Synthesis and characterisation of some amidino derivatives of the heterocyclic analogues of Benzo-TCNQ

A thesis presented for the degree of Master of Science

by

Colette A. Dunlea BSc

under the supervision of Prof Albert C. Pratt

at

DUBLIN CITY UNIVERSITY

School of Chemical Sciences

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To my parents

Declaration

I, the undersigned, hereby state that this thesis, which I now submit for assessment on the programme of study leading to the award of M Sc 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

Colette Dunlea

Colette A Dunlea

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ABSTRACT

Investigations into the synthesis of heterocyclic analogues of 11,11,12,12-tetracyano-1,4-naphthaquinodimethane have been carried out to create new acceptor compounds for investigation as electron-acceptors in the synthesis of charge-transfer complexes Many TCNQ charge-transfer complexes exhibit interesting electrical conductor properties

Pyrolysis of a number of tetraalkylammonium salts of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile in trichlorobenzene was attempted Though successful N-methylation was achieved, this method did not permit the introduction of other alkyl groups Mannich type reactions of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile and its ammonium salt with formaldehyde in the presence of succinimide or N-methylaniline were examined but no products were formed

Investigations were conducted into the possibility of generating a Reformatsky-type organozinc reagent for reaction with N-methylphthalimide as a potential route to 2,2'-(2-methylisoindolin-1, 3-diylidene)bispropanedinitrile

Investigation of the reaction of the ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile with a variety of primary and secondary amines was undertaken This resulted in new amidine derivatives

Cyclic voltammetry measurements of these compounds showed that they were all electrochemically reversible Possible charge-transfer interactions between N,N,N',N',-tetramethyl-p-phenylenediamine and tetrathiafulvalene and some of the amidine derivatives were investigated by UV spectroscopy

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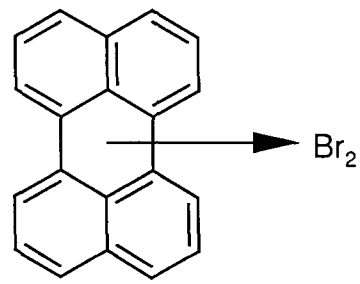
Chapter 1

1.1 Introduction

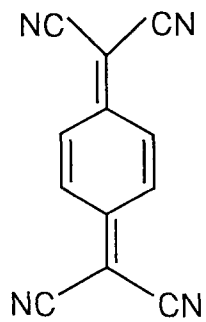
Organic solids are usually thought of as electrical insulators However, since the 1950s, many discoveries have pointed towards new organic compounds with metal-like qualities such as conductivity, and in some cases even super-conductivity It was this breakthrough in organic chemistry that has lead to the phenomenal interest in the synthesis and characterisation of a wide variety of new 'organic conductors'

In 1954 the first organic conductor was reported[1] consisting of a complex formed between a polycyclic aromatic compound, perylene and a halogen, bromine

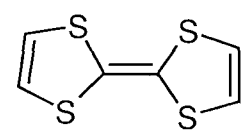


[1]

This new compound [1] comprised of a donor, (D) and an acceptor (A), which when complexed produced electrical conductivity in the range ~ 1 x 10^{-3} Scm^{-1} A very early acceptor which was developed[2a] was tetracyanoquinodimethane [2] However, the biggest breakthrough in the synthesis of these new organic conductors came in 1973, when it was discovered that single crystals of the salt tetrathiafulvalene [3] - tetracyanoquinodimethane [2] (TTF-TCNQ) showed metal-like electrical conductivity of 500 Scm^{-1} [2b,2c]



[2]



[3]

1.2 Band theory of solids

To appreciate the unique properties of these salts, an understanding of the band theory of solids is imperative (fig 1.1). When a large number of atoms or molecules congregate together in a crystalline solid, the electronic states mix resulting in two bands. These bands, the conduction band [derived from the LUMO (lowest unoccupied molecular orbitals) of the molecules], and the valence band [derived from the HOMO (highest occupied molecular orbitals) of the molecules] will extend throughout the solid only if interaction is sufficiently strong. Band filling can be compared to the Aufbau principle for atoms : electrons are filled first into the lower energy states and then into increasingly higher energy states.

In an insulator (fig 1.1a) there only exists completely filled and completely empty bands. Between these lie a large energy gap E_g, which prevents electron movement in the system. In a semi-conductor (fig 1.1b) there exists a much smaller energy gap. This allows thermal excitation of the electrons from the valence band to the conduction band resulting in an intrinsic semi-conductor. Metallic behaviour is associated with partially filled bands and it is this which allows large numbers of electrons to move easily to higher states within the band (fig 1.1c). The highest occupied state is known as the Fermi level, and it is electrons present in the energy states near this level that influence the physical properties.

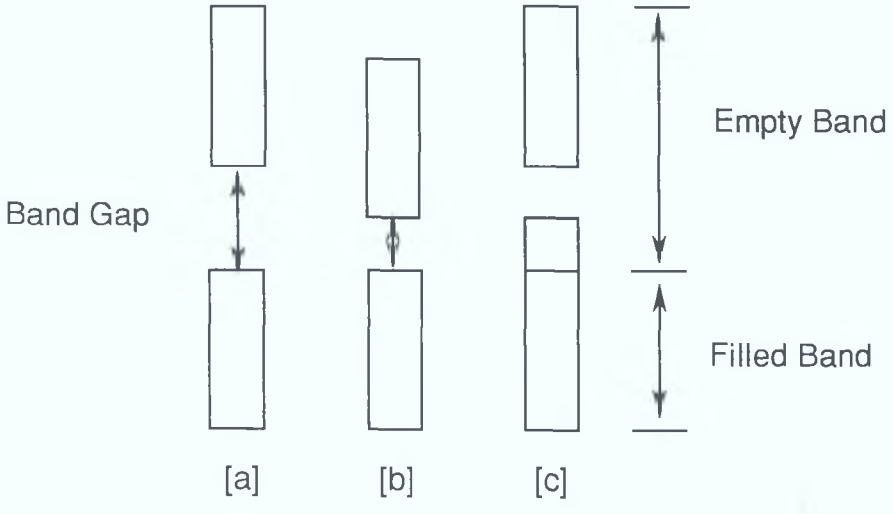


Fig 1.1 Band Structure of (a) an insulator (b) a semi-conductor (c) a metal

When the structure of the first 'organic metal' TCNQ-TTF[3] was determined by X-ray crystallography, it was found that it consisted of the acceptor and donor molecules complexed together in segregated stacks This resulted in considerable π-electron overlap and delocalisation This complex has been extensively studied due to the relative ease of growing single crystals of good size and quality and also due to its structural, electrical and magnetic properties X-ray analysis has shown that this organic metal exists with 'ring over bond' overlap, with the exocyclic carbon-carbon double bond of the acceptor lying over the ring of the molecule adjacent to it in the stack Other studies have shown that charge-transfer of TTF to TCNQ is incomplete with 0 59 electrons in the TCNQ band producing two incomplete bands[4] Hence, both stacks contribute to the complex's metallic conductivity These compounds have been labeled quasi one-dimensional metals due to their anistropic behaviour This means that electron transport is associated with one preferred direction, usually by several orders of magnitude, whereas the electrons in metals can move in three directions In the quasi one-dimensional compounds the electrons can only move in one and cannot avoid one another and tend to interact more strongly This results in more phase transitions caused by Peierls distortions and increased π-electron interactions

1.3 Superconductivity

This has been defined as the ability to conduct an electrical current without resistance A theory of superconductivity was proposed in 1957 by Bardeen, Cooper and Schrieffer now known as the BCS theory[5] They stated that this phenomenon of superconductivity arose when electrons of a conductor formed loosely bound pairs called Cooper pairs These electrons move at the same speed but in opposite directions The properties of this Cooper pair are sufficiently different from those of ordinary electrons for it to be treated as an entirely new conducting particle It is the highly coordinated motion of the Cooper pair which then brings about superconduction However, when dealing with one-dimensional systems, such as those of charge-transfer salts, some problems are encountered It was pointed out by Peierls[6] that uniform separation between adjacent planes of molecules, characteristic

of TCNQ-TTF at room temperature, is not energetically favourable at all temperatures

It is considered that conducting organic charge-transfer complexes (CTCs) are equivalent to arrays of one dimensional molecules with more electrons than required for valence bonding The extra electrons should contribute only to incomplete occupation of the conduction band whose interaction with neighbouring bands determine its width However, Peierls distortion does not allow long range order and the result is an unstable lattice at lower temperatures This causes a change in the distribution of the valence electrons The charge density of the electrons is concentrated in one region with reduced electron density in another, resulting in a charge density wave (CDW) The partially filled valence band splits into two bands, the upper being completely empty and the lower band filled This CDW results in the formation of an insulator or, at best a semi-conductor This transition typically occurs between 50 and 100 Kelvin TCNQ-TTF makes the transition to semi-conductor below 53K

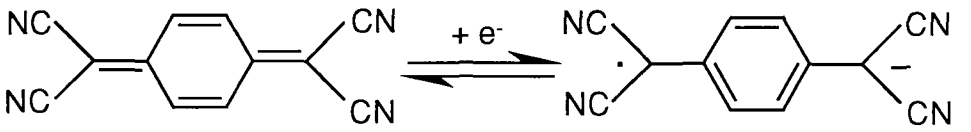
1.4 Design of charge-transfer complexes

1.4.1 Introduction

The essential attributes required to create a molecular metal include partial occupation of the band (due to electron transfer), strong intermolecular interactions (which give rise to a delocalised electronic band structure in the solid) and planar components of high symmetry and similar size Also, when a donor and acceptor overlap, the degree of charge-transfer determines whether the product will be a charge-transfer complex or a radical salt, the former resulting from partial charge-transfer with the latter as a consequence of complete charge-transfer Because our ability to induce molecules to pack within a crystal lattice in a prescribed manner is limited, it is only possible to design these complexes with respect to the properties of the individual components, the acceptor and the donor The next section of this chapter looks at each of these in turn

1.4.2 Acceptors

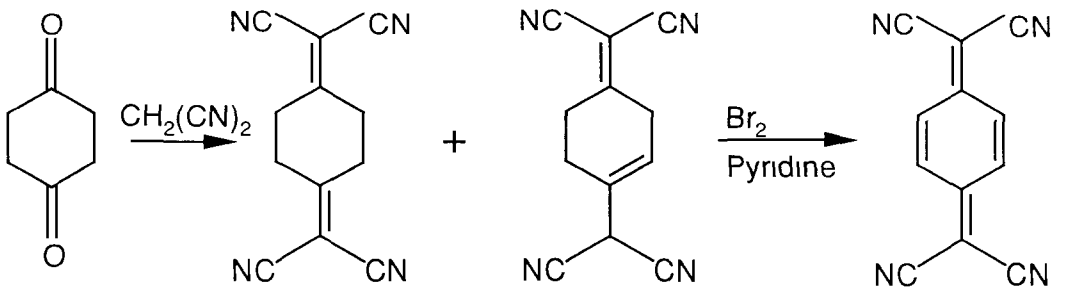
Acceptors compounds have high electron affinity due to the presence of low-lying empty π-molecular orbitals (LUMOs) When they receive an electron from a donor, resulting in reduction, it is delocalised over a number of atoms of the acceptor Examination of TCNQ, a powerful electron acceptor, allows us to see this more clearly



[2] Anion Radical

Scheme 1 01

The acceptance of an extra electron by TCNQ leads to the formation of an aromatic ring with six delocalised electrons, a highly stable system (scheme 1 01) It is the four conjugated bonds and its planar structure in association with the four electron-withdrawing cyano groups that give TCNQ its enhanced electron acceptor ability It was first synthesised by a condensation reaction of malononitrile with cyclohexane-1,4-dione [4], followed by bromination and dehyrobromination in pyridine (scheme 1 02) Its structure is based on a combination of tetracyanoethylene (TCNE), a highly electron deficient electrophilic reagent[7] and p-benzoquinones,[8] a strong electron acceptor



[4] [2]

