	67	-6	3	12	108	92	10	0	10	12	10	21	9	-4	-1	13	65	45	65
11	183	179	6	0	-5	12	167	177	5	-5	3	12	216	216	5	-4	11	12	65	34	65	-3	-1	13	197	193	4
11	65	118	65	1	-5	12	120	87	7	-4	3	12	69	9	28	-3	11	12	32	12	32	-2	-1	13	53	94	53
11	197	184	7	2	-5	12	47	20	46	-3	3	12	360	355	3	1	-11	13	70	12	69	-1	-1	13	115	121	6
11	46	29	45	-8	-4	12	103	0	12	-2	3	12	25	55	25	-2	-10	13	84	18	84	0	-1	13	196	197	4
11	160	176	8	-7	-4	12	141	144	8	-1	3	12	92	24	9	-1	-10	13	286	283	5	1	-1	13	153	142	5
11	78	49	34	-6	-4	12	58	48	57	0	3	12	117	118	7	0	-10	13	51	52	26	2	-1	13	136	145	6
11	200	198	6	-5	-4	12	77	20	77	1	3	12	148	154	6	1	-10	13	212	219	6	-9	0	13	93	8	20
11	65	16	18	-4	-4	12	20	62	19	2	3	12	68	63	14	2	-10	13	89	77	13	-8	0	13	260	267	5
11	147	135	8	-3	-4	12	311	300	3	3	3	12	84	3	17	-4	-9	13	69	86	18	-7	0	13	108	109	10
11	32	11	31	-2	-4	12	334	326	3	-9	4	12	75	24	33	-3	-9	13	53	52	53	-6	0	13	82	45	64
11	0	28	1	-1	-4	12	233	225	4	-8	4	12	42	45	15	-2	-9	13	87	24	62	-5	0	13	183	182	6
11	55	56	21	0	-4	12	72	97	72	-7	4	12	74	27	73	-1	-9	13	83	32	23	-4	0	13	160	154	6
11	98	19	12	1	-4	12	204	191	4	-6	4	12	84	2	68	0	-9	13	88	51	52	-3	0	13	60	58	59
11	76	24	75	2	-4	12	62	80	61	-5	4	12	117	108	9	1	-9	13	93	57	15	-2	0	13	309	318	3
11	35	28	34	-8	-3	12	89	23	55	-4	4	12	201	202	5	2	-9	13	48	13	25	-1	0	13	315	306	3
11	78	33	31	-7	-3	12	0	9	1	-3	4	12	362	358	3	-5	-8	13	58	72	21	0	0	13	43	5	43
11	89	49	64	-6	-3	12	156	148	7	-2	4	12	80	64	46	-4	-8	13	23	13	23	1	0	13	48	33	48
11	108	114	11	-5	-3	12	49	57	49	-1	4	12	159	149	6	-3	-8	13	178	186	7	2	0	13	118	116	8
11	86	152	85	-4	-3	12	94	62	10	0	4	12	230	235	4	-2	-8	13	81	33	21	-9	1	13	89	42	22
11	66	19	66	-3	-3	12	152	138	6	1	4	12	67	18	66	-1	-8	13	121	112	9	-8	1	13	22	47	22
11	104	13	12	-2	-3	12	222	220	4	2	4	12	270	256	4	0	-8	13	43	74	43	-7	1	13	43	104	42
11	114	48	8	-1	-3	12	72	15	16	3	4	12	118	116	9	1	-8	13	38	12	37	-6	1	13	200	204	6
11	39	58	39	0	-3	12	68	38	57	-9	5	12	24	46	23	2	-8	13	85	11	21	-5	1	13	51	5	51
11	81	55	62	1	-3	12	110	106	7	-8	5	12	66	57	19	-6	-7	13	107	24	11	-4	1	13	110	14	7
11	89	79	13	2	-3	12	100	101	8	-7	5	12	30	46	30	-5	-7	13	33	49	33	-3	1	13	138	138	6
11	35	99	34	-9	-2	12	73	107	73	-6	5	12	46	66	46	-4	-7	13	45	43	45	-2	1	13	340	334	3
11	132	140	10	-8	-2	12	65	75	65	-5	5	12	181	178	6	-3	-7	13	249	250	5	-1	1	13	53	87	52
11	94	118	57	-7	-2	12	69	2	46	-4	5	12	39	5	38	-2	-7	13	83	94	63	0	1	13	41	23	21
11	152	146	8	-6	-2	12	83	30	25	-3	5	12	78	50	69	-1	-7	13	192	160	6	1	1	13	37	40	36
11	61	2	61	-5	-2	12	205	196	5	-2	5	12	46	34	46	0	-7	13	127	127	8	2	1	13	112	101	8
11	84	64	23	-4	-2	12	80	68	11	-1	5	12	162	168	6	1	-7	13	86	0	52	-9	2	13	34	28	33
11	81	3	28	-3	-2	12	156	152	5	0	5	12	65	76	15	2	-7	13	171	191	7	-8	2	13	237	234	6
11	41	115	41	-2	-2	12	203	203	4	1	5	12	72	29	72	-6	-6	13	78	30	21	-7	2	13	290	291	4
11	85	108	63	-1	-2	12	130	124	6	2	5	12	196	210	6	-5	-6	13	99	26	12	-6	2	13	61	49	60
11	69	27	69	0	-2	12	76	83	9	3	5	12	22	5	21	-4	-6	13	49	16	48	-5	2	13	247	240	4
11	69	128	68	1	-2	12	134	145	6	-9	6	12	96	68	13	-3	-6	13	80	70	13	-4	2	13	260	241	4
11	96	95	14	2	-2	12	146	147	6	-8	6	12	136	9	7	-2	-6	13	36	82	35	-3	2	13	18	36	18
11	139	142	9	-9	-1	12	72	76	17	-7	6	12	54	28	54	-1	-6	13	157	166	7	-2	2	13	70	53	11
11	89	30	62	-8	-1	12	45	124	45	-6	6	12	77	62	76	0	-6	13	172	165	6	-1	2	13	134	144	6
11	74	41	47	-7	-1	12	48	54	48	-5	6	12	46	43	45	1	-6	13	152	153	7	0	2	13	137	139	6
11	168	191	7	-6	-1	12	35	31	35	-4	6	12	35	120	34	2	-6	13	87	81	52	1	2	13	124	106	7
11	93	88	13	-5	-1	12	179	177	6	-3	6	12	34	96	34	-7	-5	13	34	3	33	2	2	13	48	28	47
11	97	167	62	-4	-1	12	36	18	36	-2	6	12	81	114	81	-6	-5	13	63	56	17	3	2	13	154	157	7
10	63	67	19	-3	-1	12	68	4	24	-1	6	12	56	50	19	-5	-5	13	89	76	13	-9	3	13	68	23	18
10	97	82	12	-2	-1	12	332	324	3	0	6	12	29	100	28	-4	-5	13	59	42	59	-8	3	13	22	19	22
10	53	71	52	-1	-1	12	302	303	3	1	6	12	302	307	4	-3	-5	13	139	142	7	-7	3	13	37	78	37
10	33	61	33	0	-1	12	167	162	4	2	6	12	72	31	71	-2	-5	13	68	47	68	-6	3	13	249	249	5
10	33	53	32	1	-1	12	162	168	4	3	6	12	219	219	6	-1	-5	13	267	274	4	-5	3	13	208	228	5
10	174	182	7	2	-1	12	36	8	35	-9	7	12	74	93	62	0	-5	13	19	64	19	-4	3	13	71	9	30
-9	12	88	68	13	-9	0	12	38	62	38	-8	7	12	158	166	8	1	-5	13	245	257	4	-3	3	13	355	358	3

l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	n	k	l	10Fo	10Fc	10s
13	75	73	12	0	-9	14	76	79	14	0	0	14	64	51	64	3	7	14	76	84	15	-4	-2	15	130	134	8
13	78	65	11	1	-9	14	87	84	51	1	0	14	58	57	15	-7	8	14	90	2	61	-3	-2	15	39	10	39
13	0	124	1	2	-9	14	81	89	14	2	0	14	218	218	4	-6	8	14	33	101	33	-2	-2	15	51	14	51
13	115	132	8	-4	-8	14	173	177	7	-9	1	14	73	73	43	-5	8	14	152	159	8	-1	-2	15	115	98	8
13	83	92	58	-3	-8	14	70	43	39	-8	1	14	97	85	12	-4	8	14	157	157	8	0	-2	15	223	216	4
13	430	424	3	-2	-8	14	45	43	45	-7	1	14	242	262	5	-3	8	14	32	10	32	1	-2	15	65	29	65
13	107	21	15	-1	-8	14	26	4	25	-6	1	14	74	67	15	-2	8	14	60	128	59	2	-2	15	29	6	28
13	188	183	6	0	-8	14	115	125	10	-5	1	14	140	143	7	-1	8	14	40	56	39	-8	-1	15	86	81	25
13	78	38	78	1	-8	14	54	18	54	-4	1	14	318	317	4	0	8	14	70	68	50	-7	-1	15	22	64	21
13	230	234	5	2	-8	14	75	41	34	-3	1	14	42	11	41	1	8	14	0	9	1	-6	-1	15	81	66	81
13	196	204	6	-5	-7	14	41	19	41	-2	1	14	308	290	3	2	8	14	0	24	1	-5	-1	15	150	142	7
13	78	81	13	-4	-7	14	33	121	32	-1	1	14	183	181	5	-6	9	14	64	55	64	-4	-1	15	136	140	7
13	170	180	6	-3	-7	14	90	41	53	0	1	14	151	140	6	-5	9	14	34	149	33	-3	-1	15	58	123	58
13	53	100	53	-2	-7	14	137	142	8	1	1	14	297	298	3	-4	9	14	88	7	23	-2	-1	15	19	21	19
13	59	24	16	-1	-7	14	43	40	43	2	1	14	34	113	34	-3	9	14	23	101	23	-1	-1	15	69	34	68
13	102	10	9	0	-7	14	83	47	13	-9	2	14	54	77	53	-2	9	14	116	27	11	0	-1	15	62	54	14
13	112	115	9	1	-7	14	84	69	13	-8	2	14	119	1	8	-1	9	14	83	39	26	1	-1	15	81	118	65
13	86	72	12	2	-7	14	104	113	11	-7	2	14	58	36	6	0	9	14	89	65	13	2	-1	15	148	145	7
13	357	361	4	-6	-6	14	27	28	26	-6	2	14	175	178	7	-5	10	14	86	85	65	-8	0	15	85	14	20
13	59	23	59	-5	-6	14	93	87	12	-5	2	14	229	237	5	-4	10	14	49	85	49	-7	0	15	32	6	31
13	83	99	83	-4	-6	14	44	42	44	-4	2	14	77	52	23	-3	10	14	167	159	8	-6	0	15	65	56	18
13	66	53	19	-3	-6	14	110	113	10	-3	2	14	219	217	4	-2	10	14	45	54	41	-5	0	15	36	41	35
13	107	109	11	-2	-6	14	175	180	6	-2	2	14	37	47	37	0	-10	15	96	114	12	-4	0	15	73	79	14
13	162	164	7	-1	-6	14	101	60	13	-1	2	14	70	9	69	1	-10	15	92	47	57	-3	0	15	307	301	4
13	221	220	5	0	-6	14	107	14	12	0	2	14	68	24	68	2	-10	15	52	59	26	-2	0	15	62	36	15
13	77	57	13	1	-6	14	109	117	10	1	2	14	93	89	10	-3	-9	15	44	19	11	-1	0	15	54	103	53
13	34	42	33	2	-6	14	79	50	13	2	2	14	93	91	11	-2	-9	15	110	110	11	0	0	15	47	6	46
13	50	51	22	-7	-5	14	0	30	1	3	2	14	79	69	13	-1	-9	15	34	7	33	1	0	15	34	29	34
13	139	130	7	-6	-5	14	61	61	61	-9	3	14	42	96	41	0	-9	15	63	51	62	2	0	15	158	153	7
13	66	70	17	-5	-5	14	86	62	51	-8	3	14	198	199	6	1	-9	15	100	114	12	-9	1	15	46	22	35
13	250	263	5	-4	-5	14	89	92	12	-7	3	14	70	57	17	2	-9	15	48	26	47	-8	1	15	33	7	33
13	67	127	66	-3	-5	14	69	8	36	-6	3	14	144	147	8	-4	-8	15	69	104	68	-7	1	15	92	108	59
13	60	17	59	-2	-5	14	64	43	42	-5	3	14	40	34	40	-3	-8	15	79	79	78	-6	1	15	298	298	4
13	192	194	7	-1	-5	14	128	132	7	-4	3	14	76	52	27	-2	-8	15	33	54	32	-5	1	15	98	34	14
13	32	18	31	0	-5	14	157	158	6	-3	3	14	127	84	6	-1	-8	15	56	61	56	-4	1	15	336	325	4
13	142	71	6	1	-5	14	215	220	5	-2	3	14	73	45	13	0	-8	15	76	22	75	-3	1	15	66	89	16
13	60	32	59	2	-5	14	46	51	45	-1	3	14	77	60	12	1	-8	15	46	22	45	-2	1	15	234	222	4
13	101	89	11	-7	-4	14	41	3	41	0	3	14	67	41	34	2	-8	15	61	8	60	-1	1	15	90	15	13
13	71	81	16	-6	-4	14	75	14	74	1	3	14	75	35	25	-5	-7	15	127	123	9	0	1	15	100	89	9
13	61	69	60	-5	-4	14	57	74	57	2	3	14	159	163	7	-4	-7	15	78	18	25	1	1	15	84	83	12
13	194	186	6	-4	-4	14	120	113	9	3	3	14	339	324	4	-3	-7	15	69	127	68	2	1	15	36	90	35
13	112	117	9	-3	-4	14	75	60	75	-9	4	14	34	102	34	-2	-7	15	67	82	67	-9	2	15	30	48	29
13	141	141	8	-2	-4	14	44	15	43	-8	4	14	46	42	46	-1	-7	15	153	146	7	-8	2	15	77	62	77
13	149	150	7	-1	-4	14	35	27	35	-7	4	14	9	76	8	0	-7	15	149	146	8	-7	2	15	70	79	70
13	130	138	9	0	-4	14	39	28	38	-6	4	14	20	7	19	1	-7	15	221	215	6	-6	2	15	93	121	57
13	90	6	21	1	-4	14	83	46	49	-5	4	14	50	27	50	2	-7	15	77	113	77	-5	2	15	49	40	25
13	65	122	65	2	-4	14	94	108	11	-4	4	14	282	281	4	-6	-6	15	42	90	42	-4	2	15	28	9	28
13	50	21	49	-8	-3	14	90	89	13	-3	4	14	28	15	27	-5	-6	15	102	105	16	-3	2	15	88	52	11
13	65	94	65	-7	-3	14	89	82	13	-2	4	14	183	176	6	-4	-6	15	60	71	60	-2	2	15	152	147	6
13	57	5	56	-6	-3	14	96	28	15	-1	4	14	48	80	48	-3	-6	15	228	225	5	-1	2	15	78	98	59
13	64	112	63	-5	-3	14	84	7	20	0	4	14	184	174	6	-2	-6	15	328	320	4	0	2	15	181	185	6
13	79	75	79	-4	-3	14	53	23	53	1	4	14	77	4	28	-1	-6	15	302	303	4	1	2	15	29	27	28
13	106	102	10	-3	-3	14	85	63	58	2	4	14	98	97	11	0	-6	15	76	23	76	2	2	15	51	64	51
13	97	89	11	-2	-3	14	105	116	9	3	4	14	66	72	17	1	-6	15	60	47	60	3	2	15	84	68	53
13	63	56	63	-1	-3	14	134	139	6	-9	5	14	88	26	25	2	-6	15	94	107	12	-9	3	15	98	9	16
13	68	31	15	0	-3	14	158	152	6	-8	5	14	0	41	1	-7	-5	15	131	0	8	-8	3	15	278	277	5
13	54	68	53	1	-3	14	47	38	21	-7	5	14	84	125	84	-6	-5	15	58	89	58	-7	3	15	123	25	9
13	132	148	10	2	-3	14	83	9	16	-6	5	14	78	20	32	-5	-5	15	72	70	72	-6	3	15	57	115	56
13	78	62	78	-8	-2	14	79	63	32	-5	5	14	200	180	6	-4	-5	15	84	82	13	-5	3	15	123	105	9
13	26	11	25	-7	-2	14	82	3	22	-4	5	14	82	72	26	-3	-5	15	64	74	64	-4	3	15	20	68	20
13	50	76	50	-6	-2	14	10	57	10	-3	5	14	131	131	8	-2	-5	15	51	64	51	-3	3	15	169	171	6
13	77	79	76	-5	-2	14	151	136	7	-2	5	14	212	196	5	-1	-5	15	85	89	12	-2	3	15	34	16	34
13	168	172	7	-4	-2	14	80	93	12	-1	5	14	209	207	5	0	-5	15	71	13	71	-1	3	15	46	71	25
13	44	75	44	-3	-2	14	150	145	6	0	5	14	399	413	3	1	-5	15	141	150	7	0	3	15	159	152	6
13	91	86	12	-2	-2	14	46	52	45	1	5	14	133	127	8	2	-5	15	76	24	33	1	3	15	80	10	23
13	98	100	11	-1	-2	14	104	95	8	2	5	14	237	255	5	-7	-4	15	80	57	79	2	3	15	32	1	31
13	74	25	30	0	-2	14	77	81	11	3	5	14	178	183	6	-6	-4	15	84	76	13	3	3	15	120	43	8
13	110	18	10	1	-2	14	200	202	4	-8	6	14	122	107	10	-5	-4	15	59	101	58	-9	4	15	49	117	49
13	115	46	14	2	-2	14	97	98	10	-7	6	14	56	75	23	-4	-4	15	76	78	14	-8	4	15	166	170	8
13	0	73	1	-9	-1	14	49	32	49	-6	6	14	65	75	19	-3	-4	15	83	56	56	-7	4	15	172	170	7
13	88	90	57	-8	-1	14	23	81	23	-5	6	14	188	176	6	-2	-4	15	46	31	24	-6	4	15	81	71	15
13	83	49	61	-7	-1	14	83	31	55	-4	6	14	81	47	14	-1	-4	15	49	131	49	-5	4	15	124	129	9
13	177	161	7	-6	-1	14	114	115	10	-3	6	14	227	229	5	0	-4	15	129	137	8	-4	4	15	58	4	58
13	77	93	76	-5	-1	14	155	157	7	-2	6	14	131	113	8	1	-4	15	176	176	6	-3	4	15	73	59	31
13	70	51	69	-4	-1	14	78	41	56	-1	6	14	99	42	14	2	-4	15	116	114	9	-2	4	15	101	38	13
13	24	18	23	-3	-1	14	98	92	9	0	6	14	275	262	4	-8	-3	15	25	36	24	-1	4	15	76	63	76
13	112	15	10	-2	-1	14	194	193	4	1	6	14	58	0	58	-7	-3	15	23	62	23	0	4	15	157	156	7
13	96	79	14	-1	-1	14	72	68	11	2	6	14	95	93	11	-6	-3	15	45	1	44	1	4	15	206	197	5
13	73	129	72	0	-1	14	201	194	4	3	6	14	47	33	47	-5	-3	15	52	9	6	2	4	15	88	38	15
13	193	187	7	1	-1	14	117	126	8	-8	7	14	97	21	18	-4	-3	15	106	84	10	3	4	15	65	4	64
13	56	35	23	2	-1	14	55	74	54	-7	7	14	70	53	70	-3	-3	15	136	126	7	-8	5	15	53	74	53
13	49	19	29	-9	0	14	49	2	48	-6	7	14	79	55	34	-2	-3	15	119	135	8	-7	5	15	23	103	22
13	15	28	15	-8	0	14	23	2	23	-5	7	14	77	86	34	-1	-3	15	134	131	7	-6	5	15	83	103	82
14	84	114	84	-7	0	14	126	126	9	-4	7	14	136	117	9	0	-3	15	52	69	51	-5	5	15	91	61	60
14	60	60	20	-6	0	14	138	134	8	-3	7	14	87	1	54	1	-3	15	49	20	48	-4	5	15	211	204	6
14	48	13	48	-5	0	14	261	266	4	-2	7	14	31	57	30	2	-3	15	0	54	1	-3	5	15	14	29	13
14	73	77	41	-4	0	14	221	205	4	-1	7	14	22	24	21	-8	-2	15	34	52	34	-2	5	15	86	7	58
14	49	37	48	-3	0	14	295	300	3	0	7	14	72	68	15	-7	-2	15	78	78	14	-1	5	15	192	183	6
14	231	234	6	-2	0	14	142	131	6	1	7	14	87	98	13	-6	-2	15	93	4	17	0	5	15	80	49	24
14	66	3	66	-1	0	14	36	40	36	2	7	14	89	87	61	-5	-2	15	26	10	25	1	5	15	199	210	6

