New Isoindoline Electron Acceptors Analogous To Benzo-TCNQ

A thesis presented for the degree of Doctor of Philosophy

by

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at

DUBLIN CITY UNIVERSITY
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JUNE 1996

To my parents, Betty and Joe.

Declaration

I, the undersigned, hereby declare that this thesis, which I now submit for assessment on the programme of study leading to the award of Ph.D. represents the sole work of the author 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 work.

Shane Conway

Shane P. Conway

Acknowledgements

I would like to thank my supervisor Prof. Albert Pratt for his help, encouragement and guidance during the course of this work.

I am deeply indebted to both the academic staff and in particular the technical staff of the School of Chemical Sciences for their assistance during my stay. I particularly wish to thank Mick Burke most sincerely for all his help, with the aid of Maurice, Damien and Veronica. I would also like to thank Dr Robert Forster and Joe O' Kelly for their help, advice and use of their equipment for the Cyclic Voltammetry experiments, Dr Conor Long for the X-ray crystallographic data and structures, and Dr Josh Howarth and Dr Padraig James for their advice.

I also wish to express my deepest thanks to my fellow postgraduates for their friendship over the years, in particular the members of the Albert Pratt research group, Fang, Cormac F.F. O'Donnell, Mark, James (Jimmy) Delaney, Farmer, Li Jing, Ollie Egan, Rory (aka ROD), Orla, Joe, Collette, Ben, and Mauro and all the previous inmates of AG 07. I would also like to acknowledge the members of the DCU staff soccer team especially Jarlath, Liam, Stevie N. and, last and very much least, Stormin' Norman the sparks. I would also like to thank John Dennis just for talking to me.

I wish to thank all the members of my family who have supported and encouraged me throughout this work and in particular to Patricia for her help in typing this thesis.

I would also like to express my appreciation to Ana for her encouragement and patience.

Finally I wish to express my most sincere thanks to my parents for putting up with and supporting me all these years and to whom I owe everything.

Abstract

Interest in novel heterocyclic derivatives analogous to TCNQ in which the π-electrons of a carbon-carbon double bond are replaced by a lone pair of electrons on a heteroatom has led to investigation of the synthesis of *N*-alkyl derivatives of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile.

Knoevenagel condensation of *N*-methylphthalimide with malononitrile under a number of conditions yielded complex product mixtures from which the sodium and methylammonium salts of *o*-(2,2-dicyanoethenyl-1-olate-)*N*-methylbenzamide and 3-(dicyanomethylidene)phthalide were isolated as minor products.

Reaction of malononitrile with diiminoisoindoline and 1-phenylimino-3-iminoisoindoline in dimethylformamide yielded the ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile. In methanol the highly insoluble mono-condensation product was obtained and this was also the product obtained by reaction of sodio-malononitrile with phthalonitrile in methanol. 2,2'-(Isoindolin-1,3-diylidene)bispropanedinitrile was obtained from its ammonium salt by acidification.

Reaction of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile or its ammonium salt with a variety of acylating and alkylating agents did not yield the desired compounds. A very low yield of 2,2'-(2-methyl-isoindolin-1,3-diylidene)bispropanedinitrile was obtained on reaction with dimethylsulphate. Reaction of the ammonium salt with a variety of amines yielded products which X-ray crystallography showed to arise from amine addition across a cyano group. 2,2'-(2-Methyl-isoindolin-1,3-diylidene)bispropanedinitrile was successfully synthesised by heating the tetramethylammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile in 1,2-dichlorobenzene.

Cyclic voltammetry measurements of the 2,2'-(isoindolin-1,3-diylidene) bispropanedinitriles show they are electrochemically irreversibile. UV studies of the charge-transfer complexing abilities of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile and its *N*-methyl derivative with a variety of electron donors were carried out and a number of charge-transfer complexes have been synthesised. X-ray crystallography of the 1:1 complex between 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine shows that it crystallises in a mixed stacking arrangement.

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List of abbreviations

AN	anthracene
BEDT-TTF (or ET)	bis(ethylenedithiolo)tetrathiofulvalene
BEDO-TTF	bis(ethylenedioxa)tetrathiofulvalene
BTC	bis(trimethylsilyl)carbodiimide
CDW	charge density wave
C-T	charge-transfer
CV	cyclic voltammetry
DBTSF	dibenzotetraselenafulvalene
DBTTF	dibenzotetrathiafulvalene
DBTeTF	dibenzotetratellurafulvalene
DCNQI	*N,N'*-dicyano-quinone diimine
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DMA	*N,N*,-dimethylaniline
DMF	*N,N*-dimethylformamide
DMSO	Dimethylsulphoxide
ET	bis(ethylenedithiolo)tetrathiofulvalene
HMTTF	hexamethylenetetrathiafulvalene
HMTTeF	hexamethylenetetratellurafulvalene
HOMO	highest occupied molecular orbital
LDA	lithium diisopropylamide
LUMO	lowest unoccupied molecular orbital
M(dmit)	metal complex of 4,5-dimercapto-1,3-dithiole-2-thione
TCAQ	tetracyanoanthraquinone
TCNDQ	13,13,14,14-tetracyanodiphenoquinodimethane
TCNE	tetracyanoethylene
TCNEO	tetracyanoethylene oxide
TCNP	11,11,12,12-tetracyanopyrene
TCNQ	7,7,8,8-tetracyano-*p*-quinodimethane
THF	tetrahydrofuran
TMA	tetramethylammonium
TMDA	*N,N,N',N'*-tetramethly-*p*-phenylenediamine
TMTTF	tetramethylenetetrathiafulvalene
TMTSF	tetramethylenetetraselenafulvalene
TNAP	11,11,12,12-tetracyanonaphtho-2,6-quinodimethane
TSF	tetraselenafulvalene

TTF	tetrathiafulvalene
TTeF	tetratellurafulvalene
SDW	spin density wave

Chapter 1

1.A.1 Introduction

The availability of lightweight materials with high electrical conductivity and high processibility, or liquid nitrogen temperature superconductivity, would, if attainable, have phenomenal consequences for the electronics industry. Electrical power transmission without resistance would increase the efficiency of the national grid and electrical motors. Powerful supercomputers using superconducting gates with extremely fast response times, without the need for a complex cooling system, are seen as the next generation of computer. The development of powerful superconducting electromagnets could allow the realisation of high speed trains travelling along frictionless superconducting tracks by expelling an external magnetic field. Electric cars, powered by extremely light-weight batteries, and without the toxic emissions of their fossil fuel-burning counterparts, would help the pollution problems in cities and possibly reduce the damage being done to the environment.

One area of research which is attempting to make such materials a reality is that of Organic Metals. Organic Metals, while encompassing the fields of conducting polymers and conducting charge-transfer (C-T) complexes, have but one common property with that of metals, i.e. partially-filled delocalised bands. It has been the highly brittle, crystalline C-T complexes which have yielded most information on these solid state properties. While it is unlikely that these crystalline solids will replace copper as a means to making a simple electrical contact, interest in these materials lies in understanding the mechanism of charge transport and testing theoretical models. This understanding does have practical use in the design of organic photoconductors and materials to modify the surface of semiconductor electrodes. It may even give an insight into the complex rapid electron transfer processes in biological systems. Figure 1.01 gives some examples of the types of conductivities achieved in the field of Organic Metals.

1.A.2 Background

Interest in highly conducting C-T complexes came about with the discovery in 1954 of the first electrically conducting molecular compound [1] with a conductivity of ~1×10^{-3} Scm^{-1}. However the true impetus was initiated by the discovery of the highly conducting (~500 Scm^{-1}) C-T salt [2] of the acceptor, 7,7,8,8-tetracyano-*p*-quinodimethane[3] (TCNQ; 1) and the donor,

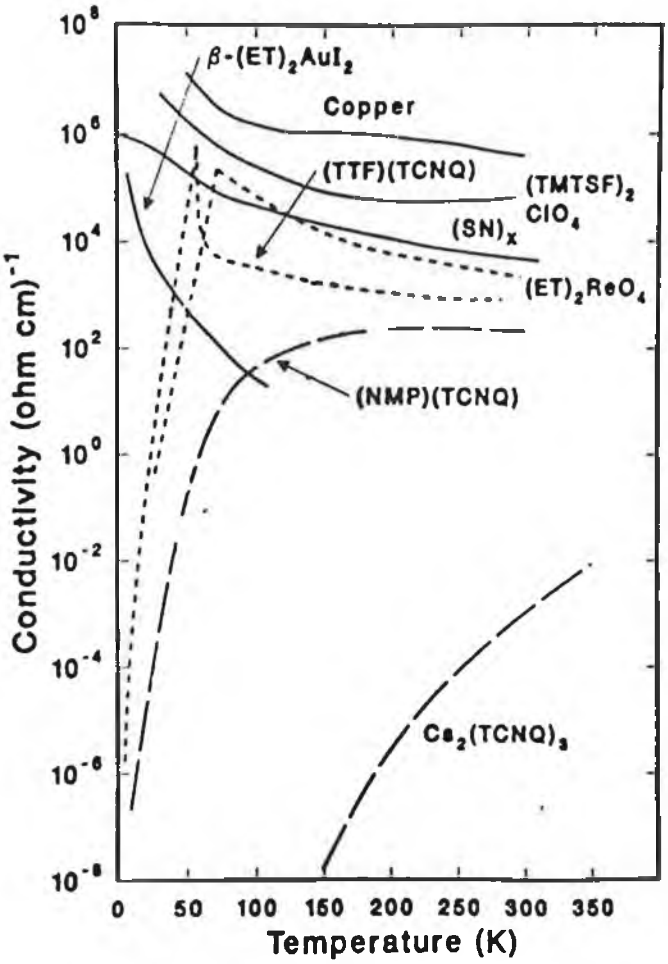
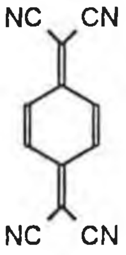


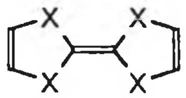
Figure 1.01. Temperature dependence of conductivity for various electrical conductors

tetrathiafulvalene [4] (TTF; 2a). While C-T complexes also exhibit interesting magnetic [5] and non-linear optical properties [6], most research has centred around achieving ever higher conductivities. In trying to reach this goal many thousands of C-T salts have been synthesised, with the ultimate, superconductivity, being first achieved in 1980 by Bechgaard and Jerome [7]. To date the highest T_c for an organic superconductor is 11.6 K at ambient pressure, [8] or 12.5 K at 0.3 Kbar of pressure,[9] for the $(ET)_2X$ (3) class of salts. A higher T_c of 40 K has been reported[10] for the newest class of organic superconductors, the fullerides, C_{60}. However these organic compounds still have a long way to go to compare with the most highly superconducting inorganic cuprates, which at present have the highest T_c= 133 K for a mercurybarium-calcium-oxide.[11] It is through continued research and co-operation between chemists and physicists that so much has been achieved in recent years. The ongoing synthesis of novel donor and acceptor molecules should further these goals or at least yield additional insights into how they may be realised.



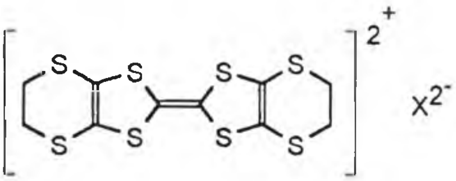
TCNQ

(1)



(a) X=S, TTF
(b) X=Se, TSeF
(c) X=Te, TTeF

(2)



$(ET)_2X$

(3)

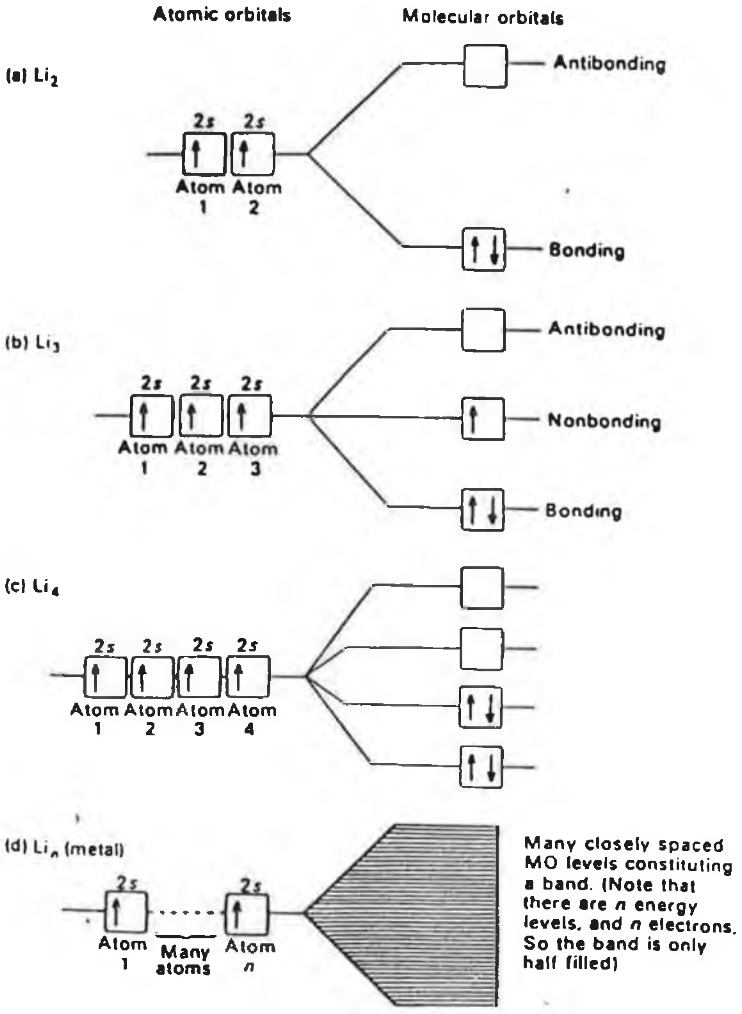


Figure 1.02 Development of molecular orbitals into bands in lithium metal.

1.A.3 Conductivity in a solid: The Band Theory

In the formation of crystalline materials, the electronic orbitals of the component atoms or molecules overlap and mix to form bands, each band containing a range of energy states or levels. These bands are filled according to Pauli's exclusion principle, with the lowest energy states being filled first and then the next highest states right up to the highest occupied state, which is known as the Fermi Level, E_F. An example of this is seen in Figure 1.02 for the overlap of the 2s-orbitals of lithium.

These bands may overlap or a gap may exist. The lower band (or valence band) is formed from the highest occupied molecular orbitals (HOMOs) and the upper (or conduction) band from the lowest unoccupied molecular orbitals (LUMOs) of the interacting species.

A simple theoretical basis for one-dimensional conduction is illustrated by the tight-binding band approximation, in which one considers a one-dimensional array or chain of N equally spaced molecules a distance c apart, Figure 1.03.

< c >
--O----O----O----O----O----O-- normal

--O-O---O-O----O-O---O-O-- distorted
< 2c >

Figure 1.03 Showing the normal separations between an array of atoms or molecules which form a one dimensional metallic conductor and the distorted separations which can occur at lower temperatures which result in the loss of electrical conductivity and the opening of a band gap.

In the isolated state each atom or molecule has an orbital with energy E_0 that overlaps with the equivalent orbitals of its two nearest neighbours. This is equivalent to the energy of an orbital before its linear combination with another orbital to give the corresponding bonding and anti-bonding molecular orbitals. The energies of these orbitals which constitute this array or band are derived from a Hückel-like tight-binding band description. These energy levels are sufficiently close in energy that an apparent continuum of allowed energy levels exist above and below the energy level of the isolated molecule E_0, Figure 1.04. This continuum is bounded within a band of width 2W and is composed of N orbitals capable of accommodating 2N electrons. The bandwidth is related to the transfer integral t (the resonance integral β in the Hückel method) by 2W=4t, Figure 1.04.

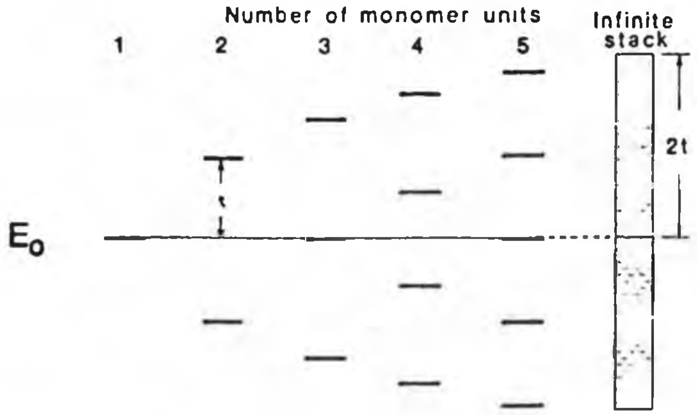


Figure 1.04 Schematic illustration of the formation of a band from the overlap of the molecular subunits in a stack

In most non-metallic solids the valence band is completely filled and the upper conduction band is completely empty. These materials are insulators or at best semiconductors as there are no empty states near the Fermi level to accommodate electrons as they gain energy during conduction. If the band gap is not too large (<2eV), Figure 1.05(b), the electrons at the Fermi level may be thermally or photo excited into the conduction band. Both these electrons and the positive holes they leave behind can move and contribute to the conductivity. Such a material is a semiconductor and conductivity increases with increased temperature. If the band gap is too large (>2eV) for the excitation of electrons across the gap then the material is an insulator, Figure 1.05(a). When there is overlap of the valence and conduction bands or there is an incomplete band, then little or no energy is required for the movement of electrons from the highest occupied states of the Fermi level into the vacant states of the conduction band, Figure 1.05(c). This defines metallic conductivity.

Thus the extent of occupation of the energy levels and the magnitude of the band gap determine the electrical properties of a material. In order to design and synthesise a material with the partially filled delocalised band of a metal a collection of atoms or molecules must be found which, when arranged in close proximity and in similar crystallographic and electronic environments, form an energetically flat extended pathway enabling the free movement of electrons. Such a situation is frequently realised when planar, conjugated molecules crystallise in a stack, as in the case for charge-transfer complexes, in which electron transfer from the donor to the acceptor provides the means for the formation of a partially filled band.

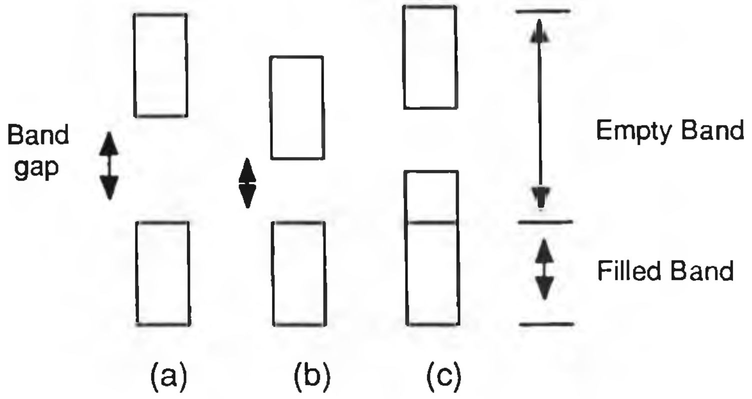


Figure 1.05 Schematic illustration of the electron occupancy of allowed energy bands in (a) an insulator, (b) a semiconductor, and (c) a metal.

1.A.4 General Properties of Charge-Transfer Complexes

Charge-transfer (C-T) complexes, or alternatively electron donor-acceptor (EDA) complexes, are associations of definite stoichiometry between two different molecules, each of closed shell electronic structures. They are frequently formed when a molecule of low ionisation potential, an electron donor (D), interacts with a molecule of relatively high electron affinity, an electron acceptor (A), (equation 1). These C-T complexes are capable of discrete absorption of light giving rise to bands in the near UV or visible spectrum which are distinct from those of either component of the complex.

$$D + A \rightleftharpoons [A,D] \longrightarrow [A^-,D^+] \qquad \text{equation 1}$$

One theory as to the nature of the binding and the characteristic electronic absorption was put forward by Mulliken.[12] His theory stated that the ground state for a complex, $\Phi_N(DA)$, was a combination of a "no-bond" structure, $\Phi(D,A)$, in which A and D are held together by dipole-dipole interactions and other intermolecular forces, and a "dative bond" structure, $\Phi(D^+\text{-}A^-)$, in which one electron has been transferred from the D to A. Thus,

$$\Phi_N(DA) = a\Phi(D,A) + b\Phi(D^+\text{-}A^-) \qquad \text{equation 2}$$

where a and b are coefficients and a>b.
The excited state of the complex, $\Phi_E(DA)$, corresponds to the combination:

$$\Phi_E(DA) = a^*\Phi(D^+\text{-}A^-) + b^*\Phi(D,A) \qquad \text{equation 3}$$

with a "dative bond" structure as the main contributor.

Thus the optical absorption characteristic of these complexes is identified with the transition $\Phi_E(DA) \leftarrow \Phi_N(DA)$. These spectral bands result from the promotion of an electron from the HOMO of D to the LUMO of A, Figure 1.06.

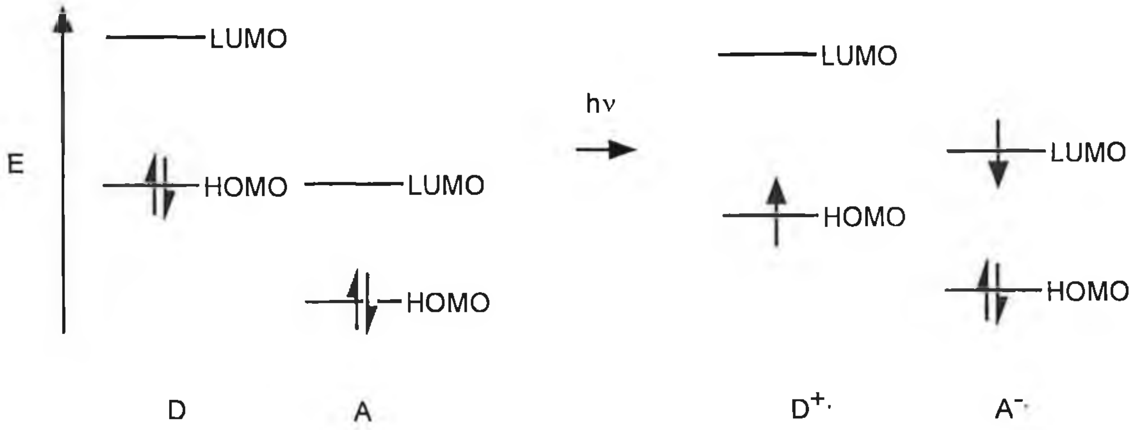


Figure 1.06 Transfer of an electron from the HOMO of D to the LUMO of A

It is important to note that for many EDA complexes the "no bond" structure is the major contributor to the ground state, i.e. a>>b in equation 2. Therefore there is little C-T in the ground state.

The magnitude of C-T, and with it the intensity of the C-T bands, is dependent on the degree of donor-acceptor overlap and on the ionisation potential of the donor and the electron affinity of the acceptor. The degree of C-T may be partial or complete, with complete C-T resulting in the formation of a radical ion salt.

1.A.4.1 Stacking formation in C-T Complexes

There are two classes of aggregation isomers into which C-T complexes may form. The first type is that in which the donors and the acceptors aggregate into mixed stacks comprising alternate D and A molecules, Figure 1.07(a). The second class involves the formation of segregated stacks of donors and acceptors, Figure 1.07.

D A D A	A D A D
A D A D	A D A D
D A D A	A D A D
A D A D	A D A D
D A D A	A D A D
(a)	(b)

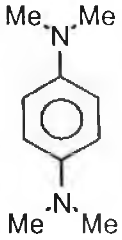
Figure 1.07 Illustration of the types of stacking motifs found in C-T complexes; (a) Mixed Stacks and (b) Segregated Stacks.

The potential ability of these two stacking systems to conduct electricity is very different. In order to conduct down a mixed stack an unpaired electron on an acceptor molecule would have to start hopping to the adjacent molecule, a donor. Since the molecular potential of this acceptor is very different from that of the donor, this will act as a large activation energy to conduction. Bringing an electron along a segregated stack of acceptors again involves the hopping of an electron onto adjacent molecules but without the large potential difference experienced in the mixed stack. Such a situation exists with the metallic complex, TTF-TCNQ, which is highly conducting and forms segregated stacks [2] in its crystalline state. However there may be some barriers, like the Coulombic repulsion U, which, if $U>>4t$, the bandwidth, may lead to the formation of a Mott-Hubbard type insulator. This occurs in complexes with half filled bands. A band becomes half filled when there is complete transfer of an electron between the donors and the acceptors and as a result there are no neutral sites in the stack for the electrons to hop to, due to an electron becoming associated with each site. The result of moving an electron from one site to another involves increased repulsion between the like charges. This usually occurs when there are either strong donors or strong acceptors in the complex. By combining donors and acceptors in which the charge transfer is incomplete, the overall valence of the stack is effectively mixed with the result that there are neutral sites in the stack capable of accommodating an electron. The degree of C-T for the TCNQ C-T complexes of TTF, TSF and TTeF have been found to be 0.59, 0.63 and 0.71 of an electron respectively.[13]

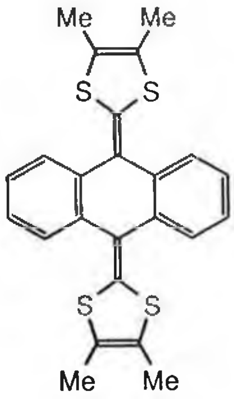
In general most segregated stacking C-T complexes are conducting while the mixed stacking complexes are insulating. However, while it has been suggested that the mixed-stack form is as, or more, thermodynamically stable,[14] it appears that both isomers may in any event coexist and the only way to ensure segregated stacking is to design molecules where the segregation is built-in.[15]

1.A.4.2 Stoichiometries in C-T Complexes

In addition to the differences in the stacking types organic C-T salts are found with differing stoichiometric ratios of donor to acceptor. TCNQ (1) alone forms a multitude of variable stoichiometric complexes with many donors including 1:1 salts with TTF (2a), a 1:1 and 2:1 salt with *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMDA; 4)[16, 17] and even a 4:1 complex with an anthraquinone derivative of TTF (5).[18] The variable stoichiometry of these complexes, even between the same donors and acceptors, is most likely determined by packing considerations. *Wheland and Gillson* have shown that complex formation methathesis occasionally affords control over stoichiometry.[19] In the case of the halide salts of TTF it is argued that the stoichiometry is determined by competition between the cost of ionising a D-A pair (I - A), ionisation potential minus the electron affinity, and the electrostatic (or Madelung) energy, E_M,of the solid that is gained by forming ions.[20]



(4)



(5)

1.A.4.3 The Unidimensionality of C-T Complexes

As mentioned previously, the partially filled delocalised band of a metal can be realised in C-T complexes when planar, conjugated molecules crystallise in segregated stacks. Because the greatest overlap of orbitals occurs along the stack, electrical conductivity is greater in this direction than in any other direction. As a result of this anisotropic behaviour these compounds have also been referred to as quasi- or pseudo-one-dimensional metals. Since C-T is usually complete or partial, the bands are usually at most half full or in any case incomplete. Unlike metals, in which electrons can avoid each other by moving in three dimensions, the quasi one-dimensional C-T salts are subject to various phase transitions due to increased electron interactions. The problem of the half filled state giving rise to a Mott-Hubbard insulator has been mentioned already. The partially filled quasi one-dimensional salts are also subject to metal to insulator (M-I) transitions at low temperatures. These are a result of lattice distortions and the formation of an antiferromagnetic state and are the principal barrier to higher conductivities.

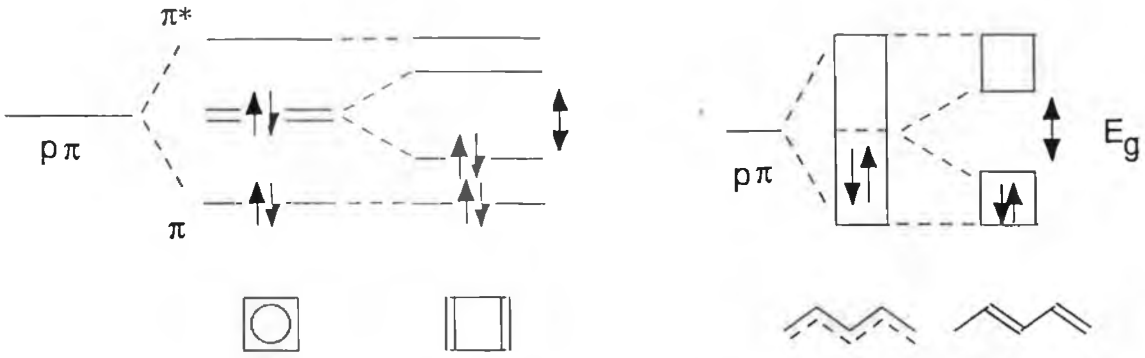
1.A.4.4 Lattice instabilities in quasi one-dimensional conductors

The nature of quasi one-dimensional C-T complexes results in certain physical restrictions on conductivity as the temperature is lowered. These lattice instabilities are characteristic of this class of conductors due to the increased electron interaction and are made up of :

(i) Peierls distortions (or Charge Density Waves (CDW))
(ii) Spin Density Waves (SDW)

(i) Peierls distortions:

By analogy with Jahn-Teller's theory, partially-filled energy bands, which are analogous to metals, are subject to geometrical distortions associated with a lowering of the total energy. An example of this is given for comparison of the Jahn-Teller effect in cyclobutadiene, Figure 1.08(a), and Peierls distortion in an extended chain made up of pπ-orbitals, Figure 1.08(b). The lower energy structure in both systems is the one where the bond lengths alternate. If the electrons were delocalised over the entire system, then the π-extended one-dimensional chain of polyacetylene would have a half-filled band and would be expected to be metallic.



(a) (b)

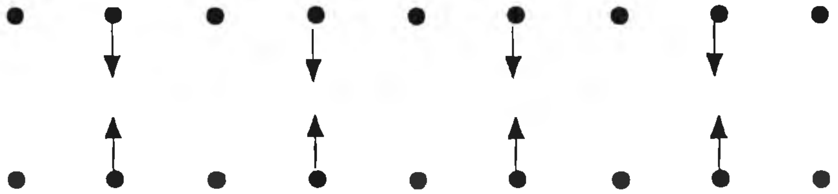
Figure 1.08 Showing the comparison in the geometric distortions of (a) Jahn-Teller effect in cyclobutadiene and (b) Peierl's distortion in an extended chain of pπ-orbitals.

These geometric distortions are variously known as Peierls[21] distortions or Charge Density Waves (CDW).[22]

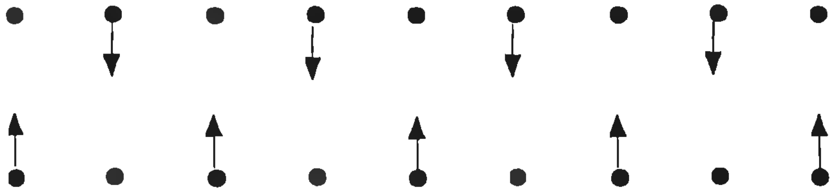
At the Fermi level there is a degeneracy and just above or below it, near-degeneracy, for any partially-filled band. There is a driving force for the system to lower its energy. In order to do this the structure must distort and thus the electrons in these degenerate states become paired, opening up a gap at the Fermi level. This is referred to as Electron-Phonon coupling. The size of the gap will determine whether the solid is insulating or semi-conducting. This pairing of electrons results in regions of the lattice having alternating high and low charge density and hence generating a CDW.

CDWs can also be thought of as electron-hole pairs as well as electron-electron pairs, Figure 1.09(a). We can think of an electron as being paired either with a hole to its right or left or with the electron opposite. As a solid is cooled towards absolute zero (0 K) there is a tendency for electrons to pair. A CDW forms when below the phase-transition temperature and the electrons are trapped in pairs. The formation of this CDW is accompanied by lattice distortions and these can be seen by x-ray diffraction.

The coupling of CDWs with lattice vibrations also shows variable effects on conductivity. The wavelength of a CDW varies with the number of electrons in the solid, *i.e.* the greater the number of electrons the shorter the wavelength. Hence the wavelength of the CDW may not match that of the original lattice. The CDW is said to be incommensurate with the original lattice spacings and is free to travel throughout the lattice until pinned by a lattice defect. CDWs which are commensurate with the lattice spacings are trapped and do not contribute to the conductivity.



(a) CDW



(b) SDW

Figure 1.09 (a) Pairing of electrons and holes in a stack giving a CDW. (b) Pairing of electron spins on adjacent molecules in a stack giving a SDW.

(ii) Spin Density Waves (SDW)

Electrons with the same spin tend to oppose one another and so prefer to pair-up with electrons of opposite spin, *i.e.* antiferromagnetically. So a SDW can be likened to two CDWs superimposed but shifted one space to the left or right, Figure 1.09(b), so that the total charge density is constant but the spin density alternates along the lattice. This antiferromagnetic phase is insulating due to the periodicity of the SDW which destroys the Fermi surface. This type of distortion is exhibited by the Bechgaard salts formed from octahedral anions[23] and these M-I transitions give way to a superconducting state under the application of high pressures.

Another cause of M-I transitions observed in the Bechgaard salts is due to the ordering of the anions at lower temperatures.[23] The lower symmetry anions undergo these transitions at higher temperatures, with the exception of the perchlorate salt, than those of the octahedral anions. These transitions can be suppressed by the application of pressure, again with the observation of a superconducting state.

1.A.5 Superconductivity

Superconductivity is the ability to conduct electricity with zero resistance. A current set up in a superconductor is not dissipated as heat, as in an ordinary conductor, but instead continues to flow forever. A theory for superconductivity in metals was put forward by Bardeen, Cooper and Schrieffer in 1957 called the BCS theory.[24]

1.A.5.1 BCS Theory of Superconductivity

The BCS theory proposed that, unlike conventional conductivity which involves the movement of free electrons in a conduction band, superconductivity involves the pairing of conduction electrons by some interelectron attraction and a condensation of these pairs, known as Cooper pairs, at some critical temperature, T_C, to form a macroscopic quantum state. This state has many unique properties including zero resistance and perfect diamagnetism, which excludes an external magnetic field from its interior, known as the Meissner effect, up to a limiting critical field strength. The mechanism for the formation of the Cooper pairs is mediated by lattice vibrations called phonons. The process begins when one electron attracts the surrounding positive ions of the crystal lattice and creates a region of lowered potential energy for itself and other electrons. Because these ions are much heavier than the electron they move more slowly and as a result this region of lowered energy persists and a second electron is attracted, Figure 1.10.

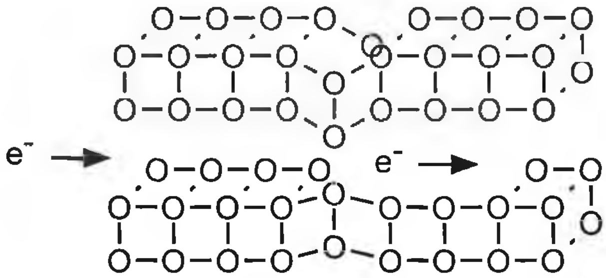


Figure 1.10 Mechanism for the formation of Cooper pairs

Interactions between the conduction electrons and the phonons take place in a region whose energy ranges from the Fermi level, E_F, to the Fermi level plus the average excitation energy of the phonon (E_F + E_V). Because the Pauli exclusion principle forbids these interactions from scattering electrons into the fully occupied states below the Fermi level, the lower states provide a passive support base for the interaction region. At T_C, the temperature is sufficiently low that thermal agitation at the Fermi surface is insufficiently large to break up the pairing process. As a result many Cooper pairs form simultaneously to create the superconducting state.

In the simplest form of the BCS theory, T_C depends linearly on the excitation energy of the system that mediates the electron pairing, the lattice vibration E_V. Consequently a decrease in the lattice vibration will decrease T_C, since the heavier lattice will vibrate at lower frequencies. Isotope substitution is one method which has been used to ascertain whether superconductive pairing is mediated by lattice vibrations.

However, while the general principles of the BCS theory probably can account for the new superconductors like the cuprates and the new organic superconductors, the mechanism for the formation of the superconducting state is still unknown. Modifications of the classic BCS theory are still required. The most likely modification is an alternative electron-pairing mechanism mediated not by phonons but by interaction of the conduction electrons with charge or electron spin fluctuations in the electronic subsystem.[25]

1.A.6 Design of Organic Metals

In the last twenty years there has been intense interest in trying to determine and understand the properties necessary to enable an organic solid conduct electricity. Ongoing research focused on the synthesis of new derivatives of both TCNQ and TTF, along with the sophisticated measurements and interpretations of the solid-state physicist, has contributed greatly to the wealth of knowledge now available. From this information certain common characteristic properties have been found in all the organic solids which conduct electricity.[26]

In order to attain the metallic state, an organic solid has to fulfil the following basic requirements ;

(i) the molecular components must be planar with extensive π-delocalisation in order to facilitate extensive overlap

(ii) the components should be of similar size and highly symmetric

(iii) the components should crystallise into a uniform structure with segregated stacking of the donors and acceptors

(iv) the degree of charge-transfer should be partial to ensure mixed valence stacks

(v) the organic solid should be capable of minimising electron - electron interactions

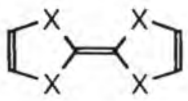
In addition to the above basic requirements, increased dimensionality, necessary for enhanced conductivity and the reduction or elimination of M-I transitions associated with the quasi-one-dimensional salts at low temperatures, is achieved by the incorporation of highly polarizable heteroatoms such as S, Se or Te on the peripheral sites of the donor and acceptors.

Since the ability of chemists to induce molecules to pack within a crystal lattice in a prescribed manner is very limited, one is restricted to controlling the key properties of the individual molecules in advance. One of the major goals for chemists in recent years has been to discover new families of donors and acceptors, using the above guidelines, which would exhibit metallic or superconductivity.

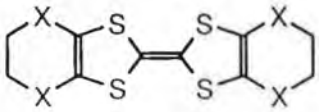
1.B Donor Molecules

1.B.1 Introduction

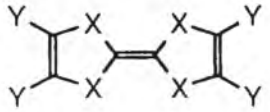
Since the discovery of the electron donating ability [4] and electrical conducting properties of TTF (2a) [2] in the early 1970s much effort has been devoted to synthesising analogues of TTF with the aim of determining the effect of structural variation on conductivity and superconductivity. The most remarkable analogues are bis(ethylenedithiolo)tetrathiofulvalene (BEDT-TTF), or ET (6a) for short, tetramethyltetraselenafulvalene (TMTSF; 7a) and bis(ethylenedioxa)-tetrathiofulvalene (BEDO-TTF; 6b), all of which form superconducting salts. Of the properties necessary for the formation of electrically conducting organic metals [26] TTF possesses the required planarity, symmetry and low oxidation potential to form both a stable cation and dication, whose stability arises from the formation of a 4n+2 π-electron Hückel-type aromatic ring system. As a result most of the research to develop new donors has centred on exploiting these properties by modifying the basic TTF unit.



(2)a: X = S, TTF
b: X = Se, TSF
c: X = Te, TTeF



(6)a: X = S, BEDT-TTF
b: X = O, BEDO-TTF



(7)a: X = Se, Y = Me, TMTSF
b: X = S, Y = Me, TMTTF
c: X = S, Y-Y = $(CH_2)_3$ HMTTF

The main direction of these efforts involves:

(i) extending the π-conjugated system in order to minimise the Coulomb repulsion in the doubly ionised state of the donor; this is achieved by incorporation of cyclic or vinylogous spacers between the two 1,3-dithiole rings;

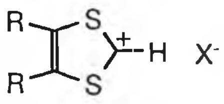
(ii) the replacement of the sulphur atoms with selenium and tellurium in order to increase the bandwidth and increase both the inter and intrastack Se-Se and Te-Te interactions which result in increased dimensionality; the increased polarisability of Se and Te should also reduce the on-site Coulomb repulsion;

(iii) synthesising TTF derivatives with substituents on the peripheral 2,3 and 6,7 positions to modify the electronic properties of the parent π-system and to increase the intermolecular interaction.

Since the numbers of donors synthesised in the last 20 years is enormous only the more important ones will be discussed here.

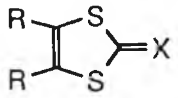
1.B.2 General synthesis of TTF and its derivatives

The most widely used routes to TTF derivatives proceed via coupling of 1,3-dithiolium salts (8) or 1,3-dithiole-2-thiones (9a) or -2-ones (9b).



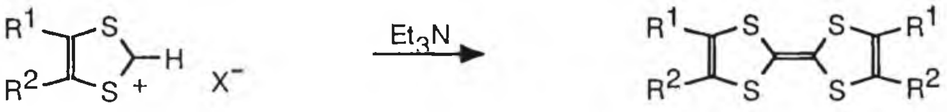
(8)

or



(9) a: X= S
b: X= O

The 1,3-dithiolium salts are coupled via the generation of a stabilised carbene, by deprotonation of the cation with a base, which can then attack the positive C2 centre of another cation. This method has been used for the synthesis of TTF (2a) [4] and its derivatives TMTTF (7b)[27] and HMTTF (7c),[28] Scheme 1.01.

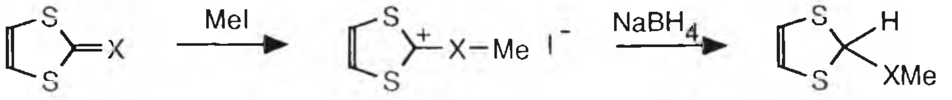


(8) a: $R^1 = R^2 = H$, $X^- = HSO_4^-$
b: $R^1 = R^2 = Me$, $X^- = ClO_4^-$
c: $R^1 - R^2 = (CH_2)_3$, $X^- = ClO_4^-$

(2) a: $R^1 = R^2 = H$, TTF
(7) b: $R^1 = R^2 = Me$, TMTTF
(7) c: $R^1 - R^2 = (CH_2)_3$, HMTTF

Scheme 1.01

The 1,3-dithiolium and 1,3-diselenium salts possessing a hydrogen in the 2 position are obtained by the alkylation of the corresponding 1,3-dithiolo-2-thione or -2-selenone with an alkylating agent, usually methyliodide, Scheme 1.02.



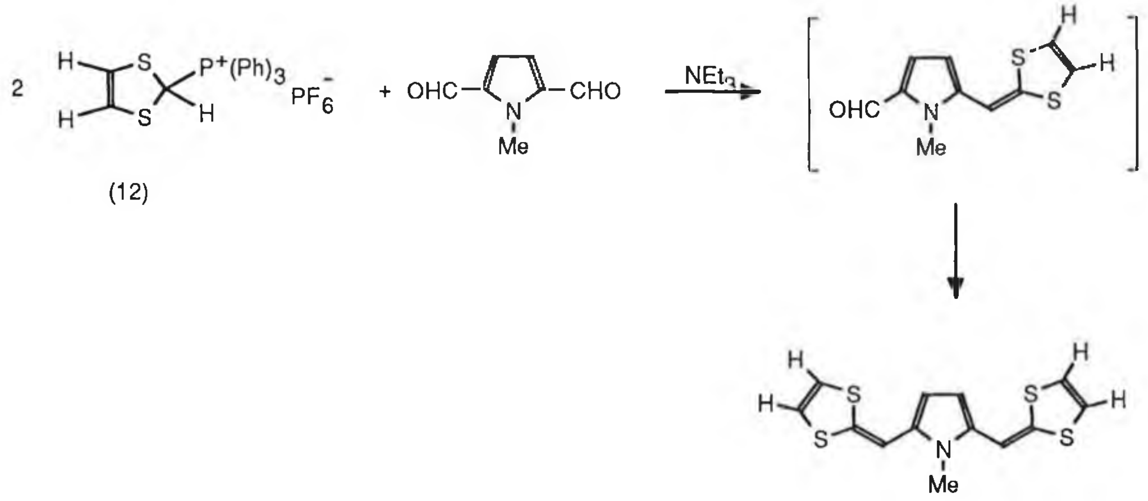
(10) a: X = S
b: X = Se
C: X = O

(11) a: X = S
b: X = Se

Scheme 1.02

This is followed by reduction of these salts with sodium borohydride, $NaBH_4$, which generates the 2-alkylthio- (11a) or 2-alkylseleno-1,3-dithiols (11b), and finally treatment of these with a strong acid like fluoroboric acid, or perchloric acid.

The reaction of 1,3-dithiolium cations with trialkylphosphines or phosphites give Wittig and Wittig-Horner phosphonium salts (12), which are the key intermediates in the synthesis of the vast array of vinylogues of TTF,[29] obtained by their reaction with aldehydes in the presence of base, Scheme 1.03.[30]

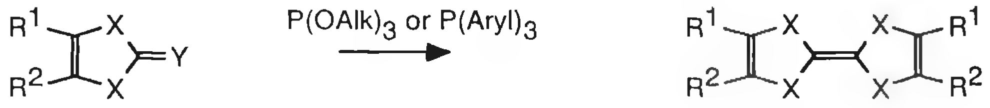


(12)

Scheme 1.03

The phosphoranes formed by the removal of a proton by base, usually triethylamine or butyllithium, can also couple with other 1,3-dithiolium salts to yield hybrid or unsymmetrical TTFs.

The 1,3-dithiolo-, and 1,3-diseleno-, -2-thiones, -2-selenones and -2-ones (13a-c) are also coupled using trialkyl or triaryl phosphines or trialkyl phosphites *via* desulfurisation, deselenation and deoxygenation. While this route has proven to be useful for selenones, which are more reactive, desulphurisation-coupling was only successful when electron-withdrawing substituents were present in the 4- and 5- positions of the 1,3-dithiole-2-thiones,[31] Scheme 1.04.



(13) a: R^1 - R^2 = $S(CH_2)_2S$, X = S, Y = O	(6a) BEDT-TTF
b: R^1 = R^2 = H, X = Se, Y = Se	(2b) TSeF
c: R^1 = R^2 = Me, X = Se, Y = S	(7a) TMTSF

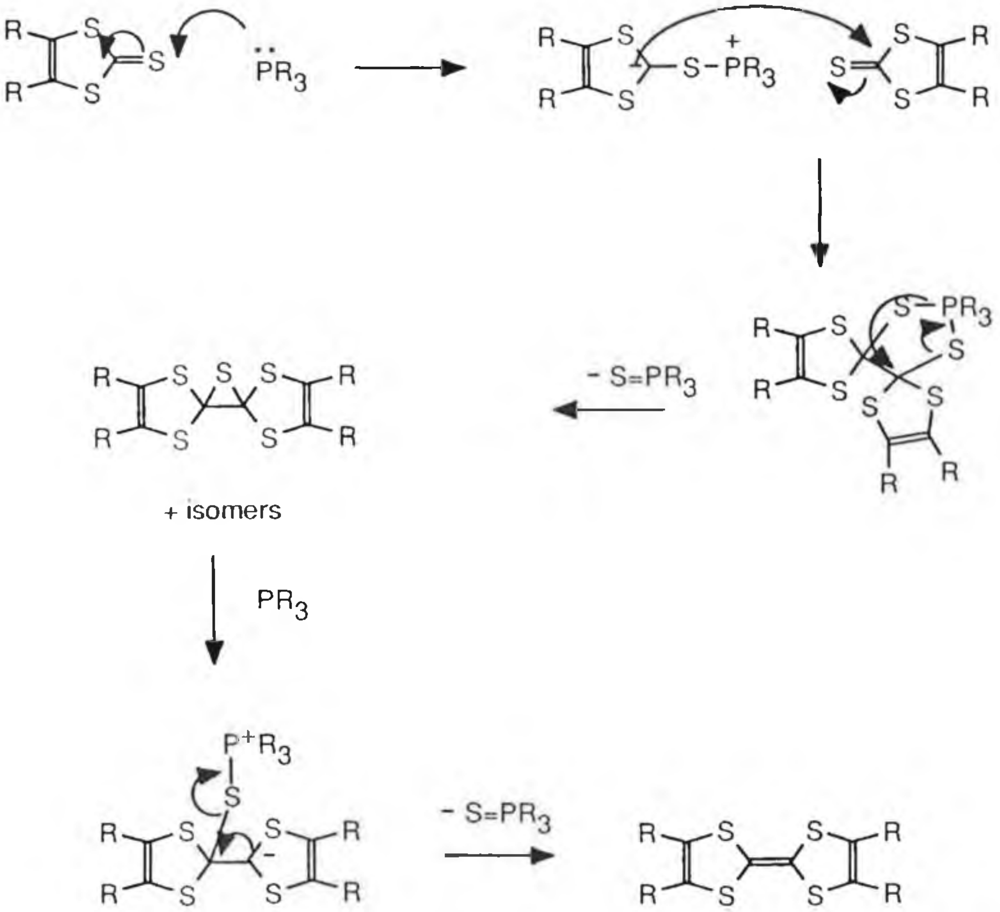
Scheme 1.04

It has been suggested[32] that in the majority of cases these TTF derivatives are most likely formed by reactions of the carbene with their precursor, or occasionally by reactions not involving carbenes at all, rather than by bimolecular carbene coupling, Scheme 1.05. This method of coupling is the most widespread but it does have its limitations in that the synthesis of unsymmetrical derivatives will yield mixtures of isomers.

An alternative to the phosphine or phosphite coupling has been the use of dicobaltoctacarbonyl, $Co_2(CO)_8$. This coupling reagent may be preferable in that it allows for a wider range of substituents.[33]

1.B.3 Peripherally substituted TTF analogues

Of the many modifications which have been carried out to improve the electronic properties of the parent TTF π-system, introduction of heteroatoms on its peripheral 2,3- and 6,7- positions have been the most exciting. These substituents were expected to increase interchain interactions, thus increasing the dimensionality and suppressing the M-I transitions to insulating or semiconducting states associated with one-dimensional systems.



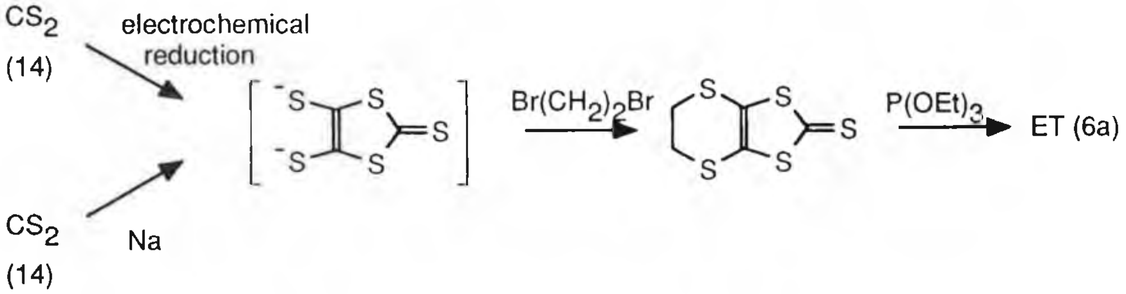
Scheme 1.05

1.B.3.1 TMTTF (7b) and HMTTF (7c)

Tetramethyltetrathiafulvalene, TMTTF (7b), and hexamethylenetetrathiafulvalene, HMTTF (7c), were the first compounds to suggest that peripheral substitution may actually improve the conductivity. While comparison of the room temperature conductivities of their TCNQ salts did not show any improvement (500, 350, 500 Scm^{-1} for TTF-TCNQ, TMTTF-TCNQ and HMTTF-TCNQ respectively), their σ_{max} did show improvement (2×10^4, 5×10^3, and 2×10^3 Scm^{-1} at T_{max}= 59, 60 and 75K respectively before the onset of a M-I transition).

1.B.3.2 Bis(ethylenedithiolo)tetrathiofulvalene (BEDT-TTF) or ET (6a).

Of the large number of organic superconductors known to date the majority are derived from ET. ET was the first sulphur-based donor to exhibit superconductivity and, contrary to previous conditions found necessary for good conduction, it was non-planar with the peripheral ethylene groups preventing good p-overlap between the donor molecules. ET was first synthesised[34] using carbon disulphide, CS_2 (14), as the starting material according to Scheme 1.06. This procedure has since been improved upon.[35]



Scheme 1.06

The ET family of superconductors can be divided into two main structural types according to the mode of the internal arrangement of the donor molecules. They are the β-phase and the κ-phase. An α and θ phase also exist but are less common. In the β-phase superconductors the ET layers are composed of loose stacks which are parallel to each other, giving rise to a "corrugated sheet" type 2-D network (Figure 1.11), in which the S-S interstack contact distances are less than the intrastack distances. In β-$(ET)_2AuI_2$, interstack $d_{S\text{-}S} \leq 3.60$Å, the van der Waals radius sum for S, whereas the intrastack $d_{S\text{-}S} \geq 3.60$ Å).[36] This 2-dimensionality is reflected in the anisotropy of the electrical conductivity, which for $(ET)_2ClO_4(C_2H_3Cl_3)_{0.5}$ [37] is a hundred to a thousand times higher in the sheet direction than in the stack direction.

The "corrugated sheet" of donor molecules is sandwiched between sheets of anions. The first ET salt synthesised, $(ET)_2ClO_4(C_2H_3Cl_3)_{0.5}$,[37] and the first ET based superconductor, $(ET)_2ReO_4$,[37] (T_C~2 K at pressures >4 kbar), exhibit a similar corrugated sheet network.

On replacing the tetrahedral and octahedral anions so successful in the Bechgaard salts (15), with a linear anion, the first ambient pressure superconductor $\beta(ET)_2\ I_3$ (T_C = 1.4 - 1.6 K) [37] was obtained.

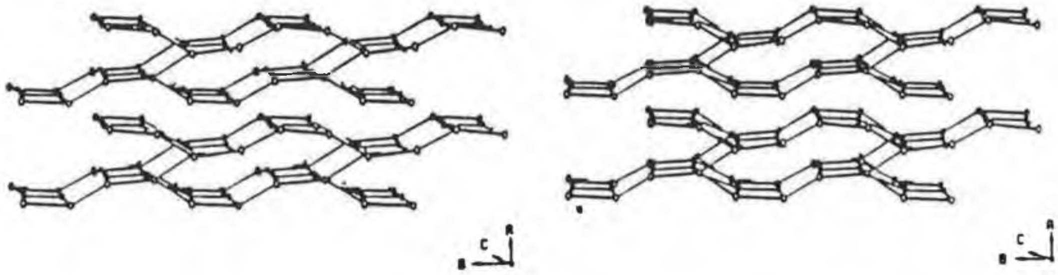
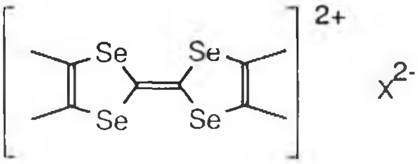


Figure 1.11 Corrugated sheet network of ET.cations found in β-phase salts.



(15)

By replacing the I_3^- anion with other linear anions of shorter length, it was believed that the S-S interstack distances would shorten and decrease the H atom cavity volume surrounding the anion. The IBr_2^- anion, ~7% shorter than I_3, gave $\beta(ET)_2\ IBr_2$, with an average shortening of the interstack S-S distances of ~ 0.02 A and resulting in a rise in T_C by a factor of 2-3.[37] With the discovery that anion disorder inhibits the onset of superconductivity, even on applying pressure up to 5 kbar,[38] it was proposed[36] that new ambient-pressure organic superconductors in the $\beta(ET)_2X$ class would contain centrosymmetric anions of specific length, close to that of IBr_2^- but less than I_3^-. This was vindicated by the synthesis of $\beta(ET)_2$ (I-Au-I)[36] with T_C= ~5 K at ambient pressure, and the length of the anion, I-Au-I, being intermediate between that of IBr_2^- and I_3^-.

Following this line of investigation into the effects of anion length led to the synthesis of the first organic compound, $(ET)_2Cu(NCS)_2$, to have T_C > 10 K at ambient pressure.[39] However this salt was found to have a different layer packing, called κ-phase type. κ-Phase type superconductors are comprised of ET dimers, with each dimer orientated orthogonally to its neighbour, giving rise to a zig-zag type pattern, Figure 1.12.

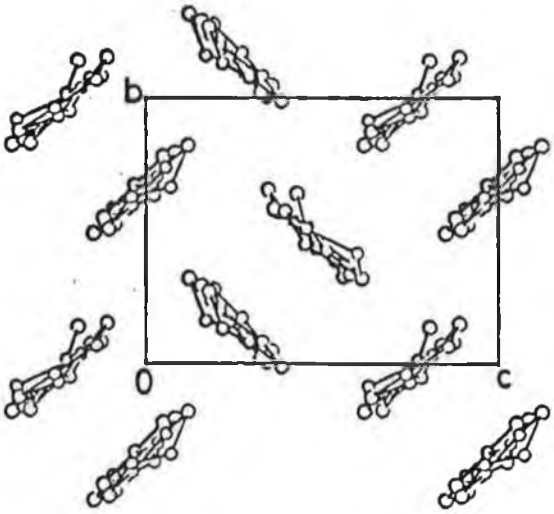


Figure 1.12 Zig-zag packing mode of ET cations in κ-phase type superconductors.

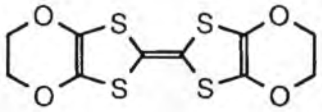
This results in the formation of a 2-D S-S network with the intercellular $d_{S-S} <$ 3.6 Å. For the $\kappa(ET)_2Hg(SCN)_{3-n}X_n$, [X=Cl (n=1, 2), F, Br, I (n=1)] salts, the intra-dimer S-S contact distances varied from 3.55 to 3.57 Å and the inter-dimer S-S contacts were in the range 3.40 - 3.53 Å.[40] The conducting layer of "zig-zagged" ET dimers in κ-phase salts is sandwiched by the insulting layers of V-shaped anions which arrange themselves into a 1-D flat polymer.

The search for other metal complex anions which were isostructural to $(ET)_2Cu(NCS)_2$ led to the synthesis of κ-$(ET)_2Cu[N(CN)_2]Br$ [8] which has the highest ambient pressure superconductivity (T_C=11.6 K) to date for an organic cation salt and κ-$(ET)_2Cu[N(CN)_2]Cl$,[9] a semi-conductor at ambient pressure but with a T_C=12.5 K at the slight pressure of 0.3 kbar.

At present no well-defined structure-property correlations exist for the determination of improved superconductivity in the κ-phase salts. The synthesis of new ET salts with polymer metal complex anions seems to be the most promising direction.

1.B.3.3 Bis(ethylenedioxy)-tetrathiofulvalene (BEDO-TTF; 6b)

The discovery of superconductivity in ET salts prompted the search for new donors structurally similar to BEDT-TTF. This resulted in the synthesis[41] of the oxygen equivalent of ET, BEDO-TTF (6b), with oxygen atoms replacing sulphur atoms on the periphery, giving rise to a cyclic ether analogue of TTF. This was inspired by the possibility that, if the organic superconductors were BCS superconductors, then the T_C would increase within a series of identical donors if there was a decrease in the overall molecular mass of the constituent molecules (BCS isotope effect) and, since oxygen is smaller and less polarisable than sulphur, the metallic bandwidth would decrease, the density of states near the Fermi level would increase and T_C would be raised.[42]



(6b)

Cyclic voltammetry studies showed that the first oxidation potential for BEDO-TTF is higher than that of TTF but its second is lower showing it to be better able to stabilise the dicationic state. Of the many metallic salts which BEDO-TTF forms with inorganic anions, only two have been found to be superconducting, β-$(BEDO\text{-}TTF)_3Cu_2(NCS)_3$ and $(BEDO\text{-}TTF)_2$ ReO_4 (H_2O), at ambient pressure and below 1 K and 2.5 K respectively.[39] Crystallographic analysis[42] shows that while BEDO-TTF salts give crystals of poor quality, those that have been characterised show that the salts contain sheets of donor stacks in which the interstack S-S and S-O contacts are less than the respective van der Waals radii of 3.6 Å and 3.33 Å.

While other organic superconductors exist[39] none have so far have been as promising as the ET based salts. Further investigations into why ET should exhibit superconductivity while related compounds with similar crystal-structures do not are necessary and may eventually lead to even higher transition temperatures.

1.B.3.4 Other substituted TTFs

While a huge variety of substituted TTF derivatives exist,[43] their synthesis involves several steps to give the pre-substituted 1,2-dithiolo-2-thione, -2-ketone or -2-selenone, which must then be coupled. However recent work in the synthesis of further derivatives of TTFs has involved modifying the preformed TTF. This has been achieved by the mono-lithiation and tetralithiation of TTF, which serves as the building block to a huge variety of new donors, with the ability to attach varying functionalities and to synthesise donors with multiple TTF units.

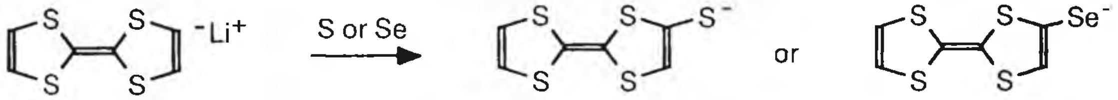
Monolithiation of TTF was first reported by Green [44] using n-butyllithium (n-BuLi) and also with lithium diisopropylamide (LDA) in ether at -70°C. The resulting mono-lithiated derivative TTFLi (16) could then be trapped with a variety of electrophiles (Scheme 1.07), *e.g.* $ClCO_2Et$, CO_2, CH_3COCl, dimethyl sulphate, HCHO. However one complication to this reaction involves the fact that TTFLi readily disproportionates at temperatures above -70°C to give di- and multi-substituted products. This method has been used in the synthesis of a huge variety of mono-substituted derivatives, linked to varying side chains through carbon,[45, 46] silicon, sulphur, selenium and tellurium.[46, 47]

(16)

R= Et, CO_2H, CH_3
R= $COC_{15}H_{31}$, $CO_2C_{16}H_{33}$, $SiMe_3$,
CO_2H, $SC_{18}H_{37}$, $TeC_{18}H_{37}$
R= $SCH_2O(CH_2)_2SiMe_3$, $SeCH_2O(CH_2)_2SiMe_3$

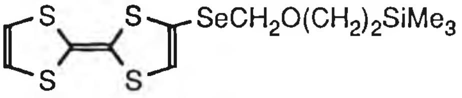
Scheme 1.07

Reaction of the mono-lithiated TTF (16) with elemental sulphur or selenium at -78°C yields the corresponding chalcogenate anion, (17) or (18), which is trapped by treating *in situ* with varying electrophiles and alkylhalides. These chalcogenate anions are reported to be considerably more reactive towards electrophiles than the lithiated TTF precursor.[47]

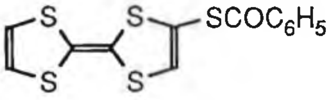


(16) (17) (18)

Trapping of the monoselenolate anion (18) with trimethylsilyl ethoxymethyl (SEM) chloride afforded a shelf-stable equivalent for the selenolate anion, (19). This could be recovered using tetrabutylammonium fluoride and the appropriate electrophile. While this method did yield the SEM derivative of the monothiolate salt, it was not recoverable as the thiolate anion. However the benzoyl derivative of the thiolate anion, (20), is a shelf stable equivalent and is regenerated with base.[48]

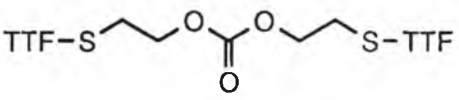


(19)

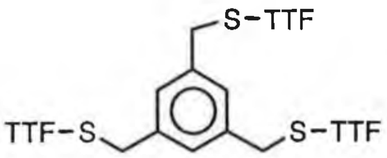


(20)

The TTF-thiolate anion has also been used to synthesise a range of new-bis and tris-TTF derivatives including (21) and (22).[48]

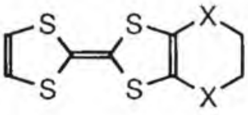


(21)

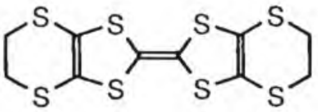


(22)

Other reactions involving the mono-lithiated TTF have led to the one-pot synthesis of the known unsymmetrical donor, EDT-TTF (23a) and EDS-TTF (23b), in low yields (10-20%).[47] On varying the molar ratios BEDT-TTF was obtained instead.

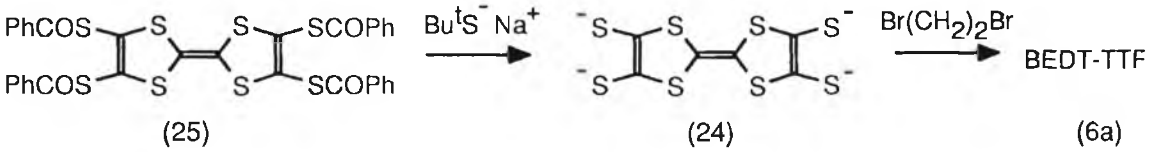


(23) a: X = S, EDT-TTF
b: X = Se, EDS-TTF



(6a) BEDT-TTF

The tetrathiolate ($TTFS_4^{4-}$; 24) [49] has also been exploited as a precursor to many tetrasubstituted TTF derivatives and like the monolithiated compound has been reacted with selenium.[50] BEDT-TTF (6a) has recently been synthesised from the tetrathiolate (24) by Hansen *et al* [51] from the tetra ester (25) by deprotection of the ester groups with sodium tert-butylthiolate, Scheme 1.08.



Scheme 1.08

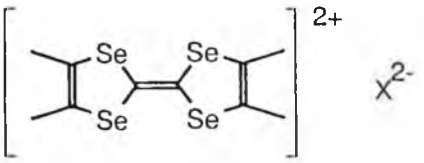
The ability of both the tetralithiated and the monolithiated tetrathiafulvalenes to undergo reaction with such a variety of electrophiles which in turn can themselves undergo a variety of further reactions, opens up a multitude of synthetic pathways to new donor compounds whose synthesis should further increase both the understanding of the structural characteristics which can lead to improved conductivity and higher temperature superconductivity.

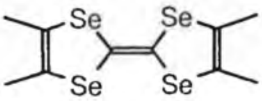
1.B.4 Selenium and Tellurium Derivatives of TTF

1.B.4.1 Selenium Derivatives of TTF

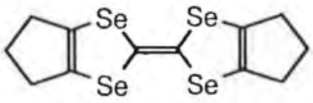
The extended d-orbital of both selenium and tellurium made them ideal replacements for sulphur in the search for increased interstack interactions, resulting in larger bandwidths and increased dimensionality. The synthesis of selenium derivatives has been far more successful than those of tellurium due to the difficulty in the synthesis of the latter. The variety of selenium derivatives is vast and many have been reported by Krief.[43] Initial indications that the replacement of sulphur with selenium would result in increased conductivity were proved correct when the 1:1 salt of TSF-TCNQ was found to have a conductivity of σ_{rt}= 800 Scm^{-1}, (TTF-TCNQ has σ_{rt}= 500 Scm^{-1}), and a M-I transition ~ 40 K, 18 K below that of TTF-TCNQ. It also has a conductivity of 10^4 Scm^{-1} at 40 K.[52]

The tetramethyltetraselenafulvalene salts $(TMTSF)_2X$ (15), where X is a monovalent inorganic anion such as PF_6^-, ClO_4^-, ReO_4^-, BFO_3^-, known as the Bechgaard salts,[7] caused a great sensation at the time of their synthesis, by becoming the first organic superconductors. Of these, the $(TMTSF)_2ClO_4$ salt was the first ambient pressure superconductor (T_c=1.3 K), which was achieved by slow cooling of the salt.[53]





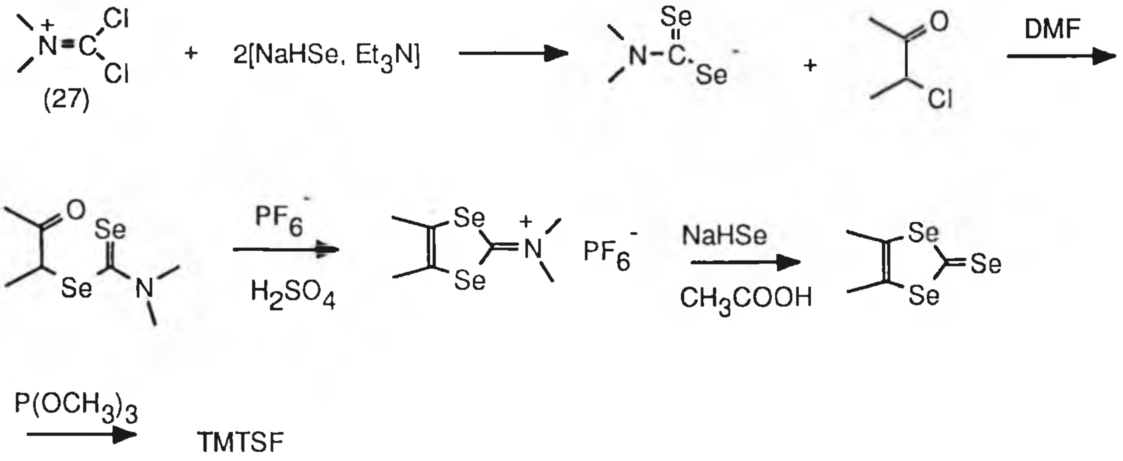
(7a)



(26)

(15) X = PF_6^-, ClO_4^-, ReO_4^-, BFO_3^-, TaF_6^- and SbF_6^-

The original syntheses[26] of TMTSF (7a) and HMTSF (26) involved the use of the extremely malodorous carbon diselenide and the highly toxic H_2Se (15 times more toxic than H_2S). An alternative routine[54] has been found using elemental selenium and dimethylphosgene iminium chloride (27), Scheme 1.09.