Scheme 1 02

1.4.2.1 Synthesis of TCNQ derivatives

There are three main categories of derivatives that have been synthesised These include

a π-extended derivatives of TCNQ

b heterocyclic derivatives of TCNQ

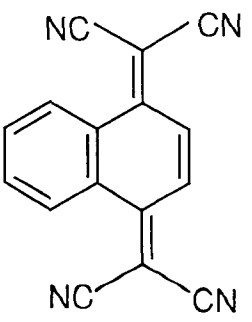
c substituted derivatives of TCNQ

By synthesising these various derivatives, it was possible to investigate the effects of planarity and their ability to stabilise the radical formed on reduction of these acceptors It was known that in TCNQ anions, the excess electron density resides on the terminal dicyanomethylene group, so this functional group has been retained in most of the following new acceptors

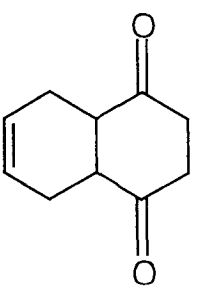
1.4.2.1a π-Extended derivatives of TCNQ

Extension of the π-system of TCNQ was investigated to synthesise products with better overlap to widen band widths The critical studies have proposed a lowering in the intramolecular Coulombic repulsion leading to highly conducting charge-transfer complexes on extension of the π-system of the TCNQ ring

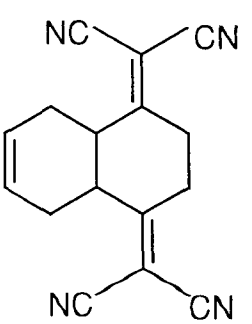
Benzo-TCNQ [5] was one of the first of the π-extended derivatives of TCNQ to be synthesised [9] This was achieved from the condensation of *cis*-2,3,5,8,9,10-hexahydro-1,4-naphthaquinone [6] with malononitrile to yield 11,11,12,12-tetracyano-(*cis*-2,3,5,8,9,10-hexahydro)naphtha-1,4-quinodimethane [7] Subsequent bromination with N-bromo-succinimide in acetonitrile/dichloromethane followed by dehydrogenation with anhydrous pyridine afforded the benzo-TCNQ compound [5]



[5]



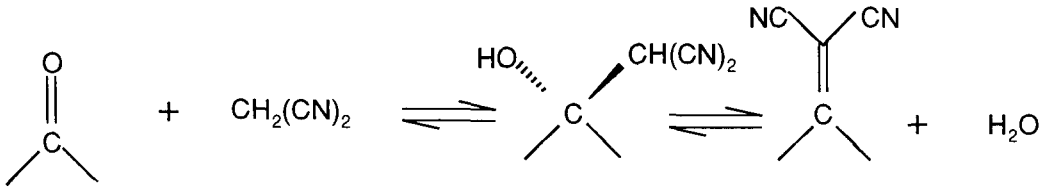
[6]



[7]

It was found to retain the π-acid character of TCNQ forming a wide range of π-complexes with many aromatic hydrocarbons including anthracene and perylene However, charge-transfer complexes were not formed with the strong donor, TTF, in constrast to what had been found for TCNQ

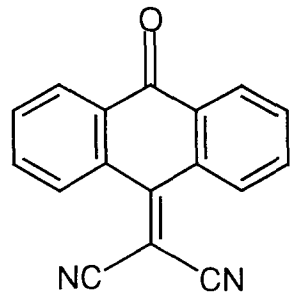
Conversion of aromatic carbonyls to dicyanomethylene groups is a condensation reaction with malononitrile which proceeds readily, scheme 1 03



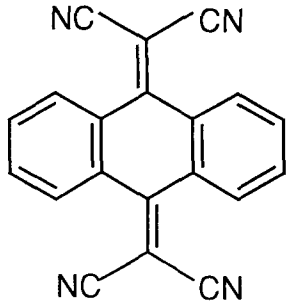
[8]

Scheme 1 03

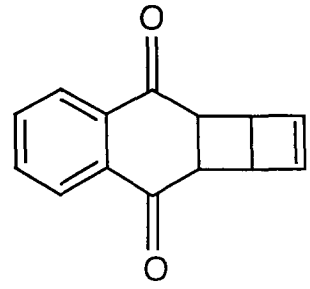
However, this does not occur for quinones such as anthraquinone, due to excessive overcrowding in the molecule This has been overcome by use of a Lewis acid, titanium tetrachloride, which effectively promotes the condensation by first activating the carbonyl functions of anthraquinone for condensation, by complexation, and subsequent irreversible removal of water from [8] [10] This condensation reaction was found to be so effective that in the synthesis of 11,11,12,12-tetracyanoanthra-9,10-quinodimethane (TCNA) [10], the monosubstituted species [9] could not be isolated, only giving [10] as the product A previous synthesis of [10] from the diketone [11] by dicyanomethylenation with a large excess of malononitrile in the presence of β-alanine and dimethylformamide[11] has also been reported This resulted in such low yields that the alternative route using the Lewis acid catalyst became the most useful method for effective dicyanomethylenation reactions of quinones



[9]



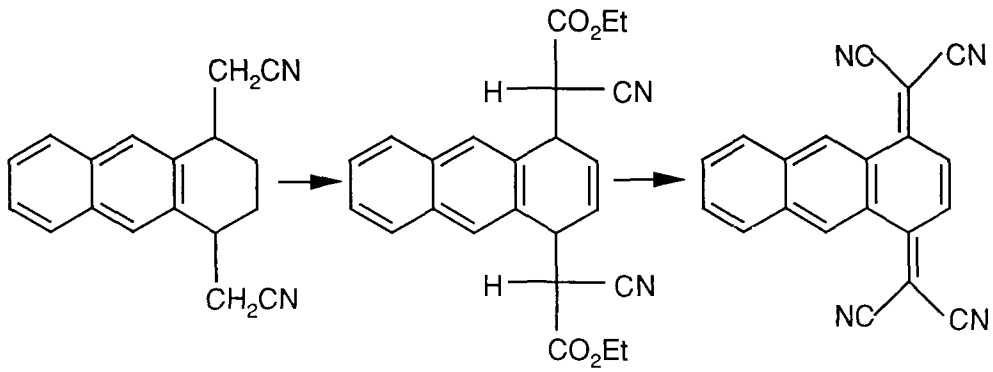
[10]



[11]

Electron affinity measurements for this new compound [10] indicated reasonably high values [10] However, attempts to synthesise charge-transfer complexes, even with strong donors such as TTF proved unsuccessful

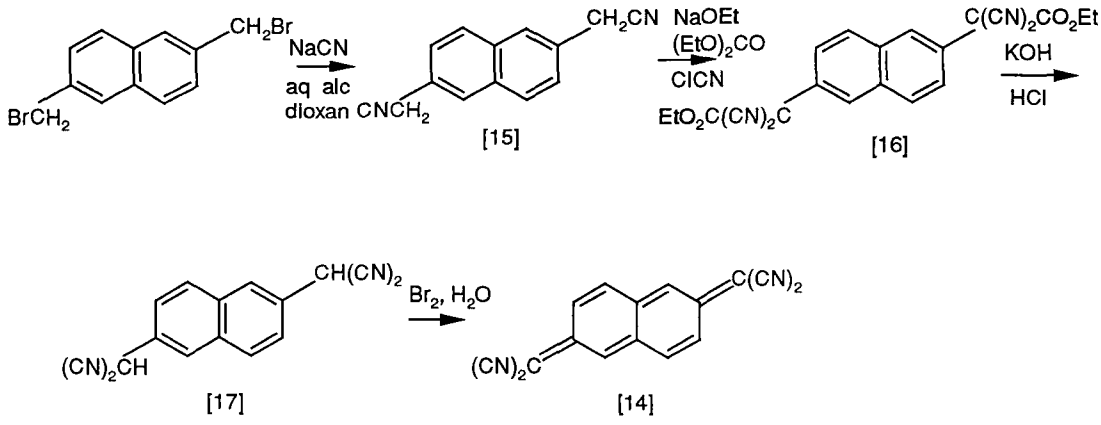
An isomer of [10] is naphtho-TCNQ [12][11] This was made from [13] using the method of Wheland and Martin,[12] scheme 1 04.



[13] [12]

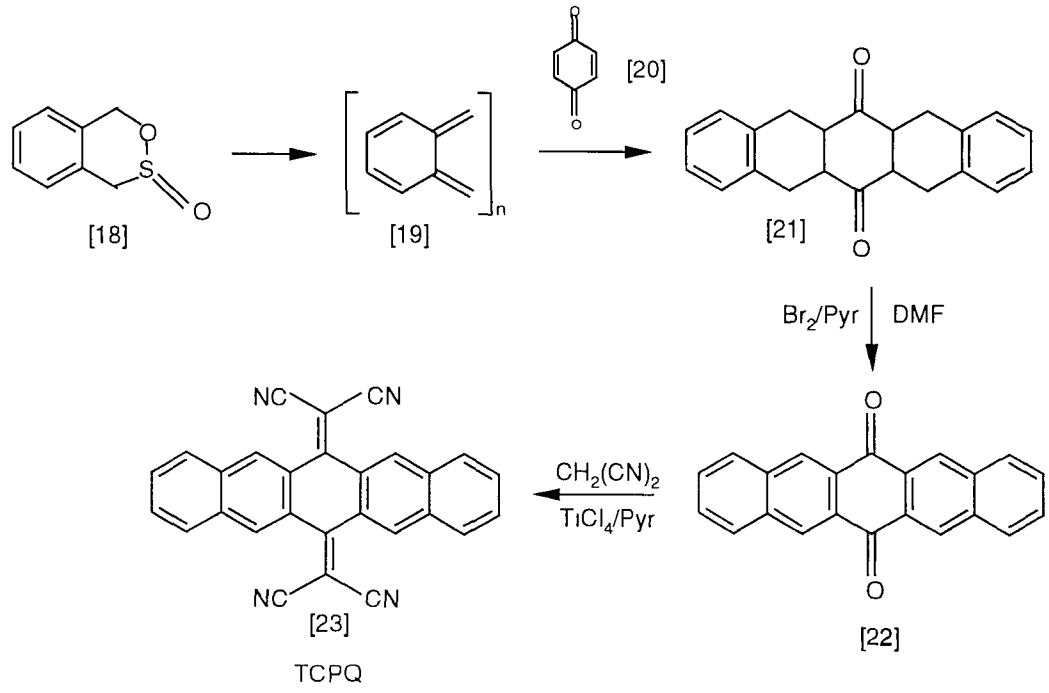
Scheme 1 04

Another π-extended TCNQ derivative, 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane (TNAP) [14] was first prepared in 1963[13] and an improved synthesis by Sandman and Garito[14] was formulated in 1973 This involved reaction of 2,6-bis(bromomethyl)naphthalene with sodium cyanide in an aqueous alcoholic dioxan solution at room temperature This yielded 2,6-naphthalenediacetonitrile [15] Subsequent reaction of [15] with sodium ethoxide and diethylcarbonate, followed by reaction of the resultant dianion with cyanogen chloride gave diethyl 2,6-naphthalene-α,α,α',α'-tetracyanodiacetate [16] TNAP was then formed on hydrolysis and decarboxylation of [16] and oxidation of the resultant product [17], scheme 1 05



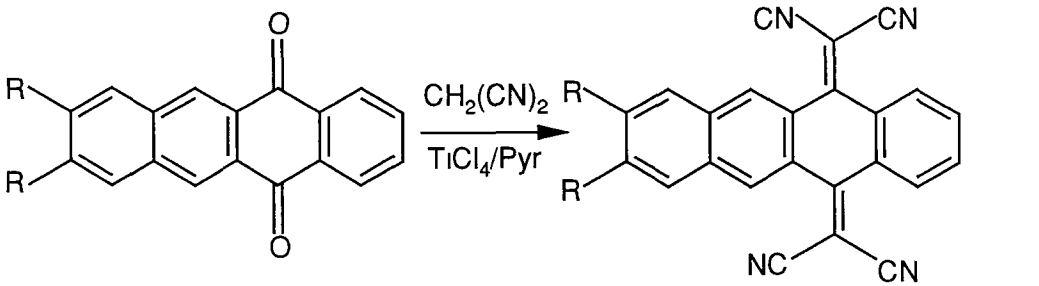
Scheme 1 05

On reaction with TTF, TNAP yielded a 1 1 complex of TTF TNAP This extended system has helped to reduce Coulombic interactions, resulting in slightly stronger electron affinity, a higher polarizability and a smaller on-site Coulomb repulsion than TCNQ itself [15] Substitution on the basic TCNQ skeleton results in π-complexes that are less conducting than those of TCNQ itself This behaviour could be explained with lower acceptor properties in some cases or to the complete charge-transfer of stronger electron acceptors in other cases [16] Here we describe the synthesis of TCNQ analogues in which the extension of the π-system has been increased systematically, scheme 1 06