l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
15	51	119	50	-3	-3	16	217	204	5	-4	5	16	169	162	7	-5	-2	17	74	56	73	-4	6	17	89	65	13
15	41	21	40	-2	-3	16	88	81	11	-3	5	16	82	105	14	-4	-2	17	78	53	77	-3	6	17	132	128	9
15	42	66	42	-1	-3	16	64	28	49	-2	5	16	30	92	30	-3	-2	17	0	96	1	-2	6	17	93	83	12
15	52	55	8	0	-3	16	141	131	7	-1	5	16	75	71	75	-2	-2	17	137	121	7	-1	6	17	0	15	1
15	149	170	8	1	-3	16	91	93	11	0	5	16	22	28	21	-1	-2	17	313	327	4	0	6	17	90	89	13
15	83	84	82	2	-3	16	90	8	18	1	5	16	81	41	54	0	-2	17	159	168	7	1	6	17	140	133	8
15	109	13	12	-8	-2	16	71	84	18	2	5	16	33	25	33	1	-2	17	56	18	56	2	6	17	126	89	10
15	109	100	10	-7	-2	16	82	65	14	3	5	16	0	17	1	2	-2	17	61	31	61	-6	7	17	84	71	84
15	82	84	13	-6	-2	16	101	99	11	-8	6	16	74	108	74	-8	-1	17	131	125	9	-5	7	17	101	100	12
15	81	98	28	-5	-2	16	53	71	52	-7	6	16	66	72	20	-7	-1	17	0	43	1	-4	7	17	47	95	47
15	183	186	6	-4	-2	16	36	27	36	-6	6	16	84	21	61	-6	-1	17	46	30	28	-3	7	17	110	30	11
15	64	21	64	-3	-2	16	90	87	11	-5	6	16	131	141	9	-5	-1	17	76	70	75	-2	7	17	118	131	10
15	126	122	9	-2	-2	16	102	88	10	-4	6	16	95	7	15	-4	-1	17	109	111	10	-1	7	17	79	80	63
15	87	59	12	-1	-2	16	304	309	4	-3	6	16	253	269	5	-3	-1	17	198	201	6	0	7	17	55	48	23
15	65	47	65	0	-2	16	121	121	8	-2	6	16	138	149	9	-2	-1	17	358	368	4	-5	8	17	77	37	16
15	107	117	16	1	-2	16	68	90	67	-1	6	16	138	142	8	-1	-1	17	74	79	74	-4	8	17	88	10	24
15	100	90	12	2	-2	16	47	54	46	0	6	16	91	88	11	0	-1	17	46	74	46	-3	8	17	81	68	80
15	45	16	45	-8	-1	16	84	18	30	1	6	16	32	55	31	1	-1	17	70	74	69	-2	8	17	42	10	42
15	201	195	6	-7	-1	16	66	60	65	2	6	16	45	30	31	2	-1	17	120	126	9	-1	8	17	60	54	60
15	161	167	7	-6	-1	16	80	64	24	-7	7	16	75	64	17	-8	0	17	60	16	59	-1	-8	18	65	20	65
15	113	94	10	-5	-1	16	105	101	10	-6	7	16	114	118	11	-7	0	17	33	58	33	0	-8	18	125	111	9
15	71	68	41	-4	-1	16	87	88	12	-5	7	16	122	143	10	-6	0	17	68	78	44	1	-8	18	78	2	29
15	69	107	68	-3	-1	16	171	166	6	-4	7	16	76	54	76	-5	0	17	44	11	43	-3	-7	18	73	43	73
15	41	15	40	-2	-1	16	107	38	9	-3	7	16	79	79	79	-4	0	17	42	21	42	-2	-7	18	64	36	63
15	64	46	64	-1	-1	16	135	136	7	-2	7	16	65	56	64	-3	0	17	184	198	6	-1	-7	18	24	46	23
15	128	105	10	0	-1	16	57	13	17	-1	7	16	33	41	32	-2	0	17	58	22	58	0	-7	18	85	104	14
15	120	1	8	1	-1	16	76	136	76	0	7	16	71	34	70	-1	0	17	326	320	4	1	-7	18	67	2	56
15	47	52	46	2	-1	16	29	77	29	1	7	16	73	2	41	0	0	17	21	1	20	2	-7	18	68	63	68
15	61	9	61	-8	0	16	86	9	69	-6	8	16	77	79	77	1	0	17	95	97	11	-4	-6	18	91	115	20
15	52	26	51	-7	0	16	56	19	56	-5	8	16	103	90	12	2	0	17	97	95	12	-3	-6	18	121	121	9
15	104	20	11	-6	0	16	105	40	13	-4	8	16	82	49	14	-8	1	17	69	28	51	-2	-6	18	0	35	1
15	110	108	10	-5	0	16	171	168	7	-3	8	16	97	84	12	-7	1	17	189	194	7	-1	-6	18	77	12	76
15	96	30	15	-4	0	16	36	37	35	-2	8	16	75	54	75	-6	1	17	53	40	23	0	-6	18	250	262	5
15	42	49	42	-3	0	16	69	54	15	-1	8	16	59	58	58	-5	1	17	72	34	72	1	-6	18	66	65	17
15	108	111	12	-2	0	16	56	56	18	0	8	16	55	51	54	-4	1	17	93	87	12	2	-6	18	91	68	16
15	133	112	9	-1	0	16	117	76	7	-4	9	16	42	58	41	-3	1	17	99	69	11	-5	-5	18	24	48	24
15	0	47	1	0	0	16	120	18	6	-3	9	16	92	18	20	-2	1	17	0	103	1	-4	-5	18	76	70	15
15	189	189	7	1	0	16	102	102	10	-2	9	16	65	106	65	-1	1	17	152	157	7	-3	-5	18	0	17	1
15	69	38	17	2	0	16	303	296	4	0	-9	17	147	137	8	0	1	17	36	16	36	-2	-5	18	75	89	75
15	33	22	32	-8	1	16	0	96	1	-3	-8	17	43	120	42	1	1	17	259	266	4	-1	-5	18	241	252	5
16	99	42	15	-7	1	16	58	77	20	-2	-8	17	73	25	37	2	1	17	134	134	8	0	-5	18	282	280	5
16	54	43	54	-6	1	16	56	48	22	-1	-8	17	102	56	13	-8	2	17	112	110	11	1	-5	18	28	47	27
16	49	38	27	-5	1	16	165	164	7	0	-8	17	0	50	1	-7	2	17	104	98	11	2	-5	18	236	246	5
16	118	114	10	-4	1	16	82	101	81	1	-8	17	42	42	41	-6	2	17	112	111	10	-6	-4	18	81	22	73
16	35	34	34	-3	1	16	121	105	8	2	-8	17	42	63	41	-5	2	17	22	34	21	-5	-4	18	53	27	52
16	125	118	9	-2	1	16	113	130	9	-4	-7	17	38	63	38	-4	2	17	80	92	14	-4	-4	18	110	114	10
16	0	48	1	-1	1	16	70	46	14	-3	-7	17	37	72	37	-3	2	17	36	100	36	-3	-4	18	104	89	10
16	74	35	30	0	1	16	40	88	40	-2	-7	17	171	168	7	-2	2	17	104	6	11	-2	-4	18	271	281	5
16	132	51	6	1	1	16	237	238	4	-1	-7	17	46	38	46	-1	2	17	77	69	14	-1	-4	18	268	271	5
16	62	25	61	2	1	16	70	23	70	0	-7	17	83	4	22	0	2	17	42	19	42	0	-4	18	133	126	8
16	113	110	10	-8	2	16	94	93	13	1	-7	17	127	115	9	1	2	17	192	192	6	1	-4	18	165	183	7
16	148	5	-5	-7	2	16	23	41	22	2	-7	17	152	169	8	2	2	17	131	131	8	2	-4	18	72	18	72
16	136	131	8	-6	2	16	62	39	61	-5	-6	17	49	101	48	3	2	17	33	16	32	-6	-3	18	90	78	20
16	18	4	18	-5	2	16	67	45	66	-4	-6	17	34	94	33	-8	3	17	103	55	16	-5	-3	18	137	134	8
16	162	167	7	-4	2	16	54	65	54	-3	-6	17	220	204	5	-7	3	17	62	19	61	-4	-3	18	106	66	12
16	19	6	18	-3	2	16	76	7	75	-2	-6	17	120	121	9	-6	3	17	191	207	6	-3	-3	18	171	159	6
16	55	57	55	-2	2	16	64	11	63	-1	-6	17	84	95	61	-5	3	17	6	37	6	-2	-3	18	173	173	7
16	107	96	10	-1	2	16	122	126	8	0	-6	17	90	36	19	-4	3	17	83	4	72	-1	-3	18	61	20	61
16	70	72	16	0	2	16	209	217	5	1	-6	17	168	174	7	-3	3	17	45	43	32	0	-3	18	289	295	4
16	42	35	41	1	2	16	403	402	3	2	-6	17	83	6	18	-2	3	17	76	71	76	1	-3	18	148	145	7
16	18	49	18	2	2	16	57	91	57	-6	-5	17	77	55	15	-1	3	17	34	12	34	2	-3	18	81	76	67
16	173	177	6	3	2	16	32	118	31	-5	-5	17	75	46	75	0	3	17	115	91	9	-7	-2	18	92	57	54
16	193	196	6	-8	3	16	48	15	47	-4	-5	17	83	17	63	1	3	17	72	89	15	-6	-2	18	128	107	9
16	211	220	6	-7	3	16	56	49	56	-3	-5	17	78	34	62	2	3	17	75	54	75	-5	-2	18	60	54	19
16	105	107	11	-6	3	16	119	101	10	-2	-5	17	31	79	31	3	3	17	47	55	9	-4	-2	18	263	274	5
16	62	4	62	-5	3	16	92	104	13	-1	-5	17	226	237	5	-8	4	17	65	6	64	-3	-2	18	178	197	7
16	86	15	19	-4	3	16	55	12	55	0	-5	17	264	261	5	-7	4	17	24	76	23	-2	-2	18	107	113	10
16	76	83	76	-3	3	16	82	30	23	1	-5	17	130	132	9	-6	4	17	86	0	56	-1	-2	18	37	81	37
16	23	27	23	-2	3	16	48	38	24	2	-5	17	196	199	6	-5	4	17	50	22	49	0	-2	18	120	118	9
16	187	194	6	-1	3	16	41	17	41	-6	-4	17	80	0	61	-4	4	17	76	43	75	1	-2	18	26	2	26
16	121	135	9	0	3	16	29	53	29	-5	-4	17	135	131	8	-3	4	17	49	35	25	2	-2	18	71	23	38
16	133	130	8	1	3	16	128	130	8	-4	-4	17	59	89	59	-2	4	17	34	5	34	-7	-1	18	122	125	10
16	282	270	4	2	3	16	124	108	9	-3	-4	17	55	52	21	-1	4	17	212	211	6	-6	-1	18	187	191	6
16	311	295	4	3	3	16	46	36	45	-2	-4	17	21	17	21	0	4	17	101	17	11	-5	-1	18	117	123	9
16	439	439	3	-8	4	16	76	87	17	-1	-4	17	21	92	21	1	4	17	78	2	54	-4	-1	18	309	314	4
16	277	275	5	-7	4	16	77	24	31	0	-4	17	122	135	9	2	4	17	38	38	37	-3	-1	18	0	68	1
16	25	36	24	-6	4	16	26	65	26	1	-4	17	360	362	4	3	4	17	64	74	63	-2	-1	18	130	66	6
16	152	139	7	-5	4	16	85	105	13	2	-4	17	172	168	6	-7	5	17	76	32	37	-1	-1	18	246	240	5
16	93	15	15	-4	4	16	124	133	9	-7	-3	17	74	68	16	-6	5	17	61	54	61	0	-1	18	260	256	4
16	49	4	48	-3	4	16	76	2	34	-6	-3	17	0	7	1	-5	5	17	82	1	24	1	-1	18	76	17	75
16	52	84	52	-2	4	16	165	162	6	-5	-3	17	51	47	50	-4	5	17	67	14	67	2	-1	18	164	179	7
16	122	137	9	-1	4	16	94	3	16	-4	-3	17	62	43	61	-3	5	17	22	17	22	-7	0	18	102	6	14
16	208	199	5	0	4	16	62	22	18	-3	-3	17	116	113	9	-2	5	17	0	1	1	-6	0	18	126	135	9
16	62	49	62	1	4	16	79	52	72	-2	-3	17	260	266	4	-1	5	17	55	50	21	-5	0	18	87	40	53
16	220	213	5	2	4	16	147	162	7	-1	-3	17	180	176	6	0	5	17	60	87	60	-4	0	18	102	99	11
16	173	182	6	3	4	16	81	76	25	0	-3	17	345	338	4	1	5	17	46	75	46	-3	0	18	240	263	5
16	72	10	34	-8	5	16	114	100	11	1	-3	17	49	34	23	2	5	17	111	98	10	-2	0	18	21	100	21
16	46	74	45	-7	5	16	0	28	1	2	-3	17	38	27	37	-7	6	17	115	137	11	-1	0	18	23	5	22
16	78	91	15	-6	5	16	201	216	6	-7	-2	17	96	22	17	-6	6	17	67	7	67	0	0	18	325	327	4
16	175	173	6	-5	5	16	148	174	8	-6	-2	17	52	35	51	-5	6	17	142	139	8	1	0	18	150	160	8

l	10Fo	10Fc	10s
18	114	135	9
18	67	104	67
18	197	194	6
18	125	127	9
18	138	143	8
18	88	101	12
18	604	604	3
18	201	201	6
18	207	211	6
18	54	92	53
18	163	173	7
18	147	137	7
18	34	18	34
18	69	54	69
18	116	28	9
18	85	89	25
18	101	109	11
18	309	303	4
18	65	64	17
18	31	39	30
18	117	120	9
18	73	42	72
18	47	79	47
18	59	12	58
18	24	17	24
18	78	59	27
18	64	82	19
18	103	98	11
18	135	22	6
18	79	9	79
18	188	200	6
18	147	142	7
18	61	79	18
18	81	45	24
18	54	39	53
18	50	61	26
18	75	78	15
18	39	24	38
18	45	47	44
18	45	38	44
18	74	21	35
18	89	84	12
18	131	140	9
18	125	66	8
18	98	68	17
18	167	163	7
18	52	26	52
18	137	138	9
18	46	45	45
18	203	211	6
18	56	61	56
18	31	42	31
18	42	19	41
18	51	36	7
18	88	38	24
18	112	80	10
18	62	16	62
18	168	157	7
18	74	130	74
18	121	105	9
18	93	4	15
18	74	74	39
18	91	38	19
18	64	58	64
18	72	124	72
18	94	42	18
18	102	108	12
19	99	23	17
19	42	112	42
19	60	48	59
19	65	75	64
19	54	2	54
19	109	107	11
19	98	43	13

h	k	l	10Fo	10Fc	10s
0	-6	19	67	33	67
1	-6	19	51	22	23
2	-6	19	149	156	8
-4	-5	19	21	17	21
-3	-5	19	78	79	78
-2	-5	19	91	55	16
-1	-5	19	23	95	23
0	-5	19	77	70	77
1	-5	19	38	10	37
2	-5	19	53	57	53
-5	-4	19	108	37	13
-4	-4	19	168	165	7
-3	-4	19	40	46	40
-2	-4	19	0	49	1
-1	-4	19	37	12	37
0	-4	19	155	163	7
1	-4	19	223	229	5
2	-4	19	74	80	68
-6	-3	19	55	43	54
-5	-3	19	100	105	11
-4	-3	19	16	16	15
-3	-3	19	196	206	6
-2	-3	19	27	36	27
-1	-3	19	78	18	24
0	-3	19	78	67	28
1	-3	19	85	62	21
2	-3	19	136	130	8
-6	-2	19	156	155	8
-5	-2	19	129	133	9
-4	-2	19	102	117	11
-3	-2	19	92	149	60
-2	-2	19	162	171	7
-1	-2	19	86	93	56
0	-2	19	218	213	6
1	-2	19	78	74	78
2	-2	19	102	110	11
-7	-1	19	74	13	35
-6	-1	19	86	47	58
-5	-1	19	61	75	61
-4	-1	19	51	83	50
-3	-1	19	59	72	58
-2	-1	19	38	44	38
-1	-1	19	275	290	5
0	-1	19	22	140	22
1	-1	19	75	62	26
2	-1	19	113	119	9
-7	0	19	120	84	10
-6	0	19	156	164	8
-5	0	19	69	28	68
-4	0	19	9	17	8
-3	0	19	166	179	7
-2	0	19	113	121	10
-1	0	19	143	149	8
0	0	19	288	293	4
1	0	19	146	134	7
2	0	19	57	31	56
-7	1	19	49	130	48
-6	1	19	41	88	41
-5	1	19	86	16	19
-4	1	19	75	150	74
-3	1	19	217	225	6
-2	1	19	85	74	62
-1	1	19	256	266	5
0	1	19	146	173	8
1	1	19	30	34	30
2	1	19	66	32	66
3	1	19	42	59	41
-7	2	19	64	44	20
-6	2	19	71	11	70
-5	2	19	92	44	16
-4	2	19	53	60	23
-3	2	19	158	148	7
-2	2	19	327	334	4
-1	2	19	50	37	50

h	k	l	10Fo	10Fc	10s
0	2	19	116	103	9
1	2	19	88	101	12
2	2	19	89	43	17
3	2	19	43	0	42
-7	3	19	49	61	49
-6	3	19	76	61	16
-5	3	19	104	22	11
-4	3	19	46	0	45
-3	3	19	138	56	5
-2	3	19	51	68	50
-1	3	19	141	152	8
0	3	19	68	54	16
1	3	19	60	82	20
2	3	19	42	75	41
-7	4	19	50	25	49
-6	4	19	99	9	14
-5	4	19	41	67	40
-4	4	19	156	154	7
-3	4	19	89	21	57
-2	4	19	153	155	7
-1	4	19	229	232	5
0	4	19	225	219	6
1	4	19	72	65	15
2	4	19	26	44	25
-6	5	19	35	10	34
-5	5	19	63	14	63
-4	5	19	71	41	70
-3	5	19	62	31	62
-2	5	19	192	198	7
-1	5	19	19	37	18
0	5	19	81	82	15
1	5	19	55	49	54
-5	6	19	88	51	73
-4	6	19	48	32	48
-3	6	19	68	56	68
-2	6	19	156	148	7
-1	6	19	80	60	14
-3	7	19	35	10	34
-2	-6	20	82	54	81
-1	-6	20	84	47	13
0	-6	20	98	64	15
1	-6	20	78	27	77
-3	-5	20	69	3	68
-2	-5	20	104	91	10
-1	-5	20	63	30	63
0	-5	20	104	111	11
1	-5	20	58	13	19
2	-5	20	65	67	64
-4	-4	20	88	60	52
-3	-4	20	24	42	23
-2	-4	20	58	28	57
-1	-4	20	121	129	9
0	-4	20	41	25	40
1	-4	20	67	22	67
-5	-3	20	77	70	77
-4	-3	20	79	10	25
-3	-3	20	120	15	8
-2	-3	20	66	16	65
-1	-3	20	98	88	11
0	-3	20	24	29	24
1	-3	20	78	33	25
2	-3	20	80	33	50
-6	-2	20	15	67	15
-5	-2	20	90	12	19
-4	-2	20	94	86	12
-3	-2	20	83	123	83
-2	-2	20	23	22	22
-1	-2	20	40	102	39
0	-2	20	46	21	45
1	-2	20	92	90	11
2	-2	20	75	16	75
-6	-1	20	73	134	73
-5	-1	20	82	5	82
-4	-1	20	70	51	69

h	k	l	10Fo	10Fc	10s
-3	-1	20	33	50	32
-2	-1	20	23	66	22
-1	-1	20	85	124	75
0	-1	20	108	109	10
1	-1	20	54	38	20
2	-1	20	75	109	75
-6	0	20	24	30	24
-5	0	20	41	108	41
-4	0	20	101	46	13
-3	0	20	69	35	40
-2	0	20	240	242	5
-1	0	20	180	189	6
0	0	20	116	134	9
1	0	20	119	90	8
2	0	20	33	12	33
-6	1	20	65	37	18
-5	1	20	118	83	10
-4	1	20	224	222	6
-3	1	20	117	15	8
-2	1	20	42	65	41
-1	1	20	249	254	5
0	1	20	69	80	69
1	1	20	53	14	22
2	1	20	73	68	72
-6	2	20	98	83	12
-5	2	20	92	86	12
-4	2	20	171	171	7
-3	2	20	110	114	10
-2	2	20	80	72	79
-1	2	20	103	10	12
0	2	20	104	95	10
1	2	20	45	43	10
2	2	20	69	62	69
-6	3	20	50	79	29
-5	3	20	113	92	10
-4	3	20	105	34	12
-3	3	20	196	203	6
-2	3	20	84	2	22
-1	3	20	88	99	62
0	3	20	79	64	26
1	3	20	115	117	10
-6	4	20	92	95	14
-5	4	20	24	45	24
-4	4	20	41	50	41
-3	4	20	75	2	34
-2	4	20	75	18	74
-1	4	20	125	118	9
0	4	20	93	87	13
1	4	20	89	52	21
-5	5	20	98	109	13
-4	5	20	54	1	54
-3	5	20	73	92	72
-2	5	20	106	15	12
-1	5	20	85	33	29
-3	6	20	43	50	42
-2	-5	21	92	19	15
-1	-5	21	22	23	21
0	-5	21	116	29	9
-4	-4	21	65	7	64
-3	-4	21	88	1	61
-2	-4	21	54	72	53
-1	-4	21	34	57	34
0	-4	21	51	86	26
-4	-3	21	77	5	27
-3	-3	21	48	31	48
-2	-3	21	63	42	63
-1	-3	21	63	22	62
0	-3	21	93	36	15
1	-3	21	54	24	54
2	-3	21	92	13	14
-5	-2	21	65	68	65
-4	-2	21	65	66	17
-3	-2	21	109	115	10
-2	-2	21	24	54	23

h	k	l	10Fo	10Fc	10s
-1	-2	21	85	79	13
0	-2	21	79	31	69
1	-2	21	94	70	11
2	-2	21	32	42	32
-5	-1	21	31	40	30
-4	-1	21	90	76	19
-3	-1	21	67	1	37
-2	-1	21	70	90	70
-1	-1	21	53	63	52
0	-1	21	85	50	53
1	-1	21	83	6	21
2	-1	21	60	73	60
-5	0	21	109	33	12
-4	0	21	145	155	8
-3	0	21	88	86	53
-2	0	21	81	11	62
-1	0	21	140	132	8
0	0	21	41	55	41
1	0	21	59	15	59
2	0	21	0	5	1
-5	1	21	77	41	30
-4	1	21	41	15	41
-3	1	21	91	104	55
-2	1	21	41	6	40
-1	1	21	76	55	15
0	1	21	118	137	10
1	1	21	73	57	73
-5	2	21	117	44	10
-4	2	21	63	72	19
-3	2	21	53	21	53
-2	2	21	53	9	53
-1	2	21	48	126	47
0	2	21	0	32	1
1	2	21	25	8	24
-5	3	21	85	16	67
-4	3	21	103	63	15
-3	3	21	0	4	1
-2	3	21	28	58	28
-1	3	21	59	11	4
0	3	21	40	37	40
-4	4	21	157	17	-5
-3	4	21	60	23	59
-2	4	21	60	33	59
-1	4	21	74	94	73
-2	-3	22	74	58	73
-1	-3	22	49	34	49
0	-3	22	25	35	24
-3	-2	22	49	71	49
-2	-2	22	25	14	25
-1	-2	22	73	39	45
0	-2	22	85	68	61
-4	-1	22	42	28	42
-3	-1	22	120	133	10
-2	-1	22	84	22	25
-1	-1	22	81	85	14
0	-1	22	25	20	24
-4	0	22	78	75	77
-3	0	22	133	72	7
-2	0	22	73	84	41
-1	0	22	71	31	15
0	0	22	49	48	49
-4	1	22	96	95	13
-3	1	22	106	27	11
-2	1	22	59	38	59
-1	1	22	104	104	11
0	1	22	43	68	42
-4	2	22	43	32	42
-3	2	22	49	38	27
-2	2	22	77	49	77
-1	2	22	58	66	21

ppendix E: Observed and Calculated Structure factors for **(189b)**.

l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
0	2053	1918	6	4	10	0	100	105	1	-8	4	1	67	63	1	-8	9	1	41	45	3	4	1	2	305	306	2
0	235	240	1	5	10	0	42	42	2	-7	4	1	35	38	2	-7	9	1	47	44	2	5	1	2	182	183	1
0	18	8	4	6	10	0	0	28	1	-6	4	1	132	141	1	-6	9	1	80	80	1	6	1	2	73	75	1
0	193	188	2	7	10	0	0	4	1	-5	4	1	0	8	1	-5	9	1	0	4	1	7	1	2	42	42	2
0	567	504	5	1	11	0	124	121	1	-4	4	1	69	71	1	-4	9	1	0	14	1	8	1	2	67	67	1
0	378	392	1	2	11	0	175	171	1	-3	4	1	243	233	1	-3	9	1	87	83	1	9	1	2	0	0	1
0	402	402	2	3	11	0	302	302	2	-2	4	1	56	55	1	-2	9	1	90	87	1	-9	2	2	35	34	3
0	228	234	1	4	11	0	56	59	1	-1	4	1	215	227	1	-1	9	1	35	25	2	-8	2	2	107	105	1
0	459	461	2	5	11	0	223	217	2	0	4	1	296	313	1	0	9	1	176	176	1	-7	2	2	67	67	1
0	94	93	1	6	11	0	63	61	1	1	4	1	397	403	2	1	9	1	0	11	1	-6	2	2	202	207	2
0	60	58	1	0	12	0	42	48	2	2	4	1	247	244	1	2	9	1	210	212	2	-5	2	2	223	222	2
0	93	93	1	1	12	0	25	23	3	3	4	1	247	245	1	3	9	1	163	163	1	-4	2	2	42	49	1
0	68	70	1	2	12	0	49	54	2	4	4	1	146	146	1	4	9	1	0	7	1	-3	2	2	168	159	1
0	214	221	1	3	12	0	47	50	2	5	4	1	136	135	1	5	9	1	0	14	1	-2	2	2	548	569	2
0	387	412	1	4	12	0	8	3	8	6	4	1	88	88	1	6	9	1	36	35	2	-1	2	2	774	689	6
0	0	11	1	5	12	0	51	51	2	7	4	1	115	115	1	7	9	1	56	55	1	0	2	2	1168	1069	8
0	36	37	1	6	12	0	29	14	3	8	4	1	58	53	1	-7	10	1	0	16	1	1	2	2	884	772	6
0	117	112	1	1	13	0	0	21	1	9	4	1	49	54	2	-6	10	1	49	43	2	2	2	2	497	520	2
0	229	231	2	2	13	0	11	22	11	-9	5	1	0	38	1	-5	10	1	63	65	1	3	2	2	0	29	1
0	237	230	2	3	13	0	21	16	5	-8	5	1	50	45	2	-4	10	1	35	34	2	4	2	2	0	20	1
0	0	9	1	4	13	0	0	2	1	-7	5	1	8	6	8	-3	10	1	122	123	1	5	2	2	57	59	1
0	53	49	1	5	13	0	45	44	2	-6	5	1	193	200	2	-2	10	1	64	62	1	6	2	2	90	88	1
0	73	70	1	-9	0	1	0	15	1	-5	5	1	133	127	1	-1	10	1	60	57	1	7	2	2	0	14	1
0	132	131	1	-7	0	1	184	179	1	-4	5	1	375	371	3	0	10	1	16	10	8	8	2	2	11	32	10
0	218	223	1	-5	0	1	139	139	1	-3	5	1	261	265	2	1	10	1	19	18	18	9	2	2	84	79	1
0	205	216	1	-3	0	1	373	384	2	-2	5	1	744	735	2	2	10	1	10	22	10	-9	3	2	81	79	1
0	367	361	2	-1	0	1	1001	917	5	-1	5	1	402	403	2	3	10	1	245	247	2	-8	3	2	55	55	1
0	148	153	1	1	0	1	396	410	1	0	5	1	248	271	1	4	10	1	0	14	1	-7	3	2	11	8	11
0	83	83	1	3	0	1	317	333	2	1	5	1	26	26	1	5	10	1	0	4	1	-6	3	2	83	82	1
0	145	139	1	5	0	1	101	94	1	2	5	1	229	236	1	6	10	1	80	79	1	-5	3	2	20	18	3
0	17	38	17	7	0	1	48	51	1	3	5	1	52	56	1	7	10	1	0	13	1	-4	3	2	49	41	1
0	41	35	2	9	0	1	82	83	1	4	5	1	300	294	2	-6	11	1	0	24	1	-3	3	2	344	364	2
0	280	297	2	-9	1	1	21	19	5	5	5	1	81	79	1	-5	11	1	84	84	1	-2	3	2	121	116	1
0	99	101	1	-8	1	1	69	65	1	6	5	1	79	79	1	-4	11	1	116	122	1	-1	3	2	270	277	2
0	264	268	2	-7	1	1	83	90	1	7	5	1	0	6	1	-3	11	1	139	136	1	0	3	2	51	51	1
0	251	256	1	-6	1	1	83	85	1	8	5	1	20	26	5	-2	11	1	106	107	1	1	3	2	99	102	1
0	176	177	1	-5	1	1	43	49	1	9	5	1	21	12	21	-1	11	1	0	10	1	2	3	2	218	224	1
0	14	2	13	-4	1	1	71	65	1	-9	6	1	83	80	1	0	11	1	256	257	4	3	3	2	411	410	2
0	45	46	1	-3	1	1	25	27	1	-8	6	1	8	34	8	1	11	1	19	14	5	4	3	2	246	240	2
0	42	50	2	-2	1	1	163	163	1	-7	6	1	134	131	1	2	11	1	97	99	1	5	3	2	68	60	1
0	35	38	2	-1	1	1	352	366	1	-6	6	1	30	31	3	3	11	1	84	80	1	6	3	2	49	51	1
0	91	90	1	0	1	1	1016	943	7	-5	6	1	167	166	1	4	11	1	146	148	1	7	3	2	139	136	1
0	363	354	2	1	1	1	115	122	1	-4	6	1	106	110	1	5	11	1	54	49	2	8	3	2	77	76	1
0	11	5	6	2	1	1	820	715	7	-3	6	1	46	45	1	6	11	1	0	1	1	9	3	2	59	57	2
0	241	241	2	3	1	1	362	376	2	-2	6	1	271	266	2	-6	12	1	0	11	1	-9	4	2	28	26	4
0	16	29	16	4	1	1	198	198	2	-1	6	1	293	290	2	-5	12	1	69	76	1	-8	4	2	0	1	1
0	21	12	3	5	1	1	64	66	1	0	6	1	695	691	1	-4	12	1	0	2	1	-7	4	2	155	157	1
0	33	26	2	6	1	1	50	48	1	1	6	1	84	82	1	-3	12	1	120	120	1	-6	4	2	64	59	1
0	0	3	1	7	1	1	23	25	3	2	6	1	0	8	1	-2	12	1	111	116	1	-5	4	2	35	27	2
0	52	52	2	8	1	1	91	86	1	3	6	1	242	241	2	-1	12	1	138	144	1	-4	4	2	47	47	1
0	19	28	19	9	1	1	45	45	2	4	6	1	132	137	1	0	12	1	39	41	1	-3	4	2	155	159	1
0	235	233	1	-9	2	1	17	8	7	5	6	1	148	150	1	1	12	1	94	97	1	-2	4	2	85	82	1
0	101	100	1	-8	2	1	54	56	1	6	6	1	64	65	1	2	12	1	169	168	1	-1	4	2	123	123	1
0	178	184	1	-7	2	1	162	161	1	7	6	1	38	42	2	3	12	1	70	73	1	0	4	2	178	172	1
0	85	91	1	-6	2	1	39	36	2	8	6	1	0	4	1	4	12	1	53	51	2	1	4	2	120	139	1
0	6	3	6	-5	2	1	102	103	1	9	6	1	24	17	5	5	12	1	107	108	1	2	4	2	45	43	1
0	73	73	1	-4	2	1	141	133	1	-8	7	1	77	77	1	6	12	1	17	13	17	3	4	2	25	18	2
0	110	114	1	-3	2	1	506	514	2	-7	7	1	22	24	5	-5	13	1	51	46	2	4	4	2	125	121	1
0	18	19	6	-2	2	1	470	480	1	-6	7	1	226	224	2	-4	13	1	0	16	1	5	4	2	0	2	1
0	11	7	11	-1	2	1	624	548	4	-5	7	1	79	82	1	-3	13	1	38	33	2	6	4	2	26	26	3
0	22	15	5	0	2	1	336	355	1	-4	7	1	6	47	6	-2	13	1	14	12	10	7	4	2	109	113	1
0	271	265	2	1	2	1	343	349	1	-3	7	1	89	96	1	-1	13	1	72	77	1	8	4	2	0	10	1
0	125	121	1	2	2	1	233	233	2	-2	7	1	118	114	1	0	13	1	17	8	16	9	4	2	20	10	5
0	189	189	2	3	2	1	205	209	1	-1	7	1	79	70	1	1	13	1	41	39	2	-9	5	2	0	25	1
0	39	40	2	4	2	1	240	235	1	0	7	1	67	73	1	2	13	1	8	9	8	-8	5	2	29	30	3
0	51	51	1	5	2	1	113	109	1	1	7	1	109	107	1	3	13	1	17	6	7	-7	5	2	85	89	1
0	61	62	1	6	2	1	23	21	3	2	7	1	324	319	3	4	13	1	27	24	4	-6	5	2	41	35	2
0	13	3	13	7	2	1	12	53	12	3	7	1	209	210	2	5	13	1	52	49	2	-5	5	2	90	91	1
0	0	0	1	8	2	1	39	45	2	4	7	1	177	181	1	-8	0	2	0	12	1	-4	5	2	137	135	1
0	172	168	1	9	2	1	44	40	2	5	7	1	83	86	1	-6	0	2	398	391	3	-3	5	2	105	98	1
0	28	30	2	-9	3	1	37	38	2	6	7	1	42	43	2	-4	0	2	633	640	2	-2	5	2	146	144	1
0	189	193	2	-8	3	1	50	51	2	7	7	1	8	24	7	-2	0	2	46	24	1	-1	5	2	233	225	1
0	177	182	1	-7	3	1	0	5	1	8	7	1	37	34	2	0	0	2	66	68	1	0	5	2	90	79	5
0	90	90	1	-6	3	1	0	8	1	-8	8	1	31	30	3	2	0	2	1745	1589	7	1	5	2	199	208	1
0	119	124	1	-5	3	1	137	137	1	-7	8	1	42	43	2	4	0	2	392	385	2	2	5	2	153	149	1
0	47	45	2	-4	3	1	338	331	2	-6	8	1	22	22	4	6	0	2	65	70	1	3	5	2	10	1	9
0	37	35	2	-3	3	1	334	332	2	-5	8	1	213	216	2	8	0	2	57	51	1	4	5	2	41	33	1
0	51	52	2	-2	3	1	40	42	1	-4	8	1	16	19	6	-9	1	2	14	6	14	5	5	2	23	16	3
0	106	104	1	-1	3	1	279	286	1	-3	8	1	138	138	1	-8	1	2	23	22	4	6	5	2	0	0	1
0	0	10	1	0	3	1	49	53	1	-2	8	1	119	113	1	-7	1	2	56	56	1	7	5	2	14	15	8
0	146	148	1	1	3	1	0	3	1	-1	8	1	69	69	1	-6	1	2	19	10	4	8	5	2	26	35	4
0	250	260	2	2	3	1	345	354	2	0	8	1	29	23	2	-5	1	2	48	47	1	9	5	2	40	40	2
0	46	51	2	3	3	1	86	79	1	1	8	1	40	39	1	-4	1	2	81	81	1	-9	6	2	29	26	4
0	0	3	1	4	3	1	18	1	3	2	8	1	19	8	3	-3	1	2	251	246	2	-8	6	2	75	76	1
0	61	56	1	5	3	1	52	45	1	3	8	1	70	66	1	-2	1	2	287	308	1	-7	6	2	11	35	10
0	0	12	1	6	3	1	144	143	1	4	8	1	81	75	1	-1	1	2	1309	1190	5	-6	6	2	4	0	4
0	432	425	3	7	3	1	61	63	1	5	8	1	96	98	1	0	1	2	550	489	7	-5	6	2	0	3	1
0	125	128	1	8	3	1	0	10	1	6	8	1	60	62	1	1	1	2	636	573	6	-4	6	2	288	290	2
0	160	158	1	9	3	1	0	2	1	7	8	1	55	56	1	2	1	2	1125	1005	7	-3	6	2	43	45	1
0	162	155	1	-9	4	1	90	89	1	8	8	1	0	18	1	3	1	2	405	413	2	-2	6	2	364	359	2