Scheme 1.09

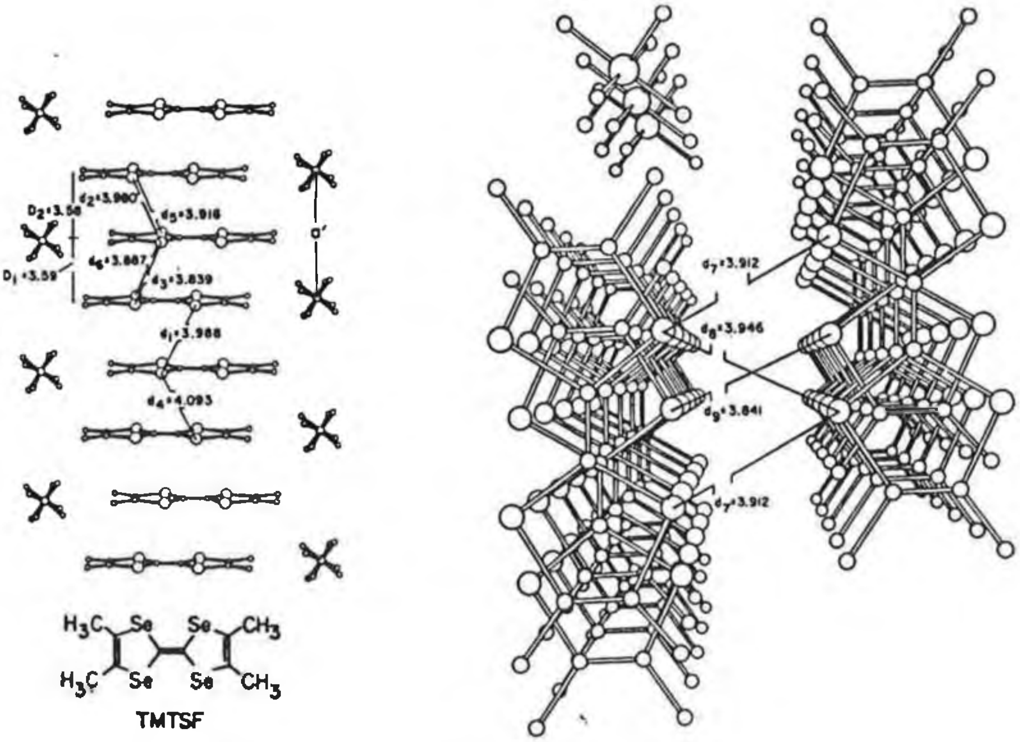
1.B.4.1.1 Synthesis of salts of TMTSF

Single crystals of $(TMTSF)_2X$ are obtained by electrochemical oxidation according to equation 4.

$$2n\,(\text{TMTSF}) + n\text{X} \xrightarrow{-ne^-} [(\text{TMTSF})_2\text{X}]n \qquad \text{equation 4}$$

Using a low constant current, the solvent (redistilled, dried and deoxygenated, usually THF or CH_2Cl_2) and the tetrabutylammonium salt of the appropriate anion are placed in the cathode compartment of a H-shaped cell, while at the anode the solvent, the anionic salt and the TMTSF are introduced. Platinum electrodes are placed in the cell and it is through oxidation of the donor at the anode that the crystals begin to grow. These 2:1 salts are all isostructural, independent of whether tetrahedral or octahedral salts are used. The TMTSF molecules are found to stack in a zig-zig pattern, with the highest conductivity along the stacking direction, Figure 1.13(a). In addition to this, there are short interstack Se-Se interactions, d< 4.0Å (van der Waals radius for Se) between the TMTSF molecules, which results in a sheet-like 2-D network with sheets of anions separating the donor sheets, Figure 1.13(b).

The anions themselves play no role in the electrical conductivity, which occurs through the network of Se-Se interactions but their symmetry and ordering do. Bechgaard [53(b)] found that the octahedral (centrosymmetric) salts, (X=PF_6^-, TaF_6^-, SbF_6^-) all exhibit high metallic conductivity with M-I transitions occurring between 12 and 18 K. Unlike the one-dimensional salts found before, the M-I transition found in these salts was the effect of a spin-density wave (SDW) distortion rather than a charge-density wave (CDW). The salts of TMTSF containing the non-centrosymmetric, tetrahedral anions (with the exception of a perchlorate salt) showed ambient pressure phase transitions at much higher temperatures (~40 K and ~130 K for BF_4^- and ReO_4^- respectively).[23]



(a) (b)

Figure 1.13 View of the crystal structure of (TMTSF)$_2$BrO$_4$ (a) perpendicular to the stacking direction showing the zig-zag pattern of the salt and (b) looking down the stacking direction showing the short interstack interactions.

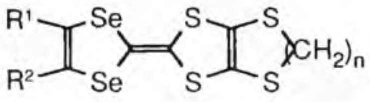
These transitions are associated with the ordering of the anions. The tetrahedral anions occupy two statistically equivalent positions and so are disordered. As the temperature is lowered the anions become ordered giving rise to a Peierls type instability. The application of pressure resulted in all but one, (the NbF_6^- salt), of the octahedral anions salt of TMTSF becoming superconducting at a critical pressure, P_c (6.5→12 kbar) at low temperatures (T_c ~0.4 -1.4 K). This is not surprising in light of the findings of Williams *et al*[37] that the decrease in the ratio of interstack to intrastack Se-Se distances is nearly 2:1, as the temperature is lowered, as compared to the room temperature Se-Se distances (~3.9 - 4.0 Å) which results in greater delocalisation through greater interchain interactions.

The perchlorate salt, $(TMTSF)_2ClO_4$, is unique among the TMTSF salts in that not only is the anion tetrahedral but it is superconducting at ambient pressure.[53(a)] One reason suggested for this, by Williams *et al*,[37] is again related to anion ordering. It was noted that in the $(TMTSF)_2$ X systems the anions reside in a "methyl group H-atom cavity". Thus the perchlorate anion resides in an asymmetric H-atom environment, with hydrogen-type bonding between H_2C---H---$OClO_3^-$, which "freezes" the anion in a disordered position even on cooling. However, the perchlorate salt has to be cooled slowly for this "freezing" to be achieved. This ability to maintain its order within the lattice along with its smaller cell volume (as compared with the larger octahedral anion) may account for its superconductivity at ambient pressure.

1.B.4.1.2 Derivatives of TSF

The ready coupling of 1,3-diselenole-2-selenones by the common phosphite coupling method had led to the synthesis of unsymmetrical dithiadiselenafulvalenes,[55] compounds (28 a-d). Of these the DMET donor (28a) which is a hybrid between TMTSF and BEDT-TTF, has been found to form seven superconducting salts.[39]

For the preparation of (28a), it was found that using 1,3-dithiolo-2-one gave a better yield and a cleaner reaction than the corresponding -2-thione and -2-selenone. The desired cross-coupling products were formed along with the symmetrical products BEDT-TTF and TMTSF, in a surprisingly higher ratio than expected[55] and the components were separated by chromatography.



(28) a: $R^1 = R^2 =$ Me, n = 2

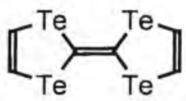
b: R^1-$R^2 = (CH_2)_3$, n = 2

c: $R^1 = R^2 =$ Me, n = 3

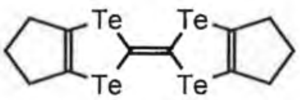
d: R^1-$R^2 = (CH_2)_3$, n = 3

1.B.4.2 Tellurium Derivatives

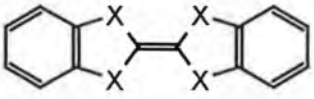
In order to see whether the anticipated effects of increased bandwidths and more polarizable donors were possible by replacement of the sulphur atom in TTF with tellurium, to give tetratellurafulvalene TTeF (2c), chemists had to wait until 1982 for the synthesis of the first tetratellurafulvalene, hexamethylenetetratellurafulvalene HMTTe (29).[56]



(2c)



(29) HMTTeF



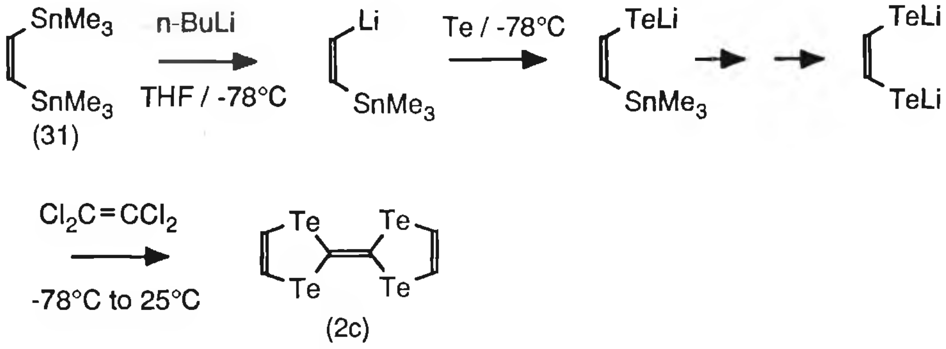
(30) a: X = S, DBTTF
b: X = Se, DBTSeF
c: X = Te, DBTTeF

The synthesis of dibenzotetratellurafulvalene,[57] DBTTeF (30c), soon followed. Cyclic voltammetry showed that DBTTeF had a lower oxidation potential than DBTSF (30b) but the same as its sulphur analogue (30a). This was explained by two factors which have opposite effects in the series S, Se, Te. These are that, while the ionisation potential decreases in the series S> Se> Te, the differences in the orbital interactions between carbon and the series members become smaller due to longer bond lengths. This has a stabilising effect on the HOMO making it more difficult to remove an electron. The separation between the first and second oxidation potentials ($\Delta E = E_{1/2}^{1} - E_{1/2}^{2}$) decreases in the series DBTTF> DBTSF> DBTTeF. This is consistent with the predicted effect of the heteroatom change on the on-site Coulomb repulsion.

The highly elusive, tetratellurafulvalene, TTeF (2c) was eventually synthesised in 1987, by Cowan and coworkers.[58] TTeF was prepared by treating 1,2-bis(trimethylstannyl)-1,3-butadiene (31) with n-butyllithium at -78 °C and then with microcrystalline tellurium at the same temperature. After all the tellurium had reacted, the first two steps were repeated and 0.5 equivalents of tetrachloroethylene was added at -78 °C to react with 1,2-dilithioditelluride. After chromatography, TTeF was isolated pure, Scheme 1.10. Cyclic voltammetry showed that TTeF had a first oxidation potential intermediate between that of TSF and TTF, similar to the case with the analogues dibenzofulvalenes.

The anticipated enhanced conductivity was obtained when the TCNQ complex of TTeF was synthesised by recrystallisation from a carbon disulphide solution[59] in a glove box, due to easy air oxidation of TTeF. TTeF-TCNQ was found to have a room temperature conductivity σ_{RT} ~1,800 Scm^{-1}. Like TTF-TCNQ, TTeF-TCNQ consisted of segregated stacks of TTeF molecules and TCNQ molecules and had a charge-transfer of 0.71 of an electron. Unlike its sulphur and selenium counterparts, it did not undergo a phase transition at low temperatures, nor did it undergo a transition to a superconducting state.

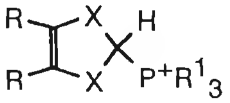
While the tetramethyltetratellurafulvalene still remains to be synthesised, other extended alkyl substituted TTeFs have been reported [13] in an attempt to improve their poor solubility and to permit investigation into their ability to form salts with inorganic anions.



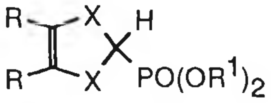
Scheme 1.10

1.B.5 Extended-π-Donors

Recent attention in the field of electron donor molecules has been directed at the synthesis of π-extended donors. The key to the synthesis of these compounds involves the reaction of the 1,3-dithiol-2yl- or 1,3-diselenol-2yl-phosphonium salts(32a and 32b) or the phosphonates (33a and 33b) with an aldehyde in the presence of BuLi in a Wittig or Wittig-Horner condensation reaction.



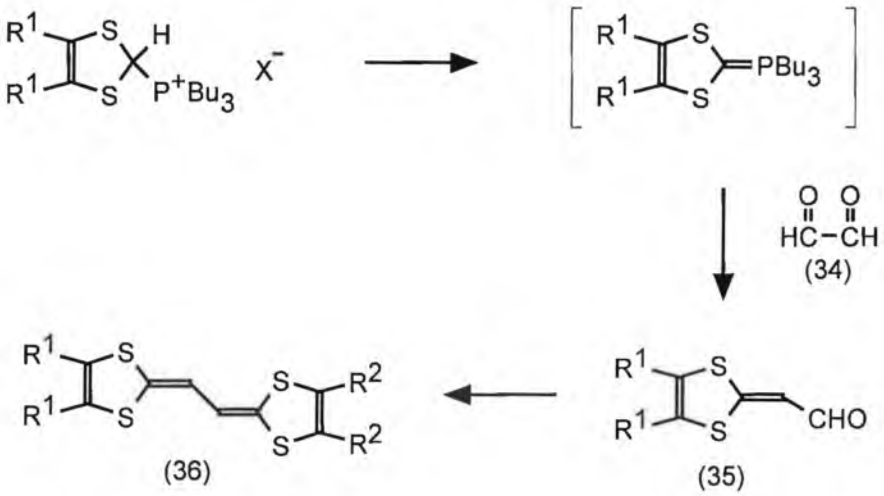
(32) a: X = S
b: X = Se



(33) a: X = S
b: X = Se

This method was used by Yoshida *et al* to prepare the first vinylogous TTFs[60] using the dialdehyde, glyoxal (34), Scheme 1.11.

This synthetic approach was also used to synthesise both symmetrical and unsymmetrical vinylogues of BEDT-TTF.[61] Vinylogous TTF was obtained from (36; R_1=R_2=CO_2Me) by decarbomethoxylation using lithium bromide/H_2O in Hexamethylphosphoric triamide HMPA.

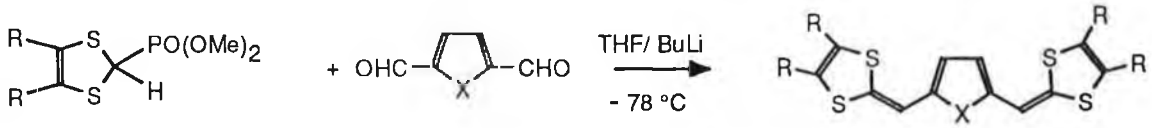


Scheme 1.11

A third double bond was also introduced by the reductive coupling of the aldehyde (35) in Scheme 1.11 above using titanium trichloride, lithium aluminium hydride and tributylamine in THF. On comparing the cyclic voltammetry data of the two vinylogous TTF compounds with that of TTF itself, it was found that in the derivative with two double bonds, the difference in the first and second oxidation potentials, $\Delta E = E\frac{1}{2}^{1} - E\frac{1}{2}^{2}$, were less than that for TTF. In the case of the dithiole units separated by three double bonds, the ΔE value decreased to zero, with only one oxidation wave being discernible.

Incorporation of various heterocyclic ring systems, including pyrrole, thiophene and furan, between the 1,3-dithiole rings has also been carried out. These reactions also take advantage of the reaction between the previously mentioned phosphoranes or phosphonates with the dialdehyde of the corresponding heterocycle.[31] Some examples include the extended ET (40a-c) and TTF (39a-c) systems, Scheme 1.12.

If the incorporation of a heterocycle can be viewed as two dithiole rings separated by four carbon-carbon double bonds then, by analogy with the behaviour of the two dithiole rings separated by three ethylene bonds, there should be little or no difference in the first and second oxidation potentials ($\Delta E = E\frac{1}{2}^{1} - E\frac{1}{2}^{2}$). This was found to be the case with the furan derivative (39a), which had ΔE= 0.00 V.[31] This small ΔE value is ascribable to the decreased intermolecular Coulomb repulsion in the dicationic state. The role of the heteroaromatic ring and the heteroatom also influence strongly the ΔE values. These are determined by the stability of the aromatic system when considering the various radical cation resonance structures and by the ability of the heteroatom to bear a positive charge in the dicationic state, the order of importance being pyrrole> furan> thiophene.



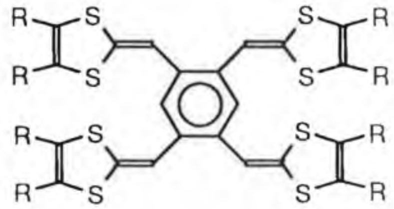
(37) a: $R = H$
b: $R\text{-}R = S(CH_2)_2S$

(38) a: $X = O$
b: $X = NMe$
c: $X = S$

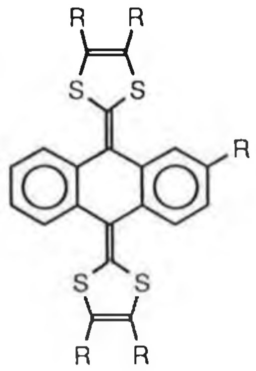
(39) a: $R = H, X = O$
b: $R = H, X = NMe$
c: $R = H, X = S$
(40) a: $R\text{-}R = S(CH_2)_2S, X = O$
b: $R\text{-}R = S(CH_2)_2S, X = NMe$
c: $R\text{-}R = S(CH_2)_2S, X = S$

Scheme 1.12

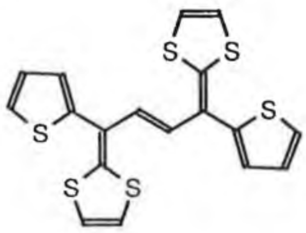
Many other extended analogues of TTF exist with some being synthesised not only with a view to reducing on-site Coulomb repulsion but also to enhance dimensionality through the greater number of intra and inter S-S contacts by increasing the number of sulphur heterocyclic moieties. Some examples of these include (41),[62] (42),[63] (43),[64] which were again synthesised by Wittig and Wittig-Horner reactions. They all form C-T complexes with TCNQ and (41) has formed microcrystalline inorganic salts with $Bu_4N^+X^-$ ($X=ClO_4^-$, BF_4^- and I_3^-).



(41)



(42)

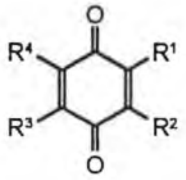


(43)

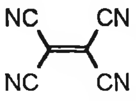
1.C Acceptors

1.C.1 Introduction

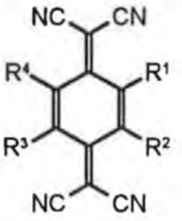
The ability of planar organic acceptor compounds to form C-T complexes derives from the presence of low-lying empty π-molecular orbitals (LUMOs) and also from their ability to stabilise the radical formed on reduction by distributing the odd electron over several atoms. For this reason *p*-benzoquinone (44a), and its tetra-halo derivatives (44 b,c,d), the anils, are strong electron acceptors and have been found to form highly conducting 1:1 C-T complexes with TTF and TMTTF. [65] The replacement of two halides with cyano groups gives a stronger acceptor, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, (DDQ; 44e). The fully cyano-substituted anil, tetracyano-1,4-benzoquinone, cyanil (44f), is the strongest acceptor that has been isolated in the neutral form.[66] It has a reduction potential more than 0.3 V greater than DDQ and tetrafluoro-TCNQ (46b).



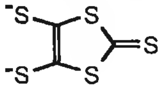
(44) a: $R^1 = R^2 = R^3 = R^4 = H$
b: $R^1 = R^2 = R^3 = R^4 = F$
c: $R^1 = R^2 = R^3 = R^4 = Br$
d: $R^1 = R^2 = R^3 = R^4 = Cl$
e: $R^1 = R^2 = Cl$, $R^3 = R^4 = CN$
f: $R^1 = R^2 = R^3 = R^4 = CN$



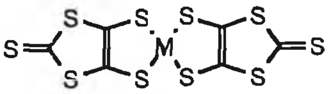
(45) TCNE



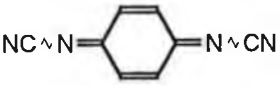
(46) a: $R^{(1-4)} = H$
b: $R^{(1-4)} = F$



(47)



(48) M(DMIT)



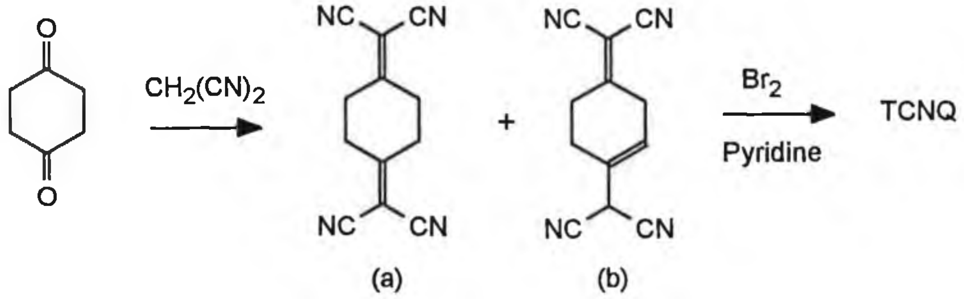
(49) DCNQI

Olefins containing strongly electron-withdrawing groups also act as acceptor molecules. Tetracyanoethylene (TCNE; 47) is a highly electron-deficient and strongly electrophilic reagent and forms C-T complexes with cycloalkanes[67], alkenes, alkynes and their aryl derivatives.[68] By combining the acceptor abilities of both TCNE and the *p*-benzoquinones, a powerful electron acceptor was conceived, 7,7,8,8-tetracyano-p-quinodimethane (TCNQ; 46a), whose electron acceptor ability was soon recognised.[3]

Since the discovery of one-dimensional electrical conductivity in the TCNQ-TTF complex, much effort has been devoted to the synthesis of novel donor and acceptor systems. The discovery that derivatives of TTF, TMTSF and ET, formed superconducting salts in the absence of an organic acceptor, directed the attention away from acceptor molecules. Consequently, while there has been a considerable amount of research carried out on acceptors during the last twenty years, most of the recent work has been carried out by only a few groups around the world. This research has focused mainly on the preparation of derivatives of TCNQ but also on two novel families of acceptor molecules; those of the metal complexes of the 4,5-dimercapto-1,3-dithiole-2-thione ligand (47), M(dmit)$_2$ (48) and *N,N'*-dicyano-quinone diimine (DCNQI; 49). Both of these form highly conducting complexes, with the former exhibiting superconductivity.

1.C.2 Synthesis of TCNQ

The synthesis of TCNQ was first described in 1962.[69] It was synthesised by the condensation of malononitrile with cyclohexane-1,4-dione, followed by bromination and dehydrobromination of 1,4-bis(dicyanomethylene)cyclohexane in the presence of pyridine, Scheme 1.13. The reaction can be carried out in benzene in the presence of a small amount of acetic acid and ammonium acetate (this gives a mixture of isomers before bromination) or in water in the presence of β-alanine, which gives one of the isomers (b) in higher yield.



Scheme 1.13

1.C.2.1 Synthesis of TCNQ Derivatives

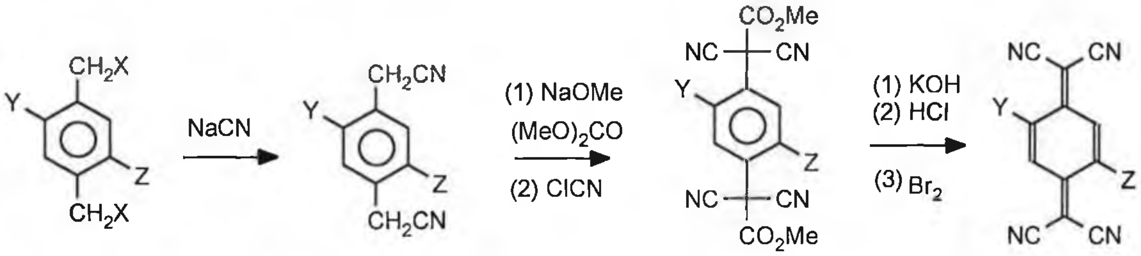
Because of the unusual stability and electrical properties of TCNQ, it has been desirable to investigate the steric and electronic effects of ring substitution. The main direction of efforts has involved:

(i) substituting various electron-withdrawing and electron-donating groups onto the 2-, 3-, 4- and 5- positions of the TCNQ ring; this allows "fine-tuning" of the electron-affinity and can also affect the crystal packing and stoichiometry of the C-T complex;

(ii) extending π-conjugation of the TCNQ unit both annularly and linearly; this can reduce the onsite Coulomb repulsion and the better overlap increases the bandwidth;

(iii) introducing larger, more highly polarisable heteroatoms, such as oxygen, nitrogen and sulphur, into the acceptor, either into the TCNQ ring itself or into adjacent fused-ring systems; this also reduces the onsite Coulomb repulsion and also increases both the inter- and intra-molecular interaction and thus widens the bandwidth.

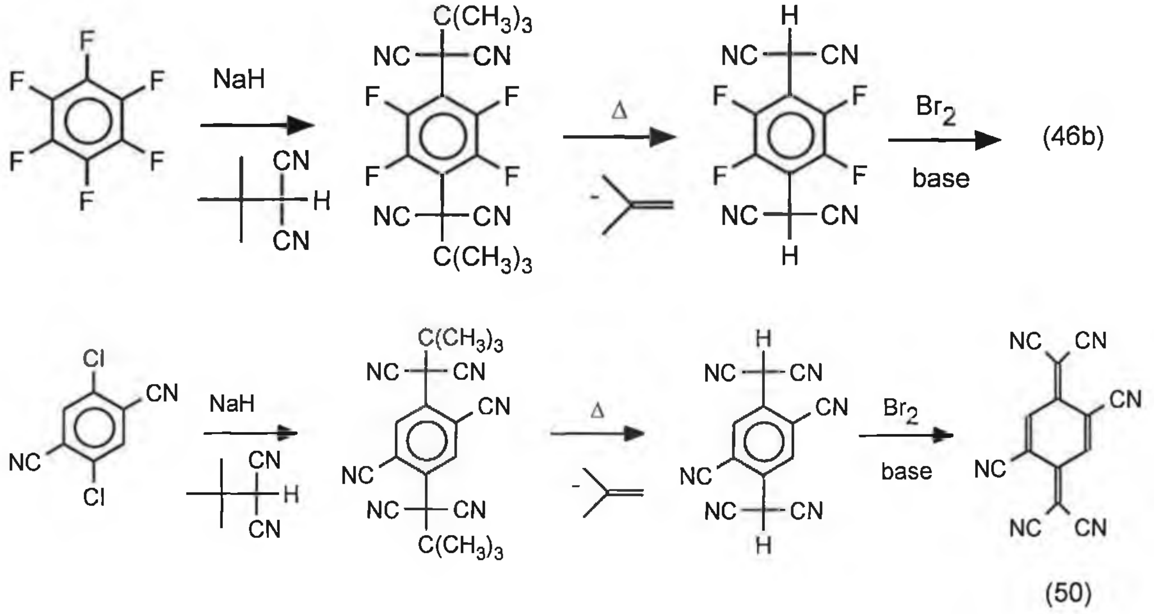
The alkyl derivatives, 2-methyl-, 2-propyl-, and 2,5-dimethyl-TCNQ, were synthesised by a similar procedure to that of TCNQ.[70] The synthesis of about 20 derivatives with different substituents on the 3- and 6- positions[71] has been carried out according to Scheme 1.14. These substituents include alkyl, alkoxy, halogeno, thioalkyl and cyano groups.



Scheme 1.14

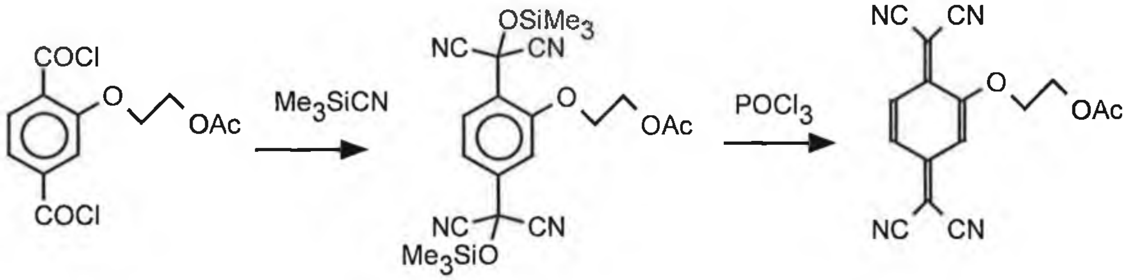
The 1,4-di(cyanomethyl)benzene derivatives were synthesised from the corresponding *p*-xylylenedihalides. The synthesis of the tetrafluoro- and 2,5-dicyano-TCNQ derivatives, (46b) and (50) respectively, was carried out by the condensation of *t*-butyl-malononitrile with hexafluorobenzene and 3,6-dichloro-1,4-dicyanobenzene respectively in the presence of sodium hydride, followed by thermolysis and oxidation as before, Scheme 1.15.

A convenient alternative to cyanogenchloride, CNCl, used in Scheme 1.15, is 2-chlorobenzylthiocyanate. This compound is shelf-stable and non-toxic. It has been used to synthesise a range of TCNQ derivatives[72] and has the advantage that, unlike CNCl, it is a selective cyanating agent and does not react with highly stabilised anions. Therefore tricyanomethane products are not formed and there is no need to insert the protecting ester groups. It is also versatile in that it has been used in a one-pot procedure for the synthesis of TCNQ derivatives bearing electron-withdrawing, electron-donating or fused ring groups.[72]



Scheme 1.15

Terephthaloyl chloride (51) when treated with an excess of trimethylsilanecarbonitrile produces a 1,4-bis[dicyano (trimethylsiloxy) methyl]benzene. Treatment of this with phosphorous oxychloride removed the siloxy group, Scheme 1.16.

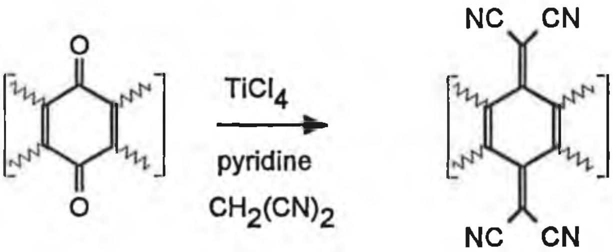


(51)

Scheme 1.16

1.C.2.2 Alternative routes to TCNQ derivatives

(i) Knoevenagel condensation of malononitrile with the corresponding quinones in the presence of Lehnert's reagent ($TiCl_4$ and pyridine),[73] Scheme 1.17.



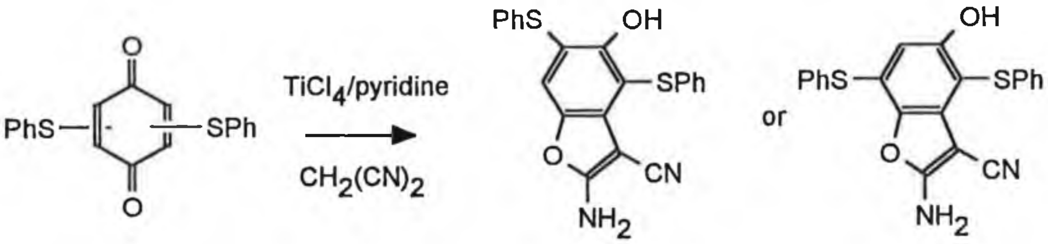
Scheme 1.17

This method has been useful in its simplicity, in that it affords ready replacement of the carbonyl moiety of the quinone/arylketone with a dicyanomethylene. Many TCNQ derivatives[74] have been synthesised in this way, including many π-extended TCNQ derivatives.

However this method is not always applicable. A 1,4-addition of malononitrile to the quinone ring of 2,5- and 2,6-diphenylthiobenzoquinones[75] (52a and b) (Scheme 1.18) and a 1,6-addition of malononitrile to the initially formed mono-dicyanomethyl quinone(53), giving a tricyano derivative (54) (Scheme 1.19), have been reported.[76]

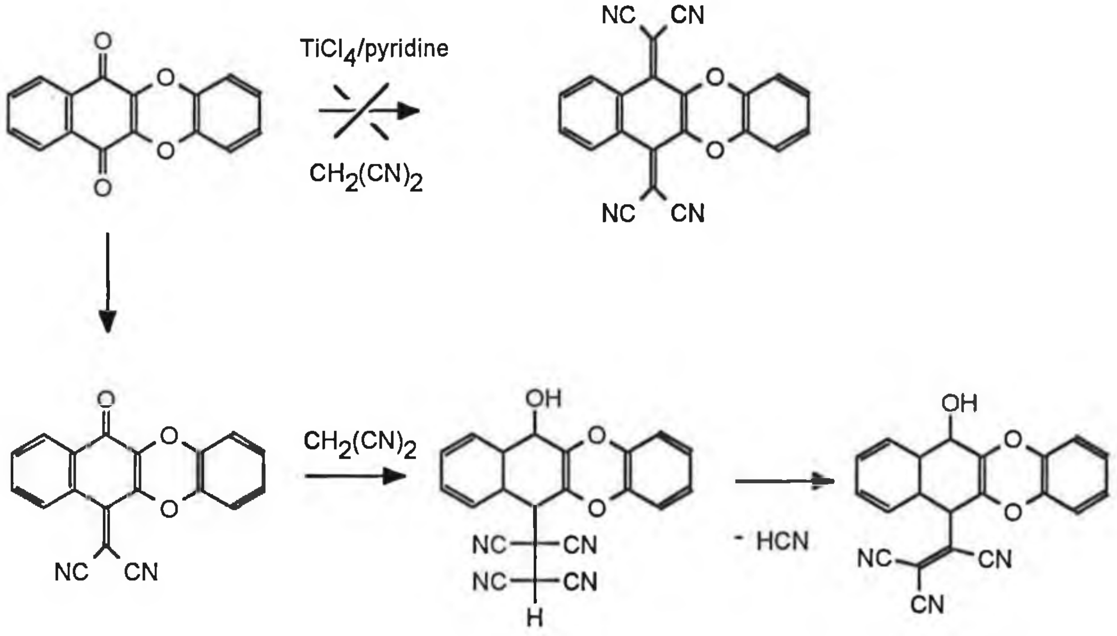
(ii) Palladium(0) catalysed reactions.

Phenylenedimalononitrile and some alkyl and alkoxy derivatives were also synthesised by the palladium(0) catalysed reaction between dicyanomethanide and the corresponding 1,4-diiodo- or dibromo-benzenes.[77] Many hetero-TCNQ analogues have also been synthesised by this method, Scheme 1.20.



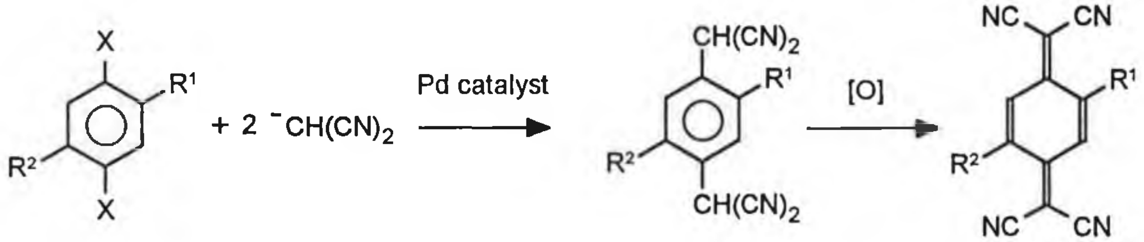
(52) a: 2,5 isomer
b: 2,6 isomer

Scheme 1.18



(53) (54)

Scheme 1.19

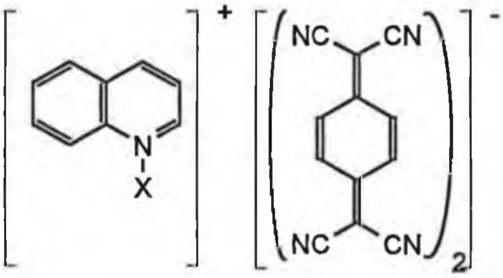


a: X= I, R^1= R^2= H
b: X= Br, R^1= R^2= H
c: X= I, R^1= R^2= Me, Et or OMe

Scheme 1.20

1.C.3 TCNQ C-T Complexes

Initial evidence of the electrical conducting ability of TCNQ was found as far back as 1963 when it was reported that the 1:2 salts of quinolinium-(TCNQ)$_2$ (55a) and *N*-methylquinolinium-(TCNQ)$_2$ (55b) were found to have a room temperature conductivity, σ_{rt}, of ~100 Scm^{-1}.[78] The discovery of TTF-TCNQ was to be the milestone by which the synthesis of future C-T salts would be measured and it has also been the most extensively studied. The crystal structure of TTF-TCNQ was found to be made up of segregated columnar stacks of planar donor and acceptor molecules with the inter-molecular stacking distances less than the van der Waals stacking distances for the neutral species. [2] It was also found to exhibit metallic behaviour between 293K (σ_{rt}=500 Scm^{-1}) and 59 K (σ_{max}=~10^4 Scm^{-1}) and undergo a M-I transition at 53 K.[79]



(55) a: X= H

b: X= Me

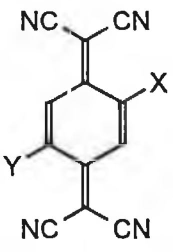
The degree of C-T, ρ, has been found to be incomplete, with 0.59 electrons [80] being transferred to the TCNQ stack. TTF-TCNQ has also been found to be highly anisotropic in its conductivity, with higher conductivity in the stacking direction than in any other direction.

The key features of TTF-TCNQ which make it so highly conducting is the similarity in size and symmetry of the donor and acceptor molecules. Both are planar molecules with extensive π-delocalisation throughout the molecule and both the ionisation potential of TTF and the electron-affinity of TCNQ favour partial electron transfer.

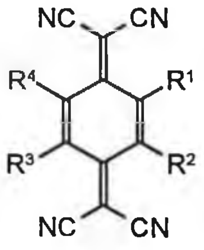
TCNQ also forms C-T complexes with a variety of TTF derivatives.[81] TTeF-TCNQ [82] was found to have σ_{rt}=1800+/-300 Scm^{-1} and is metallic in behaviour down to 90-100 K. This increase in room temperature conductivity can be accounted for by the expected increase in the donor overlap.

1.C.3.1 C-T Complexes of Non-ring fused TCNQ Derivatives

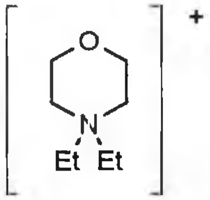
In the search to identify the requirements for enhanced conductivity in compounds similar to TCNQ and TTF, Wheland and Gillson synthesised about 80 conductive C-T complexes [19] with the majority of the acceptors being derivatives of TCNQ and were able to correlate electrical conductivity with redox potentials, steric effects and heavy atom substitution[83]. In looking for trends in a series of complexes of TCNQ derivatives with TTF, it was found that the stronger acceptors for which complete electron transfer was most likely, TCNQ(CN)$_2$ (56a) and TCNQF$_4$ (46b), gave poorly conductive complexes with compaction resistivities of 10^6 and 5000 Ωcm respectively, whereas the weaker electron acceptors, TCNQ (46a) and TCNQClCH$_3$ (56b), gave highly conductive complexes with compaction resistivities of 0.1 and 0.2 Ωcm respectively. It appears that conductivity is associated with moderately strong acceptors, *i.e.* those with a redox potential between -0.02 V and +0.35 V, in combination with moderately strong donors with a first redox potential between 0.1 V and 0.4 V, such that the redox potentials are closely matched, *i.e.* (E_{1A}-E_{1D} <0.25 V). However these correlations are subject to strict crystal structure. Substitution of the TCNQ ring with increasingly bulky groups appears to have only minor effects until five to six side chain carbons or oxygens are introduced. The resistivity of TTF complexes of TCNQEt$_2$ (56c) and TCNQ-*i*-Pr$_2$ (56d) increases from 0.05 to 2.10 Ωcm. TMTCNQ (57) has been reported to be non-planar,[72c] with strong deformation of the TCNQ skeleton into a boat-conformation owing to the steric factor and in addition to its weak π-acidity fails to form C-T complexes with TTF or TMTTF.[74] Similar steric effects have also been observed for TCNQBr$_2$ (56e) and TCNQCl$_2$ (56f). The X-ray structure of neutral (56e) [72b] shows that while the molecule is essentially planar, the exocyclic carbon-carbon double bond bends in the plane of the ring away from the adjacent bromine atoms and that the cyanide group adjacent to the bromine is slightly non-linear unlike the cyanide group removed from the bromine which is almost linear. This is presumed to be a steric effect. Compound (56e) also forms four complexes with 4,4-diethylmorpholinium (58) of stoichiometries 1:1, 1:2, 2:3 and 3: 4 with all four complexes being insulators at 293 K.[84] The X-ray crystal structure of the 1:2 complex [85] shows that the



(56) a: X= Y= CN
b: X= Cl, Y= Me
c: X= Y= Et
d: X= Y= i-Pr
e: X= Y= Br
f: X= Y= Cl



(57) R$^{(1-4)}$= Me

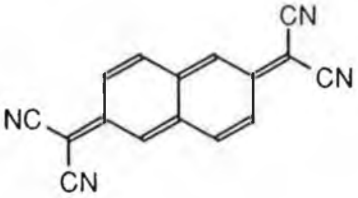


(58)

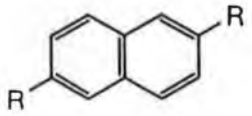
(56e) dimerises in columns similar to the 1:1 complex but with a peculiar interdimer twisted ring-ring overlap. This intra-stack "mirror image flip" and twisting of the $TCNQBr_2$ molecules has been explained as a way of efficiently minimising steric repulsion between bulky bromine atoms. The poor conductivity of these complexes has been associated with increased electron affinity of (56e) (0.41 V compared with 0.17 V for TCNQ)[19] which seems to result in complete electron transfer.[84]

1.C.3.2 C-T Complexes of π-extended TCNQ Derivatives

In an effort to achieve the metallic state, the Coulomb interaction must be minimised.[86] This is achieved by designing acceptor compounds with electron-withdrawing groups at diametrically distant points on the molecule and is manifested by a lowering of the difference, $\Delta E_{1/2}$, of the first and second half-wave reduction potentials of the acceptor ($E^1{}_{1/2}$-$E^2{}_{1/2}$). The first π-extended TCNQ derivative to be synthesised was TNAP (59), synthesised [70] from 2,6-dimethylnaphthalene (60a) by a method similar to that used for the synthesis of TCNQ. This method has since been improved by increasing the yield of the intermediate 2,6-naphthalenediacetonitrile (60b)[87] and also by the adoption of a novel synthesis of 2,6-naphthalenedimalononitrile (60c).



(59)



(60) a: R= Me

b: R= CH_2CN

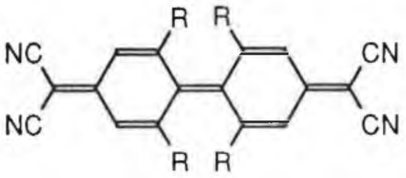
c: R= $CH(CN)_2$

d: R= CH_2Br

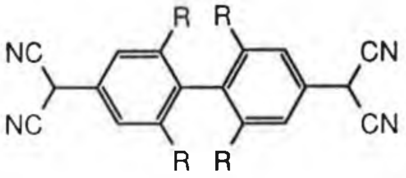
TNAP was also synthesised by Bryce *et al* [72b] in three steps from 2,6-bis(bromomethyl)naphthalene (60d) in a poorer yield. TNAP is a stronger π-acid than TCNQ and the smaller $\Delta E_{1/2}$ value shows that there is a reduction of the on-site Coulombic repulsion. However while TTF-TNAP has been found to be a poorer conductor (σ_{rt}=40 Scm^{-1}) than its TCNQ counterpart (σ_{rt}=500 S cm^{-1}), HMTSF-TNAP has been found to be highly conducting with

σ_{300K}=2400+/-600 Scm^{-1} rising to 15,000 Scm^{-1} at T=50 K and its extrapolated zero temperature conductivity is at least 250 Scm^{-1}.[88]

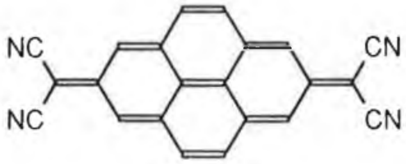
In the search for new acceptors with the desirable features of a π-extended system combined with the high symmetry of TCNQ, a number of groups[89] attempted to synthesise 13,13,14,14-tetracyanodiphenoquinodimethane (TCNDQ; 61a) but this resulted in the recovery of polymeric materials attributed to the high instability of TCNDQ due to the repulsive interaction of the "biphenylic hydrogens". TCNDQ was finally synthesised, along with its more stable bridged analogue TCNTHPQ (61b), by dideprotonation of 4,4'-bis(dicyanomethyl)biphenyl (62a) and 2,7-bis(dicyanomethyl)-4,5,9,10-tetrahydropyrene (62b) respectively to give the corresponding dianion which in turn was electrochemically oxidised.[90] TCNTHPQ and its pyrene analogue (TCNP; 63) have also been synthesised by a similar method with final oxidation, or dehydrogenation step, being carried out using DDQ.[91] These all show two reversible reduction potentials but



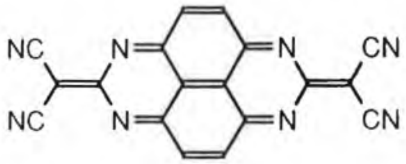
(61) a: R= H, TCNDQ
b: R= CH_2CH_2, TCNTHPQ



(62) a: R= H
b: R= CH_2CH_2



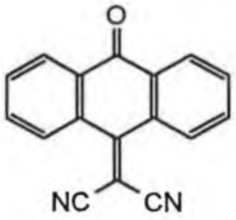
(63) TCNP



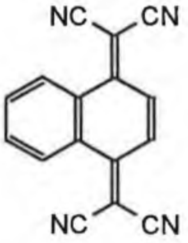
(64) TCQQ

with the $\Delta E_{1/2}$ values (0.16, 0.23 and 0.30 V for TCNDQ, TCNTHPQ and TCNP respectively) less than those for TCNQ (0.56 V), and showing reduction of the on-site Coulomb repulsion. C-T complexes of TCNDQ with TTF and TCNTHPQ with TTF and TMTTF (σ_{rt}=0.2 Scm^{-1}) have also been obtained. The nitrogen analogue of TCNP, TCQQ (64) has also been reported [92] and the presence of the more electronegative nitrogens resulted in no oxidation potential being observed in the range from -0.88 to +1.8 V.

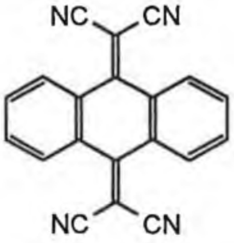
Outlined in Table 1.0 are most of the π-extended TCNQ derivatives that have been synthesised in recent years and a comparison of their reduction redox potentials. A general trend which is apparent is that the strength of the acceptors appears to be reduced as increasing numbers of fused benzenoid rings are added. This marked decrease has been attributed to the deviation of the dicyanomethylene groups from planarity as a result of the close proximity of *peri*-hydrogens. This has been verified by the X-ray crystal studies of 10-dicyanomethyleneanthrone (65),[97] benzo-TCNQ (66),[98] TCAQ (67) [99] and the sulfur containing compounds (68) and (69).[96] All of these exhibit the same butterfly shape distortions, with the central ring bent into boat form, and that this may be due to steric hindrances, is further supported by the fact that the dicyanomethylene group nearest the sulphur atom in (68) is more coplanar with the rings than the other due to the absence of the *peri*-hydrogen. Furthermore, (69) with its additional fused ring, as with the other extended acceptors, should be more severely distorted from planarity and this has been confirmed from the UV spectrum and the shifting of the conjugated cyano groups in the FT-IR. These extended TCNQ derivatives all fail to form C-T complexes with TTF and this can be attributed to their reduced planarity. In addition some of these compounds show a third additional electron reduction to the trianion. It has been suggested that this additional electron is taken up by the less charged residual arenediyl fragment which is the next LUMO. These NLUMOs are similar in shape and energy to the comparable LUMOs of dialkyl-substituted hydrocarbons.[100]



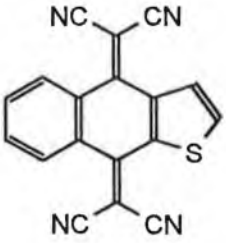
(65)



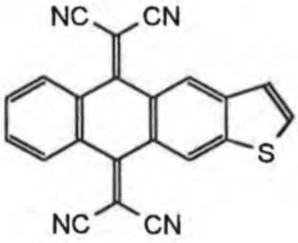
(66)



(67)

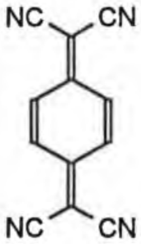
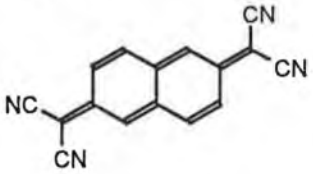
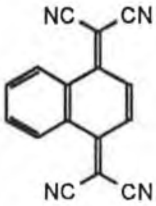
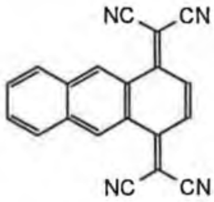
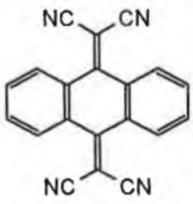


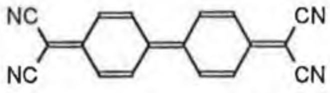
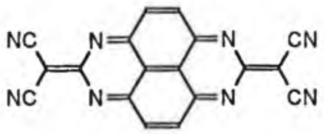
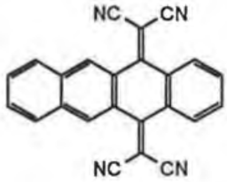
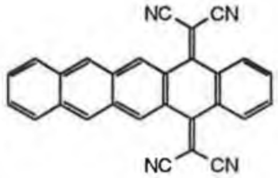
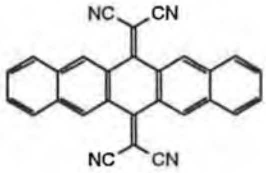
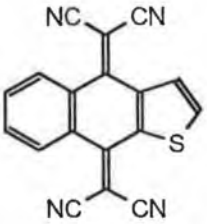
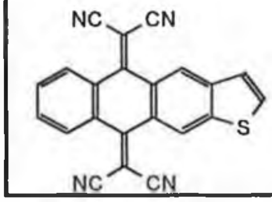
(68)



(69)

Table 1.0 Cyclic Voltammetric data for π-extended TCNQ derivatives (in volts)

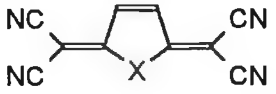
compound	solvent	$E_{1/2}^1$	$E_{1/2}^2$	$\Delta E_{1/2}$	$E_{1/2}^3$	ref.
 TCNQ	CH3CN	0.08 0.17	-0.48 -0.37	0.56 0.54		93
 TNAP		0.23	-0.13	0.36		94
 benzo-TCNQ		-0.04	-0.41	0.37		95
 naphtho-TCNQ		-0.18	-0.48	0.03		95
 TCAQ		-0.285			-2.06	95

 TCNDQ	0.13	-0.03	0.16		94
 TCQQ	not measurable (>+1.8 V)				94
	-0.44	-0.93	0.49	-1.85	95
	-0.50	-0.92	0.42	-1.54	95
	-0.57	-0.91	0.34	-1.61	95
		-0.18 (2e)			96
		-0.37 (2e)			96

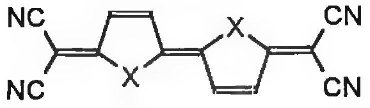
1.C.4 Heteroquinoid Electron Acceptors

In contrast to the extensively studied tetracyanoquinodimethane (TCNQ), it is only recently that heteroquinoid analogues of TCNQ have been synthesised and examined as potential acceptors. These heteroquinoid analogues are derived from selenophene (70b), furan (70c), and most importantly, thiophene (70a). It was believed that the increased intra- and inter-molecular interactions of the chalcogens, which were so successful for the donors, would be as effective for the acceptors. In addition, the heterocyclic systems would also avoid the steric interactions in linearly conjugated systems by assuming the *trans* configuration, and could also reduce the amount of interaction between dicyanomethylene groups and *peri*-hydrogens.

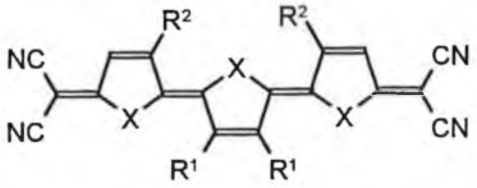
(70) a:X= S
b:X= Se
c:X= O



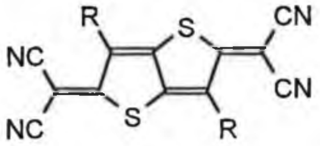
(71) a:X= S
b:X= Se
c:X= O



(72) a:X= S
b:X= Se
c:X= O

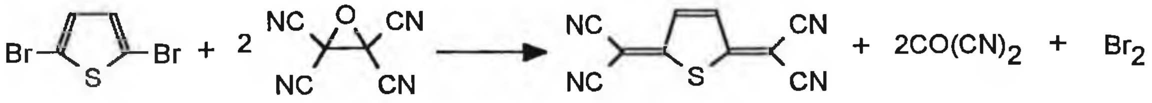


(73)a:X= S, R^1=R^2= H
b:X= O, R^1=R^2= H
c:X= O, R^1= H, R^2= Br



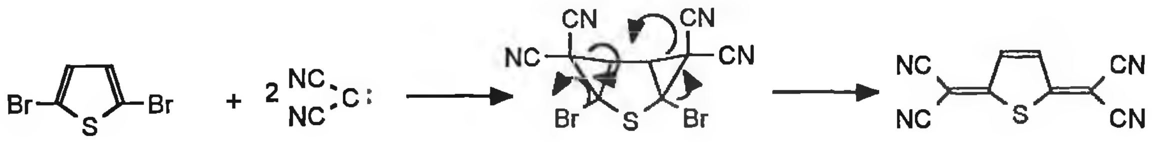
(74) a:R= H
b:R= Br

The first heteroquinoid TCNQ, or hetero-TCNQ, to be synthesised was 2,5-bis(dicyanomethylene)-2,5-dihydrothiophene (71a), which was discovered serendipitously by Gronowitz and Uppström while investigating cycloaddition reactions of tetracyanoethylene oxide (TCNEO) with dihalothiophenes.[101] On reacting TCNEO with 2,5-dibromothiophene a red liquid and a yellow solid were obtained which were found to be carbonyl cyanide and (71a) respectively, Scheme 1.21.



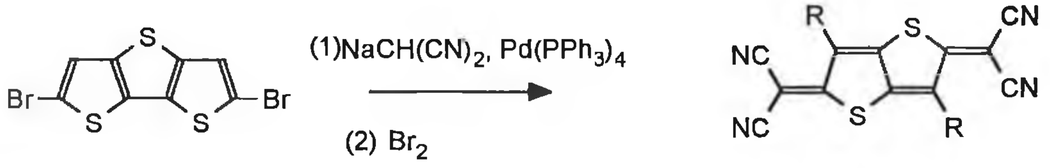
Scheme 1.21

The mechanism for this reaction was thought to be rather complex, the most likely being the 2,3- and 4,5-cycloaddition of the carbene, dicyanomethylene, to the 2,5-dibromothiophene followed by the rearrangement shown below. The carbene and carbonyl cyanide are generated by the thermal dissociation of TCNEO. A weak support for this mechanism is the presence of tetracyanoethylene as a minor by-product.



The selenoquinoid and furanoquinoid analogues, (71b)[101] and (71c),[102] were also synthesised by a similar method, as was their extended analogues, compounds (72a),[103] (72 b and c),[102] (73a)[103] and (74a and b).[104]

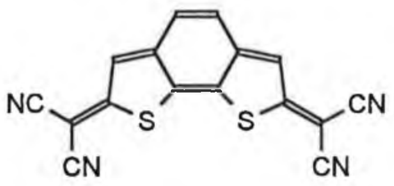
Some hetero-TCNQs were also synthesised by Pd(0) catalysed substitution of the corresponding halides of the heteroaromatics with sodium dicyanomethanide, followed by appropriate oxidation using bromine, DDQ, or lead tetraacetate, Scheme 1.22. This method has been used to synthesise the acceptors (73a and b),[102] (75),[104] (76) to (78)[105] and (79)[106].



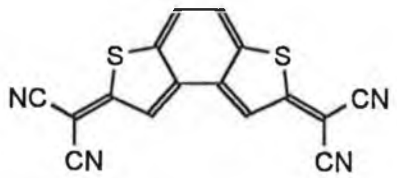
(75)

Scheme 1.22

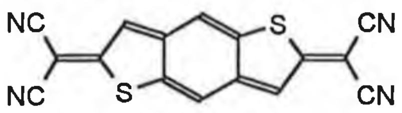
A reaction path for this method has postulated the initial formation of an arylpalladium intermediate,[107] Scheme 1.23, which may be able to undergo insertion of the stabilised anion with loss of halide, giving intermediate (80) which then rearranges to give the substituted product.



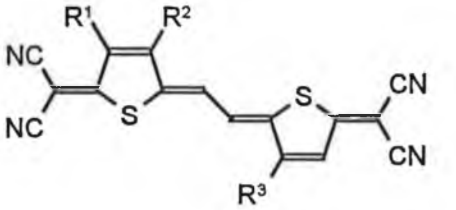
(76)



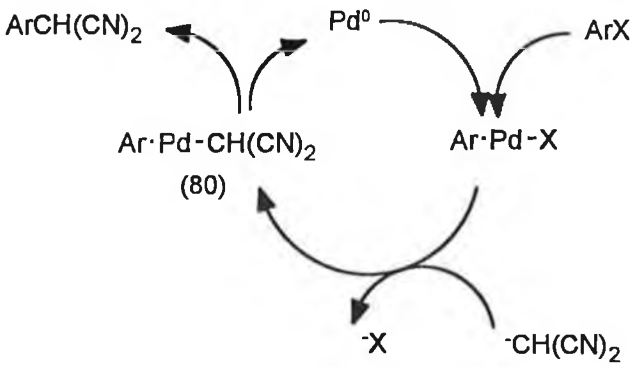
(77)



(78)



(79)a:$R^1=R^2=R^3=$ H
b:$R^1=$ H, $R^2=R^3=$ Br
c:$R^1=R^2=$ Br, $R^3=$ H



Scheme 1.23

1.C.4.1 Acceptor Properties of Hetero-TCNQs

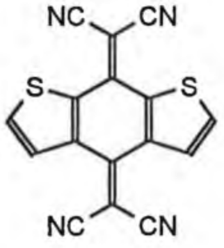
Compound (71a) was found to have poor acceptor ability, $E_{1/2}{}^1= +0.07$, $E_{1/2}{}^2= -0.50$ V, with the selenoquinoid and furanoquinoid analogues being poorer again, $E_{1/2}{}^1= +0.03$, $E_{1/2}{}^2= -0.51$ V, and $E_{1/2}{}^1= +0.03$, $E_{1/2}{}^2= -0.55$ V, respectively.[102] The furanoquinoid acceptor (71c) is a poorer acceptor because, although oxygen is more electronegative and would be expected to be a better acceptor, this same property reduces the aromaticity of the resultant furan ring of the dianion. The conjugated homologues of these heteroquinoids were also investigated. These were found to be poorer acceptors but showed enhanced ability to reduce the on-site Coulomb repulsion, with terheteroquinoid conjugation leading to a coalescence of the first and second redox potentials. However, in spite of their poor electron acceptor ability, they were still capable of forming some C-T complexes with TTF. It was found that, for the TTF complexes with (71a) and its extended homologues, (72a) and (73a), the conductivity of the complexes increased in line with the extended conjugation from $6.7x10^{-9}$, 2.2×10^{-4} to 3.3×10^{-3} Scm^{-1} respectively.[103] Acceptor ability was enhanced by introduction of additional electron-withdrawing substituents. The 3,6-dibromo derivative (74b) of the condensed homologue, 2,5-bis(dicyanomethylene)-2,5-dihydrothieno[3,2-b]thiophene (74a), has been found to be a better acceptor than TCNQ, i.e. $E_{1/2}{}^1$= +0.25, $E_{1/2}{}^2$= -0.13 V, ΔE= 0.38 for the dibromo derivative and $E_{1/2}{}^1$= +0.25, $E_{1/2}{}^2$= -0.47 V, ΔE= 0.72 for TCNQ. Compounds (74a) and (74b) form highly conducting C-T complexes with many donors, especially HMTTeF, whose 1:1 complex with (74a) and 2:1 complex with (74b) have room temperature pressed pellet conductivities of 140 and 170 Scm^{-1} respectively.[104]

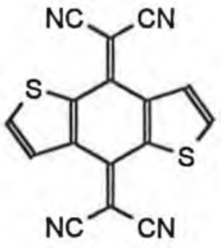
A crystal structure of (74a) and BEDT-TTF[108] has shown that (74a) is planar and forms a segregated stack structure along the a-axis, nearly perpendicular to the molecular plane. Intermolecular S-S contact distances between alternately stacked components are slightly longer than the van der Waals radius (3.70 Å). There are, however, several short contacts within the plane. There are interactions between the S atoms of adjacent BEDT-TTF molecules (3.64 and 3.59 Å) and the nitrogen atoms of the acceptor (3.33 Å). There are also interactions between the S atoms of the acceptor (3.48 Å) which shows their potential as multi-dimensional organic metals.

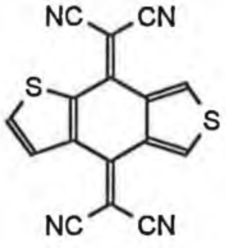
Recently, condensed benzothiophenes (76)-(78) have been synthesised.[105] These were investigated because the weak electron affinity of the other hetero-TCNQs was mainly attributed to the lesser aromaticity of the aromatic sextets arising from the heteroquinoid reduction. The benzothiophenes have the ability to form strongly aromatic benzenoid intermediates on reduction and should therefore form strong electron acceptors without the need for the introduction of more electronegative groups which can interfere with the crystal packing and intermolecular interactions. These acceptors show improved electron acceptor ability compared to TCNQ and the reduced ΔE values show enhanced reductions of the on-site Coulomb repulsions.

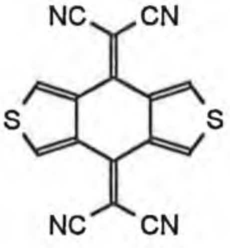
In an attempt to eliminate the distorting effect on the planarity due to the steric interaction between the dicyanomethylene groups and the *peri*-hydrogens of benzannulated derivatives of TCNQ, like TCAQ, a number of new acceptors have been synthesised which are heterocyclic rings fused to TCNQ.

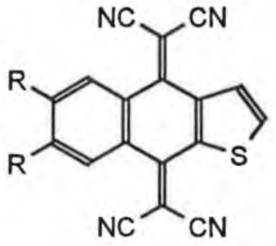
It was also hoped that the presence of the heteroatoms would also lead to increased intra- and intermolecular interactions. The four isomeric benzothiophene analogues (81)-(84) of TCAQ all showed two reversible one-electron reduction potentials, with (81) and (82) showing potentials close to that of TCNQ, $E_{1/2}^1$= +0.13, $E_{1/2}^2$= -0.19 V, ΔE= 0.32, and $E_{1/2}^1$= +0.13, $E_{1/2}^2$= -0.21 V, ΔE= 0.34, respectively and (83) and (84) showing weaker acceptor ability.[109]

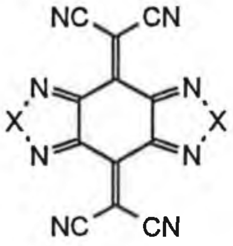

(81)

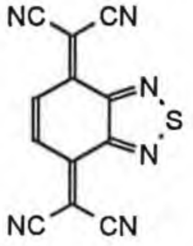

(82)


(83)


(84)


(85) a:R= H
b:R= Cl


(86) a:X= S
b:X= Se


(87)

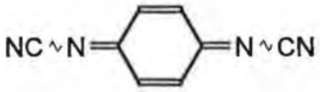
This has been attributed to the formation of a stable aromatic benzothiophene on reduction of (81) and (82). This improved acceptor ability suggests that the acceptors are planar and this is enhanced by their ability to form highly conducting C-T complexes with TTF; (81):TTF and (82):TTF have pellet conductivitys of 0.89 and 4.78 Scm^{-1} respectively. The mono-thiophene fused derivatives of TCAQ, (85a and b), which contained an annulated benzene ring, still exhibited a butterfly shape with the central benzene ring taking on a boat conformation due to the steric interactions of the *peri*-hydrogens with the cyano groups.[110]

X-ray structural analysis of TCNQs fused with 1,2,5-thiadiazole (86a) and 1,2,5-selenadiazole (86b) rings show that they are planar and crystallise in sheetlike networks with short sulphur to cyano and selenium to cyano contacts.[111] The mono-fused 1,2,5-dithiazole derivative (87) was found to have improved acceptor ability over the bis-fused homologue with a first reduction potential of $E_{1/2}^1$= +0.12 V, compared with $E_{1/2}^1$= -0.02 V for (86a).

Compound (87) also formed more highly conducting C-T complexes with TTF and its derivatives indicating that the inclusion behaviour shown by C-T complexes of (86a), whose extra heterocyclic ring gave rise to the formation of inclusion cavities, were diminished.[112] The X-ray structure of (87) showed that the planar molecule forms a coplanar dyad by hydrogen bonding with the cyano groups and the hydrogens on the adjacent quinodimethane ring. Although there is no S-S or S-N heteroatom interaction in the crystal , the dyad formation of (87) shows the possibility that the negative charge can be delocalised over two molecules in the anion radical salts, which is another approach to reducing the on-site Coulomb repulsion.

1.C.5 *N,N'*-Dicyano-*p*-quinodiimine (DCNQI) Acceptors

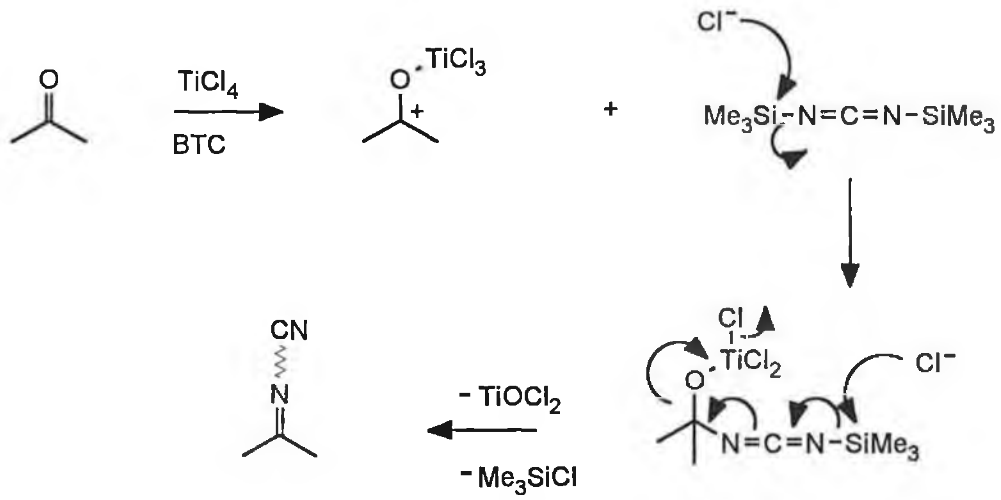
An alternative family of acceptor molecules with the same Würster type redox system as TCNQ is the *N,N'*-dicyano-*p*-quinodiimine (DCNQI; 88) family which was discovered by Hünig and coworkers.[113] This family of acceptors has several distinct features which make it attractive as a novel group of acceptors. One of the main advantages is that of its facile one-step synthesis from the corresponding quinone. Secondly, owing to the small angle formed by the =N-CN group, the planarity of the acceptor molecule remains virtually unaltered even upon tetrasubstitution. Finally DCNQI has essentially the same redox potentials[114] ($E_1^{1/2}$=+0.39 and $E_2^{1/2}$= -0.25 V) as TCNQ ($E_1^{1/2}$= +0.39 and $E_2^{1/2}$= -0.28 V) and this can be varied easily by appropriate substitution with more electronegative groups. Furthermore, the symmetries and energies of the LUMOs of DCNQI and TCNQ have been found to be almost identical.[115]



(88)

1.C.5.1 Synthesis of DCNQI and its derivatives

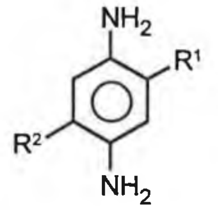
The synthesis of DCNQI can be carried out in a one-pot reaction by a method which can be applied to non-enolizing ketones and a whole variety of substituted benzo-, naphtho- and anthraquinones, Scheme 1.24 .



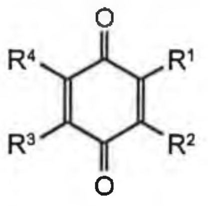
Scheme 1.24

The crucial reagents in this reaction are bis(trimethylsilyl)carbodiimide (BTC) and titanium tetrachloride ($TiCl_4$). This reaction counts among the few reactions involving condensation at the carbonyl group of a quinone. While an alternative synthesis using 1,4-substituted *p*-phenylenediamines (89a-c) exists,[116] this has its limitations in that it involves more than one step, gives intermediates which are difficult to handle, and a lesser variety of derivatives compared to the quinones, since only a few substituted phenylenediamines are easily accessible. The use of cyanide as well as fluoride catalysts did work for some difficult to enolise ketones but not for some quinones which tend to undergo 1,4-addition and are more readily reduced.[113] This was overcome with the use of a Lewis acid. A variety of Lewis acids were investigated including aluminium chloride, tin(IV) chloride, ether-borontrifluoride, and triisopropoxytitanium chloride all of which were found to be inactive or caused decomposition of the *p*-benzoquinone. Finally the highest yields were obtained using titanium tetrachloride especially when added first to the quinone.