Scheme1 06

In the synthesis of 15,15,16,16-tetracyano-6,13-pentacenequinodimethane (TCPQ) [23], the initial step involved reaction of p-benzoquinone [20] with o-quinomethane [19] which was generated in situ from the 1,4-dihydro-2,3-benzothiin-3-oxide [18] [17] This product was then easily oxidised by bromine/pyridine in dimethylformamide to give [22], the pentacenedione Compound [23] was subsequently formed on reaction of [22] with malononitrile using pyridine as base, in the presence of titanium tetrachloride as catalyst



[24a-c]

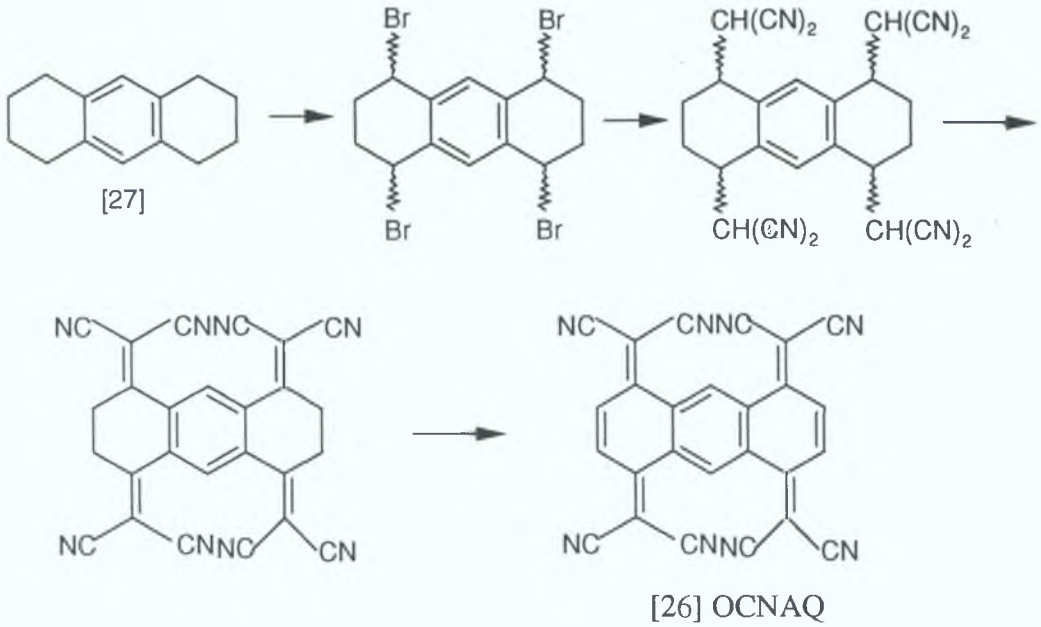
[25a-c]

a R=H
b R=CH_3O
c R=(-CH=CH-)$_2$-

Scheme 1 07

The quinones [24a-c], were similarly converted to the corresponding substituted tetracyanonaphthacenequinodimethanes [25a,b] and tetracyanopentacene quinodimethane [25c] respectively, scheme 1 07 Cyclic voltammetry indicated for TCPQ that it is a poorer electron acceptor than TCNQ [18] However, the small difference between midpoint potential for the first and second reduction (ΔE = 0 34 V) compared to that of TCNQ (ΔE = 0 56 V) suggests, that the intramolecular Coulomb repulsion is reduced in TCPQ [23] owing to the extension of the π-system

The synthesis of 11,11,12,12,13,13,14,14-octacyano-1,4 5,8-anthraquino-tetradimethane (OCNAQ)[19] [26] is outlined below, scheme 1 08



[27]

[26] OCNAQ

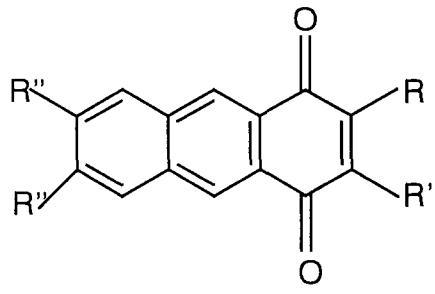
Scheme 1.08

Introduction of an electron into OCNAQ results in equal sharing of the charge density by both TCNQ nuclei. It was expected that the charge dispersal resulting from the reduction of the on-site Coulomb repulsion would enhance OCNAQ's ability to accept an electron. Its synthesis consisted of bromination of octahydroanthracene [27] with N-bromosuccinimide, followed by dicyanomethylation with excess sodiomalononitrile with a successive bromination-dehydrobromination procedure yielding [26]. Cyclic voltammetry has confirmed[19] that it is a stronger acceptor than TCNQ and it has formed CTCs with both TTF and tetraethylammonium iodide.

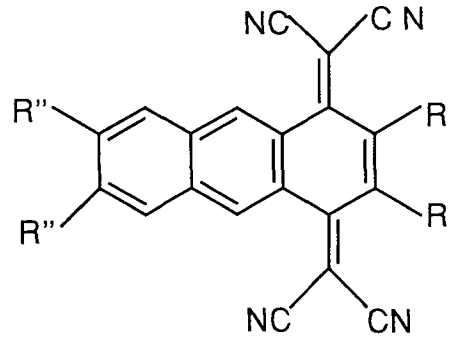
Theoretical studies suggest that the extension of the π-system of the TCNQ ring would result in a lowering of the intramolecular Coulomb repulsion leading to highly conducting charge-transfer complexes. However, when the π-system is extended laterally on both sides, the steric hindrance of the aromatic peri-hydrogens with the dicyanomethylene groups of the TCNQ moiety results in highly distorted molecules exhibiting poor acceptor abilities.[20] Thus, the synthesis of π-extended molecules was undertaken because these possible acceptors are less sterically hindered than the 2,3-5,6 benzene-fused TCNQ derivatives previously described.[16]

1,4-TCAQs [29] have been prepared from corresponding substituted anthracenediones [28], by reaction with malononitrile in the presence of titanium tetrachloride,[21] (Lehnert's reagent). The presence of different substituents in the 2 and

3 positions of the TCNQ allows fine-tuning of the acceptor abilities of these molecules



[28]

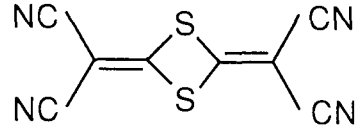


[29]

1.4.2.1b Heterocyclic derivatives of TCNQ

The inclusion of heteroatoms in CTCs contribute to increased interstack and intrastack interactions These then enhance the conductivity and stabilisation of the metallic state

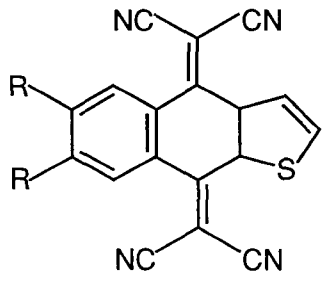
In the first example of a heterocyclic derivative of TCNQ, the carbon to carbon double bond in a cyclic system was replaced by a sulphur atom [30] [22] This is a system isoelectronic to TCNQ and of comparable stability



[30]

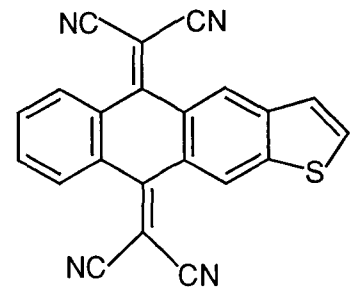
This was easily synthesised from 1,1-dichloro-2,2-dicyanoethylene and dipotassium 2,2-dicyanoethylene-1,1-dithiolate in dichloromethane Compound [30] has shown electron acceptor ability by formation of a 1 1 charge-transfer salt with the donor molecule TTF This salt, however, proved to be electrically insulating

π-Extended systems with one sulphur atom include [31] and [32].[23] These



[31a] R = H

[31b] R = Cl

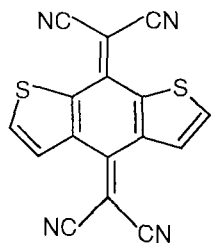


[32]

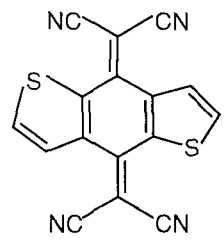
compounds were synthesised by a titanium tetrachloride-catalysed condensation reaction from the corresponding quinones at room temperature Both molecules showed poor reduction potential and did not form crystalline complexes when treated with TTF and LiI Compound [32] also demonstrated a highly distorted structure from X-ray analysis

Synthesis of [31b][24] was carried out by methods similar to that above Acceptor ability measurements are comparable to those of TCNQ, indicating a two electron transfer Substitution with chlorine, an electron withdrawing group, significantly decreased the reduction potential when compared to [31a] Overall, however, replacement of the benzene ring with a thiophene ring leads to better acceptors, due both to electronic factors as well as reduced steric hindrance This is due to sulphur atoms in the ring preventing unfavourable steric interaction found in the TCNQ-type derivatives between the peri-hydrogens of the π-system and the cyano groups

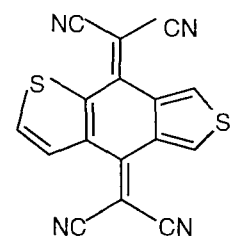
Synthesis of heterocyclic derivatives of TCNQ with greater than one heteroatom have also been investigated [25] These included [33]-[36]



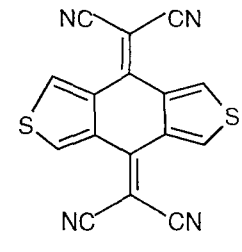
[33]



[34]



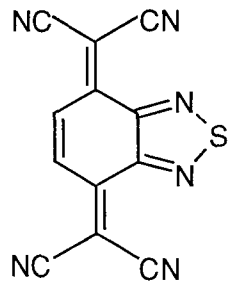
[35]



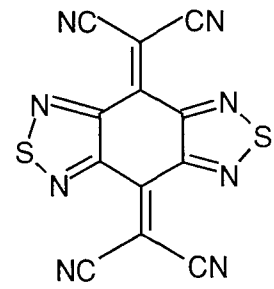
[36]

It was anticipated that fusion of a larger number of thiophene units onto the TCNQ molecule would have a greater effect on the properties of the charge-transfer salts and would enable better models for molecular design of synthetic metals Both [33] and [34] formed 1 1 charge-transfer complexes with TTF while [35] and [36] did not This was due to the ability of [33] and [34] to gain aromatic stabilisation on reduction Also, these two compounds had reduction potential values comparable to that of TCNQ while cyclic voltammetry results indicated [35] and [36] to be weak acceptors For compounds [35] and [36] the intramolecular Coulombic repulsion is reduced as the two sulphur atoms are located further apart in the molecules This explains the inability of these compounds to form charge-transfer compounds with TTF

Heterocyclic derivatives of TCNQ, [37] and [38], containing different types of heteroatoms have also been examined [26]



[37]