k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
5	2	13	9	13	-4	12	2	48	53	2	-8	4	3	8	27	7	-7	9	3	14	18	14	7	1	4	109	107	1
5	2	171	170	3	-3	12	2	11	3	11	-7	4	3	90	88	1	-6	9	3	0	14	1	8	1	4	121	115	1
5	2	95	88	1	-2	12	2	112	111	1	-6	4	3	0	16	1	-5	9	3	134	137	1	9	1	4	65	64	1
5	2	155	151	1	-1	12	2	81	85	1	-5	4	3	74	70	1	-4	9	3	77	83	1	-9	2	4	44	37	2
5	2	63	66	1	0	12	2	127	129	1	-4	4	3	131	137	1	-3	9	3	156	150	1	-8	2	4	48	48	2
5	2	34	27	2	1	12	2	29	33	3	-3	4	3	43	46	1	-2	9	3	126	130	1	-7	2	4	8	4	7
5	2	78	81	1	2	12	2	74	73	1	-2	4	3	93	91	1	-1	9	3	51	49	1	-6	2	4	0	7	1
5	2	0	6	1	3	12	2	46	42	2	-1	4	3	425	424	2	0	9	3	72	72	1	-5	2	4	200	195	1
5	2	20	2	4	4	12	2	93	93	1	0	4	3	256	244	1	1	9	3	37	37	2	-4	2	4	59	67	1
5	2	31	35	3	5	12	2	43	38	2	1	4	3	323	328	2	2	9	3	0	7	1	-3	2	4	461	466	2
7	2	43	38	2	6	12	2	55	50	2	2	4	3	365	360	2	3	9	3	255	252	2	-2	2	4	247	263	2
7	2	92	89	1	-5	13	2	19	1	19	3	4	3	168	160	1	4	9	3	7	9	7	-1	2	4	81	82	1
7	2	54	53	1	-4	13	2	67	63	1	4	4	3	54	59	1	5	9	3	153	157	1	0	2	4	0	9	1
7	2	59	57	1	-3	13	2	56	56	2	5	4	3	89	90	1	6	9	3	0	6	1	1	2	4	238	242	2
7	2	69	68	1	-2	13	2	8	16	8	6	4	3	77	82	1	7	9	3	46	45	2	2	2	4	372	382	2
7	2	0	7	1	-1	13	2	47	47	2	7	4	3	19	13	5	-7	10	3	23	20	5	3	2	4	197	194	2
7	2	148	148	1	0	13	2	105	106	1	8	4	3	135	137	1	-6	10	3	16	4	7	4	2	4	100	98	1
7	2	86	98	1	1	13	2	71	69	1	9	4	3	0	45	1	-5	10	3	72	67	1	5	2	4	108	109	1
7	2	57	54	1	2	13	2	0	10	1	-9	5	3	0	0	1	-4	10	3	186	194	1	6	2	4	117	120	1
7	2	120	112	1	3	13	2	49	52	2	-8	5	3	170	169	1	-3	10	3	96	100	1	7	2	4	0	5	1
7	2	155	147	1	4	13	2	20	17	6	-7	5	3	112	110	1	-2	10	3	54	50	1	8	2	4	35	33	2
7	2	78	80	1	5	13	2	0	24	1	-6	5	3	265	272	2	-1	10	3	159	160	1	9	2	4	60	57	1
7	2	158	162	1	-9	0	3	0	15	1	-5	5	3	56	55	1	0	10	3	98	103	1	-9	3	4	100	98	1
7	2	158	162	1	-7	0	3	145	154	1	-4	5	3	205	205	2	1	10	3	39	37	2	-8	3	4	0	7	1
7	2	65	65	1	-5	0	3	298	293	2	-3	5	3	64	64	1	2	10	3	236	231	2	-7	3	4	185	187	1
7	2	0	14	1	-3	0	3	50	57	1	-2	5	3	445	429	2	3	10	3	112	112	1	-6	3	4	50	49	1
7	2	0	5	1	-1	0	3	1757	1625	6	-1	5	3	219	224	1	4	10	3	45	51	2	-5	3	4	112	112	1
8	2	46	46	2	1	0	3	790	703	6	0	5	3	507	517	1	5	10	3	35	36	3	-4	3	4	110	112	1
8	2	45	46	2	3	0	3	254	255	2	1	5	3	85	82	1	6	10	3	18	19	6	-3	3	4	66	72	1
8	2	0	26	1	5	0	3	0	7	1	2	5	3	116	121	1	7	10	3	19	8	6	-2	3	4	218	227	1
8	2	76	78	1	7	0	3	221	227	2	3	5	3	163	170	1	-6	11	3	21	31	20	-1	3	4	69	73	1
8	2	30	26	2	9	0	3	25	26	4	4	5	3	124	133	1	-5	11	3	0	6	1	0	3	4	440	449	1
8	2	138	135	1	-9	1	3	27	33	3	5	5	3	85	85	1	-4	11	3	0	8	1	1	3	4	8	10	7
8	2	141	147	1	-8	1	3	19	10	5	6	5	3	0	6	1	-3	11	3	33	38	2	2	3	4	22	20	2
8	2	209	208	2	-7	1	3	98	98	1	7	5	3	93	89	1	-2	11	3	0	3	1	3	3	4	564	554	2
8	2	33	28	1	-6	1	3	231	227	2	8	5	3	82	81	1	-1	11	3	0	2	1	4	3	4	6	17	5
8	2	356	351	3	-5	1	3	0	5	1	9	5	3	37	41	3	0	11	3	34	23	11	5	3	4	31	23	2
8	2	231	235	2	-4	1	3	249	231	1	-9	6	3	12	11	12	1	11	3	133	135	1	6	3	4	74	73	1
8	2	12	1	9	-3	1	3	91	96	1	-8	6	3	0	15	1	2	11	3	310	300	2	7	3	4	133	138	1
8	2	132	136	1	-2	1	3	488	510	2	-7	6	3	119	122	1	3	11	3	15	13	15	8	3	4	57	56	1
8	2	37	43	2	-1	1	3	667	614	4	-6	6	3	153	155	1	4	11	3	175	165	1	9	3	4	47	46	2
8	2	47	48	2	0	1	3	382	410	10	-5	6	3	167	167	1	5	11	3	0	2	1	-9	4	4	27	22	4
8	2	18	5	18	1	1	3	289	298	1	-4	6	3	125	128	1	6	11	3	78	71	1	-8	4	4	16	20	7
8	2	12	16	11	2	1	3	343	362	2	-3	6	3	316	306	2	-6	12	3	19	17	6	-7	4	4	72	73	1
9	2	0	10	1	3	1	3	193	181	1	-2	6	3	227	233	2	-5	12	3	8	13	8	-6	4	4	32	34	2
9	2	61	63	1	4	1	3	210	216	2	-1	6	3	257	249	1	-4	12	3	47	45	2	-5	4	4	218	218	2
9	2	19	15	6	5	1	3	191	189	1	0	6	3	128	126	1	-3	12	3	64	64	1	-4	4	4	393	394	3
9	2	107	112	1	6	1	3	75	77	1	1	6	3	185	173	1	-2	12	3	0	15	1	-3	4	4	297	302	2
9	2	153	152	1	7	1	3	26	29	3	2	6	3	160	163	1	-1	12	3	74	75	1	-2	4	4	260	260	2
9	2	128	134	1	8	1	3	76	76	1	3	6	3	132	136	1	0	12	3	41	36	9	-1	4	4	155	164	1
9	2	16	14	5	9	1	3	28	25	3	4	6	3	90	89	1	1	12	3	15	5	15	0	4	4	0	3	1
9	2	208	209	2	-9	2	3	0	10	1	5	6	3	0	13	1	2	12	3	60	56	1	1	4	4	49	46	1
9	2	41	39	11	-8	2	3	47	53	2	6	6	3	148	150	1	3	12	3	14	11	13	2	4	4	128	131	1
9	2	64	65	1	-7	2	3	49	50	1	7	6	3	37	41	2	4	12	3	37	38	2	3	4	4	106	108	1
9	2	169	164	1	-6	2	3	0	26	1	8	6	3	61	58	1	5	12	3	42	34	2	4	4	4	254	253	2
9	2	140	137	1	-5	2	3	191	189	1	-8	7	3	36	33	3	-5	13	3	16	1	8	5	4	4	36	38	2
9	2	91	96	1	-4	2	3	48	51	1	-7	7	3	56	51	2	-4	13	3	55	49	2	6	4	4	65	67	1
9	2	73	66	1	-3	2	3	88	88	1	-6	7	3	218	215	2	-3	13	3	14	14	14	7	4	4	0	36	1
9	2	16	34	15	-2	2	3	1073	942	8	-5	7	3	51	48	1	-2	13	3	0	11	1	8	4	4	12	4	11
9	2	0	4	1	-1	2	3	418	426	1	-4	7	3	127	128	1	-1	13	3	0	3	1	9	4	4	98	98	1
10	2	51	50	2	0	2	3	36	36	1	-3	7	3	9	40	8	0	13	3	16	31	16	-9	5	4	59	59	2
10	2	83	78	1	1	2	3	170	176	1	-2	7	3	57	55	1	1	13	3	64	66	1	-8	5	4	0	6	1
10	2	64	69	1	2	2	3	157	152	1	-1	7	3	41	42	1	2	13	3	0	11	1	-7	5	4	54	55	1
10	2	158	163	1	3	2	3	75	74	1	0	7	3	310	303	5	3	13	3	8	10	8	-6	5	4	25	31	3
10	2	72	66	1	4	2	3	124	122	1	1	7	3	80	76	1	4	13	3	35	31	3	-5	5	4	121	128	1
10	2	151	155	1	5	2	3	116	112	1	2	7	3	6	39	5	-8	0	4	43	43	2	-4	5	4	132	128	1
10	2	71	78	1	6	2	3	70	68	1	3	7	3	0	5	1	-6	0	4	27	23	2	-3	5	4	247	236	2
10	2	201	203	2	7	2	3	80	78	1	4	7	3	135	134	1	-4	0	4	108	108	1	-2	5	4	0	9	1
10	2	151	145	1	8	2	3	82	80	1	5	7	3	0	11	1	-2	0	4	318	317	2	-1	5	4	198	194	1
10	2	252	248	2	9	2	3	17	8	16	6	7	3	109	110	1	0	0	4	1041	919	6	0	5	4	234	238	2
10	2	71	71	1	-9	3	3	0	23	1	7	7	3	23	19	4	2	0	4	1166	1038	8	1	5	4	0	7	1
10	2	136	132	1	-8	3	3	72	68	1	8	7	3	39	38	2	4	0	4	260	255	2	2	5	4	358	354	2
10	2	143	139	1	-7	3	3	127	135	1	-8	8	3	0	13	1	6	0	4	90	86	1	3	5	4	131	129	1
10	2	0	12	1	-6	3	3	26	30	3	-7	8	3	43	42	2	8	0	4	35	36	3	4	5	4	204	200	2
10	2	21	33	21	-5	3	3	108	112	1	-6	8	3	0	41	1	-9	1	4	0	11	1	5	5	4	125	131	1
11	2	16	6	8	-4	3	3	101	98	1	-5	8	3	208	210	2	-8	1	4	80	83	1	6	5	4	93	93	1
11	2	0	13	1	-3	3	3	81	81	1	-4	8	3	48	46	1	-7	1	4	13	2	10	7	5	4	8	15	7
11	2	44	50	2	-2	3	3	491	510	2	-3	8	3	98	100	1	-6	1	4	19	21	4	8	5	4	0	0	1
11	2	13	28	12	-1	3	3	427	432	2	-2	8	3	224	218	2	-5	1	4	0	10	1	-9	6	4	0	20	1
11	2	10	7	10	0	3	3	745	659	3	-1	8	3	77	77	1	-4	1	4	118	114	1	-8	6	4	57	58	2
11	2	253	265	2	1	3	3	134	144	1	0	8	3	95	95	1	-3	1	4	72	71	1	-7	6	4	41	44	2
11	2	57	58	1	2	3	3	0	2	1	1	8	3	12	8	8	-2	1	4	429	447	2	-6	6	4	213	211	2
11	2	148	151	1	3	3	3	107	100	1	2	8	3	104	94	1	-1	1	4	329	346	1	-5	6	4	47	51	1
11	2	201	208	2	4	3	3	171	167	1	3	8	3	93	91	1	0	1	4	780	699	15	-4	6	4	160	157	1
11	2	47	42	2	5	3	3	105	103	1	4	8	3	35	35	2	1	1	4	93	100	1	-3	6	4	92	96	1
11	2	208	207	2	6	3	3	37	36	2	5	8	3	14	3	14	2	1	4	858	731	6	-2	6	4	87	91	1
11	2	34	36	3	7	3	3	171	172	1	6	8	3	91	91	1	3	1	4	215	225	1	-1	6	4	392	378	2
11	2	0	13	1	8	3	3	0	11	1	7	8	3	0	15	1	4	1	4	561	568	2	0	6	4	209	200	1
12	2	30	21	3	9	3	3	46	45	2	8	8	3	41	45	2	5	1	4	26	23	2	1	6	4	180	171	1
12	2	0	44	1	-9	4	3	52	48	2	-8	9	3	0	7	1	6	1	4	135	137	1	2	6	4	338	329	2

l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
4	83	81	1	0	12	4	177	177	2	-2	4	5	379	391	2	3	9	5	176	173	1	1	2	6	290	289	2
4	0	3	1	1	12	4	184	186	1	-1	4	5	54	49	1	4	9	5	0	3	1	2	2	6	75	69	1
4	0	9	1	2	12	4	41	39	2	0	4	5	333	336	2	5	9	5	51	48	2	3	2	6	0	12	1
4	46	43	2	3	12	4	38	35	2	1	4	5	80	70	1	6	9	5	18	18	6	4	2	6	0	18	1
4	21	50	20	4	12	4	23	22	4	2	4	5	134	137	1	7	9	5	0	28	1	5	2	6	185	186	1
4	0	11	1	5	12	4	73	75	1	3	4	5	91	99	1	-7	10	5	28	30	4	6	2	6	314	323	2
4	19	8	6	-5	13	4	65	59	1	4	4	5	123	116	1	-6	10	5	32	29	3	7	2	6	0	13	1
4	192	185	1	-4	13	4	0	17	1	5	4	5	68	69	1	-5	10	5	0	12	1	8	2	6	151	151	1
4	0	36	1	-3	13	4	0	6	1	6	4	5	203	210	2	-4	10	5	79	73	1	9	2	6	22	18	5
4	74	71	1	-2	13	4	10	15	9	7	4	5	0	20	1	-3	10	5	68	74	1	-9	3	6	67	66	1
4	184	184	1	-1	13	4	0	0	1	8	4	5	113	111	1	-2	10	5	87	88	1	-8	3	6	37	35	2
4	87	85	1	0	13	4	78	84	2	-9	5	5	0	18	1	-1	10	5	140	144	1	-7	3	6	64	66	1
4	109	98	1	1	13	4	66	64	1	-8	5	5	20	31	19	0	10	5	61	60	2	-6	3	6	77	79	1
4	116	111	1	2	13	4	46	44	2	-7	5	5	57	60	1	1	10	5	252	258	2	-5	3	6	281	292	2
4	47	42	1	3	13	4	72	73	1	-6	5	5	27	23	3	2	10	5	44	42	2	-4	3	6	255	259	2
4	236	233	2	4	13	4	63	60	1	-5	5	5	117	118	1	3	10	5	161	162	1	-3	3	6	118	121	1
4	204	206	1	-9	0	5	19	12	18	-4	5	5	0	8	1	4	10	5	249	250	2	-2	3	6	108	106	1
4	32	40	2	-7	0	5	188	184	1	-3	5	5	27	34	2	5	10	5	20	19	5	-1	3	6	174	179	1
4	48	52	1	-5	0	5	291	287	2	-2	5	5	553	546	2	6	10	5	56	58	2	0	3	6	117	111	1
4	56	54	1	-3	0	5	529	515	2	-1	5	5	304	296	2	-6	11	5	9	3	9	1	3	6	151	153	1
4	48	48	2	-1	0	5	510	531	2	0	5	5	210	197	1	-5	11	5	51	42	2	2	3	6	164	166	1
4	33	34	3	1	0	5	813	716	5	1	5	5	0	9	1	-4	11	5	0	25	1	3	3	6	311	300	3
4	48	50	2	3	0	5	557	562	2	2	5	5	237	224	2	-3	11	5	61	66	1	4	3	6	59	61	1
4	42	45	2	5	0	5	184	200	2	3	5	5	0	15	1	-2	11	5	201	216	1	5	3	6	50	51	1
4	19	5	6	7	0	5	277	279	2	4	5	5	0	19	1	-1	11	5	167	171	1	6	3	6	20	30	20
4	34	39	3	9	0	5	0	29	1	5	5	5	62	64	1	0	11	5	77	80	1	7	3	6	43	43	2
4	123	122	1	-9	1	5	41	34	2	6	5	5	27	35	3	1	11	5	57	56	1	8	3	6	33	38	3
4	38	41	2	-8	1	5	125	123	1	7	5	5	64	70	1	2	11	5	67	71	1	-9	4	6	0	14	1
4	48	48	1	-7	1	5	64	63	1	8	5	5	0	13	1	3	11	5	66	70	1	-8	4	6	176	168	1
4	66	65	1	-6	1	5	37	43	2	-9	6	5	23	34	23	4	11	5	32	34	3	-7	4	6	78	77	1
4	26	34	2	-5	1	5	149	148	1	-8	6	5	30	32	3	5	11	5	34	40	3	-6	4	6	45	49	2
4	80	78	1	-4	1	5	66	66	1	-7	6	5	85	88	1	6	11	5	63	58	1	-5	4	6	8	8	8
4	83	84	1	-3	1	5	134	146	1	-6	6	5	0	17	1	-5	12	5	83	75	1	-4	4	6	180	176	1
4	65	68	1	-2	1	5	558	568	2	-5	6	5	32	32	2	-4	12	5	59	52	1	-3	4	6	248	252	2
4	35	32	2	-1	1	5	317	331	2	-4	6	5	166	168	1	-3	12	5	62	61	1	-2	4	6	0	12	1
4	79	82	1	0	1	5	216	239	4	-3	6	5	51	53	1	-2	12	5	71	75	1	-1	4	6	262	250	1
4	0	4	1	1	1	5	932	810	8	-2	6	5	60	55	1	-1	12	5	0	6	1	0	4	6	131	127	1
4	34	30	2	2	1	5	127	130	1	-1	6	5	158	172	1	0	12	5	24	15	4	1	4	6	272	267	1
4	20	12	20	3	1	5	96	94	1	0	6	5	367	367	2	1	12	5	42	40	2	2	4	6	16	2	3
4	0	6	1	4	1	5	96	99	1	1	6	5	159	160	1	2	12	5	11	21	11	3	4	6	187	185	1
4	62	58	2	5	1	5	98	92	1	2	6	5	224	218	2	3	12	5	98	89	1	4	4	6	79	74	1
4	0	16	1	6	1	5	209	213	1	3	6	5	45	40	1	4	12	5	0	17	1	5	4	6	141	142	1
4	46	47	2	7	1	5	41	35	2	4	6	5	72	66	1	5	12	5	52	42	2	6	4	6	0	9	1
4	64	58	1	8	1	5	21	18	5	5	6	5	0	26	1	-4	13	5	56	53	2	7	4	6	161	168	1
4	42	41	2	9	1	5	0	22	1	6	6	5	20	24	19	-3	13	5	19	2	18	8	4	6	0	14	1
4	175	174	1	-9	2	5	50	48	2	7	6	5	0	8	1	-2	13	5	11	20	10	-9	5	6	58	58	2
4	46	47	1	-8	2	5	60	62	1	8	6	5	21	45	20	-1	13	5	66	59	1	-8	5	6	90	87	1
4	0	6	1	-7	2	5	101	104	1	-8	7	5	0	7	1	0	13	5	30	36	4	-7	5	6	141	134	1
4	157	152	1	-6	2	5	49	47	1	-7	7	5	0	1	1	1	13	5	17	17	6	-6	5	6	66	65	1
4	54	50	1	-5	2	5	62	59	1	-6	7	5	119	120	1	2	13	5	42	37	2	-5	5	6	39	40	2
4	98	100	1	-4	2	5	26	29	2	-5	7	5	61	65	1	3	13	5	32	28	3	-4	5	6	29	35	2
4	91	92	1	-3	2	5	559	558	2	-4	7	5	30	34	2	4	13	5	8	0	8	-3	5	6	203	195	1
4	172	174	1	-2	2	5	327	341	2	-3	7	5	32	32	2	-8	0	6	102	97	1	-2	5	6	134	123	1
4	0	10	1	-1	2	5	397	409	2	-2	7	5	113	110	1	-6	0	6	69	65	1	-1	5	6	102	97	1
4	117	114	1	0	2	5	202	203	2	-1	7	5	23	12	3	-4	0	6	57	57	1	0	5	6	34	36	1
4	0	11	1	1	2	5	437	435	2	0	7	5	141	135	1	-2	0	6	191	187	1	1	5	6	50	40	1
4	55	50	2	2	2	5	111	116	1	1	7	5	126	128	1	0	0	6	661	680	2	2	5	6	174	174	1
4	18	15	18	3	2	5	45	45	1	2	7	5	0	18	1	2	0	6	203	211	1	3	5	6	0	1	1
4	43	50	2	4	2	5	191	190	1	3	7	5	107	109	1	4	0	6	90	89	1	4	5	6	126	125	1
4	118	115	1	5	2	5	22	21	3	4	7	5	53	50	1	6	0	6	194	189	2	5	5	6	111	114	1
4	62	58	1	6	2	5	90	88	1	5	7	5	37	37	2	8	0	6	0	10	1	6	5	6	15	5	7
4	59	54	1	7	2	5	0	3	1	6	7	5	0	13	1	-9	1	6	6	3	6	7	5	6	16	22	15
4	115	123	1	8	2	5	74	74	1	7	7	5	0	33	1	-8	1	6	86	87	1	8	5	6	87	78	1
4	209	213	4	9	2	5	60	55	1	8	7	5	49	43	2	-7	1	6	62	62	1	-8	6	6	99	100	1
4	108	110	1	-9	3	5	62	55	1	-8	8	5	19	11	19	-6	1	6	39	36	2	-7	6	6	114	112	1
4	256	265	2	-8	3	5	0	23	1	-7	8	5	20	7	5	-5	1	6	0	19	1	-6	6	6	77	75	1
4	0	30	1	-7	3	5	185	177	1	-6	8	5	76	78	1	-4	1	6	172	164	1	-5	6	6	250	252	2
4	0	1	1	-6	3	5	85	84	1	-5	8	5	111	111	1	-3	1	6	72	73	1	-4	6	6	212	209	2
4	126	127	1	-5	3	5	60	61	1	-4	8	5	75	74	1	-2	1	6	260	273	2	-3	6	6	56	55	1
4	15	17	11	-4	3	5	255	258	2	-3	8	5	60	59	1	-1	1	6	140	133	1	-2	6	6	12	3	11
4	91	89	1	-3	3	5	33	40	1	-2	8	5	0	7	1	0	1	6	466	472	4	-1	6	6	39	47	1
4	0	26	1	-2	3	5	160	163	1	-1	8	5	111	112	1	1	1	6	411	421	2	0	6	6	319	317	2
4	63	71	1	-1	3	5	58	53	1	0	8	5	47	42	1	2	1	6	290	294	2	1	6	6	48	51	8
4	20	15	5	0	3	5	260	264	1	1	8	5	118	116	1	3	1	6	255	260	2	2	6	6	114	117	1
4	88	87	1	1	3	5	129	134	1	2	8	5	167	170	1	4	1	6	467	490	3	3	6	6	78	78	1
4	166	178	1	2	3	5	89	93	1	3	8	5	153	158	1	5	1	6	24	24	3	4	6	6	35	32	2
4	103	107	1	3	3	5	201	191	2	4	8	5	3	1	3	6	1	6	187	192	1	5	6	6	38	41	2
4	41	42	2	4	3	5	91	90	1	5	8	5	149	155	1	7	1	6	120	119	1	6	6	6	38	38	2
4	0	15	1	5	3	5	71	74	1	6	8	5	0	4	1	8	1	6	56	55	2	7	6	6	79	83	1
4	118	118	1	6	3	5	70	73	1	7	8	5	0	4	1	9	1	6	0	5	1	8	6	6	41	40	2
4	56	58	1	7	3	5	152	151	1	-7	9	5	36	31	3	-9	2	6	40	40	2	-8	7	6	19	18	6
4	34	32	3	8	3	5	0	8	1	-6	9	5	151	156	1	-8	2	6	57	55	1	-7	7	6	23	3	22
4	90	86	1	9	3	5	14	21	14	-5	9	5	170	164	1	-7	2	6	76	70	1	-6	7	6	28	33	3
4	105	101	1	-9	4	5	0	23	1	-4	9	5	163	164	1	-6	2	6	0	2	1	-5	7	6	228	228	2
4	12	23	12	-8	4	5	67	70	1	-3	9	5	76	76	1	-5	2	6	96	98	1	-4	7	6	13	23	13
4	71	68	1	-7	4	5	10	19	10	-2	9	5	37	27	2	-4	2	6	51	44	1	-3	7	6	67	66	1
4	14	11	13	-6	4	5	13	16	12	-1	9	5	45	43	1	-3	2	6	189	193	2	-2	7	6	147	146	1
4	56	52	1	-5	4	5	45	41	1	0	9	5	90	88	1	-2	2	6	239	236	1	-1	7	6	44	48	1
4	85	89	1	-4	4	5	118	113	1	1	9	5	158	160	1	-1	2	6	276	275	2	0	7	6	52	45	1
4	0	14	1	-3	4	5	81	81	1	2	9	5	81	80	1	0	2	6	333	338	1	1	7	6	234	237	2