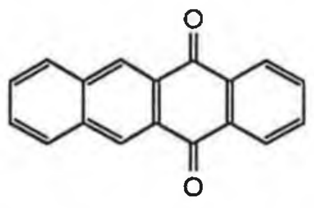
This method has proved very versatile giving reasonable yields for a broad range of substituted *p*-benzoquinones (90a-e),[113, 116, 117] including those with bulky substituents and differing redox potentials as well as 1,4-naphthoquinones,[113, 116, 117] 9,10-anthraquinones,[113, 116,] 1,4-anthraquinones[118] and the highly extended quinones (91) and (92).[119]



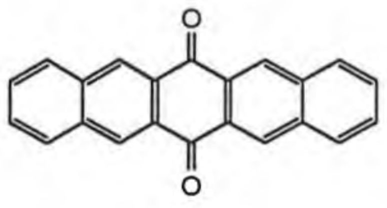
(89) a: $R^1=R^2=$ H
b: $R^1=R^2=$ Me
c: $R^1=R^2=$ Cl



(90) a:$R^1=R^2=R^3=R^4=$ H
b:$R^1=$ Me, $R^2=R^3=R^4=$ H
c:$R^1=R^3=$ Me, $R^2=R^4=$ H
d:$R^1=R^2=R^3=R^4=$ Me
e:$R^1=R^3=$ Me, $R^2=R^4=$ Me

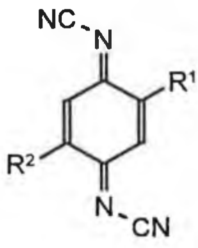


(91)

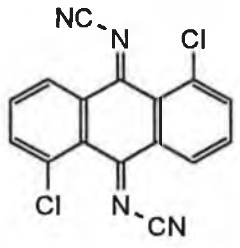


(92)

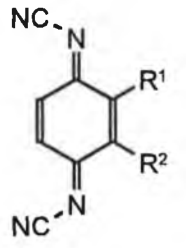
The N-CN group of the bifunctional dicyanimines may occupy *syn* and *anti* positions with respect to the neighbouring ring atoms, so that a maximum of four isomers is possible. In all the DCNQI derivatives the configuration of the cyano group is determined by the substituent pattern. In general the 2,5-substituted and 2,3-substituted dicyanimines exist only in that configuration in which the CN moiety prefers the *anti* position to the ring substituents. Accordingly the *anti* configuration is observed in substituent types (93) and (94) [115]and the *syn* configuration in types (95) and (96). This has been verified by ^{13}C and ^{1}H NMR data of these compounds.[113, 116] The non-substituted DCNQI compound (88) can be found as a *syn* /*anti* mixture according to ^{13}C NMR spectroscopy. The tetrasubstituted dicyanimines undergo rapid isomerisation which is evident from the NMR, with the number of NMR signals



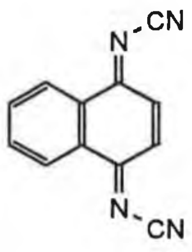
(93)



(94)



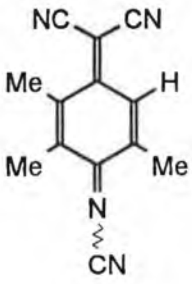
(95)



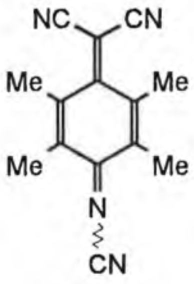
(96)

R^1 and R^2 can be Me , Et, *i*Pr, *t*Bu, Ph, Cl, F, Br, I, OMe, SMe *etc.*

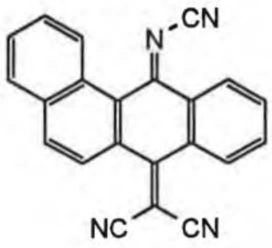
being strongly diminished. The monosubstituted derivatives also exist as a mixture of *syn /anti* isomers with one cyano group fixed in the *anti* position. Molecular mechanical studies on the DCNQI derivative of 2-methylanthraquinone predicted this and was in agreement with the NMR results.[118] It also indicated that the anthraquinone DCNQI derivatives were nearly planar. This has been found to be the case even for the tetrasubstituted DCNQI derivative of the 2-methyl-9,10-anthraquinone as demonstrated by X-ray analysis. X-ray structural analysis of the tri- and tetramethyl-substituted hybrid derivatives of DCNQI and TCNQ, (97) and (98),[120] showed that (98) is strongly distorted into a boat conformation with greater deformation about the bulkier $=C(CN)_2$ than about the =NCN group. In contrast (97) is essentially planar since the N-CN group can easily adopt an enlarged dihedral angle. A similar situation was also found for another TCNQ-DCNQI hybrid acceptor, (99), which showed a slight deviation from planarity, again with the greater deviation occuring about the $=C(CN)_2$ group.[119]



(97)



(98)



(99)

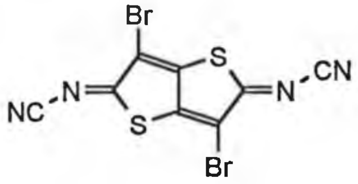
As stated already DCNQI itself has similar redox reduction potentials to TCNQ. The acceptor ability can then be improved by introducing more electronegative substituents (tetrachloro-DCNQI has $E_1^{1/2}$= +0.76 and $E_2^{1/2}$= +0.16 V).[113] Nearly all the DCNQI derivatives show two one-electron reversible reduction waves to the corresponding anion and dianion. However a continuous trend has been found which shows that increased benzannulation results in a shift of the first reduction potentials toward more negative values[121] and this leads to a reduction of the on-site Coulomb repulsion. The lower reduction potentials can be improved as before by introducing more electronegative substituents.

1.C.5.2 C-T Complexes of DCNQI

Charge-Transfer complexes have been successfully obtained from a number of derivatives of DCNQI and various donors. One of the first synthesised, and the first to yield crystals of sufficient quality to give an X-ray crystal structure, was that of *N,N'*-dicyano-1,4-naphthoquinonediimine (96) and TTF.[122] This complex has a 1:1 stoichiometry of donor to acceptor and σ_{300K} = 25 Scm^{-1}. The fact that this acceptor forms a C-T complex with TTF while its TCNQ analogue does not, due to non-planarity enforced on it by the $=C(CN)_2$ group, demonstrates the advantage of the =NCN group over the $=C(CN)_2$. The complex consists of separated stacks of donors and acceptors which occur in pairs, and which are equidistant at room temperature. It is suggested that an electrostatic interaction between the negatively charged N-atoms on the *syn* configured =N-CN groups and the sulphur atoms of the TTF was responsible for this. This interaction causes two stacks of the acceptor to crystallise in pairs in such a way that the unsubstituted part of the naphthalene skeleton are facing each other. The complex exhibits metallic behaviour and undergoes a phase-transition to a semiconducting state at 140 K.

In the X-ray structure of the DCNQI-TTF. 2 H_2O,[123] the donors and acceptors crystallise out in segregated stacks in chess-board-like arrangement. Both donors and acceptors are skewed in the same direction which is in contrast to TCNQ-TTF, in which the donors and acceptors were skewed in opposite directions. However both complexes crystallise in the same space group, P 2_1/c. The degree of charge transfer has been found to be 0.48 electrons which is one of the prerequisites for metallic conductivity in that there is incomplete charge transfer. DCNQI-TTF. 2 H_2O shows a single crystal conductivity of σ_{rt} = 1-10 Scm^{-1} and exhibits semiconductor behaviour in that its conductivity decreases as the temperature decreases.

One DCNQI derivative which has shown very high conductivity, ($\sigma_{\text{(single crystal)}}$ = 200 Scm^{-1}), and which is one of the best conducting C-T complexes with TMTSeF as donor, is the heteroquinoid acceptor 2,5-bis(cyanoimino)-3,6-dibromo-2,5-dihydrothieno-[3,2-b]thiophene (100).[124] This novel group of S-heteroquinoid acceptors were investigated to see if the properties of the DCNQI system were retained if incorporated into a heteroquinoid system. These new acceptors were synthesised from the corresponding quinones as before, but using higher temperatures. Compound (100) also formed C-T complexes with TTF, TMTTF, TTT, and BEDT-TTF. The crystal structure of (100)-TTF shows segregated stacks of donors and acceptors which are almost equidistant at room temperature. (100)-TTF also exhibits metallic behaviour and undergoes a transition to a semi-conducting state at 160 K.

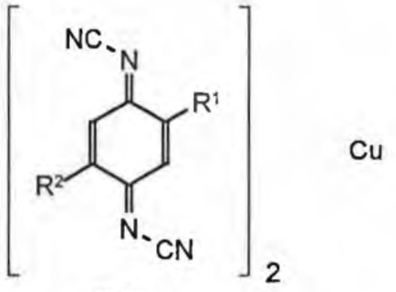


(100)

1.C.5.3 DCNQI Radical Anion Salts

In addition to forming C-T complexes with organic donor molecules, the DCNQI family of acceptors also form radical ion salts. By far the most important DCNQI derivatives to form radical ion salts are the 2,5-disubstituted DCNQIs which form 2:1 salts with metals,[123] including the alkalis, thallium , rubidium, silver and, most importantly copper. Unusually, all these metal salts crystallise in the same space group or at least in subgroups.[123, 125] All the non-copper metals are very similar in that the metal-to-N interactions of the cyano group are close to the van der Waals radius of nitrogen and the ionic radius of the metal ions, which suggests that Coulomb interactions are present. This has been found to be the case with the non-copper radical ion salts. They behave as metal-like semiconductors, showing a gradual increase in conductivity on lowering the temperature and then at a particular temperature , ~100 K, they undergo a sudden phase transition to a semiconducting state. This is characteristic of one-dimensional conductors which are prone to phase transitions at low temperatures.

Of the metal radical ion salts to be mentioned thus far, the copper salts deserve special mention. The (2,5-dimethyl-DCNQI)$_2$ Cu salt in particular, was found to be highly conductive with a single-crystal conductivity of 800 Scm^{-1} which increases continually as the temperature is lowered, giving a conductivity, σ, of 500 000 Scm^{-1} at 3.5 K.[126] Radical anions with such extremely high electrical conductivities were previously unheard of. The crystal structure of (2,5-dimethyl-DCNQI)$_2$Cu consists of stacks of copper ions, with each copper ion being coordinated in a distorted tetrahedral manner to the N-atoms of four cyano groups. Thus each copper ion stack is surrounded by four DCNQI stacks.



(101)

Group M
a:R^1 = Me, R^2 = Me
b:R^1 = Me, R^2 = I
c:R^1 = Cl, R^2 = I
d:R^1 = Br, R^2 = I
e:R^1 = Me, R^2 = OMe
f:R^1 = Br, R^2 = OMe
g:R^1 = I, R^2 = OMe
h:R^1 = OMe, R^2 = OMe
i:R^1 = I, R^2 = I

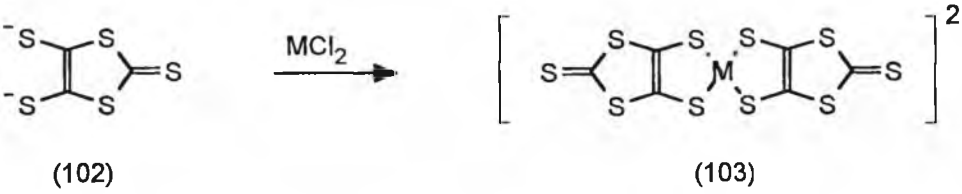
Group M-I
j:R^1 = Cl, R^2 = Cl
k:R^1 = Cl, R^2 = Me
l:R^1 = Cl, R^2 = Br
m:R^1 = Br, R^2 = Me
n:R^1 = Br, R^2 = Br
o:R^1 = Cl, R^2 = OMe

Electron transport in these salts takes place along the acceptor stacks, with conductivity along the cation stacks being ruled out due to the intra-cation stack separation being too large.(Cu-Cu 3.88 Å for $(2,5\text{-Me}_2\text{-DCNQI})_2\text{Cu}$ and 2.56 Å for Cu metal). The 2,5-disubstituted-DCNQI metal salts, $(R^1,R^2\text{-DCNQI})_2$ Cu (101), can be classified into two groups according to the temperature dependence of their conductivities at ambient pressure: Group M salts, (101a-i), which show metallic behaviour down to low temperatures.[123, 127] Group M-I salts, (101j-o),[123, 127] which undergo a M-I transition in the temperature range $T_{M\text{-}I}$= 160- 230 K. Analysis of these salts[127, 128] suggests that the solid-state behaviour of the Cu salts is dependent on the size of the substituents, with large substituents, OMe and I, giving rise to stable metallic states and combinations of small substituents giving rise to phase transitions, $(2,5\text{-Me}_2\text{-DCNQI})_2\text{Cu}$ being an exceptional case. The electronic behaviour is also dependent on the different electronic properties of the substituents.

In addition to these substituent effects, crystal structure studies at various temperatures show the importance of the tetrahedral coordination of the acceptor groups to the metal.[127, 129] This structural feature introduces a new packing motif of the molecular conductor, in which the one-dimensional columns, as a result of being tetrahedrally coordinated to the copper cation, becomes three-dimensional due to the interaction between the pπ orbital of the organic molecules and the 3d orbitals of the cation. This gives rise to a "multi-Fermi surface" which is not susceptible to phase transitions. Any "flattening" or deformation of the coordination tetrahedron (or N-Cu-N angle) results in a decrease in the number of d orbitals participating in the pπ-3d mixing and so weakens the multi-Fermi surface nature, which leads to the formation of a gap by a CDW.

1.C.6 Metal(dmit)$_2$ Acceptors

The general emphasis of much of the recent synthetic work in the area of C-T complexes has been on the development of systems with enhanced interstack interactions, leading to increased dimensionality. These efforts are motivated by the desire to avoid the metal-to-insulator transitions which are associated with 1-D metals on cooling to low temperatures. This approach has also been applied to π-acceptor molecules. These acceptors are metal complexes of the sulphur ligand, 4,5-dimercapto-1,3-dithiole-2-thione (102), and are known as M(dmit)$_2$ acceptors (103) for short. The most important complexes to date have been obtained from nickel, platinum and palladium as the metal and these metal complexes have been synthesised[130] from the dithiolate (102) and the metal-dichloride, Scheme 1.25. These are planar molecules and the sulphur ligand moieties allow for both intra- and inter-stack interactions. The nature of the metal atom plays an important role in determining the structural and physical properties of the complexes which are formed.



Scheme 1.25

M(dmit)$_2$ acceptors form complexes with a variety of cations/donors, the most important being TTF and tetramethyl ammonium cations, which give superconducting complexes. These complexes are usually synthesised by a metathesis reaction by slow interdiffusion, in a three compartment "H-tube" under an inert atmosphere, of saturated acetonitrile solutions of the counter cation, e.g. $(TTF)_3(BF_4)_2$, and the appropriate metal salt $(n\text{-}Bu_4N^+)_2$ $[M(dmit)_2]^{2-}$. Or alternatively by electrocrystallisation in a U-tube in a method similar to that described before for the radical cation salts of BEDT-TTF in the donors section.[131]

The first $M(dmit)_2$ acceptor to exhibit superconductivity was $TTF[Ni(dmit)_2]_2$, on the application of 7 kbar of pressure.[132] At room temperature and ambient pressure, it had a conductivity of σ_{rt}= 300 Scm^{-1} along the stacking axis and displayed metallic behaviour right down to 4 K, where σ_{max}= 1.5 x 10^5 Scm^{-1}, without undergoing a phase transition.[133] The crystal structure of $TTF[Ni(dmit)_2]_2$ indicates that the essentially planar TTF and $Ni(dmit)_2$ molecules stack in distinct columns parallel to the b axis, which is the direction of highest conductivity. These columns give alternate sheets of donor and acceptor molecules parallel to the b,c plane. The interatomic separations between adjacent molecules in either the TTF and $Ni(dmit)_2$ stacks are not shorter than the sum of the van der Waals radii.[133] However the inter-stack S-S distances are shorter (3.45- 3.54 Å) than the van der Waals radii separation (3.70 Å). Even shorter S-S distances have been found between the terminal S atoms of $Ni(dmit)_2$ molecules and the S atoms of the TTF molecules (3.39 Å). Despite this enhanced interaction the electronic structure of this, and other salts, are quasi one-dimensional.[39]

Replacement of Ni with Pd in the TTF complex gives $TTF[Pd(dmit)_2]_2$.[131] This complex has a room temperature conductivity of σ_{rt} = 750 Scm^{-1} along the stacking axis. It exhibits a metallike conductivity down to 220 K, at which point it undergoes a gradual transition to a semiconducting state. The metallike behaviour of this complex is maintained once it is not cooled below 220 K. Crystals which were cooled below the transition temperature were found to remain semiconducting even after storage at room temperature for periods of up to 12 days. Such behaviour is indicative of a structural phase transition at 220 K and this was confirmed by the observation of 3 different phases by X-ray diffraction studies. The first phase refers to the metallic phase, which is the structural phase before the crystal is cooled. This phase is isomorphous with the analogous nickel derivative. The second phase corresponds to the semiconducting phase on cooling the crystal down to the phase transition temperature. And finally the third phase corresponds to warming the second phase back to room temperature, which gives a crystal structure distinct from that of the first phase.

The platinum complex, $TTF[Pt(dmit)_2]_3$, unlike its nickel and palladium counterparts, is semiconducting throughout the temperature range 300 to 100 K and has a room temperature conductivity of just σ_{rt} = 20 Scm^{-1}.[131] The structure of $TTF[Pt(dmit)_2]_3$, like the stoichiometry, is distinct from that of both its nickel and palladium derivatives. It consists of alternate layers, parallel to the ab plane, of TTF and $Pt(dmit)_2$ molecules, the acceptor layer consisting of both $Pt(dmit)_2$ monomers and dimers. In the acceptor layers the monomers and dimers are stacked alternately in columns. The two $Pt(dmit)_2$ units of the dimer are distorted from planarity and results in increased intermolecular-interatomic distances within a dimer. S-S contacts less than the van der Waals radii are observed between monomers and dimers within a stack and within dimers within a stack and between either monomers or dimers belonging to adjacent stacks. Unusually the conductivity is much lower than anticipated. It has been suggested that this may be due to the opening of a band gap at the Fermi surface as a result of the alternate stacking of the monomers and dimers. It is clear that the nature of the metal atom has an important role in determining the structural and physical properties of the $M(dmit)_2$ acceptors.

Superconductors based on π-acceptor molecules and closed-shell cations have also been found. The first of these was $(Me)_4N[Ni(dmit)_2]_2$, with a superconducting transition under 3.2 kbar at T_c= 3.0 K and at T_c= 5.0 K under 7 kbar of pressure.[39] The crystal structure consists of sheets of $Ni(dmit)_2$ molecules and $(Me)_4N$ cations alternatively piled up parallel to each other, with the cation sheets separating the conductive acceptor sheets. In the acceptor sheet, the molecules are stacked in 1-D columns with the direction of adjacent columns at an angle of 52.2 ° to each other. This results in two 1-D Fermi surfaces with different orientations being superposed and giving rise to a multi-Fermi surface which is stable against lattice-modulation waves.

The palladium derivative, ß-$(Me)_4N[Pd(dmit)_2]_2$, was also found to be a superconductor above 6 kbar. The mid-point transition temperature was T= 6.2 K at 6.5 kbar.[134] The crystal structure[135] is isostructural with $(Me)_4N[Ni(dmit)_2]_2$ except for the cation sites. The $Pd(dmit)_2$ molecules form dimeric 1-D stacks, with the two anions forming a eclipsed configuration within the dimers and between the dimers the anions are displaced sideways with respect to each other. The Pd atoms within the dimers are also displaced out of the plane of the molecule by 0.07 Å towards each other. There are many S-S contacts which are shorter than the van der Waals distance (3.70 Å) along the a and b directions but intermolecular transverse interactions are small. As a result the complex is essentially 1-D. Because of the strong dimeric nature of this complex, intermolecular interaction within the dimers is much stronger than the inter-dimer, it is suggested that the conduction band is considered to be formed from the HOMO of $M(dmit)_2$ instead of the LUMO.[134] At high pressure, the dimeric nature is diminished and the LUMO may form the conduction band.

1.C.7 Fullerenes as Acceptors

The newest and more unusual acceptor molecules to be recently discovered are the spheroidal fullerenes, C_{60} (103), or Buckminsterfullerene, in particular. These acceptors are particularly interesting in that, although they are not planar like conventional organic acceptors, they do have radiating π-orbitals which form a 3-D electronic pathway which can form both conducting and superconducting complexes with both alkali and alkaline earth metals.[136] The highest transition temperature T_C to date is for the cesium doped C_{60}, Cs_3C_{60}, which has a T_C= 40 K under a pressure of 15 kbar.[10] The ability of fullerenes to function as acceptors has been attributed to their intermediate hybridisation and surface topology. Because of the curvature of the surface, σ-bonds at the conjugated carbon deviate from planarity so that a π-bond is no longer of purely p-orbital character and the σ-bonds no longer contain completely s-orbital character. This rehybridisation results in the hybridisation of the fullerenes being intermediate between that of graphite (sp^2) and diamond (sp^3) *i.e.* $sp^{2.28}$. This means that as a consequence of the lower energy 2s-orbital mixing with the π-orbital, the molecular orbitals which form from these rehybridised π-orbitals will have enhanced electron affinity. In addition to this, the fullerenes, in order to form their spherical structure, are made up of benzene-like 6-membered rings and conjugated 5-membered rings. It is the presence of these 5-membered rings and their associated stability which results in the fullerenes having six low-lying triply-degenerate molecular orbitals.

(103)

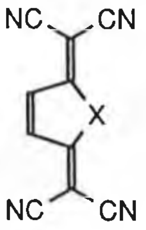
The acceptor ability of C_{60}, determined by solution electrochemistry and referenced to the standard calomel electrode, gave a first reduction potential, $E^1_{1/2}$= -0.399 V in dichloroethane. This gave a $E^1_{1/2}$= -0.422 V in acetonitrile, on conversion using an empirical relation between the E_{redox} values in acetonitrile and dichloroethane for a number of acceptors and donors. This reduction potential suggests that C_{60} is a much poorer acceptor than TCNQ ($E^{1}_{1/2}$= 0.222 V in acetonitrile).[137] This poor acceptor ability was also reflected in its inability to form C-T complexes with a wide variety of organic donors including some derivatives of TTF.[137] While some donors, *e.g.* octamethylene-TTF and BEDT-TTF, did give black crystals, with what seems to be C-T bands around 12 x 10^3 cm^{-1}, their IR spectra suggest they have neutral ionicity and are insulating (OMTTF complex has σ_{rt}= 10^{-8} Scm^{-1}). This suggests that much stronger organic donors are necessary to form conducting C-T complexes.

Chapter 2

Results and Discussion

2.A.1 Introduction

It can be seen in Chapter 1 that most of the acceptors synthesised in recent years have been derivatives of TCNQ, the majority of these having π-extended systems. The remainder are the heterocyclic-TCNQ analogues, usually derivatives of compounds (105-107). These compounds, including (109), are said to be iso-π-electronic with TCNQ by virtue of the presence of a heteroatom within the ring system. The lone pair of p-π electrons on the heteroatom is capable of contributing to the mesomeric bond system.

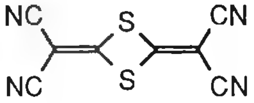


(105) X= S

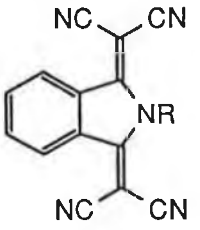
(106) X= Se

(107) X= O

(108) X= NR

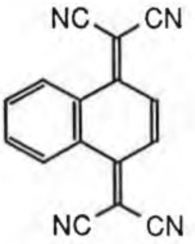


(109)



(110) R= H

(111) R= Me, Et, acyl, *etc.*

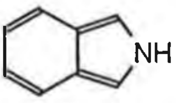


(112)

To date there have been no reports of the nitrogen analogue of (105), system (108). One- and two-electron reduction of (105-108) should result in the formation of a 4n+2 π-electron cyclic planar system whose potential aromaticity should result in a lower reduction potential and a stabilising effect on the anion radical. Since the degree of aromaticity decreases in the order thiophene > pyrrole > furan, the acceptor ability of (108) should be expected to be at least intermediate between that of (105) and (107). An additional advantage of the pyrrole system would be the ability to "fine tune" the properties of the pyrrolidine ring by varying the substituents at the nitrogen. This would also allow for the possibility of attaching a variety of functionalities, which can increase the solubility of these compounds, in addition to the introduction of polymerisable groups which may increase their applications.

With these possibilities in mind it was intended to investigate the synthesis of the isoindoline analogue of (108), (110), and its *N*-substituted derivatives (111), which are iso-π-electronic with the TCNQ derivative, benzo-TCNQ (112). These compounds were of interest in order to determine the effects of *N*-substitution on electron acceptor ability and on the formation of C-T transfer complexes with various donors, whose electrical properties would be of interest. Compound (110) should form a 10 π-electron isoindole, or benzo[c]pyrrole, intermediate on one- and two- electron reduction. Of the series benzo[c]furan (113a), benzo[c]pyrrole (113b) and benzo[c]thiophene (113c), (113b) has been calculated to be the most aromatic.[138]

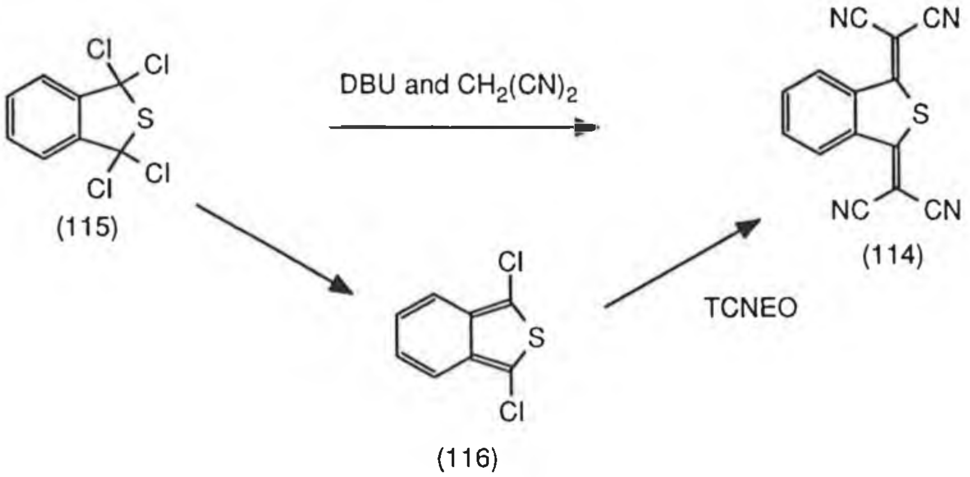
(113a)



(113b)

(113c)

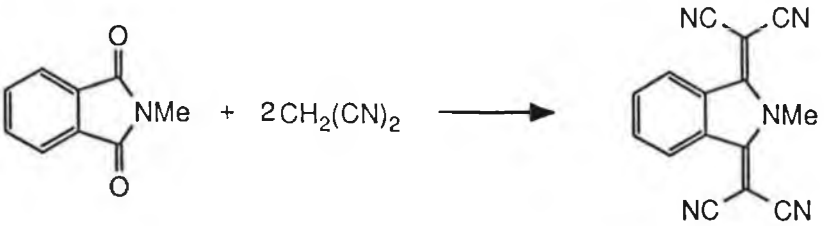
The sulphur analogue of (110), compound (114) has been previously reported[139] and cyclic voltammetry studies showed two reversible redox waves. Compound (114) was synthesised from (115) in 5% yield by warming (115) with 1,8-diazabicyclo[5.4.0]undec-7-ene, (DBU), in DMF or alternatively, in 25% yield, from (115) via the dichloride (116) which was treated with tetracyanoethylene oxide (TCNEO), Scheme 2.01.



Scheme 2.01

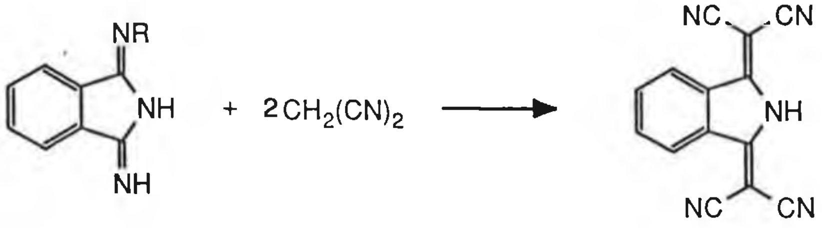
We investigated two possible routes to (110) and its *N*-substituted derivatives (111). The first involved the Knoevenagel condensation of malononitrile with a phthalimide, *e.g.* *N*-methylphthalimide (117), Scheme 2.02. This route was initially considered attractive as a readily accessible supply of starting materials, the *N*-substituted phthalimides, was available.

The second route investigated involved the condensation reaction of malononitrile with the imidines (118a) and (118b) to give (110), Scheme 2.03. *N*-Substitution reactions of (110) were then investigated.



(117)

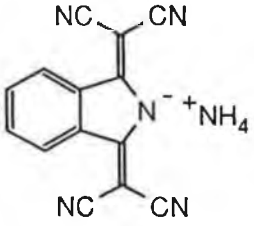
Scheme 2.02



(118) a: R= H
b: R= Ph

Scheme 2.03

In this Chapter the results of these investigations are discussed as well as the reactivity of the salt (119) with various amines. The following Chapters, three and four respectively, will deal with the determination of the electron-accepting ability of the acceptors (110), and (111, R= Me), by cyclic voltammetry and a study of their charge-transfer properties.



(119)

2.A.2 Knoevenagel Condensations of *N*-Methylphthalimide

2.A.2.1 The Knoevenagel Reaction

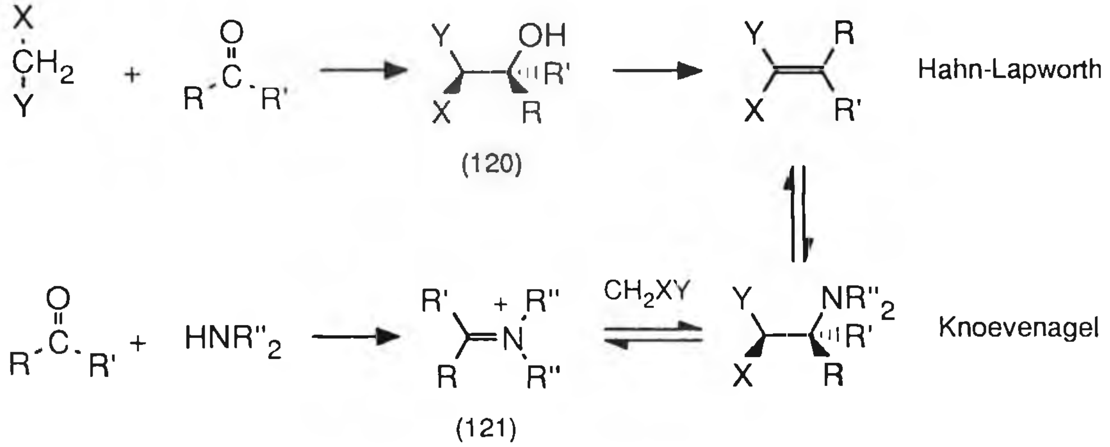
The Knoevenagel condensation is effected by treating a carbonyl with an active methylene compound, usually in the presence of at least a catalytic amount of base or sometimes acid. The active methylene group usually contains two electron-withdrawing groups, although the condensation can be effected using a strong base when only one strongly electron-withdrawing group is present. The active methylene compounds can include malonates, acetoacetates, acetonitriles, malononitrile, 1,3-diones and barbituric acid. A variety of aldehydes can be used for these reactions but the use of ketones is limited due to their lower reactivity.

The catalysts used are of great importance. The more common ones include primary, secondary and tertiary amines or their corresponding ammonium salts. By far the most widely used catalysts are pyridine, alone or in the presence of a small amount of piperidine, and ammonium salts such as ammonium or piperidinium acetate.

The use of the Lewis acid titanium tetrachloride in the presence of pyridine, known as Lehnert's reagent, in tetrahydrofuran or 1,4-dioxan as solvent, has proved to give effective yields of the olefin derivatives for reactions with less reactive ketones.[73]

Two different mechanisms, depending mainly on the base used, have been proposed[140] for the reaction of an active methylene group with a carbonyl group. One mechanism, the Hahn-Lapworth mechanism, postulates the formation of an intermediate β-hydroxy adduct (120), Scheme 2.04. This mechanism is suggested for bases such as tertiary amines and pyridine. The β-hydroxy adduct (120) is also formed as the intermediate when the sodium salt of the active methylene compound is used.

Knoevenagel suggested that when primary and secondary amines are used as catalysts, the condensation of the aldehyde and the amine takes place first to give an iminium salt (121) which then reacts with the active methylene compound, Scheme 2.04. This is then followed by elimination of the amine.

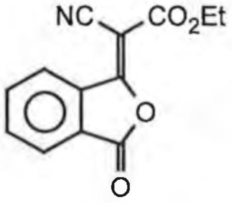


Scheme 2.04

It has been shown that weak bases producing solutions of pH 7.5-8.0 are the most efficient. However, when malononitrile is used with stronger bases to effect more rapid condensation, the yield is found to be lower because of telomerisation of the malononitrile. In general, the presence of tertiary amines in Knoevenagel condensations, with or without acid, causes the reaction to proceed *via* the β-hydroxy intermediate. For primary and secondary amines the two mechanisms compete, the formation of the iminium intermediate being dependent on the bulkiness of the amine and the carbonyl compound.

While reports of the Knoevenagel reaction of activated methylene compounds with an extensive range of aldehydes and ketones are numerous, such reactions with phthalimides have not been reported. A search of the chemical literature to date has yielded reports of two attempted Knoevenagel reactions with the related compound phthalic anhydride.[141, 142]

The first of these reported the reaction of ethylcyanoacetate with phthalic anhydride in benzene using sodium as the catalyst to give ethyl cyano(phthalidylidene)acetate (122) in 9% yield.[141] This method had been previously reported by Sorm *et al.*[143] without any mention of yield or stereochemistry. In an attempt to increase the yield, triethylamine was used as the base in toluene. This gave the benzofulvalene derivative (123).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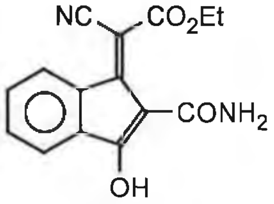
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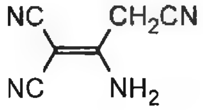
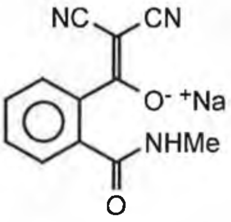

(124)

In an effort to synthesise (111, R= Me), the Knoevenagel reaction of malononitrile with *N*-methylphthalimide was attempted using a variety of bases, see Scheme 2.02. These were sodium, triethylamine and sodium hydride. The initial reaction conditions used were based on those reported by Renfrew and Bostock for the reaction of ethylcyanoacetate with phthalic anhydride.[141]

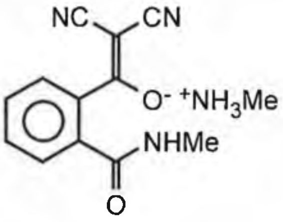
When sodium was used as the base a complex mixture of products was obtained and from this a small quantity of the malononitrile dimer, 2-amino-1-propene-1,1,3-tricarbonitrile (124) was isolated and its identity confirmed by comparison with data.[144] The dimer (124) had previously been synthesised by Carboni *et al.*[144(a)] in a very similar manner by treating a solution of malononitrile in ether or tetrahydrofuran with sodium and hydrolysing the resulting solid with a strong mineral acid.

The alternative method reported,[141] using triethylamine as base for the reaction of ethylcyanoacetate with phthalic anhydride, was also attempted for the reaction of malononitrile with *N*-methylphthalimide, but due to the complexity of the reaction mixture formed, isolation of products was not attempted. Renfrew and Bostock also reported that the Knoevenagel reaction of phthalic anhydride was attempted with other active methylene compounds including malononitrile, under the same conditions as those for ethylcyanoacetate, but only stated that no products related to the benzofulvalene (123) were isolated.

When the Knoevenagel reaction was attempted using sodium hydride as the base an off-white solid was recovered which, on the basis of its spectra, was probably the sodium salt intermediate (125). This solid was obtained by trituration with ethyl acetate of the oil obtained on evaporation of the reaction solvent. Attempts to recrystallise the solid failed due to its insolubility in most organic solvents. It could be dissolved in boiling ethanol or methanol but this resulted in the observation of further products by TLC. The salt was found to be readily soluble in water giving an orange/red solution. The ^{1}H NMR spectrum of (125) showed a broad one proton NH multiplet at 8.08 ppm, a four proton aromatic multiplet between 7.60 and 7.27 ppm and a three proton doublet, *J*= 4.9 Hz, at 2.69 ppm. The ^{13}C NMR spectrum showed a methyl carbon absorption at 26.2 ppm, the C_2 carbon absorption of the 2,2-dicyanovinylidene group at 48.8 ppm, two cyano absorptions at 120.9 and 122.07, and six aromatic absorptions between 127.0 and 140.0 ppm. The 2,2-dicyanovinylidene C_1 carbon and carboxamide carbon absorptions were found at 168.41 and 189.47 ppm respectively. The IR spectrum confirmed the presence of amide NH, cyano, and amide carbonyl absorptions.



(125)



(126)

On dissolving the sodium salt (125) in water, and acidifying with 10% hydrochloric acid, a small quantity of an off-white solid precipitated. This was filtered off and recrystallised from ethanol, giving the methylammonium salt (126), whose structure was confirmed by spectral and elemental analysis.

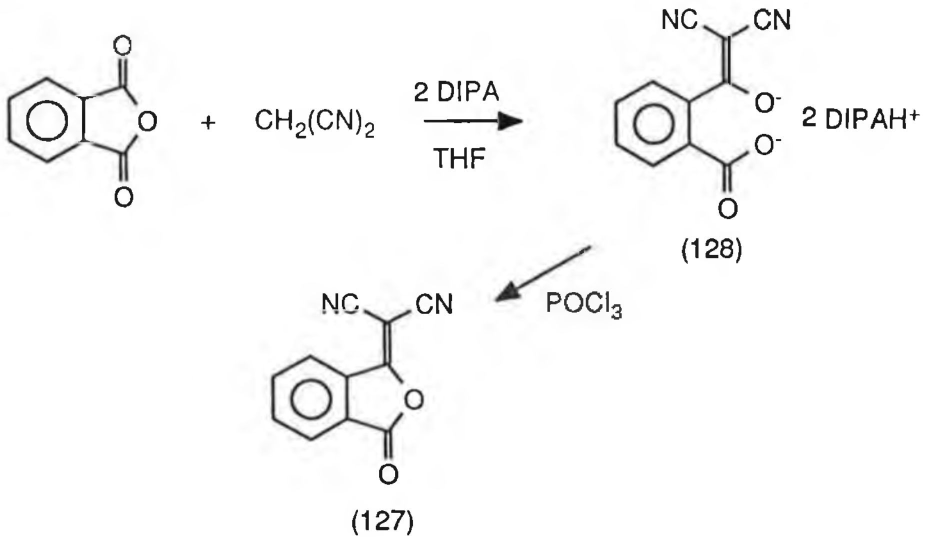
The ^{1}H NMR spectrum of this compound, in DMSO-d_6, was identical to that of the sodium salt (125) but with an additional three proton methyl singlet at 2.34 ppm and a broad three proton singlet, infringing on the four proton aromatic multiplet, at 7.50 ppm, arising from the methylammonium group. As in the ^{1}H NMR spectrum for the sodium salt, a broad one proton multiplet at 8.10 ppm, and a three proton doublet, J= 4.9 Hz, at 2.68 ppm were observed. When the ^{1}H NMR spectrum was measured in methanol-d_4 the broad peak centred at 7.55 ppm and the amido NH at 8.06 ppm disappeared and the doublet observed at 2.68 ppm appeared as a singlet.

The red filtrate remaining on removal of the methylammonium salt (126), from the acidified solution, was extracted with ethyl acetate. This yielded a red oil which was found to be a complex mixture of products whose components could not be isolated in a pure state by column chromatography.

The ethyl acetate filtrate remaining from the trituration of the sodium salt yielded unreacted *N*-methylphthalimide.

Since acidification of the sodium salt (125) failed to yield the desired compound, ring-closure was attempted by heating the solution under reflux. The reaction was carried out as before, followed by heating under reflux when all the malononitrile had been added. The white solid which precipitated on cooling was filtered off and was found to be unchanged sodium salt (125).

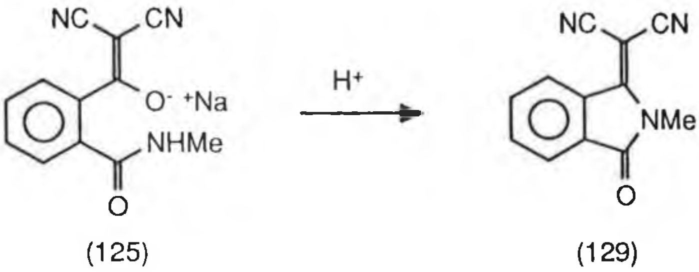
Concentration of the filtrate gave a red oil from which two products were obtained. The first, a grey crystalline solid, was obtained from a white solid which precipitated from an ethyl acetate solution of the red oil on acidification. On attempting to recrystallise the white solid from boiling ethyl acetate an insoluble grey solid remained. This was removed from the hot solution by filtration and identified as the methylammonium salt (126). A small quantity of another white product was obtained from the filtrate. This was identified as the pseudo anhydride 3-(dicyanomethylidene)phthalide (127) by comparison of its NMR and IR spectra with those in the literature.[142] The pseudo anhydride (127) has been reported before by Moore and Ji-Heung.[142] They found that the related Knoevenagel reaction of malononitrile with phthalic anhydride using diisopropylamine (DIPA) as the base gave the salt (128) which on reaction with phosphorous oxychloride gave the pseudo anhydride (127), Scheme 2.05.



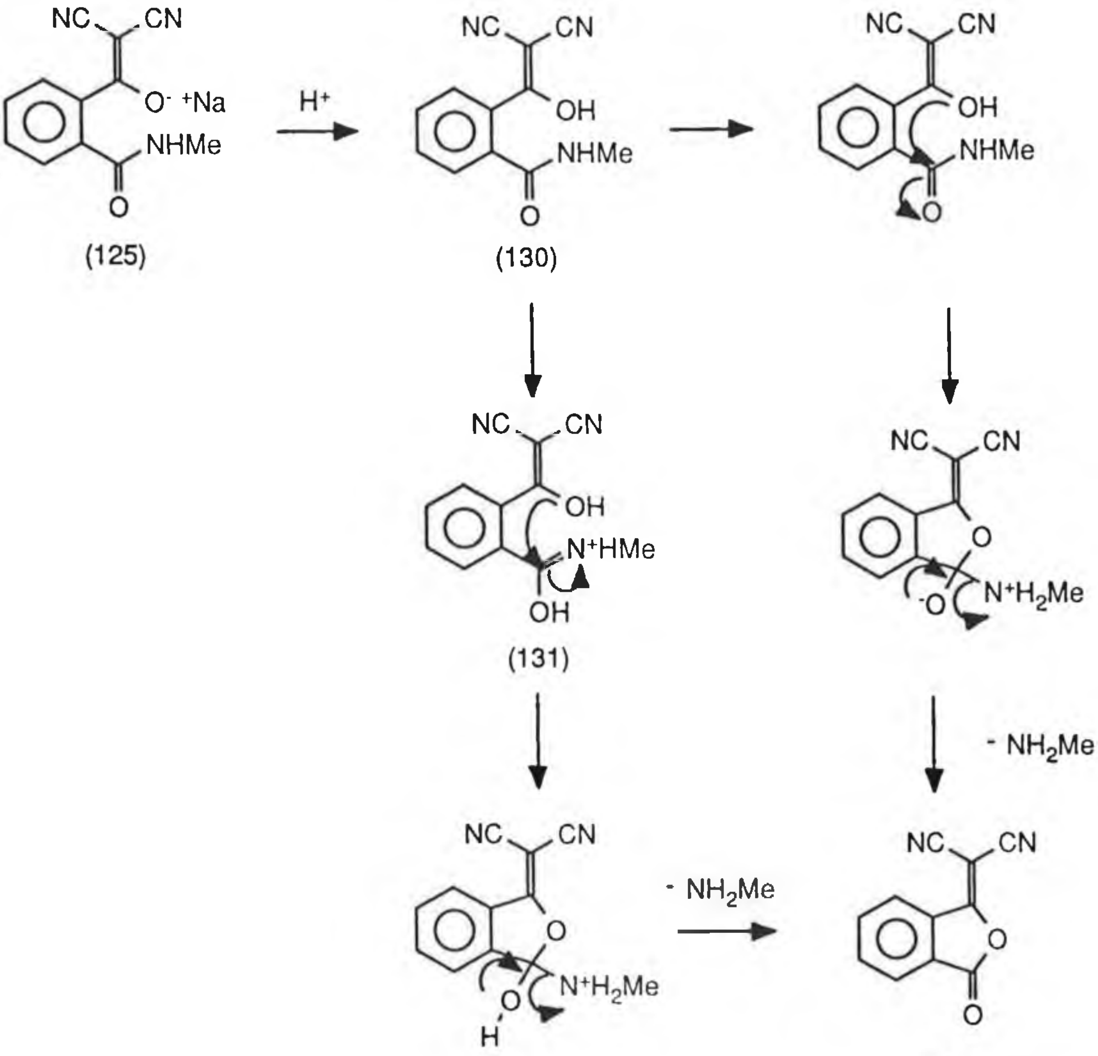
Scheme 2.05

The ^1H NMR spectrum of (127) showed a four proton aromatic multiplet between 8.11 and 8.44 ppm. The ^{13}C NMR spectrum showed the presence of the dicyanomethylene carbon absorption at 65.15 ppm, two cyano absorptions at 110.4 and 111.9 ppm, six aromatic absorptions between 125.9 and 137.4 ppm, the 2,2-dicyanovinylidene C_1 carbon absorption at 162.4 ppm and the carbonyl absorption of the lactone at 170.4 ppm.

It was hoped that acidification of the sodium salt (125) would yield the *N*-substituted pseudo phthalimide (129), Scheme 2.06. However it is apparent from the results that instead of removal of a molecule of water, a molecule of the amine is lost on ring-closure to give the pseudo anhydride (127). This most probably occurs via attack by the enolic OH at the adjacent amido group of (130) or alternatively, under the acidic conditions, at the electron difficient iminium carbon of (131), Scheme 2.07, resulting in the elimination of methylamine and the formation of (127). The methylamine released during the formation of (127) is responsible for the formation of the methylammonium salt (126). Such a mechanism would explain the products obtained in this reaction.

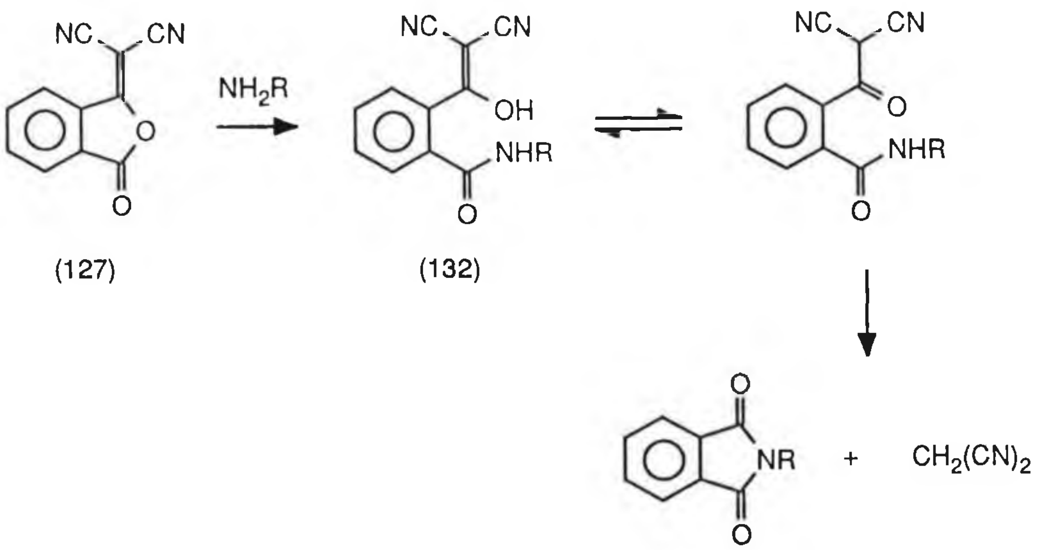


Scheme 2.06



Scheme 2.07

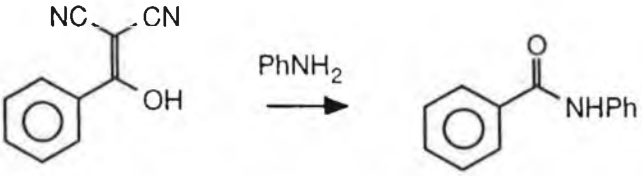
Studies on the nucleophilic attack by amines on the pseudo anhydride (127) at room temperature have been reported.[142] It was found, on following the reaction by NMR spectroscopy, that nucleophilic attack occurred at the carbonyl, rather than the 2,2-dicyanovinylidene C_1 carbon, resulting in ring-opening to give an acid-amine salt. This slowly dissociated to the intermediate (132) which then underwent subsequent imidisation, Scheme 2.08. It was postulated that elimination of malononitrile anion rather than hydroxide was favoured by the enhanced stability granted to the leaving group by the two electron-withdrawing nitriles.



(127) (132)

Scheme 2.08

This was further supported by the discovery that the reaction of aniline with (hydroxyphenylmethylene)propanedinitrile (133) gave benzanilide (134) on heating the salt initially formed at elevated temperatures,[145] Scheme 2.09.



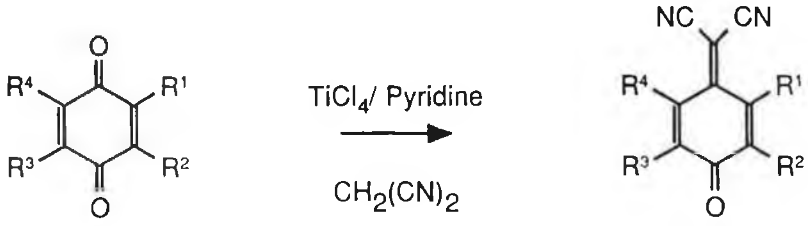
(133) (134)

Scheme 2.09

Our findings show that an alternative ring-closure to that reported for intermediate (132) can also occur, yielding the pseudo anhydride (127). One explanation for this may be attributed to the acidic conditions. Under such conditions it is possible that the enol tautomer of intermediate (130) is promoted, and the possibility of the formation of the iminium intermediate (131), having a more electron deficient carbon than that of the unprotonated amide, may favour nucleophilic attack by the enol OH at the carboxamide group to yield (127). The conditions used by Moore were in essence basic and so intermediate (132) may have favoured the keto form, due to the enhanced delocalisation granted by the two nitriles, making the amide nitrogen the better nucleophile resulting in the formation of the corresponding *N*-substituted phthalimide.

2.A.2.2 Knoevenagel Condensations using Titanium Tetrachloride

The most obvious problem in trying to carry out the Knoevenagel condensation with phthalimides was to encourage the elimination of water and thus prevent ring opening. In an effort to possibly achieve this, the reaction of *N*-methylphthalimide (117) with malononitrile in the presence of titanium tetrachloride was investigated. Titanium tetrachloride, in the presence of pyridine, known as Lehnert's reagent, has been used to effect dehydration of amides to nitriles.[146] There are also several reports of titanium tetrachloride being used to effect Knoevenagel condensations at sterically hindered ketones, by aiding the elimination of water, to synthesise electron acceptors.[147] The tetrasubstituted benzoquinones (135) have been reported[120] to yield the dicyanomethylidene derivatives (136) using Lehnert's reagent in dry dichloromethane, Scheme 2.10, and (138) has been synthesised from (137)[95] by refluxing in pyridine, Scheme 2.11.



(135)

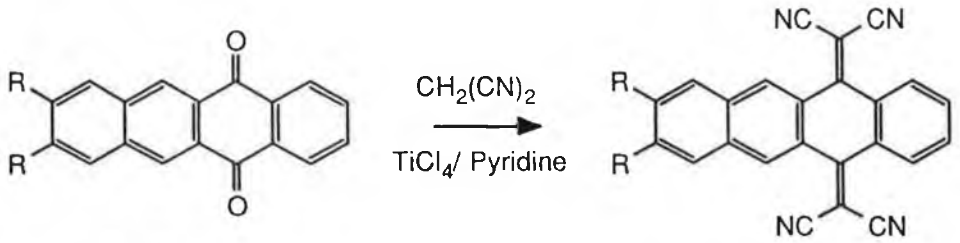
(136)

$R^1 = R^2 = R^3 = R^4 = Me$

$R^1 = H, R^2 = R^3 = R^4 = Me$

$R^1 = R^2 = H, R^3 = R^4 = \text{-S-}(CH_2)_2\text{-S-}$

Scheme 2.10



(137)

(138)

R= H, CH_3O, (-CH=CH-)$_2$

Scheme 2.11

The Knoevenagel condensation of malononitrile with (117) using Lehnert's reagent was investigated. Treatment of (117) with malononitrile and

Lehnert's reagent in dry dichloromethane at room temperature did not give any products and only unreacted *N*-methylphthalimide was recovered. An alternative, and more vigorous procedure attempted, involved heating the reaction under reflux for 14 hours in dry pyridine. A small amount of a white solid was filtered from the hot solution and pyridine was distilled from the filtrate to concentrate it to one fifth of its volume. This yielded a crystalline solid which was highly hygroscopic, and which formed an oily red liquid almost immediately. On acidification this yielded *N*-methylphthalimide . This white solid was titanium dioxide and may have formed due to the pyridine not being totally anhydrous. It did not dissolve in water or any organic solvents and did not show any characteristic peaks in its IR spectrum.

(139a) (139b)

The failure of titanium tetrachloride to effect condensation in the reaction of malononitrile with (117) may possibly be related to the stability of the chloride salt intermediate (139) formed by complexation of titanium tetrachloride at the carbonyl oxygen. This might be sufficiently stabilised by delocalisation of electron density from the nitrogen to reduce its reactivity towards attack by a malononitrile anion. The hygroscopic solid recovered from the reaction in pyridine may possibly have been the salt (139).

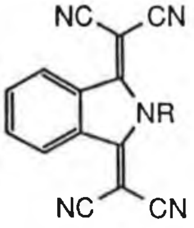
2.A.3 Conclusion

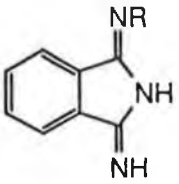
The propensity of (117) to undergo ring opening on nucleophilic attack by sodio-malononitrile to give salt (125), and the failure of this salt to undergo ring closure to the desired *N*-substituted pseudo phthalimide, makes this route non-viable for the synthesis of *N*-substituted derivatives of (110). Our results are interesting in that they show that the ring closure of the probable intermediate (132), proposed by Moore for the reaction of amines with the pseudo anhydride (127) to give phthalimides, can alternatively, under the acidic conditions of our reaction, give the pseudo anhydride (127). Attempts to avoid ring-opening, by effecting condensation in the presence of titanium tetrachloride were not successful.

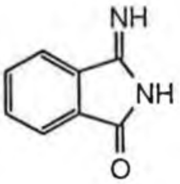
Section 2.B

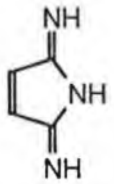
2.B.1 Condensation Reactions with Imidines

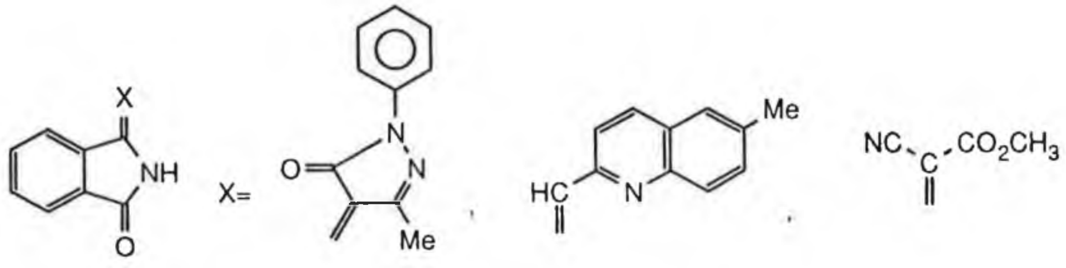
Since the reaction of malononitrile with *N*-methylphthalimide (117) did not yield the desired compound an alternative approach to synthesise (111) was investigated. The propensity of the exocyclic imino group of the imidines (118a and b), the oxo-isoindoline (140) and the succinimidine (141), to undergo base condensation with primary amines and various active methylene compounds was extensively investigated during the 1950s by Elvidge and co-workers.[148, 149]


(111) R= alkyl *etc.*


(118) a: R= H
b: R= Ph

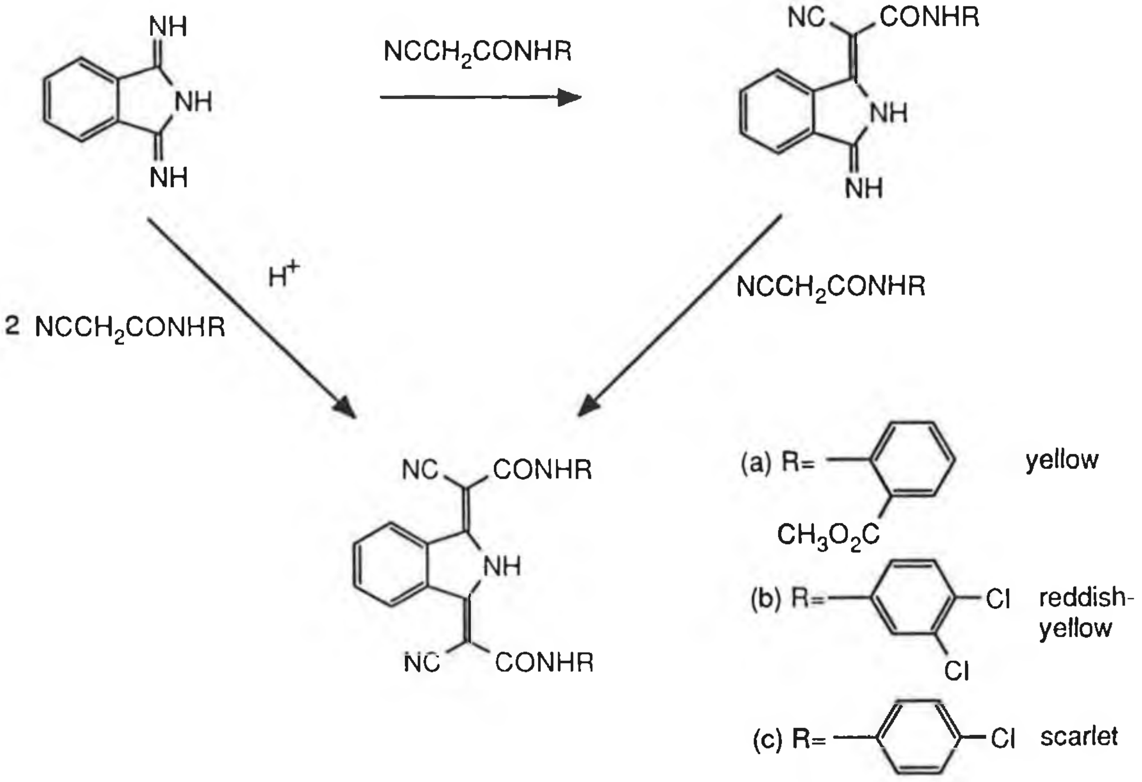

(140)


(141)



(142)

It was found[148] that while the imino groups were readily reactive, the carbonyl groups of (140) showed no tendency at all to react with bases with the elimination of water. Similar findings were reported in two patents[150] in which the monocondensation products from reactions with an array of active methylene reagents were recognised as useful dye intermediates *e.g.* (142). Similar monocondensation compounds as well as their biscondensation equivalents had been previously reported.[149, 151] Some of these biscondensation compounds have outstanding pigment properties and have found applications in paint manufacture[152] and electrophotographic applications.[150(b), 153] As a result quite a number of patents[154] have been published on this rather novel class of pigments known as the isoindoline pigments. These isoindoline compounds are synthesised, in high yields and under mild conditions, from the condensation of (118a) and an active methylene compound, Scheme 2.12. The monocondensation product can be isolated or reacted further with more active methylene compound. For the synthesis of unsymmetrical pigments the monocondensation product is isolated and then reacted with an alternative active methylene compound or amino compound.

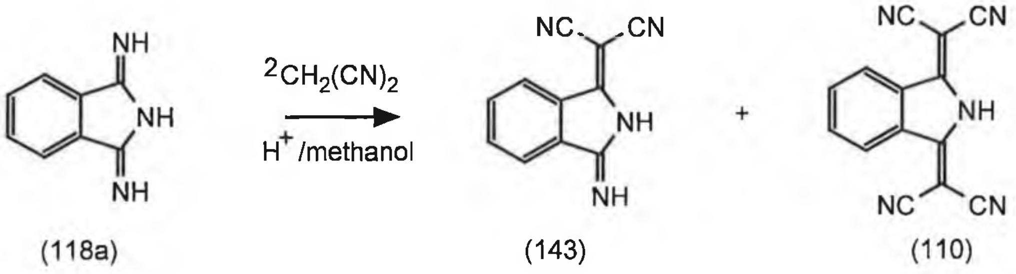


Scheme 2.12

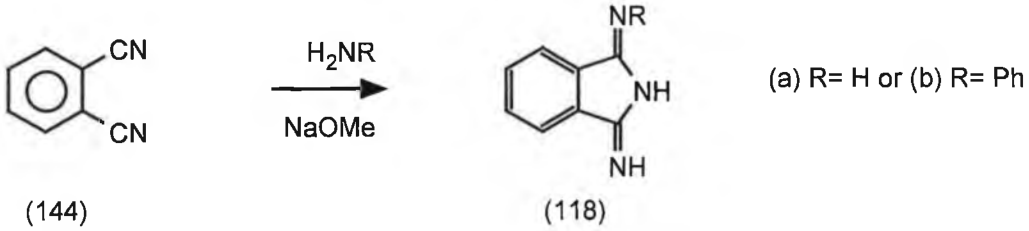
The isoindoline pigments have produced considerable interest not just because of their facile synthesis from easily available raw materials but also because of the broad variety of shades which are obtainable. This variety is not solely due to the differing substituents but is also due to the varying morphologies of the compounds in the solid state.[152] Such crystal structure variations can also affect the fastness properties of the pigments[152] and the intermolecular forces of attraction, such as hydrogen bonding, which influence the important property of insolubility in these compounds.

The isoindoline pigments have now become a new area for exploitation as dyestuffs with varied applicability. These compounds show outstanding colour fastness and when mixed with different organic and inorganic pigments give rise to a broad spectrum of shades and metallic finishes with outstanding weathering resistance. They have also found applications as charge generating agents in electrophotographic two-layer recording materials.[150(b), 153]

The synthesis of (110), by reaction of (118a) with malononitrile, was previously reported in a French patent[151] according to Scheme 2.13. It was reported that one mole equivalent of acetic acid was added to catalyse the reaction during which the monocondensation product (143) precipitated from the methanolic solution and the bis-condensation product (110) remained in solution and was precipitated by acidification. We found that a more convenient and improved method was achieved by using either (118a), or (118b), with dimethylformamide as the solvent.



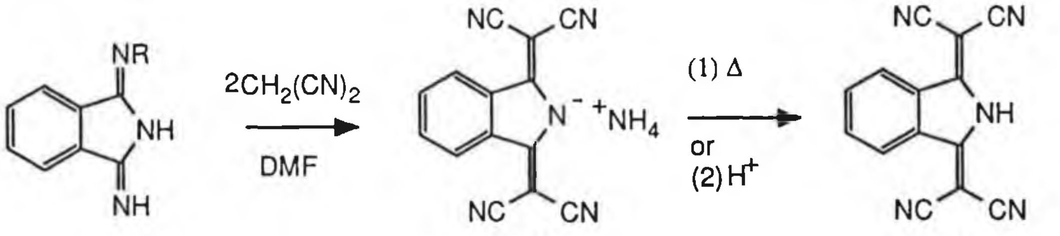
Scheme 2.13



Scheme 2.14

Compound (118a) was synthesised[155] by bubbling ammonia through a methanolic solution of (144), Scheme 2.14(a), and its structure confirmed by ^{1}H and ^{13}C NMR, and IR spectroscopy. The synthesis of (118b) was carried out according to a previously reported procedure[156] which involved reacting aniline with phthalonitrile in the presence of a base, sodium methoxide, Scheme 2.14(b). Its structure was supported by its ^{1}H and ^{13}C NMR spectra and its IR spectrum.

On addition of the malononitrile to (118a), or (118b), in DMF at room temperature, an immediate condensation reaction took place with the elimination of ammonia. This gave the ammonium salt of (110), (119), which was isolated by precipitation with chloroform, Scheme 2.15.



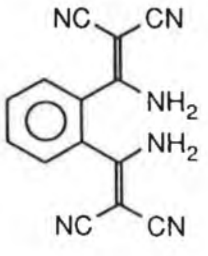
(118) a: R= H
b: R= Ph

(119)

(110)

Scheme 2.15

The ^{1}H NMR spectrum of (119) in pyridine-d_5 displayed a broad four proton NH singlet at 9.29 ppm and two symmetrical two proton aromatic multiplets at 7.30 and 8.35 ppm. On the basis of the symmetrical nature of the peaks in the ^{1}H NMR spectrum and the ^{13}C NMR spectrum, which showed the C_2 carbon absorption of the 2,2-dicyanovinylidene group at 54.63 ppm, two cyano absorptions at 116.27 and 117.14 ppm, three aromatic absorptions at 123.25, 131.04, and 138.0 ppm, and the 2,2-dicyanovinylidene C_1 carbon absorption at 172.0 ppm, it was also possible that the isomeric compound (145) had been formed. The elemental analysis obtained was consistent with both structures. However in dimethyl sulphoxide-d_6, as well as the four proton symmetrical aromatic multiplet between 7.58 and 8.05 ppm, a four proton 1:1:1 triplet, (J= 50 Hz), was observed at 7.07 ppm arising from ^{14}N/^{1}H spin-spin coupling, the ^{14}N nucleus having spin 1 rather than a half. Nuclei with spins greater than a half are quadrupolar and generally relax so rapidly in a non-cubic environment that all resolved couplings to them are lost. However the ammonium cation is unusual in that the nitrogen is in a cubic environment and so relaxes slowly thus allowing the ^{14}N/^{1}H couplings to be resolved. The ^{1}H NMR spectrum of the ammonium cation in acidified H_2O/D_2O gives a $J(^{14}N\text{-}^{1}H)$ ~ 52 Hz,[157] very similar to that displayed for (119) and providing conclusive evidence that the product was the ammonium salt (119) rather than the isomeric compound (145).



(145)

Of the two methods available for the synthesis of the ammonium salt (145), the method using (118b) as starting material was the preferred, because of its more convenient synthesis which did not require the use of gaseous ammonia.

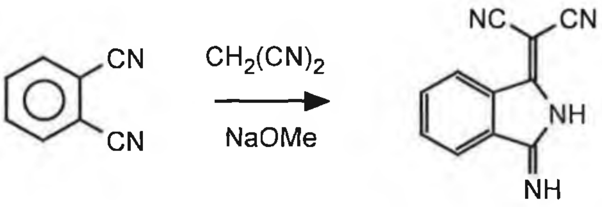
The protonation of (119) to give (110) was achieved by two methods. The first involved the pyrolysis of (119) under an atmosphere of nitrogen, which yielded (110) as an orange/brown powder. The second, and more convenient method, involved acidification of a methanolic solution of (119), by addition of dilute hydrochloric acid, which gave (110) as a fine yellow powder. Both the orange/brown solid and the yellow powder showed identical IR, ^{1}H and ^{13}C NMR spectra. The structural assignment of (110) was supported by the relevant IR, ^{1}H and ^{13}C NMR spectra and by elemental analysis and mass spectroscopy.