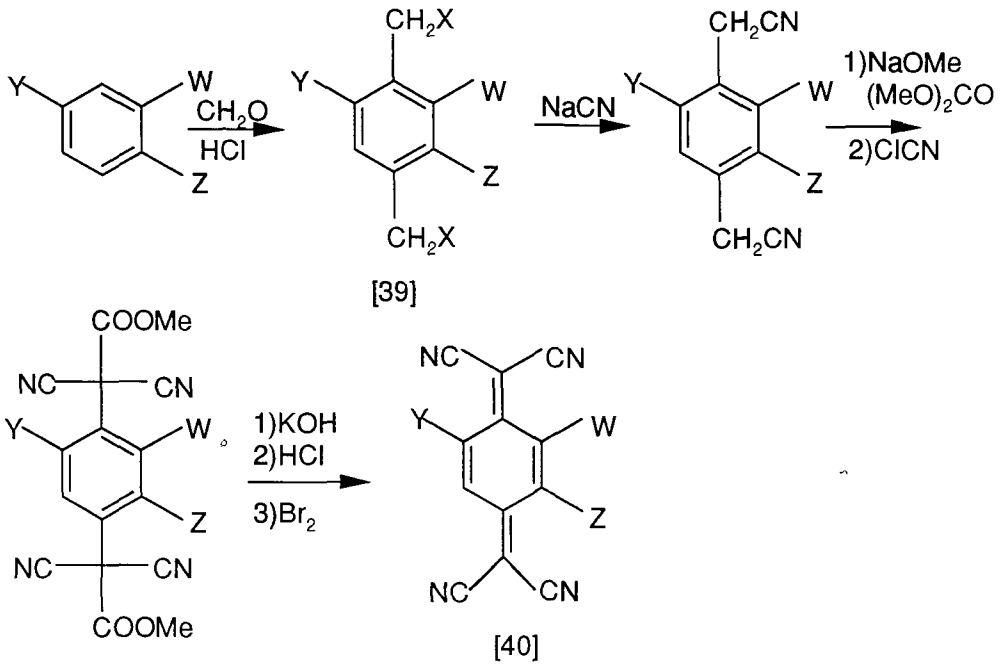
[38]

It was thought that due to the sulphur and carbon-nitrogen double bond interheteroatom interactions, there may be a contribution to the suppression of metal-insulator (M-I) transitions Compound [38] only formed a semi-conducting CTC on reaction with TTF, due to mixed stack formation caused by heteroatom interactions and inclusion behaviour This problem was overcome by removal of one of the heteroatom components to give [37] X-ray analysis indicated that [37] was a planar compound It was found that [37] gave highly conducting charge-transfer complexes with TTF, in contrast to [38] Elimination of the heterocycles prevents formation of inclusion cavities

1.4.2.1c Substituted TCNQ derivatives

To preserve planarity, which is essential for charge-transfer complex formation, substituents attached to the ring must be non-bulky Deviations from planarity arise from steric interactions between dicyanomethylene groups and the peri-hydrogens

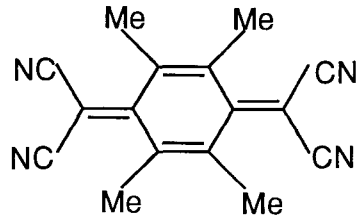
Wheland and Martin[12] synthesised an extensive range of substituted 7,7,8,8-tetracyanoquinodimethanes The substituents on the ring included halogens, alkoxy and alkyl groups



Scheme 1 09

The synthesis (scheme 1 09) involved starting with the corresponding p-xylylene dihalide [39] The substituents on this benzene ring were then retained in the final substituted TCNQ compound [40]

Rosenau et al[27] synthesised 2,3,5,6-tetramethyl-7,7,8,8-tetracyano-p-quino-dimethane [41], a tetrasubstituted TCNQ derivative by reaction of 1,4-diiodo-2,3,5,6-tetramethylbenzene with malononitrile, sodium methoxide, CuI and hexamethylphosphoric acid triamide (HMPT) (a method used for the preparation of arylmalononitriles) and subsequent oxidation of the product yielded the tetrasubstituted derivative



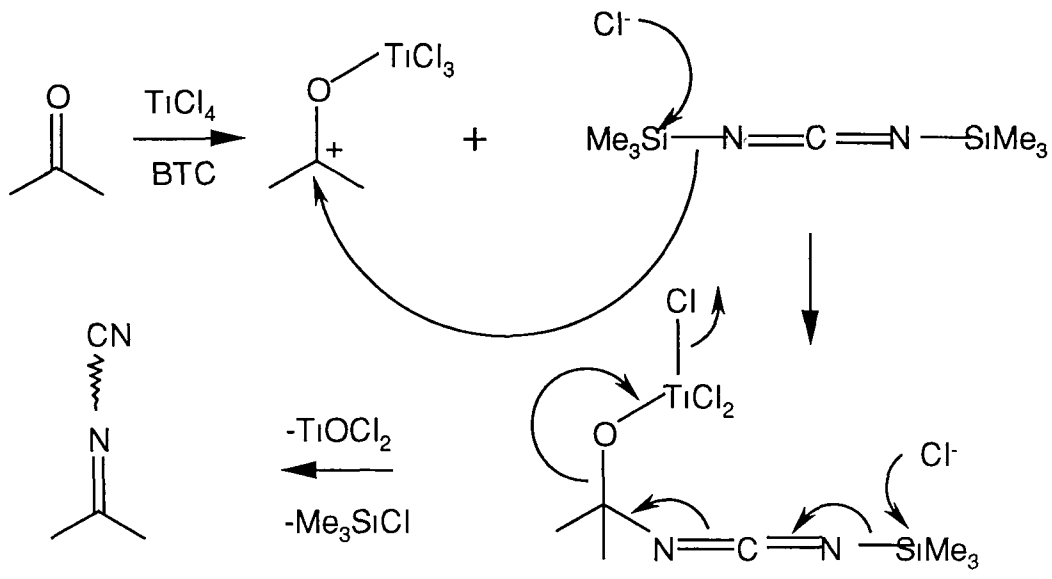
[41]

Because this was a sterically crowded molecule, the resultant X-ray structure indicated a very strong deformation of the TCNQ skeleton with the cyano groups also deviating from linearity This extra bulk strongly influences the packing of the compound and as a result reduces its ability to form electron donor-acceptor complexes

Comparison of the reduction potentials of substituted TCNQs have shown that as the number and size of alkyl groups are increased, the acceptor ability decreases [28]

1.4.2.2 Alternative electron acceptors : N, N'-dicyanoquinonediimines (DCNQIs)

Replacement of the classical acceptor TCNQ with DCNQI acceptors has opened new routes for organic conducting materials Some steric drawbacks were associated with the Y-shaped $=C(CN)_2$ groups, so in 1984 Aumuller and Hunig replaced this group with the L-shaped =NCN [29] The synthesis of these new compounds involves a one-step conversion of >C=O to >C=NCN This method is applicable to non-enolizing ketones and p-quinones The synthesis involves the use of bis(trimethylsilyl)carbodiimide with titanium tetrachloride as an auxiliary agent The mechanism is given in scheme 1 10

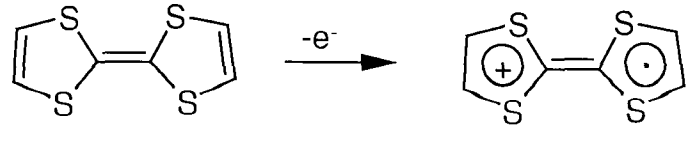


Scheme 1 10

Owing to the small angle formed by the =NCN in this class of compounds, even tetrasubstitution has almost no effect on planarity This strong tendency to preserve planarity is of great importance in charge-transfer complex formation These compounds were found to have acceptor strength comparable to TCNQ However, it was found that DNCQI and its derivatives, on formation of organic metals, did not undergo Peierls distortion even at low temperatures [30] The 1 2 copper salt of 2,5-dimethyl-DCNQI was found to have a conductivity of σ (3 5K) = 5 x 10^5 Scm^{-1} An analogous $(TCNQ)_2Cu$ salt was found only to have semiconducting abilities

1.4.3 Donors

These species must be able to readily donate an electron to an electron-deficient acceptor, have a planar, symmetrical structure to allow for increased overlap in the formation of organic metals and on oxidation to the cation and dication, sustain stable characteristics TTF is one of the best known donors and displays all of the above attributes



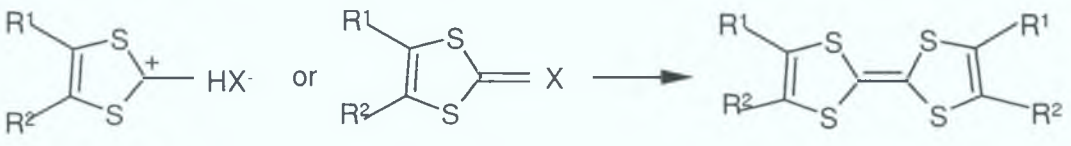
Scheme 1 11

It consists of four large sulphur heteroatoms and a conjugated system. These heteroatoms each contain two lone pairs of electrons, one of which resides in an orbital in the plane of the molecule, the other in an orbital at right angles to the plane. There is an overlap of the double bonds and the four orbitals at right angles to the plane giving a total of 14 delocalised electrons. TTF, on losing an electron to form a radical cation, scheme 1.11, forms a species with aromatic properties due to the fact that there are now 13 remaining delocalised electrons shared unequally between the two rings, one containing six, the other seven. It is the ring with the six electrons, characteristic of an aromatic compound, and overall delocalisation which contribute to its stability as a donor.

Since the discovery in 1972 that TTF possesses both electron donating ability and its ability to form highly conducting C-T complexes with TCNQ, extensive investigations into the synthesis of improved donors based on TTF have been carried out. A brief outline of the synthesis of the more important donors is given here.

1.4.3.1 Synthesis of TTF

The synthesis of TTF [3] has followed various routes.[31] It generally proceeds via a coupled reaction of 1,3-dithiolium salts, 1,3-dithiole-2-thiones or 1,3-dithiole-2-ones, scheme 1.12.



[42] X = BF_4^-
X = PF_6^-

[43] X = S
[45] X = O

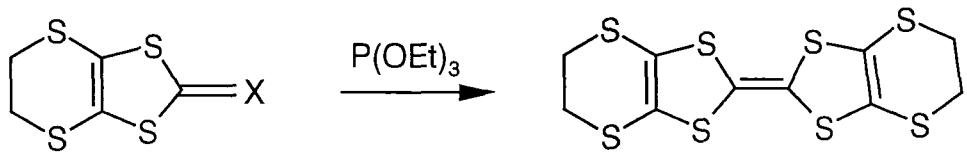
[3] $R^1 = R^2 = H$
[46] $R^1 = R^2 = -(CH_2)_3-$
[47] $R^1 = R^2 = CH_3$

Scheme 1.12

This method has also been applied to the synthesis of some TTF derivatives, hexamethylenetetrathiafulvalene, (HMTTF) [46][32] and tetramethyltetrathiafulvalene (TMTTF) [47].[33] These were the first compounds to indicate that substitution in the 2, 3 and 6, 7 positions of TTF can actually improve conductivity. TTF gave a value

of σ_{max} = 2 x 10^4 Scm^{-1}, with TMTTF and HMTTF values equal to 5 x 10^3, and 2 x 10^3 Scm^{-1} at T_{max} = 59, 60 and 75 K respectively

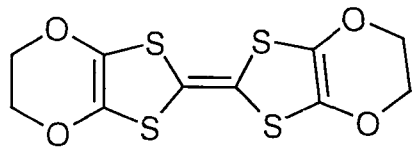
An interesting sulphur-based donor, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) (ET) [50] has been shown to exhibit superconductivity [34] Due to its extension of the basic TTF molecule and the intermolecular interactions of the sulphur atom, this has led to increased dimensionality which contributes to suppression of the M-I transition Various routes have been reported for the synthesis of ET,[35,36] the most common of which has been through the coupling of 4,5-bisalkylthio-1,3-dithiol-2-thione [48] or the analogous 2-ones [49], scheme 1 13



[48] X = S, [49] X = O [50]

Scheme 1 13

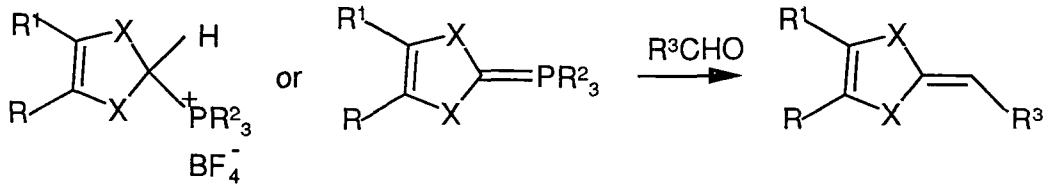
The oxygen equivalent of ET, bis(ethylenedioxo)tetrathiafulvalene[37] (BEDO-TTF) [51], has also been synthesised by replacing the sulphur atoms on the periphery with oxygen atoms This led to the first oxygen-containing donors