k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
7	6	91	103	1	7	0	7	81	81	1	8	5	7	36	31	3	-5	12	7	0	2	1	0	4	8	93	89	1
7	6	98	104	1	-9	1	7	69	59	1	-8	6	7	0	9	1	-4	12	7	0	5	1	1	4	8	118	125	1
7	6	53	57	1	-8	1	7	36	36	2	-7	6	7	9	5	9	-3	12	7	0	23	1	2	4	8	199	200	1
7	6	81	85	1	-7	1	7	0	8	1	-6	6	7	119	119	1	-2	12	7	76	79	1	3	4	8	96	95	1
7	6	55	52	1	-6	1	7	0	6	1	-5	6	7	90	94	1	-1	12	7	11	11	11	4	4	8	123	120	1
7	6	23	26	4	-5	1	7	91	88	1	-4	6	7	0	23	1	0	12	7	71	75	1	5	4	8	28	36	3
8	6	9	4	9	-4	1	7	129	132	1	-3	6	7	184	178	1	1	12	7	27	20	3	6	4	8	7	15	7
8	6	21	24	5	-3	1	7	32	34	1	-2	6	7	78	74	1	2	12	7	31	32	3	7	4	8	0	12	1
8	6	113	115	1	-2	1	7	201	195	1	-1	6	7	229	229	2	3	12	7	51	49	2	8	4	8	23	38	22
8	6	95	93	1	-1	1	7	78	72	1	0	6	7	209	215	1	4	12	7	62	61	1	-8	5	8	82	79	1
8	6	105	108	1	0	1	7	33	26	1	1	6	7	330	334	3	-4	13	7	41	46	3	-7	5	8	110	110	1
8	6	61	66	1	1	1	7	51	46	1	2	6	7	199	200	2	-3	13	7	0	12	1	-6	5	8	19	3	19
8	6	117	118	1	2	1	7	51	57	1	3	6	7	126	126	1	-2	13	7	29	22	3	-5	5	8	138	139	1
8	6	66	63	1	3	1	7	356	353	3	4	6	7	138	135	1	-1	13	7	82	89	1	-4	5	8	31	29	2
8	6	198	192	1	4	1	7	126	135	1	5	6	7	16	14	6	0	13	7	60	53	1	-3	5	8	17	18	17
8	6	0	12	1	5	1	7	127	130	1	6	6	7	135	136	1	1	13	7	8	13	8	-2	5	8	200	198	2
8	6	61	61	1	6	1	7	79	89	1	7	6	7	18	24	18	2	13	7	17	20	7	-1	5	8	192	181	1
8	6	136	140	1	7	1	7	52	48	2	8	6	7	45	49	2	3	13	7	11	10	11	0	5	8	0	2	1
8	6	42	44	2	8	1	7	0	20	1	-8	7	7	43	45	2	-8	0	8	0	3	1	1	5	8	75	66	1
8	6	83	87	1	-9	2	7	0	20	1	-7	7	7	0	25	1	-6	0	8	24	16	3	2	5	8	94	91	1
8	6	0	39	1	-8	2	7	37	38	2	-6	7	7	58	62	1	-4	0	8	0	19	1	3	5	8	50	51	1
8	6	70	66	1	-7	2	7	15	47	14	-5	7	7	20	1	20	-2	0	8	219	226	2	4	5	8	36	37	2
9	6	0	22	1	-6	2	7	112	110	1	-4	7	7	92	87	1	0	0	8	613	617	3	5	5	8	112	115	1
9	6	35	38	3	-5	2	7	27	28	3	-3	7	7	66	66	1	2	0	8	102	112	1	6	5	8	36	33	2
9	6	0	30	1	-4	2	7	379	374	3	-2	7	7	46	41	1	4	0	8	45	44	1	7	5	8	20	22	5
9	6	134	137	1	-3	2	7	96	96	1	-1	7	7	106	100	1	6	0	8	382	388	2	8	5	8	33	31	3
9	6	18	24	18	-2	2	7	374	365	2	0	7	7	155	160	1	8	0	8	76	84	1	-8	6	8	17	29	16
9	6	25	27	3	-1	2	7	166	165	1	1	7	7	48	45	1	-9	1	8	25	20	4	-7	6	8	31	36	3
9	6	30	28	2	0	2	7	478	497	8	2	7	7	201	204	2	-8	1	8	0	26	1	-6	6	8	77	75	1
9	6	64	68	2	1	2	7	230	231	1	3	7	7	92	92	1	-7	1	8	77	82	1	-5	6	8	53	55	1
9	6	92	93	1	2	2	7	129	126	1	4	7	7	130	130	1	-6	1	8	0	11	1	-4	6	8	19	19	18
9	6	0	26	1	3	2	7	180	176	1	5	7	7	26	30	3	-5	1	8	77	76	1	-3	6	8	230	236	2
9	6	194	191	1	4	2	7	145	145	1	6	7	7	25	26	4	-4	1	8	50	55	1	-2	6	8	147	145	1
9	6	206	208	2	5	2	7	10	6	9	7	7	7	30	33	3	-3	1	8	34	33	1	-1	6	8	140	139	1
9	6	156	156	1	6	2	7	68	75	1	-8	8	7	24	13	5	-2	1	8	338	334	2	0	6	8	131	130	1
9	6	110	108	1	7	2	7	58	58	1	-7	8	7	52	53	2	-1	1	8	125	131	1	1	6	8	173	174	1
9	6	0	5	1	8	2	7	87	85	1	-6	8	7	115	118	1	0	1	8	379	367	1	2	6	8	11	39	11
10	6	20	12	6	-9	3	7	22	24	5	-5	8	7	191	188	1	1	1	8	204	204	2	3	6	8	64	62	1
10	6	14	6	14	-8	3	7	130	128	1	-4	8	7	78	81	1	2	1	8	92	87	1	4	6	8	50	52	1
10	6	0	0	1	-7	3	7	31	29	3	-3	8	7	152	159	1	3	1	8	75	80	1	5	6	8	96	100	1
10	6	120	127	1	-6	3	7	135	133	1	-2	8	7	105	105	1	4	1	8	171	173	1	6	6	8	11	10	11
10	6	0	7	1	-5	3	7	199	201	1	-1	8	7	109	102	1	5	1	8	292	297	2	7	6	8	15	13	9
10	6	184	191	1	-4	3	7	189	193	2	0	8	7	154	147	2	6	1	8	237	244	2	-8	7	8	33	37	3
10	6	145	146	1	-3	3	7	16	21	15	1	8	7	80	81	1	7	1	8	12	14	11	-7	7	8	77	75	1
10	6	19	23	5	-2	3	7	71	74	1	2	8	7	42	44	2	8	1	8	86	87	1	-6	7	8	102	103	1
10	6	359	363	2	-1	3	7	110	112	1	3	8	7	0	6	1	-9	2	8	71	67	1	-5	7	8	32	26	3
10	6	0	17	1	0	3	7	125	122	1	4	8	7	0	4	1	-8	2	8	39	38	2	-4	7	8	210	217	2
10	6	154	149	1	1	3	7	73	73	1	5	8	7	37	33	2	-7	2	8	77	79	1	-3	7	8	118	116	1
10	6	110	112	1	2	3	7	105	102	1	6	8	7	12	10	11	-6	2	8	34	34	2	-2	7	8	120	121	1
10	6	22	22	5	3	3	7	93	94	1	7	8	7	21	38	21	-5	2	8	17	22	17	-1	7	8	93	94	1
10	6	0	28	1	4	3	7	145	146	1	-7	9	7	0	11	1	-4	2	8	53	58	1	0	7	8	137	137	1
11	6	0	7	1	5	3	7	147	147	1	-6	9	7	0	16	1	-3	2	8	262	273	2	1	7	8	0	13	1
11	6	57	50	2	6	3	7	0	27	1	-5	9	7	118	115	1	-2	2	8	0	10	1	2	7	8	148	148	1
11	6	59	56	1	7	3	7	0	6	1	-4	9	7	42	46	2	-1	2	8	57	59	1	3	7	8	125	122	1
11	6	26	24	4	8	3	7	64	64	1	-3	9	7	50	53	2	0	2	8	0	23	1	4	7	8	81	76	1
11	6	85	80	1	-9	4	7	0	11	1	-2	9	7	14	11	13	1	2	8	248	246	2	5	7	8	102	105	1
11	6	0	11	1	-8	4	7	62	65	1	-1	9	7	127	129	1	2	2	8	205	196	2	6	7	8	0	5	1
11	6	81	87	1	-7	4	7	86	80	1	0	9	7	92	92	1	3	2	8	78	70	1	7	7	8	0	16	1
11	6	149	154	1	-6	4	7	47	50	2	1	9	7	115	120	1	4	2	8	18	14	18	-7	8	8	62	64	2
11	6	123	122	1	-5	4	7	217	225	2	2	9	7	159	163	1	5	2	8	0	9	1	-6	8	8	78	74	1
11	6	0	3	1	-4	4	7	197	203	2	3	9	7	286	284	2	6	2	8	101	102	1	-5	8	8	45	47	2
11	6	81	76	1	-3	4	7	316	315	3	4	9	7	15	36	15	7	2	8	24	21	4	-4	8	8	91	90	1
11	6	44	43	2	-2	4	7	152	157	1	5	9	7	90	91	1	8	2	8	0	2	1	-3	8	8	200	206	2
12	6	39	42	2	-1	4	7	289	278	2	6	9	7	0	8	1	-9	3	8	79	70	1	-2	8	8	52	49	1
12	6	16	24	16	0	4	7	334	333	1	-7	10	7	27	24	4	-8	3	8	146	144	1	-1	8	8	155	162	1
12	6	69	72	1	1	4	7	310	313	2	-6	10	7	17	33	16	-7	3	8	48	46	2	0	8	8	86	87	1
12	6	0	9	1	2	4	7	115	117	1	-5	10	7	16	25	15	-6	3	8	171	172	1	1	8	8	119	122	1
12	6	0	16	1	3	4	7	68	62	1	-4	10	7	0	13	1	-5	3	8	60	65	1	2	8	8	222	228	2
12	6	14	27	13	4	4	7	71	69	1	-3	10	7	179	184	1	-4	3	8	0	21	1	3	8	8	0	11	1
12	6	73	72	1	5	4	7	37	36	2	-2	10	7	57	60	1	-3	3	8	101	107	1	4	8	8	124	128	1
12	6	110	106	1	6	4	7	59	63	1	-1	10	7	55	53	1	-2	3	8	123	117	1	5	8	8	45	49	2
12	6	20	3	20	7	4	7	0	15	1	0	10	7	111	120	1	-1	3	8	118	118	1	6	8	8	0	6	1
12	6	27	22	3	8	4	7	17	18	7	1	10	7	26	27	3	0	3	8	139	134	2	7	8	8	23	14	5
12	6	49	51	2	-9	5	7	27	28	4	2	10	7	36	26	2	1	3	8	154	142	1	-7	9	8	33	29	3
13	6	17	14	8	-8	5	7	120	117	1	3	10	7	102	100	1	2	3	8	67	69	1	-6	9	8	26	27	4
13	6	68	63	1	-7	5	7	45	39	2	4	10	7	56	57	1	3	3	8	77	72	1	-5	9	8	17	3	7
13	6	12	13	11	-6	5	7	155	150	1	5	10	7	53	51	2	4	3	8	153	148	1	-4	9	8	109	111	1
13	6	64	64	1	-5	5	7	197	200	1	6	10	7	102	100	1	5	3	8	91	93	1	-3	9	8	64	67	1
13	6	120	120	1	-4	5	7	156	162	1	-6	11	7	10	8	9	6	3	8	104	109	1	-2	9	8	0	16	1
13	6	100	94	1	-3	5	7	191	202	1	-5	11	7	8	33	8	7	3	8	58	52	1	-1	9	8	48	50	1
13	6	79	74	1	-2	5	7	0	34	1	-4	11	7	40	37	2	8	3	8	0	19	1	0	9	8	78	80	1
13	6	82	71	1	-1	5	7	230	220	2	-3	11	7	65	71	1	-9	4	8	39	37	3	1	9	8	17	24	6
0	7	22	33	22	0	5	7	483	483	4	-2	11	7	37	31	2	-8	4	8	21	27	5	2	9	8	41	42	2
0	7	41	40	2	1	5	7	96	94	1	-1	11	7	82	86	1	-7	4	8	127	127	1	3	9	8	0	1	1
0	7	47	50	1	2	5	7	27	23	2	0	11	7	67	72	1	-6	4	8	115	119	1	4	9	8	63	64	1
0	7	445	443	2	3	5	7	83	85	1	1	11	7	111	114	1	-5	4	8	93	95	1	5	9	8	48	40	2
0	7	234	233	1	4	5	7	93	91	1	2	11	7	74	77	1	-4	4	8	38	42	2	6	9	8	54	51	2
0	7	139	143	1	5	5	7	47	51	1	3	11	7	19	20	19	-3	4	8	66	60	1	-6	10	8	0	18	1
0	7	24	12	2	6	5	7	76	72	1	4	11	7	28	28	3	-2	4	8	23	30	3	-5	10	8	144	143	1
0	7	53	57	1	7	5	7	39	37	2	5	11	7	44	39	2	-1	4	8	151	145	1	-4	10	8	0	3	1

l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
8	74	76	1	-1	3	9	40	41	1	-5	9	9	46	45	2	-7	3	10	8	16	7	6	8	10	0	31	1
8	115	111	1	0	3	9	99	96	1	-4	9	9	0	1	1	-6	3	10	65	67	1	-6	9	10	31	33	4
8	0	30	1	1	3	9	55	51	1	-3	9	9	27	31	3	-5	3	10	30	31	3	-5	9	10	14	38	14
8	38	41	1	2	3	9	175	165	1	-2	9	9	65	64	1	-4	3	10	173	179	1	-4	9	10	40	36	2
8	39	45	2	3	3	9	71	73	1	-1	9	9	42	44	2	-3	3	10	23	24	3	-3	9	10	25	19	4
8	43	41	2	4	3	9	25	19	3	0	9	9	197	195	1	-2	3	10	178	186	1	-2	9	10	74	74	1
8	280	277	3	5	3	9	117	118	1	1	9	9	36	35	2	-1	3	10	29	26	2	-1	9	10	49	51	2
8	0	8	1	6	3	9	22	28	4	2	9	9	110	104	1	0	3	10	78	80	2	0	9	10	12	21	12
8	82	79	1	7	3	9	35	36	3	3	9	9	118	121	1	1	3	10	0	16	1	1	9	10	95	93	1
8	0	9	1	8	3	9	14	3	13	4	9	9	0	2	1	2	3	10	39	36	2	2	9	10	171	177	1
8	59	58	2	-8	4	9	0	4	1	5	9	9	75	75	1	3	3	10	202	198	2	3	9	10	48	44	2
8	0	7	1	-7	4	9	125	121	1	6	9	9	25	25	5	4	3	10	18	14	5	4	9	10	0	5	1
8	88	95	1	-6	4	9	59	60	1	-6	10	9	9	5	8	5	3	10	85	88	1	5	9	10	91	87	1
8	75	70	1	-5	4	9	229	226	2	-5	10	9	55	49	2	6	3	10	61	62	1	-6	10	10	0	4	1
8	35	31	3	-4	4	9	31	35	2	-4	10	9	56	61	2	7	3	10	17	13	8	-5	10	10	19	5	18
8	133	129	1	-3	4	9	175	176	1	-3	10	9	0	8	1	-8	4	10	54	55	2	-4	10	10	72	72	1
8	86	83	1	-2	4	9	81	82	1	-2	10	9	20	19	20	-7	4	10	0	24	1	-3	10	10	59	62	1
8	28	29	3	-1	4	9	132	131	1	-1	10	9	20	19	19	-6	4	10	38	41	2	-2	10	10	76	77	1
8	69	68	1	0	4	9	66	68	1	0	10	9	104	105	1	-5	4	10	259	259	2	-1	10	10	151	155	1
8	70	69	1	1	4	9	231	224	2	1	10	9	0	21	1	-4	4	10	0	20	1	0	10	10	20	15	20
8	21	21	5	2	4	9	230	239	2	2	10	9	181	177	1	-3	4	10	165	175	1	1	10	10	51	45	2
8	20	3	19	3	4	9	267	267	2	3	10	9	163	162	1	-2	4	10	70	77	1	2	10	10	0	39	1
8	9	6	9	4	4	9	35	36	2	4	10	9	76	76	1	-1	4	10	8	8	8	3	10	10	0	11	1
8	0	8	1	5	4	9	76	81	1	5	10	9	16	15	9	0	4	10	68	64	1	4	10	10	0	7	1
8	17	6	8	6	4	9	18	17	6	-5	11	9	43	45	2	1	4	10	132	131	1	5	10	10	83	77	1
8	0	13	1	7	4	9	17	11	16	-4	11	9	20	34	6	2	4	10	50	48	1	-5	11	10	7	2	6
8	48	51	1	-8	5	9	0	22	1	-3	11	9	89	90	1	3	4	10	249	248	2	-4	11	10	8	13	8
8	53	49	2	-7	5	9	59	57	2	-2	11	9	14	8	13	4	4	10	18	29	5	-3	11	10	73	74	1
8	88	89	1	-6	5	9	127	128	1	-1	11	9	32	21	3	5	4	10	45	41	2	-2	11	10	32	31	3
8	80	72	1	-5	5	9	228	235	2	0	11	9	35	43	13	6	4	10	0	9	1	-1	11	10	15	10	9
8	23	37	22	-4	5	9	82	84	1	1	11	9	53	52	2	7	4	10	0	15	1	0	11	10	24	28	10
8	39	33	3	-3	5	9	91	96	1	2	11	9	83	78	1	-8	5	10	62	64	2	1	11	10	0	0	1
8	33	28	3	-2	5	9	15	3	15	3	11	9	0	18	1	-7	5	10	79	80	1	2	11	10	20	4	5
8	23	16	5	-1	5	9	66	67	1	4	11	9	19	2	18	-6	5	10	13	4	13	3	11	10	0	16	1
8	0	13	1	0	5	9	113	114	1	-4	12	9	0	23	1	-5	5	10	113	115	1	4	11	10	9	36	8
8	11	5	10	1	5	9	27	28	2	-3	12	9	48	48	2	-4	5	10	0	14	1	-4	12	10	13	13	13
8	0	8	1	2	5	9	0	37	1	-2	12	9	79	77	1	-3	5	10	0	1	1	-3	12	10	0	5	1
9	42	36	2	3	5	9	21	13	4	-1	12	9	83	76	1	-2	5	10	81	83	1	-2	12	10	16	18	10
9	43	40	2	4	5	9	97	91	1	0	12	9	23	20	22	-1	5	10	192	188	1	-1	12	10	0	31	1
9	155	150	1	5	5	9	80	83	1	1	12	9	45	46	2	0	5	10	36	38	1	0	12	10	42	42	2
9	27	33	2	6	5	9	78	83	1	2	12	9	74	72	1	1	5	10	33	31	2	1	12	10	0	8	1
9	56	57	1	7	5	9	0	2	1	3	12	9	39	34	2	2	5	10	172	172	1	2	12	10	14	14	14
9	0	9	1	-8	6	9	47	46	2	-3	13	9	62	60	2	3	5	10	14	38	13	3	12	10	12	5	12
9	70	72	1	-7	6	9	39	35	2	-2	13	9	0	16	1	4	5	10	53	49	1	-2	13	10	20	17	19
9	16	16	15	-6	6	9	86	89	1	-1	13	9	69	65	1	5	5	10	0	13	1	-1	13	10	29	27	4
9	17	7	7	-5	6	9	142	144	1	0	13	9	66	64	1	6	5	10	12	4	12	0	13	10	0	5	1
9	29	18	4	-4	6	9	89	87	1	1	13	9	0	12	1	7	5	10	63	61	1	-7	0	11	50	47	2
9	80	84	1	-3	6	9	75	76	1	2	13	9	10	6	10	-8	6	10	42	37	3	-5	0	11	97	98	1
9	50	50	2	-2	6	9	18	10	5	-8	0	10	91	94	1	-7	6	10	0	28	1	-3	0	11	184	178	1
9	118	114	1	-1	6	9	51	49	1	-6	0	10	226	226	2	-6	6	10	100	99	1	-1	0	11	485	477	3
9	50	55	1	0	6	9	105	103	1	-4	0	10	17	37	16	-5	6	10	146	154	1	1	0	11	88	87	1
9	47	48	1	1	6	9	150	147	1	-2	0	10	232	239	2	-4	6	10	173	175	1	3	0	11	46	48	1
9	182	175	1	2	6	9	114	120	1	0	0	10	241	241	1	-3	6	10	163	166	1	5	0	11	105	110	1
9	45	43	1	3	6	9	42	39	2	2	0	10	89	90	1	-2	6	10	14	5	8	7	0	11	40	42	2
9	507	502	2	4	6	9	51	50	1	4	0	10	43	45	2	-1	6	10	111	109	1	-8	1	11	0	2	1
9	60	60	1	5	6	9	80	82	1	6	0	10	58	58	1	0	6	10	23	18	6	-7	1	11	93	93	1
9	220	215	2	6	6	9	49	42	2	-9	1	10	44	39	2	1	6	10	116	119	1	-6	1	11	0	10	1
9	12	7	11	7	6	9	0	9	1	-8	1	10	0	12	1	2	6	10	104	102	1	-5	1	11	0	8	1
9	248	252	2	-8	7	9	0	5	1	-7	1	10	49	42	2	3	6	10	106	109	1	-4	1	11	15	2	14
9	88	97	1	-7	7	9	0	5	1	-6	1	10	0	17	1	4	6	10	20	5	19	-3	1	11	31	33	2
9	185	196	1	-6	7	9	118	122	1	-5	1	10	148	151	1	5	6	10	0	39	1	-2	1	11	51	53	1
9	23	29	4	-5	7	9	0	4	1	-4	1	10	75	73	1	6	6	10	0	19	1	-1	1	11	40	36	1
9	129	138	1	-4	7	9	98	99	1	-3	1	10	106	105	1	7	6	10	91	86	1	0	1	11	151	143	1
9	17	22	7	-3	7	9	35	29	2	-2	1	10	142	139	1	-7	7	10	25	33	4	1	1	11	121	114	1
9	68	60	1	-2	7	9	182	180	1	-1	1	10	242	235	2	-6	7	10	20	23	6	2	1	11	0	3	1
9	0	36	1	-1	7	9	25	29	3	0	1	10	184	191	3	-5	7	10	40	38	2	3	1	11	141	135	1
9	0	33	1	0	7	9	344	345	2	1	1	10	0	44	1	-4	7	10	119	120	1	4	1	11	168	170	1
9	33	33	2	1	7	9	50	48	1	2	1	10	142	145	1	-3	7	10	15	17	8	5	1	11	148	149	1
9	0	20	1	2	7	9	64	62	1	3	1	10	0	24	1	-2	7	10	216	221	2	6	1	11	0	21	1
9	102	102	1	3	7	9	83	86	1	4	1	10	46	45	1	-1	7	10	0	20	1	7	1	11	49	56	2
9	38	30	2	4	7	9	35	33	2	5	1	10	129	133	1	0	7	10	94	91	1	-8	2	11	0	25	1
9	319	324	3	5	7	9	76	78	1	6	1	10	44	42	2	1	7	10	0	28	1	-7	2	11	18	13	17
9	229	231	2	6	7	9	0	3	1	7	1	10	0	6	1	2	7	10	38	44	2	-6	2	11	68	76	1
9	102	104	3	7	7	9	30	27	3	-8	2	10	0	7	1	3	7	10	60	62	1	-5	2	11	66	67	1
9	168	172	1	-7	8	9	18	9	8	-7	2	10	45	46	2	4	7	10	50	48	1	-4	2	11	196	203	2
9	251	244	2	-6	8	9	0	6	1	-6	2	10	34	38	2	5	7	10	18	21	18	-3	2	11	19	23	19
9	63	60	1	-5	8	9	98	97	1	-5	2	10	81	90	1	6	7	10	17	29	16	-2	2	11	91	95	1
9	220	222	2	-4	8	9	103	106	1	-4	2	10	52	53	1	-7	8	10	83	84	1	-1	2	11	136	132	1
9	191	191	1	-3	8	9	67	63	1	-3	2	10	18	28	4	-6	8	10	0	3	1	0	2	11	19	22	4
9	54	53	1	-2	8	9	201	200	2	-2	2	10	129	135	1	-5	8	10	0	30	1	1	2	11	172	170	1
9	34	37	3	-1	8	9	140	139	1	-1	2	10	53	53	1	-4	8	10	0	0	1	2	2	11	0	5	1
9	45	47	2	0	8	9	70	70	1	0	2	10	20	27	2	-3	8	10	0	19	1	3	2	11	11	12	11
9	40	39	3	1	8	9	0	3	1	1	2	10	0	11	1	-2	8	10	70	69	1	4	2	11	82	82	1
9	28	25	4	2	8	9	0	13	1	2	2	10	124	123	1	-1	8	10	47	48	2	5	2	11	113	113	1
9	0	11	1	3	8	9	76	75	1	3	2	10	20	16	4	0	8	10	44	43	2	6	2	11	0	23	1
9	52	47	1	4	8	9	0	13	1	4	2	10	166	174	1	1	8	10	196	196	1	7	2	11	35	40	3
9	69	66	1	5	8	9	0	22	1	5	2	10	117	120	1	2	8	10	163	165	1	-8	3	11	42	44	2
9	40	41	2	6	8	9	0	14	1	6	2	10	16	21	15	3	8	10	0	0	1	-7	3	11	28	22	4
9	213	216	2	-7	9	9	103	97	1	7	2	10	91	90	1	4	8	10	59	56	1	-6	3	11	20	9	19
9	118	119	1	-6	9	9	46	42	2	-8	3	10	26	20	4	5	8	10	22	28	5	-5	3	11	77	73	1