The IR spectrum showed the presence of two NH bands at 3243 and 3189 cm^{-1} and two conjugated nitrile peaks at 2240 and 2227 cm^{-1}. A large hypsochromic shift in the maximum absorption of the salt (119) (496 nm) relative to that of the neutral compound (110) (408 nm) in the UV/visible spectrum was observed and this was attributed to the lower conjugation of (110). The ^{1}H NMR spectrum showed two multiplets at 7.79 and 8.19 ppm, each integrating for two protons, and corresponding to the aromatic protons of the symmetrical product. A broad singlet at 4.85 ppm which integrated for one proton corresponded to the NH of the pyrrolidine ring. The ^{13}C NMR spectrum was consistent with the assigned structure and showed a total of seven different carbons. The C_2 carbon absorption of the 2,2-dicyanovinylidene group was observed at 56.54 ppm, the two cyano carbon absorptions at 114.65 and 115.66 ppm and the three aromatic carbon absorptions at 123.84, 132.83 and 134.90 ppm. The 2,2-dicyanovinylidene C_1 carbon absorption was observed at 166.27 ppm. Compound (110) was highly insoluble in most solvents and could only be recrystallised from a mixture of dimethylformamide and methanol to give bright orange needles.

2.B.2 Synthesis of 2-(3-Iminoisoindolin-1-diylidene)propanedinitrile (143)

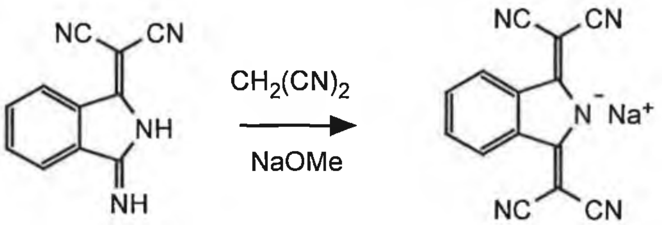
An alternative synthetic route to (110) involved the reaction of phthalonitrile (144) with malononitrile in the presence of sodium methoxide. This gave compound (143) in a one-pot synthesis, Scheme 2.15. The IR, ^{1}H and ^{13}C NMR spectra and elemental analysis were consistent with the assigned structure. The IR spectrum showed the presence of a broad NH peak at

2,990 cm^{-1} as well as a carbon-nitrogen double bond stretch at 1610 cm^{-1}. A conjugated nitrile stretch was also apparent at 2222 cm^{-1}. The ^1H NMR spectrum showed the presence of two broad, one proton, NH singlets at 9.95 and 3.37 ppm, with the former being due to the highly deshielded imino proton. Also present were four aromatic proton absorptions as two two proton multiplets at 7.7 and 9.95 ppm. The ^{13}C NMR spectrum showed the presence of the highly shielded C_2 carbon absorption of the 2,2-dicyanovinylidene group at 59.14 ppm, two cyano carbon absorptions at 114.83 and 115.63 ppm, and four aromatic absorptions between 122.91 and 132.0 ppm and two more at 137 and 171.9 ppm. An imino carbon absorption was observed at 134.18 ppm and the 2,2-dicyanovinylidene C_1 carbon absorption at 175.81 ppm. The high insolubility of compound (143) in most solvents made it difficult to react further. However reaction of (143) with sodio-malononitrile in boiling methanol gave the sodium salt of (110), (146), Scheme 2.16.



(144) (143)

Scheme 2.15



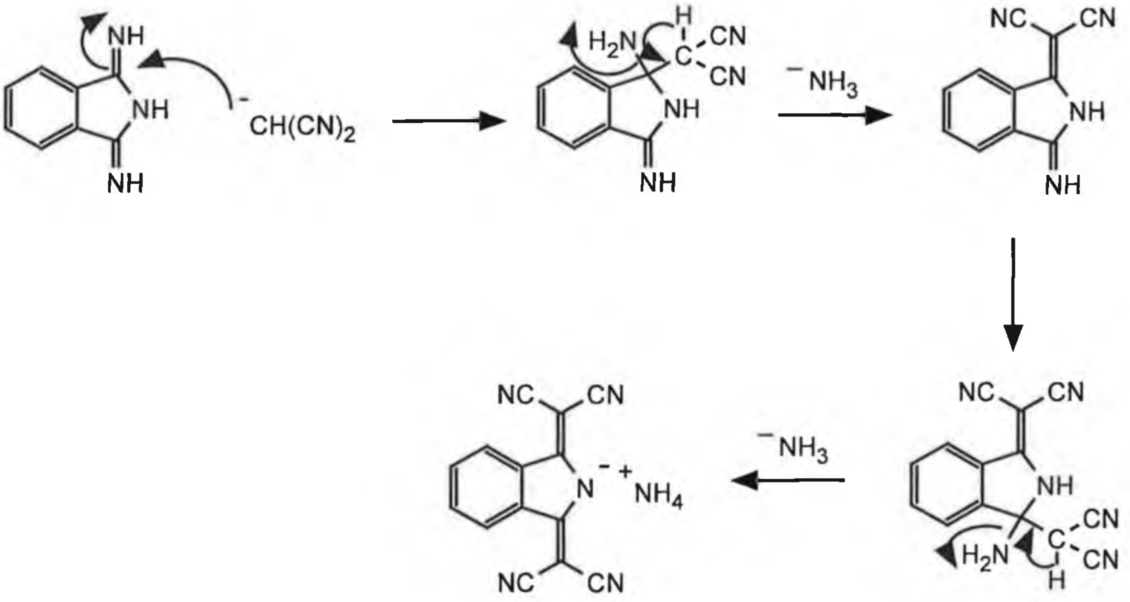
(143) (146)

Scheme 2.16

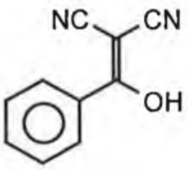
Structural elucidation of (146) was made on the basis of IR, ^1H and ^{13}C NMR spectra. The absence of a NH stretching frequency in the IR spectrum and a NH absorption in the ^1H NMR spectrum were the most remarkable differences between (146) and (110). The ^1H NMR spectrum of the sodium salt was very simple and only showed two symmetric aromatic multiplets at 7.61 and 8.21 ppm, each integrating for two protons. The solid was heated to 360 °C without melting, further suggesting the formation of a salt. Comparison of the IR and ^1H and ^{13}C NMR spectra of (146) with that of compound (146) recovered form the attempted benzoylation of (110) using benzoyl chloride and sodium hydroxide as the base, see page 88 Section 2.C, confirmed the structure.

2.B.3 Discussion

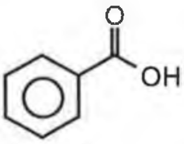
The formation of (110) is thought to occur *via* the mechanism shown in Scheme 2.17. When (118b) was used as the starting material the elimination of aniline was observed by TLC. The isolation of compound (110) as its ammonium salt (119) is not surprising when the potential acidity of (110) is considered. The carbonyl analogue of (110), phthalimide, is relatively acidic with a pKa of ~ 9. Studies of the analogy between oxygen and $C(CN)_2$ have been carried out[158] and the pKa values of $C(CN)_2$-H acids are up to 4.5 units smaller than those of the corresponding OH acids. Similarly compound (147) is found to be more acidic, (pKa= ~1),[159] than its carbonyl equivalent benzoic acid (148),(pKa= 4.2).[160]



Scheme 2.17

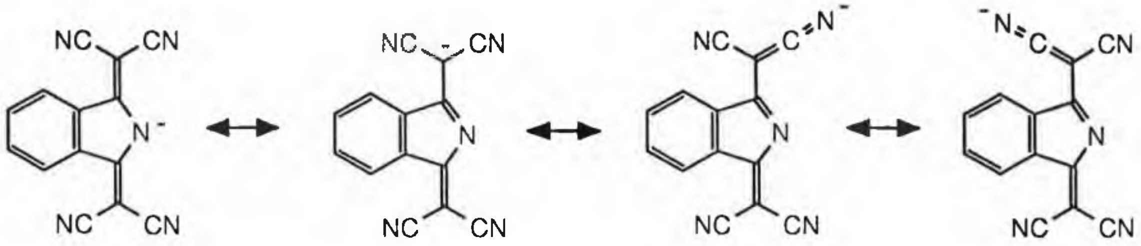


(147)



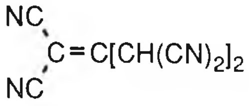
(148)

As a result of the greater electronegativity of the cyano groups, coupled with the fact that resonances that stabilise the conjugate base of an acid result in the acid having a higher stability than otherwise expected, it could be expected that (110) would be even more acidic than phthalimide. The stability of the anion of (110) is further enhanced by the presence of four strongly electron withdrawing groups in conjugation with the nitrogen of the isoindolin-1,3-diylidene system which can give rise to a number of different mesomers, four of which are shown below in Scheme 2.18. This additional resonance allows for even greater delocalisation of the charge.



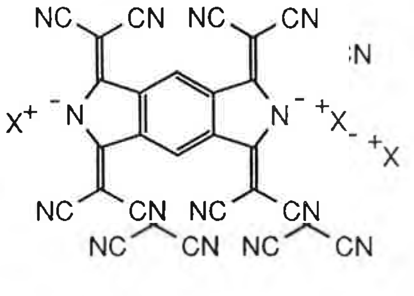
Scheme 2.18

Such enhanced delocalisation has given rise to the unusually high acidity of 2-dicyanomethylene-1,1,3,3-tetracyanopropene (149), which has a first pKa below -8.5 and a second pKa at -2.5.[161] The acidity of (110) was simply verified by the addition of sodium carbonate to a solution of (110) in dimethylformamide with the immediate evolution of carbon dioxide gas.



$(NC)_2C=C[CH(CN)_2]_2$

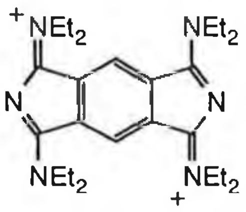
(149)



(150)

(a): $X^+ = Na^+$

(b): $X^+ =$



Salts of compounds structurally similar to (110) have also been reported. Gompper *et al.* reported the synthesis of the bis analogue of (110) as two salts (150a) and (150b). These were synthesised from the tetrafluoroborate salt of cation (b) by reaction with sodio-malononitrile.[162] The vast differences in the shades of the (110) isolated by the two methods, brown/orange for the pyrolysis method, bright yellow by acidification with dilute hydrochloric acid and then the bright orange needles obtained on recrystallisation, can be explained by the different morphologies in which (110) was isolated using these methods.

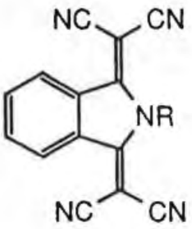
2.B.4 Conclusions

Several advantages are gained in using the improved synthesis of (110) from the ammonium salt (119). The synthesis and isolation of (119) makes for a more easily purified compound and it can be used as a highly soluble equivalent of (110), whose insolubility makes it an excellent pigment[151] but restricts its use for further reaction. Although the more direct route to compound (143), and ultimately the sodium salt (146), from phthalonitrile (144), Scheme 2.16, gives a viable route for the synthesis of (110), the poor solubility of (143) in most organic solvents makes this route less attractive.

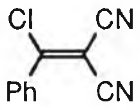
Section 2.C

2.C.1 *N*-Substituted derivatives of 2,2'-(Isoindolin-1,3-diylidene) bispropanedinitrile (110)

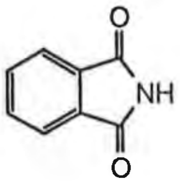
Investigations into the synthesis of novel *N*-substituted compounds of (110) were carried out, primarily to determine the effects of varying substituents on the electron acceptor ability of these isoindoline derivatives. The ability of these *N*-substituted compounds to form C-T complexes would then be investigated. In addition, it was hoped that such substitutions would result in improved solubility properties and allow for the attachment of a broad range of functional groups including polymerisable substituents.



(110) R= H
(151) R= Me
(152) R= Ph



(153)

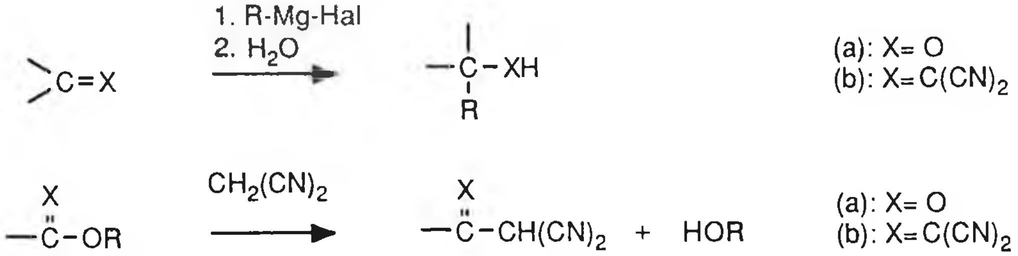


(154)

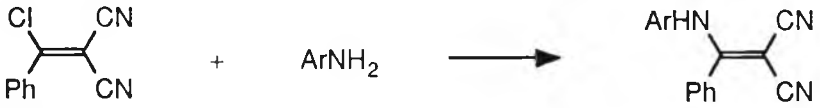
On searching the literature it was found that the methyl- and phenyl-derivatives of (110), (151) and (152), had been reported as charge carriers in an electro-conductive support by the BASF A.-G. company in a patent.[153] However the patent gave no indication or reference as to how these compounds were synthesised. They only described the synthesis of (110).

We were interested in finding viable methods for the *N*-substitution of (110) in high yields. The analogy between the $C(CN)_2$ group and oxygen has previously been made and many similarities in the reactivity and properties of carbonyl compounds and their alkylidenemalononitrile analogues have been found.[163] Some examples include, the addition reactions of a Grignard and the addition-elimination Knoevenagel reaction shown in Scheme 2.19 and the reaction of an amine with the acyl chloride analogue (153)[159] in Scheme 2.20.

With this in mind we speculated that (110) might also undergo the same *N*-substitution reactions as its oxygen analogue, phthalimide (154). *N*-Substituted phthalimides are synthesised by first generating the sodium or potassium salt of phthalimide and then reacting the salt with a substrate containing a displaceable group such as an alkyl or acyl halide, or an alkyl tosylate or sulphonate. These *N*-substituted phthalimides are extensively used in the Gabriel synthesis of primary amines.[164] The Gabriel type *N*-substitution reaction of (110) with a variety of substrates was investigated and these shall now be discussed.



Scheme 2.19

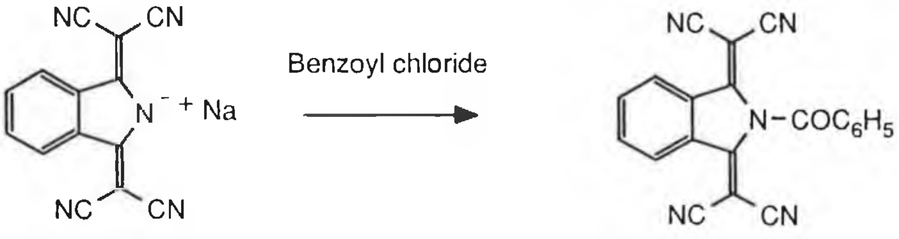


(153)

Scheme 2.20

2.C.1.1 Gabriel Type *N*-substitution reactions of (110)

Benzoylation of (110) by a number of methods was attempted, Scheme 2.21. These included the Schotten-Baumann method, which involved generating the sodium salt of (110), (146), using sodium hydroxide, and stirring the resulting suspension with benzoyl chloride at room temperature.

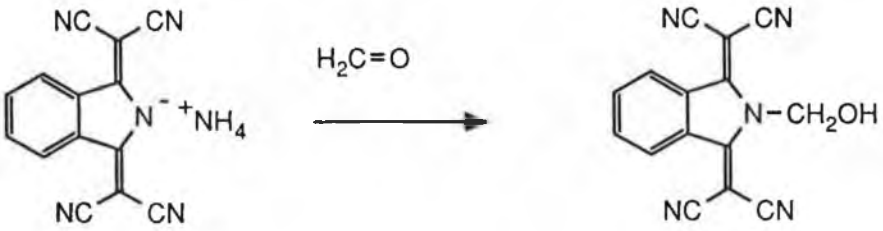


(146)

Scheme 2.21

This yielded a yellow powder which was identified, from its spectral data, as the sodium salt of (110) on comparison with a previously characterised sample. The more vigorous conditions of heating the sodium salt of (110), generated from the ammonium salt (119) by reaction with sodium hydride, with benzoyl chloride under reflux in tetrahydrofuran, or alternatively heating (110) under reflux with benzoyl chloride in pyridine, were also attempted. No new products were observed on following these reactions by TLC. Work-up of the reaction mixture in pyridine gave (110), identified by comparison of its spectra with that of the known compound . Similar results were also obtained on attempted acylation with acetic anhydride and attempted tosylation with tosylchloride.

The Mannich type reaction of the ammonium salt (119) with formalin (36% formaldehyde solution in water) was investigated, Scheme 2.22, to establish whether a hydroxymethyl group could be appended to (110). The aim of this reaction was to introduce a functional group onto (110) which could then undergo a multitude of reactions offering a wider range of substituents. A similar reaction between phthalimide (154) and formalin was reported to give *N*-(hydroxymethyl)phthalimide.[165] The ammonium salt of (110) was treated with formalin and heated under reflux.



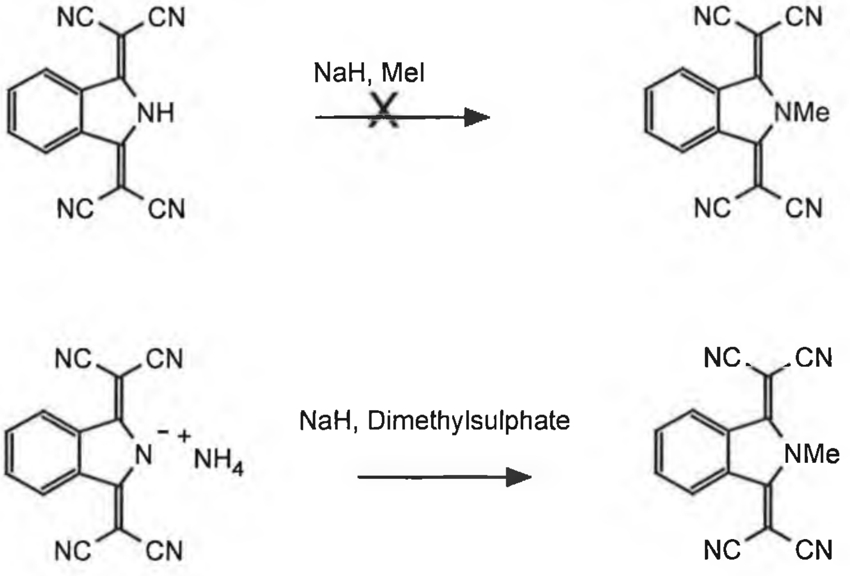
(119)

Scheme 2.22

TLC showed no new products were formed. The spectral data for the yellow solid obtained on terminating the experiment were consistent with those for (110).

N-Methylation of (110) was initially attempted using methyl iodide but the yellow solid recovered, on terminating the reaction, was identified as the sodium salt of (110) by comparison of its IR and melting point with those of an authentic sample. *N*-Substitution of (110) was finally achieved when methylation was accomplished in a very poor yield using dimethylsulphate as the reagent, Scheme 2.23. Reaction of the sodium salt of (110) with dimethylsulphate showed the formation of a much faster eluting principal compound, and a number of minor products nearer the baseline, on following the reaction by TLC. This faster moving product was eventually isolated by column chromatography using tetrahydrofuran as the mobile phase. The ^{1}H NMR spectrum of this compound in chloroform-d$_1$ showed three peaks in total, two symmetrical aromatic multiplets at 7.19 and 8.67 ppm, integrating for two protons each, and a third peak, a three proton singlet at 4.17 ppm, assigned to the *N*-methyl group.

A further indication that methylation had taken place was apparent from the IR spectrum which showed the absence of NH bands above 3150 cm^{-1}.



(151)

Scheme 2.23

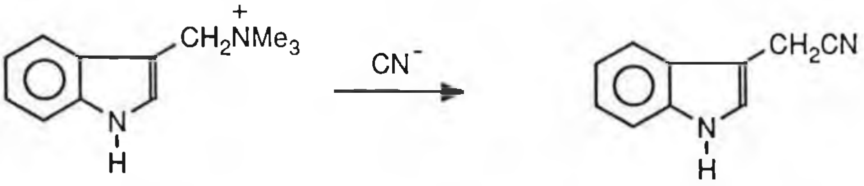
On carrying out a ^{13}C NMR experiment in dimethylsulphoxide-d_6, some heating was necessary in order to dissolve the compound. The ^{13}C NMR spectrum obtained showed an unexpectedly large number of carbon absorptions. TLC of the ^{13}C NMR sample no longer showed just one product but several products indicating that the compound was unstable when heated in dimethylsulphoxide. On the basis of the ^1H NMR and IR spectra this compound was believed to be the N-methylated derivative (151). This assignment was confirmed by comparison of the ^1H NMR, IR spectra and melting point of (151) synthesised by this method with those of the same compound synthesised from the tetramethylammonium salt discussed in the next section. The poor yield of this reaction and the need to use highly toxic dimethylsulphate meant an alternative and safer synthesis was needed.

2.C.1.2 Alternative Methods for *N*-Substitution of (110)

2.C.1.2.1 Methylation using the tetramethylammonium (TMA) salt (155)

The use of quaternary ammonium salts in nucleophilic displacement reactions have been rare and suffer from poor yields and lack of generality.

Some examples include the nucleophilic displacements on gramine quaternary salts,[166] Scheme 2.24.

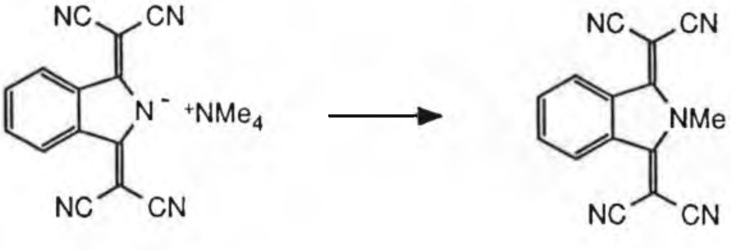


Scheme 2.24

In the Hofmann degradation of amines, cleavage of quaternary ammonium hydroxides is the final step. The pyrolysis of tetramethylammonium hydroxide, $NMe_4^+OH^-$, under vacuum has been found to yield trimethylamine, dimethyl ether and methanol.[167] One mechanism proposed suggested that the formation of the ether may be explained by the abstraction of a proton from the tetramethylammonium group by the OH^- group to give a nitrogen ylide. This ylide, which can behave like a carbene, can then react with the methanol present, which may be formed initially by nucleophilic displacement of a methyl group from the tetramethylammonium cation by a hydroxide anion, or by reaction of the ylide with a small amount of water, to form an ether. Similar results were also obtained from tetramethylammonium alkoxides.[168] Demethylation of triethylmethylammonium cation in the dry state and also in non-protic solvents by thiophenoxide has also been reported.[169]

It was decided that this approach may provide a viable way of obtaining (151). We found on heating the tetramethylammonium (TMA) salt (155) in 1,2-dichlorobenzene that (151) was obtained, Scheme 2.25.

The TMA salt (155) was isolated in 60% yield by mixing an aqueous solution of tetramethylammonium chloride with a solution of (119) in methanol. The IR, ^1H NMR and ^{13}C NMR spectra, and elemental analysis of (155) were all consistent with the assigned structure. The ^1H NMR spectrum showed four aromatic protons as two symmetric multiplets at 7.56 and 8.14 ppm and twelve methyl protons as a singlet at 3.41 ppm. The ^{13}C NMR spectrum showed the C_2 carbon absorption of the 2,2-dicyanovinylidene group at 54.06 ppm, a triplet at 54.43 ppm, J = 15 Hz, which corresponded to the methyl carbons of the tetramethylammonium cation, two nitrile carbon absorptions at 116.32 and 117.20 ppm, three aromatic absorptions at 122.9, 131.4 and 137.33 ppm and a 2,2-dicyanovinylidene C_1 carbon absorption at 171.87 ppm. The methyl carbon absorption at 54.43 ppm occurs as a triplet due to coupling of the ^{14}N nucleus with that of ^{13}C. Couplings between ^{13}C and the abundant isotope ^{14}N, which has a natural abundance of 99.6 % and $I = 1$, are usually not measurable. This is because ^{14}N has a nuclear quadrupole moment which results in a more effective mode of relaxation which is usually so fast that the coupling effects are not observed. ^{13}C-^{14}N splittings however are observed in special cases such as tetraalkylammonium ions, isonitriles and diazomethanes, where the nitrogen nucleus is in a relatively symmetrical environment and so the electric field gradient at the ^{14}N nucleus is zero or sufficiently small. A typical $J(^{13}C, ^{14}N)$ value is of the order of 10 Hz.[170]



(155) (151)

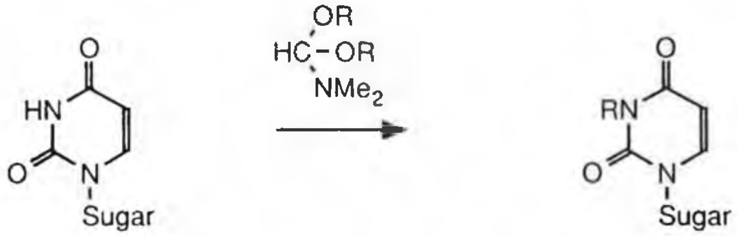
Scheme 2.25

Heating the TMA salt (155) under reflux in 1,2-dichlorobenzene for 150 hours gave (151) as black/purple needles, Scheme 2.25. Recrystallisation of these needles, and the solid remaining from evaporating off the 1,2-dichlorobenzene from the filtrate, gave (151) as an orange/yellow crystalline solid in 54% yield. The ^1H NMR spectrum of (151) showed only three different types of proton. Four aromatic protons were observed as two symmetric multiplets at 7.98 and 8.65 ppm, in the ratio 2:2, and a three proton singlet at 4.10 ppm corresponding to the methyl protons at the 2 position of the isoindolin-1,3-diylidene ring system. The symmetrical nature of the molecule was further supported by the ^{13}C NMR spectrum which showed a methyl carbon absorption at 37.49 ppm, the C_2 absorption of 2,2-dicyanovinylidene group at 61.90 ppm, only two cyano carbon absorptions at 113.76 and 114.52 ppm and three aromatic carbon absorptions between 125.70 and 135.30 ppm. The 2,2-dicyanovinylidene C_1 carbon absorption was found at 160.92 ppm.

A less convenient method for the synthesis of (151) involved heating the salt (155) under a vacuum of 0.5 mmHg at 180 °C for twelve hours. During the course of the reaction a yellow solid sublimed onto the sides of the reaction vessel. This was removed by washing the sides of the reaction vessel with acetone. TLC showed that this yellow product was made up of two main compounds with very similar R_f values. Attempts to separate the individual components were unsuccessful. The ^1H NMR spectrum in chloroform-d_1 showed that there were two pairs of aromatic protons. The major component showed a pair of symmetric aromatic multiplets, which occurred at 7.86 and 8.67 ppm and which integrated for a total of four protons. A singlet at 4.18 ppm which integrated for three protons was also observed. These values corresponded with the chemical shifts observed for the pure compound, (151), obtained using dimethylsulphate as the methylating agent and of that obtained by heating (155) in 1,2-dichlorobenzene. This verified that one of the products of this method was (151). The ^{13}C NMR spectrum, also in chloroform-d_1, was more complicated and showed many carbon absorptions with 5 cyano absorptions observed between 116.0 and 111.0 ppm along with a total of 9 aromatic absorptions.

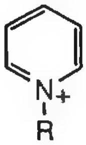
2.C.1.2.2 Attempted Benzylation of 2,2'-(Isoindolin-1,3-diylidene) bispropanedinitrile (110)

Apart from the tetraalkylammonium salts previously mentioned, other highly specific methods of *N*-alkylation exist. Compounds containing acidic NH groups undergo alkylation by amide acetals at the nitrogen atom. This exceptionally selective reaction was used until recently with nucleosides,[171] Scheme 2.26



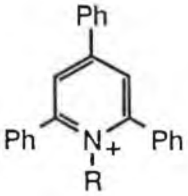
Scheme 2.26

The discovery that (110) could be methylated using dimethylsulphate, or its tetramethylammonium salt, suggested that other substituents could also be appended by synthesising substrate salts with appropriate leaving groups. One such group is the pyridinium salts, (156)-(160), extensively investigated and developed by Katritzky[172] for the conversion of aliphatic amino groups into leaving groups. These pyridinium salts can transfer *N*-substituents to a wide range of nucleophiles such as halides and oxygen-, sulphur-, nitrogen-, phosphorus- and carbon-nucleophiles. A variety of *N*-substituted phthalimides (161) has been prepared in high yields from the potassium salt of phthalimide with the appropriately *N*-substituted 2,4,6-triphenylpyridinium tetrafluoroborates (157) by pyrolysis or by heating under reflux in dimethylformamide.[173]



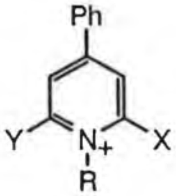
(156)

R= Me, Et, i-Pr, etc.

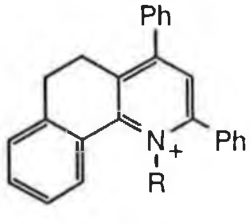


(157)

R= Me, t-Bu, Ph, $NO_2C_6H_4$

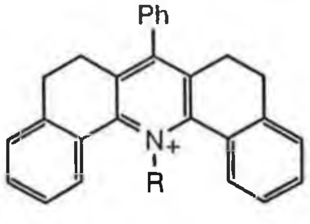


(158) a: Y= Ph, X= Me, t-Bu, 2-thienyl
b: Y= X= Me
c: Y= X= Mesityl



(159)

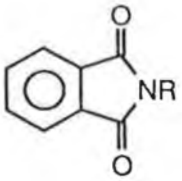
R= Me, n-Bu, Benzyl, Ph



(160)

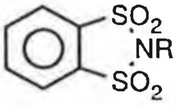
R= Me, n-Bu, Benzyl, Ph

N-Substituted o-benzenesulphonimides (162) have also been investigated as potential alkylating agents because of the expected high charge stabilisation of the anion.[174] However these compounds were found to be relatively inert on heating with nucleophiles under reflux in dimethylformamide with low recovery of the imide.



R= Alkyl (C1-C6), i-Pr, benzyl, $ClC_6H_4CH_2$(o), etc

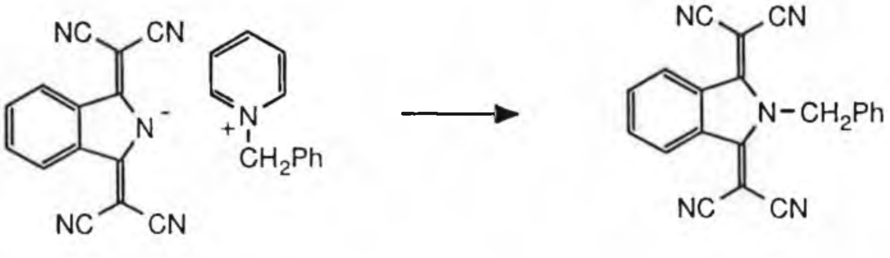
(161)



R= CH_2Ph and CH_2CH_2Ph

(162)

We attempted to benzylate compound (110), based on Katritzky's method, by first forming the benzylpyridinium salt of (110), (163), and then heating this salt in 1,2-dichlorobenzene as done previously with the TMA salt (155), Scheme 2.27. The unsubstituted pyridinium salt was investigated because these substrate salts had been successfully used to convert the very poor nucleophile trifluoroacetic acid to its corresponding ester by solvolysis of trifluoroacetic acid with a variety of *N*-substituted pyridinium salts and also because it was more easily synthesised than the alternative pyridinium salts. In addition it is known that steric hindrance of the attacking nucleophile affects the rate of the displacement reaction[172(b)] and while the displacement rates are also dependent on the substituents on the pyridinium ring, with the salts (159) and (160) being shown to be better substrates for reaction with sodium acetate than the 2,4,6-triphenylpyridinium salt,[175] it was considered that such steric effects may not occur if the unsubtituted pyridinium salt were utilised.



(163)

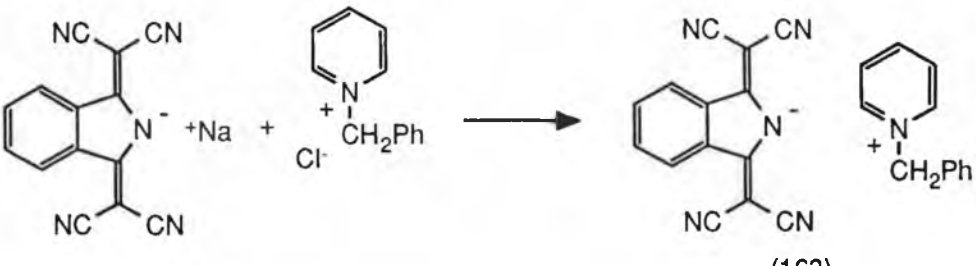
(164)

Scheme 2.27

The *N*-benzyl derivative was chosen as this *N*-substituent has been found to be more easily transferred to the nucleophile than the other aliphatic *N*-substituents[172(b)] and has been displaced in reactions with some nucleophiles where other aliphatic *N*-substituents have not.[175]

Mixing a methanol solution of the sodium salt of (110) with benzylpyridinium chloride, synthesised by heating benzyl chloride and pyridine together, gave the benzylpyridinium salt (163), Scheme 2.28. This was supported by the IR, ^{1}H and ^{13}C NMR spectra and by elemental analysis. The ^{1}H and ^{13}C NMR spectra of the benzylpyridinium cation compare very well with those of the benzylpyridinium perchlorate salt reported by Katritzky.[176] The aromatic protons for the anion of (110) were found at 7.62 and 8.08 ppm, with both multiplets integrating for two protons each. The carbon absorptions for the anion of (110) were found at 54.4 ppm for the C_2 carbon of the 2,2-

dicyanovinylidene group, at 116.3 and 117.3 ppm for the cyano carbons, aromatic carbons at 122.9, 131.4 and 137.4 ppm and the 2,2-dicyanovinylidene C_1 carbon at 171.9 ppm.



(163)

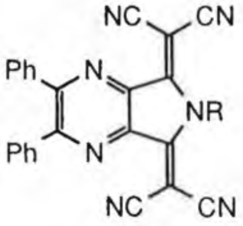
Scheme 2.28

Heating salt (163) under reflux in 1,2-dichlorobenzene for sixteen hours resulted in the formation of a black solution as found for the corresponding TMA salt (155). Although a very small quantity of a fast eluting compound was observed by TLC, the amount generated was insufficient to be isolated. A black non-eluting decomposition product was obtained on filtering the solution and this was insoluble in all the solvents tried. Starting material was also recovered from the filtrate, on evaporation to dryness.

2.C.2 Discussion

The same influences which determine the acidity of (110) also contribute to its poor nucleophilicity. The lone pair of electrons in the 2-position of the anion of (110) are highly delocalised. As a result it is not too surprising that the standard methods of substitution, involving nucleophilic reaction with an alkyl or acyl halide, were not successful. Although methylation with dimethylsulphate was effective, the poor yields obtained and need to use such a highly toxic methylating agent made this method very unattractive.

The reports of highly specific methods[166, 171] for alkylating weakly nucleophilic substrates show the need for finding alternative methods of alkylation when standard methods are not successful. The tetramethylammonium salt method reported here was successful and provided reasonable yields. The formation of (151) is thought to occur *via* a displacement reaction between the weakly nucleophilic anion of (110) and the tetramethylammonium group. This is consistent with the findings of Musher[167] who reported that for the related Hofmann degradation of various tetramethylammonium salts of various anions, hydrogen abstraction was favoured for strong bases, while weaker bases, like the halides, were thought to undergo a displacement reaction. The attempted *N*-benzylation of (110) using the benzylpyridinium salt (163) failed to yield sufficient quantities of the new product observed by TLC. A similar type displacement reaction would be expected to take place for this reaction, with generation of pyridine as the leaving group. While there are fewer reports by Katritzky of the use of the unsubstituted *N*-alkylpyridinium salts (156), they have been shown to alkylate even the most poorly nucleophilic compounds such as trifluoroacetic acid which gave the corresponding ester as the solvolysis product.[177] Considering these reports, it is evident that the anion of (110) is extremely non-nucleophilic. It was also reported that the *N*-substituted pyridinium salts underwent hydrolysis to give the corresponding alcohols at temperatures between 60 and 100 °C.[177] The possibility that the *N*-benzyl-derivative (164) is unstable at the temperature at which the reaction was carried out seems plausible but attempts to effect reaction at lower temperatures were not successful. Interestingly, the methods for *N*-alkylation reported here, the tetraalkylammonium salt method and the *N*-benzylpyridinium salt method, have since been applied to the pyrazine analogue of (110), (165a),[178] and have successfully yielded the *N*-methyl, -ethyl and -benzyl derivatives (165b) under similar conditions. Why these methods should work effectively for the pyrazine analogue and not (110) is not understood.



(165)

a:R= H
b:R= Me, Et and Benzyl

Comparison of the UV/visible spectra of (110), its ammonium salt (119) and its *N*-methyl derivative (151) in acetonitrile show varying λ_{max}, see Figure 2.1. The λ_{max} of (110) compared with (119) occur at much shorter wavelengths, 386 and 408 nm compared with 466 and 496 nm. This difference can be attributed to the greater auxochromic effect of the anion, which results in greater conjugation, compared with the protonated NH compound. Comparison of the UV/visible spectra of (110) and (151) shows that *N*-alkyl substitution slightly enhances the auxochromic effect of the ring nitrogen with λ_{max} associated with the *N*-methyl derivative occuring at slightly longer wavelengths, (394 and 416 nm). The use of a more polar solvent, *N,N*-dimethylformamide, shows a significant effect on the UV/visible spectrum of (110). Comparison of the UV/visible spectrum of (110) and its ammonium salt in *N,N*-dimethylformamide, Figure. 2.2, shows that both are identical. This shows that in solution the better solvating ability of the *N,N*-dimethylformamide enhances deprotonation of (110) resulting in the formation of the more highly conjugated anionic system. The *N*-methyl derivative (151) however cannot undergo deprotonation and thus shows little change in its λ_{max} values, see Figure 2.2.

2.C.3 Conclusion

In light of these findings it is apparent that the substantial anionic charge stabilisation, granted by the dicyanomethylene groups, makes (110) a poor nucleophile thus making it extremely difficult to carry out standard alkylation and acylation reactions. In spite of this it seems worthwhile that alkylation of (110) with other substituted pyridinium salts should be investigated to determine if these methods are more effective.

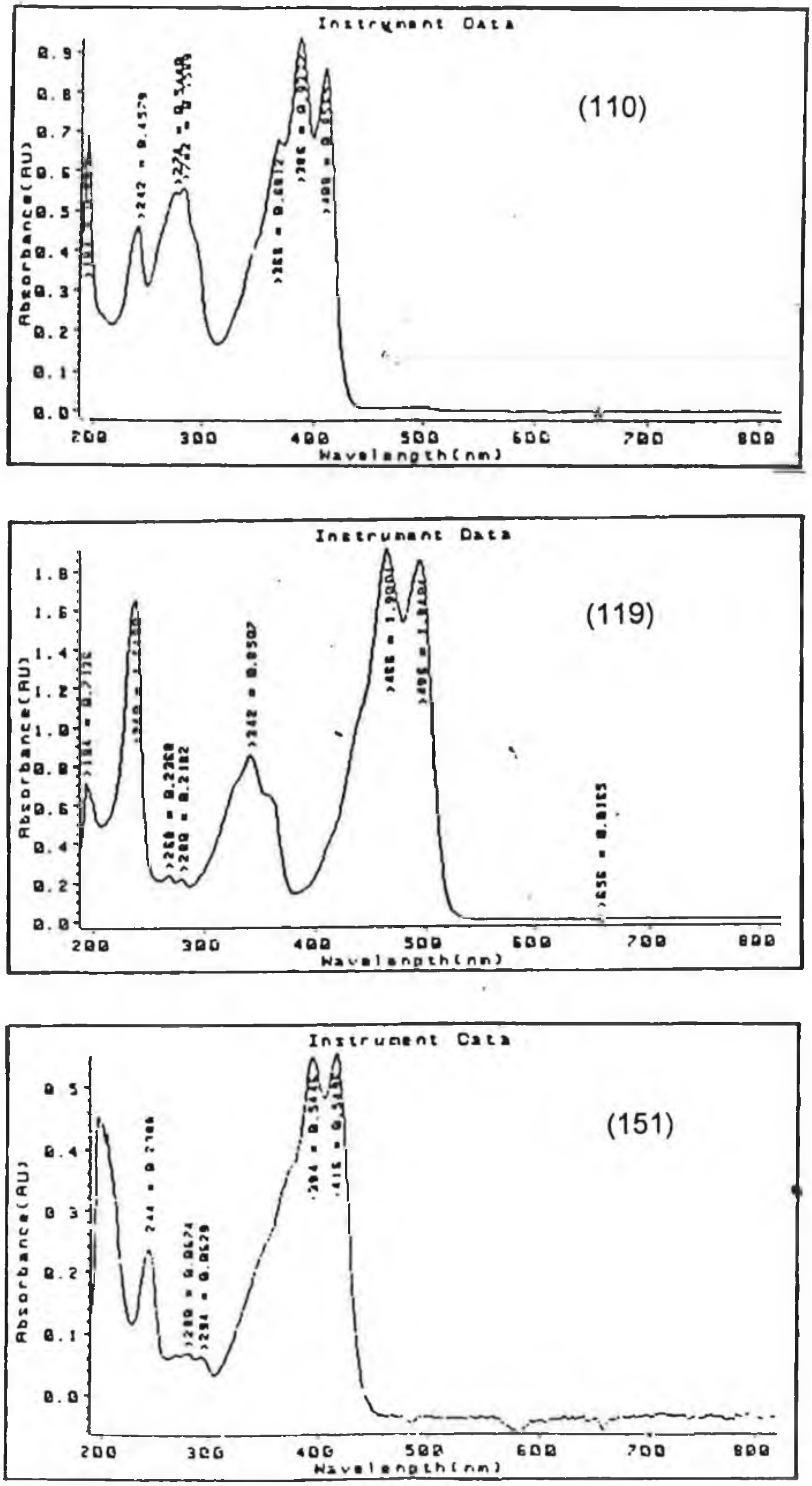


Figure 2.1 UV/visible spectra of (110), (119) and (151) in acetonitrile.

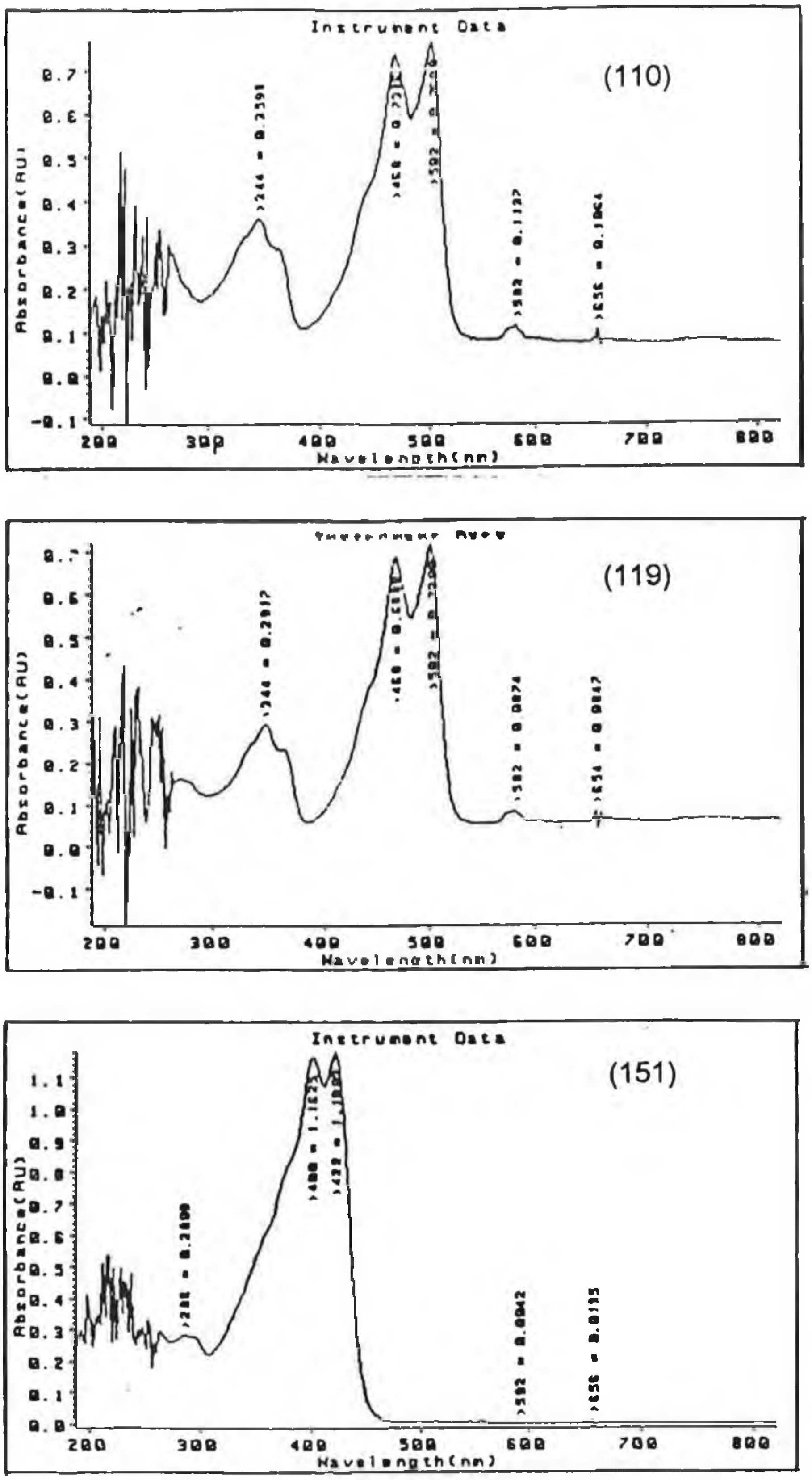


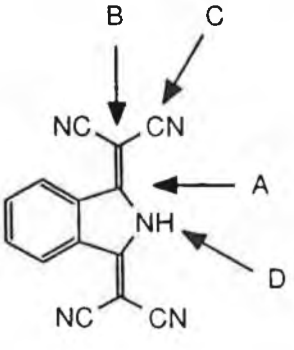
Figure 2.2 UV/visible spectra of (110), (119) and (151) in dimethylformamide.

Section 2.D

2.D.1 Reactions of 2,2'-(Isoindolin-1,3-diylidene)bispropanedinitrile (110) with Amines

Apart from reports of the pigment properties and uses of (110) in the patent literature there has been no report of the chemistry of this compound. As stated previously, the reactions of carbonyl compounds and their analogues, the alkylidenemalononitriles, have shown many similarities.[159, 163] Some of these have been mentioned already, (see Scheme 2.19 and 2.20, Section 2.C).. We have found (Section 2.C) that it was extremely difficult to achieve *N*-substitution of (110), the alkylidenemalononitrile analogue of phthalimide, and that methods used for the synthesis of *N*-substituted phthalimides were not effective for (110). This was attributed to the poorer nucleophilicity of the nitrogen in the 2-position of the ring, due to the greater delocalisation of the anionic charge, resulting from the presence of highly electron-withdrawing dicyanomethylene groups. On the basis of a possible similarity in the chemistry of phthalimide and (110), we were interested in investigating the reactivity of (110) towards amines. Nucleophilic attack on an *N*-substituted phthalimide by hydrazine, the final step in the Gabriel synthesis of amines,[164] occurs at the carbonyl carbon resulting in ring-opening and subsequent elimination of an amine bearing the *N*-substituent. The possibility of an analogous reaction occurring between (110) and an amine, or of nucleophilic attack by the amine occurring at another position, was of interest in view of the possible products which could be formed. These shall now be discussed.

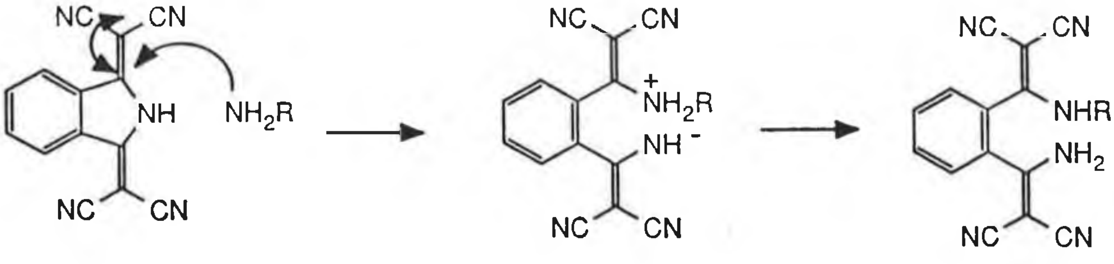
There are four principal sites on (110) at which an amine could attack and these are shown below as A, B, C and D, Scheme 2.29.



(110)

Scheme 2.29

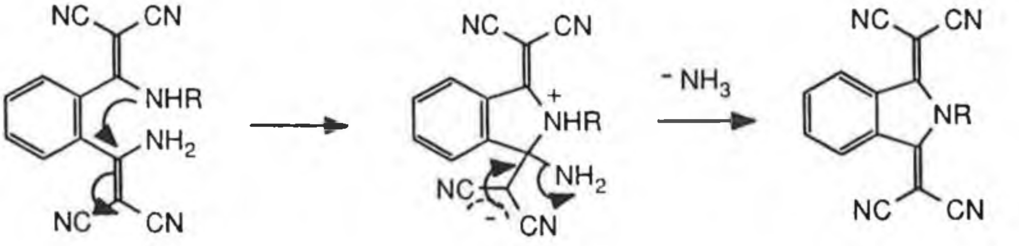
Nucleophilic attack at site A, by analogy with phthalimide, could result in ring-opening, giving intermediate (166), Scheme 2.30.



(166)

Scheme 2.30

Intermediate (166) could then undergo ring-closure, followed by elimination of ammonia, to give an *N*-substituted derivative of (110), (167), Scheme 2.31. Equally possible is the alternative ring-closure to (110), with loss of the amine.



(166)

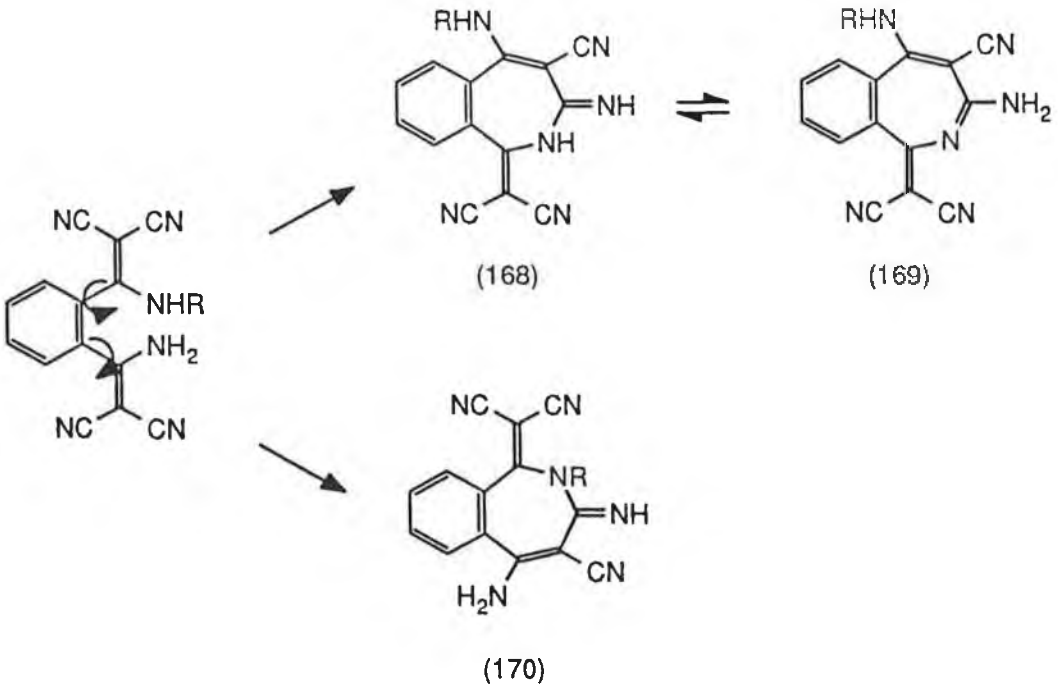
(167)

Scheme 2.31

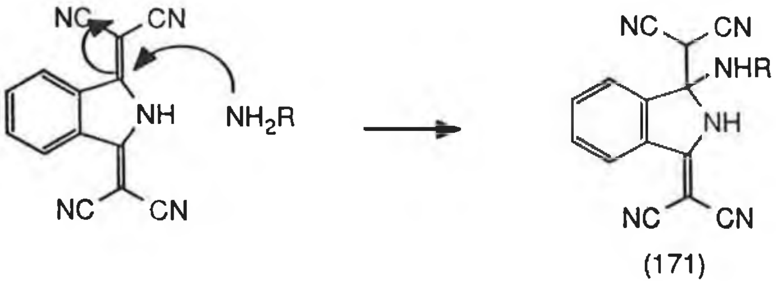
Alternatively either moiety in the 1- and 2- positions of the benzene ring of (166) could rotate freely around the carbon-to-carbon single bond giving rise to the formation of a seven-membered ring system (168-170). This could occur *via* addition of either nucleophilic amino group to a cyano on the adjacent dicyanoethenylamino group, Scheme 2.32.

Nucleophilic attack at postion A could also give an addition reaction across the carbon-to-carbon double bond of the dicyanovinylidene group giving adduct (171), Scheme 2.33.

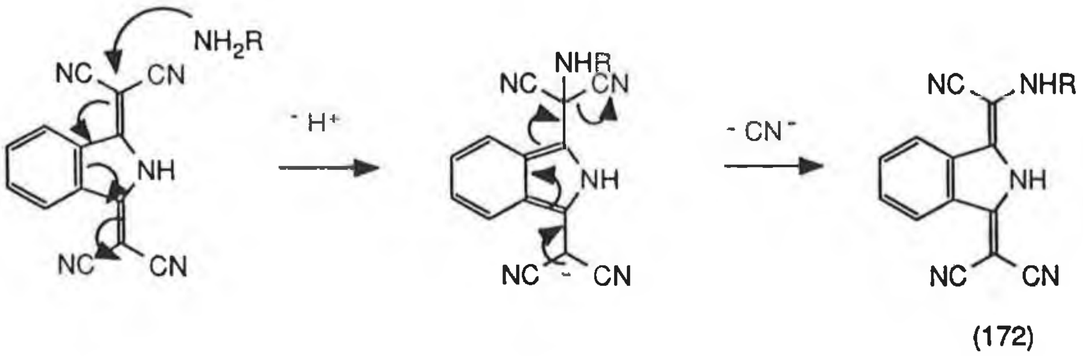
Attack by an amine at site B of (110) could result in a 1,6-addition-elimination reaction giving (172), Scheme 2.34. Similar addition-elimination reactions of amines with TCNQ[179] and other alkylidenemalononitrile compounds have been reported,[180] *e.g.* Scheme 2.35.



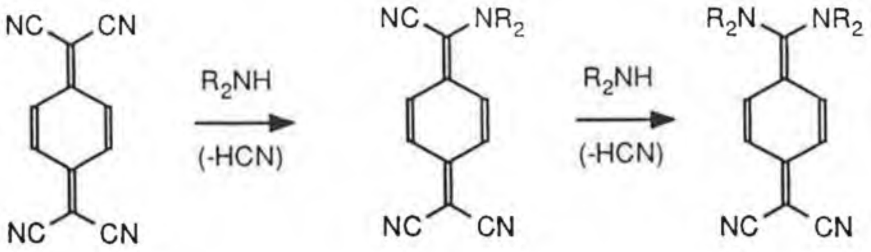
Scheme 2.32



Scheme 2.33

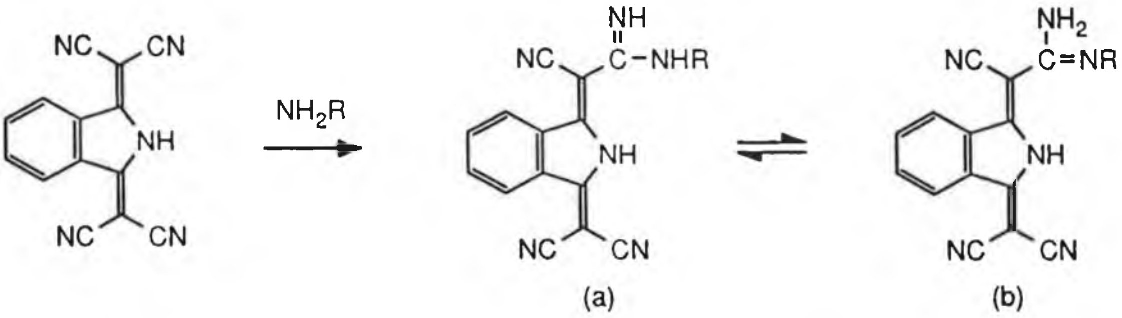


Scheme 2.34



Scheme 2.35

Reaction at site C, or at any of the cyano groups, could result in 1,2-addition of the amine to a cyano group resulting in the formation of an amidine, (173), which can exist in tautomeric forms (a) and (b), Scheme 2.36.

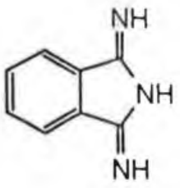


(173)

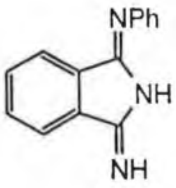
Scheme 2.36

In light of the acidic nature of (110) reaction at site D would result in the formation of the corresponding alkylammonium salt of (110) by abstraction of the acidic proton by the amine. It would seem likely that this reaction would be the first step in any reactions between (110) and an amine. This is verified by the isolation of the ammonium salt (119) from the Knoevenagel condensation of malononitrile with the imidines (118a) and (118b), in which the ammonia generated by the condensation reaction deprotonated (110). Immediate deprotonation of the related compound, (174), with alkali has also been reported.[149]

Because of the poor solubility of (110) in common solvents, the ammonium salt (119) was used in its place for the reactions with various amines in a variety of solvents. The results of these experiments will be discussed in the next section.

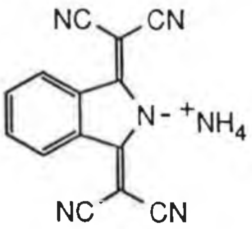


(118a)



(118b)

(174)



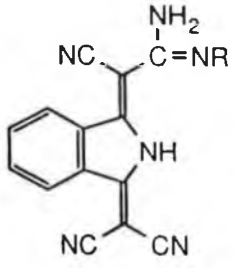
(119)

2.D.2 Reactions of Amines with the Ammonium Salt (119)

2.D.2.1 Reaction of Benzylamine with (119)

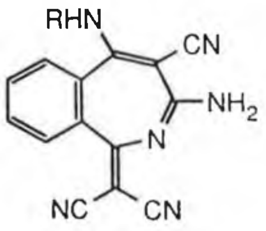
A solution of the ammonium salt (119) in 1,4-dioxan was treated with benzylamine and heated under reflux for four hours. During the course of the reaction the formation of a new product, which precipitated from solution as an orange solid, was observed by TLC and was isolated by filtration. It was found to be insoluble in most organic solvents and was recrystallised from a DMF/ethanol mixture.

The ^1H NMR spectrum showed four unsymmmetrical aromatic multiplets at 8.29, 8.11, 7.62 and 7.36 ppm whose integrations were in the ratio 1:1:2:5 respectively. The five proton aromatic multiplet at 7.36 ppm was assigned to the benzyl aromatic protons. Also present were two broad singlets at 10.29 and 9.25 ppm whose integrations were in the ratio 1:2 respectively which were assigned as NH and NH_2 protons and a two proton singlet at 4.67 ppm was assigned to the methylene protons of the benzyl group. The unsymmetrical nature of the aromatic multiplets, and the presence of two NH absorptions in the ratio 1:2, suggested that, of the products postulated in the introduction, the product was probably the amidine (175) or either of the two benzoazepines (176) or (177). The absence of a dicyanomethyl signal in the proton NMR

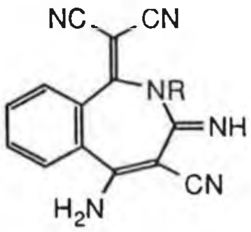


(175)

where $R=CH_2Ph$

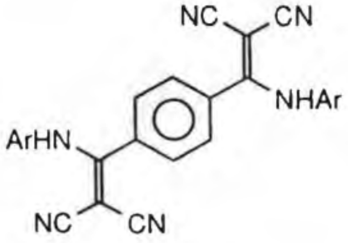


(176)



(177)

spectrum eliminated the possibility of an addition reaction at the 2,2-dicyanovinylidene C_1 carbon as in Scheme 2.33. The ^{13}C NMR spectrum further supported the hypothesis that the structure was unsymmetrical and showed the correct number of different carbon absorptions for the structures postulated. A total of 19 different carbon absorptions were observed of which 10 were aromatic. Four of these were attributed to the benzyl group, three of which were assigned conclusively with the aid of a C-H correlation spectrum, and the remaining six aromatic absorptions to the isoindolin-1,3-diylidene ring. Only three cyano carbon absorptions were observed, at 114.66, 115.35 and 116.80 ppm. Since a 1,6-addition elimination reaction would have given a product having a total of 18 different carbons, see Scheme 2.34, this possibility was disregarded. The carbon absorption at 44.9 ppm was assigned to the methylene carbon of the benzyl group and the carbon at 57.25 ppm, by comparison with the carbon NMR spectrum of (110) and various derivatives of bis[2,2-dicyano-1-(phenylamino)vinyl]benzene (178),[159] was assigned as the

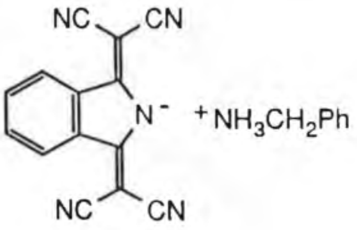


(178)

C_2 carbon of the 2,2-dicyanovinylidene group, which is common to all three possible structures. The IR spectrum showed two NH stretching bands at 3382 and 3321 cm^{-1}. Since the NH stretching bands were sharp, and the characteristically very broad band of an imino NH stretch was absent, this suggested that either isomer (175) or (176) was the most probable structure. However on the basis of this information alone it was not possible to determine which structure was correct and further evidence was needed, either an X-ray crystal structure of the product, which was not possible due to the inability to grow adequate crystals, or a crystal structure of a compound which was structurally very similar and whose spectral data would also be very similar, and which by comparison would allow the true structure to be assigned.

Recrystallisation of the solid obtained on evaporating the filtrate, gave the benzylammonium salt (179). The structure of (179) was assigned on the basis of ^1H, ^{13}C NMR and IR spectral data and was confirmed by X-ray structural analysis.

The ^1H NMR spectrum of (179) showed a broad singlet overlapping a symmetrical aromatic multiplet at 8.52 ppm, giving a total integration of five protons, and a symmetrical two proton aromatic multiplet at 7.65 ppm. The addition of deuterium oxide D_2O to the ^1H NMR spectrum sample resulted in the disappearance of the broad singlet, leaving a two proton aromatic multiplet at 8.52 ppm, and verifying the presence of the three exchangeable protons of the benzylammonium cation. The symmetrical aromatic peaks at 8.52 and 7.65 corresponded to the aromatic protons of the anion of (110). The five aromatic protons of the benzylammonium cation were observed as a multiplet at 7.45 ppm and the two methylene protons occurred as a singlet at 4.5 ppm.



(179)

The symmetrical nature of the molecule was also apparent from the ^{13}C NMR spectrum which showed a total of seven different aromatic peaks between 123 and 138 ppm and two cyano peaks at 116.24 and 117.19 ppm. The C_1 and C_2 absorptions of the 2,2-dicyanovinylidene group were observed at 171.97 and 53.89 ppm respectively and the methylene carbon absorption at 42.28 ppm. The C-H correlation spectrum showed that the three aromatic carbon absorptions at ~ 128 ppm corresponded to the benzylammonium group and the absorptions at 122.8 and 131.3 corresponded to the anion of (110), as did the quaternary aromatic absorption at 137.38 by comparison with the carbon NMR spectra of the ammonium salt (119) and the tetramethylammonium salt (155). Comparison of the UV/visible spectrum of (179) with that of (119), and (155), showed that they had identical λ_{max} values, see Figure 2.3. The strong similarities in the ^1H, ^{13}C NMR and UV/visible spectra suggested that the orange solid was the benzylammonium salt.

In order to confirm the structure of (179) an X-ray crystal structure analysis was carried out. Compound (179) gave orange cubic crystals on recrystallisation from acetonitrile. The crystal structure data showed that (179) was monoclinic with space group P48 symmetry. The crystal structure is shown in Figure 2.4(a) and (b) and the corresponding bond lengths and bond angles are given in Tables 2.1 and 2.2 respectively.