[51]

1.4.3.2 π-Extended TTFs

To reduce on-site Coulombic repulsion in the doubly ionised state of the donor, π-extension between the two dithiole units is carried out The general route towards these TTF derivatives involves the reaction of a 1,3-dithiole [52a] or a 1, 3-diselelole phosphonium salt [52b] or phosphorane [53] via Wittig or Wittig-Horner reaction with an aldehyde, scheme 1 14

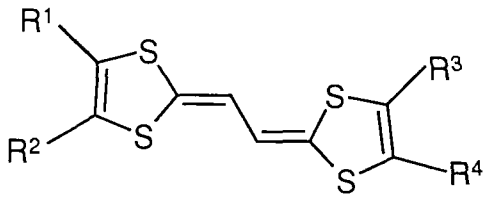


[52a] X = S [53] a X = S [54] a X = S

[52b] X = Se b X = Se b X = Se

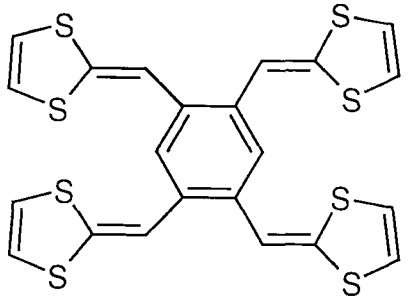
Scheme 1 14

The first vinyl analogue of TTF was synthesised by Yoshida[38] in 1983, ethanediylidene-2,2'-bis(1,3-dithiole) (EDBDT) [55] and consisted of two 1,3-dithiole rings connected by sp^2 hybridised carbons

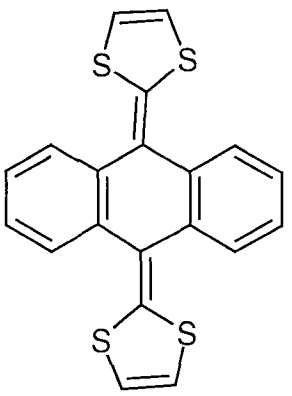


[55]

Many extended analogues of TTF have been made with increased numbers of sulphur heterocyclic moieties[39] These have contributed to reducing on-site Coulombic repulsions and have also augmented dimensionality through increased numbers of S-S intra- and inter-chain contacts Both [56] and [57] have been synthesised via Wittig and Wittig-Horner reaction



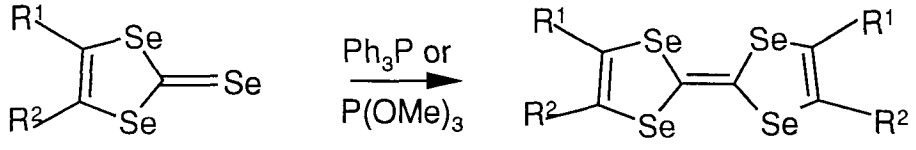
[56]



[57]

1.4.3.3 Selenium derivatives of TTF

It has been found that larger, more polarizable chalcogens stabilise radical cations, affording greater overlap of the orbitals, thereby producing wider conduction bands Both selenium and tellurium were the ideal replacements for sulphur due to their extended d-orbital It was found that the synthesis of selenium derivatives was far more facile when compared to that of the tellurium derivatives [40] Tetramethyltetraselenafulvalene (TMTSF) [59a] and tetraselenafulvalene (TSF) [59b] were synthesised by phosphine or phosphite coupling of compounds [58a] and [58b], scheme 1 15



[58] a $R^1 = R^2 = Me$ [59] a $R^1 = R^2 = Me$

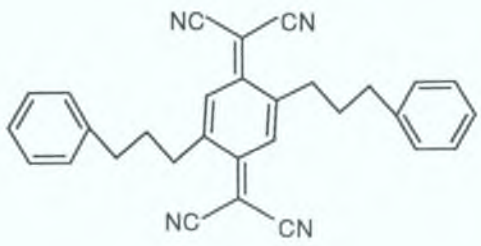
[58] b $R^1 = R^2 = H$ [59] b $R^1 = R^2 = H$

Scheme 1 15

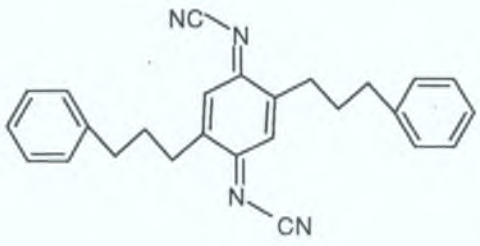
In the synthesis of the 1 1 salt of TSF-TCNQ, it was found to have a room temperature conductivity of $\sigma = 800$ Scm^{-1} [41] Its M-I transition occurred at ~ 40 K, 18 K below that of TTF-TCNQ, indicating its enhanced metal qualities due the incorporation of the selenium heteroatom $(TMTSF)_2PF_6$ was found to be the first organic superconductor which state was induced at 12 Kbar pressure and 0 9 K [42] In this case the material can be made superconducting if the Peierls distortion is suppressed by modification of TTF-TCNQ

1.4.4 Single-component donor-acceptor complexes

In recent times, new single-component D-A organic semiconductors derived from TCNQ have been synthesised [43] In one example, the acceptor TCNQ and DCNQI moieties are covalently linked to a weak donor, a phenyl ring, by three methylene units It was intended that they would exist as donor-acceptor-donor (D-A-D) systems



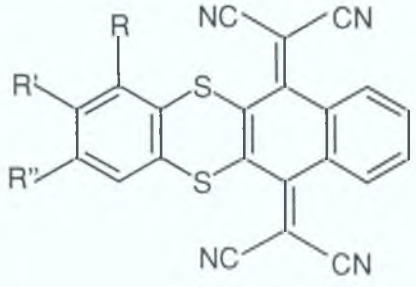
[60]



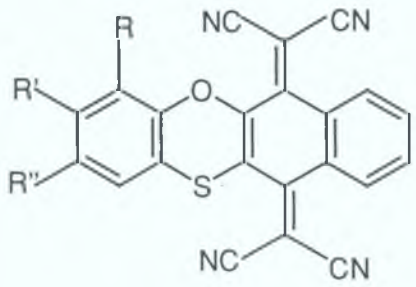
[61]

It was anticipated that by having both acceptor and donor moieties present in the same organic molecule, there could be better control over conductivity and the donor to acceptor ratio. Synthesis of both compounds [60] and [61] was a multistep procedure starting with the diketone analogue. Cyclic voltammetry indicated that the disubstitution did not alter their electrochemical properties. In fact, there was little deviation from that of the central TCNQ and DCNQI rings. These compounds behaved like disubstituted derivatives rather than charge-transfer complexes.

In an second example,[21] single component donor-acceptor compounds where these moieties were linked by two sulphur atoms (or S/O atoms), were investigated.



[62]



[63]

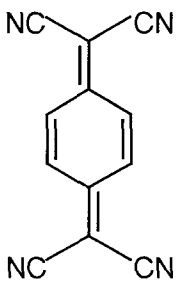
Synthesis was via a titanium tetrachloride catalysed condensation reaction from the corresponding quinones of [62] and [63]. These target molecules had several advantages. Firstly, it was possible to tune the degree of electron transfer by varying the substituents due to the fact that there was a fixed donor:acceptor stoichiometric ratio. Secondly, fusion of the benzene ring to the TCNQ moiety contributed to a decrease in on-site Coulombic repulsion. Thirdly, the solid-state crystal packing could be adjusted by varying the intermolecular connectivity. Finally, heteroatoms in the molecule may have reinforced the intermolecular interactions in the solid state. UV/visible spectroscopy of these compounds indicated the presence of an intramolecular electronic transfer from donor to acceptor moiety.[21]

Chapter 2

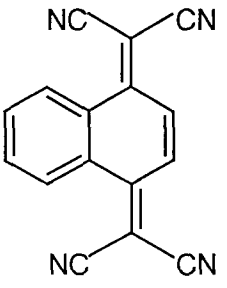
Investigation of the synthesis of N-alkyl derivatives of benzo-TCNQ

2.1 Introduction

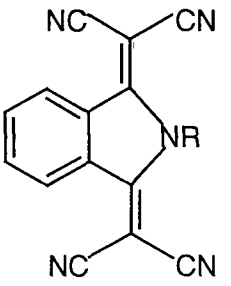
In chapter 1 it was seen that there has been significant interest in the synthesis of TCNQ [3] derivatives This was due to the ability of these compounds to combine with a wide variety of donors forming charge-transfer complexes It was found that many of these complexes have high conducting abilities while others possess superconductive qualities The useful properties of these TCNQ analogues have thus prompted our interest in the synthesis of new heterocyclic compounds analogous to TCNQ It was anticipated that by introducing heteroatoms into the TCNQ moiety or adjacent fused rings, the acceptor ability might be modified favourably by changes in Coulomb repulsion and also in intermolecular interaction



[3]



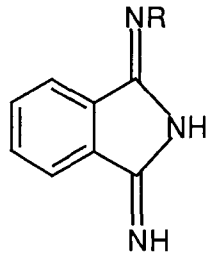
[64]



[65] R = H
[66] R = Me

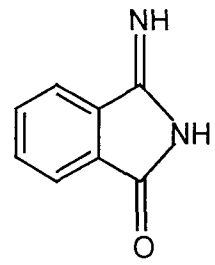
Previously compounds [65] and [66] had been reported [44,45] The methyl derivative [66] has been reported in a patent by the BASF Company, but experimental details have not been indicated Previous work[44] in our laboratory also investigated the synthesis of the methyl derivative [66], achieved in a number of steps Due to the success of this synthesis, we decided to base further reactions on it in an attempt to synthesise a range of N-substituted derivatives of benzo-TCNQ [64] It was anticipated that this would produce a range of new acceptor compounds including those with a potential for linking the acceptors intramolecularly to other systems

The precursors to [65] and [66] are imidines Extensive investigations of these compounds had been carried out by Elvidge and co-workers in the 1950s [46] This work involved base condensation reactions of the imidines [67a,67b], the oxo-isoindoline [68] and succinimidine [69] with various methylene compounds

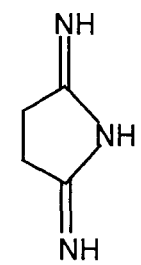


[67a] R = H

[67b] R = Ph



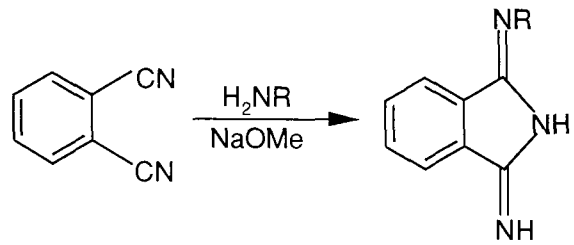
[68]



[69]

Results indicated that the exocyclic imino group of [67-69] was readily reactive with a variety of active methylene compounds whereas the carbonyl group of [68] proved unreactive on addition of a base [46(a)] It was this reactivity with active methylene compounds which proved to be a key-step in the synthesis of [65] and [66]

To synthesise [65] and [66] the first step involved either the synthesis of [67a] or [67b] Compound [67a], 1,3-diiminoisoindoline was synthesised[47] by reaction of ammonia with phthalonitrile [70], scheme 2 01 Elvidge synthesised [67b] by reaction of phthalonitrile with one equivalent of aniline [48]