h	k	l	10Fo	10Fc	10s
11	0	3	1	1	9
11	20	8	4	2	9
11	0	14	1	3	9
11	87	88	1	4	9
11	90	88	1	5	9
11	0	11	1	-5	10
11	39	43	2	-4	10
11	0	34	1	-3	10
11	140	139	1	-2	10
11	64	62	1	-1	10
11	84	81	1	0	10
11	64	63	1	1	10
11	41	37	2	2	10
11	51	55	2	3	10
11	78	81	1	4	10
11	15	12	14	-4	11
11	14	2	13	-3	11
11	4	4	4	-2	11
11	101	104	1	-1	11
11	73	69	1	0	11
11	54	57	3	1	11
11	74	74	1	2	11
11	12	0	11	3	11
11	18	10	5	-3	12
11	183	191	1	-2	12
11	47	48	2	-1	12
11	79	80	1	0	12
11	38	34	3	1	12
11	48	43	2	2	12
11	20	21	6	-8	0
11	20	23	6	-6	0
11	0	1	1	-4	0
11	106	109	1	-2	0
11	84	83	1	0	0
11	51	54	1	2	0
11	114	118	1	4	0
11	125	130	1	6	0
11	121	121	1	-8	1
11	125	122	1	-7	1
11	36	35	2	-6	1
11	11	12	10	-5	1
11	23	29	4	-4	1
11	12	1	11	-3	1
11	50	52	2	-2	1
11	23	26	5	-1	1
11	0	12	1	0	1
11	16	12	8	1	1
11	47	51	2	2	1
11	164	167	1	3	1
11	112	110	1	4	1
11	46	48	1	5	1
11	0	16	1	6	1
11	8	4	8	7	1
11	0	7	1	-8	2
11	11	12	11	-7	2
11	66	68	1	-6	2
11	35	36	3	-5	2
11	0	13	1	-4	2
11	86	86	1	-3	2
11	93	100	1	-2	2
11	0	2	1	-1	2
11	124	125	1	0	2
11	41	43	2	1	2
11	138	138	1	2	2
11	139	139	1	3	2
11	88	89	1	4	2
11	0	16	1	5	2
11	100	101	1	6	2
11	28	30	3	7	2
11	0	22	1	-8	3
11	59	60	2	-7	3
11	0	5	1	-6	3
11	82	84	1	-5	3
11	64	66	1	-4	3
11	18	0	18	-3	3
11	142	149	1	-2	3
11	58	57	1	-1	3
11	123	122	1	0	3
11	53	57	2	1	3
11	113	111	1	2	3
11	33	33	3	3	3
11	8	14	8	4	3
11	8	27	8	5	3
11	35	40	3	6	3
11	15	10	10	-8	4
11	0	2	1	-7	4
11	13	5	13	-6	4
11	0	9	1	-5	4
11	15	21	15	-4	4
11	0	14	1	-3	4
11	15	21	5	-4	4
11	105	106	1	-2	4
11	108	106	1	-1	4
11	82	85	2	0	4
11	164	171	1	1	4
11	175	173	1	2	4
11	43	43	2	3	4
11	10	17	9	4	4
11	113	119	1	5	4
11	53	50	2	6	4
11	95	91	1	-7	5
11	107	109	1	-6	5
11	146	146	1	-5	5
11	71	74	1	-4	5
11	42	43	2	-3	5
11	14	26	13	-2	5
11	19	22	5	-1	5
11	123	120	1	0	5
11	131	129	1	1	5
11	209	204	2	2	5
11	38	41	2	3	5
11	0	20	1	4	5
11	65	71	1	5	5
11	36	36	3	6	5
11	21	32	21	-7	6
11	44	46	2	-6	6
11	60	64	2	-5	6
11	11	14	10	-4	6
11	212	221	2	-3	6
11	142	139	1	-2	6
11	229	235	2	-1	6
11	48	49	1	0	6
11	89	91	1	1	6
11	0	10	1	2	6
11	28	34	3	3	6
11	0	0	1	4	6
11	0	13	1	5	6
11	41	31	2	6	6
11	108	103	1	-7	7
11	12	13	11	-6	7
11	22	22	5	-5	7
11	43	40	2	-4	7
11	88	85	1	-3	7
11	112	113	1	-2	7
11	165	163	1	-1	7
11	181	176	1	0	7
11	0	1	1	1	7
11	151	153	1	2	7
11	0	14	1	3	7
11	54	50	1	4	7
11	75	73	1	5	7
11	72	65	1	6	7
11	0	9	1	-6	8
11	0	17	1	-5	8
11	0	14	1	-4	8
11	86	87	1	-3	8
11	0	4	1	-2	8
11	108	107	1	-1	8
11	39	46	2	0	8
11	34	32	3	1	8
11	0	9	1	2	8
11	56	59	2	3	8
11	28	23	4	4	8
11	24	19	5	5	8
11	0	11	1	6	8
11	55	59	2	-7	9
11	103	104	1	-6	9
11	0	3	1	-5	9
11	41	40	9	-4	9
11	0	9	1	-3	9
11	14	11	10	-2	9
11	34	22	3	-1	9
11	61	61	1	0	9
11	48	47	2	1	9
11	44	41	2	2	9
11	19	14	18	3	9
11	35	40	3	4	9
11	40	37	2	5	9
11	0	5	1	-7	10
11	38	36	2	-6	10
11	38	37	2	-5	10
11	0	3	1	-4	10
11	0	4	1	-3	11
11	0	13	1	-2	11
11	0	17	1	-1	11
11	28	28	3	0	11
11	26	25	4	1	11
11	25	31	4	2	11
11	14	23	14	3	12
11	92	84	1	4	12
11	14	21	14	5	6
11	86	83	1	-5	0
11	183	184	1	-3	0
11	279	278	2	-1	0
11	170	165	1	1	0
11	0	4	1	3	0
11	8	26	7	5	0
11	45	42	2	-8	1
11	37	36	3	-7	1
11	14	8	13	-6	1
11	101	108	1	-5	1
11	17	20	17	-4	1
11	61	55	1	-3	1
11	217	215	2	-2	1
11	0	21	1	-1	1
11	170	167	2	0	1
11	134	129	1	1	1
11	160	154	1	2	1
11	0	5	1	3	1
11	164	167	1	4	1
11	46	46	2	5	1
11	21	22	5	6	1
11	47	38	2	-8	2
11	0	18	1	-7	2
11	67	68	1	-6	2
11	42	36	2	-5	2
11	152	152	1	-4	2
11	37	39	2	-3	2
11	243	248	2	-2	2
11	48	51	1	-1	2
11	134	135	1	0	2
11	17	5	6	1	2
11	17	26	17	2	2
11	117	112	1	3	2
11	62	64	1	4	2
11	32	26	3	5	2
11	0	37	1	6	2
11	8	2	8	-7	3
11	8	21	7	-6	3
11	24	26	4	-5	3
11	0	0	1	-4	3
11	74	78	1	-3	3
11	44	47	2	-2	3
11	0	33	1	-1	3
11	121	122	3	0	3
11	101	104	1	1	3
11	43	47	2	2	3
11	125	126	1	3	3
11	86	89	1	4	3
11	104	102	1	5	3
11	19	17	6	6	3
11	21	24	6	-7	4
11	0	9	1	-6	4
11	99	104	1	-5	4
11	0	20	1	-4	4
11	129	131	1	-3	4
11	14	22	14	-2	4
11	102	100	1	-1	4
11	95	103	1	0	4
11	0	5	1	1	4
11	148	148	1	2	4
11	110	110	1	3	4
11	82	83	1	4	4
11	100	99	1	5	4
11	0	21	1	6	4
11	0	6	1	-7	5
11	0	3	1	-6	5
11	0	24	1	-5	5
11	0	15	1	-4	5
11	27	17	4	-3	5
11	104	110	1	-2	5
11	120	118	1	-1	5
11	0	12	1	0	5
11	0	44	1	1	5
11	24	19	4	2	5
11	37	42	2	3	5
11	16	15	16	4	5
11	20	18	20	5	5
11	17	12	9	6	5
11	0	18	1	-7	6
11	46	50	2	-6	6
11	55	63	2	-5	6
11	30	33	3	-4	6
11	79	88	1	-3	6
11	68	70	1	-2	6
11	105	100	1	-1	6
11	111	109	1	0	6
11	9	15	8	1	6
11	56	53	1	2	6
11	39	34	2	3	6
11	27	20	4	4	6
11	20	23	5	5	6
11	305	305	2	-7	0
11	76	72	1	-6	1
11	45	40	2	-5	1
11	81	81	1	-4	1
11	38	38	2	-3	1
11	0	7	1	-2	1
11	39	32	2	-1	1
11	23	20	5	0	1
11	0	18	1	1	1
11	130	128	1	2	1
11	21	22	4	3	1
11	64	60	1	4	1
11	76	72	1	5	1
11	45	40	2	6	1
11	81	81	1	-7	2
11	109	109	1	-6	2
11	22	29	5	-5	2
11	128	129	1	-4	2
11	26	29	3	-3	2
11	102	102	1	-2	2
11	109	112	1	-1	2
11	128	128	1	0	2
11	27	26	3	1	2
11	107	109	1	2	2
11	152	159	1	3	2
11	41	41	2	4	2
11	11	8	11	5	2
11	44	37	2	6	2
11	54	53	2	7	2
11	12	14	12	-8	3
11	40	35	2	-7	3
11	81	82	1	-6	3
11	35	33	2	-5	3
11	161	172	1	-4	3
11	104	102	1	-3	3
11	48	52	1	-2	3
11	125	127	1	-1	3
11	24	25	3	0	3
11	72	75	1	1	3
11	158	158	1	2	3
11	0	7	1	3	3
11	46	50	2	-3	4
11	112	112	1	-2	4
11	0	13	1	-1	4
11	18	2	7	0	4
11	0	4	1	1	4
11	0	23	1	2	4
11	17	10	16	-1	5
11	20	23	5	0	5
11	305	305	2	-7	0
11	15	21	1	-6	1
11	13	23	1	-5	1
11	58	53	1	-4	1
11	39	34	2	-3	1
11	27	20	4	-2	1
11	183	184	1	-1	1
11	279	278	2	0	1
11	170	165	1	1	1
11	0	4	1	2	1
11	8	26	7	3	1
11	45	42	2	4	1
11	37	36	3	5	1
11	14	8	13	6	1
11	101	108	1	7	1
11	17	20	17	8	1
11	61	55	1	9	1
11	217	215	2	10	1
11	0	21	1	11	1
11	170	167	2	12	1
11	134	129	1	13	1
11	160	154	1	14	1
11	0	5	1	15	1
11	164	167	1	16	1
11	46	46	2	17	1
11	21	22	5	18	1
11	47	38	2	19	1
11	0	18	1	20	1
11	67	68	1	21	1
11	42	36	2	22	1
11	152	152	1	23	1
11	37	39	2	24	1
11	243	248	2	25	1
11	48	51	1	26	1
11	134	135	1	27	1
11	17	5	6	28	1
11	17	26	17	29	1
11	117	112	1	30	1
11	62	64	1	31	1
11	32	26	3	32	1
11	0	37	1	33	1
11	8	2	8	34	1
11	8	21	7	35	1
11	24	26	4	36	1
11	0	0	1	37	1
11	74	78	1	38	1
11	44	47	2	39	1
11	0	33	1	40	1
11	121	122	3	41	1
11	101	104	1	42	1
11	43	47	2	43	1
11	125	126	1	44	1
11	86	89	1	45	1
11	104	102	1	46	1
11	19	17	6	47	1
11	21	24	6	48	1
11	0	9	1	49	1
11	99	104	1	50	1
11	0	20	1	51	1
11	129	131	1	52	1
11	14	22	14	53	1
11	102	100	1	54	1
11	95	103	1	55	1
11	0	5	1	56	1
11	148	148	1	57	1
11	110	110	1	58	1
11	82	83	1	59	1
11	100	99	1	60	1
11	0	21	1	61	1
11	0	6	1	62	1
11	0	3	1	63	1
11	0	24	1	64	1
11	0	15	1	65	1
11	27	17	4	66	1
11	104	110	1	67	1
11	120	118	1	68	1
11	0	12	1	69	1
11	0	44	1	70	1
11	24	19	4	71	1
11	37	42	2	72	1
11	16	15	16	73	1
11	20	18	20	74	1
11	17	12	9	75	1
11	0	18	1	76	1
11	46	50	2	77	1
11	55	63	2	78	1
11	30	33	3	79	1
11	79	88	1	80	1
11	68	70	1	81	1
11	105	100	1	82	1
11	111	109	1	83	1
11	9	15	8	84	1
11	56	53	1	85	1
11	39	34	2	86	1
11	27	20	4	87	1
11	20	23	5	88	1
11	305	305	2	89	1
11	76	72	1	90	1
11	45	40	2	91	1
11	81	81	1	92	1
11	38	38	2	93	1
11	0	7	1	94	1
11	39	32	2	95	1
11	23	20	5	96	1
11	0	18	1	97	1
11	130	128	1	98	1
11	21	22	4	99	1
11	64	60	1	100	1
11	76	72	1	101	1
11	45	40	2	102	1
11	81	81	1	103	1
11	109	109	1	104	1
11	22	29	5	105	1
11	128	129	1	106	1
11	26	29	3	107	1
11	102	102	1	108	1
11	109	112	1	109	1
11	128	128	1	110	1
11	27	26	3	111	1
11	107	109	1	112	1
11	152	159	1	113	1
11	41	41	2	114	1
11	11	8	11	115	1
11	44	37	2	116	1
11	54	53	2	117	1
11	12	14	12	118	1
11	40	35	2	119	1
11	81	82	1	120	1
11	35	33	2	121	1
11	161	172	1	122	1
11	104	102	1	123	1
11	48	52	1	124	1
11	125	127	1	125	1
11	24	25	3	126	1
11	72	75	1	127	1
11	158	158	1	128	1
11	0	7	1	129	1
11	46	50	2	130	1
11	112	112	1	131	1
11	0	13	1	132	1
11	18	2	7	133	1
11	0	4	1	134	1
11	0	23	1	135	1
11	17	10	16	136	1
11	20	23	5	137	1
11	305	305	2	138	1

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
14	0	6	1	1	9	14	20	30	20	3	4	15	18	29	18	-6	2	16	0	2	1	-5	0	17	38	33	3
14	21	4	21	2	9	14	27	26	4	4	4	15	56	59	2	-5	2	16	47	46	2	-3	0	17	0	28	1
14	13	17	13	3	9	14	53	49	2	5	4	15	0	5	1	-4	2	16	28	37	4	-1	0	17	0	3	1
14	39	45	2	-3	10	14	29	15	4	-6	5	15	21	17	6	-3	2	16	174	168	1	1	0	17	97	96	1
14	141	141	1	-2	10	14	0	5	1	-5	5	15	49	43	2	-2	2	16	77	78	1	3	0	17	43	43	2
14	11	12	10	-1	10	14	0	5	1	-4	5	15	17	16	8	-1	2	16	133	130	1	-5	1	17	32	19	3
14	245	250	2	0	10	14	0	4	1	-3	5	15	0	7	1	0	2	16	36	38	2	-4	1	17	65	54	1
14	177	180	1	1	10	14	13	8	13	-2	5	15	54	56	2	1	2	16	0	40	1	-3	1	17	48	49	2
14	104	102	1	-7	0	15	15	4	15	-1	5	15	0	23	1	2	2	16	39	32	2	-2	1	17	21	21	5
14	121	116	1	-5	0	15	65	64	1	0	5	15	68	65	2	3	2	16	86	84	1	-1	1	17	0	14	1
14	68	69	1	-3	0	15	78	73	1	1	5	15	123	122	1	4	2	16	0	12	1	0	1	17	49	47	1
14	93	98	1	-1	0	15	35	39	2	2	5	15	71	68	1	-6	3	16	0	31	1	1	1	17	0	0	1
14	0	4	1	1	0	15	0	3	1	3	5	15	29	23	3	-5	3	16	55	58	2	2	1	17	0	3	1
14	0	49	1	3	0	15	198	188	1	4	5	15	0	30	1	-4	3	16	0	15	1	3	1	17	12	20	12
14	30	33	4	5	0	15	88	85	1	-5	6	15	12	33	12	-3	3	16	21	14	21	-5	2	17	0	10	1
14	0	21	1	-7	1	15	74	72	1	-4	6	15	12	14	12	-2	3	16	29	20	3	-4	2	17	18	16	7
14	0	21	1	-6	1	15	81	76	1	-3	6	15	0	-1	1	-1	3	16	57	52	1	-3	2	17	37	36	3
14	101	105	1	-5	1	15	97	95	1	-2	6	15	16	36	15	0	3	16	25	23	11	-2	2	17	52	50	2
14	80	84	1	-4	1	15	0	8	1	-1	6	15	0	5	1	1	3	16	0	10	1	-1	2	17	15	11	9
14	79	76	1	-3	1	15	126	127	1	0	6	15	68	74	1	2	3	16	59	65	2	0	2	17	0	9	1
14	76	79	1	-2	1	15	119	121	1	1	6	15	78	73	1	3	3	16	0	6	1	1	2	17	0	13	1
14	49	47	2	-1	1	15	63	67	1	2	6	15	0	31	1	4	3	16	12	14	12	2	2	17	27	32	4
14	33	27	3	0	1	15	51	53	1	3	6	15	46	47	2	-5	4	16	34	29	3	3	2	17	0	2	1
14	33	36	3	1	1	15	11	12	11	4	6	15	28	26	4	-4	4	16	9	10	8	-5	3	17	53	48	2
14	0	41	1	2	1	15	59	60	1	-5	7	15	45	43	2	-3	4	16	100	101	1	-4	3	17	45	48	2
14	0	15	1	3	1	15	21	15	5	-4	7	15	0	34	1	-2	4	16	33	30	3	-3	3	17	96	95	1
14	19	15	7	4	1	15	0	34	1	-3	7	15	42	43	2	-1	4	16	75	78	1	-2	3	17	65	63	1
14	12	25	11	5	1	15	46	47	2	-2	7	15	0	30	1	0	4	16	46	47	10	-1	3	17	93	94	1
14	51	45	2	-7	2	15	0	3	1	-1	7	15	94	88	1	1	4	16	58	60	2	0	3	17	60	61	1
14	99	97	1	-6	2	15	46	39	2	0	7	15	18	20	7	2	4	16	33	31	3	1	3	17	22	30	21
14	94	92	1	-5	2	15	67	72	1	1	7	15	64	60	1	3	4	16	0	21	1	2	3	17	8	5	8
14	57	55	1	-4	2	15	44	43	2	2	7	15	8	4	7	4	4	16	18	24	8	3	3	17	75	73	1
14	18	10	13	-3	2	15	0	2	1	3	7	15	20	15	6	-5	5	16	16	20	10	-5	4	17	0	5	1
14	0	11	1	-2	2	15	97	96	1	-4	8	15	0	26	1	-4	5	16	0	13	1	-4	4	17	19	24	19
14	53	50	2	-1	2	15	31	29	3	-3	8	15	56	46	2	-3	5	16	45	42	2	-3	4	17	54	57	2
14	0	14	1	0	2	15	81	81	1	-2	8	15	21	20	6	-2	5	16	71	78	1	-2	4	17	0	3	1
14	0	39	1	1	2	15	61	61	1	-1	8	15	39	32	3	-1	5	16	72	69	1	-1	4	17	0	16	1
14	25	0	5	2	2	15	26	28	4	0	8	15	56	54	1	0	5	16	0	7	1	0	4	17	82	85	2
14	41	37	3	3	2	15	37	43	3	1	8	15	0	34	1	1	5	16	129	124	1	1	4	17	8	3	8
14	0	23	1	4	2	15	22	13	5	2	8	15	23	17	5	2	5	16	35	37	3	2	4	17	30	34	4
14	0	12	1	5	2	15	39	33	3	-3	9	15	0	1	1	3	5	16	78	75	1	3	4	17	0	3	1
14	69	74	1	-6	3	15	15	21	14	-2	9	15	23	23	5	-5	6	16	11	11	11	-4	5	17	0	4	1
14	60	50	1	-5	3	15	86	89	1	-1	9	15	41	37	2	-4	6	16	63	57	2	-3	5	17	0	4	1
14	42	36	1	-4	3	15	57	64	2	0	9	15	70	68	2	-3	6	16	14	25	14	-2	5	17	75	73	1
14	178	166	1	-3	3	15	23	19	5	1	9	15	0	17	1	-2	6	16	63	58	2	-1	5	17	20	12	6
14	0	6	1	-2	3	15	69	75	1	-6	0	16	54	46	2	-1	6	16	98	95	1	0	5	17	31	32	2
14	19	16	18	-1	3	15	85	85	1	-4	0	16	65	61	1	0	6	16	0	6	1	1	5	17	83	78	1
14	15	4	14	0	3	15	116	119	1	-2	0	16	138	139	1	1	6	16	45	45	2	2	5	17	26	26	4
14	20	26	7	1	3	15	169	164	1	0	0	16	51	53	1	2	6	16	60	56	2	-3	6	17	9	0	8
14	37	35	3	2	3	15	0	7	1	2	0	16	47	45	2	3	6	16	58	54	2	-2	6	17	64	58	2
14	0	19	1	3	3	15	49	47	2	4	0	16	0	9	1	-4	7	16	20	8	6	-1	6	17	20	15	6
14	0	36	1	4	3	15	20	14	20	-6	1	16	65	66	2	-3	7	16	23	25	5	0	6	17	34	36	6
14	23	26	5	5	3	15	60	55	2	-5	1	16	70	66	1	-2	7	16	59	57	2	1	6	17	91	89	1
14	22	33	22	-6	4	15	9	26	8	-4	1	16	0	12	1	-1	7	16	0	7	1	2	6	17	12	20	12
14	71	73	1	-5	4	15	23	26	5	-3	1	16	56	53	2	0	7	16	70	67	2	-2	7	17	27	27	4
14	14	9	14	-4	4	15	65	63	1	-2	1	16	19	37	18	1	7	16	17	9	8	-1	7	17	0	24	1
14	34	31	3	-3	4	15	69	72	1	-1	1	16	19	22	6	2	7	16	25	24	4	0	7	17	103	98	1
14	0	22	1	-2	4	15	54	60	2	0	1	16	42	40	12	-3	8	16	16	17	13	1	7	17	18	0	17
14	34	32	3	-1	4	15	49	49	2	1	1	16	0	13	1	-2	8	16	39	35	3						
14	59	49	2	0	4	15	89	86	1	2	1	16	51	44	2	-1	8	16	43	38	2						
14	25	32	4	1	4	15	83	79	1	3	1	16	21	16	6	0	8	16	21	27	6						
14	0	11	1	2	4	15	0	3	1	4	1	16	20	16	6	1	8	16	21	12	21						

dix F: Observed and Calculated Structure factors for (227).