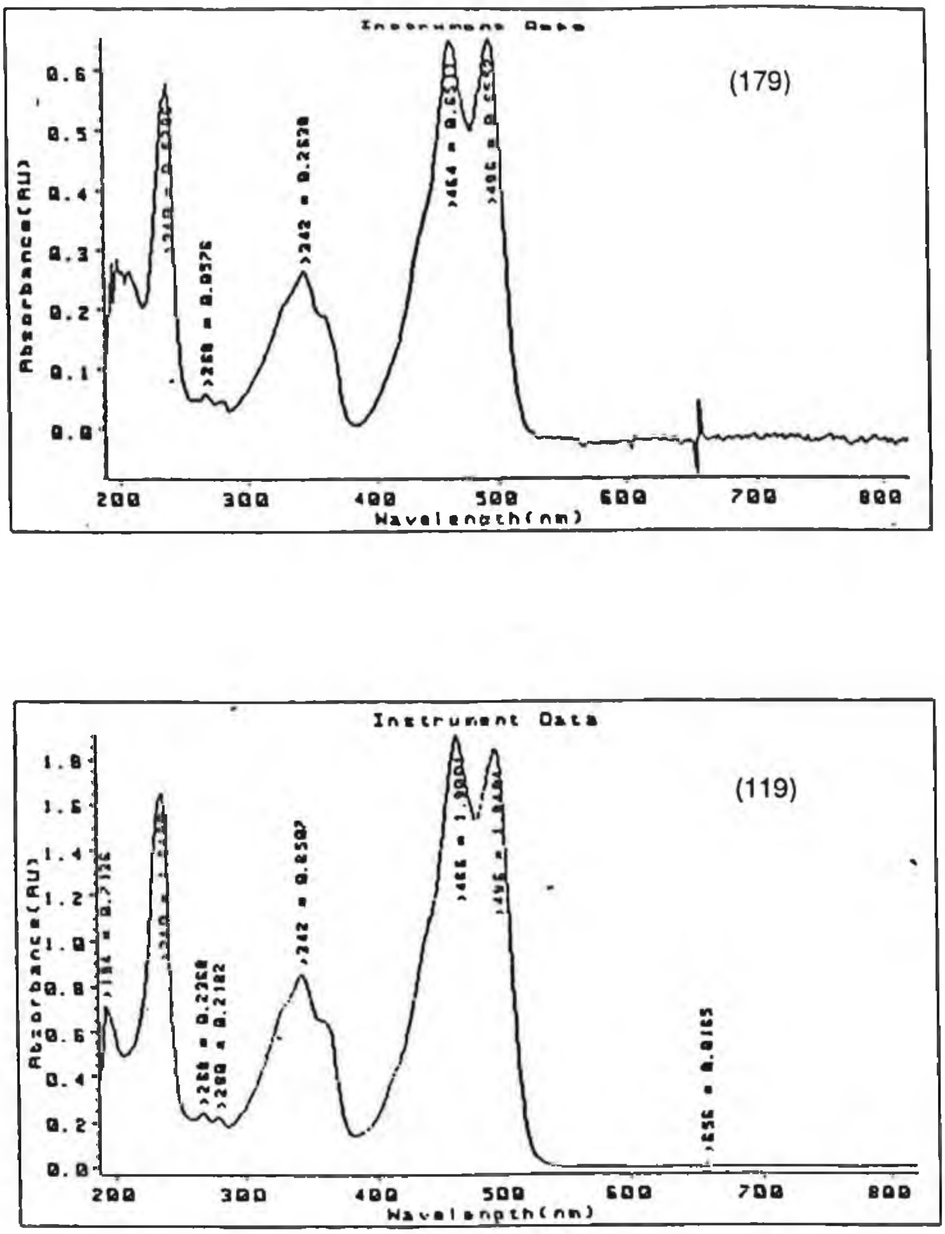


Figure 2.3 UV/Visible spectra of (a) (179) and (b) (119)

Table 2.1 Bond lengths [Å]

N(1)-C(8)	1.347(10)
N(1)-C(1)	1.388(10)
N(2)-C(10)	1.113(12)
N(3)-C(11)	1.150(11)
N(4)-C(13)	1.169(12)
N(5)-C(14)	1.132(11)
N(6)-C(21)	1.487(5)
C(1)-C(9)	1.374(10)
C(1)-C(2)	1.519(11)
C(2)-C(3)	1.350(12)
C(2)-C(7)	1.395(5)
C(3)-C(4)	1.363(13)
C(4)-C(5)	1.381(6)
C(5)-C(6)	1.423(14)
C(6)-C(7)	1.413(12)
C(7)-C(8)	1.440(12)
C(8)-C(12)	1.384(11)
C(9)-C(11)	1.369(11)
C(9)-C(10)	1.418(12)
C(12)-C(13)	1.428(12)
C(12)-C(14)	1.475(10)
C(15)-C(16)	1.35(2)
C(15)-C(20)	1.39(2)
C(15)-C(21)	1.494(6)
C(16)-C(17)	1.49(2)
C(17)-C(18)	1.55(2)
C(18)-C(19)	1.16(2)
C(19)-C(20)	1.25(2)

Table 2.2 Bond angles [deg]

C(8)-N(1)-C(1)	107.0(3)
N(1)-C(1)-C(9)	125.4(7)
N(1)-C(1)-C(2)	108.6(7)
C(9)-C(1)-C(2)	126.0(7)
C(3)-C(2)-C(7)	121.2(10)
C(3)-C(2)-C(1)	133.7(9)
C(7)-C(2)-C(1)	104.8(9)
C(4)-C(3)-C(2)	117.9(8)
C(3)-C(4)-C(5)	125.0(10)
C(4)-C(5)-C(6)	117.5(11)
C(7)-C(6)-C(5)	117.3(10)
C(2)-C(7)-C(6)	121.0(10)
C(2)-C(7)-C(8)	106.6(9)
C(6)-C(7)-C(8)	132.4(10)
N(1)-C(8)-C(12)	119.2(7)
N(1)-C(8)-C(7)	112.8(7)
C(12)-C(8)-C(7)	127.5(7)
C(11)-C(9)-C(1)	121.3(8)
C(11)-C(9)-C(10)	120.1(7)
C(1)-C(9)-C(10)	118.2(7)
N(2)-C(10)-C(9)	177.6(10)
N(3)-C(11)-C(9)	173.6(10)
C(8)-C(12)-C(13)	122.4(7)
C(8)-C(12)-C(14)	125.0(7)
C(13)-C(12)-C(14)	112.6(7)
N(4)-C(13)-C(12)	176.6(11)
N(5)-C(14)-C(12)	175.7(10)
C(16)-C(15)-C(20)	119.4(5)
C(16)-C(15)-C(21)	118.2(11)
C(20)-C(15)-C(21)	122.4(12)
C(15)-C(16)-C(17)	115.4(11)
C(16)-C(17)-C(18)	114.8(11)
C(19)-C(18)-C(17)	120.1(12)
C(18)-C(19)-C(20)	125(2)
C(19)-C(20)-C(15)	125(2)
N(6)-C(21)-C(15)	112.9(3)

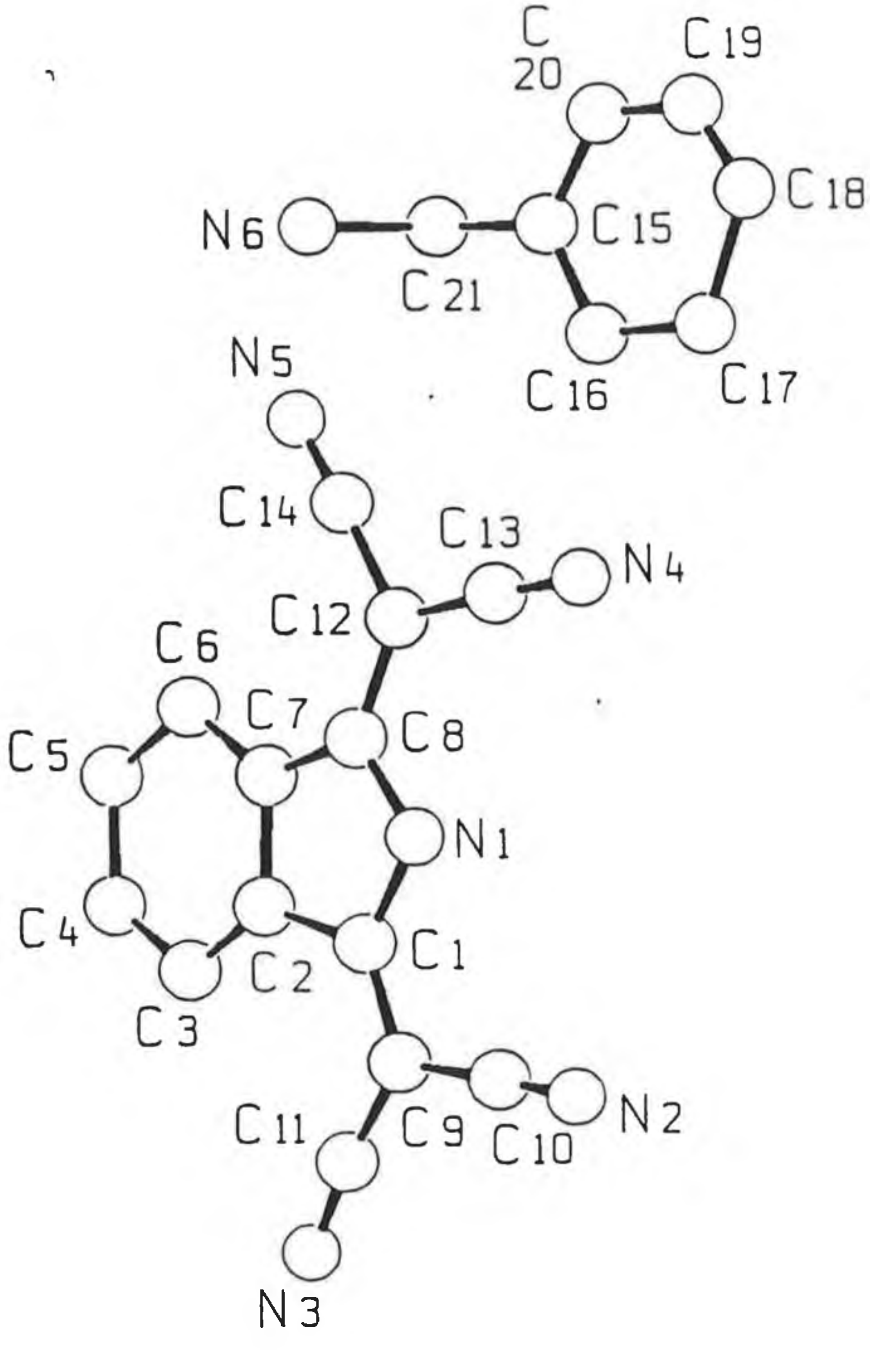


Figure 2.4(a) SCHAKAL drawing of the crystal structure of (179)

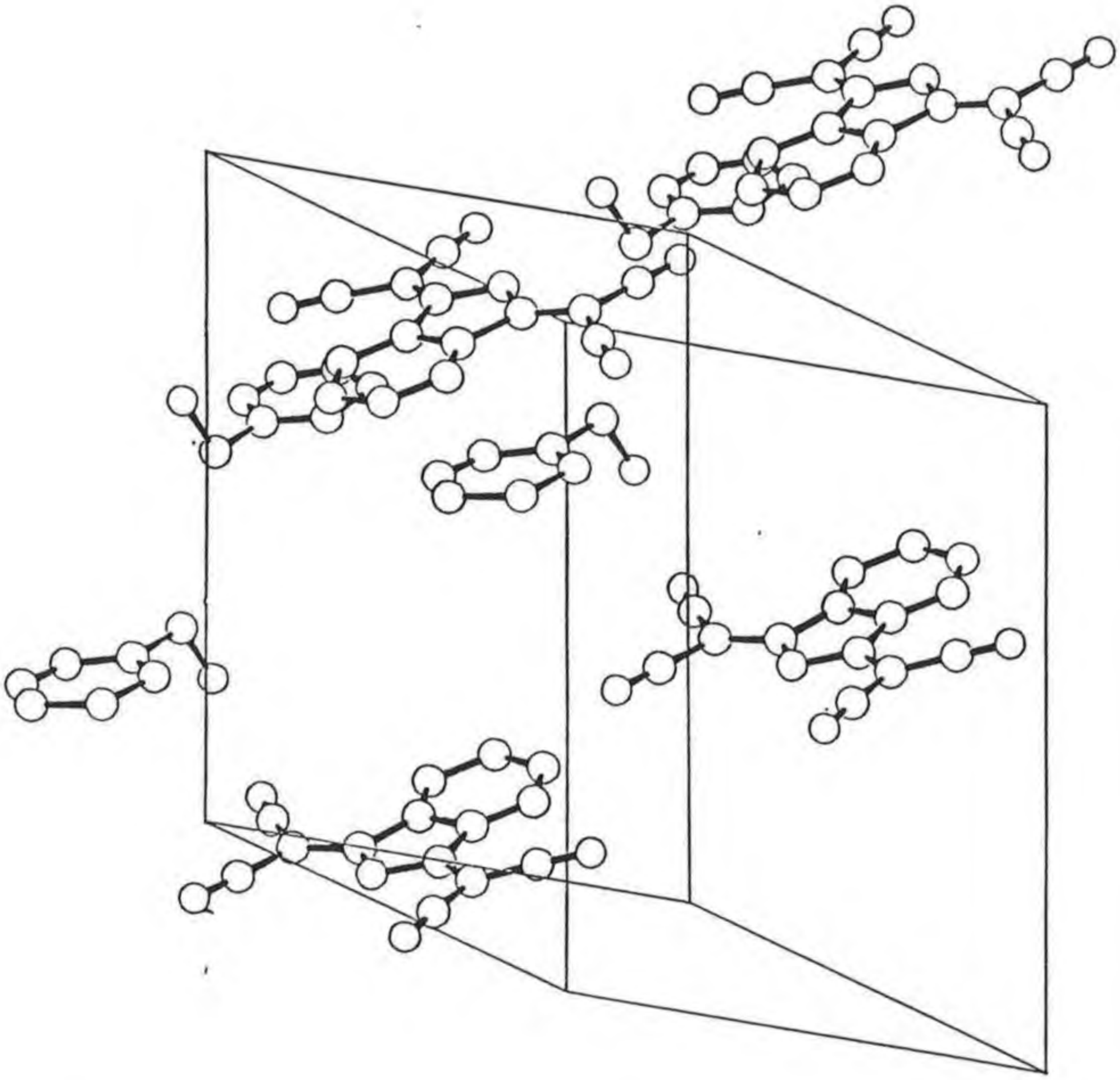
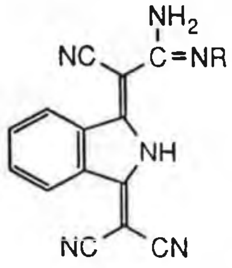


Figure 2.4(b) SCHAKAL representation of the unit cell of (179)

The crystal structure confirmed conclusively that the compound isolated from the filtrate was in fact the corresponding benzylammonium salt (179).

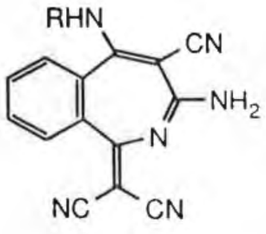
2.D.2.2 Reaction of n-Propylamine with (119)

Treatment of (119) with n-propylamine under the same conditions as used for the benzylamine reaction, with heating under reflux being maintained for 22 hours, gave a similar result. The new product which was observed by TLC precipitated from solution. The ^1H NMR spectrum was consistent with that of the benzylamino derivative, in that the same unsymmetrical character was observed in the aromatic peaks. Three aromatic multiplets integrated in the ratio 1:1:2 as before and two different NH proton peaks, with an integration ratio of 1:2, were also present. The main difference, on comparing the two proton NMR spectra, was the expected difference in the *N*-substituent of the amine used. The *N*-propyl group gave the expected splitting pattern, a triplet, multiplet and triplet with J= 7.4 Hz, and an integration ratio of 2:2:3. By the same reasoning arrived at for the benzylamino adduct discussed previously, three possible structures were postulated for the product, (180), (181) and (182). The ^{13}C NMR spectrum was also consistent with these findings and showed the correct number of different peaks for the postulated structures.



(180)

where R= Propyl



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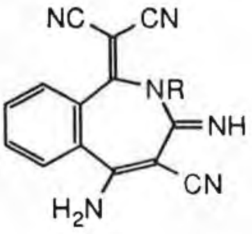


(182)

The unsymmetrical structure of the product was verified by the observation of six different aromatic absorptions between 123 and 138 ppm and three cyano absorptions at 115.15, 115.95, and 117.18 ppm. The three propyl carbons were observed at 11.65, 21.09 and 44.2 ppm. The carbon observed at 56.96 ppm was assigned as the C_2 carbon of the 2,2-dicyanovinylidene group by comparison with the findings for the benzylamine derivative. All the carbon absorptions observed occurred at chemical shifts very similar to those found for the corresponding carbons of the benzylamino derivative, (see Table 2.7 in Discussion Section, pg 129). This showed that the propyl and benzyl derivatives had essentially the same basic structure. The IR spectrum showed the presence of three sharp NH stretching bands at 3350, 3278 and 3205 cm^{-1}. The absence of a broad imino NH stretch again suggested (179) and (180) were the most probable structures. The UV/visible spectra of both derivatives were also found to be essentially the same, Figure 2.5, and this further confirmed the same type of structure for both derivatives.

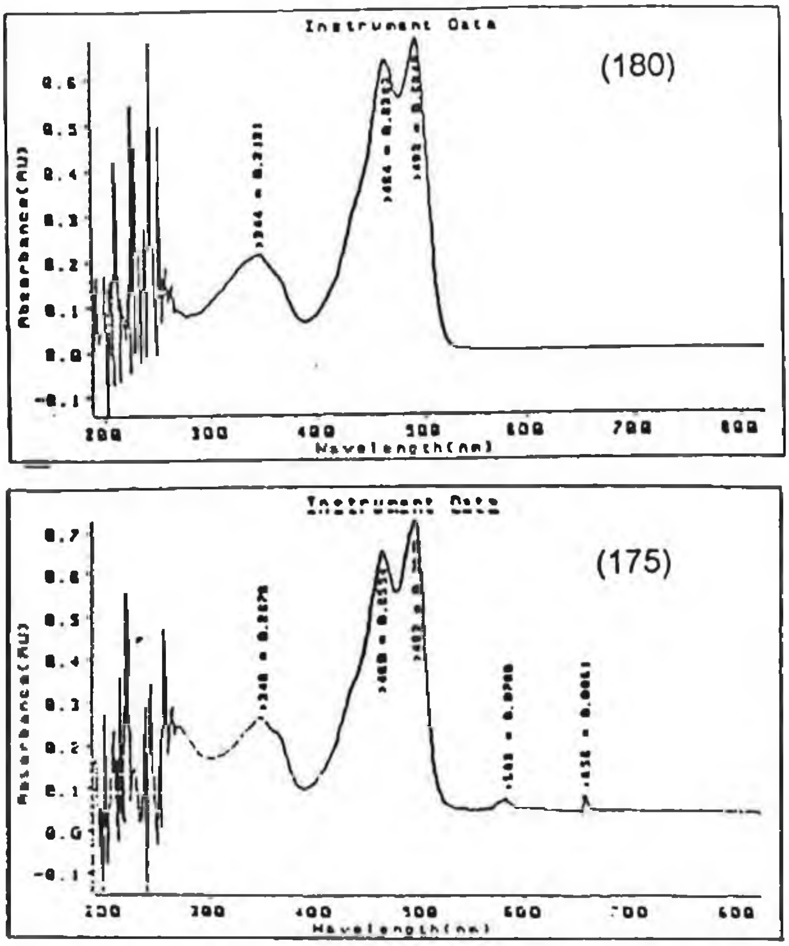
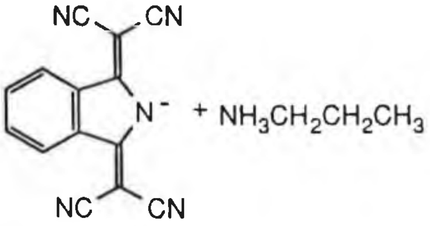


Figure 2.5 UV/Visible spectra of (a) Propylamino derivative (180) and (b) Benzylamino derivative (175)

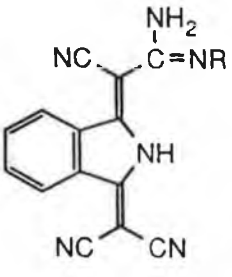
The ^{1}H, and ^{13}C NMR spectra of the solid isolated from the filtrate of the propylamine reaction with (119) were consistent with the assigned structure (183). The ^{1}H NMR spectrum showed a symmetrical two proton multiplet at 8.07 ppm and another symmetrical aromatic multiplet overlapping with a broad singlet at 7.59-7.62 ppm integrating for a total of five protons. These corresponded to the aromatic protons of the anion of (110) and the NH$_3$ protons of the propylammonium cation. The propyl protons gave a splitting pattern consistent with that expected and integrated for a total of seven protons. The ^{13}C NMR spectrum, (see Table 2.8, discussion section pg 131), showed three aromatic carbon absorptions, two cyano absorptions, and two absorptions corresponding to the C_1 and C_2 carbons of the 2,2-dicyanovinylidene group as expected for the symmetrical structure of the anion of (110). The remaining three carbon absorptions corresponded to the *N*-propyl group. Since the ^1H, and ^{13}C NMR, and UV/visible spectra were essentially identical to those of the benzylammonium salt, except for the differences due to the different *N*-alkyl substituents, it was concluded that assigned structure (183) was correct.



(183)

2.D.2.3 Reaction of Isopropylamine with (119)

The reaction of isopropylamine with (119) gave results very similar to those for the propylamine and benzylamine reactions. The new product observed by TLC was again found to have unsymmetrical aromatic proton NMR absorptions in the ratio 1:1:2 and two types of NH protons integrating in the ratio 1:2. The other protons observed corresponded to the isopropyl group and were found as a multiplet at 3.94 ppm and a doublet at 1.26 ppm in a ratio of 1:6. Three possible structures were postulated as before, (184)-(186). The ^{13}C NMR spectrum showed the correct number of carbons for the structures postulated, with six different aromatic carbon absorptions, three cyano absorptions and the C_2 carbon absorption of the 2,2-dicyanovinylidene group, as well as the remaining carbon absorptions, being observed at very similar



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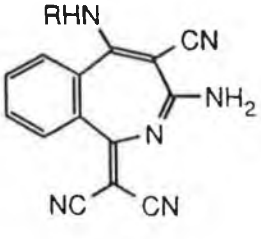

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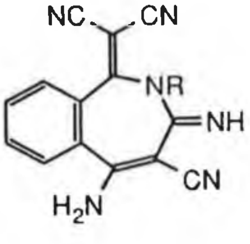
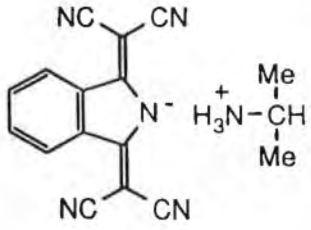


(186)

where R= Isopropyl

chemical shifts to those found for the corresponding benzylamino and propylamino derivatives, (see Table 2.7). The main difference, on comparing the carbon NMR spectra, was the observation of the different number of carbon absorptions corresponding to the different *N*-alkyl groups. The equivalent methyl carbon absorptions for the isopropyl group were found at 21.6 ppm and the remaining CH carbon absorption was found at 43.6 ppm. The IR spectrum showed the presence of three sharp NH stretching bands at 3424, 3341 and 3233 cm^{-1} as before. The UV/visible spectrum was identical to that of the propylamino derivative and it was concluded that the reaction of isopropylamine with (119) gave a product with a correspondingly analogous structure.

Once again the product isolated from the filtrate was identified as the corresponding salt, the isopropylammonium salt (187), on comparison of the ^1H and ^{13}C NMR spectra, and the UV/visible spectra, with those of the benzylammonium salt. Two symmetrical aromatic multiplets were observed as before with a broad three proton singlet, corresponding to the NH protons of the isopropylammonium cation, infringing on the multiplet at 7.62 ppm. The isopropyl protons were observed as a one proton multiplet at 3.26 ppm and a six proton doublet, *J*= 6.4 Hz, at 1.13 ppm. Also present was a broad one proton OH singlet at 4.36 ppm, a two proton quartet at 3.41 ppm, *J*= 6.8 Hz, and a three proton triplet, *J*= 6.8 Hz, at 1.03 ppm which corresponded to ethanol, present as a solvent of crystallisation. The disappearance of the broad five proton multiplet at 7.62 ppm, giving instead a two proton multiplet, and the broad singlet at 4.36 ppm on addition of deuterium oxide to the NMR sample confirmed the presence of exchangeable NH and OH protons. The ^{13}C NMR spectrum was also very similar to those of the previous alkylammonium salts, (see Table 2.8). The symmetrical structure of the salt was apparent from the presence of three aromatic absorptions, two cyano absorptions, and the C_1 and C_2 carbon absorptions of the 2,2-dicyanovinylidene group, all occuring at chemical shifts similar to those of the other salts and the anion of (110). The main difference was the observation of carbons corresponding to the isopropyl

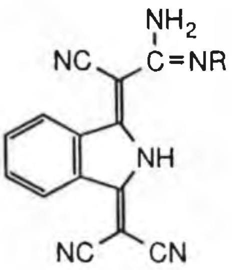


(187)

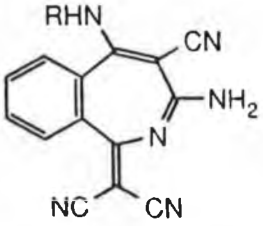
group and the ethanol, which gave a total of four carbons between 19 and 54 ppm. The UV/visible spectrum was also identical to those of the previous alkylammonium salts and thus on the basis of the strong similarities of all the spectral properties it was concluded that the assigned structure (187) was correct.

2.D.2.4 Reaction of n-Butylamine with (119)

Treatment of (119) with n-butylamine under reflux for six hours in ethanol gave an orange precipitate in high yield. The precipitate was assigned as one of the three possible structures (188)-(190) on the basis of the strong similarities in the ^1H, ^{13}C NMR and IR spectra, and by comparison of its UV/visible spectrum, with those of the previous alkylamino derivatives. The unsymmetrical aromatic multiplets were observed as before in the ratio 1:1:2 as were the two NH absorptions, in the ratio 1:2, at 10.8 and 8.7 ppm respectively. The remaining absorptions in the proton NMR spectrum corresponded to the n-butyl group, observed as a series of multiplets between 3.3 and 0.9 ppm and which gave a total integration for nine protons.

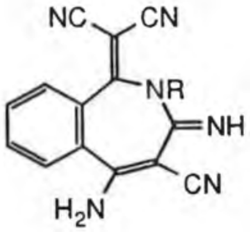


(188)



R= n-butyl

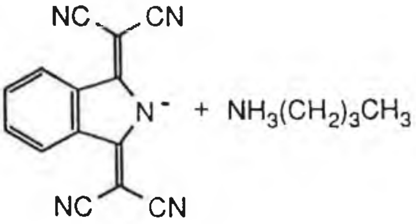
(189)



(190)

The ^{13}C NMR spectrum was very similar to those of the previous *N*-alkyl derivatives (see Table 2.7) the main difference being the number of carbon absorptions observed for the different *N*-alkyl group. The butyl group appeared as four peaks between 13.4 and 42.3 ppm. The IR spectrum showed two NH stretches at 3326 and 3270 cm^{-1} and comparison of the UV/visible spectrum of the n-butylamino derivative with that of the isopropylamino derivative showed they had identical λ_{max} values again demonstrating that the n-butylamino derivative of (110) had essentially a structure analogous to those of the other amino derivatives.

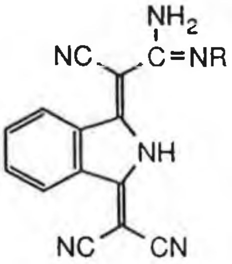
Comparison of the ^1H, ^{13}C NMR and UV/visible spectra with those of the other alkylammonium salts showed that the product obtained from the filtrate was the butylammonium salt (191). Two symmetrical aromatic multiplets, in the ratio 2:2, were observed at 8.07 and 7.62 ppm with a broad three proton singlet at 7.58 ppm, corresponding to the NH protons of the butylammonium cation, infringing on the multiplet at 7.62 ppm. The butyl group gave the anticipated splitting pattern and integrated for a total of nine protons. The carbon NMR spectrum showed three aromatic absorptions, two cyano absorptions, the C_1 and C_2 carbon absorptions of the 2,2-dicyanovinylidene group all occuring at chemical shifts similar to those of the other salts, (see Table 2.8). Also present were four carbons between 13.5 and 38.6 ppm corresponding to the butyl group.



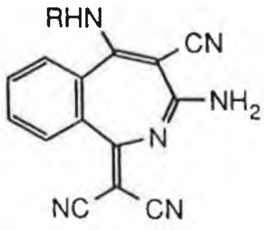
(191)

2.D.2.5 Reaction of Cyclohexylamine with (119)

Treatment of cyclohexylamine with (119) in pyridine under reflux for 11 hours gave a new product which was isolated by precipitation from water. This product exhibited similar unsymmetrical character in its ^1H NMR spectrum and showed the presence of two NH absorptions in the ratio of 1:2 as before with the main difference being the observation of a total of eleven protons as six multiplets corresponding to the cyclohexyl group. The ^{13}C NMR spectrum was essentially the same (see Table 2.7), as the other alkylamino derivatives the only difference being the observation of four carbon absorptions between 24 and 51 ppm corresponding to the cyclohexyl group. The UV/visible spectrum was identical to the previous alkylamino derivatives and on the basis of the previous findings it was concluded that the cyclohexylamino derivative also had the same structure, either (192), (193) or (194), as the other derivatives.

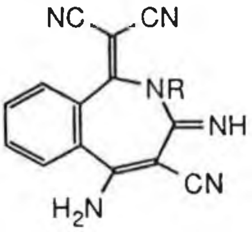


(192)



R= Cyclohexyl

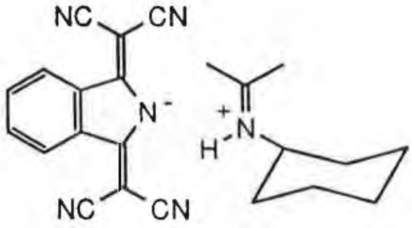
(193)



(194)

While no salts were obtained from this reaction, as had been obtained with the other amines, one unusual product which was recovered while investigating this reaction was the *N*-isopropylidenecyclohexylammonium salt (195).

Salt (195) was obtained as an orange cubic crystalline solid by recrystallisation, from acetone, of a red oil obtained when cyclohexylamine and the ammonium salt (119) were stirred together at room temperature in acetone and the acetone evaporated off. The IR, ^{1}H and ^{13}C NMR spectra and elemental analysis were in agreement with the assigned structure.



(195)

The ^{1}H NMR spectrum showed the characteristic symmetrical peaks for the four aromatic protons of the anion of (110) at 8.0 and 7.6 ppm, and a broad NH proton absorption at 12.2 ppm corresponding to the protonated imino nitrogen. Apart from the cyclohexylamino proton absorptions which integrated for a total of 11 protons, two additional three proton absorptions corresponding to the isopropylidene methyl protons were observed at 2.34 and 2.32 ppm. The ^{13}C NMR spectrum showed a total of fourteen different absorptions, three aromatics at 122.9, 131.4 and 137.4 ppm, two cyano at 116.3 and 117.3 ppm, the 2,2-dicyanovinylidene C_1 carbon absorption at 178.9 ppm and a carbon absorption at 53.9 ppm corresponding to the 2,2-dicyanovinylidene C_2 carbon, all of which corresponded to the anion of (110) (see Table 2.8). Six alkyl carbon absorptions were observed between 20.9 and 56.4 ppm. These corresponded to four cyclohexyl carbons and two methyl carbons of the isopropylidene group. The carbon absorption at 172.0 ppm corresponded to the imino carbon. The structure was conclusively confirmed by X-ray crystallography.

The single crystals required for the X-ray analysis were obtained by recrystallisation from acetone. The crystal structure analysis data showed that the salt was triclinic with space group P-1 symmetry. The crystal structure is shown in Figure 2.6 and the relevant bond lengths and bond angles are given in Tables 2.3 and 2.4.

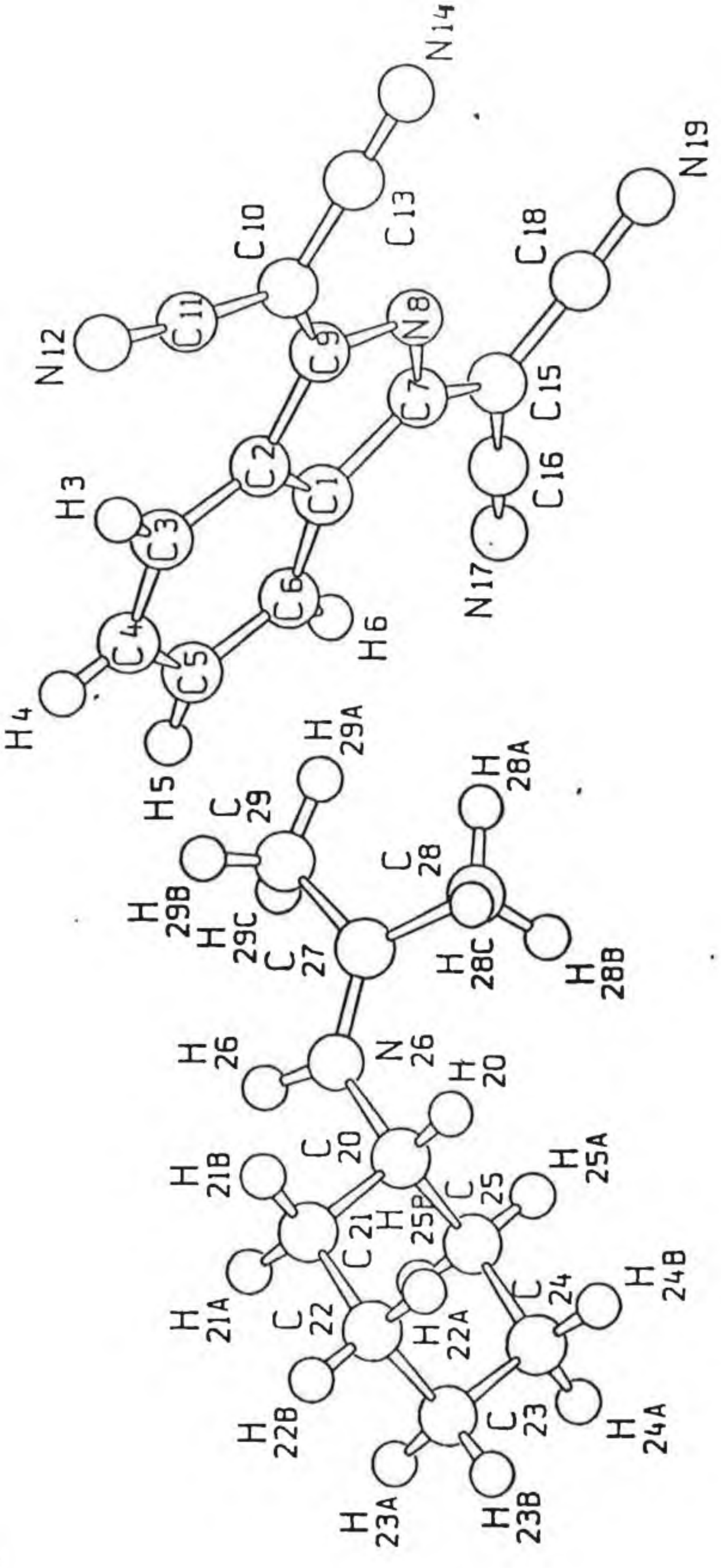
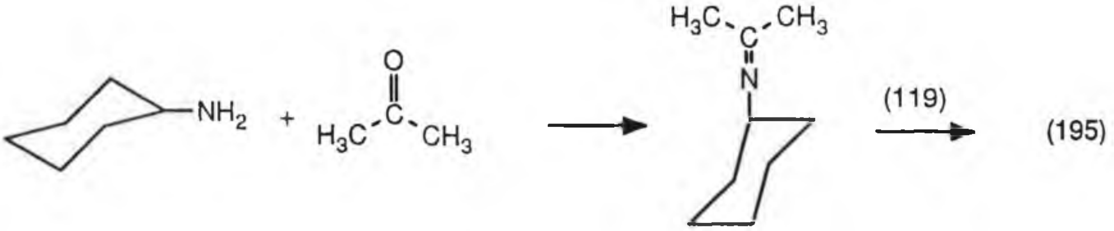


Figure 2.6 SCHAKAL drawing of the crystal structure of salt (195)

The formation of (195) may be explained by the condensation reaction of the cyclohexylamine with acetone, giving *N*-isopropylidenecyclohexylamine (196), Scheme 2.37, which is subsequently protonated to give the corresponding iminium salt (195).



(196)

Scheme 2.37

Table 2.3 showing bondlengths for (195)

Table 2.3 Bondlengths [Å]

C(1)-C(6)	1.384(5)	C(13)-N(14)	1.141(4)
C(1)-C(2)	1.400(4)	C(15)-C(16)	1.421(5)
C(1)-C(7)	1.473(4)	C(15)-C(18)	1.424(5)
C(2)-C(3)	1.383(4)	C(16)-N(17)	1.147(4)
C(2)-C(9)	1.474(4)	C(18)-N(19)	1.146(4)
C(3)-C(4)	1.381(5)	C(20)-N(26)	1.478(4)
C(5)-C(4)	1.378(5)	C(20)-C(21)	1.514(4)
C(5)-C(6)	1.386(5)	C(20)-C(25)	1.515(4)
C(7)-N(8)	1.370(4)	C(21)-C(22)	1.513(5)
C(7)-C(15)	1.374(4)	C(22)-C(23)	1.510(5)
N(8)-C(9)	1.361(4)	C(23)-C(24)	1.517(5)
C(9)-C(10)	1.383(4)	C(24)-C(25)	1.528(5)
C(10)-C(11)	1.421(5)	N(26)-C(27)	1.278(4)
C(10)-C(13)	1.426(5)	C(27)-C(29)	1.476(5)
C(11)-N(12)	1.150(4)	C(27)-C(28)	1.477(5)

2.D.2.6 Reaction of n-Octylamine and n-Decylamine with (119)

Results similar to those for the other amines were observed on treating (119) with n-octylamine or with n-decylamine. The new product in each of these reactions precipitated from solution. The ^{1}H and ^{13}C NMR spectra of each indicated unsymmetrical structures consistent with previous findings. The n-octylamino product showed two broad NH singlets at 10.7 and 8.5 ppm in the ratio 1:2 as before as well as unsymmetrical aromatic multiplets integrating in the ratio 1:1:2. The remaining protons corresponded to the n-octyl protons and these integrated for total of seventeen protons. The ^{13}C NMR spectrum was very similar to those of the previous *N*-alkyl derivatives (see Table 2.7) with the main difference being for the carbons of the *N*-alkyl group. Eight carbons corresponding to the n-octyl group were observed between 14 and 42 ppm.

Table 2.4 showing bondangles for (195)

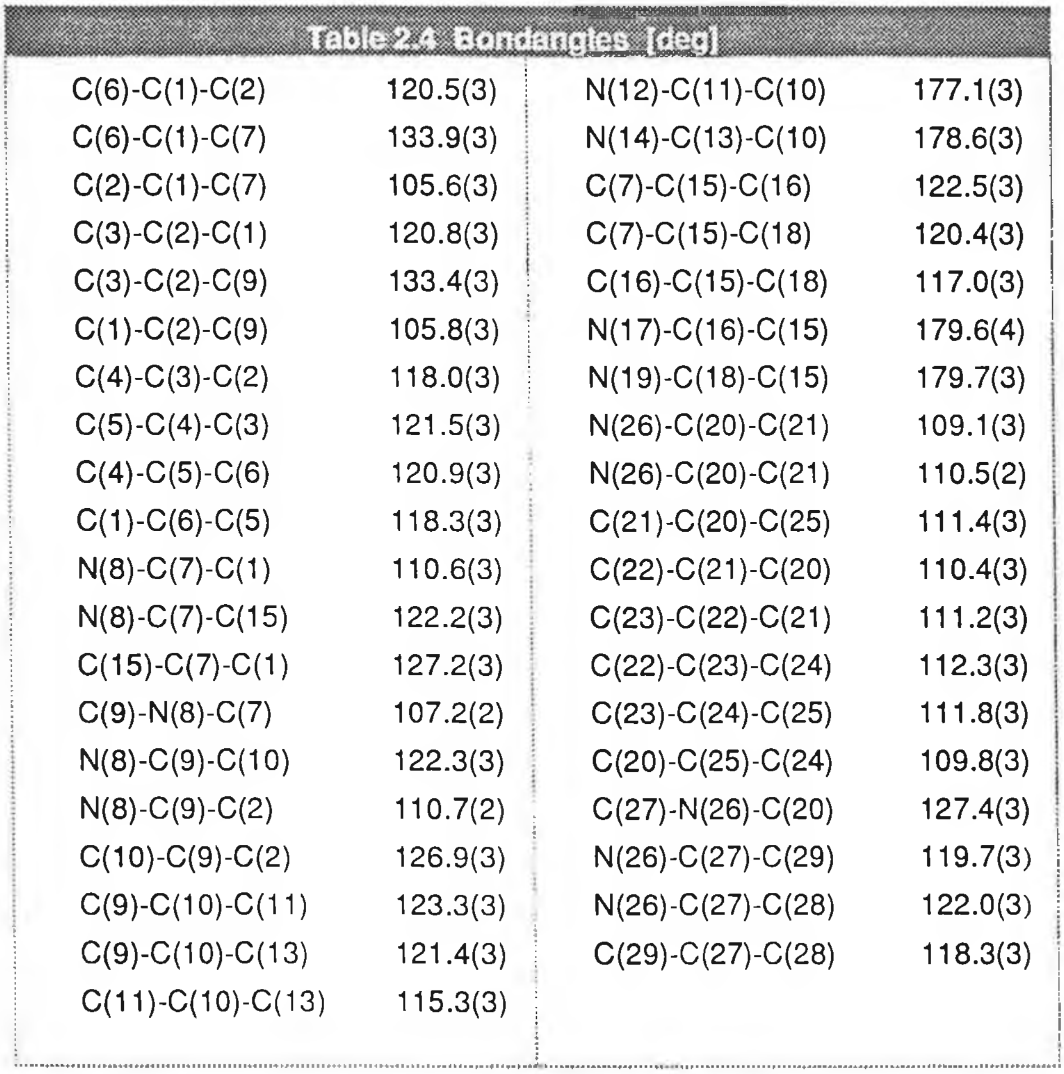
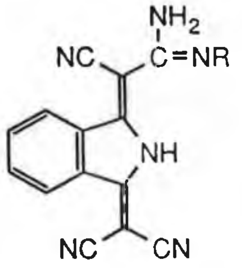


Table 2.4 Bondangles [deg]

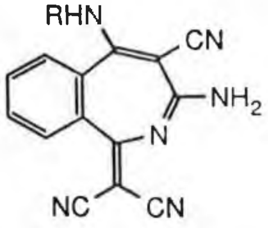
C(6)-C(1)-C(2)	120.5(3)	N(12)-C(11)-C(10)	177.1(3)
C(6)-C(1)-C(7)	133.9(3)	N(14)-C(13)-C(10)	178.6(3)
C(2)-C(1)-C(7)	105.6(3)	C(7)-C(15)-C(16)	122.5(3)
C(3)-C(2)-C(1)	120.8(3)	C(7)-C(15)-C(18)	120.4(3)
C(3)-C(2)-C(9)	133.4(3)	C(16)-C(15)-C(18)	117.0(3)
C(1)-C(2)-C(9)	105.8(3)	N(17)-C(16)-C(15)	179.6(4)
C(4)-C(3)-C(2)	118.0(3)	N(19)-C(18)-C(15)	179.7(3)
C(5)-C(4)-C(3)	121.5(3)	N(26)-C(20)-C(21)	109.1(3)
C(4)-C(5)-C(6)	120.9(3)	N(26)-C(20)-C(21)	110.5(2)
C(1)-C(6)-C(5)	118.3(3)	C(21)-C(20)-C(25)	111.4(3)
N(8)-C(7)-C(1)	110.6(3)	C(22)-C(21)-C(20)	110.4(3)
N(8)-C(7)-C(15)	122.2(3)	C(23)-C(22)-C(21)	111.2(3)
C(15)-C(7)-C(1)	127.2(3)	C(22)-C(23)-C(24)	112.3(3)
C(9)-N(8)-C(7)	107.2(2)	C(23)-C(24)-C(25)	111.8(3)
N(8)-C(9)-C(10)	122.3(3)	C(20)-C(25)-C(24)	109.8(3)
N(8)-C(9)-C(2)	110.7(2)	C(27)-N(26)-C(20)	127.4(3)
C(10)-C(9)-C(2)	126.9(3)	N(26)-C(27)-C(29)	119.7(3)
C(9)-C(10)-C(11)	123.3(3)	N(26)-C(27)-C(28)	122.0(3)
C(9)-C(10)-C(13)	121.4(3)	C(29)-C(27)-C(28)	118.3(3)
C(11)-C(10)-C(13)	115.3(3)		

The aromatic proton absorptions of the n-decylamino derivative were unsymmetrical as before, with two broad NH peaks, in the ratio 1:2, being observed at 10.8 and 8.6 ppm. The other protons present occurred between 3.29 and 0.79 ppm and these integrated in total for 21 protons, corresponding to the n-decyl protons. The ^{13}C NMR spectrum was very similar to those of the previous *N*-alkyl derivatives (see Table 2.7) with the expected difference of ten carbon absorptions being observed between 14 and 42 ppm, corresponding to the n-decyl carbons. Both the n-octyl and n-decyl derivatives had essentially identical UV/visible spectra. Unfortunately a crystal structure of neither of these products could be obtained. Once again on the basis of the strong similarities in the spectral data between all the *N*-alkyl derivatives it was concluded that the products obtained from the reaction of n-octyl and n-decyl amine with (119) were either the amidines (197) and (198) or the benzoazepines (199) and (200) or (201) and (202).



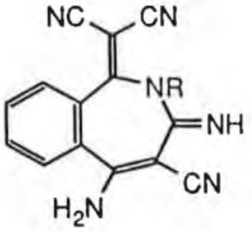
(197) R= n-octyl

(198) R= n-decyl



(199) R= n-octyl

(200) R= n-decyl



(201) R= n-octyl

(202) R= n-decyl

While both the filtrates from the n-octylamine reaction and the n-decylamine reaction gave black oils on evaporating off the solvents, only the n-decylammonium salt was obtained, by precipitation of a chloroform solution of the oil with light petroleum. Attempts to isolate the n-octylammonium salt in a similar manner were unsuccessful. The ^{1}H NMR spectrum of the n-decylammonium salt again showed two symmetrical aromatic multiplets at 8.08 ppm, integrating for two protons, and another at 7.6 ppm which overlapped with a broad singlet which together gave a total integration for five protons. The remaining protons were observed as four multiplets at 2.7, 1.48, 1.18 and 0.8 ppm, in the ratio 2:2:14:3, corresponding to the n-decyl protons. The ^{13}C NMR spectrum showed the same symmetrical character of the salt as before, with three aromatic carbon absorptions, two cyano absorptions, and two absorptions corresponding to the 2,2-dicyanovinylidene C_1 and C_2 carbons being observed which corresponded to the anion of (110), (see Table 2.8). The remaining ten carbons between 14 and 48 ppm corresponded to the decyl group. On the basis of the strong similarities in the spectral data with the conclusively identified benzylammonium salt it was concluded that the solid isolated was the n-decylammonium salt.

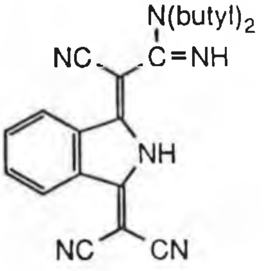
Since it had not been possible to obtain crystals of adequate quality for X-ray crystal structure determination of the possible amidine/benzoazepine products obtained from reaction of (119) with the primary amines just described, it was decided to investigate the reaction the reaction of a secondary amine with (119). The use of a secondary amine might also be expected to yield products with fewer possible tautomers.

2.D.2.7 Reaction of *N,N*-Dibutylamine with (119)

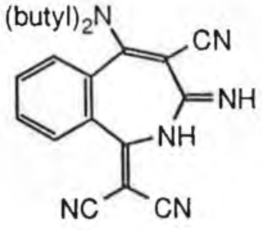
Treatment of the ammonium salt (119) with the secondary amine *N,N*-dibutylamine under reflux in ethanol for six hours gave almost complete conversion to a new product. This new product was isolated as a red solid by evaporation of the ethanol and recrystallisation from acetonitrile gave red needles. The identity of this new product was determined by ^{1}H, ^{13}C NMR and IR spectral data and its structure was confirmed conclusively by X-ray crystal structure analysis.

The ^{1}H NMR spectrum showed many similarities to those of the primary amine products mentioned already. Three unsymmetrical aromatic multiplets were observed at 8.3, 8.2 and 7.7 ppm respectively in the ratio 1:1:2 as before. Two broad NH peaks were also observed at 9.6 and 9.0 ppm and integrated in the ratio 1:1. The remaining protons integrated for a total of eighteen protons and these occurred as four multiplets between 3.6 and 0.9 ppm and corresponded to the *N,N*-dibutyl group. The ^{13}C NMR spectrum also showed many similarities to those of the primary amine products (see Table 2.7), with the main difference being the number of different carbon absorptions corresponding to the *N*-alkyl substituents. Thus four carbon absorptions were observed between 13 and 29 ppm, corresponding to the butyl carbons. Six aromatic carbon absorptions were observed as before between 123 and 138 ppm as were three cyano absorptions at 116.8, 118.2 and 118.5 ppm. The C_2 carbon absorption of the 2,2-dicyanovinylidene group was also found at 50.8 ppm. The IR spectrum showed a NH stretch at 3340 cm^{-1} and the UV/visible spectrum showed λ_{max} at 482, 460 and 336 nm, slightly shorter wavelengths than those of the previous addition products. On the basis of the spectral information two possible structures, (203) and (204), were postulated. Fortunately this compound yielded crystals of sufficient quality for X-ray structural analysis to allow the exact structural assignment be made.

Crystals of good quality for X-ray structural determination of the *N,N*-dibutylamine adduct of (110) were obtained as scarlet needles by recrystallisation from dimethylformamide. The single crystal X-ray structure conclusively identified the product to be 2-cyano-*N*^{1},*N*^{1}-dibutyl-2-(3-dicyanomethyleneisoindolin-1-diylidene)acetamidine (203). The structure is triclinic, with P-1 symmetry and is shown in Figure 2.7.



(203)



(204)

The relevant bond lengths and bond angles are shown in Tables 2.5 and 2.6. The crystal structure shows that the molecule is essentially planar except for the 2-cyano-*N*^{1},*N*^{1}-dibutylacetamidino group which is twisted out of the plane due to the steric bulk of the *N,N*-dibutylamino group.

2.D.3 Discussion

At the outset of these reactions we were interested in seeing how and where an amine would react with compound (110). On the basis of the strong similarities found in the proton and carbon NMR data of the products from the reaction of (119) with primary amines and those for (203), it was concluded that the products of the addition reactions of the primary amines were also amidines, Scheme 2.38. The unsymmetrical character of the aromatic multiplets, in the ratio 1:1:2, was common to all the amidines. Two NH proton peaks in the ratio 1:2 in the ^{1}H NMR spectrum, showing the presence of an NH and an NH_2 group, were found in the primary amine derivatives, confirming that these amidines exist in the tautomeric form (173b) (Scheme 2.36). The *N,N*-dibutyl derivative (203) exhibited two one proton NH absorptions and can only exist in one form as expected. The common carbon absorptions of the ^{13}C NMR spectra of all the amidines, with the *N*-alkyl peaks omitted, are shown in Table 2.7. It is clear from the table that essentially the same carbon skeleton is common to all structures. The slight variations in the chemical shifts for some of the absorptions for (203) can be attributed to reduced conjugation in the system due to the greater steric bulk of the *N,N*-dibutylacetamidino group compared with the other amidines, as also evident from the UV/visible spectra.

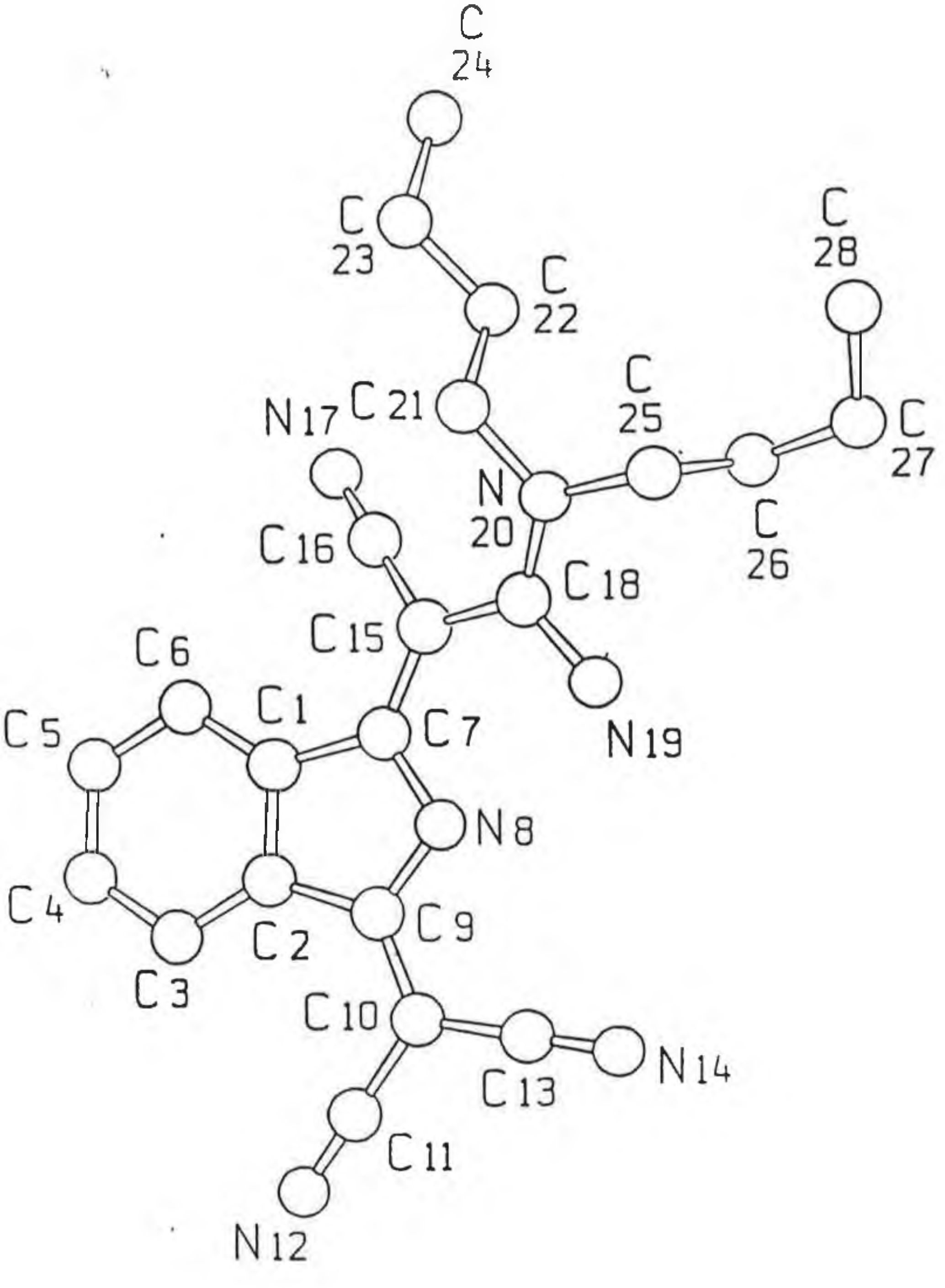
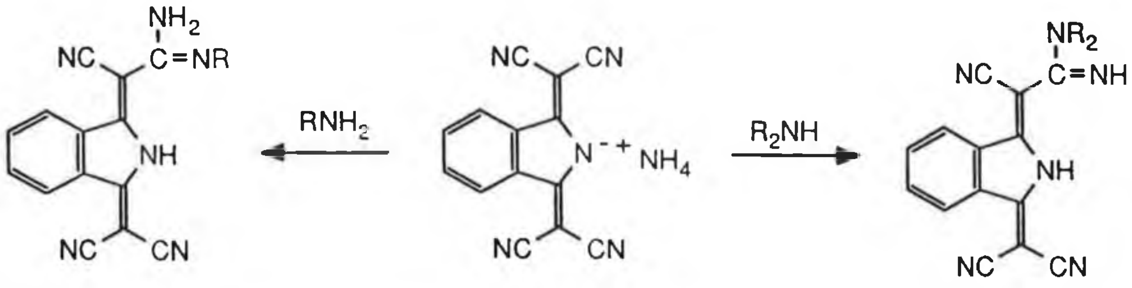


Figure 2.7 SCHAKAL drawing of the crystal structure of (203)

Table 2.5 showing the bondlengths for (203)

Table 2.5 Bond lengths [Å]

N(1)-C(8)	1.347(10)
N(1)-C(1)	1.388(10)
N(2)-C(10)	1.113(12)
N(3)-C(11)	1.150(11)
N(4)-C(13)	1.169(12)
N(5)-C(14)	1.132(11)
N(6)-C(21)	1.487(5)
C(1)-C(9)	1.374(10)
C(1)-C(2)	1.519(11)
C(2)-C(3)	1.350(12)
C(2)-C(7)	1.395(5)
C(3)-C(4)	1.363(13)
C(4)-C(5)	1.381(6)
C(5)-C(6)	1.423(14)
C(6)-C(7)	1.413(12)
C(7)-C(8)	1.440(12)
C(8)-C(12)	1.384(11)
C(9)-C(11)	1.369(11)
C(9)-C(10)	1.418(12)



(175): R= benzyl
(180): R= propyl
(184): R= isopropyl
(188): R= butyl
(192): R= cyclohexyl
(197): R= octyl
(198): R= decyl

(119)

(203): R= butyl

Scheme 2.38

Table 2.6 showing the bondangles for (203)

Table 2.6 Bond angles [deg]

C(9)-N(8)-C(7)	107.9(2)
C(18)-N(20)-C(21)	125.1(2)
C(18)-N(20)-C(25)	120.3(2)
C(21)-N(20)-C(25)	113.7(2)
C(6)-C(1)-C(2)	119.8(2)
C(6)-C(1)-C(7)	134.4(2)
C(2)-C(1)-C(7)	105.5(2)
C(3)-C(2)-C(1)	121.1(2)
C(3)-C(2)-C(9)	133.4(2)
C(1)-C(2)-C(9)	105.5(2)
C(2)-C(3)-C(4)	118.2(3)
C(5)-C(4)-C(3)	121.1(3)
C(4)-C(5)-C(6)	121.1(2)
C(1)-C(6)-C(5)	118.7(2)
N(8)-C(7)-C(15)	123.0(2)
N(8)-C(7)-C(1)	109.9(2)
C(15)-C(7)-C(1)	127.1(2)
N(8)-C(9)-C(10)	120.8(2)
N(8)-C(9)-C(2)	111.0(2)
C(10)-C(9)-C(2)	128.1(2)
C(9)-C(10)-C(13)	120.4(2)
C(9)-C(10)-C(11)	122.5(2)
C(13)-C(10)-C(11)	117.0(2)
N(12)-C(11)-C(10)	179.5(3)
N(14)-C(13)-C(10)	178.3(3)
C(7)-C(15)-C(16)	116.7(2)
C(7)-C(15)-C(18)	123.8(2)
C(16)-C(15)-C(18)	119.0(2)
N(17)-C(16)-C(15)	177.0(3)
N(19)-C(18)-N(20)	119.4(2)
N(19)-C(18)-C(15)	117.7(2)
N(20)-C(18)-C(15)	122.8(2)
N(20)-C(21)-C(22)	113.6(2)
C(23)-C(22)-C(21)	111.7(2)
C(22)-C(23)-C(24)	113.7(3)
N(20)-C(25)-C(26)	113.2(2)
C(25)-C(26)-C(27)	113.0(2)
C(28)-C(27)-C(26)	115.2(3)

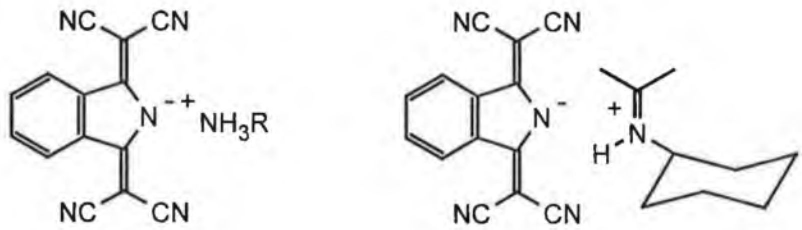
Table 2.7 ^{13}C NMR Spectra* of 2-Cyano-N-alkyl-2-(3-dicyanomethyleneisoindolin-1-diylidene)acetamidines

Compound	(175)	(180)	(184)	(188)	(192)	(197)	(198)	(203)
N-Substituent	Benzyl	Propyl	Isopropyl	Butyl	Cyclohexyl	Octyl	Decyl	Dibutyl
C2 of 2,2-dicyanovinylidene group	57.25	56.96	56.36	56.9	56.8	56.9	57.0	50.8
Cyano C	114.66, 115.35, 116.8	115.15 115.95 117.18	114.8 115.3 116.7	115.1 115.9 117.1	115.2 115.8 117.2	114.9 115.7 116.9	115.1 115.9 117.1	116.8 118.2 118.5
Aromatic C	123.12 123.44 131.03 131.46 135.0 137.97	123.25 123.61 131.21 131.66 134.97 137.98	122.6 123.0 130.6 131.1 134.3 137.4	123.2 123.5 131.1 131.5 134.9 137.9	123.2 123.5 131.2 131.6 134.9 137.9	122.9 123.3 130.8 131.2 134.7 137.7	123.2 123.5 131.1 131.5 134.9 137.9	122.7 122.9 131.0 131.1 137.7 137.8
Benzyl Aromatic Cs	127.05 127.19 128.01 135.54							
Other non-alkyl C	71.37 159.56 167.26 170.1	71.95 159.1 166.79 170.25	71.5 157.4 166.1 169.8	71.9 158.9 166.7 170.1	71.9 157.7 166.7 170.3	71.59 158.7 166.5 169.9	71.8 158.9 166.7 170.2	73.2 159.2 165.4 171.5

*: in DMSO-d_6 and referenced to 39.49 ppm.

Comparison of the UV/visible spectrum of (203) with the spectra of the other acetamidines synthesised from primary amines, showed that there was a 10 nm hypsochromic shift for the UV/visible spectrum of (203), whose λ_{max} in DMF occurs at 482 and 460 nm compared with 492 and 460 nm for the adducts of the primary amines. This suggests that there is less deviation from planarity for the acetamidines derived from the primary amines due to their lesser steric bulk.

The recovery of the alkylammonium salts, Scheme 2.39, and the *N*-isopropylidenecyclohexylammonium salt (195) from the reaction of the alkylamines with (119) is not surprising in light of the acidic nature of (110).



(179): R= benzyl
(183): R= propyl
(187): R= isopropyl
(191): R= butyl

(195)

Scheme 2.39

These salts were also identified by comparison of their spectral data with those of the conclusively identified benzylammonium salt (179). They all showed the same symmetrical character in the aromatic multiplets of their proton NMR spectra, with a three proton NH singlet, corresponding to the alkyl ammonium group, infringing on one of the aromatic multiplets. Comparison of the carbon NMR spectra, Table 2.8, with the absorptions corresponding to the different alkyl groups omitted, showed the same symmetrical character for all the salts and that the absorptions all occurred at very similar chemical shift values.

The reactions of the amines with (119) are summarised in Table 2.9 and are thought to involve an initial proton exchange between the ammonium cation and the alkylamine releasing ammonia and forming the alkylammonium salt. It is the alkylammonium salt which then reacts to give the amidine product . This was verified by taking the n-propylammonium salt (183) and heating it under reflux in 1,4-dioxan to give the corresponding amidine (180).

Table 2.8 ^{13}C NMR spectra* of the anion of the alkylammonium salts of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (110).

Salt	**Aromatic C**	**C_1 of 2,2-dicyanovinylidene group**	**C_2 of 2,2-dicyanovinylidene group**	**Cyano C**
Benzyl Ammonium (179)	122.83, 131.27, 137.38	171.97	53.89	116.24, 117.19
Propyl ammonium (183)	122.9, 131.3, 137.5	172.1	54.0	116.4, 117.3
Isopropyl ammonium (187)	122.93, 131.37, 137.48	172.07	56.08	116.35, 117.3
Butyl ammonium (191)	122.9, 131.4, 137.5	172.1	54.1	116.3, 117.3
Isopropylidene-cyclohexyl ammonium (195)	122.9, 131.4, 137.4	172.0	53.9	116.3, 117.3
Decyl ammonium	123.5, 131.3, 138.3	172.5	54.8	116.7, 117.4

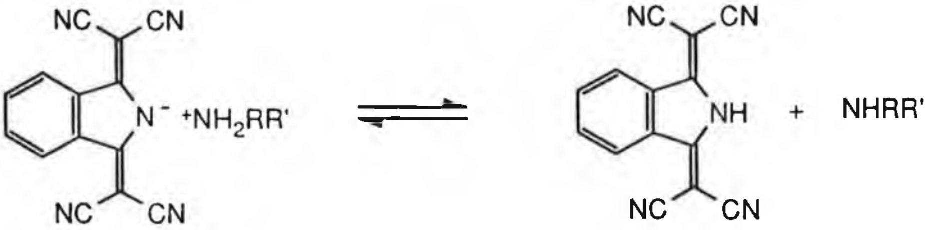
*: all spectra were measured in DMSO-d_6 except for the n-decylammonium salt which was determined in acetone-d_6.

Why nucleophilic attack does not occur at the 1-position of the isoindolin-1,3-diylidene ring may somehow be resonance related. By analogy with the nitrogen in an amide group, the lone pair on the nitrogen in the 2-position of the isoindolin-1,3-diylidene ring can delocalise into the adjacent 2,2-dicyanovinylidene groups, thus making the adjacent carbons in the 1- and 3-positions less prone to nucleophilic attack due to the greater stability granted by the resonance structures.

Table 2.9 Summary of the reactions of various amines with (119)

Amine	Solvent	Amidine % Yield	Salt % Yield
benzylamine	1,4-dioxan	46	28
n-propylamine	1,4-dioxan	65	8
isopropylamine	1,4-dioxan	47	25
n-butylamine	ethanol	77	17
N,N-dibutylamine	ethanol	94	-
cyclohexylamine	pyridine	64	-
n-octylamine	1,4-dioxan	27	-
n-decylamine	ethanol	30	-

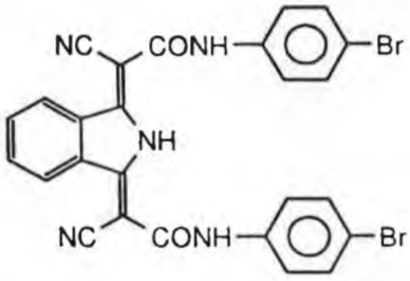
Formation of the amidines from the corresponding alkylammonium salts probably involves an equilibrium between the alkylammonium salt of (110) and the neutral components (Scheme 2.40), maintaining a small concentration of the free amine. 1,2-Addition of the amine across a cyano group of (110) can then occur.



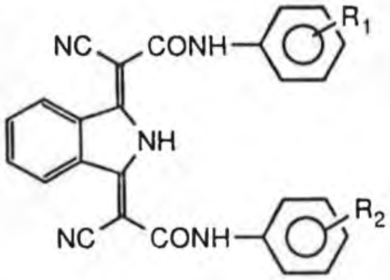
Scheme 2.40

The X-ray crystal structure of (203) shows that addition of the *N,N*-dibutylamine occurs at the cyano group farthest from the aromatic ring, giving the *Z*-isomer, and that there is significant twisting of the *N,N*-dibutylacetamidino group out of the plane of the molecule due to the steric bulk of *N,N*-dibutyl group. Were addition to occur at the cyano group adjacent to the benzene ring, this would result in greater steric strain in the system due to unfavourable interaction between the *N,N*-dibutylacetamidino group and the *peri* hydrogen of the aromatic ring.

As mentioned previously the greater steric bulk of the *N,N*-dibutylacetamidino group of (203) is apparent from comparison of its UV/visible spectrum with those of the primary amine derivatives in that its λ_{max} occurs at a shorter wavelength due to reduced conjugation. Interestingly the primary amine derivatives all exhibit essentially the same solution-phase UV/visible spectrum yet show various shades of orange and even a yellow in their solid state. It has been reported[152] that some pigments can crystallise in different phases and these can have different colour properties. For example, pigment (205) exists in two phases, α and β, which give a yellow and scarlet pigment respectively and the phase obtained is dependent on the solvent used in their synthesis. Standard solvents give the yellow pigment and solvents like DMF give the scarlet pigment. Thus these morphological effects on pigment shade and colour may explain why (203) occurs as a scarlet red crystalline solid with λ_{max} values at shorter wavelengths, 482 and 460 nm, compared to the varying orange powders found for the primary amine derivatives, all with λ_{max} values at 492 and 460 nm.



(205)



(206)

The UV/visible spectra of (206), with various substituents, have λ_{max} values at 495 and 498 nm in DMF and these occur at values similar to those for the primary amine derivatives and this further supports the assigned amidine structures.

2.D.4 Conclusions

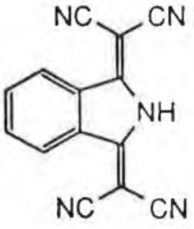
It is apparent from the reactions carried out on (110), via its ammonium salt (119), that it is not prone to nucleophilic attack at the sp^2-hybridised carbon adjacent to the nitrogen as is the carbonyl carbon of phthalimide. Thus it seems that similarities in the reactivity of carbonyl compounds and their alkylidenemalononitrile analogues does not hold for phthalimide and (110) and unfortunately did not provide a route to the *N*-alkyl derivatives of (110). The amidines in Scheme 2.38, which have not been reported before, show poor solubility in nearly all organic solvents and may be of use as pigments. Further studies with a greater range of nucleophiles may yield further related isoindoline pigments with a greater variety of shades and good pigment properties.

Chapter 3

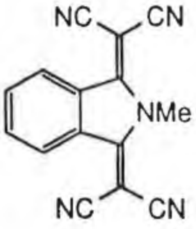
3.0 Cyclic Voltammetric Analysis

3.1 Introduction

Cyclic Linear Sweep Voltammetry (CV) is a popular technique for characterising the electrochemical properties of new species and has proven useful for determining the electron affinity and electron donating ability of compounds. This method is well reported[181] and has allowed the electron acceptor ability of novel acceptor groups to be compared with those already known and gives a good indication as to the potential C-T forming abilities of new acceptor groups. In this chapter, the results of the electrochemical studies on the acceptor molecules (110) and (151) shall be reported.



(110)



(151)

In a typical CV experiment,[182] the applied potential at the working electrode, measured with respect to a reference electrode, is varied linearly with time at a controlled sweep rate and the resulting current is measured. Typical sweep rates range from 0.04 to about 1,000 V/sec. It is customary to record the current as a function of potential, which is equivalent to recording the current versus time. A typical CV is shown in Figure 3.1.

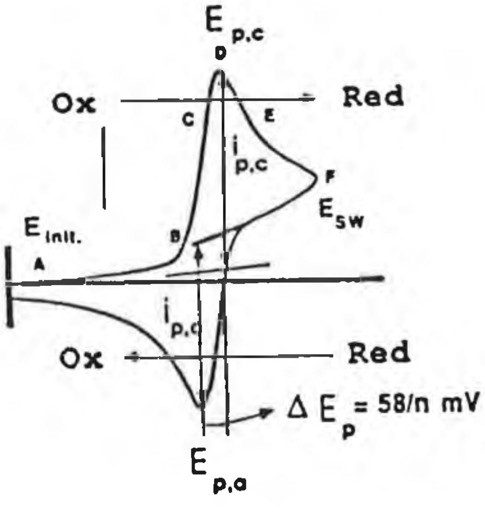


Figure 3.1 Typical Cyclic Voltammogram for a freely diffusing species.

During the forward sweep of a species O for reduction to a species R, the scan is begun well positive of the formal potential $E^{o'}$ for the process, position (A), and no current flows at this initial potential. As the electrode potential approaches $E^{o'}$, a current begins to flow, (B), and as the potential becomes more negative the current continues to grow, (C), as the surface concentration of the neutral species at the working electrode drops. As the potential moves past $E^{o'}$ the surface concentration drops to near zero, mass transfer of the neutral species to the surface reaches a maximum, (D), and then declines as the depletion effect sets in and the current decays, (E). By reversing the potential at (F) and sweeping in a positive direction, the large concentration of oxidisable anion radical R, in the vicinity of the electrode, generates a reversal current which gives a curve having a shape much like that of the forward sweep.

In a cyclic voltammogram the parameters of most importance are: the peak potentials $E_{p,c}$ and $E_{p,a}$ (c = cathodic and a = anodic), their difference $\Delta E_{p,}$ and the peak currents $i_{p,c}$ and $i_{p,a}$. These parameters give important information as to the reversibility of the electrochemical system. If an electrochemical system follows the Nernst equation (equation 5), or an equation derived from it, the system is said to be reversible or Nernstian.

$$E = E^{o'} + RT/nF \ln C_O/C_R \qquad \text{equation 5}$$

where E is the applied potential, $E^{o'}$ is the formal potential, R is the Gas Constant, T is the absolute Temperature, F is the Faraday Constant, n is the number of electrons per molecule of oxidised or reduced species, C_O is the concentration of oxidised species in mol/cm^3, and C_R is the concentration of reduced species in mol/cm^3.