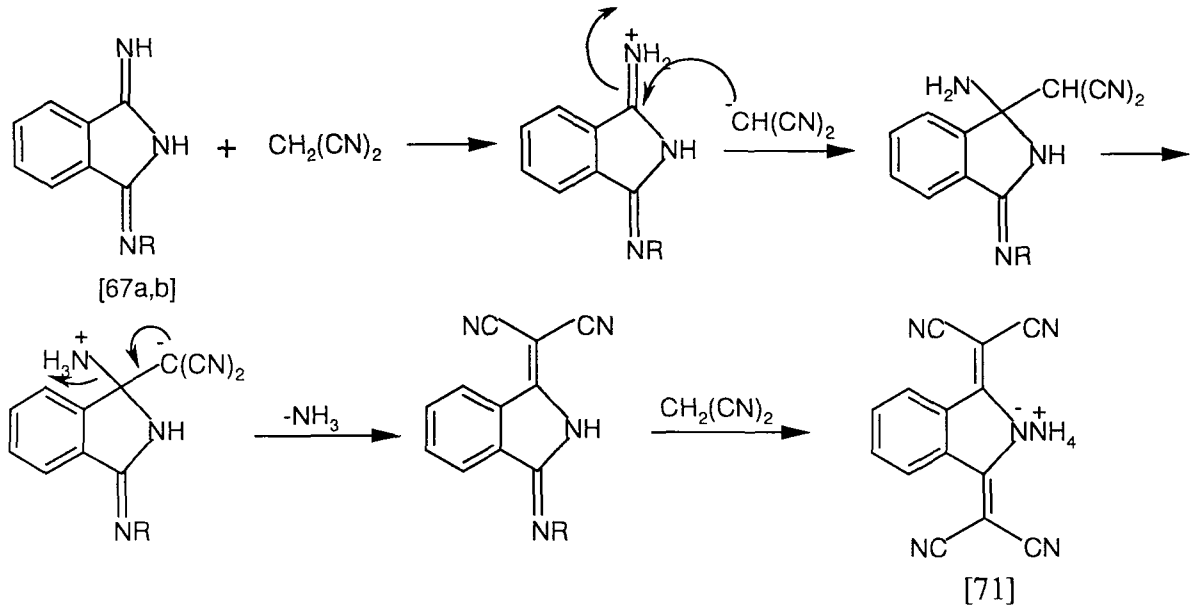


a R = H
b R = Ph

[70] [67a, b]

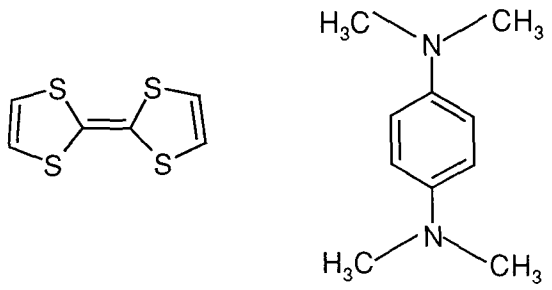
Scheme 2 01

The ammonium salt [71] was then synthesised[44] by addition of malononitrile to [67a] or [67b] in dimethylformamide at room temperature Acidification of the salt [71] then yielded the N-analogue [65] of benzo-TCNQ A possible mechanism for this reaction is given in scheme 2 02



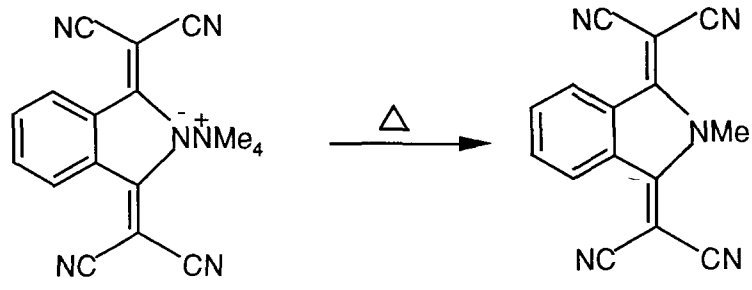
Scheme 2 02

It was thought that the active methylene compound attacked at the imino carbons of [67a, b] producing [71] and ammonia or aniline respectively Electron-acceptor ability of [65] was then confirmed by formation of charge-transfer complexes with the donors TTF [3] and TMDA [72] [44]



[3] [72]

The N-methyl analogue was synthesised[44] from [71] in two further steps They involved the conversion of [71] to the tetramethylammonium salt [73] followed by its subsequent pyrolysis This led to [66], scheme 2 03



[73] [66]

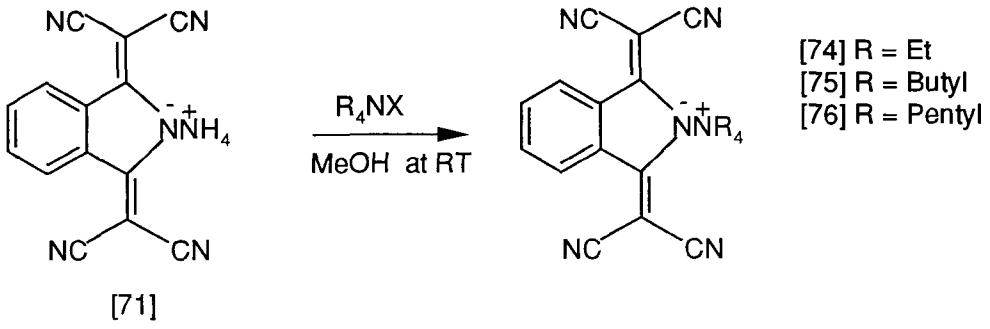
Scheme 2 03

This synthesis of [66] then formed the model for the attempted synthesis of a range of new acceptors, N-alkyl derivatives of benzo-TCNQ

2.2 Synthesis of tetraalkylammomum salts of [65]

A series of tetraalkylammonium salts of [65] was produced according to the method previously reported for that of [73] [44] The ammonium salt [71] was added to a methanolic solution of tetramethylammonium chloride producing [73] ^{1}H-NMR spectroscopy indicated two sets of aromatic multiplets integrating for two protons each There was only one other peak present at 3 08 ppm, a singlet representing twelve methyl protons This data alone pointed towards a very symmetrical compound ^{13}C-NMR spectroscopy confirmed the symmetrical characteristics of the product by the presence of three aromatic carbons Two nitrile absorptions were observed at 117 23 and 116 28 ppm with the C_1 and C_2 carbon absorption of the 2,2-dicyanovinylidene group appearing at 59 73 and 172 73 ppm respectively The methyl absorption at 54 34 ppm occurred as a triplet due to coupling with ^{14}N ^{13}C-^{14}N splittings are observed[49] when the nitrogen nucleus is in a relatively symmetrical environment, such as tetraalkylammonium salts It arises because ^{14}N has a spin of one and is quadrupolar In non-cubic surroundings, the nuclei generally relax so rapidly that all resolved couplings to them are lost In this case however, the nitrogen is in a cubic environment and so relaxes slowly producing the triplet This data in conjunction with IR spectroscopy results confirm that the product is the tetramethylammonium salt [73]

A series of new tetraalkylammonium salts [74]-[76] was synthesised, scheme 2 10 Compound [74] was synthesised from [71] and tetraethylammonium



Scheme 2 04

bromide ^{1}H-NMR data indicated similar results to those of [73] Two sets of aromatic multiplets at 7 63 and 7 17 ppm and a quartet at 2 72 with a triplet at 0 67 ppm integrating for 2 2 8 12 protons were observed This indicated a symmetrical product The ^{13}C-NMR spectrum contained nine unique carbons As for [73], there were three aromatic carbons, two nitrile absorptions, two dicyanovinylidene absorptions and two peaks observed for the aliphatic carbons of the tetraethylammonium group A C-H NMR correlation spectrum was run for this sample and all the salts to distinguish between the two closely occurring absorptions at ~ 50 ppm, table 2 1

Table 2 1 C-H Correlation results for the tetraethylammonium salt [74] of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile

^{1}H NMR Peaks /δ (ppm)	**^{13}C NMR Peaks / δ (ppm)**
0 67	7 09
2 72	54 01
7 17	131 46
7 63	122 94

It indicated that absorption at 54 01 ppm was due to the methylene carbon while the nearby absorption at 51.34 ppm represented the C_2 of the dicyanovinylidene group

This data confirmed that the product from the reaction was [74] and microanalysis results matched the molecular formula of the structure of [74]

Using tetrabutylammonium iodide and [71], the tetrabutylammonium salt [75] was synthesised The IR, ^{1}H and ^{13}C spectra and microanalysis were consistent with the assigned structure of [75] The ^{1}H-NMR spectrum confirmed that the product was symmetrical with the presence of two aromatic multiplets at 8 09 and 7 64 ppm in the ration 2 2 Aliphatic protons were observed as four multiplets between 3 15 and 0 90 ppm. These peaks integrated for a total of 36 protons The ^{13}C-NMR spectrum also indicated a symmetrical compound Eleven signals were observed, four of these belonging to the tetrabutylammonium group The presence of a dicyano substituted carbon entity with peaks at 116 22, 117 22 and 53 92 ppm was also observed The C_1 carbon of the dicyanovinylidene group was present at 172 00 ppm The remaining three carbons were assigned as aromatic A C-H correlation spectrum was used here also to distinguish between the C_2 absorption of the dicyanovinylidene and the alkyl carbon attached to the nitrogen

Synthesis of the tetrapentylammonium salt [76] of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile involved the use of the salt, tetrapentylammonium iodide In this case also, spectral results and microanalysis were in agreement with the structure [76] The ^{1}H-NMR spectrum consisted of two sets of aromatic multiplets and a total of five multiplets in the aliphatic region between 3 14 and 0 91 ppm indicative of the pentyl protons The ^{13}C-NMR spectrum showed twelve unique carbons and was consistent with the presence of a tetrapentylammonium cation Cyano carbons occurred at 116 44 and 117 44 ppm, with the C_1 and C_2 of the dicyanovinylidene group at 172 21 and 54 14 ppm respectively This data also indicated that [76] was a symmetrical tetraalkylammonium salt

Table 2 2 compares the ^{13}C-NMR data for all of the tetraalkylammonium salts [73-76] and the ammonium salt [71]

Table 2 2 ^{13}C NMR data for tetraalkylammonium salts [73-76]

	71 δ/ppm	**73** δ/ppm	**74** δ/ppm	**75** δ/ppm	**76** δ/ppm
Cyano C	115 74 116 74	117 23 116 28	117 28 116 31	116 22 117 22	116 44 117 44
C=C(CN)$_2$	171 48	172 02	172 06	172 00	172 21
C=**C**(CN)$_2$	53 44	59 73	51 34	53 92	54 14
Quaternary Aromatic C	136 91	137 42	137 45	137 44	137 65
Aromatic CH	130 90 122 40	131 36 122 88	131 46 122 94	131 34 122 88	131 57 123 04
Alkyl C	_____	54 34	7 09 54 01	13 45 19 19 23 05 57 23	13 92 20 94 21 77 28 13 57 84

This comparison in chemical shift values indicates the strong similarities between all of these compounds confirming that they are all salts of the known compound [71] IR data for the compounds synthesised indicated similar results with cyano peaks occurring between 2203 and 2206 cm^{-1} in all cases A final comparison of [71] with the tetraalkylammonium salts [73-76] using UV/visible spectroscopy showed identical spectra with λ_{max} at 490 nm in each case The combination of the microanalysis results, IR, UV/visible and NMR spectroscopy has thus proven that the products of the reactions of [71] with tetraalkylammonium halides are the required salts [73-76]

2.3 Attempted N-alkylation using the tetraalkylammonium salts [73-76]

N-Methylation of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile [65] was previously achieved [44] by heating the tetramethylammonium salt [73] under reflux in 1,2-dichlorobenzene for 150 hours In our work, the pyrolysis was attempted using a higher boiling, slightly less polar solvent, 1,2,4-trichlorobenzene This solvent was

thought to contribute to a reduction in reaction times due to its higher boiling point. Also, this is a less-polar solvent which helps to increase the rate of reaction when dealing with a charged nucleophile and charged substrate.[50] It is an Sn2-type reaction where there is a charge separation in the transition state leading to uncharged products. The non-polar environment thus favours the formation of the uncharged species. It was anticipated that these two factors could lead to a more efficient result in the synthesis of the N-methyl derivative [66].