h	k	l	10Fo	10Fc	10s
0	0	0	897	796	4
0	0	0	528	554	1
0	0	0	133	129	3
0	0	0	201	201	1
0	0	0	278	283	2
0	0	0	14	12	14
0	0	0	71	66	2
0	0	0	48	54	4
0	0	0	25	7	11
0	0	0	79	74	1
0	0	0	15	25	15
0	0	0	368	371	2
0	0	0	390	388	2
0	0	0	74	77	1
0	0	0	82	82	2
0	0	0	124	129	1
0	0	0	148	151	1
0	0	0	83	80	2
0	0	0	135	138	1
0	0	0	459	476	3
0	0	0	455	459	1
0	0	0	98	105	1
0	0	0	73	70	1
0	0	0	84	87	3
0	0	0	101	103	3
0	0	0	43	45	3
0	0	0	64	59	3
0	0	0	22	4	15
0	0	0	452	449	1
0	0	0	703	708	5
0	0	0	220	223	1
0	0	0	23	21	4
0	0	0	189	185	1
0	0	0	41	41	3
0	0	0	125	122	3
0	0	0	143	143	3
0	0	0	35	38	5
0	0	0	1259	1120	7
0	0	0	387	410	1
0	0	0	97	92	1
0	0	0	403	404	2
0	0	0	199	200	2
0	0	0	21	33	10
0	0	0	40	36	3
0	0	0	181	186	1
0	0	0	38	35	19
0	0	0	18	13	18
0	0	0	637	642	2
0	0	0	360	359	1
0	0	0	117	116	1
0	0	0	178	167	1
0	0	0	108	102	1
0	0	0	213	214	1
0	0	0	166	166	1
0	0	0	19	19	18
0	0	0	60	59	3
0	0	0	38	37	2
0	0	0	812	833	6
0	0	0	133	138	2
0	0	0	361	357	2
0	0	0	102	102	1
0	0	0	25	13	4
0	0	0	115	126	1
0	0	0	0	3	1
0	0	0	0	7	1
0	0	0	84	87	2
0	0	0	856	882	1
0	0	0	324	333	2
0	0	0	169	151	1
0	0	0	44	51	4
0	0	0	107	104	1
0	0	0	15	5	15
0	0	0	14	13	14
0	0	0	25	24	25
0	0	0	39	34	14
0	0	0	216	215	2
0	0	0	483	488	1
0	0	0	106	106	1
0	0	0	100	100	1
0	0	0	118	119	1
0	0	0	38	35	3
0	0	0	23	28	10
0	0	0	34	25	14
0	0	0	114	116	2
0	0	0	66	62	3
0	0	0	337	340	2
0	0	0	140	136	1
0	0	0	730	707	3
0	0	0	118	117	1
0	0	0	15	26	15
6	9	0	61	57	4
7	9	0	121	120	2
8	9	0	68	66	2
9	9	0	96	90	5
0	10	0	269	261	2
1	10	0	109	106	1
2	10	0	539	529	2
3	10	0	0	24	1
4	10	0	85	96	1
5	10	0	86	78	3
6	10	0	201	199	1
7	10	0	47	43	3
8	10	0	57	48	3
1	11	0	369	358	2
2	11	0	239	227	3
3	11	0	295	297	2
4	11	0	32	25	3
5	11	0	170	178	1
6	11	0	53	65	3
7	11	0	48	32	3
8	11	0	57	54	3
0	12	0	106	111	1
1	12	0	46	49	2
2	12	0	180	178	1
3	12	0	139	133	1
4	12	0	0	2	1
5	12	0	133	136	1
6	12	0	59	69	2
7	12	0	94	96	2
8	12	0	45	43	7
1	13	0	97	95	1
2	13	0	10	34	10
3	13	0	243	249	1
4	13	0	66	69	2
5	13	0	85	74	2
6	13	0	51	45	3
7	13	0	43	32	11
8	13	0	23	8	13
0	14	0	46	42	3
1	14	0	137	138	1
2	14	0	127	126	1
3	14	0	235	232	1
4	14	0	186	182	2
5	14	0	26	24	8
6	14	0	58	62	2
7	14	0	49	49	3
8	14	0	11	13	10
1	15	0	122	118	2
2	15	0	263	247	1
3	15	0	59	65	3
4	15	0	0	4	1
5	15	0	49	45	3
6	15	0	57	60	3
7	15	0	52	43	3
8	15	0	79	75	2
0	16	0	30	21	5
1	16	0	96	98	1
2	16	0	41	48	3
3	16	0	100	112	1
4	16	0	145	140	3
5	16	0	61	60	3
6	16	0	0	2	1
7	16	0	5	24	5
8	16	0	0	5	1
1	17	0	91	93	1
2	17	0	0	30	1
3	17	0	148	141	1
4	17	0	193	186	1
5	17	0	185	180	1
6	17	0	26	2	8
7	17	0	28	24	13
0	18	0	91	94	2
1	18	0	59	62	4
2	18	0	109	106	1
3	18	0	0	3	1
4	18	0	84	83	2
5	18	0	27	23	6
6	18	0	0	10	1
7	18	0	0	4	1
1	19	0	38	55	4
2	19	0	127	128	2
3	19	0	86	80	2
4	19	0	23	24	7
5	19	0	134	136	1
6	19	0	29	21	10
7	19	0	0	29	1
0	20	0	193	197	2
1	20	0	253	245	1
2	20	0	193	192	1
3	20	0	128	126	1
4	20	0	95	89	2
5	20	0	20	26	20
6	20	0	24	24	23
7	20	0	0	34	1
0	21	0	87	86	2
1	21	0	112	113	2
2	21	0	11	30	11
3	21	0	111	106	4
4	21	0	95	98	2
5	21	0	20	25	20
6	21	0	77	82	3
0	22	0	52	48	4
1	22	0	88	74	3
2	22	0	0	7	1
3	22	0	117	113	2
4	22	0	0	13	1
5	22	0	68	58	3
6	22	0	37	37	8
1	23	0	19	31	19
2	23	0	21	21	14
3	23	0	56	58	5
4	23	0	85	81	2
5	23	0	29	2	10
6	23	0	55	44	4
0	24	0	64	67	2
1	24	0	51	57	17
2	24	0	48	44	3
3	24	0	13	24	13
4	24	0	62	63	3
5	24	0	0	10	1
6	24	0	65	60	2
0	25	0	0	10	1
1	25	0	93	92	2
2	25	0	19	31	19
3	25	0	0	10	1
4	25	0	54	47	4
5	25	0	63	61	3
6	25	0	58	44	8
0	26	0	54	47	4
1	26	0	13	19	12
2	26	0	0	8	1
3	26	0	51	54	3
4	26	0	0	24	1
1	27	0	63	61	3
2	27	0	58	44	8
3	27	0	63	64	3
4	27	0	48	45	4
5	28	0	55	50	5
1	28	0	0	12	1
2	28	0	31	28	9
3	28	0	0	4	1
1	29	0	23	29	11
2	29	0	0	8	1
0	30	0	23	27	23
-9	1	1	120	119	3
-8	1	1	179	176	2
-7	1	1	121	128	2
-6	1	1	0	19	1
-5	1	1	123	118	1
-4	1	1	180	177	1
-3	1	1	376	383	2
-2	1	1	268	279	2
-1	1	1	91	95	1
0	1	1	463	474	1
1	1	1	578	595	2
2	1	1	679	690	2
3	1	1	72	72	1
4	1	1	172	169	1
5	1	1	114	114	2
6	1	1	89	83	2
7	1	1	27	25	8
8	1	1	52	50	4
9	1	1	29	45	12
-9	2	1	34	44	9
-8	2	1	179	181	2
-7	2	1	253	255	2
-6	2	1	0	2	1
-5	2	1	36	40	4
-4	2	1	87	85	1
-3	2	1	53	54	2
-2	2	1	0	17	1
-1	2	1	225	224	2
0	2	1	611	628	1
1	2	1	1379	1179	8
2	2	1	640	653	2
3	2	1	103	92	1
4	2	1	180	175	1
5	2	1	162	163	1
6	2	1	207	206	2
7	2	1	49	49	4
8	2	1	56	53	4
9	2	1	0	9	1
-9	3	1	35	23	8
-8	3	1	62	62	4
-7	3	1	108	108	2
-6	3	1	103	109	2
-5	3	1	26	20	5
-4	3	1	73	62	2
-3	3	1	77	83	1
-2	3	1	157	163	1
-1	3	1	592	612	2
0	3	1	891	922	1
1	3	1	34	32	3
2	3	1	30	27	4
3	3	1	260	266	2
4	3	1	21	27	8
5	3	1	64	70	2
6	3	1	111	111	2
7	3	1	107	105	2
8	3	1	34	26	6
9	3	1	16	5	15
-9	4	1	0	17	1
-8	4	1	158	155	2
-7	4	1	57	54	4
-6	4	1	131	130	2
-5	4	1	36	38	4
-4	4	1	241	228	2
-3	4	1	92	99	1
-2	4	1	334	340	2
-1	4	1	1280	1121	8
0	4	1	462	478	2
1	4	1	651	675	2
2	4	1	415	428	2
3	4	1	343	344	3
4	4	1	217	214	2
5	4	1	51	47	3
6	4	1	15	28	15
7	4	1	102	100	2
8	4	1	50	45	5
9	4	1	35	10	7
-9	5	1	31	20	9
-8	5	1	106	103	2
-7	5	1	183	189	2
-6	5	1	60	55	3
-5	5	1	126	125	1
-4	5	1	240	237	2
-3	5	1	40	40	2
-2	5	1	87	87	1
-1	5	1	1076	1105	2
0	5	1	335	352	2
1	5	1	1024	1046	2
2	5	1	306	290	2
3	5	1	322	317	2
4	5	1	0	2	1
5	5	1	152	159	1
6	5	1	96	94	2
7	5	1	74	71	3
8	5	1	0	8	1
-9	6	1	23	14	16
-8	6	1	22	26	22
-7	6	1	242	248	2
-6	6	1	0	10	1
-5	6	1	72	74	2
-4	6	1	0	23	1
-3	6	1	45	46	2
-2	6	1	298	301	2
-1	6	1	706	752	2
0	6	1	400	409	2
1	6	1	658	669	2
2	6	1	361	360	3
3	6	1	473	456	3
4	6	1	128	127	1
5	6	1	107	110	2
6	6	1	29	37	8
7	6	1	63	71	3
8	6	1	0	14	1
-9	7	1	38	39	8
-8	7	1	65	68	3
-7	7	1	36	40	6
-6	7	1	64	63	3
-5	7	1	85	91	2
-4	7	1	228	222	2
-3	7	1	25	29	5
-2	7	1	543	537	2
-1	7	1	277	348	2
0	7	1	421	432	2
1	7	1	296	297	2
2	7	1	46	46	2
3	7	1	0	26	1
4	7	1	56	51	2
5	7	1	310	298	3
6	7	1	47	50	4
7	7	1	58	61	4
8	7	1	51	50	5
-9	8	1	23	27	22
-8	8	1	54	60	4
-7	8	1	39	36	5
-6	8	1	175	179	2
-5	8	1	53	47	3
-4	8	1	112	106	1
-3	8	1	80	79	2
-2	8	1	203	217	2
-1	8	1	0	216	-1
0	8	1	522	535	2
1	8	1	50	47	2
2	8	1	264	253	2
3	8	1	57	60	2
4	8	1	22	18	8
5	8	1	40	42	4
6	8	1	91	90	2
7	8	1	44	35	5
8	8	1	48	51	5
-9	9	1	0	2	1
-8	9	1	46	46	5
-7	9	1	53	47	4
-6	9	1	202	200	2
-5	9	1	0	12	1
-4	9	1	321	313	3
-3	9	1	341	332	3
-2	9	1	12	20	11
-1	9	1	514	551	3
0	9	1	368	374	2
1	9	1	357	342	3
2	9	1	138	137	1
3	9	1	36	29	4
4	9	1	154	149	1
5	9	1	0	14	1
6	9	1	133	142	2
7	9	1	69	76	3
8	9	1	67	61	4
9	9	1	215	215	2
-9	10	1	0	2	1
-8	10	1	119	112	2
-7	10	1	175	169	2
-6	10	1	278	271	2
-5	10	1	62	61	3
-4	10	1	107	102	1
-3	10	1	192	178	1
-2	10	1	57	56	2
-1	10	1	0	137	-1
0	10	1	112	115	1
1	10	1	125	123	1
2	10	1	47	40	3
3	10	1	178	178	1
4	10	1	190	182	1
5	10	1	215	215	2
6	10	1	55	56	4
7	10	1	45	34	5
8	10	1	11	48	10
-9	11	1	0	5	1
-8	11	1	33	10	7
-7	11	1	67	73	3
-6	11	1	0	9	1
-5	11	1	8	0	8
-4	11	1	193	178	1
-3	11	1	89	94	2
-2	11	1	601	591	3
-1	11	1	0	209	-1
0	11	1	172	171	1
1	11	1	105	110	1
2	11	1	413	407	3
3	11	1	224	221	2
4	11	1	203	192	1
5	11	1	115	119	2
6	11	1	69	67	3
7	11	1	31	35	8
8	11	1	92	88	3
-8	12	1	0	1	1
-7	12	1	23	22	12
-6	12	1	145	152	2
-5	12	1	0	15	1
-4	12	1	109	105	2
-3	12	1	222	216	2
-2	12	1	407	400	3
-1	12	1	419	453	3
0	12	1	18	0	8
1	12	1	73	68	2
2	12	1	500	507	3
3	12	1	60	58	3
4	12	1	55	51	3
5	12	1	17	32	17
6	12	1	54	52	4
7	12	1	61	63	4
8	12	1	20	0	20
-8	13	1	107	105	3

h	k	l	10Fo	10Fc	10s
1	0	1	8	8	1
1	91	1	91	91	2
1	0	1	8	8	1
1	91	1	89	89	2
1	186	1	181	181	1
1	253	1	242	242	2
1	0	1	74	74	-1
1	170	1	158	158	1
1	103	1	105	105	1
1	71	1	74	74	2
1	160	1	153	153	1
1	164	1	167	167	2
1	65	1	67	67	3
1	128	1	135	135	2
1	65	1	63	63	4
1	24	1	14	14	15
1	50	1	50	50	5
1	27	1	9	9	9
1	94	1	90	90	2
1	109	1	110	110	2
1	0	1	4	4	1
1	104	1	100	100	2
1	237	1	241	241	2
1	73	1	85	85	3
1	198	1	203	203	2
1	81	1	91	91	2
1	34	1	31	31	5
1	45	1	50	50	4
1	205	1	209	209	2
1	63	1	61	61	3
1	75	1	75	75	3
1	67	1	60	60	4
1	0	1	4	4	1
1	0	1	10	10	1
1	0	1	4	4	1
1	75	1	75	75	3
1	144	1	137	137	2
1	210	1	206	206	2
1	77	1	77	77	2
1	125	1	116	116	2
1	0	1	71	71	-1
1	36	1	41	41	4
1	212	1	204	204	2
1	49	1	38	38	3
1	107	1	111	111	2
1	0	1	3	3	1
1	127	1	120	120	2
1	56	1	58	58	4
1	0	1	9	9	1
1	0	1	4	4	1
1	41	1	38	38	6
1	50	1	55	55	4
1	124	1	123	123	2
1	59	1	65	65	3
1	200	1	198	198	2
1	58	1	66	66	3
1	163	1	185	185	2
1	113	1	120	120	2
1	118	1	113	113	2
1	202	1	202	202	2
1	164	1	159	159	1
1	214	1	210	210	2
1	23	1	47	47	23
1	34	1	32	32	6
1	0	1	2	2	1
1	22	1	23	23	22
1	0	1	1	1	1
1	0	1	10	1	1
1	104	1	107	107	2
1	18	1	11	11	18
1	50	1	51	51	4
1	46	1	45	45	4
1	87	1	134	134	4
1	186	1	187	187	1
1	112	1	104	104	2
1	86	1	87	87	2
1	90	1	90	90	3
1	46	1	39	39	5
1	25	1	9	9	9
1	14	1	20	20	14
1	48	1	46	46	6
1	0	1	9	9	1
1	36	1	38	38	7
1	37	1	38	38	6
1	125	1	119	119	2
1	36	1	30	30	6
1	0	1	19	19	1
1	0	1	78	78	1
1	109	1	112	112	2
1	85	1	81	81	2
2	18	1	259	247	2
3	18	1	261	258	2
4	18	1	39	25	5
5	18	1	60	59	4
6	18	1	36	26	7
7	18	1	0	31	1
-7	19	1	0	17	1
-6	19	1	26	34	11
-5	19	1	129	127	2
-4	19	1	50	47	4
-3	19	1	117	100	2
-2	19	1	154	150	2
-1	19	1	0	36	1
0	19	1	86	99	3
1	19	1	94	88	2
2	19	1	91	87	3
3	19	1	139	136	2
4	19	1	35	37	6
5	19	1	26	39	10
6	19	1	37	28	7
-7	20	1	35	27	8
-6	20	1	18	35	18
-5	20	1	38	41	6
-4	20	1	0	10	1
-3	20	1	96	94	3
-2	20	1	42	55	6
-1	20	1	17	41	17
0	20	1	90	97	3
1	20	1	20	40	19
2	20	1	0	17	1
3	20	1	95	92	3
4	20	1	28	7	8
5	20	1	28	28	10
6	20	1	0	9	1
-6	21	1	53	55	5
-5	21	1	20	19	19
-4	21	1	133	129	2
-3	21	1	32	35	8
-2	21	1	110	102	2
-1	21	1	0	29	-1
0	21	1	0	10	-1
1	21	1	117	122	2
2	21	1	107	109	2
3	21	1	29	25	8
4	21	1	14	36	14
5	21	1	33	34	8
6	21	1	35	20	8
-6	22	1	31	42	10
-5	22	1	21	1	20
-4	22	1	58	69	4
-3	22	1	113	99	2
-2	22	1	0	6	1
-1	22	1	139	133	2
0	22	1	201	208	2
1	22	1	186	181	2
2	22	1	119	117	2
3	22	1	119	118	2
4	22	1	56	55	4
5	22	1	0	2	1
6	22	1	111	98	3
-6	23	1	52	41	5
-5	23	1	24	2	23
-4	23	1	80	78	3
-3	23	1	82	73	3
-2	23	1	40	45	6
-1	23	1	0	4	-1
0	23	1	0	48	-1
1	23	1	29	51	10
2	23	1	96	89	3
3	23	1	0	3	1
4	23	1	39	28	6
5	23	1	19	5	18
-5	24	1	63	64	4
-4	24	1	37	16	6
-3	24	1	71	79	4
-2	24	1	29	44	9
-1	24	1	36	32	6
0	24	1	125	126	2
1	24	1	0	42	1
2	24	1	11	25	11
3	24	1	41	39	6
4	24	1	47	51	6
5	24	1	28	9	11
-5	25	1	0	6	1
-4	25	1	48	50	6
-3	25	1	56	68	5
-2	25	1	74	65	3
-1	25	1	0	2	1
0	25	1	0	20	-1
1	25	1	53	40	4
2	25	1	62	68	4
3	25	1	0	22	1
4	25	1	77	73	4
5	25	1	21	0	20
-6	26	1	0	12	1
-5	26	1	0	3	1
-4	26	1	15	6	14
-3	26	1	53	58	5
-2	26	1	0	13	1
-1	26	1	9	15	8
0	26	1	0	1	1
1	26	1	23	25	22
2	26	1	51	46	5
3	26	1	0	30	-1
-5	27	1	108	90	3
-4	27	1	35	22	7
-3	27	1	0	18	1
-2	27	1	72	64	4
-1	27	1	0	4	1
0	27	1	0	18	1
1	27	1	50	49	6
2	27	1	0	37	1
3	27	1	50	42	5
-5	28	1	81	77	4
-4	28	1	0	13	1
-3	28	1	0	14	1
-2	28	1	64	54	5
-1	28	1	40	33	6
0	28	1	258	267	2
1	28	1	34	37	6
2	28	1	187	189	1
3	28	1	394	379	3
4	28	1	490	488	3
5	28	1	211	205	2
6	28	1	371	382	2
-6	29	1	58	60	1
-5	29	1	1458	1293	9
-4	29	1	834	848	2
-3	29	1	51	46	2
-2	29	1	555	533	3
-1	29	1	218	224	2
0	29	1	244	241	2
1	29	1	149	153	2
2	29	1	120	115	2
3	29	1	55	58	5
-4	30	1	0	23	1
-3	30	1	50	52	4
-2	30	1	183	184	1
-1	30	1	150	156	1
0	30	1	236	238	2
1	30	1	48	47	2
2	30	1	12	8	11
-3	31	1	531	536	2
-2	31	1	48	39	2
-1	31	1	740	783	2
0	31	1	528	537	3
1	31	1	285	294	3
2	31	1	121	116	1
3	31	1	233	239	2
-3	32	1	236	232	2
-2	32	1	333	335	2
-1	32	1	347	370	2
0	32	1	300	302	2
1	32	1	689	698	2
2	32	1	431	447	3
3	32	1	69	71	2
4	32	1	236	239	2
5	32	1	97	92	2
6	32	1	13	7	12
7	32	1	14	32	13
8	32	1	0	32	1
-3	33	1	32	35	9
-2	33	1	92	87	3
-1	33	1	125	132	2
0	33	1	27	29	7
1	33	1	167	166	1
2	33	1	131	123	1
3	33	1	62	68	4
4	33	1	0	22	1
5	33	1	77	73	4
6	33	1	21	0	20
-6	34	1	0	12	1
-5	34	1	0	3	1
-4	34	1	15	6	14
-3	34	1	53	58	5
-2	34	1	0	13	1
-1	34	1	9	15	8
0	34	1	0	1	1
1	34	1	23	25	22
2	34	1	51	46	5
3	34	1	0	30	-1
-5	35	1	108	90	3
-4	35	1	35	22	7
-3	35	1	0	18	1
-2	35	1	72	64	4
-1	35	1	0	4	1
0	35	1	0	18	1
1	35	1	50	49	6
2	35	1	0	37	1
3	35	1	50	42	5
-5	36	1	81	77	4
-4	36	1	0	13	1
-3	36	1	0	14	1
-2	36	1	64	54	5
-1	36	1	40	33	6
0	36	1	258	267	2
1	36	1	34	37	6
2	36	1	187	189	1
3	36	1	394	379	3
4	36	1	490	488	3
5	36	1	211	205	2
6	36	1	371	382	2
-6	37	1	58	60	1
-5	37	1	1458	1293	9
-4	37	1	834	848	2
-3	37	1	51	46	2
-2	37	1	555	533	3
-1	37	1	218	224	2
0	37	1	244	241	2
1	37	1	149	153	2
2	37	1	120	115	2
3	37	1	55	58	5
-4	38	1	0	23	1
-3	38	1	50	52	4
-2	38	1	183	184	1
-1	38	1	150	156	1
0	38	1	236	238	2
1	38	1	48	47	2
2	38	1	12	8	11
-3	39	1	531	536	2
-2	39	1	48	39	2
-1	39	1	740	783	2
0	39	1	528	537	3
1	39	1	285	294	3
2	39	1	121	116	1
3	39	1	233	239	2
-3	40	1	236	232	2
-2	40	1	333	335	2
-1	40	1	347	370	2
0	40	1	300	302	2
1	40	1	689	698	2
2	40	1	431	447	3
3	40	1	69	71	2
4	40	1	236	239	2
5	40	1	97	92	2
6	40	1	13	7	12
7	40	1	14	32	13
8	40	1	0	32	1
-3	41	1	32	35	9
-2	41	1	92	87	3
-1	41	1	125	132	2
0	41	1	27	29	7
1	41	1	167	166	1
2	41	1	131	123	1
-3	42	2	574	577	2
-2	42	2	487	489	2
-1	42	2	59	58	1
0	42	2	21	25	5
1	42	2	78	79	1
2	42	2	411	421	3
3	42	2	397	397	3
4	42	2	188	183	1
5	42	2	54	55	3
6	42	2	40	44	5
7	42	2	93	91	3
8	42	2	0	45	1
-9	42	2	11	6	10
-8	42	2	30	20	8
-7	42	2	146	148	2
-6	42	2	35	32	5
-5	42	2	0	24	1
-4	42	2	323	307	3
-3	42	2	161	161	1
-2	42	2	40	42	2
-1	42	2	282	298	2
0	42	2	250	254	2
1	42	2	654	663	2
2	42	2	118	124	1
3	42	2	314	302	3
4	42	2	35	35	4
5	42	2	60	62	3
6	42	2	131	132	2
7	42	2	0	11	1
8	42	2	0	12	1
-9	42	2	78	76	4
-8	42	2	62	66	4
-7	42	2	18	5	18
-6	42	2	20	13	10
-5	42	2	62	57	2
-4	42	2	352	338	3
-3	42	2	408	404	3
-2	42	2	75	80	1
-1	42	2	115	115	1
0	42	2	210	213	2
1	42	2	194	187	1
2	42	2	375	365	3
3	42	2	272	268	2
4	42	2	0	10	1
5	42	2	0	10	1
6	42	2	51	50	4
7	42	2	0	2	1
8	42	2	54	53	5
-9	42	2	60	55	4
-8	42	2	71	76	3
-7	42	2	42	50	5
-6	42	2	69	70	2
-5	42	2	80	78	2
-4	42	2	126	124	1
-3	42	2	290	277	2
-2	42	2	181	177	1
-1	42	2	0	3	1
0	42	2	160	160	1
1	42	2	265	263	2
2	42	2	169	157	1
3	42	2	28	40	5
4	42	2	157	154	1
5	42	2	20	8	12
6	42	2	67	65	3
7	42	2	50	43	4
8	42	2	0	16	1
-9	42	2	90	87	3
-8	42	2	56	47	4
-7	42	2	111	113	2
-6	42	2	176	181	2
-5	42	2	160	168	1
-4	42	2	28	10	4
-3	42	2	180	166	1
-2	42	2	116	109	1
-1	42	2	150	151	1
0	42	2	60	57	2
1	42	2	456	459	3
2	42	2	38	45	3
3	42	2	58	63	2
4	42	2	96	96	2
5	42	2	136	138	2
6	42	2	19	12	18
7	42	2	31	43	8
8	42	2	0	1	1
-9	42	2	0	12	1
-8	42	2	80	84	3
-7	42	2	27	36	9
-6	42	2	21	29	20
-5	42	2	25	20	7
-4	42	2	115	112	1
-3	43	2	122	125	1
-2	43	2	499	495	3
-1	43	2	375	374	3
0	43	2	167	172	1
1	43	2	74	78	2
2	43	2	226	220	2
3	43	2	137	130	1
4	43	2	98	95	2
5	43	2	130	126	2
6	43	2	51	51	4
7	43	2	53	58	4
8	43	2	40	36	7
-9	43	2	153	151	3
-8	43	2	75	74	3
-7	43	2	86	83	2
-6	43	2	47	46	4
-5	43	2	31	29	5
-4	43	2	65	64	2
-3	43	2	25	12	5
-2	43	2	138	135	1
-1	43	2	419	417	3
0	43	2	104	97	1
1	43	2	165	167	1
2	43	2	36	29	4
3	43	2	170	166	1
4	43	2	66	64	3
5	43	2	62	66	3
6	43	2	43	52	5
7	43	2	43	40	5
8	43	2	52	52	5
-9	43	2	98	87	3
-8	43	2	77	77	3
-7	43	2	49	58	4
-6	43	2	259	260	2
-5	43	2	0	7	1
-4	43	2	36	41	4
-3	43	2	129	119	1
-2	43	2	141	143	1
-1	43	2	0	13	1
0	43	2	132	120	1
1	43	2	84	79	1
2	43	2	334	319	3
3	43	2	161	148	1
4	43	2	91	88	2
5	43	2	55	58	4
6	43	2	112	116	2
7	43	2	10	8	10
8	43	2	0	1	1
-9	43	2	15	20	15
-8	43	2	105	113	3
-7	43	2	98	101	2
-6	43	2	96	96	2
-5	43	2	48	46	4
-4	43	2	29	32	5
-3	43	2	129	136	1
-2	43	2	74	72	2
-1	43	2	85	77	2
0	43	2	63	65	2
1	43	2	80	77	2
2	43	2	121	106	1
3	43	2	17	7	16
4	43	2	97	95	2
5	43	2	47	40	4
6	43	2	58	51	4
7	43	2	0	0	1
8	43	2	51	50	6
-9	43	2	12	22	12
-8	43	2	0	10	1
-7	43	2	153	157	2
-6	43	2	129	127	2
-5	43	2	150	153	2
-4	43	2	52	51	3
-3	43	2	157	158	1
-2	43	2	336	325	3
-1	43	2	375	370	3
0	43	2	438	414	3
1	43	2	119	113	1
2	43	2	95	98	2
3	43	2	0	7	1
4	43	2	0	15	1
5	43	2	137	145	2
6	43	2	192	199	2
7	43	2	38	37	7
8	43	2	54	42	5
-9	43	2	0	3	1
-8	43	2	0	6	1
-7	43	2	85	75	2
-6	43	2	18	16	15
-5	43	2	0	18	1
-4	43	2	0	83	1