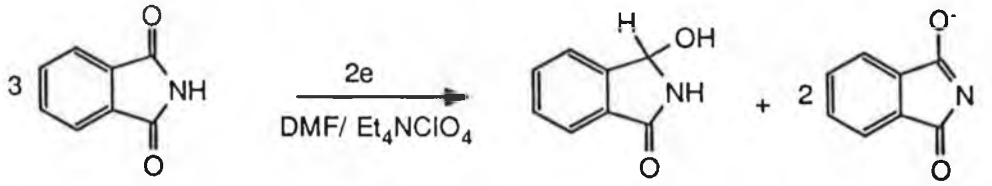
For an electrochemically reversible system the difference in the peak potentials, ΔE_p, at 25°C is 0.059/n V. For a chemically reversible system the ratio of the peak currents $i_{p,c}/i_{p,a}$ is unity since both the oxidised and reduced species are chemically stable. A cause of non-reversibility, which can occur for organic species, is if a chemical reaction occurs at the electrode resulting in the generation of a new organic entity leading to the initial product of electron transfer being lost.

3.2 Electrochemical Studies of (110) and (151)

Figures 3.2 and 3.3 show the cyclic voltammograms of (110) and (151) respectively, measured in dimethylformamide at room temperature, where the supporting electrolyte was lithium perchlorate. A hanging mercury drop electrode was used as the working electrode and a Ag/AgCl electrode as the reference electrode. Dimethylformamide was used as the solvent as this was the only solvent in which (110) was sufficiently soluble. It is apparent from both CVs that neither species was reversible, under the chemical conditions used and at the timescale employed, suggesting that the reduction products formed were chemically unstable.

In the CV of (110) (Figure 3.2), the potential was scanned between -0.2 and -2.0 V at a sweep rate of 0.1 V/s. The resulting voltammogram showed the formation of a reduction peak at E_p = -1.09 V and there was evidence of a subsequent reduction product past -2.0 V as observed by the continued increase in the current. In an effort to see if the reduction wave at -1.09 V was reversible, the potential range between -0.4 to -1.3 V was scanned with varying sweep rates. Figures 3.4 to 3.6 show the CVs for (110) measured at decreasing sweep rates, from 0.5 V/s to 0.01 V/s, and it is evident from these that the species in solution was irreversible.

We have found, by UV/visible studies, that (110), due to its acidity, exists as its anionic form in DMF (see Chapter 2 Section 2.C). This suggests that the species which is being reduced in solution is the anion of (110) and not the neutral acceptor. It has been reported that the electrochemical studies of phthalimide have been complicated due to the acidic NH proton but in spite of its acidity the anion radical of phthalimide was observable[183] by cyclic voltammetry in DMF and the first reduction peak (E_p= -1.49 V *vs* SCE) was reversible at a sweep rate of 20 V/s. At slower sweep rates self-protonation occured giving products which gave anomalous currents. See Scheme 4.01.



Scheme 4.01

We have found that the anion of (110) shows irreversible electrochemical behaviour, even at millisecond timescales. The irreversibility of (110) most likely results from the formation of an unstable reduction product, the identity of

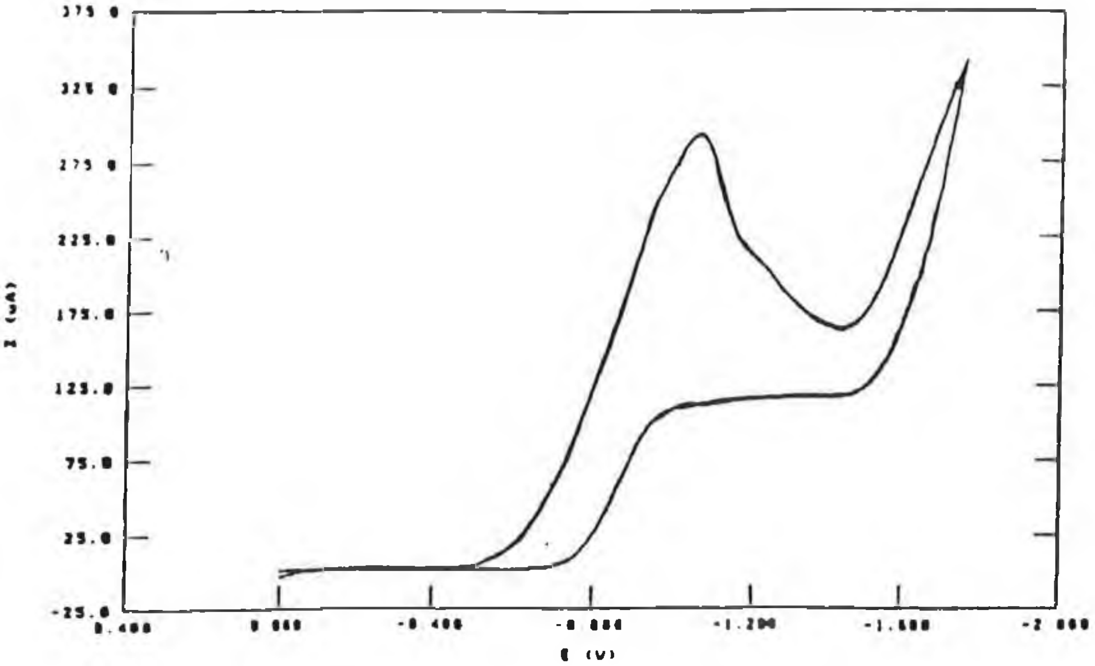


Figure 3.2 Cyclic Voltammogram of (110) in 0.1 M lithium perchlorate in Dimethylformamide at a hanging mercury-drop electrode, scan rate 0.1 V/s.

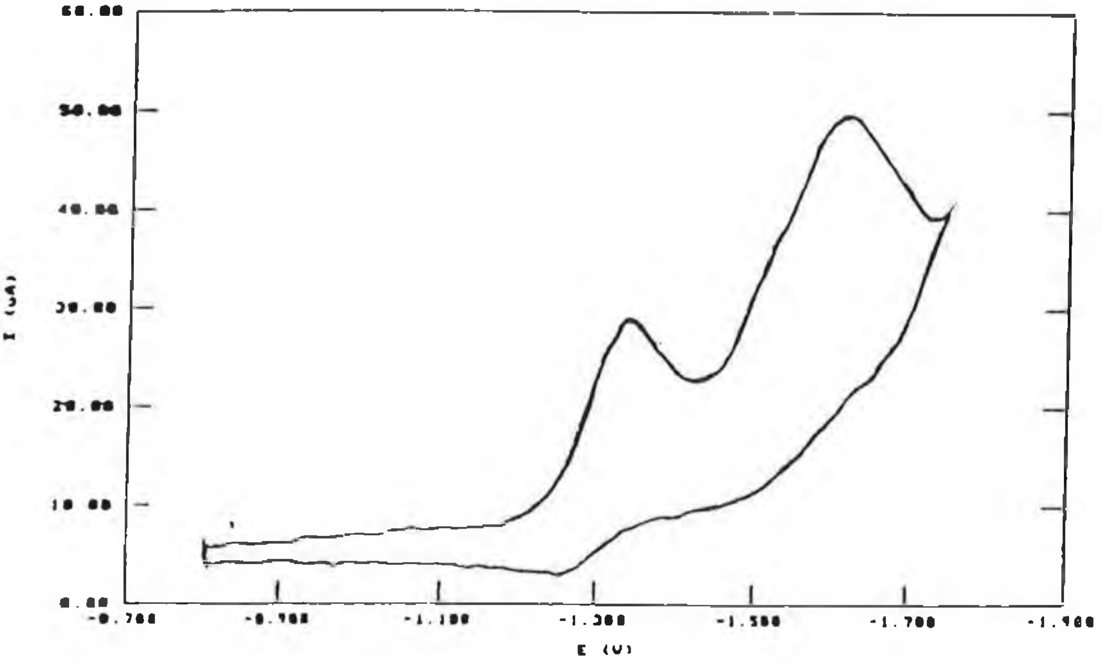


Figure 3.3 Cyclic Voltammogram of (151) in 0.1 M lithium perchlorate in Dimethylformamide at a hanging mercury-drop electrode, scan rate 0.1 V/s.

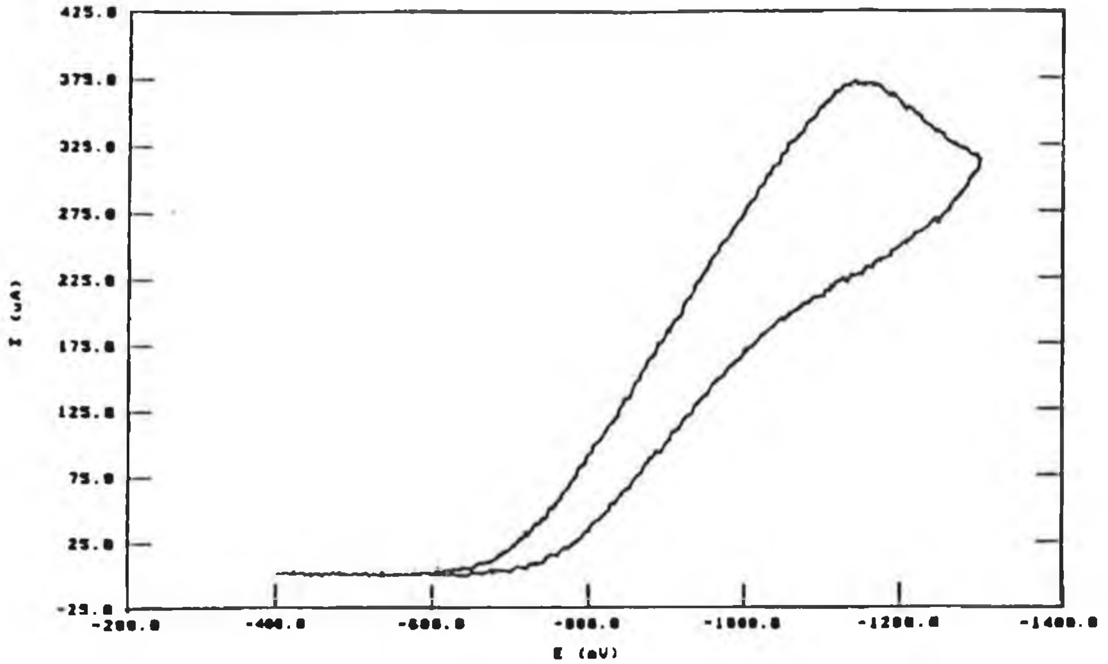


Figure 3.4 Cyclic Voltammogram of (110) in 0.1 M lithium perchlorate in Dimethylformamide at a hanging mercury-drop electrode, scan rate 0.5 V/s.

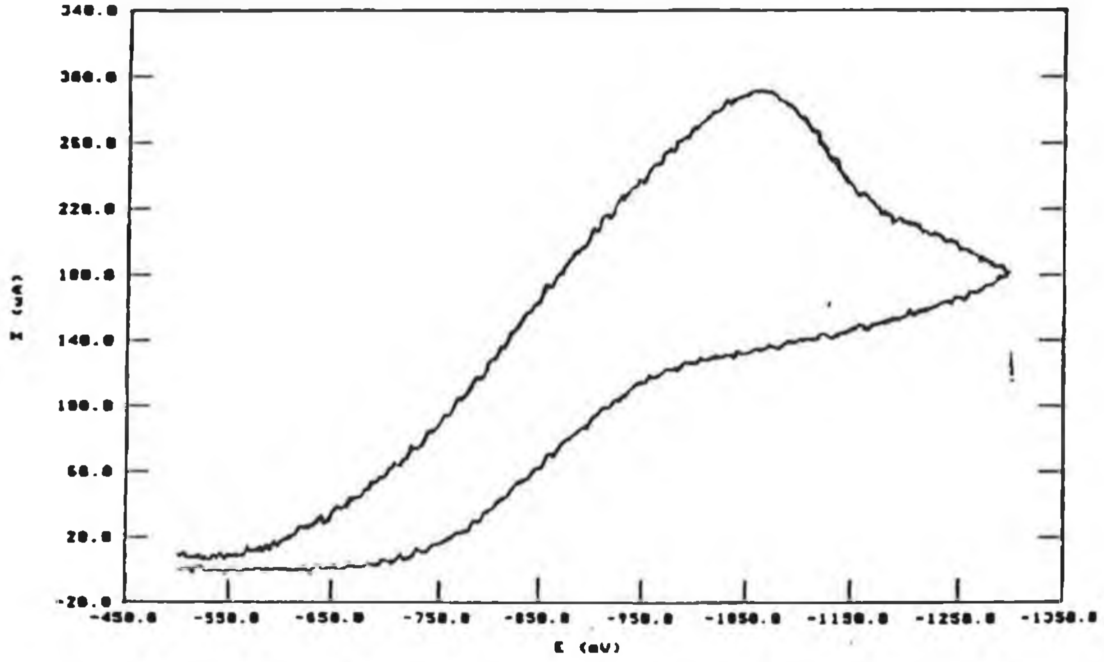


Figure 3.5 Cyclic Voltammogram of (110) in 0.1 M lithium perchlorate in Dimethylformamide at a hanging mercury-drop electrode, scan rate 0.1 V/s.

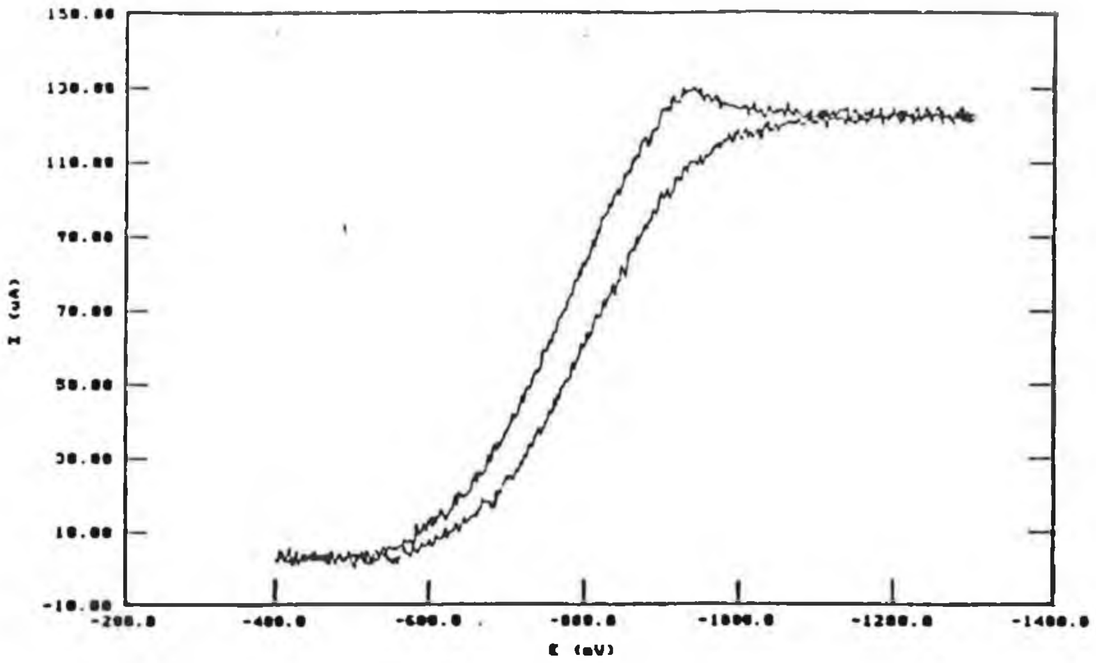


Figure 3.6 Cyclic Voltammogram of (110) in 0.1 M lithium perchlorate in Dimethylformamide at a hanging mercury-drop electrode, scan rate 0.01 V/s.

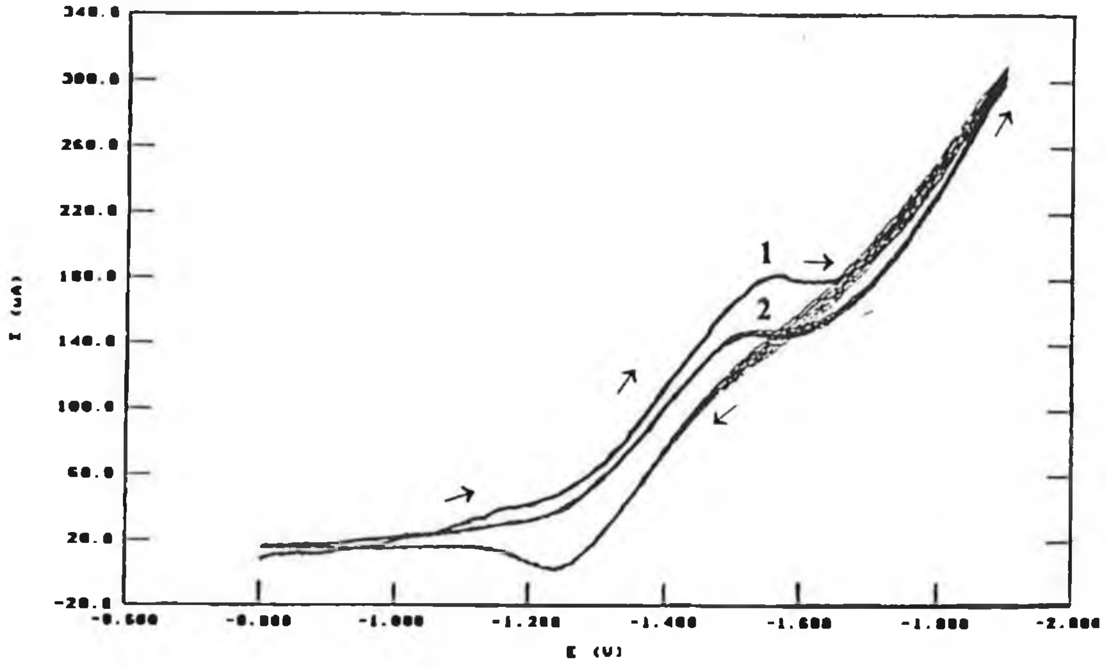
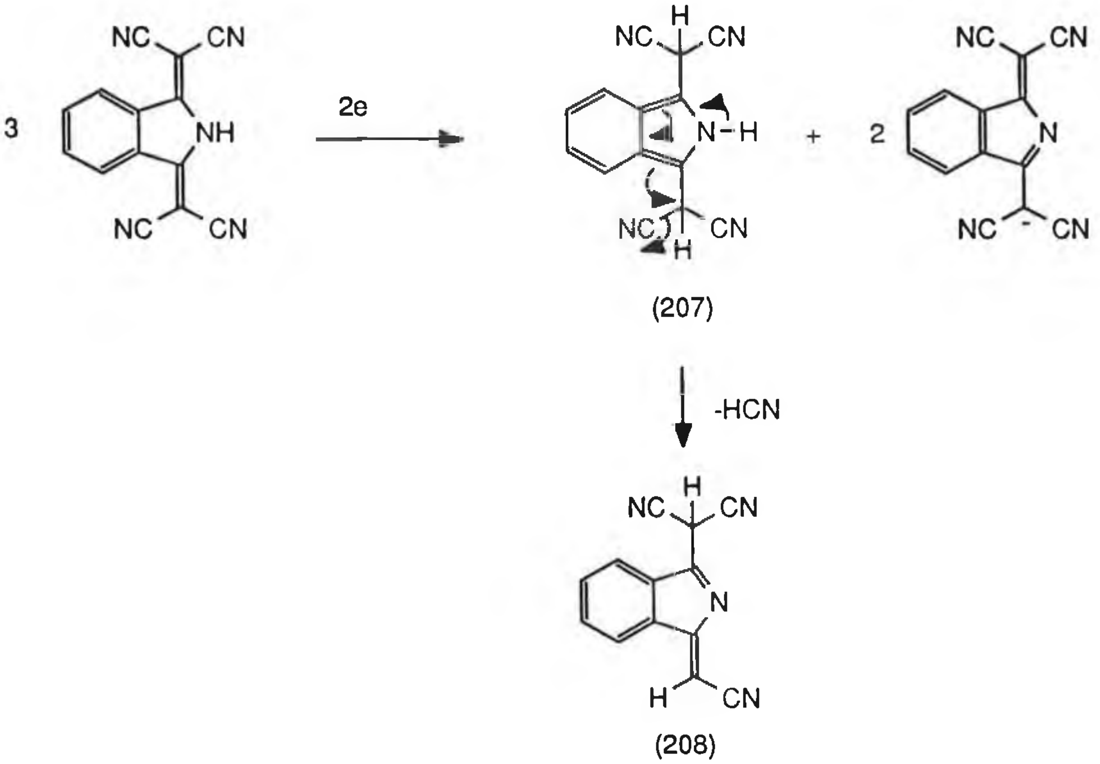
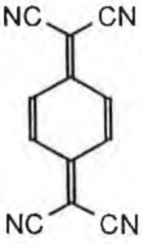


Figure 3.7 Cyclic Voltammogram of (151) in 0.1 M lithium perchlorate in Dimethylformamide at a hanging mercury-drop electrode, scan rate 5.0 V/s.

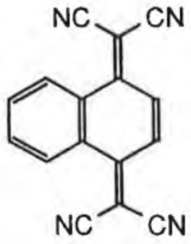
which is unknown. Such a product may possibly result from an analogous reaction to that for phthalimide in Scheme 4.01, giving the 1,3-disubstituted isoindole (207) which in turn could lose hydrogen cyanide giving the isoindolenine (208). Scheme 4.02. Since the half wave potential $E_{1/2}$ for (110), or its anion, cannot be determined, because of the non-reversibility of the reduction wave, it is not possible to compare its acceptor ability accurately with that of TCNQ (1), which has $E_{1/2}(1) = -0.12$, $E_{1/2}(2) = -0.72$ V in DMF, or its isoelectronic equivalent benzo-TCNQ (112), $E_{1/2}(1) = -0.30$, $E_{1/2}(2) = -0.73$ V in DMF.



Scheme 4.02



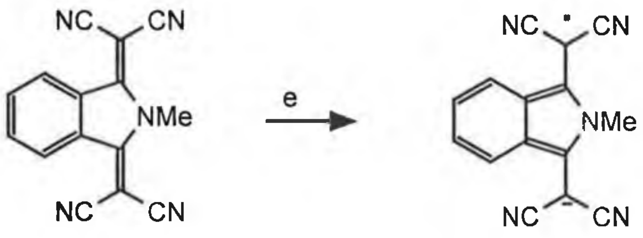
(1)



(112)

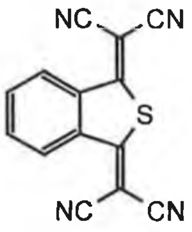
While the deprotonation associated with the formation of the anion of (110) is not possible for (151), its CV also showed non-reversibilty on reduction (Figure 3.3). Two reduction waves were observed at -1.35 and -1.62 V. In an effort to determine whether the second reduction wave was associated with (151) itself or with the formation of a new species on reduction of (151), the sweep rate was increased from 0.1 V/s to 5.0 V/s. Increasing the sweep rate in cyclic voltammetry decreases the amount of time taken for each scan, thus reducing the likelihood that the product of electron transfer will undergo a following chemical reaction. Figure 3.7 shows that on increasing the sweep rate only a single redox couple is observed at approximately -1.400 V, corresponding to reduction of (151). That a single redox couple is observed suggests that the kinetics of the chemical reaction that follows electron transfer are relatively slow, and that by employing a relatively fast sweep rate, 5 V/s, this chemical reaction can be out run. Under the circumstances, an electron can be injected into (151) and removed before significant chemical decomposition has occurred. When Figures 3.3 and 3.7 are compared, there are two significant differences in the voltammetric responses observed for the reduction of (151). First, in the higher sweep rate experiment (Figure 3.7) a significant oxidation response is observed corresponding to the re-oxidation of electrochemically reduced (151). Second, there is a difference of approximately 50 mV in the half-wave potential for the irreversible redox reaction of Figure 3.3 compared to the formal potential of the quasi-reversible response illustrated in Figure 3.7. This difference is expected since the position of the irreversible wave is controlled in part by the rate constant of the following chemical reaction. Moreover, because of the higher currents that are observed in Figure 3.7, there will be a larger iR drop, where i is the total current flow and R is the resistance of the electrolytic solution, which tend to shift the formal potential of the voltammetric response shown in Figure 3.3 in a negative potential direction.

As a result of the non-reversibility of (151) it was not possible to compare the reduction peak potential at E_p = -1.35 V with the half wave potentials of (1) and (112). However, the reduction peak potential does give some indication of the electron acceptor ability of (151) and the stability of the anion radical formed. The reduction peak potential observed suggests that (151) is not a strong acceptor and its irreversibility shows that the anion radical is unstable. One explanation for the instability of the anion radical of (151), initially considered, was the formation of an isoindole intermediate (209) which might form on one electron reduction of (151). Although *N*-substituted isoindoles are stabilised when strongly electron withdrawing groups are present in the C_1 and C_3 postions,[184] the excess negative charge may reduce this stability.



(209)

However (114), the sulphur analogue of (110), shows two reversible reduction waves in dichloromethane[139] at $E_{1/2}(1) = -0.31$, and $E_{1/2}(2) = -0.78$ V, and this compound would be expected to form similar benzo[c]thiophene radical anion intermediates. This suggests that either the isoindole derivative is less stable than its sulphur analogue or that some other chemical reaction is taking place at the electrode.



(114)

Conclusions

Due to the limitations in the use of dimethylformamide as the solvent for the electrochemical studies of (110), it cannot be conclusively stated how the acceptor ability of (110) compares to that of (1) or the iso-electronic (112). The electrochemical studies of (151), however, show that the radical anion intermediates are not stable and are not electrochemically reversible. Although the half-wave potentials cannot be calculated, comparison of the first reduction potential E_p with the half-wave reduction potentials of (112) shows that (151) is not as good an acceptor as (112). This suggests that in order for (151), and possibly (110), to form C-T complexes, more strongly donating donor groups may be necessary. Since the reduction potential obtained for (110) is less than that of (151), and is most likely due to the reduction of the anion of (110), it is possible that the electron affinity of the neutral acceptor may be greater than that of (151).

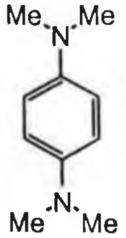
Chapter 4

4.0 Charge-Transfer Studies of 2,2'-(Isoindolin-1,3-diylidene) bispropanedinitrile (110) and 2,2'-(2-Methylisoindolin-1,3-diylidene) bispropanedinitrile (151)

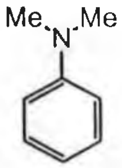
4.1 Introduction

As stated previously in Chapter 1, (Section 1.A), when an electron donor D and an electron acceptor A interact, their physical properties are perturbed and new properties arise which can be attributed to the formation of a charge-transfer complex. These new properties are responsible for the observation of new bands in the UV/visible spectrum which are not attributable to either the donor D or the acceptor A. UV/visible spectroscopy provides one of the most widely used methods for the study of both strong and weak C-T complexes and it also provides a reliable means of determining the thermodynamic properties of these complexes.[185] However weak electron-donor-acceptor interactions give complexes which last sufficiently long for intermolecular C-T to occur but are sometimes unstable and cannot be isolated as a solid complex. As a result their concentrations are less than the donor and acceptor concentrations and thus it may be difficult to observe their C-T bands in solution by UV/visible spectroscopy.

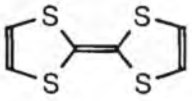
In an effort to see which donors might potentially form stable C-T complexes with the acceptors (110) and (151), UV/visible studies were carried out with a range of donors, (2a) and (210)-(212), and the spectrum of the solution of the complex recorded to determine whether C-T was taking place. The method employed involved adding a sufficient quantity of the acceptor to a fixed volume of a suitable solvent in a quartz cell and then recording the spectrum. The donor was then added to this solution in known quantities and the spectrum recorded again. A spectrum of the donor in the same solvent was also recorded and the formation of the new C-T band could then be seen on comparison of the spectra. Fortunately (110) was sufficiently soluble in dichloromethane and tetrahydrofuran to permit the measurement of its



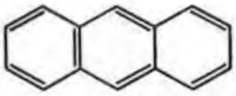
(210) TMDA



(211) DMA



(2a) TTF


(212) AN

UV/visible spectrum, which allowed for the determination of the C-T complexing ability of the neutral compound. The C-T complex was subsequently isolated by mixing together concentrated solutions of the donor and the acceptor in an appropriate solvent, filtering it off if it formed on standing, or else by evaporating off the solvent and recrystallising the complex from an alternative solvent.

In this chapter the UV/visible studies for the acceptors (110) and (151) with a variety of donors are reported along with the C-T complexes isolated, and the X-ray crystal structure of the C-T complex of (110) with *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMDA).

4.2 Charge-Transfer Complex of (110) with *N,N,N',N'*-Tetramethyl-*p*-phenylenediamine (TMDA)

Because of the acidity of the NH group in (110) it was of interest to see whether (110) would form a C-T complex or a salt with the strong donor *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMDA; 210). On adding TMDA to (110) in dichloromethane, and measuring the UV/visible spectrum, a new broad intense band was observed at 500-680 nm with λ_{max} = 642 nm, attributed to the formation of a C-T band, (Figure 4.01).

On combining a concentrated solution of (110) in tetrahydrofuran with a two molar equivalent solution of TMDA in acetonitrile a black/dark green solution formed immediately and green/black needles precipitated. Elemental analysis showed that a 1:1 C-T complex had been formed. The X-ray crystal structure permitted determination of the stacking pattern found in the complex.

4.2.1 X-ray Crystal Structure of the 1:1 C-T complex of (110)-TMDA

Crystals of the 1:1 complex of (110)-TMDA (Figure 4.02), suitable for X-ray crystallography, were obtained from acetonitrile as black/dark green needles. The 1:1 complex crystallised in a monoclinic crystal system in the P121/n space group. The relevant bond lengths and bond angles are given in Table 4.01.

The crystal packing diagram (Figure 4.03) shows the infinite one-dimensional alternate or mixed stacking of the donor (TMDA) and the acceptor (110) in the complex. The highly planar nature of (110), an important prerequisite for the synthesis of electrically conducting C-T complexes, can be seen in Figure 4.04. To calculate the distance between the two components within a stack of the C-T complex the mean plane of the nitrile component of (110) was calculated and the orthogonal distance of any atom on the adjacent

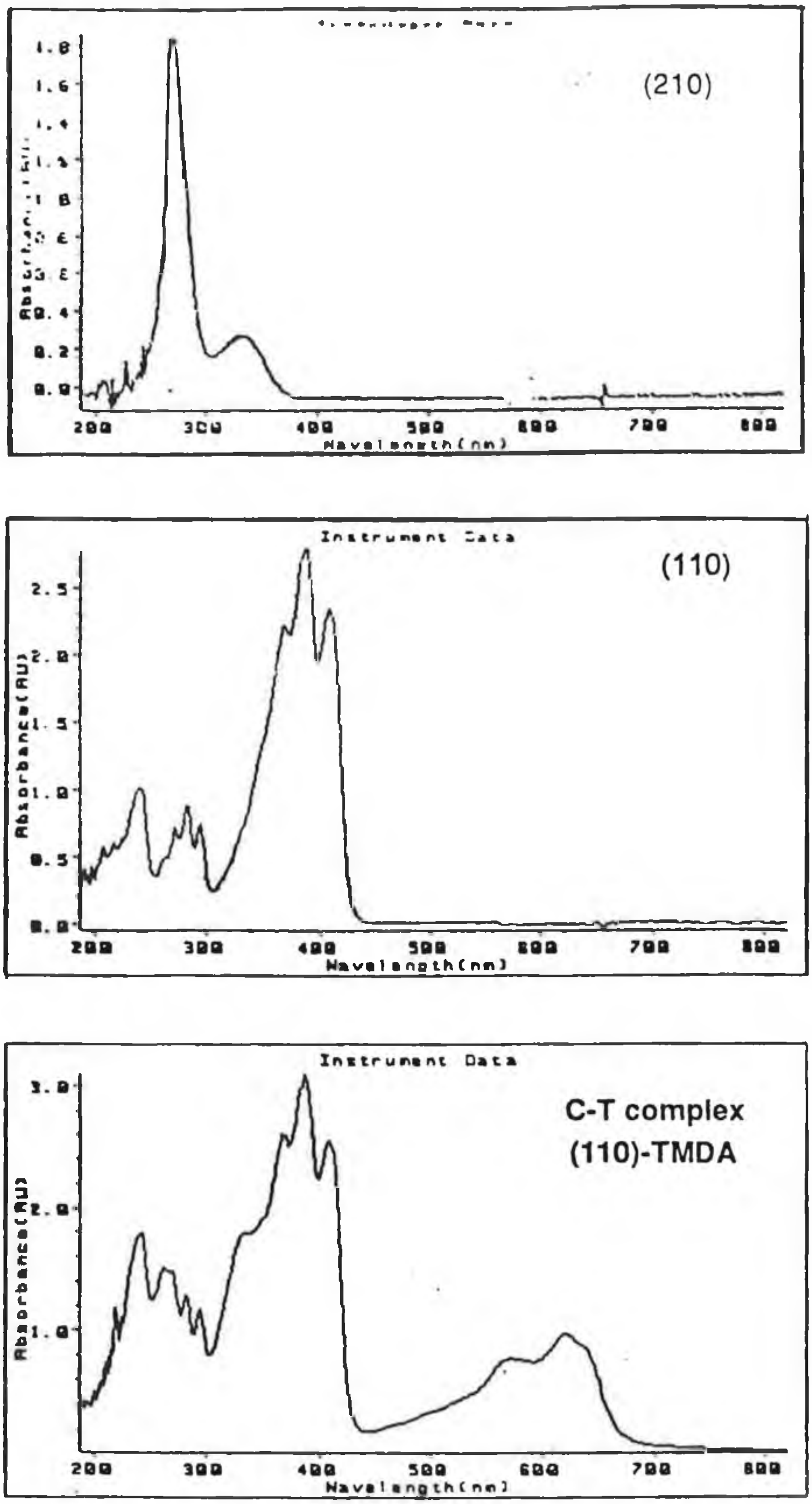


Figure 4.01 UV/visible spectra of TMDA (210), (110) and the Charge-Transfer complex (110)-TMDA.

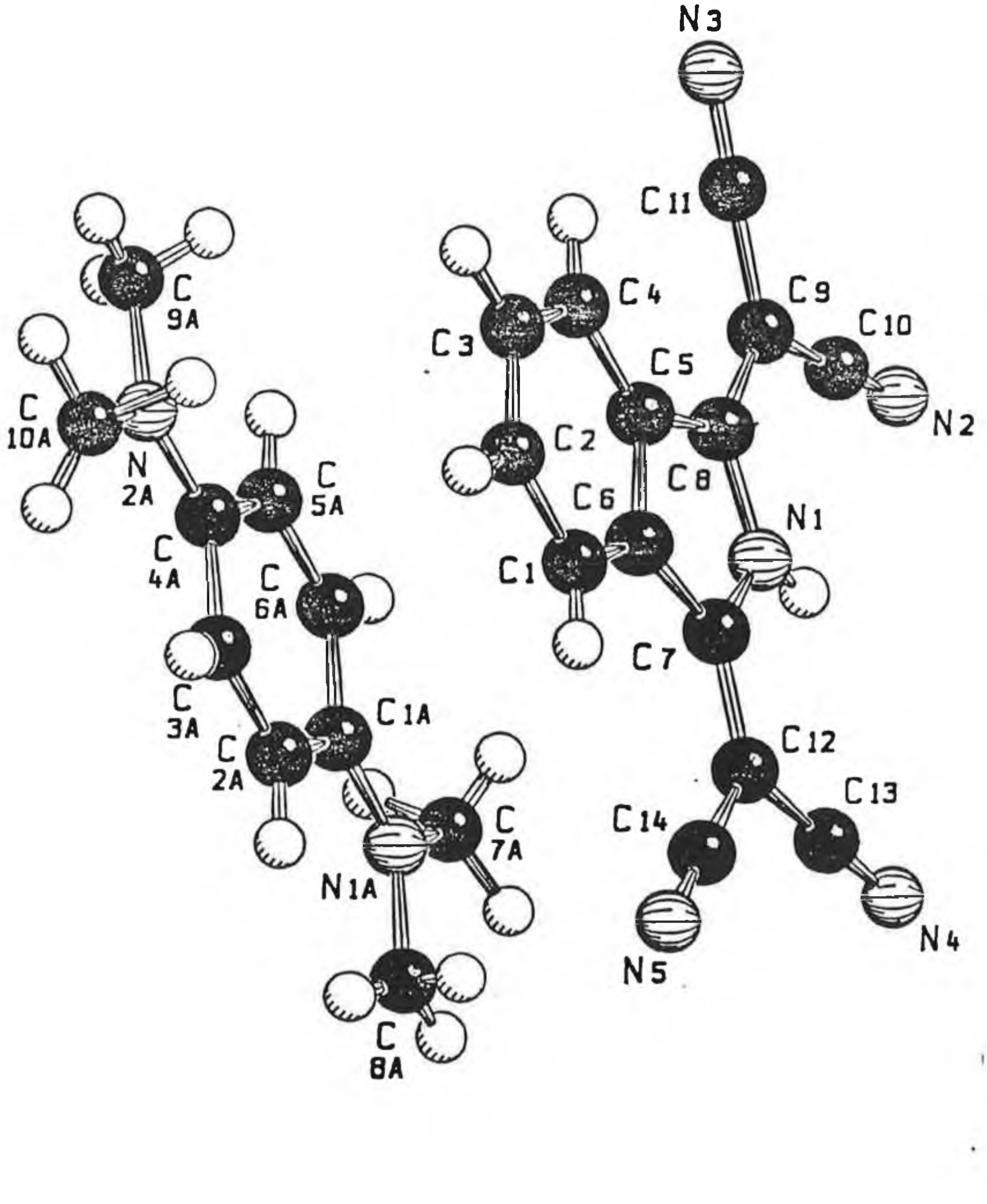


Figure 4.02 SCHAKAL drawing of the crystal structure of the 1:1 complex of (110)-TMDA.

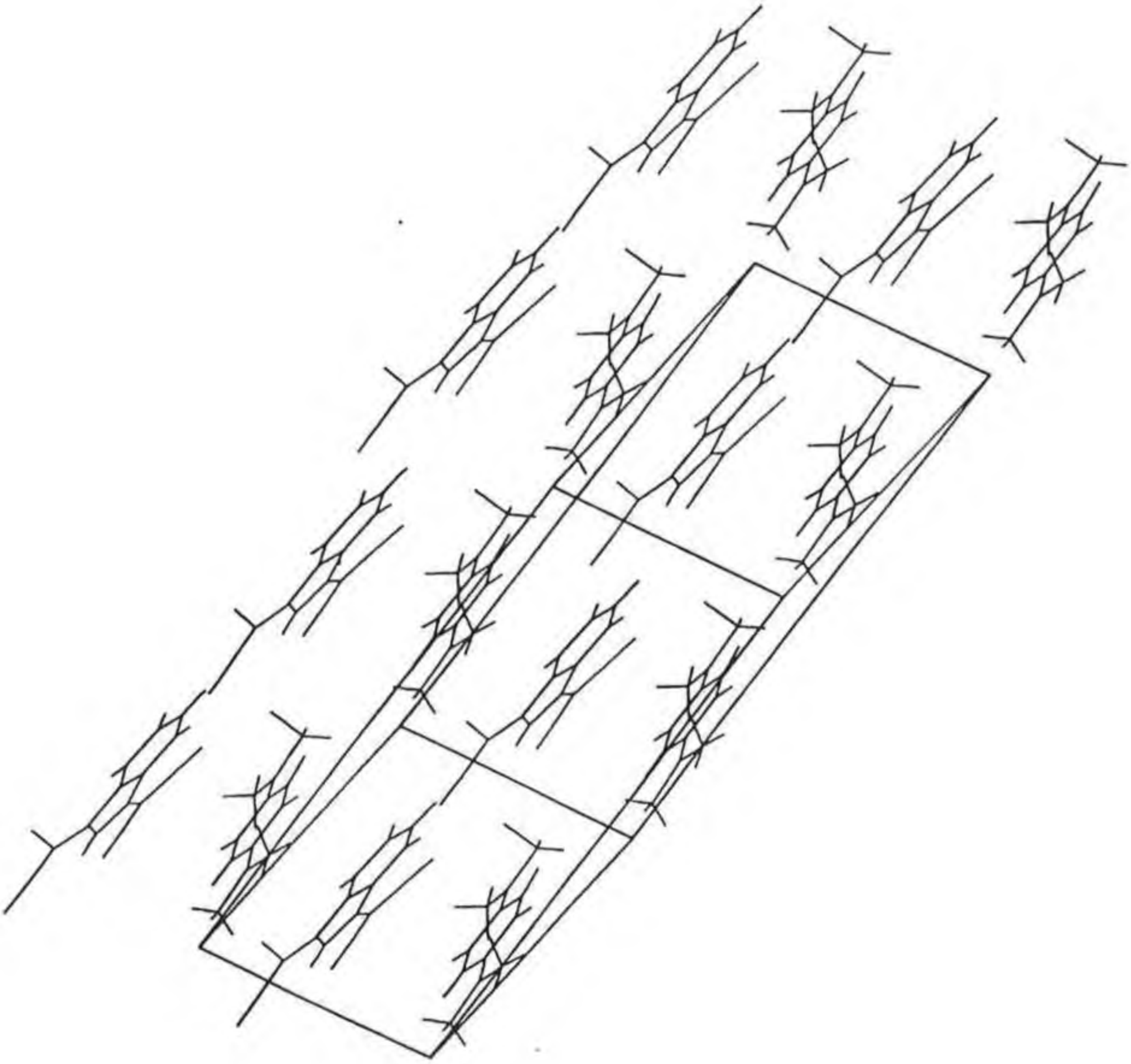


Figure 4.03 SCHAKAL illustration of the alternate or mixed stacking found in the crystal structure of the 1:1 complex of (110)-TMDA.

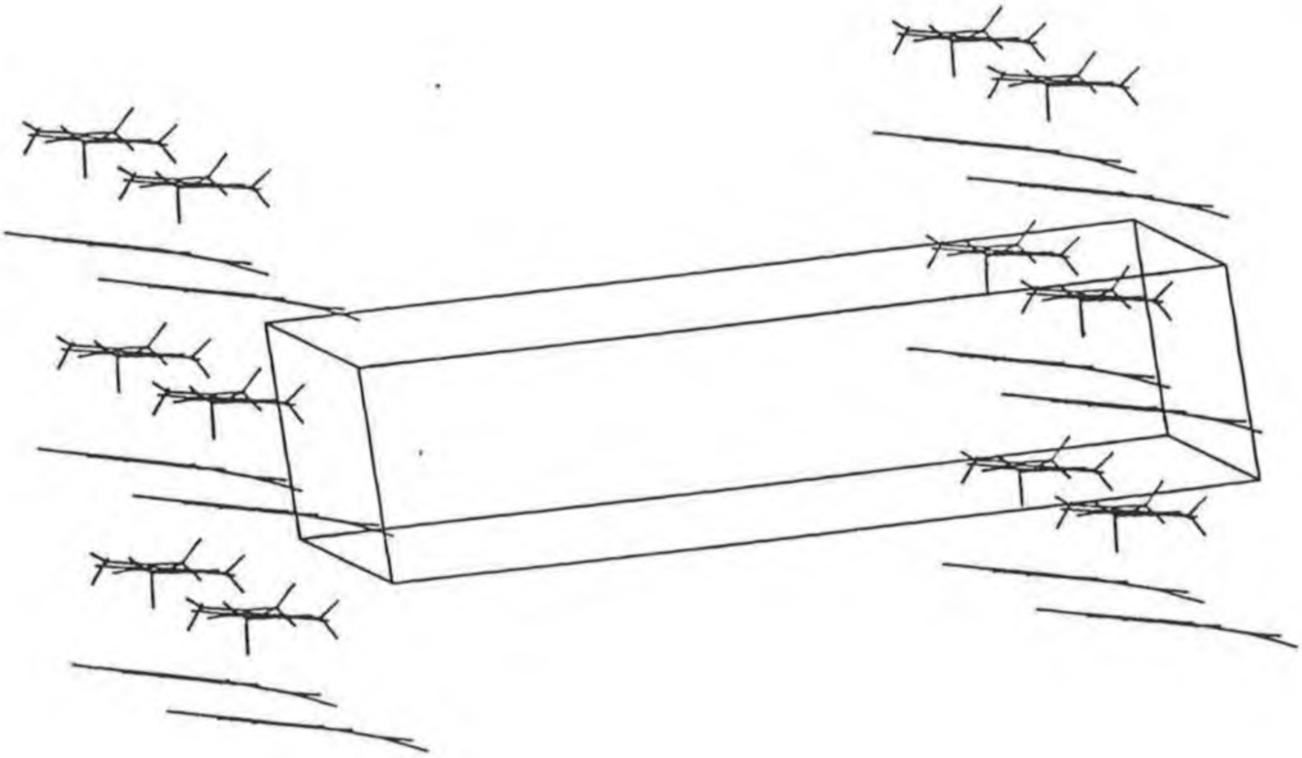


Figure 4.04 Alternative perpective of the SCHAKAL illustration of the stacking motif found in the crystal structure of the 1:1 complex of (110)-TMDA.

Table 4.01 showing the bond lengths and bond angles for (110)-TMDA

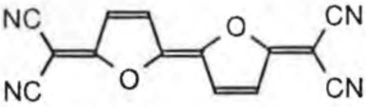
Bond lengths (Å)		Bond angles (deg)	
N(1A)-C(1A)	1.355(5)	C(1A)-N(1A)-C(7A)	121.2(4)
N(1A)-C(7A)	1.455(6)	C(1A)-N(1A)-C(8A)	122.1(4)
N(1A)-C(8A)	1.454(6)	C(7A)-N(1A)-C(8A)	116.7(4)
N(2A)-C(4A)	1.337(5)	C(4A)-N(2A)-C(9A)	122.2(4)
N(2A)-C(9A)	1.444(6)	C(4A)-N(2A)-C(10A)	121.7(4)
N(2A)-C(10A)	1.472(6)	C(9A)-N(2A)-C(10A)	116.2(4)
C(1A)-C(2A)	1.411(5)	N(1A)-C(1A)-C(2A)	121.3(4)
C(1A)-C(6A)	1.411(5)	N(1A)-C(1A)-C(6A)	121.2(3)
C(2A)-C(3A)	1.362(6)	C(2A)-C(1A)-C(6A)	117.5(4)
C(3A)-C(4A)	1.418(6)	C(3A)-C(2A)-C(1A)	120.8(4)
C(4A)-C(5A)	1.416(5)	C(2A)-C(3A)-C(4A)	122.0(4)
C(5A)-C(6A)	1.351(6)	N(2A)-C(4A)-C(5A)	121.2(4)
N(1)-C(7)	1.344(5)	N(2A)-C(4A)-C(3A)	122.4(4)
N(1)-C(8)	1.346(5)	C(5A)-C(4A)-C(3A)	116.4(4)
N(2)-C(10)	1.150(6)	C(6A)-C(5A)-C(4A)	121.8(4)
N(3)-C(11)	1.142(6)	C(5A)-C(6A)-C(1A)	121.5(4)
N(4)-C(13)	1.143(6)	C(7)-N(1)-C(8)	108.1(3)
N(5)-C(14)	1.132(5)	C(6)-C(1)-C(2)	119.4(5)
C(1)-C(6)	1.374(6)	C(1)-C(2)-C(3)	120.7(5)
C(1)-C(2)	1.375(7)	C(4)-C(3)-C(2)	120.8(5)
C(2)-C(3)	1.383(7)	C(3)-C(4)-C(5)	118.4(5)
C(3)-C(4)	1.381(7)	C(4)-C(5)-C(6)	120.7(4)
C(4)-C(5)	1.385(6)	C(4)-C(5)-C(8)	133.6(4)
C(5)-C(6)	1.399(5)	C(6)-C(5)-C(8)	105.8(4)
C(5)-C(8)	1.467(5)	C(1)-C(6)-C(5)	120.0(4)
C(6)-C(7)	1.467(5)	C(1)-C(6)-C(7)	135.0(4)
C(7)-C(12)	1.375(5)	C(5)-C(6)-C(7)	105.0(3)
C(8)-C(9)	1.378(5)	N(1)-C(7)-C(12)	121.6(4)
C(9)-C(10)	1.417(7)	N(1)-C(7)-C(6)	110.8(3)
C(9)-C(11)	1.428(6)	C(12)-C(7)-C(6)	127.6(4)
C(12)-C(14)	1.425(6)	N(1)-C(8)-C(9)	121.0(4)
C(12)-C(13)	1.434(6)	N(1)-C(8)-C(5)	110.2(3)
		C(9)-C(8)-C(5)	128.7(4)
		C(8)-C(9)-C(10)	119.8(4)
		C(8)-C(9)-C(11)	123.6(4)
		C(10)-C(9)-C(11)	116.5(4)
		N(2)-C(10)-C(9)	179.3(5)
		N(3)-C(11)-C(9)	179.4(5)
		C(7)-C(12)-C(14)	125.0(4)
		C(7)-C(12)-C(13)	120.3(4)
		C(14)-C(12)-C(13)	114.7(4)
		N(4)-C(13)-C(12)	178.0(5)
		N(5)-C(14)-C(12)	178.2(6)

donor molecule was then determined. These distances are shown in Table 4.02. It can be seen that the nearest mean plane contact distance between the donor and acceptor is 3.41 Å and the farthest is 3.60 Å, similar to the interplanar distances (~3.5 Å) found in other mixed stack complexes[186] and are

Table 4.02 Mean plane contact distances between the (110) and TMDA

Donor Atoms	Mean plane orthogonal distance (Å)
C1a	3.5400
C2a	3.4335
C3a	3.4128
C4a	3.5012
C5a	3.5770
C6a	3.5988
N1a	3.6027
N2a	3.5168

greater than those for segregated stack complexes (~3.2 Å). Figure 4.04 also shows the two-dimensional alternating stacking structure of the complex and in addition it can be seen that the donor and acceptor components of the stacks are tilted out of the plane normal to the stacking direction. The sheet-like nature of the donors and acceptors in the alternate stacks is also seen in Figure 4.03. This mixed stacking motif of the complex is the most common arrangement [187] and is consistent with complexes composed of strong donors, such as TMDA and TTF, and weak electron acceptors, such as (110) and the extended furanoquinoid TCNQ analogue (213).[102]



(213)

The other structural feature of interest from the X-ray crystal analysis is the relative orientations of the component molecules to each other. This can be seen in Figure 4.05, which gives a side view of the D-A pair, and Figure 4.06, which shows the relative overlap of the two component molecules by projection of the mean plane of the donor onto that of the acceptor. Both these figures show that there is half a ring displacement of the aromatic rings of each component. Such a half ring displacement was postulated by Mulliken [12(a)] to yield maximised C-T interactions in π-π complexes, by allowing maximum overlap of the filled donor orbital and the empty acceptor orbital. While similar

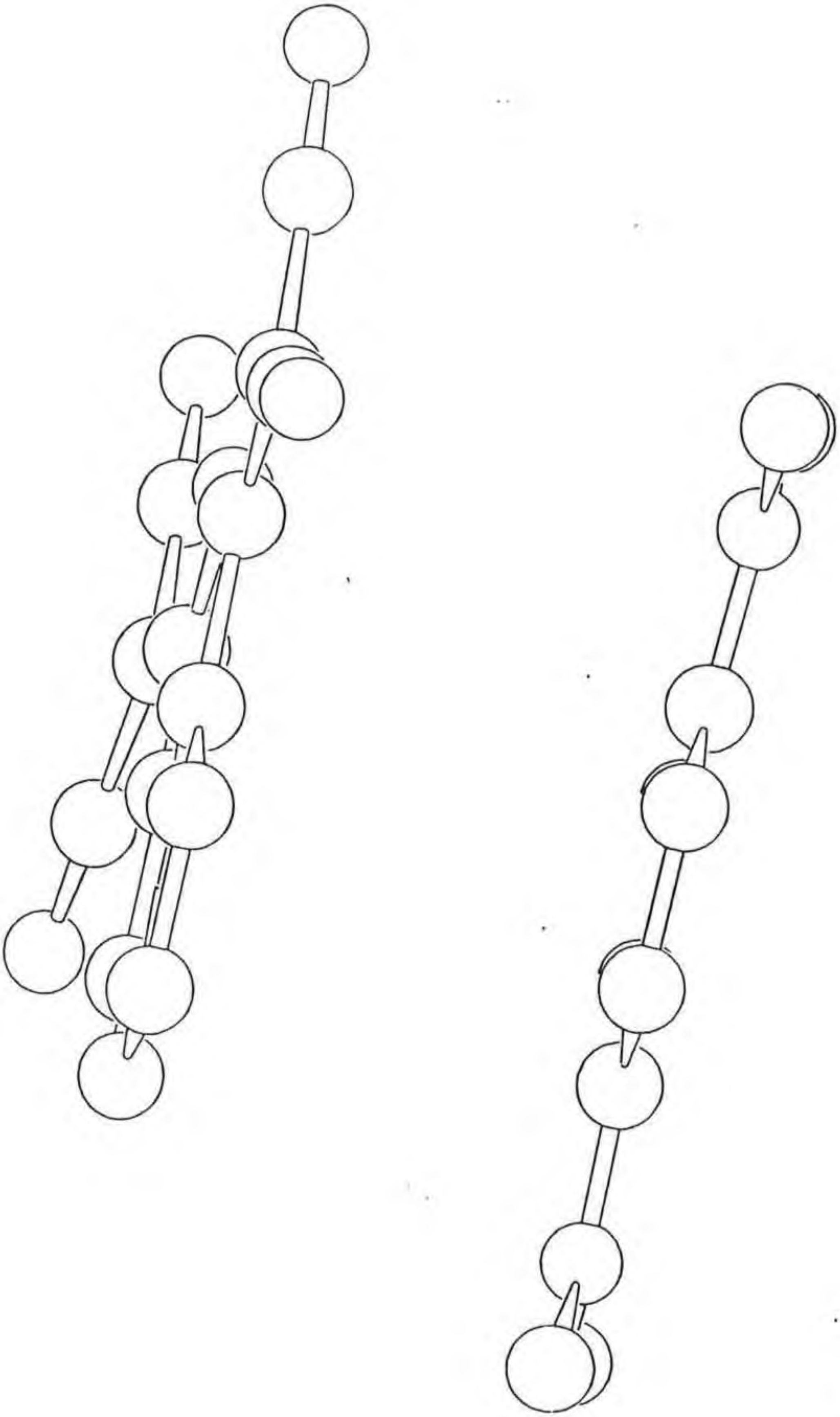


Figure 4.05 Side view of the relative orientation of the donor molecule to the acceptor molecule in (110)-TMDA.

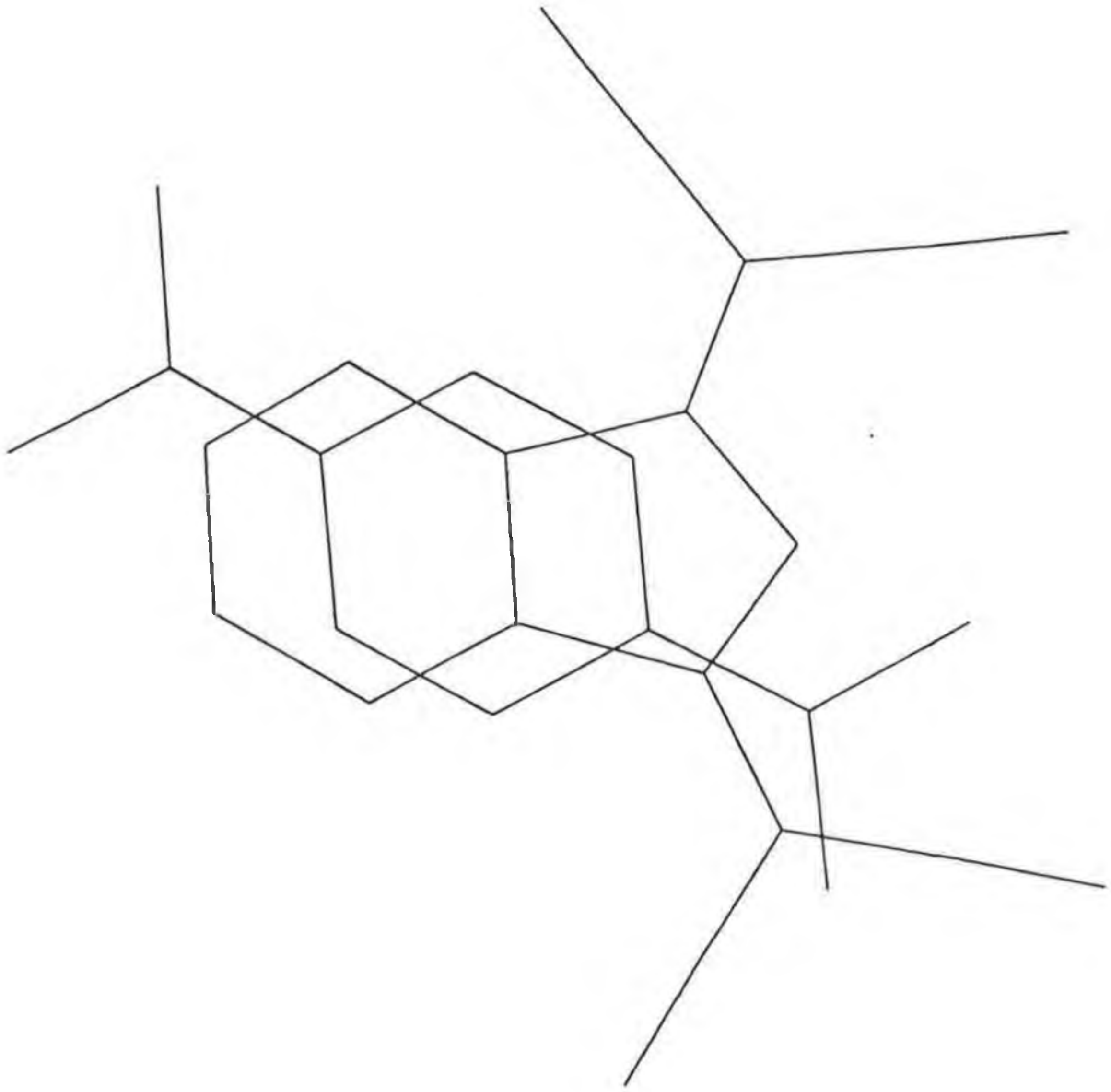
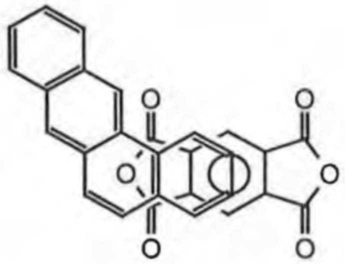


Figure 4.06 Orthogonal view, showing how the donor molecule and the acceptor overlap in (110)-TMDA.

half ring displacements can be seen in the 1:1 complexes of pyromellitic dianhydride-benz[*a*]anthracene (214) and naphthalene-d_8-tetrachlorophthalic anhydride (215),[188] it has been suggested[187(a)] that Mulliken did not take into account dispersion forces, which tend to be largest in orientations bringing maximum polarisabilities into play and which are associated with short interplanar spacings. Mulliken later conceded that electrostatic forces may be responsible, and sometimes predominantly, for the stability of weak π-π complexes, but he stated that dispersion-force contribution to the stability was only important in the vapour state since their effects were approximately cancelled in the formation of complexes in solution.[12(b)] Similar findings to Mullikens were also reported by Wallwork[189] who, on investigating the structure and relative disposition of components in C-T complexes, claimed that where C-T forces might be expected to be more significant in determining the structure (*e.g.* from low ionisation potential of the donor) the relative orientation and positions of the component donor and acceptor are found to be such as to allow the maximum overlap between their π-molecular orbitals. However it seems that since short interplanar separations are not in evidence in the (110)-TMDA complex, as compared with the interplanar spacing of 3.27 and 3.24 Å for the 1:1 and 2:1 complexes of TCNQ with TMDA, and since there seems to be no particular overlap of the polarisable groups, (the carbon to carbon double bond of the acceptor and the nitrogens of the donor), this may suggest that C-T interaction contributes to the relative orientation of TMDA and (110) which may result from maximum donor-acceptor orbital overlap.



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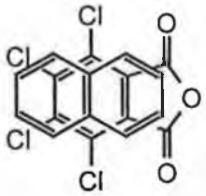
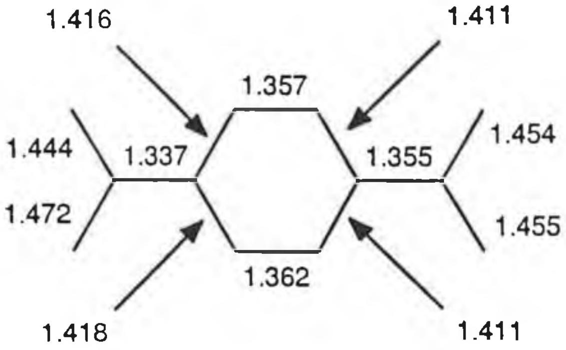


(215)

We also compared (110)-TMDA with the 2:1 and a 1:1 complexes of TCNQ with TMDA. The X-ray crystal structures of both the 1:1 complex [16] and the 2:1 complex[17] show segregated stacking of the TMDA and the TCNQ molecules with interplanar spacing of 3.27 and 3.24 Å respectively, suggesting a stronger C-T interaction than that found in (110)-TMDA. Comparison of the bond lengths of the aromatic ring system for the TMDA molecule in the complex with (110), with those for the 1:1 and 2:1 complexes for TMDA with TCNQ, (Table 4.03), shows similar values and on examining the bond lengths it is evident that the TMDA molecule has pseudo-quinonoidal character, structure (216), confirming that C-T has taken place between TMDA and (110).



(216)

Table 4.03 Comparison of the bondlengths found in TMDA in the neutral form and in C-T complexes with TCNQ and (110)

	Bond lengths (Å)			
Bond	2:1 TCNQ-TMDA	1:1 TCNQ-TMDA	1:1 (110)-TMDA	TMDA[190]
C1A-C2A	1.418	1.416	1.411	1.402
C1A-C6A			1.411	1.400
C2A-C3A	1.367	1.374	1.362	1.398
C5A-C6A			1.357	1.382
C3A-C4A	-	-	1.418	1.392
C4A-C5A			1.416	1.394
C4A-N2A	1.373	1.365	1.337	1.420
C1A-N1A			1.355	1.407
N1A-C8A	1.458	1.474	1.454	1.412
N2A-N10A			1.472	1.445

Further evidence for the occurrence of C-T is also apparent from the marked low wavenumber shift of the nitrile stretching vibration, 2198 cm^{-1} for the complex, compared with 2227 cm^{-1} for neutral (110). Such shifts are indicative of C-T in which the coupling of conduction electrons and intramolecular phonons affect the vibrational modes of the complex components and result in a shifting of frequencies.[191]

4.3 Attempted C-T Complex formation of (110) with other donors

It seemed likely that the structurally similar, yet slightly poorer donor relative to TMDA, *N,N*-dimethylaniline (DMA; 211) would give analogous results with (110). However, when DMA was added to a solution of (110) it did not show the formation of a new C-T band but instead showed the formation of the anion of (110), corresponding to the dimethylanilinium salt of (110), (Figure 4.07). This was confirmed by comparing its spectrum with that of the ammonium salt (119) (Figure 4.08) which was shown to be identical to the UV spectra of the alkylammonium salts reported in Chapter 2, Section D. Mixing solutions of the DMA and (110) in THF did not show any darkening of the resulting solution, usually an indication that C-T has taken place.

The use of a strong donor which would not deprotonate (110) was then investigated. The addition of increasing amounts of the strongly electron-donating compound TTF to a fixed concentration of (110) in acetonitrile resulted in the formation of a C-T band with λ_{max} = 460 nm (Figure 4.09). On adding a solution of (110) in tetrahydrofuran to a concentrated one molar equivalent solution of TTF in acetonitrile, an immediate colour change in the solutions, from light yellow to green, was observed. Attempts to isolate sufficient quantities of the dark green flake crystals, observed on evaporating off the solvent mixture, failed on attempting to recrystallise the complex from a variety of solvents and thus it was not possible to determine the ratio of donor to acceptor in the complex formed.

In order to determine whether complex formation with weaker donor systems was possible, spectroscopic studies on the addition of anthracene (AN) to a solution of (110) in tetrahydrofuran were carried out. Figure 4.10 shows the effect of adding increasing amounts of AN to the acceptor. The formation of a new C-T band at 450-520 nm, as two broad peaks, was observed. Although these bands are similar to those observed at 466 and 496 nm on the dropwise addition of water to a solution of (110) in THF (Figure 4.11), the considerably broadened nature of the bands due to the addition of AN and the different λ_{max} values suggest that C-T occurs. The bands due to the addition of water were identical to those of anion of (110) (see Figure 4.08) and these disappeared on addition of a drop of concentrated hydrochloric acid to the aqueous THF solution, confirming their assignment as being due to the anion of (110). It seems likely that due to the acidic nature of (110) and the amphoteric nature of water that the anion is formed on addition of water. The possibility of the formation of the anion of (110) on addition of AN is unlikely.

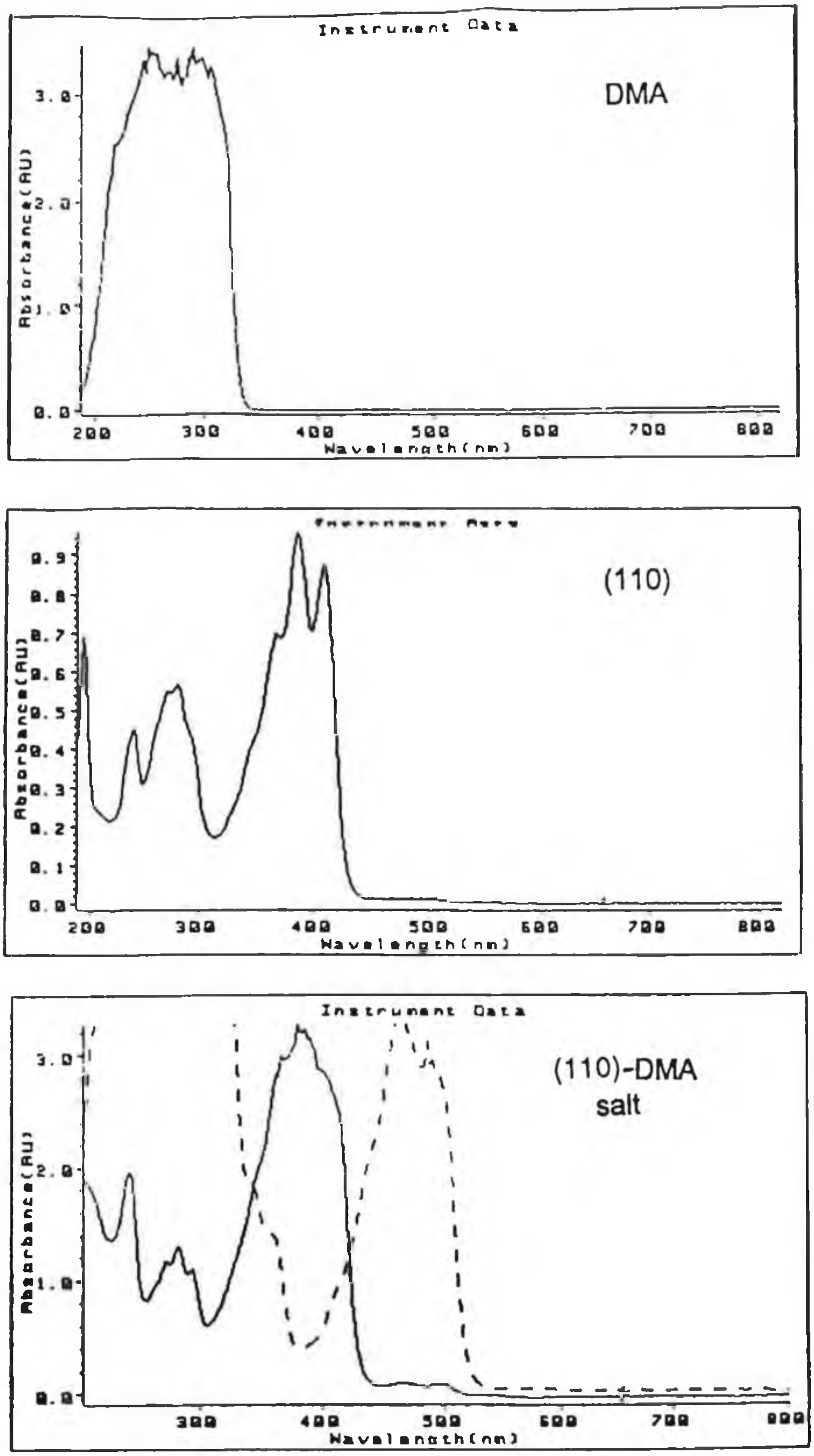


Figure 4.07 UV/visible spectra of DMA (211), (110) and the (110)-DMA salt.