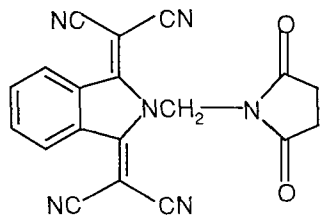
The tetramethylammonium salt [73] was heated under reflux for 24 hours in 1,2,4-trichlorobenzene. The progress of the reaction was monitored by TLC and slow formation of a fast running yellow band was observed increasing in intensity as the reaction progressed. Column chromatography and recrystallisation afforded 2,2'-(2-methyl-isoindolin-1,3-diylidene)bispropanedinitrile [66]. The IR, ^{1}H and ^{13}C-NMR spectra were consistent with the assigned structure. ^{13}C-NMR spectroscopy showed eight signals, three of which were aromatic and two representing the cyano groups. The three remaining carbons were present at 37.59, 160.92 and 61.90 ppm representing the methyl carbon and the C_1 and C_2 carbons of the dicyanovinylidene group respectively. ^{1}H-NMR data indicated a pair of multiplets at 8.65 and 7.98 ppm in the aromatic region with a singlet at 4.10 ppm representing the methyl group. This NMR data was consistent with the expected symmetry of the compound. The IR spectrum showed a strong nitrile band at 2224 cm^{-1}. These results confirmed that the product obtained was identical to that previously attained in 1,2-dichlorobenzene. Comparison of the synthesis of [66] in 1,2-dichlorobenzene and 1,2,4-trichlorobenzene have shown dramatic differences in reaction times.[44] This was due mainly to the higher boiling point of 1,2,4-trichlorobenzene. Similar yields of [66] were found in each case. This result then favoured the use of 1,2,4-trichlorobenzene for the following reactions.

The pyrolysis of each of the three new salts [74-76] was then attempted under similar reaction conditions to that reported above. The reactions were monitored by TLC which indicated a complex mixture of products in all cases with numerous decomposition products near the baseline. The reactions were repeated under a blanket of nitrogen gas to maintain an inert atmosphere. However, in this case also, a complex mixture of products was still observed. On comparison of these reactions with the successful N-methylation reaction, the main difference between the starting

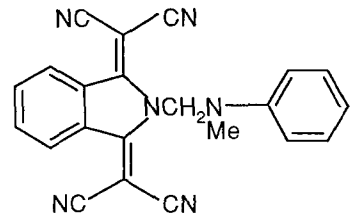
materials is the presence of a β-hydrogen on compounds [74-76] This may render them susceptible to elimination reactions producing a variety of products instead of the N-alkyl derivative of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile and the trialkylamine Problems using alkylammonium salts in nucleophilic displacement reactions have been reported [51] These have resulted in poor yields and side-reactions It is these problems which may have contributed to the failure of these N-alkylation reactions

2.4 Attempted N-alkylation of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile [65] and its ammonium salt [71]

The initial attempt to synthesise a range of N-alkylated analogues of benzo-TCNQ involving pyrolysis of their tetraalkylated ammonium salts proved unsuccessful An alternative approach was then considered This entailed an investigation into the synthesis of compounds of the type [77] and [78] which should then produce the desired N-methyl analogue of benzo-TCNQ via sodium borohydride mediated C-N cleavage [52]

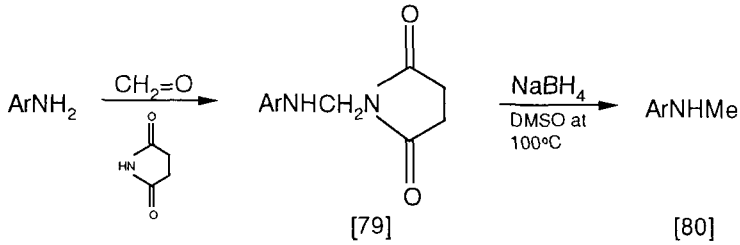


[77]



[78]

In the past, it had been found that primary arylamines, when reacted with formaldehyde and succinimide,[53] gave good yields of the corresponding N-(arylaminomethyl)succinimides [79], scheme 2 05

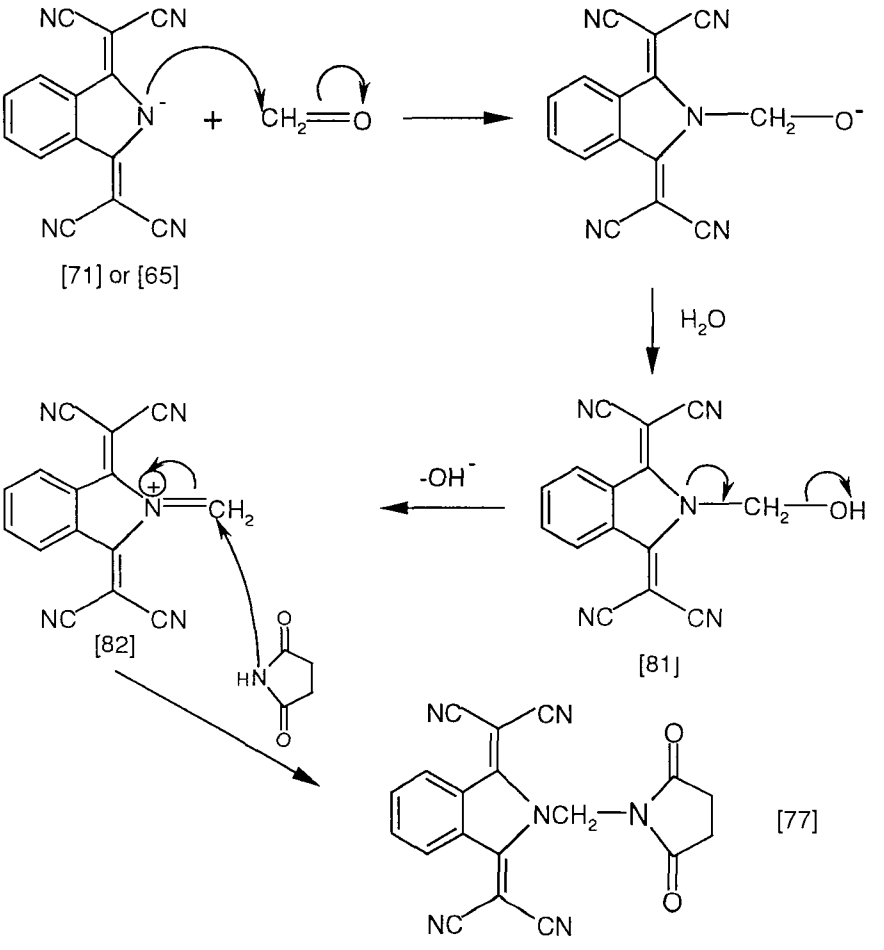


[79] [80]

Scheme 2 05

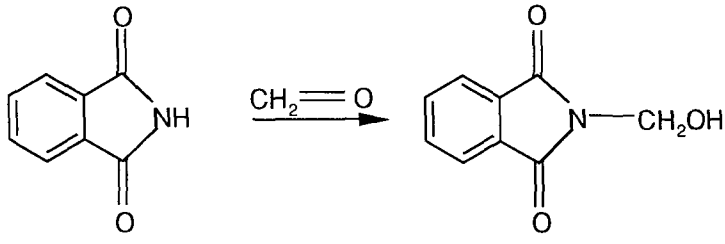
Treatment of these amino-succinimide derivatives with sodium borohydride in dimethylsulphoxide afforded the N-methylaromatic amines [80] The presence of ester, amide or nitrile functions did not affect the ease with which the reaction occurred It was known that attack on secondary amines was also possible by similar methods [54] However, some problems had been encountered in previous N-alkylation reactions Direct stoichiometric N-methylation of an aromatic amine usually required separation of the desired N-methylamino compound from unwanted N,N-dimethyl amino compound and unreacted starting material,[55] while Eschweiler-Clarke N-alkylation[56] was complicated by the formation of tertiary amines as well as other products

In our study, three separate attempts were made to synthesise 2,2'-(2-methylisoindol-1,3-diylidene)bispropanedinitrile [66] In the first two cases, [71] or [65] were reacted with formaldehyde and succinimide This was an attempted one-pot synthesis and the proposed reaction mechanism is given in scheme 2 06



Scheme 2 06

It was hoped that formaldehyde would undergo nucleophilic attack by [71] or [65] to produce [81] Previously, an analogous reaction to this had been reported [57] Phthalimide [83] and formaldehyde had reacted to give N-(hydroxymethyl)phthalimide [84], scheme 2 07

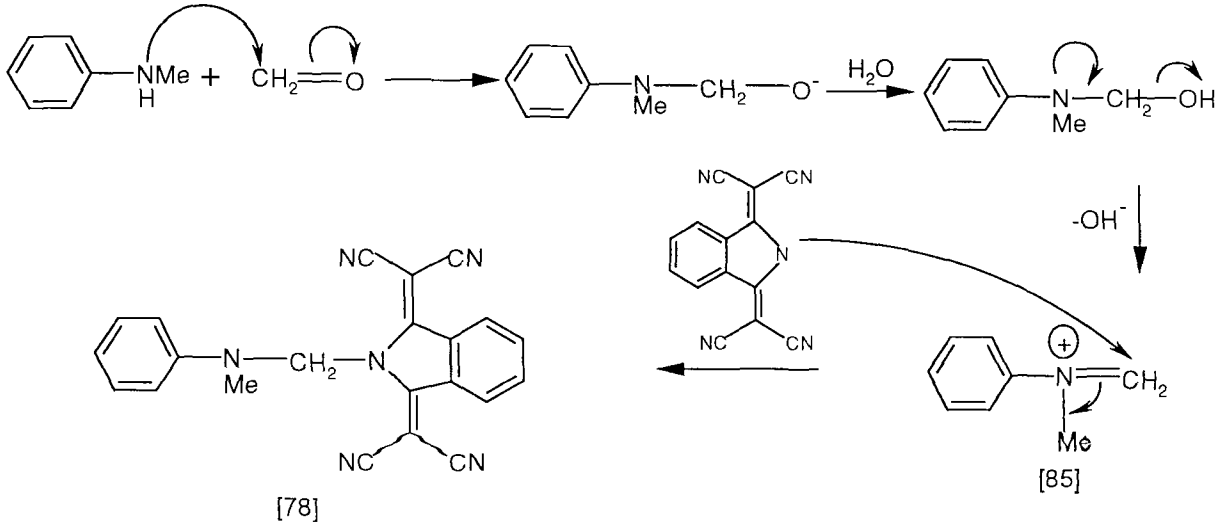


[83] [84]

Scheme 2 07

In our reaction, it was anticipated that elimination of the hydroxyl group might then give the iminium cation [82], which might then be attacked by succinimide, resulting in the formation of a C-N bond This is an aminoalkylation reaction which is comparable to the Mannich reaction However, in both cases, the orange solid that precipitated from solution was found to be [65], confirmed by spectral comparison This implied that ammonia was lost from [71] in the first case, with no reaction occurring in the second

A third reaction was then attempted N-Methylaniline was used as the nucleophile to attack formaldehyde A similar reaction mechanism was proposed, scheme 2 08, involving the iminium cation intermediate [85]



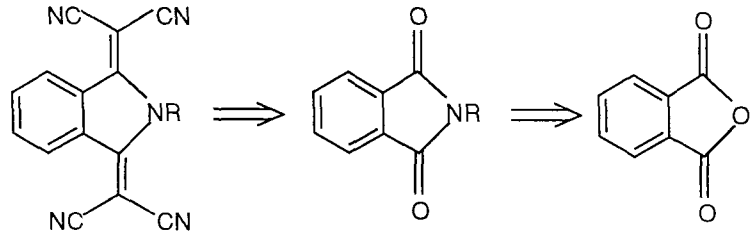
[78] [85]

Scheme 2 08

In this case also, only unchanged [65] was recovered It is thought that these reactions may not have occurred due to non-nucleophilicity of the anion of [65], arising from increased stabilisation of the anionic charge due to the presence of the two dicyanomethylene groups

2.5 Attempted reaction of bromomalononitrile with N-methylphthalimide in the presence of zinc

In the previous sections (2 3 and 2 4), it was found that direct N-alkylation of [65] had not been possible The main problem was the alkylation of the central nitrogen after the dicyanomethylene groups had been attached Perhaps by starting with an N-alkyl analogue and subsequently introducing the dicyanomethylene groups, a new approach to the synthesis of 2,2'-(2-alkylisoindolin-1,3-diylidene)-bispropanedinitriles [86] could be developed A suggested retrosynthetic sequence using N-alkylphthalimides [87] as the N-alkyl analogue is given below, scheme 2 09