l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
2	0	31	-1	-3	19	2	0	0	1	-3	27	2	43	50	7	-7	5	3	94	98	2	-3	10	3	319	312	3
2	0	1	1	-2	19	2	36	56	7	-2	27	2	58	60	5	-6	5	3	69	67	3	-2	10	3	198	202	2
2	15	10	14	-1	19	2	77	166	7	-1	27	2	52	54	5	-5	5	3	180	174	1	-1	10	3	285	273	2
2	312	313	3	0	19	2	58	55	4	0	27	2	64	57	4	-4	5	3	0	21	1	0	10	3	176	182	1
2	83	80	2	1	19	2	163	162	2	1	27	2	0	17	1	-3	5	3	392	387	3	1	10	3	493	482	3
2	129	131	2	2	19	2	91	96	2	2	27	2	0	15	1	-2	5	3	75	72	1	2	10	3	82	87	2
2	11	22	10	3	19	2	222	212	2	3	27	2	0	19	1	-1	5	3	195	192	1	3	10	3	163	164	1
2	42	40	5	4	19	2	74	65	3	-3	28	2	47	27	6	0	5	3	141	131	1	4	10	3	89	85	2
2	0	6	1	5	19	2	0	2	1	-2	28	2	0	2	1	1	5	3	125	123	1	5	10	3	0	31	1
2	75	71	4	6	19	2	24	5	24	-1	28	2	0	19	1	2	5	3	175	171	1	6	10	3	0	11	1
2	0	42	1	-7	20	2	15	34	15	0	28	2	0	19	1	3	5	3	0	8	1	7	10	3	58	50	4
2	144	147	2	-6	20	2	61	61	4	1	28	2	37	36	8	4	5	3	16	9	16	-9	11	3	0	16	1
2	133	128	2	-5	20	2	67	69	3	2	28	2	16	17	15	5	5	3	15	22	15	-8	11	3	34	33	7
2	46	53	4	-4	20	2	127	126	2	-2	29	2	11	14	10	6	5	3	0	11	1	-7	11	3	156	146	2
2	103	104	2	-3	20	2	56	48	4	-1	29	2	65	65	4	7	5	3	78	78	3	-6	11	3	103	101	2
2	102	118	2	-2	20	2	15	71	15	0	29	2	0	6	1	8	5	3	53	50	5	-5	11	3	146	150	2
2	250	244	2	-1	20	2	122	142	3	-9	1	3	56	56	4	-9	6	3	84	81	3	-4	11	3	8	11	7
2	143	147	1	0	20	2	67	65	3	-8	1	3	68	68	3	-8	6	3	39	36	5	-3	11	3	38	41	4
2	95	87	2	1	20	2	45	54	5	-7	1	3	35	26	6	-7	6	3	196	194	2	-2	11	3	19	18	18
2	146	153	2	2	20	2	18	5	18	-6	1	3	66	65	2	-6	6	3	124	128	2	-1	11	3	151	148	1
2	122	118	2	3	20	2	13	3	13	-5	1	3	209	197	2	-5	6	3	152	149	1	0	11	3	95	99	2
2	28	27	8	4	20	2	83	72	3	-4	1	3	52	44	2	-4	6	3	27	27	5	1	11	3	55	60	3
2	0	11	1	5	20	2	73	70	4	-3	1	3	326	329	3	-3	6	3	0	4	1	2	11	3	219	215	2
2	0	14	1	6	20	2	0	12	1	-2	1	3	226	224	2	-2	6	3	127	128	1	3	11	3	50	46	4
2	45	42	6	-7	21	2	16	13	15	-1	1	3	97	95	1	-1	6	3	70	63	1	4	11	3	26	12	8
2	47	51	5	-6	21	2	50	51	6	0	1	3	263	267	2	0	6	3	173	173	1	5	11	3	69	74	3
2	24	6	10	-5	21	2	0	21	1	1	1	3	114	117	1	1	6	3	53	55	2	6	11	3	0	5	1
2	0	6	1	-4	21	2	108	107	3	2	1	3	471	477	3	2	6	3	267	262	2	7	11	3	0	4	1
2	97	98	2	-3	21	2	32	42	8	3	1	3	391	405	3	3	6	3	125	116	1	-9	12	3	63	51	4
2	21	29	20	-2	21	2	49	76	6	4	1	3	306	303	3	4	6	3	64	66	3	-8	12	3	41	41	6
2	70	69	2	-1	21	2	0	34	-1	5	1	3	45	48	4	5	6	3	0	18	1	-7	12	3	104	106	2
2	109	135	3	0	21	2	0	55	1	6	1	3	87	86	3	6	6	3	46	29	4	-6	12	3	86	86	3
2	0	45	1	1	21	2	144	140	2	7	1	3	0	17	1	7	6	3	28	28	10	-5	12	3	40	40	5
2	124	123	1	2	21	2	136	138	2	8	1	3	68	66	4	-9	7	3	41	33	6	-4	12	3	11	19	11
2	122	118	2	3	21	2	98	90	2	-9	2	3	0	21	1	-8	7	3	27	26	9	-3	12	3	195	194	1
2	178	183	1	4	21	2	0	25	1	-8	2	3	112	107	2	-7	7	3	152	151	2	-2	12	3	108	111	1
2	102	101	2	5	21	2	50	45	5	-7	2	3	62	57	3	-6	7	3	137	137	2	-1	12	3	106	104	1
2	79	79	3	-6	22	2	0	10	1	-6	2	3	67	65	2	-5	7	3	125	126	2	0	12	3	50	43	3
2	76	75	3	-5	22	2	0	18	1	-5	2	3	28	30	6	-4	7	3	7	15	7	1	12	3	33	32	5
2	10	27	10	-4	22	2	0	12	1	-4	2	3	590	568	3	-3	7	3	405	395	3	2	12	3	139	131	2
2	0	19	1	-3	22	2	20	24	20	-3	2	3	136	140	1	-2	7	3	65	68	2	3	12	3	155	152	2
2	29	11	9	-2	22	2	0	10	-1	-2	2	3	16	20	9	-1	7	3	44	44	2	4	12	3	27	26	9
2	0	12	1	-1	22	2	91	143	5	-1	2	3	223	224	2	0	7	3	129	127	1	5	12	3	51	55	4
2	74	70	3	0	22	2	47	47	5	0	2	3	205	202	2	1	7	3	285	278	2	6	12	3	40	25	6
2	77	75	3	1	22	2	67	63	3	1	2	3	86	81	1	2	7	3	0	22	1	7	12	3	0	25	1
2	0	9	1	2	22	2	58	53	4	2	2	3	15	2	14	3	7	3	264	250	2	-8	13	3	0	21	1
2	51	39	3	3	22	2	55	55	5	3	2	3	204	198	1	4	7	3	7	9	6	-7	13	3	17	26	17
2	116	153	3	4	22	2	47	48	5	4	2	3	212	218	2	5	7	3	191	193	2	-6	13	3	92	90	2
2	134	132	2	5	22	2	48	46	6	5	2	3	173	177	2	6	7	3	0	8	1	-5	13	3	84	82	2
2	0	3	1	-6	23	2	0	6	1	6	2	3	90	93	3	7	7	3	18	9	18	-4	13	3	103	106	2
2	56	63	3	-5	23	2	39	42	6	7	2	3	51	52	5	-9	8	3	0	3	1	-3	13	3	162	154	1
2	97	101	2	-4	23	2	0	21	1	8	2	3	30	2	9	-8	8	3	0	44	1	-2	13	3	372	363	3
2	108	109	2	-3	23	2	9	30	8	-9	3	3	76	79	3	-7	8	3	104	100	2	-1	13	3	7	20	7
2	87	77	3	-2	23	2	85	84	3	-8	3	3	60	65	3	-6	8	3	175	173	2	0	13	3	85	84	2
2	47	45	4	-1	23	2	0	99	-1	-7	3	3	91	92	2	-5	8	3	176	174	1	1	13	3	70	73	2
2	54	50	4	0	23	2	48	58	5	-6	3	3	70	67	3	-4	8	3	15	20	14	2	13	3	241	233	2
2	22	7	22	1	23	2	0	27	1	-5	3	3	13	9	12	-3	8	3	81	92	2	3	13	3	46	40	4
2	7	21	6	2	23	2	44	46	6	-4	3	3	17	0	13	-2	8	3	144	144	1	4	13	3	92	90	2
2	34	32	7	3	23	2	130	125	2	-3	3	3	170	165	1	-1	8	3	202	203	2	5	13	3	68	71	3
2	35	24	6	4	23	2	71	73	4	-2	3	3	91	90	1	0	8	3	115	114	1	6	13	3	96	95	3
2	138	131	2	5	23	2	27	25	13	-1	3	3	84	81	1	1	8	3	142	136	1	7	13	3	21	13	21
2	32	28	6	-5	24	2	0	16	1	0	3	3	310	315	3	2	8	3	122	113	1	-8	14	3	96	100	3
2	106	100	2	-4	24	2	56	50	4	1	3	3	0	3	1	3	8	3	144	136	1	-7	14	3	106	111	2
2	126	149	3	-3	24	2	77	71	3	2	3	3	9	33	9	4	8	3	0	21	1	-6	14	3	52	45	4
2	0	2	-1	-2	24	2	0	54	1	3	3	3	253	253	2	5	8	3	108	109	2	-5	14	3	17	18	17
2	105	102	2	-1	24	2	0	70	-1	4	3	3	118	117	2	6	8	3	76	90	3	-4	14	3	111	109	2
2	88	95	3	0	24	2	0	26	1	5	3	3	79	82	3	7	8	3	0	15	1	-3	14	3	24	17	7
2	125	116	2	1	24	2	0	26	1	6	3	3	86	94	3	-9	9	3	42	38	6	-2	14	3	126	127	2
2	62	61	3	2	24	2	0	23	1	7	3	3	0	36	1	-8	9	3	0	33	1	-1	14	3	77	79	2
2	45	40	5	3	24	2	11	15	10	8	3	3	0	10	1	-7	9	3	46	50	4	0	14	3	53	54	3
2	42	39	5	4	24	2	0	7	1	-9	4	3	24	23	23	-6	9	3	95	84	2	1	14	3	52	49	3
2	61	57	4	-5	25	2	0	6	1	-8	4	3	0	25	1	-5	9	3	55	54	3	2	14	3	0	25	1
2	0	32	1	-4	25	2	29	42	9	-7	4	3	32	34	6	-4	9	3	107	102	2	3	14	3	12	6	11
2	53	46	4	-3	25	2	0	16	1	-6	4	3	224	223	2	-3	9	3	97	83	1	4	14	3	37	43	6
2	36	43	7	-2	25	2	39	55	7	-5	4	3	89	87	2	-2	9	3	156	149	1	5	14	3	56	63	4
2	0	2	1	-1	25	2	97	98	3	-4	4	3	0	10	1	-1	9	3	108	105	1	6	14	3	38	28	6
2	34	45	7	0	25	2	68	71	4	-3	4	3	199	186	2	0	9	3	96	97	1	-8	15	3	0	4	1
2	0	26	-1	1	25	2	18	22	17	-2	4	3	226	222	2	1	9	3	28	39	5	-7	15	3	52	56	4
2	0	86	-1	2	25	2	15	17	14	-1	4	3	552	538	2	2	9	3	0	8	1	-6	15	3	0	3	1
2	76	76	2	3	25	2	28	0	10	0	4	3	379	379	3	3	9	3	94	99	2	-5	15	3	76	81	3
2	290	279	2	4	25	2	25	38	24	1	4	3	266	274	2	4	9	3	14	11	14	-4	15	3	56	52	3
2	75	77	3	-4	26	2	45	31	5	2	4	3	405	390	3	5	9	3	19	4	19	-3	15	3	54	53	3
2	0	1	1	-3	26	2	33	18	8	3	4	3	8	12	7	6	9	3	56	58	4	-2	15	3	87	80	2
2	74	68	3	-2	26	2	26	34	25	4	4	3	146	150	2	7	9	3	0	19	1	-1	15	3	0	0	1
2	0	41	1	-1	26	2	0	6	1	5	4	3	125	125	2	-9	10	3	91	82	3	0	15	3	137	128	1
2	0	3	1	0	26	2	0	5	1	6	4	3	32	15	7	-8	10	3	134	133	2	1	15	3	121	126	2
2	36	33	7	1	26	2	58	59	4	7	4	3	39	38	6	-7	10	3	150	152	2	2	15	3	74	71	3
2	79	71	3	2	26	2	0	13	1	8	4	3	25	31	24	-6	10	3	210	208	2	3	15	3	34	21	6
2	81	87	3	3	26	2	9	3	9	-9	5	3	67	69	4	-5	10	3	270	270	2	4	15	3	0	26	1
2	0	10	1	-4	27	2	34	3	8	-8	5	3	33	37	7	-4	10	3	18	12	11	5	15	3	64	68	3

l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
3	0	1	1	0	22	3	64	66	4	-5	2	4	160	159	1	0	7	4	7	1	7	-8	13	4	54	53	5
3	56	45	5	1	22	3	137	135	2	-4	2	4	275	270	2	1	7	4	237	232	2	-7	13	4	0	24	1
3	50	49	5	2	22	3	93	84	3	-3	2	4	305	304	3	2	7	4	83	88	2	-6	13	4	153	161	2
3	68	62	3	3	22	3	93	83	3	-2	2	4	232	244	2	3	7	4	0	16	1	-5	13	4	50	56	4
3	110	109	2	4	22	3	0	18	1	-1	2	4	217	219	2	4	7	4	25	14	9	-4	13	4	25	20	8
3	120	121	2	-6	23	3	0	5	1	0	2	4	96	93	1	5	7	4	14	23	13	-3	13	4	0	5	1
3	161	163	2	-5	23	3	24	11	23	1	2	4	46	51	3	6	7	4	36	48	7	-2	13	4	0	11	1
3	0	11	1	-4	23	3	14	0	14	2	2	4	53	57	3	7	7	4	16	4	15	-1	13	4	0	9	1
3	126	129	2	-3	23	3	0	22	1	3	2	4	51	52	3	-9	8	4	23	20	18	0	13	4	46	51	4
3	43	43	4	-2	23	3	28	71	27	4	2	4	0	4	1	-8	8	4	46	51	6	1	13	4	96	109	2
3	43	32	4	-1	23	3	24	50	24	5	2	4	13	35	13	-7	8	4	186	182	2	2	13	4	53	56	4
3	0	1	1	0	23	3	42	51	7	6	2	4	64	58	3	-6	8	4	109	107	2	3	13	4	64	71	3
3	54	48	4	1	23	3	0	41	1	7	2	4	0	8	1	-5	8	4	17	8	16	4	13	4	27	32	10
3	52	53	4	2	23	3	0	6	1	-9	3	4	96	99	3	-4	8	4	172	163	1	5	13	4	45	51	5
3	0	13	1	3	23	3	35	29	8	-8	3	4	37	25	6	-3	8	4	130	134	1	6	13	4	38	35	7
3	22	10	21	4	23	3	11	15	11	-7	3	4	50	55	4	-2	8	4	141	142	1	-8	14	4	0	8	1
3	19	22	19	-5	24	3	0	14	1	-6	3	4	0	18	1	-1	8	4	237	221	2	-7	14	4	18	10	17
3	0	4	1	-4	24	3	0	37	1	-5	3	4	51	52	3	0	8	4	267	275	2	-6	14	4	169	170	2
3	62	56	4	-3	24	3	28	26	10	-4	3	4	134	124	1	1	8	4	104	100	2	-5	14	4	101	97	2
3	60	75	4	-2	24	3	0	29	1	-3	3	4	306	314	3	2	8	4	108	109	2	-4	14	4	15	16	14
3	144	149	2	-1	24	3	0	3	1	-2	3	4	171	165	1	3	8	4	173	174	1	-3	14	4	60	63	3
3	9	14	8	0	24	3	125	117	2	-1	3	4	121	122	1	4	8	4	41	33	4	-2	14	4	88	95	2
3	139	142	2	1	24	3	34	37	7	0	3	4	167	161	1	5	8	4	86	91	3	-1	14	4	51	52	3
3	119	116	2	2	24	3	73	67	3	1	3	4	155	146	1	6	8	4	55	63	4	0	14	4	79	80	2
3	73	75	3	3	24	3	0	20	1	2	3	4	273	285	2	7	8	4	28	12	10	1	14	4	34	40	6
3	95	103	2	4	24	3	37	31	8	3	3	4	150	150	1	-9	9	4	43	44	6	2	14	4	53	49	4
3	152	151	2	-5	25	3	20	23	19	4	3	4	153	155	2	-8	9	4	51	53	4	3	14	4	109	108	2
3	69	57	3	-4	25	3	72	73	4	5	3	4	0	8	1	-7	9	4	9	42	9	4	14	4	68	63	3
3	156	153	2	-3	25	3	21	39	20	6	3	4	0	26	1	-6	9	4	34	49	7	5	14	4	11	10	11
3	62	58	4	-2	25	3	0	2	1	7	3	4	48	53	5	-5	9	4	79	85	2	6	14	4	26	29	13
3	0	11	1	-1	25	3	20	29	19	-9	4	4	0	8	1	-4	9	4	82	89	2	-8	15	4	0	2	1
3	17	10	17	0	25	3	15	51	14	-8	4	4	52	59	4	-3	9	4	194	196	1	-7	15	4	54	36	4
3	52	48	4	1	25	3	48	50	6	-7	4	4	43	35	5	-2	9	4	0	21	1	-6	15	4	91	85	3
3	158	154	2	2	25	3	0	17	1	-6	4	4	98	104	2	-1	9	4	171	162	1	-5	15	4	9	22	9
3	23	3	11	3	25	3	0	0	1	-5	4	4	97	97	2	0	9	4	101	101	1	-4	15	4	89	91	2
3	34	30	6	-4	26	3	32	32	9	-4	4	4	122	118	1	1	9	4	17	3	17	-3	15	4	181	177	2
3	46	57	6	-3	26	3	0	22	1	-3	4	4	198	197	2	2	9	4	59	61	3	-2	15	4	0	2	1
3	72	64	3	-2	26	3	11	43	10	-2	4	4	315	326	3	3	9	4	28	25	8	-1	15	4	87	87	2
3	21	82	12	-1	26	3	18	42	18	-1	4	4	124	115	1	4	9	4	22	10	22	0	15	4	27	2	6
3	61	67	3	0	26	3	24	16	23	0	4	4	100	102	1	5	9	4	56	65	4	1	15	4	106	105	2
3	86	80	3	1	26	3	62	64	5	1	4	4	55	51	2	6	9	4	24	23	13	2	15	4	262	256	2
3	66	57	3	2	26	3	0	27	1	2	4	4	18	11	12	7	9	4	54	40	5	3	15	4	113	106	2
3	20	67	19	-3	27	3	0	32	1	3	4	4	72	76	2	-9	10	4	0	3	1	4	15	4	55	53	4
3	42	18	5	-2	27	3	67	58	4	4	4	4	38	39	5	-8	10	4	0	12	1	5	15	4	0	32	1
3	11	28	11	-1	27	3	0	30	1	5	4	4	30	31	7	-7	10	4	42	43	5	6	15	4	57	56	5
3	15	25	15	0	27	3	0	33	1	6	4	4	0	9	1	-6	10	4	119	117	2	-8	16	4	9	21	9
3	0	27	1	1	27	3	22	33	21	7	4	4	40	41	6	-5	10	4	77	81	2	-7	16	4	42	44	5
3	22	29	21	2	27	3	35	31	8	-9	5	4	28	19	10	-4	10	4	46	51	3	-6	16	4	68	71	4
3	0	31	1	-2	28	3	0	10	1	-8	5	4	41	58	6	-3	10	4	167	167	1	-5	16	4	131	126	2
3	32	37	7	-1	28	3	0	29	1	-7	5	4	23	50	22	-2	10	4	306	288	3	-4	16	4	184	182	2
3	57	55	4	0	28	3	0	15	1	-6	5	4	84	77	2	-1	10	4	48	35	3	-3	16	4	20	9	19
3	0	22	1	1	28	3	0	7	1	-5	5	4	265	269	2	0	10	4	78	85	2	-2	16	4	71	63	3
3	9	45	8	-9	0	4	83	75	3	-4	5	4	139	138	1	1	10	4	149	149	1	-1	16	4	59	60	3
3	79	81	3	-8	0	4	69	72	3	-3	5	4	55	53	2	2	10	4	156	153	1	0	16	4	9	9	8
3	0	11	1	-7	0	4	27	23	8	-2	5	4	149	140	1	3	10	4	104	106	2	1	16	4	81	81	3
3	74	73	3	-6	0	4	46	45	4	-1	5	4	195	193	2	4	10	4	146	149	2	2	16	4	46	52	5
3	177	170	2	-5	0	4	161	168	1	0	5	4	43	34	3	5	10	4	55	56	4	3	16	4	44	46	5
3	39	37	7	-4	0	4	357	345	3	1	5	4	0	12	1	6	10	4	32	24	8	4	16	4	47	45	5
3	47	45	6	-3	0	4	445	440	3	2	5	4	9	1	9	-9	11	4	0	6	1	5	16	4	21	20	21
3	18	4	18	-2	0	4	335	318	2	3	5	4	13	22	13	-8	11	4	18	9	18	-8	17	4	0	29	1
3	0	41	1	-1	0	4	59	58	2	4	5	4	191	196	2	-7	11	4	69	67	3	-7	17	4	0	14	1
3	41	38	5	0	0	4	362	351	3	5	5	4	101	106	2	-6	11	4	59	57	4	-6	17	4	0	25	1
3	39	29	5	1	0	4	450	451	3	6	5	4	23	34	22	-5	11	4	104	111	2	-5	17	4	72	64	3
3	0	32	1	2	0	4	295	290	3	7	5	4	0	10	1	-4	11	4	81	79	2	-4	17	4	114	109	2
3	107	104	2	3	0	4	74	72	2	-9	6	4	16	1	16	-3	11	4	76	78	2	-3	17	4	79	81	3
3	52	57	4	4	0	4	39	28	5	-8	6	4	28	27	8	-2	11	4	13	7	13	-2	17	4	67	61	3
3	62	66	4	5	0	4	64	72	3	-7	6	4	120	127	2	-1	11	4	17	17	16	-1	17	4	6	4	6
3	21	0	21	6	0	4	85	91	3	-6	6	4	21	24	11	0	11	4	91	94	2	0	17	4	12	9	12
3	43	42	6	7	0	4	0	23	1	-5	6	4	0	19	1	1	11	4	57	44	3	1	17	4	18	32	18
3	39	34	7	-9	1	4	81	78	3	-4	6	4	45	39	3	2	11	4	185	173	1	2	17	4	161	150	2
3	84	78	3	-8	1	4	0	4	1	-3	6	4	284	273	2	3	11	4	40	37	5	3	17	4	98	95	3
3	0	7	1	-7	1	4	120	122	2	-2	6	4	0	18	1	4	11	4	55	57	4	4	17	4	92	92	3
3	36	39	8	-6	1	4	56	58	3	-1	6	4	104	101	1	5	11	4	40	41	6	5	17	4	0	4	1
3	83	79	3	-5	1	4	113	105	2	0	6	4	170	157	1	6	11	4	30	15	9	-7	18	4	13	17	12
3	115	114	2	-4	1	4	203	195	2	1	6	4	183	180	1	-9	12	4	49	46	6	-6	18	4	0	14	1
3	7	14	6	-3	1	4	18	18	10	2	6	4	108	111	2	-8	12	4	0	16	1	-5	18	4	82	86	3
3	0	28	-1	-2	1	4	471	473	3	3	6	4	126	127	2	-7	12	4	97	97	3	-4	18	4	49	42	4
3	0	51	1	-1	1	4	431	421	3	4	6	4	116	120	2	-6	12	4	240	250	2	-3	18	4	65	65	3
3	70	71	3	0	1	4	138	138	1	5	6	4	0	4	1	-5	12	4	105	110	2	-2	18	4	13	5	12
3	92	93	3	1	1	4	114	125	1	6	6	4	0	4	1	-4	12	4	109	107	2	-1	18	4	17	7	16
3	160	151	2	2	1	4	132	132	1	7	6	4	22	29	21	-3	12	4	38	42	5	0	18	4	77	76	3
3	8	4	8	3	1	4	127	137	2	-9	7	4	0	3	1	-2	12	4	295	285	2	1	18	4	150	139	2
3	114	108	3	4	1	4	93	95	2	-8	7	4	34	36	7	-1	12	4	165	163	1	2	18	4	72	66	3
3	0	10	1	5	1	4	75	79	3	-7	7	4	169	173	2	0	12	4	31	21	5	3	18	4	19	16	19
3	25	13	12	6	1	4	31	28	8	-6	7	4	136	134	2	1	12	4	62	70	3	4	18	4	41	37	6
3	29	24	8	7	1	4	22	33	20	-5	7	4	86	82	2	2	12	4	91	89	2	5	18	4	0	36	1
3	0	24	1	-9	2	4	42	41	6	-4	7	4	11	26	10	3	12	4	107	113	2	-7	19	4	47	42	6
3	43	44	5	-8	2	4	0	12	1	-3	7	4	80	75	2	4	12	4	0	19	1	-6	19	4	21	25	20
3	68	81	4	-7	2	4	0	21	1	-2	7	4	181	178	1	5	12	4	90	100	3	-5	19	4	117	117	2
3	114	116	3	-6	2	4	19	1	18	-1	7	4	42	35	3	6	12	4	0	18	1	-4	19	4	35	33	7