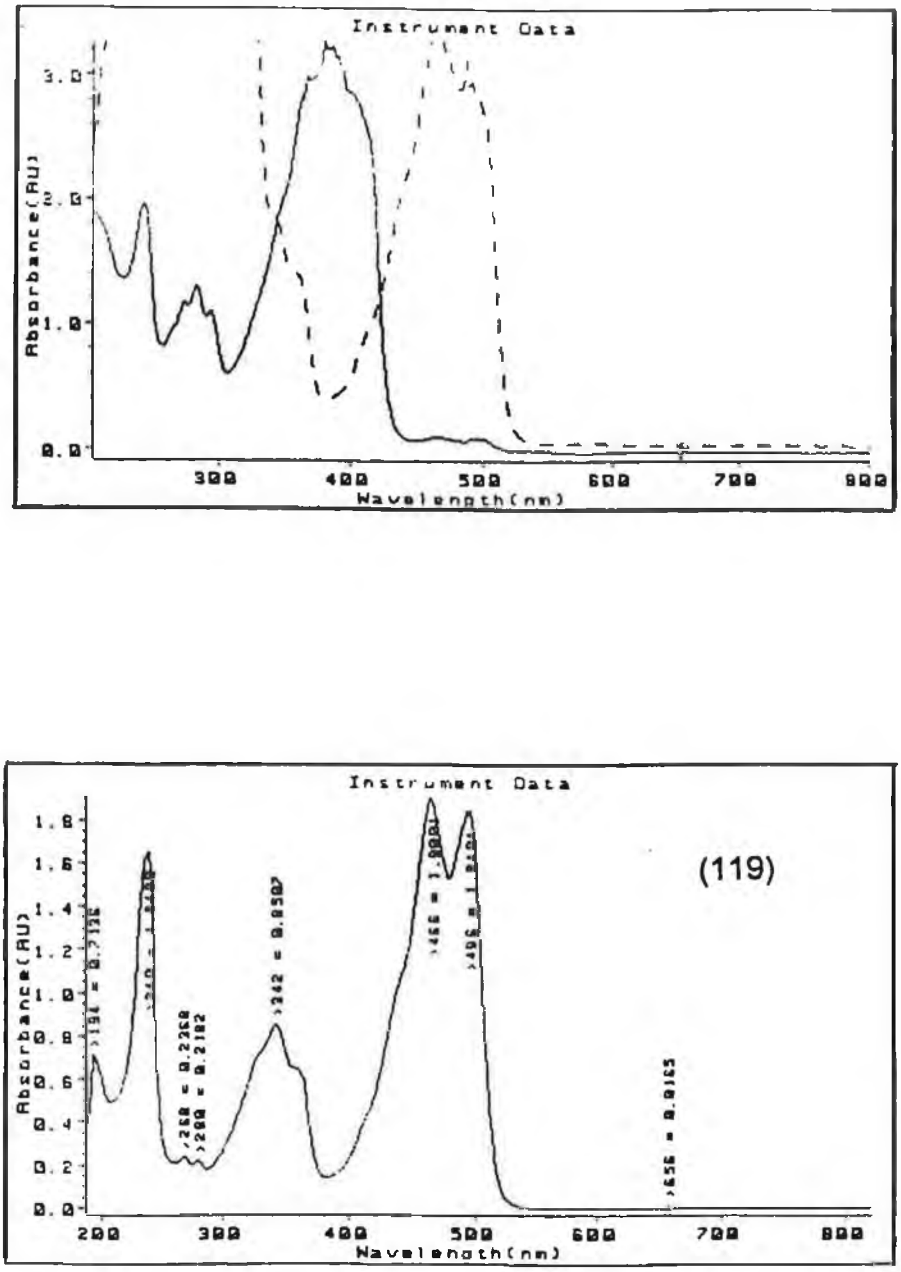


Figure 4.08 UV/visible spectra of Dimethylammonium salt of (110) and the ammonium salt (119)

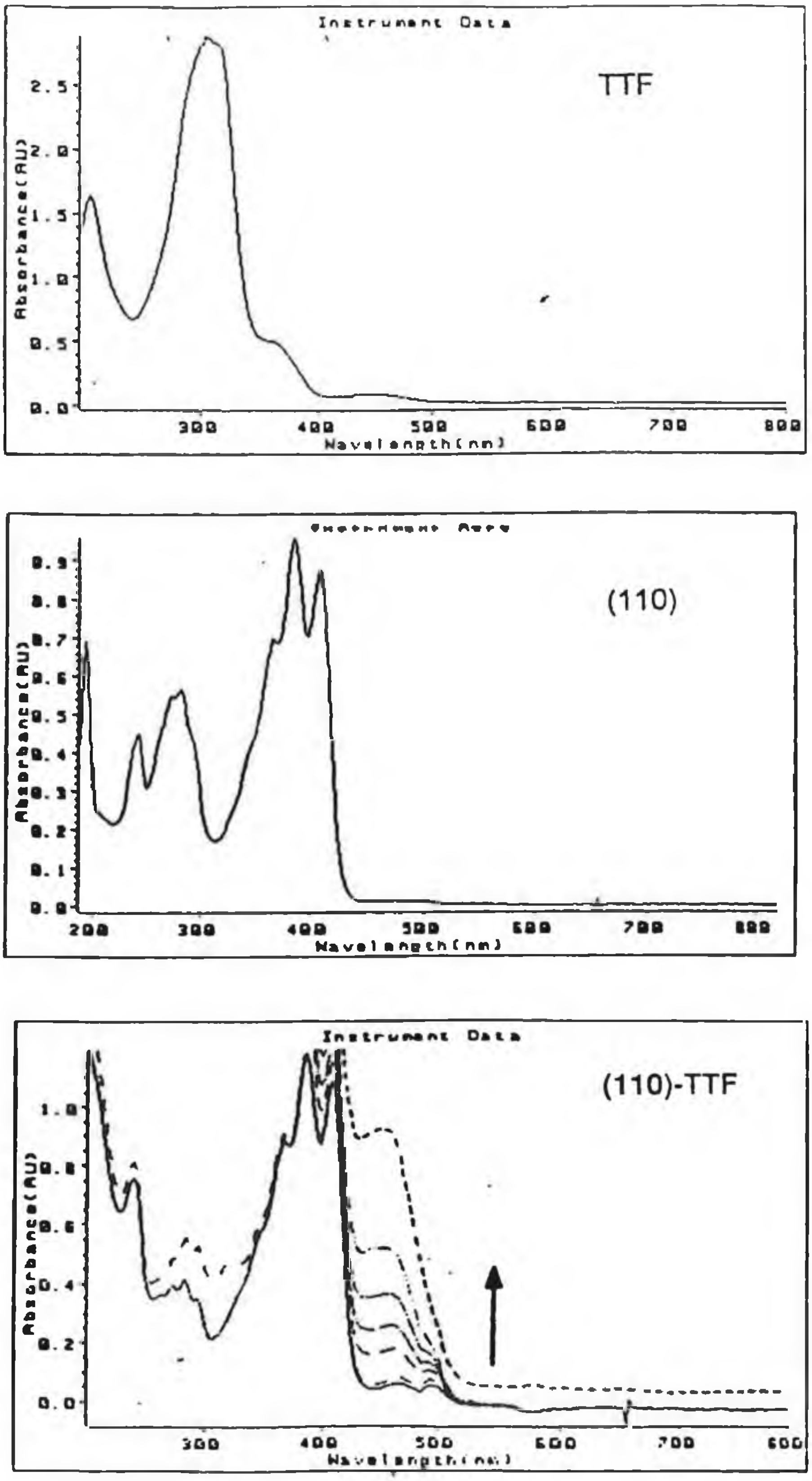


Figure 4.09 UV/visible spectra of TTF (2a), (110) and the Charge-Transfer complex (110)-TTF.

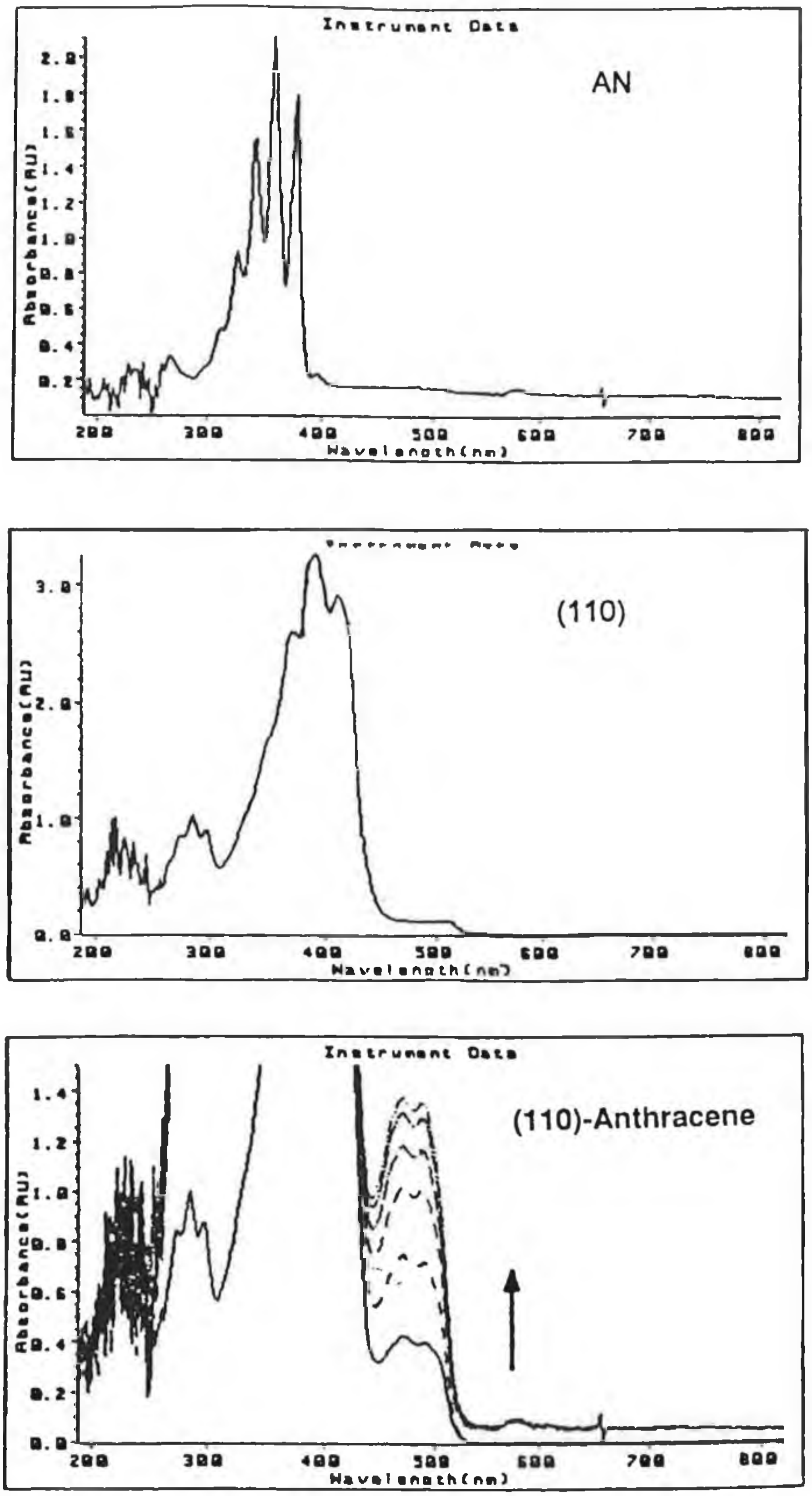


Figure 4.10 UV/visible spectra of AN (212), (110) and the Charge-Transfer complex (110)-AN.

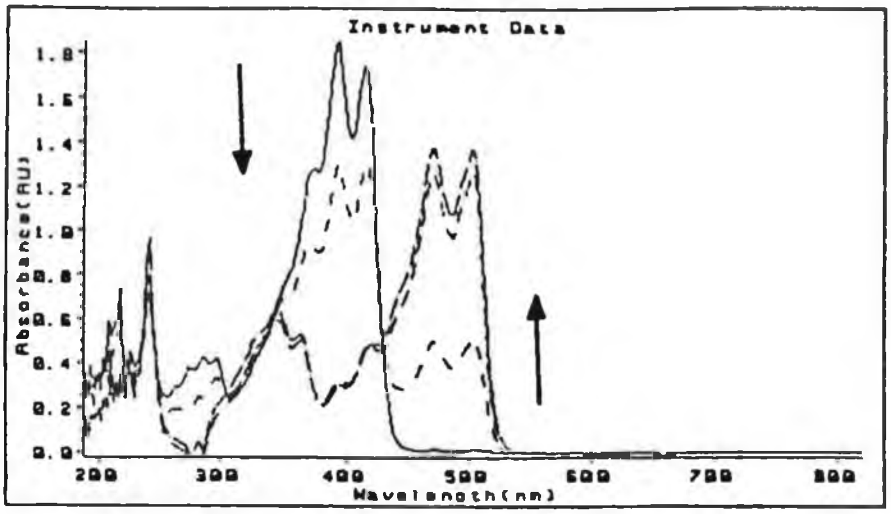


Figure 4.11 UV/visible spectrum of (110) showing the formation of bands due to the anion on drop-wise addition of water to (110)

Mixing equimolar THF solutions of (110) and AN gave a resulting dark orange/red coloured solution which was in strong contrast with the pale yellow solution of (110) and the colourless solution of AN. On concentration of the solution and storing under argon, the resulting claret coloured solution yielded large black/metallic purple needles of the C-T complex. It was found that on filtering in air these needles were unstable, readily changing from purple to yellow. On filtering under argon the complex remained stable and this suggested that the C-T complex formed was susceptible to gradual oxidation from atmospheric oxygen.

Charge-Transfer Complexes of (151) with various donors.

The C-T complex forming ability of (151) was also investigated in a similar manner. Figure 4.12 shows the effects of adding increasing amounts of TMDA to a solution of (151) in acetonitrile. The UV/visible absorption spectrum shows the formation of a C-T band which tails out to 700 nm. This band can be attributed to the formation of a C-T complex between (151) and TMDA. By combining two concentrated solutions of (151) and TMDA in tetrahydrofuran a dark green solution was obtained. The tetrahydrofuran was removed and the green solid obtained was recrystallised from acetonitrile giving a 2:1 complex of

(151)-TMDA based on its elemental analysis. A shift in the cyano peak in the IR spectrum was also observed for the complex, with the cyano stretching band occurring at 2221 cm^{-1} compared with 2224 cm^{-1} for the neutral acceptor. While these results showed that (151) was capable of forming a C-T complex, the small bathochromic shift to longer wavelengths suggested that the degree of transfer was not as great as for the corresponding complex of (110), in which there was a shift of 29 cm^{-1}. This suggests that (151) is not as strong an acceptor as (110). Unfortunately attempts to obtain crystals of sufficient quality for X-ray crystallography were not successful.

It was hoped that a C-T complex with DMA might be obtained for (151) as it did not have the same complication of an acidic NH as (110). However the addition of increasing quantities of DMA to a solution of (151) in acetonitrile showed no formation of a C-T band (Figure 4.13). The combination of (151) and DMA in equimolar quantities in THF showed no colour change for the resulting solution and it was concluded that no C-T had taken place.

When the more strongly electron-donating compound, TTF, was added to a solution of (151) in acetonitrile the formation of a C-T band was observed with λ_{max} = 452 nm and this was attributed to the formation of a C-T complex between (151) and TTF (Figure 4.14). Dark green plates of the complex of (151)-TTF were obtained from the dark green solution which formed when two concentrated solutions of (151) and TTF were mixed. The ratio of the components in the complex was determined by elemental analysis as 1:1. A shift in the cyano stretching frequency peak in the IR spectrum was also observed, with the cyano peak occurring at 2213 cm^{-1} compared with 2224 cm^{-1} observed for the neutral acceptor, suggesting that the degree of C-T from TTF to (151) is slightly greater than for TMDA.

The ability of (151) to form a C-T complex with the weak donor, anthracene, was also investigated. The UV/visible spectrum recorded after the addition of AN to a solution of (151) (Figure 4.15) showed that the weaker donor was not capable of forming a C-T complex with (151) and no complex was formed on mixing equimolar solutions of the donor and acceptor together.

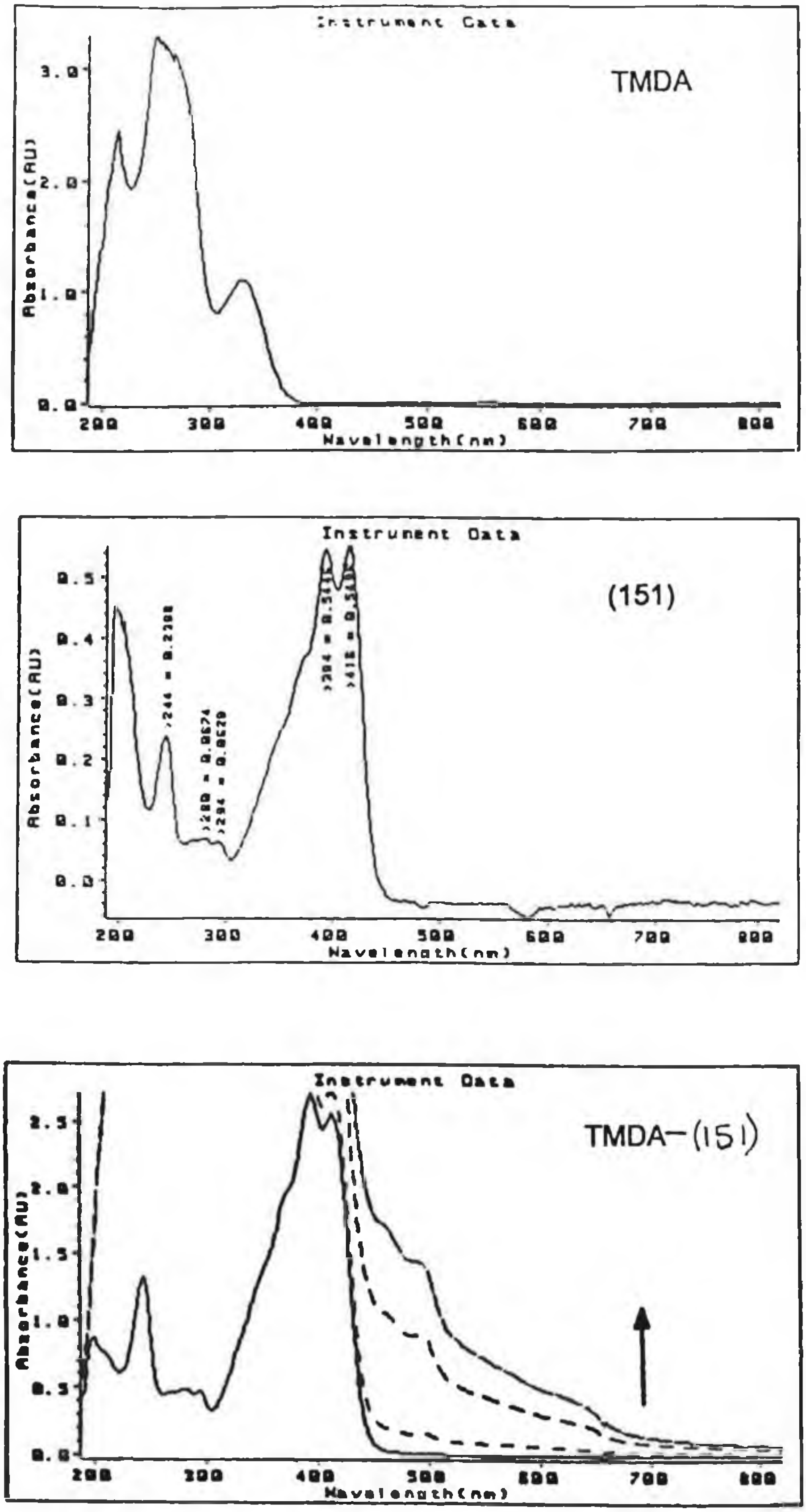


Figure 4.12 UV/visible spectra of TMDA, (151) and the Charge-Transfer complex (151)-TMDA.

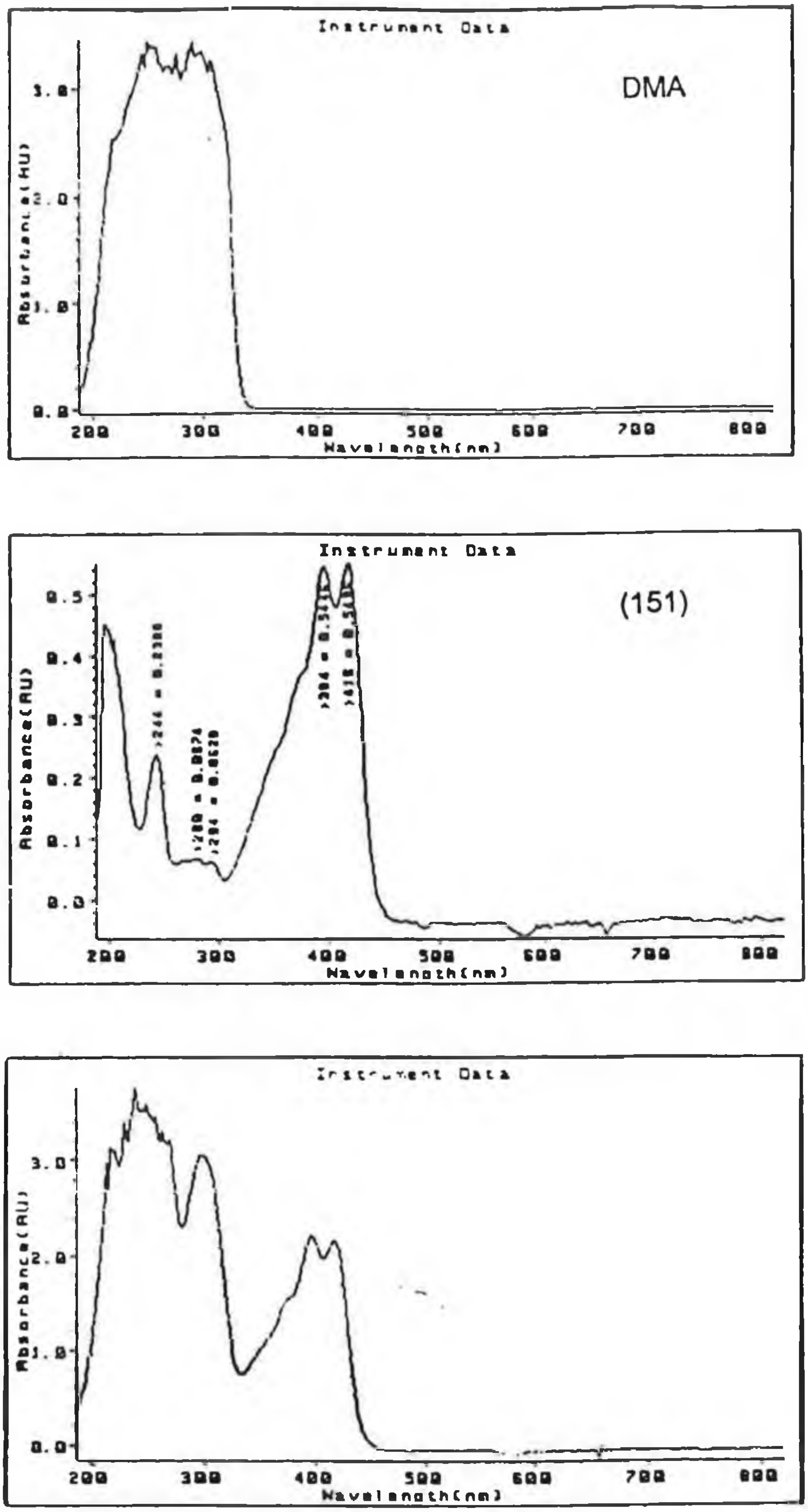


Figure 4.13 UV/visible spectra of DMA, (151) and the DMA/(151) mixture.

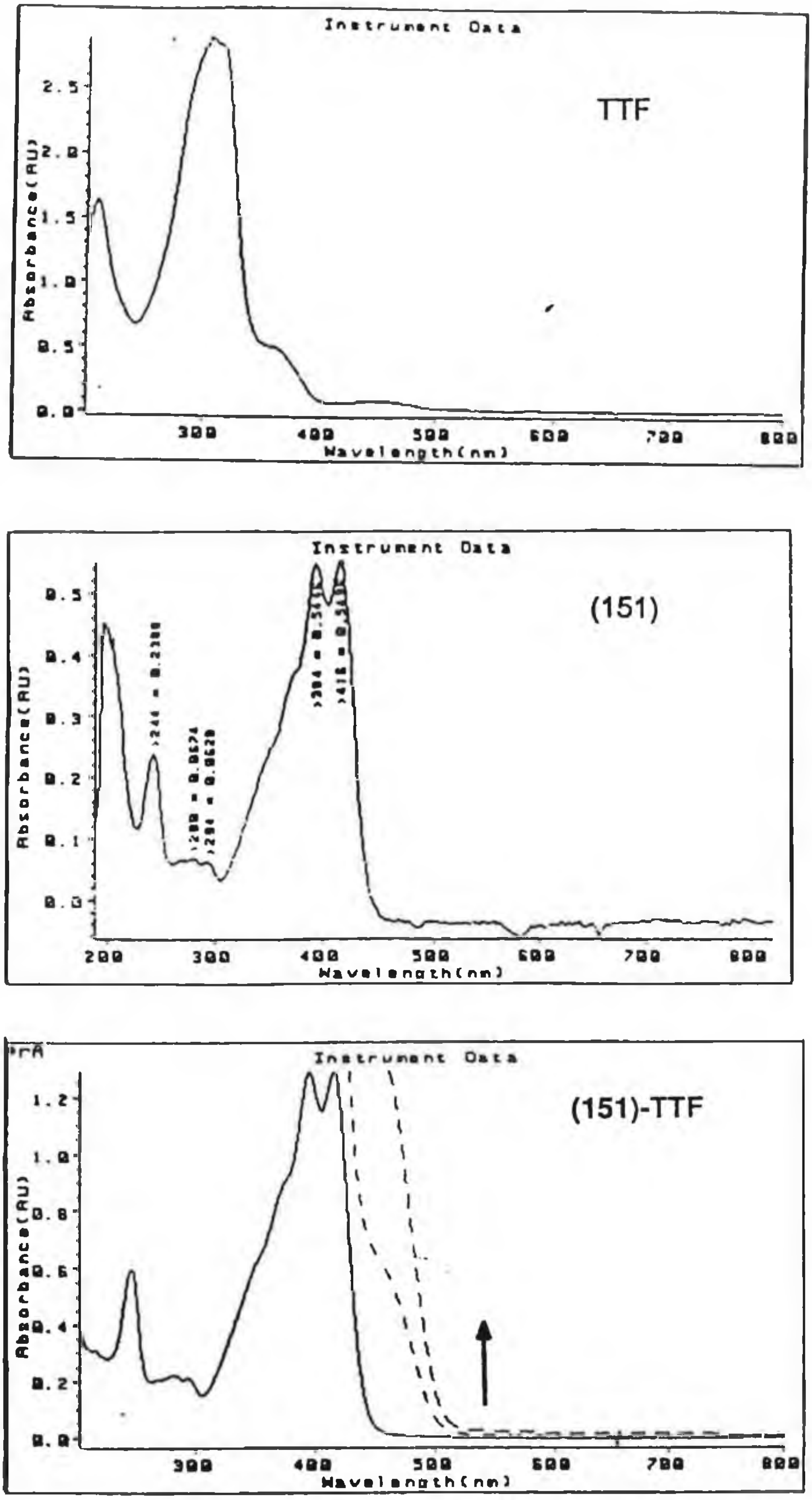


Figure 4.14 UV/visible spectra of TTF, (151) and the Charge-Transfer complex (151)-TTF.

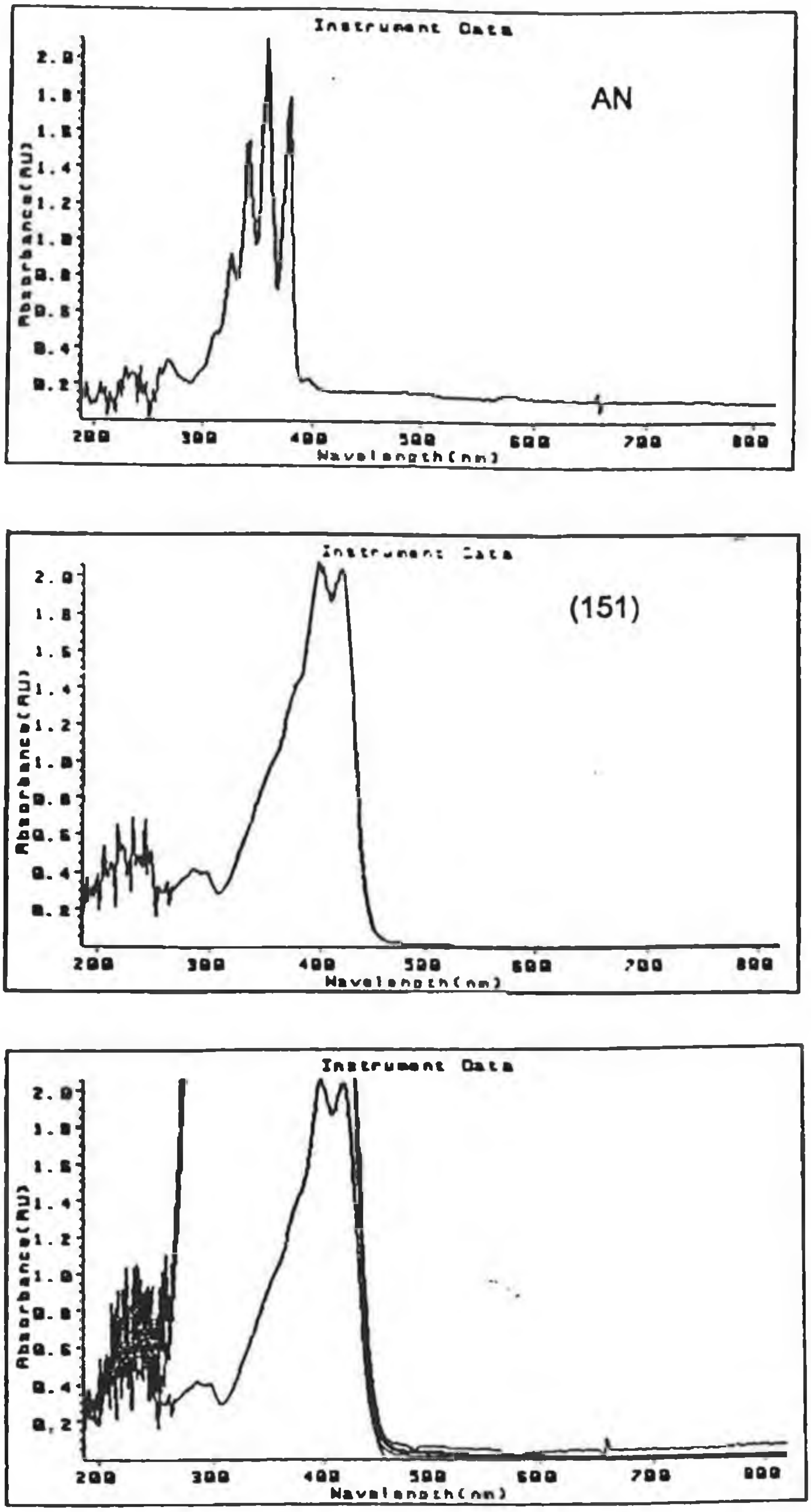
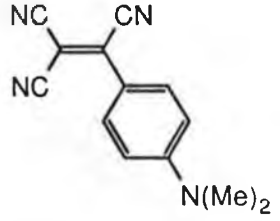


Figure 4.15 UV/visible spectra of AN, (151) and the AN/(151) mixture.

4.5 Discussion

It is clear from the UV/visible spectral data, and from the complexes isolated, that both (110) and (151) are capable of forming C-T complexes with a variety of donors. These results are summarised in Table 4.1. It is apparent from this data that while it was difficult to determine the electron accepting ability of (110) and (151) by electrochemical methods, it appears that (110) is a better acceptor than its *N*-methyl analogue. This is suggested from the greater shift in the nitrile stretching frequencies for the cyano groups in (110)-TMDA compared with those for (151)-TMDA and (151)-TTF and from the ability of (110) to form a C-T complex with a weak donor such as anthracene. This is not too surprising in that the methyl group may reduce the electron affinity of (151), and in addition it may also reduce the degree of intermolecular interaction which in turn influences the degree of overlap required for strong C-T interaction. However, since no X-ray crystal structure was obtained for any of the complexes of (151) and since the cyclic voltammetry studies of the previous chapter were inconclusive, this remains to be verified.

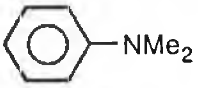
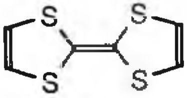
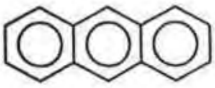
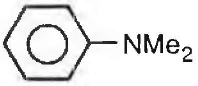
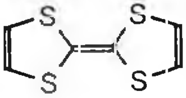
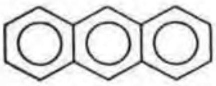
The parallel, face-to-face close crystal packing of the essentially planar TMDA and (110) molecules in mixed stacks confirmed that (110) was capable of forming a C-T complex. Such mixed stacking systems have been found to be poor electrical conductors.[192] The mixed-stacking arrangement of the donors and the acceptors and the greater interplanar spacings also show, by comparison of (110)-TMDA with the 1:1 and 2:1 complexes of TCNQ with TMDA, that (110) is not as strong an acceptor as TCNQ.



(217)

Why DMA should form a salt with (110) and TMDA should form a complex is difficult to explain, especially when TMDA is a stronger base than DMA. It is known that some electron donor-acceptor systems not only immediately form C-T complexes but these can more slowly form new species by irreversible chemical reaction.[188] One such example is the formation of *N,N*-dimethyl-4-tricyanoaniline (217), formed by the reaction of *N,N*-dimethylaniline with tetracyanoethylene. This reaction[193] was studied

Table 4.1 Charge-Transfer complexes of (110) and (151) with various donors

Acceptor	Donor	C-T Complex	mp, °C	C-T λ_{max} (solvent)/nm
(110)		black/dark green needles	154-155	624 (dichloromethane)
(110)		none- forms a salt		
(110)		green powder	-	450 (CH_3CN)
(110)		violet needles	unstable	450-520 (THF)
(151)		green needles	198	465 (CH_3CN)
(151)		none		
(151)		green plates	190 (d)	452 (CH_3CN)
(151)		none		

spectrophotometrically by UV/visible spectroscopy and was found to occur via a 1:1 π-complex between the reactants. The UV/visible spectral studies of (110) and DMA do not show any C-T band and thus it appears that the dimethylanilinium salt of (110) is formed immediately. One potential explanation for the salt formation is that, if DMA did form a C-T complex it may not be as stable as that formed by TMDA since the cation radical formed by DMA would have a less delocalised charge. As stated in the introduction, the absorption bands of weak C-T complexes are difficult to observe since their concentrations are less than those of the donor and the acceptor and thus this may explain why no C-T is observed.[185] As a result there may be a greater gain in stability if DMA reacts with (110) and forms the ionic salt.

4.6 Conclusions

At the outset of this work our goal was to synthesise (110) and some *N*-substituted derivatives and to investigate their ability to form C-T complexes. While we have found difficulty in synthesising a range of *N*-substituted derivatives of (110) we have been able to determine that (110) and its *N*-methyl derivative (151) can form C-T complexes. While the electrochemical studies did not give conclusive results and consequently did not allow for an accurate comparison of the electron affinity of (110) and (151) with benzo-TCNQ and TCNQ it did suggest that these new acceptors would form complexes with strong donors. This indeed has been found to be the case. However, while we have concluded that under the conditions of the electrochemical studies it was most likely the anion of (110) which was being reduced, the ability of the neutral compound to form C-T complexes was unsure. It can be seen from the C-T studies that (110) is capable of forming C-T complexes, even with the weak donor anthracene and in addition can form a stronger complex than (151) with TMDA. Single crystal conductivity measurements have yet to be carried out on the 1:1 complex of (110)-TMDA but since the complex is made up of mixed stacks and such stacking arrangements are poorly conducting, it would be predicted that at best this complex would be semiconducting.

Chapter 5

EXPERIMENTAL

Introductory Remarks

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AC 400 instrument operating at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR. All spectra were recorded using deuterated dimethylsulphoxide (DMSO-d_6) as solvent unless otherwise stated (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet, brm = broad multiplet, and brs = broad singlet). Chemical shifts are given in parts per million (ppm) and coupling constants (*J*) are given in Hertz (Hz).

Infra-red (IR) spectra were recorded on a Perkin-Elmer 983G IR spectrophotometer or a Nicolet 205 FT-IR for KBr pellets unless otherwise stated.

Ultraviolet (UV) spectra were recorded on a Hewlett-Packard 8452A diode array UV-Vis spectrophotometer. The units for ε are $dm^3mol^{-1}cm^{-1}$. Spectrograde dimethylformamide (DMF) was used as the solvent unless otherwise stated.

Melting point determinations were recorded using a Griffin melting point apparatus and are uncorrected. Elemental analyses were carried out by the Microanalytical Laboratory at University College Dublin.

Thin layer chromotography (TLC) was carried out using silica gel TLC plates containing a fluorescent indicator (Riedel de Haen, δ_C cards SiF, layer thickness 0.2mm).

Mass Spectra were recorded on a VG12 250 Mass spectrometer

Attempted Knoevenagel Reactions of Malononitrile with *N*-Methylphthalimide

Using sodium as the base and toluene as solvent

Malononitrile (0.33 g, 0.0049 moles) was added to sodium (0.11 g, 0.0049 moles) in dry toluene and left stirring on a boiling water-bath for 1.5 hours and then stirred overnight at room temperature giving a creamy-white suspension. *N*-Methylphthalimide (117) (0.50 g, 0.0031 moles) was added and the reaction mixture heated under reflux. After three hours a yellow "gum" formed on the sides of the reaction flask. Heating at reflux was continued for a further 4 hours. The reaction mixture was added to water, acidified and extracted with ethyl acetate and the combined extracts dried over magnesium sulphate. This gave a green/brown solid (0.6 g) on evaporating the ethyl acetate. TLC of this solid showed it to be a complex mixture of products and *N*-methylphthalimide.

One product was isolated by dissolving the impure solid in tetrahydrofuran. On adding light petroleum a solid precipitated which formed a brown oil on standing. The oil and the yellow supernatant were separated. TLC showed the oil to be a complex mixture of products and the supernatant showed one major and two minor products. The solvent was removed from the supernatant to give a solid. This solid was purified by adding it to hot toluene, in which it was mainly insoluble and filtering hot. TLC showed this removed the minor impurities. The insoluble solid was then recrystallised from water to give 2-amino-1-propene-1,1,3-tricarbonitrile (0.043 g); mp 170-171 °C (lit.,[194] 171-173 °C); ν_{max}: 3345, 3233, 3205, 2920, 2265, 2223, 2205, 1657, 1554, 1447, 1383 and 909 cm^{-1}; δ_H (acetone-d$_6$): 7.12 (brs, 2H, NH) and 3.70 ppm (s, 2H, CH); δ_C (acetone-d$_6$): 23.25 (CH_2), 54.13 ($=\underline{C}(CN)_2$), 114.17, 114.61, 115.23 (CN) and 118.38 ppm ($=\underline{C}NH_2$). IR and NMR spectra were in good agreement with those found in the literature.[144]

Using sodium hydride as the base and dry tetrahydrofuran as solvent

Dry light petroleum (40-60)(10 cm^3) was added to sodium hydride (60% suspension in oil; 0.99 g, 0.025 moles), the suspension swirled and the solvent/oil solution removed with a Pasteur pipette once the mixture had settled. A solution of *N*-methylphthalimide (2.00 g, 0.012 moles) in dry tetrahydrofuran (60 cm^3) was added. Malononitrile (1.64 g, 0.025 moles) in dry tetrahydrofuran (50 cm^3) was added dropwise to the *N*-methylphthalimide/sodium hydride suspension. The reaction mixture was stirred for 15 hours. An orange oil was obtained on evaporating off the tetrahydrofuran. Trituration of the oil with ethyl acetate, followed by filtration, gave the sodium salt of *o*-(2,2-dicyanoethenyl-1-olate-)-*N*-methylbenzamide (125) as an off-white solid (3.10 g); mp 230-234 °C.; ν_{max}: 3399, 3075, 2989, 2947, 2221, 2199, 2189, 2164, 2158, 1656, 1628, 1596, 1441, 1412, 1369, 1312, 1162, 984, 951, 919, 841, 773, 743, 696 and 621 cm^{-1}; δ_H: 8.08 (brm, 1H, NH), 7.60-7.27 (m, 4H, aromatic H), 2.69 ppm (d, *J* 4.9, 3H, NHC$\underline{H}_3$); δ_C: 26.2 (methyl amino C), 48.8 (=$\underline{C}$(CN)$_2$), 120.9 and 122.0 (CN), 127.4, 127.8, 128.2, 129.0, 135.1 and 141.4 (aromatic C), 168.4 ($\underline{C}$=C(CN)$_2$) and 189.4 ppm (carboxamide C). The salt could not be recrystallised due to its insolubility in nearly all organic solvents tried and its ready solubility in water. It was found to be soluble in boiling ethanol and methanol but the resulting solution showed additional products by TLC.

On dissolving the salt in water (150 cm^3) and acidifying with 10% v/v hydrochloric acid an off-white solid precipitated from solution. This was filtered giving a grey solid (0.22 g) and this was recrystallised from ethanol to give the methylammonium salt of *o*-(2,2-dicyanoethenyl-1-olate-)-*N*-methylbenzamide (126) as grey crystals (0.09 g), mp 163-164 °C ; ν_{max}: 3309, 3129, 2991, 2871, 2757, 2207, 2193, 2165, 1709, 1632, 1596, 1492, 1406, 1360, 1331, 1266, 1169, 963, 919, 842, 782, 751, 728 and 702 cm^{-1}; δ_H: 8.06 (m, 1H, NH), 7.55-7.27 (m with broad shoulder, 7H, NH$_3$ and aromatic H), 2.68 (d, *J* 4.9, 3H, NHC$\underline{H}_3$) and 2.34 ppm (s, 3H, Me); δ_H (methanol-d$_4$): 7.56-7.45 (m, 4H, aromatic H), 2.88 (s, 3H, NHC$\underline{H}_3$) and 2.52 ppm (s, 3H, methylammonium H); δ_C (methanol-d$_4$): 25.4 (methyl ammonium C), 26.9 (methyl amino C), 52.6 (=$\underline{C}$(CN)$_2$), 120.6 and 122.2 (CN), 128.8, 129.1, 130.2, 131.0, 135.9 and 141.0 (aromatic C), 171.7 ($\underline{C}$=C(CN)$_2$) and 193.7 ppm (carboxamide C). (Found: C, 60.31; H, 4.95; N, 21.75% $C_{13}H_{14}N_4O_2$ requires: C, 60.45; H, 5.46; N, 21.69%).

The aqueous filtrate remaining on filtering off the methylammonium salt was extracted with ethyl acetate and the extract dried over magnesium sulphate. Evaporation of the ethyl acetate gave a red oil. TLC of the oil showed it to be a complex mixture of products. Attempts were made to isolate these products by column chromatography but without success.

The ethyl acetate filtrate remaining from the trituration of the sodium salt was evaporated off giving an oil. A small quantity of a white crystalline solid was isolated on heating the oil in ethanol. This was identified as *N*-methylphthalimide (TLC, IR and mp).

Using sodium hydride as base, tetrahydrofuran as solvent and heating under reflux

Dry light petroleum (40-60) (10 cm^3) was added to sodium hydride (60% suspension in oil; 0.99 g, 0.025 moles), the suspension swirled and the solvent/oil solution removed with a Pasteur pipette once the mixture had settled. A solution of *N*-methylphthalimide (2.00 g, 0.012 moles) in dry tetrahydrofuran (70 cm^3) was added. Malononitrile (1.64 g, 0.025 moles) in dry tetrahydrofuran (50 cm^3) was added dropwise to the *N*-methylphthalimide/sodium hydride suspension. The reaction mixture was heated under reflux for three hours. A white solid (1.07 g) precipitated on cooling and was filtered off. This was found to be identical to the sodium salt (125) (TLC, IR, ^1H NMR). On acidification with 10% dilute hydrochloric acid an off-white solid precipitated. This was identified as the methylammonium salt (126) (IR, melting point and NMR).

A red oil was obtained from the tetrahydrofuran filtrate remaining after filtering off the white solid, by evaporating off the tetrahydrofuran. This oil was dissolved in ethyl acetate and on acidification with 10% dilute hydrochloric acid (40 cm^3), a white solid precipitated. On trying to recrystallise this solid (0.92 g) from ethyl acetate an insoluble solid was isolated on filtering hot. This was found to be the methylammonium salt of *o*-(2,2-dicyanoethenyl-1-olate-)-*N*-methylbenzamide (126) as grey crystals (0.29 g) (TLC, IR, ^1H and ^{13}C NMR, mp).

On evaporating the ethyl acetate filtrate which was remaining after filtering off the methylammonium *o*-(2,2-dicyanoethenyl-1-olate-)-*N*-methylbenzamide salt (126) hot, an orange crystalline solid (0.124 g) was obtained. This was recrystallised twice from toluene to give 3-(dicyanomethylidene)phthalide (127) as a white solid (0.043 g); mp 155 °C(lit.,[142] 157.5 °C); ν_{max}: 2238, 1835, 1617, 1590, 1472, 1380, 1308, 1279, 1215, 1181, 1145, 1099, 1022, 972, 877, 792, 781, 788 and 701 cm^{-1}; δ_H (acetone-d_6): 8.44 (d, 1H, aromatic), 8.24 (d, 1H, aromatic), 8.18 (m, 1H, aromatic) and 8.11ppm (m,1H, aromatic); δ_C (acetone- d_6): 65.15 ($=\underline{C}(CN)_2$), 110.4 and 111.9(CN), 125.9. 126.3, 127.8, 134.9, 136.5 and 137.4 (aromatic C), 162.4 ($\underline{C}=C(CN)_2$) and 170 4 ppm (C=O). This structural assignment was made on comparing these IR, ^{1}H and ^{13}C NMR spectra and mp values with those of the known compound.[142]

Using pyridine as base, dichloromethane as solvent and titanium tetrachloride

Titanium tetrachloride (2.94 g; 50% solution, 0.0078 moles) was added to a solution of *N*-methylphthalimide (0.50 g, 0.0031 moles) in dry dichloromethane (40 cm^3) and stirred at 20 °C for 30 minutes under argon. Dry pyridine (1.23 g, 0.0155 moles) and malononitrile (1.52 g, 0.0078 moles) in dichloromethane (10 cm^3) was added dropwise. The pale yellow solution was left stirring for 11 hours. The solution was added to water (100 cm^3), extracted with ethyl acetate and dried over magnesium sulphate, giving a pale yellow solid (0.57 g) on evaporating off the solvent. This was recrystallised from ethanol to give *N*-methylphthalimide as a white solid (IR and melting point).

Using pyridine as base and solvent and titanium tetrachloride

Titanium tetrachloride (5.80 g; 50% solution, 0.0155 moles) was added to a solution of *N*-methylphthalimide (1.00 g, 0.0062 moles) in dry pyridine (30 cm^3) under nitrogen. Malononitrile (1.16 g, 0.176 moles) in pyridine (20 cm^3) was added to the warmed suspension and heated under reflux for 14 hours. The dark red solution was filtered hot to remove a small quantity of white solid and the filtrate concentrated to a fifth of its volume, yielding a crystalline solid on cooling. This crystalline solid was found to be highly hygroscopic on filtering and passed through the filter paper into the filtrate. On adding water to the filtrate, an off-white solid precipitated which was filtered off and washed with dilute hydrochloric acid (10%) and water. On recrystallising from ethanol, the off-white crystalline solid (0.62 g) was found to be *N*-methylphthalimide (IR, melting point and TLC).

Synthesis of 1,3-Diiminoisoindoline (118a)

Dry light petroleum (40-60)(10 cm^3) was added to sodium hydride (80% dispersion in oil ; 0.54 g, 0.025 moles), the suspension swirled and the solvent/oil solution removed with a Pasteur pipette once the mixture had settled. Methanol (10 cm^3) was added gradually with care and the resulting sodium methoxide suspension added to a solution of phthalonitrile (5.00 g, 0.03 moles) in methanol (110 cm^3). Ammonia was then bubbled through the stirred solution for one hour. The reaction mixture was heated under reflux for 3 hours with continued bubbling of ammonia through the solution. The hot solution was filtered to remove a very small amount of grey solid. The solvent was removed by rotary evaporation giving a green viscous oil which yielded a yellow solid on scratching with a glass rod. Recrystallisation from methanol/ diethyl ether (70:30) using decolourising charcoal yielded bright yellow crystals of 1,3-diiminoisoindoline (118a) (2.17 g, 49%), m.p.(methanol) 195-196 °C (lit.,[148] 196 °C); ν_{max}: 3281, 3255, 2984 (broad, C=$\underline{\text{NH}}$), 1693, 1530, 1468, 1312, 1276, 1177, 1158, 1136, 1081, 1015, 950, 891, 776, 745, 708 and 695 cm^{-1}; λ_{max} (CH_3OH): 344 (ε= 1 893, br sh), 316 (3 595), 260 (16 113) and 232 (16 796); δ_H: 8.8 (brs, 2H, NH), 7.85 (m, 2H, aromatic), 7.55 (m, 2H, aromatic), and 3.85 ppm (brs, 1H, NH); δ_C (methanol-d_4): 119.98 and 129.94 (aromatic C), 134.36 (quaternary aromatic C) and 169.75 ppm ($\underline{\text{C}}$=NH).

Synthesis of 3-Phenylimino-1-iminoisoindoline (118b)

Dry light petroleum (40-60)(10 cm^3) was added to sodium hydride (80% dispersion in oil ; 1.68 g, 0.031 moles), the suspension swirled and the solvent/oil solution removed with a Pasteur pipette once the mixture had settled. Methanol (40 cm^3) was added gradually with care and the resulting sodium methoxide suspension added to a solution of phthalonitrile (20.02 g, 0.156 moles) in methanol (350 cm^3). Aniline (14.57 g, 0.156 moles) was added and the mixture was heated under reflux for two and a half hours and then filtered hot to remove a very small amount of navy-blue solid (phthalocyanines). Removal of the solvent yielded a crude yellow solid (20.50 g). This was recrystallised twice from ethanol to give 3-phenylimino-1-iminoisoindoline (118b) as a microcrystalline solid (18.5 g, 54 %), m.p. 203 °C (d), (lit.,[156] 203 °C); ν_{max}: 3031, 1692, 1604, 1594, 1530, 1432, 1332, 1290, 1215, 1128, 1100, 999, 908, 780, 743, 720, 697 and 644 cm^{-1}; λ_{max} (CH_3OH): 372 (ε= 4 585), overlapping with 348 (4 713), 314 (4 538) and 232 (12 866); δ_H: 8.72 (brs, 1H, NH), 8.51 (brs, 1H, NH) and 6.99 - 7.94 ppm (m, 9H, aromatic); δ_C: 119.78, 120.78, 121.47, 123.19, 123.71, 128.15, 129.12, 130.11, 130.93, 135.21, 140.56, and 150.39 (aromatic C), 165.10 and 171.58 ppm ($\underline{\text{C}}$=N); m/z 221 ($M^{+\cdot}$ 100%), 205 (15), 194 (21), 129 (22), 102 (23), 93 (33), 77 (67) and 65 (20).

Ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (119)

Method (a): Using 1,3-Diiminoisoindoline (118a)

Malononitrile (9.53 g, 0.144 moles, 20% excess) was added dropwise to a stirring solution of 1,3-diiminoisoindoline (118a) (10.09 g, 0.06 moles) in dimethylformamide (100 cm^3) at room temperature. The colour of the solution changed immediately from a light green/yellow colour to dark red, accompanied by the distinct smell of ammonia. Addition of chloroform caused a red solid to precipitate. Filtration followed by recrystallisation from methanol gave the ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (119), as dark red crystals (12.22 g, 78%). The salt underwent a gradual colour change from red to light brown at 180-200 °C, and decomposed at 348-349 °C; ν_{max}: 3181, 3091, 2211, 1612, 1577, 1501, 1450, 1432, 1307, 1259, 1195, 1164, 1096, 920, 770, 749 and 704 cm^{-1} ; λ_{max} (CH_3CN): 496 (ε= 25 905), 466 (27 120), 360 (9 612), 344 (12 259) and 240 nm (9 331) ; δ_H (pyridine-d_5): 9.29 (brs, 4H, NH), 8.35 (m, 2H, aromatic), and 7.3 ppm (m, 2H, aromatic); δ_H: 8.05 (m, 2H, aromatic), 7.58 (m, 2H, aromatic) and 7.07 ppm (1:1:1 t, *J* 50, 4H, NH); δ_C: 54.63 ($C{=}\underline{C}(CN)_2$), 116.27 and 117.14 (CN), 123.25 and 131.04 (aromatic C), 138.0 (quaternary aromatic C), 172.02 ppm ($\underline{C}{=}C(CN)_2$). (Found: C, 64.53; H, 3.04; N, 32.4%. $C_{14}H_8N_6$ requires: C, 64.61; H, 3.07; N, 32.3%).

Method (b): Using 3-Phenylimino-1-iminoisoindoline (118b)

Malononitrile (9.42 g, 0.143 moles, 10% excess) was added dropwise to a stirring solution of 3-phenylimino-1-iminoisoindoline (118b) (15.00 g, 0.068 moles) in dimethylformamide (130 cm^3) at room temperature. The colour of the solution changed immediately from a yellow colour to dark red, accompanied by the distinct smell of ammonia. Addition of chloroform caused a red solid to precipitate. Filtration followed by recrystallisation from methanol gave the ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (119) as dark red crystals (15.63 g, 89%). This gave identical mp, IR, and NMR spectra as method (a).

2,2'-(Isoindolin-1,3-diylidene)bispropanedinitrile (110)
Method (a): Pyrolysis of (119)

The ammonium salt (119) (1.00 g, 0.0385 moles) was placed in a 250 cm^3 round-bottomed flask and heated at *ca* 180-200 °C on a sandbath under a nitrogen atmosphere for 5 hours. During this time the compound changed from a dark red to a dull orange/brown solid (0.70 g, 75%). Recrystallisation from dimethylformamide/ethanol 20:80 gave shiny orange needles of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (110), m.p. 349-350 °C (d.) (lit.,[151] 350 °C) ; ν_{max}: 3243, 3189, 2818, 3004, 2240, 2227, 1865, 1701, 1685, 1664, 1612, 1470, 1449, 1414, 1398, 1321, 1244, 1207, 1170, 1158, 1102, 1014, 916, 793, 752, 691 and 652 cm^{-1}; λ_{max} (CH_3CN): 408 (ε= 65 884), 386 (71 823), 366 sh (56 400), 282 (42 838), 274 (41 846), 242 (35 223) and 194 nm (53 261) ; δ_H: 8.19 and 7.79 (m, 4H, aromatic) ,and 4.85 ppm (brs, 1H, NH) ; δ_C: 56.54 ($=\underline{C}(CN)_2$), 114.65 and 115.66 (CN), 132.83 and 123.84 (aromatic carbons), 134.9 (aromatic C) and 166.27 ppm ($\underline{C}=C(CN)_2$); m/z 243 (M^+, 100%), 216 (9), 189 (18), 153 (9), 129 (8), 99 (13), 73 (18), 55 (19), 39 (39) and 28 (94). (Found: C, 69.24; H, 2.16; N, 29.1%. $C_{14}H_5N_5$ requires: C, 69.13; H, 2.08; N, 29.1%).

Method (b): Acidification of (119)

To a solution of (119) (3.27 g, 0.0125 moles) in methanol (70 cm^3) was added 1%^{v}/v HCl (100 cm^3) causing a fine yellow solid to precipitate. This was filtered and the solid washed several times with water and dried to give 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (110) (2.27 g, 76%). This gave the same IR, UV, NMR spectral data as before and the same melting point. It could be used in this state or recrystallised from dimethylformamide/methanol 20:80.

2-(3-Iminoisoindolin-1-diylidene)bispropanedinitrile (143)

Dry light petroleum (40-60)(10 cm^3) was added to sodium hydride (80% dispersion in oil ; 1.96 g, 0.06 moles), the suspension swirled and the solvent/oil solution removed with a Pasteur pipette once the mixture had settled. Methanol (15 cm^3) was added gradually with care and the resulting sodium methoxide suspension added to a solution of phthalonitrile (144) (3.05 g, 0.02 moles) in methanol (60 cm^3). Malononitrile (1.98 g, 0.03 moles) was then added, the pale yellow coloured solution changed to a ruby red colour. The reaction mixture was stirred at 30 °C for three hours during which a powdery yellow solid precipitated. The solid was filtered off under vacuum and recrystallised three times from acetic acid to yield 2-(3-imino-isoindolin-1-diylidene)bispropanedinitrile (143) (2.70 g, 58%), mp 210 °C (d) ; ν_{max}: 3401, 2990 (broad, C=$\underline{NH}$), 2222, 1688, 1610, 1591, 1519, 1469, 1309, 1262, 1205, 774, and 704 cm^{-1}; δ_H: 9.95 (brs, 1H, C=N$\underline{H}$)), 8.05 (m, 2H, aromatic), 7.7 (m, 2H, aromatic), and 3.37 ppm (brs, 1H, N-H); δ_C: 59.14 (=$\underline{C}$(CN)$_2$), 114.84 and 115.63 (CN), 122.91, 123.22, 131.90, 132, 137 and 171.9 ppm (aromatic C), 134.18 ($\underline{C}$=NH), 175.81 ppm ($\underline{C}$=C(CN)$_2$). (Found: C, 67.84; H, 3.11; N, 28.87%. $C_{11}H_6N_4$ requires: C, 68.03; H, 3.11; N, 28.85%).

Sodium salt of 2,2'-(Isoindolin-1,3-diylidene)propanedinitrile (146)

Dry light petroleum (40-60)(10 cm^3) was added to sodium hydride (80% dispersion in oil ; 0.026 g, 0.0009 moles), the suspension swirled and the solvent/oil solution removed with a Pasteur pipette once the mixture had settled. Methanol (4 cm^3) was added gradually with care and the resulting sodium methoxide suspension was added to a suspension of 2-(3-imino-isoindolin-1-diylidene)bispropanedinitrile (143) (0.015 g, 0.0007 moles) in methanol (20 cm^3). Malononitrile (0.081 g, 0.0012 moles, 58% excess) was added and the suspension heated under reflux for one and a half hours. The orange solution was then evaporated to dryness to give an orange solid. On recrystallising from ethyl acetate 2-(3-imino-isoindolin-1-diylidene)bispropanedinitrile (143) (0.04 g) was isolated (verified by IR and melting point) by filtering the ethyl acetate suspension hot. The sodium salt of 2,2'-(Isoindolin-1,3-diylidene)bispropanedinitrile (146) was isolated from the filtrate as an orange powder (0.091 g, 44%), mp > 360 °C; ν_{max}: 2218, 1676, 1598, 1583, 1493, 1461, 1386, 1309, 1264, 1196, 1164, 1155, 1096, 920, 771, 751, and 706 cm^{-1}; δ_H (acetone-d$_6$): 8.21 (m, 2H, aromatic) and 7.61 ppm (m, 2H, aromatic); δ_C (acetone-d$_6$): 55.1 (C=$\underline{C}$(CN)$_2$), 116.99 and 118.29 (CN), 122.89, 131.34 and 139.26 (aromatic C), and 173.12 ppm ($\underline{C}$=C(CN)$_2$).

Attempted Benzoylation of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (110)

Method (a): Using benzoyl chloride and aqueous sodium hydroxide

Benzoyl chloride (2 cm^3, 0.017 moles, 8 equivalents) was added in 0.5 cm^3 portions with continuous shaking to a suspension of (110) (1.00 g, 0.0021 moles) in a 5% aqueous sodium hydroxide solution. Shaking was continued until the benzoyl chloride odour disappeared. Additional sodium hydroxide solution (~3 cm^3) was added to make the suspension alkaline. It was then filtered and the solid washed with cold water. Recrystallisation from ethanol gave a yellow powder (0.36 g, 66%), the sodium salt of (110), mp >350 °C ; ν_{max}: 2227, 2217, 1677, 1598, 1583, 1497, 1463, 1387, 1310, 1265, 1198, 1096, 920, 771, 751 and 706 cm^{-1} ; δ_H: 7.94 (m, 2H, aromatic) and 7.49 ppm (m, 2H, aromatic); δ_C: 53.79 (=$\underline{C}(CN)_2$), 116.13 and 117.09 (CN), 122.72, 131.18 and 137.28 (aromatic C) and 171.88 ppm ($\underline{C}=C(CN)_2$).

Method (b): Using benzoyl chloride and pyridine

Benzoyl chloride (0.59 g, 0.0042 moles) was added dropwise from a dropping funnel to a solution of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (110) (1.0 g, 0.0041 moles) in pyridine on an ice bath and the reaction mixture was left stirring for 2.5 hours. A further 3 cm^3 of benzoyl chloride was added at 0-5 °C and the mixture was stirred overnight in the ice-bath. No new products were observed on following the reaction by TLC using ethyl acetate/light petroleum (80:20) as the mobile phase. The reaction mixture was then heated at 70 °C for 2 hours without any observable change on TLC. On pouring into cold water (100 cm^3) and adding dilute HCl (10% v/v) a yellow precipitate was obtained and filtered off. This did not dissolve in ethanol and the IR and melting point of the dried solid was found to be identical to that of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (110).

Method (c): Reaction of the sodium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (110) with benzoyl chloride

Dry light petroleum (40-60)(10 cm^3) was added to sodium hydride (80% suspension in oil; 0.07 g, 0.0023 moles), the suspension swirled and the solvent/oil solution removed with a Pasteur pipette once the mixture had settled.

A solution of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (1.0 g, 0.0021 moles) in dry tetrahydrofuran (50 cm^3) was added gradually to give the sodium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (146). Benzoyl chloride (0.29 g, 0.0021 moles) was added dropwise to the stirring sodium salt solution and was allowed to stir for 6 hours. No new products were observed on TLC using both ethyl acetate/light petroleum (80:20) and ethanol/ethyl acetate (50:50) as the mobile phase.

This reaction was repeated using a 25% excess of benzoyl chloride followed by heating under reflux for 5.5 hours. Again no change was observed on TLC using the same solvent systems.

Attempted reaction of the Ammonium salt of 2,2'-(Isoindolin-1,3-diylidene)bispropanedinitrile (119) with Formalin

The ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (119) (0.40 g, 0.0015 moles) and formalin (36% solution in water, 0.5 cm^3, 0.05 moles) in water (50 cm^3) were heated under reflux for seven hours. The water was evaporated off and the yellow solid obtained was dried (0.27g). IR and melting point data were identical with those of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (110).

Methylation of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (110)

Attempted methylation using methyliodide

Dry light petroleum (40-60)(10 cm^3) was added to sodium hydride (80% suspension in oil; 0.058 g, 0.00193 moles), the suspension swirled and the solvent/oil solution removed with a Pasteur pipette once the mixture had settled. A solution of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (110) (0.51 g, 0.00196 moles) in dry tetrahydrofuran (100 cm^3) was added gradually to control the evolution of hydrogen. Methyliodide (1.11 g, 0.0078 moles, 300% excess) in dry tetrahydrofuran (30 cm^3) was introduced from a dropping funnel into the reaction mixture. The reaction mixture was stirred for 4 hours and progress followed by TLC using 80:20 ethyl acetate/light petroleum as mobile phase. No new products were apparent. The reaction mixture was poured into iced water and a yellow solid precipitated. This was identified as the sodium salt of 2,2'-

(isoindolin-1,3-diylidene)bispropanedinitrile (146) on the basis of IR and melting point.

Methylation using Dimethyl Sulphate

Dry light petroleum (40-60)(10 cm^3) was added to sodium hydride (80% dispersion in oil, 0.118 g, 0.0039 moles), the suspension swirled and the solvent/oil solution removed with a Pasteur pipette once the mixture had settled. A solution of the ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (119) (1.02 g, 0.0039 moles) in dry tetrahydrofuran (100 cm^3) was then added, followed by dimethyl sulphate (0.51 g, 0.004 moles) and the reaction mixture heated to reflux for 7 hours. The reaction was followed by TLC using 80:20 ethyl acetate/light petroleum as the mobile phase. The formation of one principal fast eluting compound, and a number of more slowly eluting minor products near the base line, was observed. The principal product was isolated by column chromatography using tetrahydrofuran as mobile phase. This yielded a yellow/brown crystalline solid, 2,2'-(2-methylisoindolin-1,3-diylidene)bispropanedinitrile (151) (0.085 g, 8%) from acetonitrile, mp 263-264 °C; ν_{max}: 3122, 2225, 1599, 1560, 1470, 1445, 1320, 1225, 1109, 1073, 778 and 690 cm^{-1}; δ_H (chloroform-d_1): 8.67 and 7.19 (m, 4H, aromatic) and 4.17 ppm (s, 3H, Me). A ^{13}C NMR carried out in deuterated dimethyl sulphoxide, which required heating to get the solid into solution, showed a very large number of peaks. A TLC of this sample showed the formation of additional products, suggesting the compound had undergone further reaction with the solvent.

Methylation using the tetramethylammonium (TMA) salt of 2,2'-(2-methylisoindolin-1,3-diylidene)bispropanedinitrile (155)

Preparation of the TMA salt (155)

The ammonium salt (2.01 g, 0.0077 moles) was dissolved in methanol (150 cm^3) with heating. Tetramethylammonium chloride (0.96 g, 0.0088 moles) dissolved in water (20 cm^3) was added and the reaction mixture left stirring overnight and orange needles were filtered (0.62 g). Further solid was obtained from the filtrate by precipitation using water. This was vacuum filtered and dried (1.21 g). Recrystallisation twice from ethanol gave red needles of the TMA salt (155) (1.8 g, 60%), mp 251-252 °C ; ν_{max}: 3029, 2205. 1653, 1598, 1577, 1496, 1309, 1256, 1098, 947, 917, 778, 767, 745, 711 and 703 cm^{-1} ; λ_{max} (CH_3CN): 496 (ε= 83 340), 466 (87 132), 342 (40 692) and 238 nm (84 840) ; δ_H (acetone-d_6): 8.14 and 7.56 (m, 4H, aromatic) and 3.41 ppm (s, 12H, Me) ; δ_C: 54.059 (=$\underline{C}$(CN)$_2$), 54.43 (t, *J* 15, Me), 116.32 and 117.2 (CN), 122.9 and 131.4 (aromatic C), 137.33 (quaternary C) and 171.87 ppm ($\underline{C}$=C(CN)$_2$). (Found: C, 68.39; H, 4.89; N, 26.52%. $C_{18}H_{16}N_6$ requires: C, 68.34; H,5.10; N, 26.56%).

(a) Heating the dry TMA salt under vacuum

The TMA salt (155) (0.2 g, 0.0003 moles) was heated under a vacuum of 0.5 mmHg. As the salt started to melt a bright yellow solid began to sublime on the edges of the flask and the cold finger. Heating was maintained at 180 °C for 12 hours during which the starting material changed from being dark red crystals to a black solid. A small quantity (~2-3 cm^3) of clear liquid which smelled of amine was collected in the liquid nitrogen trap. The yellow solid was retrieved from the cold-finger by dissolving it in acetone and evaporating to give a yellow solid mixture (0.017 g) which manifested itself as two compounds with almost identical R_f values on TLC in a variety of solvent systems. A TLC of the black solid using 80:20 ethyl acetate/light petroleum as mobile phase showed it was composed of black baseline material and some starting material. A ^{1}H, ^{13}C NMR and an IR spectrum of the yellow mixture were recorded. ν_{max}: 3120, 3075, 2915, 2849, 2215, 1618, 1558, 1470, 1446, 1318, 1227, 1098, 1158, 785, 697 and 675 cm^{-1}; δ_H (chloroform-d_1): 8.67 (m, 2H, aromatic), 8.60 (m, 2H, aromatic), 7.86 (m, 2H, aromatic), 7.78 (m, 2H, aromatic), 5.25 (s, 1H), 4.18 (s, 3H, Me), and 3.81 ppm (s, 4H); δ_C (chloroform-d_1): many peaks observed, principal peaks at ; 31.89 and 36.77 (Me), 74.48 (C=$\underline{C}$(CN)$_2$), 111.0-116.0 (5 CN peaks), 123.76-134.31 (9 aromatic C) and 153.0-159.0 (3 peaks).

(b) Heating the TMA salt (155) in 1,2-Dichlorobenzene

The TMA salt (155) (0.90 g, 0.0028 moles) in 1,2-dichlorobenzene (20 cm^3) was heated to reflux for 150 hours during which the reaction mixture changed colour from a red to a black solution. The reaction was followed by TLC using 30:70 ethyl acetate/light petroleum as mobile phase and this showed the production of one new product. The black crystalline solid (0.71 g) which crystallised out on cooling was filtered washed three times with diethyl ether and dried. This was then recrystallised three times from acetonitrile to give 2,2'-(2-methylisoindolin-1,3-diylidene)bispropanedinitrile (151) (0.364 g). The 1,2-dichlorobenzene was removed from the filtrate by vacuum distillation to give a golden solid with the same R_f value and IR as 2,2'-(2-methylisoindolin-1,3-diylidene)bispropanedinitrile. This was recrystallised three times to give 2,2'-(2-methylisoindolin-1,3-diylidene)bispropanedinitrile (151) (0.034 g). The total yield was 0.398g (54%), mp 264 °C ; ν_{max}: 3121, 2224, 1598, 1557, 1471, 1446, 1318, 1225, 1109, 785 and 690 cm^{-1} ; λ_{max} (CH_3CN): 416 (ε= 25 247), 394 (25 017), 294, 280 and 244 nm (10 868) ; δ_H (acetone-d_6): 8.65 (m, 2H, aromatic), 7.98 (m, 2H, aromatic) and 4.10 ppm (s, 3H, Me); δ_C (acetone d_6): 37.49 (Me), 61.9 ($C{=}\underline{C}(CN)_2$), 113.76 and 114.52 (CN), 125.7, 132.1 and 135.3 (aromatic C) and 160.92 ppm ($\underline{C}{=}C(CN)_2$). (Found: C, 69.91; H, 2.87; N, 27.10%. $C_{15}H_7N_5$ requires: C, 70.03; H, 2.74; N, 27.22%).

Attempted Benzylation of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (110)

Benzylpyridinium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (163)

Dry light petroleum (40-60)(10 cm^3) was added to sodium hydride (60% dispersion in oil; 0.307 g, 0.0076 moles), the suspension swirled and the solvent/oil solution removed with a Pasteur pipette once the mixture had settled. A solution of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (110) (2.2 g, 0.0076 moles) in dry tetrahydrofuran (80 cm^3) was added gradually to give the sodium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (146). The tetrahydrofuran was then evaporated off and the sodium salt was redissolved in methanol (50 cm^3). Benzylpyridinium chloride was then prepared by heating pyridine (0.61 g, 0.0077 moles) with benzylchloride (0.97 g, 0.0076 moles) on a heating mantle for 20 minutes. The resulting clear pink solution solidified on cooling. The solution of the sodium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (110) was added to the benzyl pyridinium chloride and heated under reflux for 30 minutes. The benzylpyridinium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (163) was obtained as bright orange needles (1.95 g) on leaving to cool. The filtrate was evaporated to dryness, redissolved in boiling ethyl acetate and insoluble sodium chloride filtered off. The ethyl acetate was removed, both batches of the salt were combined and recrystallised from ethanol to give the benzylpyridinium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (163) as fine orange needles (1.52 g, 48%); mp 174-175 °C; ν_{max}: 3130, 3086, 3062, 2199, 1633, 1613, 1598, 1578, 1488, 1378, 1364, 1313, 1268, 1254, 1158, 1094, 1027, 947, 917, 817, 775, 703, 684 and 617 cm^{-1}; δ_H: 9.2 (d, *J* 5.91, 2H, pyridinium CH), 8.6 (t, *J* 7.88, 1H, pyridinium CH), 8.2 (t, *J* 7.14, 2H, pyridinium CH), 8.08 (m, 2H, aromatic), 7.62 (m, 2H, aromatic), 7.51 (m, 2H, aromatic), 7.42 (m, 3H, aromatic) and 5.84 ppm (s, 2H, benzyl CH_2); δ_C: 54.04 (=$\underline{C}(CN)_2$), 63.4 (benzyl $\underline{C}H_2$), 116.3 and 117.3 (CN), 122.9 (aromatic C), 128.5, 128.8, 129.2 and 129.4 (aromatic C), 131.4 (aromatic C), 134.2 and 137.4 (quaternary aromatic C), 144.8 and 146.0 (pyridinium CH) and 171.9 ppm ($\underline{C}=C(CN)_2$). These assignments were made with the aid of C-H correlation spectra and by comparison with benzylpyridinium perchlorate.[176] (Found: C, 74.2; H, 3.85; N, 20.61% $C_{26}H_{16}N_6.{}^1/_2H_2O$ requires C, 74.18; H, 3.95;N, 19.96%).

Attempted formation of 2,2'-(2-benzylisoindolin-1,3-diylidene)bispropanedinitrile (164)

The benzylpyridinium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (163) (0.5 g, 0.0012 moles) in 1,2-dichlorobenzene (12 cm^3) was heated under reflux for sixteen hours, during which the solution changed from a bright orange colour to a black solution. The reaction was monitored by TLC using ethyl acetate/light petroleum (40-60 °C) 80:20 as the mobile phase. A very small amount of a faster eluting product was observed. This could not be isolated due to the small concentrations involved. A non-eluting black carboniferous compound was obtained on filtering. This was insoluble in a range of solvents tried. Evaporating off the 1,2-dichlorobenzene yielded starting material (0.031 g).

Synthesis of the amidino derivatives of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (110)

The same general procedure was carried out for the syntheses of all the amidines but with varying reaction solvents and reaction times. The synthesis of 2-cyano-*N*^{2}-benzyl-2-(3-dicyanomethyleneisoindol-1-diylidene)acetamidine is given as a typical experimental procedure with any deviations or differences stated in the subsequent procedures.

2-Cyano-*N*^{2}-benzyl-2-(3-dicyanomethyleneisoindol-1-diylidene)acetamidine (175)

The ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (110) (0.50 g, 0.0019 moles) and benzyl amine (0.21 g, 0.0019 moles) in 1,4-dioxan (30 cm^3) were heated to reflux for four hours during which an orange solid precipitated. This was then filtered off from the solution and a second batch of solid precipitated, which was also filtered off. These batches were combined, dried under vacuum and recrystallised from dimethylformamide/ethanol (10:90) to yield 2-cyano-*N*^{2}-benzyl-2-(3-dicyanomethyleneisoindol-1-diylidene)acetamidine (175) (0.31 g, 46 %), mp 300-301 °C (d); ν_{max}: 3382, 3321, 2927, 2216, 2204, 1636, 1611, 1568, 1519, 1464, 1312, 1260, 1090, 879, 799, 734, 695 and 605 cm^{-1} ; λ_{max}: 492 nm (ε= 34 070), 464 (31 756) and 344 nm (10 552); δ_H: 10.29 (brs, 1H, NH), 9.25 (brs, 2H, NH_2), 8.29 (m, 1H, isoindolin-1,3-diylidene aromatic H), 8.11 (m, 1H, isoindolin-1,3-diylidene aromatic H), 7.62 (m, 2H, isoindolin-1,3-diylidene aromatic H), 7.36 (m, 5H, benzyl aromatic H) and 4.67 ppm (s, 2H, CH_2); δ_C: 44.9 (benzyl CH_2), 57.25 (=$\underline{C}(CN)_2$), 71.37, [114.66, 115.35 and 116.8 (CN)], [123.12, 123.44, 127.05, 127.19, 128.01, 131.03, 131.46, 135.00, 135.54 and 137.97 (aromatic C)], 159.56, 167.26 and 170.10 ppm, (C=N) and ($\underline{C}$=C(CN)-).

Table 5.1 showing the correlating peaks from the C-H Correlation spectrum

^{1}H NMR peaks (ppm)	^{13}C NMR peaks (ppm)
4.66	44.9
7.36	127.05, 127.19, 128.01
7.62	131.03, 131.46
8.11	123.12
8.29	123.44

(Found: C, 71.57; H, 4.14; N, 23.58%. $C_{21}H_{14}N_6$ requires: C, 71.99; H, 4.02; N, 23.99%).

The filtrate was evaporated to dryness and recrystallised from acetonitrile to give an orange crystalline solid, the benzylammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (179) (0.19 g, 28%), mp 298-299 °C; ν_{max}: 3134, 3094, 2612, 2209, 1596, 1586, 1504, 1381, 1310, 1248, 1129, 1098, 952, 848, 754 and 708 cm^{-1}; λ_{max} (CH_3CN): 496 (ε= 32 597), 464 (32 393), 342 (13 124) and 240 nm (28 786); δ_H: 8.52 (brm, 5H, isoindolin-1,3-diylidene aromatic H and NH_3), 7.65 (m, 2H, isoindolin-1,3-diylidene aromatic H), 7.45 (m, 5H, benzyl aromatic H) and 4.5 ppm (s, 2H, CH_2); on addition of D_2O to the NMR sample the multiplet at 8.52 ppm was no longer broad and integrated for 2 protons; δ_C: 42.28 (benzyl CH_2), 53.89 (=$\underline{C}(CN)_2$), 116.24 and 117.19 (CN), 122.83, 128.45, 128.57, 128.76, 131.27, 133.83 and 137.38 (aromatic C) and 171.97 ($C=C(CN)_2$).

Table 5.2 showing the correlating peaks from the C-H Correlation spectrum

^1H NMR peaks (ppm)	^{13}C NMR peaks (ppm)
4.50	42.28
7.45	128.45, 128.57, 128.76
7.65	131.27
8.52	122.83

(Found: C, 72.15; H, 4.12; N, 24.52%. $C_{21}H_{14}N_6$ requires: C, 71.99; H, 4.02; N, 23.99%).

2-Cyano-*N*^{2}-propyl-2-(3-dicyanomethyleneisoindolin-1-diylidene)acetamidine (180)

n-Propylamine (0.35 g, 0.0059 moles) was added to a solution of the ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (119) (1.50 g, 0.0058 moles) in 1,4-dioxan and heated under reflux for 22 hours. This gave 2-cyano-*N*^{2}-propyl-2(3-dicyanomethyleneisoindolin-1-diylidene)acetamidine (180) as an orange solid (1.13 g, 65%), mp 298-299 °C, gradually darkens above 200 °C; ν_{max}: 3350, 3278, 3205, 2965, 2875, 2215, 1672, 1621, 1535, 1481, 1380, 1312, 1259, 1092, 914, 773, 734, 697 and 632 cm^{-1}; λ_{max}: 492 (ε= 37 159), 460 (33 467) and 346 nm (13 664); δ_H: 10.69 (brs, 1H, NH), 8.61 (brs, 2H, NH_2), 8.03 (m, 1H, aromatic), 7.90 (m, 1H, aromatic), 7.51 (m, 2H, aromatic), 3.21 (t, *J* 7.4, 2H, N-CH_2), 1.65 (m, 2H, CH_2) and 0.92 ppm (t, *J* 7.4, 3H, Me); δ_C: 11.65 (Me), 21.09 (CH_2), 44.20 (N-CH2), 56.96 (=$\underline{C}$(CN) $_2$), 71.95, [115.15, 115.95 and 117.18] (CN), [123.25, 123.61, 131.21, 131.66, 134.97 and 137.98] (aromatic C), 159.10, 166.79 and 170.25 ppm (C=N) and ($\underline{C}$=C(CN)-). (Found: C, 67.00; H, 4.7; N, 27.91%. $C_{17}H_{14}N_6$ requires: C, 67.54; H, 4.67; N, 27.79%).

The n-propylammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile, (183) was obtained from the filtrate in 8% yield; mp 298 °C (d), gradually darkens from 180 °C; ν_{max}: 3210, 3169, 2968, 2208, 1584, 1478, 1309, 1251, 1092, 950, 917, 766 and 701 cm^{-1}; λ_{max} (CH_3CN): 496 (ε= 32 458), 464 (32 200), 342 (13 536) and 240 nm (28 747); δ_H: 8.07 (m, 2H, aromatic), 7.62-7.59 [m, (aromatic H) overlapping brs (NH3), 5H], 2.72 (t, *J* 7.6, 2H, N-CH_2), 1.53 (m, 2H, CH_2) and 0.93 ppm (t, *J* 7.4, 3H, Me); δ_C: 10.8, 20.5 and 40.5 (CH), 54.0 (=$\underline{C}$(CN) $_2$), 116.4 and 117.3 (CN), 122.9, 131.3 and 137.5 (aromatic C) and 172.1 ppm ($\underline{C}$=C(CN)$_2$). (Found: C, 67.4; H, 4.63; N, 27.86%. $C_{17}H_{14}N_6$ requires: C, 67.54; H, 4.67; N, 27.79%).

Alternative synthesis of 2-Cyano-*N*^{2}-propyl-2-(3-dicyanomethyleneisoindolin-1-diylidene)acetamidine (180)

The n-propylammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (183) (0.35 g, 0.0012 moles) in 1,4-dioxan was heated under reflux for twelve hours. An orange solid precipitated and was filtered off to give 2-cyano-*N*^{2}-propyl-2-(3-dicyanomethyleneisoindolin-1-diylidene)acetamidine (180) (0.13 g, 36%). This gave the same IR and melting point as before.

The filtrate was evaporated to dryness and the orange solid obtained was recrystallised from ethyl acetate to give the n-propylammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (183) (0.22 g, 62%). This also gave the same melting point and IR spectrum as before.

2-Cyano-*N*^{2}-isopropyl-2-(3-dicyanomethyleneisoindol-1-diylidene) acetamidine (184)

Isopropylamine (0.27 g, 0.0046 moles) was added to a solution of the ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (119) (1.00 g, 0.0038 moles) in 1,4-dioxan (40 cm^3) and heated to reflux for 24 hours. The solvent was evaporated to dryness and the orange solid obtained was recrystallised from acetonitrile to yield 2-cyano-*N*^{2}-isopropyl-2-(3-dicyanomethyleneisoindol-1-diylidene)acetamidine (184) (0.55 g, 47%); mp 272 °C; ν_{max}: 3424, 3341, 3233, 2975, 2931, 2205, 1659, 1619, 1530, 1482, 1449, 1398, 1309, 1263, 1127, 1092, 910, 769, 732 and 679 cm^{-1}; λ_{max}: 492 (ε= 35 384), 460 (31 852) and 348 nm (11 806); δ_H: 11.26 (brs, 1H, NH), 8.42 (brs, 2H, NH_2), 8.04 and 7.91 (m, 2H, aromatic H), 7.53 (m, 2H, aromatic H), 3.94 (brm, 1H, N-CH) and 1.26 ppm (d, *J* 4.9, 6H, CH_3); δ_C: 21.6 (CH_3), 43.6 (N-C), 56.36 ($=\underline{C}(CN)_2$), 71.50, [114.8, 115.3 and 116.7] (CN), [122.6, 123.0, 130.6, 131.1, 134.3 and 137.4] (aromatic C), 157.4, 166.1 and 169.8 ppm (C=N) and ($\underline{C}=C(CN)$-). (Found: C, 67.44; H, 4.69; N, 27.83%. $C_{17}H_{14}N_6$ requires: C, 67.54; H, 4.67; N, 27.79%).

The acetonitrile filtrate from the recrystallisation was evaporated to dryness and the solid obtained was added to boiling chloroform and an insoluble solid was filtered off hot. This solid was then recrystallised from ethanol to give isopropylammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (187) (0.29 g, 25%); mp 180 °C; ν_{max}: 3167, 2979, 2209, 1637, 1578, 1504, 1379, 1311, 1244, 1244, 1097, 1047, 917, 773 and 703 cm^{-1}; λ_{max} (CH_3CN): 496 (ε= 11 433), 466 (11 373), 342 (4 985) and 240 nm (10 692); δ_H: 8.07 (m, 2H, aromatic), 7.62 (brm, 5H, aromatic H and NH_3), 4.36 (brs, 1H, OH) 3.41 (q, *J* 6.8, 2H, CH_2 of ethanol), 3.26 (m, 1H, N-CH), 1.13 (d, *J* 6.4, 6H, Me of isopropyl group) and 1.03 ppm (t, *J* 6.8, 3H, Me of ethanol); on addition of D_2O to the NMR sample the broad multiplet at 7.62 ppm became a two proton multiplet and the broad peak at 4.36 ppm was no longer observed; δ_C: 18.56 and 20.39 (Me), 43.1 (N-C), 54.00 (CH_2 of ethanol), 56.08 ($=\underline{C}(CN)_2$), 116.35 and 117.3 (CN), 122.93, 131.37 and 137.48 (aromatic C) and 172.07 ppm ($\underline{C}=C(CN)_2$). (Found: C, 65.53; H, 5.59; N, 24.27%. $C_{17}H_{14}N_6.C_2H_5OH$ requires: C, 65.5; H, 5.78; N, 24.12%).

2-Cyano-N^2-butyl-2-(3-dicyanomethyleneisoindolin-1-diylidene)acetamidine (188)

The ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (119) (2.00 g, 0.0077 moles) and n-butylamine (0.57 g, 0.0077 moles) were heated under reflux in ethanol (100 cm^3) for six hours. On leaving to cool overnight an orange solid precipitated. This was filtered off and dried to yield 2-cyano-N^2-butyl-2-(3-dicyanomethyleneisoindolin-1-diylidene)acetamidine (188) (1.86 g, 77%); mp 290 °C (d); ν_{max}: 3326, 3270, 2959, 2872, 2211, 1654, 1611, 1587, 1568, 1516, 1463, 1313, 1252, 1149, 1091, 910, 781, 733, 775, 765 and 630 cm^{-1}; λ_{max}: 492 (ε= 37 516), 460 (33 598) and 348 nm (12 642); δ_H: 10.83 (brs, 1H, NH), 8.70 (brs, 2H, NH), 8.17 (m, 1H, aromatic), 8.03 (m, 1H, aromatic), 7.62 (m, 2H, aromatic), 3.3 (m, 2H, N-CH_2), 1.63 (m, 2H, CH_2), 1.38 (m, 2H, CH_2) and 0.91 ppm (t, *J* 7.4, 3H, Me); δ_C: 13.4 (Me), 19.8, 29.5 and 42.3 (CH_2), 56.9 ($=\underline{C}(CN)_2$), 71.9, [115.1, 115.9 and 117.1] (CN), [123.2, 123.5, 131.1, 131.5, 134.9 and 137.9] (aromatic C), 158.9,166.7 and 170.1 ppm (C=N) and ($\underline{C}$=C(CN)-). (Found: C, 68.06; H, 5.07; N, 26.72%. $C_{18}H_{16}N_6$ requires: C, 68.34; H, 5.09; N, 26.56%).

The filtrate was evaporated to dryness and recrystallised from chloroform to yield the n-butylammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (190) (0.42 g, 17%) as orange plates; mp 289-290 °C (d); ν_{max}: 3220, 3176, 2963, 2936, 2207, 1597, 1478, 1309, 1244, 1225, 1244, 1096, 910 and 778 cm^{-1}; λ_{max} (CH_3CN): 496 (ε= 40 556), 464 (40 354), 342 (17 438) and 240 nm (36 670); δ_H: 8.07 (m, 2H, aromatic), 7.62 (m, 2H, aromatic) overlapping with 7.58 (brs, 3H, NH_3), 2.75 (t, *J* 7.4, 2H, NCH_2), 1.45 (m, 2H, CH_2), 1.28 (m, 2H, CH_2) and 0.86 ppm (t, *J* 7.4, 3H, Me); δ_C: 13.5 (Me), 19.1, 29.1 and 38.6 (CH_2), 54.1 ($=\underline{C}(CN)_2$), 116.3 and 117.3 (CN), 122.9, 131.4 and 137.5 (aromatic C) and 172.1 ppm ($\underline{C}=C(CN)_2$). (Found: C, 68.25; H, 5.08; N, 26.82%. $C_{18}H_{16}N_6$ requires: C, 68.33; H, 5.09; N, 26.56%).

2-Cyano-N^2-cyclohexyl-2-(3-dicyanomethyleneisoindolin-1-diylidene) acetamidine (192)

Cyclohexylamine (0.39 g, 0.004 moles) was added to a solution of the ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (119) (0.51 g, 0.002 moles) in pyridine (4 cm^3) and the solution heated under reflux for eleven hours. It was then poured into water (200 cm^3) and a yellow solid precipitated. Dilute HCl (10%, 30 cm^3) was added and the solid was filtered under vacuum and washed with water. The solid was recrystallised twice from acetonitrile to give 2-cyano-N^2-cyclohexyl-2-(3-dicyanomethyleneisoindolin-1-diylidene)acetamidine (192) as fine needles (0.43 g, 64%); mp 277-278 °C; ν_{max}: 3424, 3338, 3271, 3236, 2935, 2219, 2203, 1659, 1619, 1527, 1484, 1308, 1259, 1093, 910, 795 and 725 cm^{-1}; λ_{max}: 492 (ε= 34 364), 460 (29 988) and 348 nm (12 363); δ_H: 11.25 (brd, 1H, NH), 8.4 (brs, 2H, NH_2), 8.09 (m, 1H, aromatic), 7.95 (m, 1H, aromatic), 7.5 (m, 2H, aromatic H), 3.6 (m, 1H, NCH), 1.95 (m, 2H, CH_2), 1.7 (m, 2H, CH_2), 1.55 (m, 1H, CH), 1.3 (m, 4H, CH_2) and 1.1 ppm (m, 1H, CH); δ_C: 24.2 (CH_2), 24.7 (CH_2), 31.7 (CH_2), 50.9 (CH), 56.8 (=$\underline{C}(CN)_2$), 71.9, [115.2, 115.8 and 117.2] (CN), [123.2, 123.5, 131.2, 131.6, 134.9 and 137.9] (aromatic C), 157.7, 166.7 and 170.3 ppm (C=N) and ($\underline{C}$=C(CN)-). (Found: C, 70.05; H, 5.34; N, 24.71%. $C_{20}H_{18}N_6$ requires: C, 70.16; H, 5.29; N, 24.5%)

N-Isopropylidenecyclohexylammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (195)

The ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (119) (0.52 g, 0.002 moles) in acetone (40 cm^3) was added to a solution of cyclohexylamine (0.20 g, 0.002 moles) in acetone (20 cm^3). The solution was stirred at room temperature for one and a half days, and then evaporated to give a red oil which solidified on cooling. Recrystallisation from acetone in two batches yielded the *N*-isopropylidenecyclohexylammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (195) as orange plates (0.47 g, 62%); mp 189-190 °C (d); ν_{max}: 3086, 2941, 2863, 2207, 2218, 1689, 1498, 1453, 1313, 1250, 1098, 920, 902, 766, 749 and 705 cm^{-1}; λ_{max} (CH_3CN): 496 (ε= 34 566), 464 (34 306), 342 (14 705) and 240 nm (30 982); δ_H: 12.2 (brs, 1H, NH), 8.0 (m, 2H, aromatic), 7.6 (m, 2H, aromatic), 3.8 (brs, 1H, N-CH), 2.34 (s, 3H, Me), 2.32 (s, 3H, Me), 1.8 (brm, 2H, CH_2), 1.67 (brm, 2H, CH_2), 1.53 (brm, 1H, CH), 1.28 (m, 4H, CH_2) and 1.05 ppm (m, 1H, CH); δ_C: 20.9, 23.7, 24.3, and 26.3 (CH_2), 30.5 (Me), 56.4 ($=N^+HC$), 53.9 ($=\underline{C}(CN)_2$), 116.3 and 117.3 (CN), 122.9, 131.4 and 137.4 (aromatic C), 172.0 (C=N) and 188.9 ppm ($\underline{C}=C(CN)_2$). (Found: C, 71.92; H, 5.77; N, 22.02%. $C_{20}H_{22}N_6$ requires: C, 72.23; H, 5.79; N, 21.97%).

2-Cyano-N^2-octyl-2-(3-dicyanomethyleneisoindolin-1-diylidene)acetamidine (197)

n-Octylamine (0.51 g, 0.0039 moles) was added to a suspension of the ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (119) (1.0 g, 0.0038 moles) in 1,4-dioxan (30 cm^3) This was heated under reflux for four and a half hours and a bright orange solid fell out of solution on cooling. This was filtered off and washed with diethyl ether to give 2-cyano-N^2-octyl-2-(3-dicyanomethyleneisoindolin-1-diylidene)acetamidine (197) (0.48 g). The filtrate was evaporated to give a dark red/black oil. On dissolving in hot acetone, some diethyl ether was added and a fine orange powder (0.08 g) was filtered off. The combined orange solids were recrystallised from methanol to give 2-cyano-N^2-octyl-2-(3-dicyanomethyleneisoindolin-1-diylidene)acetamidine (197) as small orange needles (0.39 g, 27%) ; mp 232-233 °C; ν_{max}: 3438, 3345, 3238, 2940, 2868, 2201,1659, 1623, 1528, 1489, 1310, 1268, 1093, 768, 730 and 694 cm^{-1} ; λ_{max}: 492 (ε= 38 656), 460 (34 258)and 348 nm (13 094); δ_H: 10.7 (brs,1H, NH), 8.5 (brs, 2H, NH), 7.95 (m,1H, aromatic), 7.85 (m,1H, aromatic), 7.4 (m, 2H, aromatic), 3.2 (m, 2H, NCH_2), 1.6 (m, 2H, CH), 1.2 (brm, 10H, CH) and 0.8 ppm (m, 3H, Me): δ_C: 13.7, 21.9, 26.4, 27.4, 28.3, 28.5, 31.2 and 42.4 (octyl CHs), 56.9 ($=\underline{C}(CN)_2$), 71.59, [114.9, 115.7 and 116.9] (CN), [122.9, 123.3, 130.8, 131.2, 134.7 and 137.7] (aromatic C), 158.7, 166.5 and 169.9 ppm (C=N) and ($\underline{C}=C(CN)$-). (Found: C, 71.06; H, 6.18, N, 22.98%. $C_{22}H_{24}N_6$ requires: C, 70.96; H, 6.45; N, 22.98%).

On evaporating the filtrate again, a black oil was recovered. Attempts to precipitate further solid by the addition of light petroleum were not successfull as a tacky oil was obtained.

2-Cyano-*N*2-decyl-2-(3-dicyanomethyleneisoindolin-1-diylidene)acetamidine (198)

n-Decylamine (1.25 g, 0.0079 moles) was added to a solution of the ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (119) (1.03 g, 0.0039 moles) in ethanol (30 cm^3). This was stirred overnight and then heated under reflux for nine and a half hours. 2-Cyano-*N*2-decyl-2-(3-dicyanomethyleneisoindolin-1-diylidene)acetamidine (198) (0.47 g, 30%) precipitated as a fine golden powder on cooling and was recrystallised from toluene, mp 204 °C ; ν_{max}: 3306, 2925, 2854, 2222, 2199, 1648, 1612, 1573, 1524, 1478, 1314, 1272, 1093, 770, 733 and 694 cm^{-1}; λ_{max}: 492 (ε= 37 776), 460 (34 085) and 346 nm (12 516); δ_H: 10.8 (brs, 1H, NH), 8.6 (brs, 2H, NH), 8.04 (m, 1H, aromatic), 7.92 (m, 1H, aromatic), 7.5 (m, 2H, aromatic), 3.23 (m, 2H, NCH_2), 1.6 (m, 2H, CH), 1.17 (brm, 14H, CH) and 0.79 ppm (m 3H, Me); δ_C: 13.9, 22.2, 26.5, 27.5, 28.5, 28.8, 28.9, 29.0, 31.4 and 42.5 (decylamino CHs), 57.0 ($=\underline{C}(CN)_2$), 71.8, [115.1, 115.9 and 117.1] (CN), [123.2, 123.5, 131.1, 131.5, 134.9 and 137.9] (aromatic C), 158.9, 166.7 and 170.2 ppm (C=N) and ($\underline{C}$=C(CN)-). (Found : C, 71.95; H, 7.08; N, 21.13%. $C_{24}H_{28}N_6$ requires C, 71.97; H, 7.05; N, 20.98%)

The filtrate gave a dark red oil on evaporating the solvent. On dissolving the oil in hot chloroform and adding light petroleum, a small amount of the n-decylammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile(0.043 g) was obtained as a yellow powder. Repeating this procedure gave a tacky, oily solid which could not be purified further. Attempts to obtain the pure salt were not successful; ν_{max}: 3165, 3025, 2928, 2851, 2212, 1641, 1578, 1481, 1377, 1309, 1258, 1193, 1188, 1098, 917, 778 and 715 cm^{-1}; δ_H : 8.08 (m, 2H, aromatic), 7.6-7.4 [m, (aromatic H) overlapping brs (NH_3), 5H], 2.7 (m, 2H, NCH_2), 1.48 (m, 2H, CH_2), 1.18 (m, 14H, CH) and 0.8 ppm (m, 3H, Me); δ_C (acetone d_6): 13.8, 22.7, 26.4, 26.6, 27.4, 27.6, 28.8, 32.0, 40.7 and 48.2 (decylamino CHs), 54.8 ($=\underline{C}(CN)_2$), 116.7 and 117.4 (CN), 123.5, 131.3 and 138.3 (aromatic C) and 172 .5 ppm ($\underline{C}=C(CN)_2$).

2-Cyano-*N*^{1},*N*^{1}-dibutyl-2-(3-dicyanomethyleneisoindol-1-diylidene) acetamidine (203)

The ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile (119) (1.6 g, 0.006 moles) and *N,N*-dibutylamine (0.81 g, 0.006 moles) were heated under reflux in ethanol (50 cm^3) for six hours. The solution was evaporated to dryness and recrystallised from acetonitrile to give 2-cyano-*N*^{1},*N*^{1}-dibutyl-2-(3-dicyanomethyleneisoindol-1-diylidene)acetamidine (203) as red needles (2.20 g, 94%); mp 212-213 °C; ν_{max}: 3340, 2950, 2867, 2218, 2195, 1648, 1604, 1584, 1561, 1478, 1370, 1314, 1258, 1234, 1116, 1087, 752, 734 and 650 cm^{-1}; λ_{max}: 482 (ε= 28 580), 460 (28 150) and 336 nm (9 070); δ_H: 9.6 (brs, 1H, NH), 9.0 (brs, 1H, NH), 8.3 (m, 1H, aromatic), 8.2 (m, 1H, aromatic), 7.7 (m, 2H, aromatic), 3.6 (m, 4H, NCH_2), 1.7 (m, 4H, CH_2), 1.4 (m, 4H, CH_2) and 0.9 ppm (m, 6H, Me); δ_C: 13.4 (Me), 13.6, 19.2 and 28.5 (CH_2), 50.8 ($=\underline{C}(CN)_2$), 73.2, [116.8, 118.2 and 118.5] (CN), [122.7, 122.9, 131.0, 131.1, 137.7 and 137.8] (aromatic C), 159.2, 165.4 and 171.5 ppm. (Found: C, 71.2; H, 6.5; N, 23.0%. $C_{22}H_{24}N_6$ requires: C, 70.9; H, 6.49; N, 22.56%).

Crystal Structure Determination

Structure analysis and refinement

All collections of crystallographic data were carried out at Trinity College Dublin except for that of the benzylammonium salt of (110), (179), which was carried out at the University of Aberdeen, Scotland.

X-Ray diffraction data were collected using Mo-Kα radiation (λ = 0.71609 Å) monochromatised with a graphite plate giving *N* independent reflections, N_0 of these being used in the structure analysis. The index range is given for each crystal. All structures were solved using the Patterson heavy atom method with partial structure expansion to find all non-hydrogens using SHELXS-86.[195] The atomic coordinates were refined with full matrix least squares refinement using SHELXL-93.[196] Hydrogen atoms were located in their calculated positions and refined with respect to the carbon and nitrogen atoms to which they were attached.

Crystal data for Benzylammonium salt (179)

Crystallised from acetonitrile to give orange cubic crystals. Crystal dimensions 0.36 X 0.42 X 0.30 mm^3. M = 350.38, monoclinic, space group $P48$, a = 11.463(10), b = 13.094(9), c = 13.563(9) Å, V = 1857(2) Å^3, Z = 4, D_x = 1.254 g/cm^3. N = 2731, N_0 = 2533, index range = $0 \leq h \leq 12$, $0 \leq k \leq 15$, $-16 \leq l \leq 14$; R = 0.0456, wR = 0.1091.

Crystal data for *N*-Isopropylidenecyclohexylammonium salt (195)

Crystallised from acetone to give almost cubic light orange crystals. Crystal dimensions 0.45 X 0.40 X 0.35 mm^3. M = 382.47, triclinic, space group P-1, a = 9.353(15), b = 10.492(19), c = 11.257(16) Å, V = 1021.1(29) Å^3, Z = 2, D_x = 1.244 g/cm^3. N = 2484, N_0 = 1957, index range = $0 \leq h \leq 9$, $-10 \leq k \leq 11$, $-11 \leq l \leq 11$; R = 0.0723, wR = 0.1272.

Crystal data for 2-Cyano-N^1,N^1-dibutyl-2-(3-dicyanomethyleneisoindol-1-diylidene)acetamidine (203)

Crystallised from dimethylformamide to give red columns. Crystal dimensions 0.40 X 0.30 X 0.25 mm^3. M = 372.47, triclinic, space group P-1, a = 8.889(10), b = 11.382(2), c = 11.748(3) Å, V = 1036.0(3) Å^3, Z = 2, D_x = 1.194 g/cm^3. N = 2731, N_0 = 2533, index range = $0 \leq h \leq 9$, $-11 \leq k \leq 11$, $-12 \leq l \leq 11$; R = 0.0479, wR = 0.1240.

Crystal data for C-T complex (110)-TMDA (210)

Crystallised from acetonitrile to give dark green/black columns. Crystal dimensions 0.40 X 0.50 X 0.60 mm^3. M = 407.48, monoclinic, space group P121/n, a = 7.3133(119), b = 29.813(2), c = 10.226(2) Å, V = 2123.1(6) Å^3, Z = 4, D_x = 1.275 g/cm^3. N = 3947, N_0 = 3731, index range = $-8 \leq h \leq 8 \leq k \leq 35$, $0 \leq l \leq 12$; R = 0.0607, wR = 0.1750.

Cyclic Voltammetry

Cyclic voltammetry was performed using an EG&G model 273 potentiostat/galvanostat interfaced to an EG&G model 174A polarographic analyser and an EG&G model 303A Scanning Mercury Drop Electrode (SMDE), all of which were relayed to a personal computer. All solutions were made up in HPLC grade dimethylformamide using 0.1 M lithium perchlorate as the electrolyte and degassed for twenty minutes using nitrogen. All potentials are quoted with respect to BAS Ag/AgCl gel-filled reference electrode, the potential of which was 35 mV more positive than that of the saturated calomel electrode (SCE), with platinum wire as the counter electrode.

Ultra-Violet Studies of C-T Complexes in Solution

C-T interactions were initially investigated using UV spectroscopy. The spectra were measured on a Hewlett Packard 8452 UV Diode Array Spectrometer using standard techniques. C-T absorption bands were determined, either by addition of one equivalent of the donor to a solution of the acceptor, or by adding increasing amounts of the donor to a fixed concentration of the acceptor, and comparing these spectra with those of the individual donor and acceptor.

All spectra were determined for freshly prepared solutions. The following solvents were used as received: acetonitrile (Labscan-HPLC grade); tetrahydrofuran (Labscan-HPLC grade dried under standard conditions)[197]; dichloromethane (Labscan- HPLC grade). Investigations with commercially available donor compounds included anthracene (212), tetrathiafulvalene (2a), *N,N*-dimethylaniline (211), and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (210), and all used without further purification.

Solutions of *N,N*-dimethylaniline (211) and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (210) were degassed with nitrogen before the UV spectra were measured.

Synthesis of C-T Complexes

(110)-TMDA complex

Compound (110) (0.278 g, 0.0014 moles) in tetrahydrofuran (10 cm^3) was added to a hot solution of TMDA (0.376 g, 0.0028 moles, two equivalents) in acetonitrile (10 cm^3) giving a dark red solution. The solvent was evaporated off and the black solid remaining was recrystallised from acetonitrile. The resulting dark green solution was left for 36 hours at room temperature. (110)-TMDA was obtained as black/green columns (0.196 g); mp 154-155 °C; ν_{max}: 2925, 2199 (CN), 1653, 1611, 1544, 1475, 1312, 1260, 1182, 1151, 1093, 978, 943, 824, 778, and 708 cm^{-1}. (Found: C, 70.69; H, 4.97; N, 24.08%. $C_{24}H_{21}N_7$. requires C, 70.74; H, 5.19;N, 24.06%).

(110)-TTF Complex

A solution of (110) (0.100g, 0.0004 moles) in THF was added to a boiling solution of TTF (0.088 g, 0.0004 moles) in acetonitrile giving a green solution. On halving the volume of solution by evaporation no solid was obtained. On storing at 0 °C for two days only a very small amount of a dark green solid had precipitated. On evaporating off all the solvent a dark green solid was obtained. Attempts to recrystallise this green solid from a number of solvents were not successful.

(110)-Anthracene Complex

Compound (110) (0.267 g, 0.0011 moles) dissolved in THF (70 cm^3) in a sonicator bath, and degassed with argon, was added to a solution of anthracene (0.197 g, 0.0011 moles) in THF (20 cm^3), also degassed, giving a dark orange /red solution. This was further degassed, stoppered and left for 48 hours. Large purple crystals were formed which were found to be unstable when filtered in air. These crystals were isolated under argon in an glove bag but were not stable for a sufficient period of time to obtain elemental analysis.

(151)-TMDA Complex

Compound (151) (0.100 g, 0.0039 moles) dissolved in THF (25 cm^3) was added to a solution of TMDA (0.064 g, 0.0039 moles) in THF (10 cm^3) giving a dark green solution. The volume was reduced to 10 cm^3 and the flask stoppered under argon. When no solid was formed after two days all the solvent was evaporated off and the resulting dark green solid was recrystallised from acetonitrile giving the 2:1 complex of (151)-TMDA as green plates (0.041 g); on heating from 100-180 °C the plates darkens to a red solid which melts at 198 °C; ν_{max}: 3125, 2918, 2868, 2812, 2221 (CN), 1561, 1519, 1472, 1445, 1386, 1319, 1279, 1212, 1110, 1075, 951, 816, 775, and 686 cm^{-1}. (Found: C, 70.19; H, 4.32; N, 24.04%. $C_{40}H_{30}N_{12}$. requires: C, 70.78; H, 4.45; N, 24.76%).

(151)-TTF Complex

A boiling solution of (151) (0.100 g, 0.0039 moles) in acetonitrile (15 cm^3) was added to a boiling solution of TTF (0.079 g, 0.0039 moles) in acetonitrile (10 cm^3) giving a dark green/brown solution. On cooling the 1:1 complex of (151)-TTF was obtained as bright green plates (0.023 g); mp 160 °C (darkens), 190 °C (d); ν_{max}: 3075, 2975, 2933, 2868, 2213 (CN), 1561, 1444, 1384, 1069, 699, 766 and 670 cm^{-1}. (Found: C, 54.34; H, 2.37; N, 14.95%. $C_{21}H_{11}N_5$ requires: C, 54.64; H, 2.40; N, 15.17%).

Chapter 6

Reference Section

1 H. Akamatu, H. Inokuchi, and Y. Matsunaga, *Nature*, 1954, **173**, 168.

2 T. E. Phillips, T. J. Kistenmacher, J. P. Ferraris, and D. O. Cowan, *Chem. Commun.*, 1973, 471.

3 L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, 1962, **84**, 3374.

4 F. Wudl, G. M. Smith, and E. J. Hufnagel, *J. Chem. Soc., Chem. Commun.,* 1970, 1453.

5 J. S. Miller and A. J. Epstein, *Angew. Chem. Int. Ed. Engl.,* 1994, **33**, 385.

6 P. N. Prasad, D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley & Sons, New York, 1991.

7 (a) D. Jerome, A. Mazand, M. Ribault, and K. Bechgaard, *J. Phys. Lett.*, 1980, **41**, L95; (b) K. Bechgaard, C. S. Jacobsen, K. Mortensen, H. J. Pedersen, and N. Thorup, *Solid State Commun.,* 1980, **33**, 1119.

8 A.M. Kini, U. Geiser, H.H. Whangbo, K. D. Carlson, J. M. Williams, W. K. Kwok, K. G. Vandervoorst, J. E. Thompson, D. L. Stupka, D. Jung, and M. H. Whangbo, *Inorg. Chem.*, 1990, **29**, 2555.

9 J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlson, U. Geiser, L. K. Montgomery, G. J. Pyrka, D. M. Watkins, J. M. Kommers, S. J. Boryschuk, A. V. S. Crouch, W. K. Kwok, J. E. Schriber, D. L. Overmyer, D. Jung, and M. V. Whangbo, *Inorg. Chem.*, 1990, **29**, 3274.

10 T. T. M. Palstra, O. Zhou, Y. Iwasa, P. E. Fleming, and B. R. Zegarski, *Solid State Commun.*,1995, **93**, 327.

11 M. Marezio, J. Caponi, P. G. Radelli, P. P. Edwards, A. R. Armstrong, and W. David, *Eur. J. of Solid State and Inorg. Chem.*, 1994, **31**, 843.

12 (a) R. S. Mulliken, *J. Am. Chem. Soc.*, 1952, **74**, 811; (b) *J. Phys. Chem*, 1952, **56**, 801; (c) R. S. Mulliken, and W. B. Person, *J. Am. Chem. Soc.*, 1969, **91**, 3409.

13 D. O. Cowan, R. D. McCullough, A. Bailey, K. Lerstrup, D. Talham, D. Herr, and M. Mays, *Phosphorous, Sulphur and Silicon*, 1992, **67**,227.

14 J. H. Perlstein, *Angew. Chem. Int. Ed. Engl.,* 1977, **16**, 519.

15 S. S. Shaik, *J. Am. Chem. Soc.*, 1982, **104**, 5328.

16 A. W. Hanson, *Acta Cryst.,*1965, **19**, 610.

17 A. W. Hanson, *Acta Cryst.,*1968, **B24**, 768.

18 M. Bryce, A. J. Moore, M. Hasan, G. J. Askell, A. T. Fraser, D. W. Clegg, M. B. Hursthouse, and A. I. Karraulov, *Angew. Chem. Int. Ed. Engl.,* 1990, **29**, 1450.

19 R. C. Wheland, and J. L. Gillson, *J. Am. Chem. Soc.*, 1976, **98**, 3916.

20 J. B. Torrance, *Mol. Cryst. Liq. Cryst.,* 1985, **126**, 55.

21 R. E. Peierls, *Quantum Theory of Solids*, Oxford University Press, Oxford, 1972.

22 (a) J. K. Burdett, *Chem. Soc. Rev.*, 1994, 299;(b) S. Brown and G. Gruner, *Sci. Am.*, 1994, April, 28.

23 S. S. P. Parkin, F. Creuzet, M. Ribault, D. Jerome, K.Bechgaard, and J. M. Fabre, *Mol. Cryst., Liq. Cryst.*, 1982, **79**, 249.

24 J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.,* 1957, **108**, 1175.

25 F. J. Adrian, and D. O. Cowan, *Chem. Eng. News*, 1992, Dec. 21, 24.

26 D. O. Cowan, A. Kini, L-Y. Chiang, K. Lerstrup, D. R. Talham, T. O. Poehler, and A. N. Bloch, *Mol. Cryst. Liq. Cryst.*, 1982, **86**, 1.

27 J. P. Ferraris, T. O. Poehler, A.N. Bloch, and D. O. Cowan, *Tetrahedron Lett.,* 1973, **27**, 2553.

28 R. V. Gemmer, *J. Org. Chem.*,1975, **40**, 3554.

29 M. V. Lakshmikathnam, and M. P. Cava, *Current Science*, 1994, **66**, 28.

30 T. K. Hansen, M. V. Lakshmikathnam, M. P. Cava, R. E. Niziurski-Mann, F. Jensen, J. Becker, *J. Am. Chem. Soc.*, 1992, **114**, 5035.

31 D Cowan, P Shu, C Hu, W Krug, T Carruthers, T Poehler, A Bloch, *Chemistry and Physics of One-dimensional Metals,* Academic Press, 1976, 25.

32 E. Bloch, *Reactions of Organosulphur Compounds*, Academic Press, New York, 1978, 222.

33 (a) P. Blanchard, M. Salle, G. Duguay, M. Jubault and A. Gorgues, *Tetrahedron Lett.*, 1992, **33**, 2685; (b) G. LeCoustmer, Y. Mollier, *J. Chem. Soc., Chem. Commun.*, 1980, 38.

34 M. Mizuno, A. F. Garito, and M. P. Cava, *J. Chem. Soc., Chem. Commun.*, 1978, 18.

35 K. S. Varma, A. Bury, N. J. Harris and A. E. Underhill, *Synthesis*, 1987, 837

36 H. H. Wang; M. A. Beno; U. Geiser; M. A. Firstone, K. S. Webb; L. Nunez, G.W. Crabtree, K. D. Carlson, J. M. Williams, L. J. Azevedo, J. F. Kwak, J.E. Schirber, *Inorg. Chem.*, 1985, **24**, 2465.

37 J. M. Williams, M. A. Beno, H. H. Wang, P. C. Leung, T. J. Enge, K. D. Carlson, *Acc. Chem. Res.*, 1985, **18**, 261.and references cited therein.

38 T. J. Emge, H. H. Wang, M. A. Beno, P. C. W. Leung, M. A. Firestone, H. C. Jenkins, J. D. Cooke, K. D. Carlson, J. M. Williams, E. L. Venturini, L. J. Azevedo, J. E. Schriber, *Inorg. Chem.*, 1985, **24**, 1736.

39 E. B. Yagubski, *Mol. Cryst. Lig. Cryst.*, 1993, **230**, 139 and references cited therein.

40 M. Z. Aldoshina, R. N. Lyubovskii, *Synth. Met.*, 1993, **55-57**, 1905.

41 T. Suzuki, H. Yamochi, G. Sradanov, K. Hinkelmann, F. Wudl, 1989, *J. Am. Chem. Soc.*, 1989, **111**, 3108.

42 F. Wudl, H. Yamochi, T. Suzuki; H. Isotalo; C. Fite; H. Kasmi; K. Liou; G. Srdanou, *J. Am. Chem. Soc.*, 1990, **112**, 2461.

43 A. Krief, *Tetrahedron*, 1986, **42**, 1209.

44 D. C. Green., *J. Org. Chem.*, 1979, **44**, 1476.

45 (a) M. R. Bryce; G. Cooke, *Synthesis*, 1991, 263; (b) J. Y. Becker, J. Berstein, S. Bittner, L. Shahal and S. Shaik, *J. Chem. Soc., Chem. Commun.*, 1991, 92.

46 M. R. Bryce, G. Cooke, A. S. Dhinsa, D. Lorcy, A. J. Moore, M. C. Petty, M. B. Hursthouse, A. I. Karaula, *J. Chem. Soc., Chem. Commun.*, 1990, 816.

47 A. J. Moore, M. R. Bryce, G. Cooke, G. J. Marshallay, P. J. Skabara, A. S. Batsanov, J. A. Howard, S. T. Daley, *J. Chem. Soc., Perkin Trans.1.*, 1993, 1403.

48 M. R. Bryce, G. J. Marshallay, A. J. Moore, *J.Org Chem.*, 1992, **57**, 4859.

49 R. McCullough, J. A. Bellot, J. Seth, *J.Org Chem.*, 1993, **58**, 6480.

50 (a) Shih-Ying Hsu, Long Y. Chiang, *J.Org Chem.*, 1987, **52**, 3444; (b) A. M. Kini, B. D. Grates, M. A. Beno, J. M. Williams, *J. Chem. Soc. Chem. Commun.*, 1989, 169.

51 T. K. Hansen, I. Hawkins, S. Varma, S. Edge, S. Larsen and A. E. Underhill, *J. Chem. Soc., Perkin. Trans. 2*, 1991, 1963.

52 E. M. Engler, V. V. Patel. *J. Am. Chem. Soc.*, 1974, **96**, 7376.

53 (a) K. Bechgaard, K. Carneiro, F. B. Rasmussen, M. Olsen, *J. Am. Chem. Soc.*, 1981, **103**, 2440; (b) K. Bechgaard, *Mol. Cryst. Liq. Cryst.*, 1982, **79**, 1.

54 A. Moradpour, V. Peyrussan, I. Johansen, K. Bechgaard, *J. Org. Chem.*,1982, **48**, 388.

55 K. Kikuchi, T. Tamiki, I. Ikemoto, K. Kobayashi, *J. Chem. Soc., Chem. Commun.*, 1986, 1472.
56 F. Wudl, and E. Aharon-Shalom, *J. Am. Chem. Soc.*, 1982, **104**, 1154.
57 K. Lerstrup, D. Talham, A. Block, T. Poehler, and D. Cowan, *J. Chem. Soc., Chem. Commun.,* 1982, 336.
58 R. D. McCullough, G. B. Kok, K. Lerstrup, D. O. Cowan, *J. Am. Chem. Soc.*, 1987, **109**, 4115.
59 M. D. Mays, R. D. McCullough, D. O. Cowan, T. O. Poehler, W. A. Bryden, and T. J. Kistenmacher, *Solid State Commun.*, 1988, **65**, 1089.
60 Z. Yoshida, T. Kawase, H. Awaji, I. Sugimoto, T. Sugimoto, and S Yoneda, *Tetrahedron Lett.*, 1983, 24, 3469.
61 A. J. Moore, M. R. Bryce, *Tetrahedron Lett.*, 1992, **33**, 1373.
62 M. Salle, A. Belysamine, A. Gorgues, M. Jubault, N. Soyer, *Tetrahedron Lett.*, 1991, **32**, 2897.
63 E. Cerrada, M. R. Bryce, A. J. Moore, *J. Chem. Soc., Perkin Trans.1*, 1993, 537.
64 A. Ohta, T. Kobayashi, H. Kato, *J. Chem. Soc. Chem Commun.*, 1993, 431.
65 J. B. Torrance, J. J. Maayerle, V. Y. Lee, K. Bechgaard, *J. Am. Chem. Soc.*, 1979, **101**, 4747.
66 C. Vazquez, J. C. Calabrese, D. A. Dixon, J. S. Miller, *J.Org.Chem.*, 1993, **58**, 65.
67 J. E. Frey, A. M. Andrews, D. G. Ankoviac, D. N. Beaman, L. E. DuPont, T. E. Elsner, S. R. Lang, M. A. Oosterbaan Zwart, R. E. Seagle, L. A. Torreano, *J. Org. Chem*, 1990, **55**, 606.
68 J. E. Frey, A. M. Andrews, S. C. Combs, S. P. Edens, J. J. Puckett, R. E. Seagle, L. A. Torreano, *J. Org. Chem*, 1992, **57**, 6460.
69 D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, 1962, **84**, 3370.
70 J. Diekmann, W.R. Hertler, and R. E. Benson, *J. Org. Chem.*, 1963, **28**, 2719.
71 R. C. Wheland, and E. L. Martin, *J. Org. Chem*, 1975, **40**, 3101.
72 (a) M. R. Bryce, M. Hasan and G. J. Ashwell, *J.Chem.Soc.,Chem.Comunn.*, 1989, 529; (b) M. R. Bryce, A. M. Grainger, M. Hasan, G. A. Ashwell, P. A. Bates and M. B. Hursthouse, *J.Chem.Soc., Perkin Trans. 1*, 1992, 611; (c) B. Rosenau, C. Krieger and H. A. Staab, *Tetrahedron Lett.*,1985, **26**, 2081
73 W. Lehnert, *Tetrahedron Lett.*, 1970, 4723.

74 (a) A. Kini, M. Mays, and D. O. Cowan, *J. Chem. Soc., Chem. Comunn.*, 1985, 286.

75 J. Y. Becker, J. Bernstein, S. Bittner, E. Harlev and J. A. R. P. Sharma, *J.Chem.Soc.,Perkin Trans. 2*, 1989, 1157.

76 T. Czekanski and M. Hanack, *J.Org.Chem.*, 1991, **56**, 1569

77 M. Uno, K. Seto, M. Masuda, W. Ueda, and S. Takahashi, *Tetrahedron Lett.*, 1985, **26**, 1553.

78 W. J. Siemons, P. E. Bierstedt and R. G. Kepler, *J.Chem.Phys.*, 1963, **39**, 3523.

79 L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Comm.*, 1973, **12**, 1125.

80 F. Denoyer, R. Comes, A. F. Garito and A. J. Heeger, *Phys.Rev.Lett.*, 1975, 35, 445.

81 (a) A. N. Bloch, T. F. Carruthers, T. O. Poehler, and D. O. Cowan, *Chemistry and Physics of One-Dimensional Metals*, Plenum Press, New York, 1977, p. 47; (b) D. O. Cowan, A. Kini, L-Y Chiang, K. Lerstrup, D. R. Talham, T. O. Poehler, and A. N. Bloch, *Mol.Cryst.Liq.Cryst.* 1982, **86**, 1; (c) M. R. Bryce and L. C. Murphy, *Nature*, **309**, 119 and references cited therein.

82 M. D. Days, R. D. McCullough, D. O. Cowan, T. O. Poehler, W. A. Bryden, and T. J. Kistenmacher, *Solid State Commun.*, 1988, **65**, 1089.

83 R C Wheland, *J. Am. Chem. Soc.*, 1976, **98**, 3926.

84 M. R. Bryce and J. A. K. Howard, *Tetrahedron Lett.*,1983, **24**, 1205.

85 M. R. Bryce and J. A. K. Howard, *Tetrahedron Lett.*,1982, **23**, 4273.

86 A. F. Garito and A. J. Heeger, *Acc.Chem.Res.*, 1973, 232.

87 D. J. Sandman and A. F. Garito, *J.Org.Chem.*, 1974, **39**, 1165.

88 K. Bechgaard, C. S. Jacobsen, and N. H. Andersen, *Sol. State.Commun.*, 1978, **25**, 875.

89 A. W. Addison, N. S. Dalal, Y. Hoyano, S. Huizinga, and L. Weiler, *Can.J.Chem.*, 1977, **55**, 4191 and references therein.

90 E. Ahaaron-Shalom, J. Y. Becker, and I. Agranat, *Nouv.J.Chim.*, 1979, **3**, 643.

91 (a) M. Maxfield, D. O. Cowan, A. N. Bloch, and T. O. Poehler, *Nouv.J.Chim.*, 1979, **3**, 647 ;(b) M. Maxfield, D. O. Cowan, A. N. Bloch, and T. O. Poehler, *J.Chem.Soc.,Chem.Commun.*, 1980, 947.

92 F Wudl, M L Kaplan, B K Teo, and J Marshall, *J.Org.Chem.*, 1977, **42**, 1666.

93 A. Aumüller and S. Hünig, *Liebigs Ann. Chem.*, 1984, 618.

94 M. L. Kaplan, R. C. Haddon, F. B. Bramwell, F. Wudl, J. H. Marshall, D. O. Cowan and S. Gronowitz, *J. Phys. Chem.*, 1980, **84**, 427.

95 N. Martin, R. Behnisch, and M. Hanack, *J. Org. Chem.*, 1989, **54**, 2563.

96 P. de la Cruz, N. Martin, F. Miguel, C. Seoane, A. Albert, F. H. Cano, A. Leverenz and M. Hanack, *Synthetic Metals*, 1992, **48**, 59.

97 J. Silverman and N. F. Yannoni, *J. Chem. Soc. B*, 1967, 194.

98 F. Iwasaki, *Acta Crystallographica Sect.B*, 1971, **B27**, 1360.

99 U. Schubert, S.Hünig, A. Aumüller, *Liebigs Ann.Chem.*, 1985, 1216.

100 F. Gerson, R. Heckendorn, D. O. Cowan, A. Kini, and M. Maxfield, *J.Am.Chem.Soc.*, 1983, **105**, 7017.

101 S. Gronowitz and B. Uppström, *Acta Chem. Scand. B*, 1974, **28**, 981.

102 H. Ishida, K. Yui, Y. Aso, T. Otsubo,and F. Ogura, B*ull. Chem. Soc. Jpn.*, 1990, **63**, 2828.

103 K. Yui, Y. Aso, T. Otsubo and F. Ogura, *J. Chem. Soc, Chem. Commun.*,1987, 1816.

104 K. Yui, H. Ishida, Y. Aso, T. Otsubo, F. Ogura, A. Kawamoto, J. Tanaka, *Bull. Chem. Soc Jpn.*, 1989, **62**, 1547.

105 S. Yoshida, M. Fujii, Y. Aso, T. Otsubo and F. Ogura, *J. Org. Chem.*, 1994, **59**, 3077.

106 M. Fujii, Y. Aso, T. Otsubo and F. Ogura, *Synth. Met.*, 1993, **55-57**, 2136.

107 M. Uno, T. Takahasi, and S. Takahashi, *J. Chem. Soc. Perkin Trans. 1*, 1990, 647.

108 Y. Aso, K. Yui, H. Ishida, T. Otsubo, F. Ogura, A. Kawamoto, and J. Tanaka, *Chem. Letters*, 1988, 1069.

109 K. Kobayashi and C. L. Gajurel, *J. Chem. Soc., Chem. Commun.*, 1986, 1779.

110 P. de la Cruz, N. Martin, F. Miguel, C. Seone, *J. Org. Chem.*, 1992, **57**, 6192.

111 (a) T. Suzuki, H. Fujii, Y. Yamashita, C. Kabuto, S. Tanaka, M. Harasawa, T. Mukai, and T. Miyashi, *J. Am. Chem. Soc*, 1992, **114**, 3034.; (b) Y. Yamashita, T. Suzuki, T. Mukai, and G. Saito, *J. Chem. Soc., Chem. Comunn.*, 1985, 1044.

112 T. Suzuki, Y. Yamashita, C. Kabuto, and T. Miyashi, *J. Chem. Soc., Chem. Commun.*, 1989, 1102.

113 A. Aumüller and S. Hünig, Angew. Chem., *Int. Ed. Engl.*, 1984, **23**, 447.

114 H. Almen, T. Bauer, S. Hünig, V. Kupcik, U. Langohr, T. Metzenthin, K. Meyer, H. Rieder, J. U. von Schütz, E. Tillsmann, and H. C. Wolf, *Angew. Chem. Int. Ed. Engl.,* 1991, **30**, 561.

115 S. Hünig and P. Erk, *Adv. Mater.*, 1991, **3**, 225.

116 A. Aumüller and S. Hünig, *Liebigs Ann. Chem.*, 1986, 142.

117 N. Martin, J. L. Segura, C. Seoane, C. Torio, A. Gonzalez, and J. M. Pingarron., *Synth. Met.,* 1994, **64**, 83.

118 E. Barranco, N. Martin, J. L. Segura, C. Seoane, P. De La Cruz, F. Langa, A. Gonzalez, and J. M. Pingarron, *Tetrahedron*, 1993, **49**, 4881.

119 N. Martin, J. A. Navarro, C. Seoane, A. Albert, F. Cano, J. Y. Becker, V. Khodorkovsky, E. Harlev, and M. Hanack, *J Org. Chem.*, 1992, **57**, 5726.

120 M. R. Bryce, S. R. Davies, A. M. Grainger, J. Hellberg, M. B. Hursthouse, M. Mazid, R. Bachmann, and F. Gerson, *J. Org. Chem.*, 1992, **57**, 1690.

121 See 118 and 119 and references cited therein.

122 A. Aumüller, E. Hadicke, S. Hünig, A. Schatzle, and J. U. von Schutz, *Angew. Chem. Int. Ed. Engl.*, 1984, **23**, 449.

123 See 115 and references cited therein.

124 E. Günther, S. Hünig, K. Peters, H. Rieder, H. G. von Schnering, J. U. von Schütz, S. Söderholm, H-P. Werner, and H. C. Wolf, *Angew. Chem. Int. Ed. Engl.*, 1990, **29**, 204.

125 M. Krebs, W. Bietsch, J. U. von Schütz, and H. C. Wolf, *Synth. Met.*, 1994, **64**, 187.

126 A. Aumüller, P. Erk, G. Klebe, S. Hünig, J. U. von Schütz, and H.-P. Werner, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 740.

127 K. Sinzger, S. Hünig, M. Jopp, D. Bauer, W. Bietsch, J. U. von Schütz, H. C. Wolf, R. K. Kremer, T. Metzenthin, R. Bau, S. I. Kahn, A. Lindbaum, C. L. Lengauer, and E. Tillmanns, *J. Am. Chem. Soc.*, 1993, **115**, 7696 and references cited therein.

128 P. Erk, H. Meixner, T. Metzenthin, S. Hünig, U. Langohr, J. U. von Schütz, H-P. Werner, H. C. Wolf, R. Burket, H. W. Helberg, and G Schaumburg, *Adv. Mater.*, 1991, **3**, 311.

129 R. Kato, H. Kobayashi and A. Kobayashi, *J. Am. Chem. Soc.*, 1989, **111**, 5224.

130 G. Steimecke, H.-J. Sieler, R. Kirmse, and E. Hoyer, *Phosphorus and Sulfur*, 1979, **7**, 49.

131 M. Bousseau, L. Valade, J-P. Legros, P. Cassoux, M. Garbauskas, and L. V. Interrante, *J. Am. Chem. Soc.*, 1986, **108**, 1908.

132 L. Brossard, M. Ribault, L. Valade, and P. Cassoux, *Physica B*, 1986, **143**, 378.

133 M. Bousseau, L. Valade, M. -F. Buniquel, P. Cassoux, M. Garbauskas, L. Interrante, and J. Kasper, *Nouv. J. Chim.*,1984, **8**, 3.

134 A. Kobayashi, H. Kobayashi, A. Miyamoto, R. Kato, R. A. Clark, and A. E. Underhill, *Chem. Lett.*, 1991, 2163.

135 A. Kobayashi, H. Kim, Y. Sasaki, K. Murata, R. Kato, and H. Kobayashi, *J. Chem. Soc. Faraday Trans.*, 1990, **86**, 361.

136 (a) R. C. Haddon, *Phil. Trans. R. Soc. Lond. A*, 1993, **343**, 53; (b) R. C. Haddon, *Acc. Chem. Res.*, 1992, **25**, 127.

137 G. Saito, T. Teramoto, A. Otsuka, Y. Sugita, T. Ban, M. Kusunoki, and K. Sakaguchi, *Synth. Met.*, 1994, **64**, 359.

138 A. R. Katritzky, *Handbook of Heterocyclic Chemistry*, Pergamon Press, Oxford, 1985, 76.

139 D. Lorcy, K. D. Robinson, Y. Okuda, J. L. Atwood, and M. P. Cava, *J. Chem. Soc., Chem. Commun.*, 1993, 345.

140 L. T. Tietze, U. Beifuss, *Comprehensive Organic Chemistry*, Pergamon Press, 1991, **Vol 2**, 341 and references cited therein.

141 A. H. Renfrew and S. B. Bostock, *J. Chem. Soc. Perkin Trans. 1*, 1977, 84.

142 J. A. Moore, Ji-Heung Kim, *Tetrahedron Lett.*, 1991, **32**, 3449.

143 F. Sorm, J. Gut and P. Kankovsky, *Coll. Czech. Chem. Commun.*, 1950, **15**, 99.

144 (a) R. A. Carboni, D. D. Coffman, and E. G. Howard, *J. Am. Chem. Soc.*, 1958, **80**, 2838;(b) Aldrich Library of NMR Spectra, 1974, **3**, 166C;(c) Aldrich Library of Infra Red Spectra, 1981, edition 3, 514G, Aldrich Chemical Co.,Inc., Milwaukee.

145 See 142 and reference cited therein.

146 W. Lehnert, *Tetrahedron Lett.*, 1971, 1501.

147 See 120 and references cited therein.

148 J. A. Elvidge, and R. P. Linstead, *J. Chem. Soc.*, 1952, 5000.

149 J. A. Elvidge, J. S. Fitt, and R. P. Linstead, *J. Chem. Soc.*, 1956, 235, and references cited therein.

150 (a) J. Kranz, French Patent No. 1 446 964, BASF AG, 1966 ; (b) G. Hoffmann and P. Neumann, DE 3 110 958, BASF AG, 1982 and references therein.

151 French Patent No. 1 537 299, Farbenfabriken Bayer Aktiengesellschaft, 1968.

152 J. von der Crone, *J. of Coatings Tech.*, 1985, **57**, 67.

153 A. Eckell, H. Eilingsfeld, A. Elzer, F. Feichtmayr, G. Hoffmann, R. J. Leyrer, P. Neumann, DE 3 110 953, BASF AG, 1982.

154 See 152 and references cited therein.

155 P. J. Brach, S. J. Grammatica, H. Ossanna, L. Weinberger , *J. Heterocyclic Chem.*, 1970, **7**, 1403.

156 P.F. Clark, J. A. Elvidge, R. P. Linstead, *J. Chem. Soc.*, 1953, 3593.

157 J. K. M. Sanders and B. K. Hunter, *Modern NMR Spectroscopy-A Guide for Chemists*, Oxford University Press, 1987, 216.

158 K. Wallenfels, K. Friedrich, J. Rieder, W. Ertel and H. K. Thieme, *Angew. Chem. Int. Ed. Engl.*, 1976, **15**, 261.

159 J. A. Moore, D. R. Robello, *Macromolecules*, 1989, **22**, 1084.

160 D. D. Perrin, B. Dempsey, E. P. Serjeant, *pKa Prediction for Organic Acids and Bases*, Chapman and Hall, London, 1981.

161 J. March, *Advanced Organic Chemistry*, Wiley & Sons, New York, 1992, fourth edition, pg 265.

162 F.Closs, R. Gompper, U. Nagel and H-U. Wagner, *Angew. Chem. Int. Ed. Engl.,* 1987, **26**, 1037.

163 (a) See 158 and references cited therein; (b) W.J. Middleton and V. A. Engelhardt, *J. Am. Chem. Soc.*, 1958, **80**, 2788.

164 M. S. Gibson and R. W. Bradshaw, *Angew. Chem. Int. Ed. Eng.*, 1968, **7**, 919.

165 S. R. Buc, *J. Am. Chem. Soc.*, 1947, **69**, 254.

166 A. R. Katritzky, *Tetrahedron*, 1980, **36**, 679, reference 3 therein.

167 W. K. Musher, *J. Am. Chem. Soc.*, 1964, **86**, 960.

168 W. K. Musher and R. R. Stevens, *J. Am. Chem. Soc.*, 1968, **90**, 3515.

169 M. Shamma, N. C. Deno, and J. F. Remar, *Tetrahedron Lett.*, 1966, 1375.

170 H-O. Kalinowski, S. Berger and S. Braun, *Carbon-13 NMR Spectroscopy*, Wiley & Sons, Chicester, 1988.

171 W. Kantlehner, *The Chemistry of Functional Groups: The Chemistry of Acid Derivatives: Supplement B, Part 1*, The Patai series, Wiley & Sons, Chichester,1979, 563.

172 (a) A. R. Katritzky, C. M. Marson, *Angew. Chem. Int. Ed. Engl.*, 1984, **23**, 420; (b) A. R. Katritzky, *Tetrahedron*, 1980, **36**, 679.

173 A. R. Katritzky, G. Liso, E. Lunt, R. C. Patel, S. S. Thind, A. Zia, *J.Chem.Soc., Perkin Trans. 1*, 1980, 849.

174 J. B. Hendrickson, S. Okano, and R. K. Bloom, *J. Org. Chem.*, 1968, 3434.

175 A. R. Katritzky, S. S. Thind, *J.Chem.Soc., Perkin Trans. 1*, 1980, 1895.

176 A. R. Katritzky, O. Rubio, M. Szajda, and B. Nowak-Wydra, *J. Chem. Research (s)*, 1984, 234.

177 A. R. Katritzky and B. Brycki, *J. Am. Chem. Soc.*, 1986, **108**, 7295.

178 J. Delaney, DCU, 1995, unpublished work.

179 W. R. Hertler, H. D. Hartzler, D. S. Acker, R. E. Benson, *J. Am. Chem.*, 1962, **84**, 3387.

180 B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, H. F. Mower, *J. Am. Chem.*, 1958, **80**, 2806.

181 See 94 and 95

182 A. J. Bard and L. R. Faulkner, *Electrochemical Methods-Fundamentals and Applications*, Wiley and Sons, Chicester, 1980.

183 J. P. Coleman, *The Chemistry of Functional Groups: The Chemistry of Acid Derivatives: Supplement B, Part* 2, The Patai series, Wiley & Sons, Chichester, 1979, 781.

184 R. Bonnett and S. A. North, *Adv. Heterocycl. Chem.,* 1981, **29**, 341.

185 R. Foster, *Molecular Association*, 1975, **Vol.1**, 151, Academic Press; (b) **Vol. 2**, 1979, 331.

186 (a) P. G. Aspen and P. G. Rasmussen, *J. Am. Chem. Soc.*, 1991, **113**, 6178 and references therein.

187 (a) C. K. Prout and J. D. Wright, *Angew. Chem. Int. Ed. Eng.*, 1968, **7**, 659; (b) J. B. Torrance, J. J. Mayerle, V. Y. Lee, K. Bechgaard, *J. Chem. Soc.*, 1979, **101**, 4747.

188 R. Foster, *The Chemistry of Functional Groups: The Chemistry of Acid Derivatives: Supplement B, Part 1*, The Patai series, Wiley & Sons, Chichester, 1979, 175.

189 S. C. Wallwork, *J. Chem Soc.*, 1961, 494.

190 I. Ikemoto, *Acta Cryst.*, B**35**, 1979, 2264.

191 J. S. Chappell, A. N. Bloch, W. A. Bryden, M. Maxfield, T. O. Poehler and D. O. Cowan, *J. Am. Chem. Soc.*, 1981, **103**, 2442.

192 M. R. Bryce, *Chem. Br.*, August 1988, 781.

193 Z. Rappoport, *J. Chem Soc.*, 1963, 4498.

194 Merck & Co. Inc., *Merck Index*, New Jersey, 1989, Edition 11, 79.

195 G. M. Sheldrick, *Acta Cryst.*, 1990, **A46**, 467.

196 G. M. Sheldrick, SHELX 93, Program for crystal structure determination, 1993.

197 D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 1980.