l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
4	106	112	2	4	1	5	161	164	2	-2	7	5	64	60	2	-3	13	5	122	123	2	-2	20	5	37	42	6
4	57	54	4	5	1	5	106	110	3	-1	7	5	81	76	2	-2	13	5	132	131	2	-1	20	5	55	48	4
4	5	3	5	6	1	5	27	9	10	0	7	5	52	47	3	-1	13	5	0	18	1	0	20	5	42	38	5
4	128	125	2	-9	2	5	0	23	1	1	7	5	0	1	1	0	13	5	0	21	1	1	20	5	0	7	1
4	167	163	2	-8	2	5	119	124	2	2	7	5	43	48	5	1	13	5	80	79	3	2	20	5	45	45	6
4	71	63	3	-7	2	5	130	136	2	3	7	5	67	67	3	2	13	5	82	79	3	3	20	5	64	60	4
4	0	28	1	-6	2	5	15	34	15	4	7	5	170	169	2	3	13	5	0	6	1	-6	21	5	48	40	5
4	0	3	1	-5	2	5	79	79	2	5	7	5	14	16	14	4	13	5	21	16	20	-5	21	5	50	43	5
4	95	89	3	-4	2	5	31	29	5	6	7	5	22	34	21	5	13	5	0	10	1	-4	21	5	28	25	10
4	42	31	6	-3	2	5	68	71	2	-9	8	5	35	41	8	-8	14	5	0	26	1	-3	21	5	0	26	1
4	24	18	13	-2	2	5	239	238	2	-8	8	5	0	27	1	-7	14	5	45	46	5	-2	21	5	0	9	1
4	57	63	4	-1	2	5	318	309	3	-7	8	5	136	139	2	-6	14	5	51	46	4	-1	21	5	86	83	3
4	133	130	2	0	2	5	18	24	11	-6	8	5	63	68	4	-5	14	5	0	9	1	0	21	5	46	50	5
4	28	38	9	1	2	5	49	53	3	-5	8	5	58	60	3	-4	14	5	37	41	6	1	21	5	0	24	1
4	48	39	4	2	2	5	145	146	1	-4	8	5	155	152	1	-3	14	5	39	42	5	2	21	5	112	108	3
4	0	2	1	3	2	5	80	80	3	-3	8	5	107	104	2	-2	14	5	40	37	5	3	21	5	19	15	19
4	75	72	3	4	2	5	29	7	8	-2	8	5	8	5	7	-1	14	5	31	33	6	-5	22	5	39	29	6
4	0	42	1	5	2	5	122	121	2	-1	8	5	17	21	14	0	14	5	174	171	2	-4	22	5	18	16	18
4	14	33	14	6	2	5	66	64	4	0	8	5	42	34	3	1	14	5	112	114	2	-3	22	5	108	103	3
4	69	67	4	-9	3	5	0	9	1	1	8	5	0	16	1	2	14	5	73	68	3	-2	22	5	147	141	2
4	77	68	4	-8	3	5	59	59	4	2	8	5	188	194	2	3	14	5	31	31	7	-1	22	5	0	16	1
4	39	24	7	-7	3	5	57	66	4	3	8	5	66	67	3	4	14	5	57	54	4	0	22	5	31	31	9
4	46	41	5	-6	3	5	30	39	7	4	8	5	90	81	3	5	14	5	11	8	10	1	22	5	39	33	6
4	52	52	4	-5	3	5	81	77	2	5	8	5	46	49	5	-8	15	5	13	10	13	2	22	5	24	10	24
4	129	128	2	-4	3	5	205	202	2	6	8	5	76	76	4	-7	15	5	38	43	7	-5	23	5	0	19	1
4	19	32	19	-3	3	5	143	146	1	-9	9	5	55	47	5	-6	15	5	0	17	1	-4	23	5	23	8	15
4	81	76	3	-2	3	5	267	256	2	-8	9	5	71	72	3	-5	15	5	110	108	2	-3	23	5	57	51	5
4	13	8	12	-1	3	5	82	88	2	-7	9	5	47	40	4	-4	15	5	91	90	2	-2	23	5	0	32	1
4	82	85	3	0	3	5	215	204	2	-6	9	5	206	207	2	-3	15	5	0	12	1	-1	23	5	41	38	6
4	67	64	4	1	3	5	110	106	2	-5	9	5	268	270	2	-2	15	5	21	15	12	0	23	5	33	9	8
4	0	2	1	2	3	5	0	13	1	-4	9	5	88	92	2	-1	15	5	55	53	4	1	23	5	55	45	5
4	0	21	1	3	3	5	40	47	5	-3	9	5	182	176	1	0	15	5	88	88	2	2	23	5	0	20	1
4	5	3	4	4	3	5	189	194	2	-2	9	5	107	110	2	1	15	5	71	57	3	-4	24	5	45	47	6
4	0	27	1	5	3	5	0	11	1	-1	9	5	0	32	1	2	15	5	76	79	3	-3	24	5	0	22	1
4	0	20	1	6	3	5	21	29	21	0	9	5	133	138	2	3	15	5	40	42	6	-2	24	5	16	27	16
4	25	51	16	-9	4	5	0	2	1	1	9	5	138	135	2	4	15	5	79	74	3	-1	24	5	51	53	6
4	26	15	10	-8	4	5	22	1	12	2	9	5	142	142	2	5	15	5	50	43	6	0	24	5	11	13	10
4	0	14	1	-7	4	5	91	98	2	3	9	5	0	28	1	-7	16	5	0	5	1	1	24	5	0	15	1
4	98	105	3	-6	4	5	139	137	2	4	9	5	40	43	5	-6	16	5	0	22	1	-3	25	5	41	39	7
4	60	65	4	-5	4	5	166	167	1	5	9	5	0	38	1	-5	16	5	103	105	2	-2	25	5	61	57	4
4	0	20	1	-4	4	5	90	93	2	6	9	5	0	7	1	-4	16	5	74	84	3	-1	25	5	50	35	6
4	0	17	1	-3	4	5	11	18	10	-9	10	5	46	27	6	-3	16	5	87	86	3	0	25	5	34	32	9
4	0	17	1	-2	4	5	267	258	2	-8	10	5	35	22	7	-2	16	5	33	34	6	-2	26	5	11	32	11
4	61	49	4	-1	4	5	155	148	1	-7	10	5	0	12	1	-1	16	5	170	160	2	-1	26	5	0	15	1
4	17	9	16	0	4	5	29	28	5	-6	10	5	170	162	2	0	16	5	45	41	5	-9	0	6	56	51	5
4	96	102	3	1	4	5	116	116	2	-5	10	5	323	330	3	1	16	5	75	67	3	-8	0	6	18	38	17
4	0	22	1	2	4	5	65	62	3	-4	10	5	169	171	2	2	16	5	0	31	1	-7	0	6	9	2	8
4	22	23	16	3	4	5	36	29	5	-3	10	5	23	16	9	3	16	5	62	66	4	-6	0	6	256	264	2
4	23	26	15	4	4	5	83	79	3	-2	10	5	0	9	1	4	16	5	21	17	20	-5	0	6	193	194	2
4	57	48	4	5	4	5	28	3	9	-1	10	5	115	107	2	5	16	5	0	18	1	-4	0	6	223	226	2
4	78	76	4	6	4	5	29	12	9	0	10	5	257	257	2	-7	17	5	30	32	10	-3	0	6	53	55	3
4	115	119	3	-9	5	5	31	8	8	1	10	5	142	136	2	-6	17	5	60	55	4	-2	0	6	106	105	2
4	12	9	12	-8	5	5	0	24	1	2	10	5	0	8	1	-5	17	5	0	15	1	-1	0	6	170	168	1
4	21	32	21	-7	5	5	33	10	5	3	10	5	146	147	2	-4	17	5	127	126	2	0	0	6	371	377	3
4	0	40	1	-6	5	5	149	144	2	4	10	5	16	1	16	-3	17	5	56	50	4	1	0	6	166	167	2
4	52	47	5	-5	5	5	77	75	2	5	10	5	34	32	8	-2	17	5	0	8	1	2	0	6	157	158	2
4	15	17	14	-4	5	5	57	52	3	6	10	5	55	53	5	-1	17	5	68	69	3	3	0	6	137	142	2
4	23	44	23	-3	5	5	54	52	3	-8	11	5	14	20	14	0	17	5	26	23	9	4	0	6	204	212	2
4	61	52	4	-2	5	5	0	13	1	-7	11	5	79	76	3	1	17	5	10	5	9	5	0	6	0	23	1
4	40	32	7	-1	5	5	132	127	1	-6	11	5	137	138	2	2	17	5	56	55	4	-9	1	6	62	59	4
4	19	34	19	0	5	5	0	9	1	-5	11	5	157	158	2	3	17	5	15	27	14	-8	1	6	0	35	1
4	22	27	21	1	5	5	198	199	2	-4	11	5	271	273	2	4	17	5	0	29	1	-7	1	6	105	109	2
4	73	67	4	2	5	5	19	3	18	-3	11	5	155	158	2	-7	18	5	59	51	4	-6	1	6	65	66	3
4	0	3	1	3	5	5	229	232	2	-2	11	5	47	54	3	-6	18	5	11	23	10	-5	1	6	57	57	3
4	0	19	1	4	5	5	47	42	5	-1	11	5	89	91	2	-5	18	5	20	47	20	-4	1	6	199	206	1
4	0	20	1	5	5	5	14	10	14	0	11	5	89	91	2	-4	18	5	0	14	1	-3	1	6	51	47	3
4	0	6	1	6	5	5	11	31	10	1	11	5	114	111	2	-3	18	5	71	76	3	-2	1	6	103	98	2
4	0	27	1	-9	6	5	0	34	1	2	11	5	75	67	3	-2	18	5	222	218	2	-1	1	6	77	73	2
4	0	2	1	-8	6	5	65	81	3	3	11	5	67	65	3	-1	18	5	58	65	4	0	1	6	193	194	1
4	0	23	1	-7	6	5	0	21	1	4	11	5	0	48	1	0	18	5	110	108	2	1	1	6	32	35	6
4	0	13	1	-6	6	5	84	83	2	5	11	5	41	28	6	1	18	5	91	89	3	2	1	6	120	112	2
4	59	46	4	-5	6	5	9	12	8	-8	12	5	81	70	3	2	18	5	0	22	1	3	1	6	44	46	5
4	34	35	8	-4	6	5	85	86	2	-7	12	5	17	1	17	3	18	5	0	3	1	4	1	6	67	62	3
4	0	31	1	-3	6	5	0	3	1	-6	12	5	0	22	1	4	18	5	43	35	7	5	1	6	0	13	1
4	0	19	1	-2	6	5	61	58	2	-5	12	5	0	17	1	-7	19	5	11	19	11	-9	2	6	28	17	10
4	8	4	8	-1	6	5	36	41	4	-4	12	5	68	69	3	-6	19	5	63	48	4	-8	2	6	0	12	1
4	0	20	1	0	6	5	35	36	4	-3	12	5	64	65	3	-5	19	5	24	16	12	-7	2	6	7	8	7
1	5	21	27	21	1	6	5	241	242	2	-2	12	5	88	78	2	-4	19	5	73	66	3	-6	2	6	96	101	2
1	5	109	121	2	2	6	5	132	138	2	-1	12	5	41	52	4	-3	19	5	0	21	1	-5	2	6	178	180	2
1	5	43	50	5	3	6	5	218	211	2	0	12	5	96	91	2	-2	19	5	22	48	21	-4	2	6	42	36	4
1	5	0	5	1	4	6	5	79	77	3	1	12	5	0	3	1	-1	19	5	41	38	6	-3	2	6	14	11	14
1	5	83	85	2	5	6	5	34	36	7	2	12	5	58	58	4	0	19	5	0	19	1	-2	2	6	0	32	1
1	5	0	11	1	6	6	5	0	7	1	3	12	5	201	196	2	1	19	5	0	3	1	-1	2	6	41	43	4
1	5	43	46	3	-9	7	5	28	25	10	4	12	5	0	27	1	2	19	5	50	47	5	0	2	6	20	20	20
1	5	91	97	2	-8	7	5	0	10	1	5	12	5	84	82	3	3	19	5	72	67	4	1	2	6	0	19	1
1	5	0	11	1	-7	7	5	52	57	4	-8	13	5	40	39	7	4	19	5	100	98	3	2	2	6	72	68	3
1	5	136	134	1	-6	7	5	67	64	3	-7	13	5	27	18	9	-6	20	5	37	20	7	3	2	6	89	91	3
1	5	76	80	2	-5	7	5	60	58	3	-6	13	5	179	179	2	-5	20	5	0	13	1	4	2	6	65	69	4
1	5	58	57	3	-4	7	5	126	121	2	-5	13	5	92	97	3	-4	20	5	69	73	4	5	2	6	71	69	4
1	5	392	405	4	-3	7	5	111	107	2	-4	13	5	64	58	3	-3	20	5	107	110	3	-9	3	6	29	29	10

k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
3	6	50	42	4	-6	9	6	121	124	2	-7	16	6	42	23	6	-1	2	7	0	35	1	-2	9	7	72	64	3
3	6	52	49	4	-5	9	6	89	90	3	-6	16	6	30	31	9	0	2	7	20	17	19	-1	9	7	34	37	6
3	6	113	118	2	-4	9	6	149	149	2	-5	16	6	46	51	5	1	2	7	101	108	2	0	9	7	168	170	2
3	6	59	57	3	-3	9	6	327	325	3	-4	16	6	59	53	4	2	2	7	89	88	3	1	9	7	0	13	1
3	6	67	65	3	-2	9	6	93	92	2	-3	16	6	137	137	2	3	2	7	20	6	20	2	9	7	58	62	4
3	6	62	58	3	-1	9	6	35	32	5	-2	16	6	47	45	5	4	2	7	16	20	15	3	9	7	54	57	5
3	6	108	109	2	0	9	6	20	32	19	-1	16	6	55	57	4	-8	3	7	22	27	19	4	9	7	0	0	1
3	6	102	98	2	1	9	6	156	155	2	0	16	6	20	25	19	-7	3	7	0	10	1	-8	10	7	29	8	9
3	6	91	93	2	2	9	6	52	55	4	1	16	6	52	60	5	-6	3	7	160	163	2	-7	10	7	61	54	4
3	6	55	53	3	3	9	6	14	31	14	2	16	6	48	38	5	-5	3	7	80	75	3	-6	10	7	49	55	5
3	6	132	139	2	4	9	6	0	6	1	3	16	6	53	47	5	-4	3	7	169	173	2	-5	10	7	70	70	3
3	6	182	180	2	5	9	6	0	24	1	-7	17	6	0	10	1	-3	3	7	62	65	3	-4	10	7	14	17	13
3	6	145	152	2	-8	10	6	21	16	21	-6	17	6	37	20	6	-2	3	7	47	40	4	-3	10	7	231	233	2
3	6	0	25	1	-7	10	6	68	65	3	-5	17	6	10	23	10	-1	3	7	77	76	3	-2	10	7	106	94	2
4	6	0	1	1	-6	10	6	104	102	2	-4	17	6	86	86	3	0	3	7	215	217	2	-1	10	7	19	2	18
4	6	0	19	1	-5	10	6	0	17	1	-3	17	6	71	73	3	1	3	7	160	162	2	0	10	7	66	62	3
4	6	115	121	2	-4	10	6	50	50	4	-2	17	6	44	44	5	2	3	7	15	2	15	1	10	7	0	49	1
4	6	123	125	2	-3	10	6	12	5	12	-1	17	6	72	68	3	3	3	7	41	46	6	2	10	7	0	9	1
4	6	153	148	2	-2	10	6	40	51	5	0	17	6	154	151	2	4	3	7	0	18	1	3	10	7	0	8	1
4	6	185	181	1	-1	10	6	27	21	7	1	17	6	27	27	10	-8	4	7	19	21	18	-7	11	7	58	47	4
4	6	80	83	2	0	10	6	121	125	2	2	17	6	35	38	8	-7	4	7	84	79	3	-6	11	7	79	76	3
4	6	143	145	1	1	10	6	0	24	1	3	17	6	50	44	6	-6	4	7	143	144	2	-5	11	7	76	74	3
4	6	62	60	3	2	10	6	59	57	3	-6	18	6	0	20	1	-5	4	7	151	152	2	-4	11	7	127	127	2
4	6	118	118	2	3	10	6	0	7	1	-5	18	6	0	16	1	-4	4	7	66	71	3	-3	11	7	51	54	4
4	6	163	164	2	4	10	6	69	65	4	-4	18	6	73	68	3	-3	4	7	79	82	2	-2	11	7	80	75	3
4	6	150	152	2	5	10	6	69	64	4	-3	18	6	64	66	4	-2	4	7	84	79	2	-1	11	7	18	11	18
4	6	74	80	3	-8	11	6	64	56	4	-2	18	6	0	7	1	-1	4	7	107	110	2	0	11	7	58	57	4
4	6	121	128	2	-7	11	6	0	11	1	-1	18	6	14	10	14	0	4	7	97	95	2	1	11	7	35	33	7
4	6	15	15	15	-6	11	6	44	44	5	0	18	6	46	41	5	1	4	7	0	9	1	2	11	7	84	83	3
5	6	58	56	4	-5	11	6	85	85	2	1	18	6	53	48	4	2	4	7	34	32	6	3	11	7	35	32	8
5	6	15	19	15	-4	11	6	197	195	2	2	18	6	94	92	3	3	4	7	32	12	7	-7	12	7	0	14	1
5	6	89	100	3	-3	11	6	150	157	2	3	18	6	0	32	1	4	4	7	0	5	1	-6	12	7	35	35	7
5	6	34	22	6	-2	11	6	91	90	2	-6	19	6	0	14	1	-8	5	7	0	24	1	-5	12	7	10	32	10
5	6	12	36	12	-1	11	6	115	110	2	-5	19	6	0	0	1	-7	5	7	18	31	17	-4	12	7	79	71	3
5	6	249	250	2	0	11	6	0	0	1	-4	19	6	26	38	12	-6	5	7	62	62	4	-3	12	7	22	6	21
5	6	19	14	11	1	11	6	123	123	2	-3	19	6	58	65	4	-5	5	7	30	27	7	-2	12	7	144	136	2
5	6	54	54	3	2	11	6	53	50	4	-2	19	6	70	73	4	-4	5	7	83	80	3	-1	12	7	135	140	2
5	6	117	113	2	3	11	6	82	77	3	-1	19	6	118	111	2	-3	5	7	97	96	2	0	12	7	62	59	4
5	6	38	31	5	4	11	6	5	28	4	0	19	6	13	23	13	-2	5	7	67	67	3	1	12	7	83	79	3
5	6	242	246	2	-8	12	6	11	21	11	1	19	6	18	30	18	-1	5	7	37	46	6	2	12	7	41	34	6
5	6	61	58	3	-7	12	6	38	37	6	2	19	6	0	13	1	0	5	7	0	7	1	3	12	7	0	2	1
5	6	32	45	8	-6	12	6	22	22	22	-6	20	6	30	10	10	1	5	7	37	27	6	-7	13	7	51	54	5
5	6	143	145	2	-5	12	6	45	41	5	-5	20	6	74	70	3	2	5	7	14	33	13	-6	13	7	66	63	4
5	6	21	22	21	-4	12	6	43	34	5	-4	20	6	0	36	1	3	5	7	113	124	2	-5	13	7	85	87	3
6	6	11	15	11	-3	12	6	9	28	9	-3	20	6	10	23	10	4	5	7	12	26	12	-4	13	7	62	60	3
6	6	35	40	7	-2	12	6	40	43	5	-2	20	6	100	105	3	-8	6	7	26	26	12	-3	13	7	22	46	21
6	6	31	26	8	-1	12	6	43	46	5	-1	20	6	145	139	2	-7	6	7	128	127	2	-2	13	7	173	175	2
6	6	78	79	3	0	12	6	0	20	1	0	20	6	0	3	1	-6	6	7	75	75	3	-1	13	7	0	10	1
6	6	328	322	3	1	12	6	254	257	2	1	20	6	19	5	18	-5	6	7	81	85	3	0	13	7	22	39	22
6	6	117	118	2	2	12	6	99	103	3	2	20	6	64	55	4	-4	6	7	64	67	3	1	13	7	0	9	1
6	6	20	19	11	3	12	6	49	52	4	-5	21	6	0	19	1	-3	6	7	233	231	2	2	13	7	0	2	1
6	6	88	94	2	4	12	6	0	8	1	-4	21	6	0	15	1	-2	6	7	121	115	2	3	13	7	71	75	4
6	6	0	22	1	-8	13	6	0	16	1	-3	21	6	36	29	7	-1	6	7	42	37	4	-7	14	7	0	19	1
6	6	77	77	2	-7	13	6	0	19	1	-2	21	6	32	40	9	0	6	7	18	7	18	-6	14	7	29	31	10
6	6	69	71	3	-6	13	6	71	72	3	-1	21	6	18	14	18	1	6	7	13	16	13	-5	14	7	21	3	20
6	6	44	44	4	-5	13	6	0	0	1	0	21	6	0	18	1	2	6	7	67	71	4	-4	14	7	24	2	10
6	6	74	74	3	-4	13	6	31	29	7	1	21	6	33	13	8	3	6	7	15	45	14	-3	14	7	0	31	1
6	6	28	14	10	-3	13	6	275	271	2	-4	22	6	22	2	21	4	6	7	0	0	1	-2	14	7	82	79	3
6	6	28	12	10	-2	13	6	123	127	2	-3	22	6	0	0	1	-8	7	7	0	3	1	-1	14	7	79	72	3
7	6	0	27	1	-1	13	6	35	15	6	-2	22	6	0	0	1	-7	7	7	63	66	4	0	14	7	53	43	4
7	6	65	65	4	0	13	6	108	110	2	-1	22	6	100	100	3	-6	7	7	55	52	4	1	14	7	54	60	5
7	6	70	66	3	1	13	6	0	26	1	0	22	6	19	20	18	-5	7	7	0	22	1	2	14	7	47	43	6
7	6	45	45	5	2	13	6	0	10	1	1	22	6	42	29	6	-4	7	7	34	41	7	3	14	7	0	1	1
7	6	114	115	2	3	13	6	0	24	1	-4	23	6	69	66	4	-3	7	7	49	50	4	-7	15	7	19	20	19
7	6	179	176	2	4	13	6	42	41	7	-3	23	6	0	20	1	-2	7	7	0	9	1	-6	15	7	40	30	6
7	6	53	53	3	-8	14	6	0	19	1	-2	23	6	0	16	1	-1	7	7	66	64	3	-5	15	7	15	2	14
7	6	186	186	1	-7	14	6	47	51	5	-1	23	6	30	34	12	0	7	7	178	177	2	-4	15	7	45	42	5
7	6	95	91	2	-6	14	6	57	58	4	0	23	6	57	53	5	1	7	7	39	42	5	-3	15	7	111	110	2
7	6	0	2	1	-5	14	6	168	166	2	-2	24	6	0	0	1	2	7	7	149	149	2	-2	15	7	0	31	1
7	6	145	148	2	-4	14	6	120	126	2	-1	24	6	58	55	5	3	7	7	20	18	19	-1	15	7	51	53	5
7	6	48	51	4	-3	14	6	82	89	3	-8	1	7	51	53	5	4	7	7	31	19	9	0	15	7	96	89	3
7	6	49	50	5	-2	14	6	98	92	2	-7	1	7	0	32	1	-8	8	7	43	37	6	1	15	7	25	28	13
7	6	18	24	17	-1	14	6	146	145	2	-6	1	7	133	135	2	-7	8	7	68	58	3	2	15	7	75	69	4
7	6	28	20	11	0	14	6	0	14	1	-5	1	7	0	14	1	-6	8	7	52	52	4	-6	16	7	54	51	5
8	6	104	108	3	1	14	6	0	4	1	-4	1	7	106	103	2	-5	8	7	76	76	3	-5	16	7	0	16	1
8	6	93	89	3	2	14	6	53	58	5	-3	1	7	0	30	1	-4	8	7	197	203	2	-4	16	7	0	22	1
8	6	37	35	6	3	14	6	0	24	1	-2	1	7	70	77	3	-3	8	7	115	119	2	-3	16	7	0	4	1
8	6	89	87	2	4	14	6	0	7	1	-1	1	7	14	15	13	-2	8	7	24	12	10	-2	16	7	92	87	3
8	6	192	187	2	-7	15	6	56	58	5	0	1	7	130	130	2	-1	8	7	22	25	14	-1	16	7	13	28	12
8	6	131	130	2	-6	15	6	55	60	4	1	1	7	77	73	3	0	8	7	111	116	2	0	16	7	79	83	3
8	6	0	23	1	-5	15	6	59	56	4	2	1	7	78	82	3	1	8	7	60	56	4	1	16	7	55	57	5
8	6	47	33	3	-4	15	6	10	42	9	3	1	7	100	111	3	2	8	7	80	82	3	2	16	7	20	24	20
8	6	0	11	1	-3	15	6	29	17	8	4	1	7	36	28	7	3	8	7	28	35	10	-6	17	7	0	11	1
8	6	35	51	7	-2	15	6	184	183	2	-8	2	7	21	11	21	4	8	7	68	61	4	-5	17	7	65	53	4
8	6	126	120	2	-1	15	6	59	60	4	-7	2	7	18	37	17	-8	9	7	0	8	1	-4	17	7	69	64	4
8	6	72	70	3	0	15	6	10	48	9	-6	2	7	27	9	9	-7	9	7	40	38	6	-3	17	7	36	38	7
8	6	60	52	4	1	15	6	22	3	22	-5	2	7	234	234	2	-6	9	7	10	25	10	-2	17	7	62	59	4
8	6	15	39	15	2	15	6	67	69	4	-4	2	7	129	123	2	-5	9	7	120	120	2	-1	17	7	53	46	4
9	6	0	22	1	3	15	6	11	16	10	-3	2	7	51	52	4	-4	9	7	0	23	1	0	17	7	25	40	14
9	6	43	37	5	4	15	6	21	24	20	-2	2	7	61	65	3	-3	9	7	163	158	2	1	17	7	51	43	5