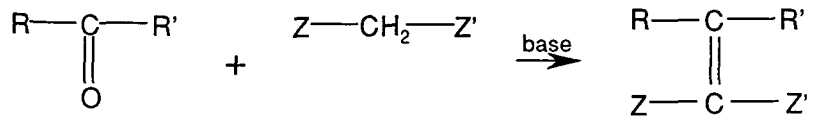


[86] [87] [88]

Scheme 2 09

N-Alkylphthalimide [87] can be readily synthesised from phthalic anhydride [88] and the appropriate N-alkylamine [58]

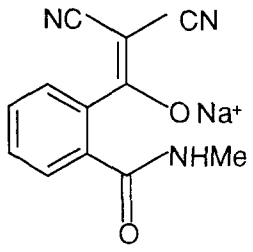
Previously, a sequence based on this had been attempted involving a Knoevenegal condensation reaction [44] This reaction is generally applied to the condensation of aldehydes and ketones with compounds of the form $Z\text{-}CH_2\text{-}Z'$ or Z-CHR-Z' where Z and Z' are electron withdrawing groups, scheme 2 10



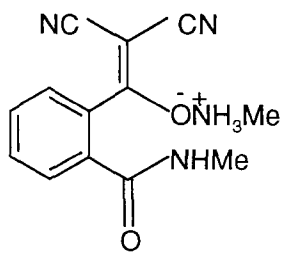
[89]

Scheme 2 10

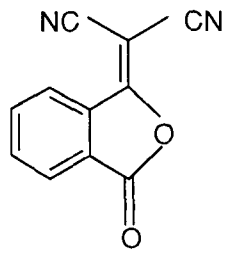
However, in the reported case,[44] the Knoevenegal reaction was extended to phthalimides A variety of bases were reacted with malononitrile The resulting carbanion, $(CN)_2HC^-$, then reacted with the carbonyl group of the N-alkylphthalimide In the particular case where sodium hydride was used as the base and N-methylphthalimide as the N-alkyl analogue, it was found that the product was the sodium salt [90] When internal ring closure of [90] was attempted, two products, the methylammonium salt [91] and a pseudoanhydride [92] were obtained



[90]

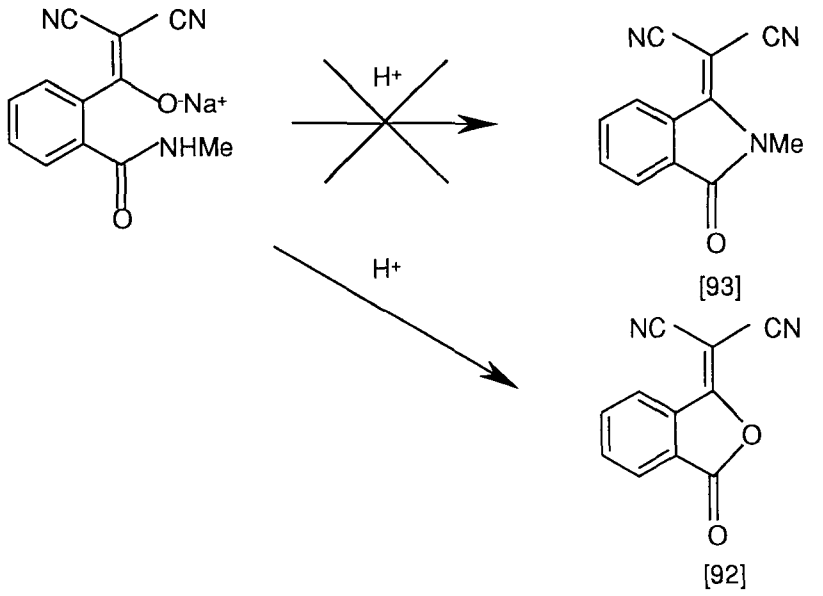


[91]



[92]

It had been hoped that acidification of [90] would yield the N-substituted pseudophthalimide [93] However, it appears that a molecule of amine is lost in the cyclisation reaction and not a molecule of water as would be required for the production of [93], scheme 2 11



Scheme 2 11

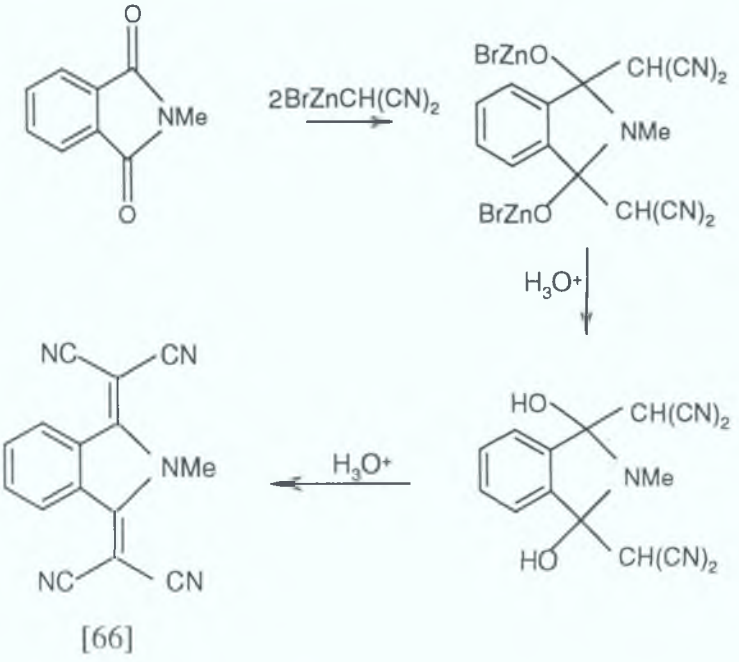
In our approach, it was proposed that N-methylphthalimide might again be used as the starting material for the synthesis of 2,2'-(2-methylisoindolin-1,3-diylidene)-bispropanedinitrile [66] However, in this case the reaction procedure employed was that of the Reformatsky reaction The Reformatsky reaction[59] is generally applicable for the conversion of aldehydes and ketones to β-hydroxy esters, hence extending their carbon chain The reaction involves treating the carbonyl containing compound normally with zinc and an α-haloester, and is analogous to the Grignard reaction, with (ROOC)(ZnBr)C< as an intermediate analogous to RMgX In the present case we wished to replace the carbonyl oxygen with $C(CN)_2$ to yield the desired N-methyl analogue of benzo-TCNQ Bromomalononitrile was investigated as a source of the desired dicyanomethylene extending group N-Methylphthalimide was synthesised by reaction of phthalic anhydride with methylamine in glacial acetic acid[58] while bromomalononitrile was synthesised by reaction of malononitrile with bromine [60]

$$CH_2(CN)_2 \xrightarrow[0\ ^{o}C,\ 4\ hrs]{Br_2} BrCH(CN)_2 + HBr$$

A search of the chemical literature to date did not yield any reports of the Reformatsky reaction using bromomalononitrile However, in one report,[61] a reaction of $RCHBrCO_2Et$ (R = H, Me) with phthalimide yielded the corresponding enamide

esters. This was a clear indication of the possibility of phthalimide use in the Reformatsky reaction.

The attempted Reformatsky-type reaction involved the addition of a solution of bromomalononitrile and N-methylphthalimide to dried zinc dust. The proposed reaction is given in scheme 2.12 below. A standard Reformatsky reaction using ethyl bromoacetate and benzaldehyde was also carried out to check that the dried zinc dust used in the reaction in scheme 2.12 was active. It proved to be with formation of the desired product, ethyl 3-phenyl-3-hydroxypropanoate.



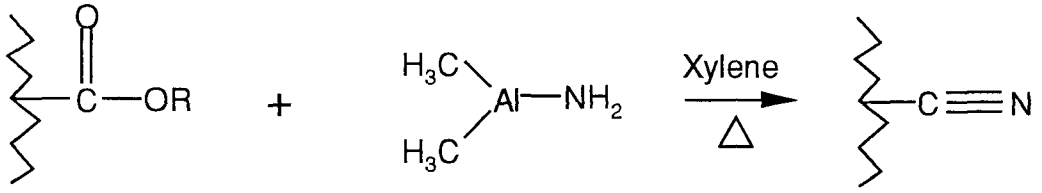
[66]

Scheme 2.12

However, the spectral data for the solid obtained from the attempted reaction in scheme 2.12 was consistent with that of N-methylphthalimide.

It appears that the failure of the reaction may have been due to the lack of formation of the hoped-for organozinc intermediate. This was apparent when no self-sustaining exothermic reaction was observed on addition of the carbonyl compound and bromomalononitrile to zinc, possibly due the absence of a coordinating ester oxygen atom in bromomalononitrile. In the standard Reformatsky reactions using α-haloesters, the oxygen atom helps to stabilise the intermediate as the zinc enolate where the electronegative oxygen bearing the negative charge is better able to cope with this charge than a carbon atom.

An alternative reaction is suggested for the future This involves using an α-haloester and N-methylphthalimide $BrCH(COOEt)_2$ has been used[62] successfully in the Reformatsky reaction The resultant product's ester groups could then conveniently converted to nitriles[63] by treatment of the ester functionalities with dimethylaluminium amides in refluxing xylene, scheme 2 13

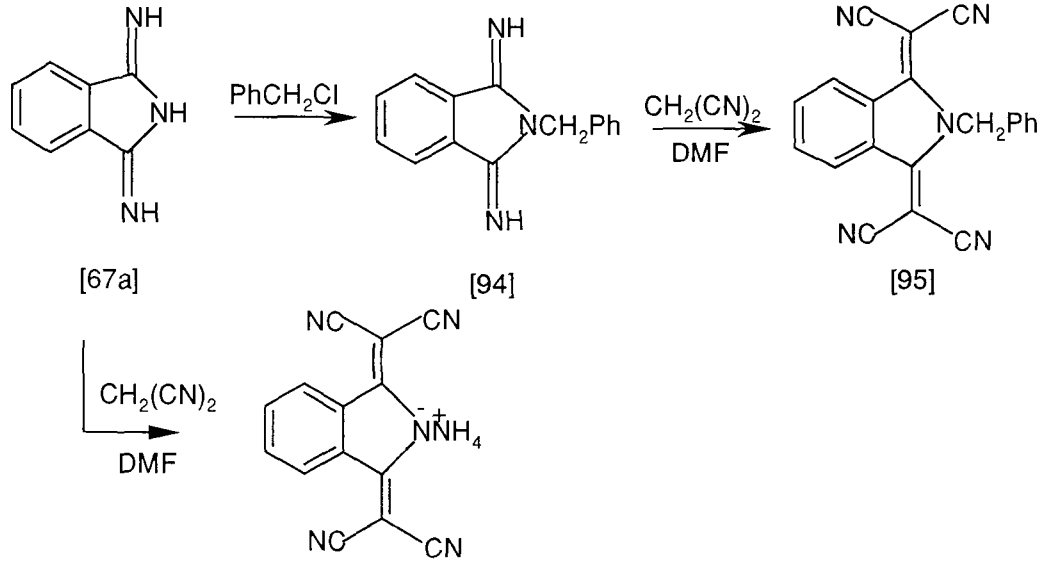


Scheme 2 13

2.6 Attempted benzylation of diiminoisoindoline

Due to the problems encountered in the direct N-alkylation of [65] and the inability to induce dicyanomethylenation of the carbonyl oxygen of N-methyl phthalimide by a Reformatsky-type reaction, an alternative synthesis was proposed

It was anticipated that by attaching a benzyl group to the central nitrogen of [67a], compound [94] might be obtained The N-benzyl derivative of benzo-TCNQ [95] might then be produced by reaction of [94] with malonomtrile in dimethylformamide, a dicyanomethylenation step, analogous to that already well-established[46] for conversion of [67a] to [71]



Scheme 2 14

On addition of sodium hydride to [67a], there was an evolution of hydrogen indicating that a possible reactive intermediate, the anion of [67a], had been generated Addition of the benzylating agent however, resulted in a complex mixture of products It was thought that due to the multiple NH groups present in [67a], many sites were available for anion generation, thus resulting in this complex mixture

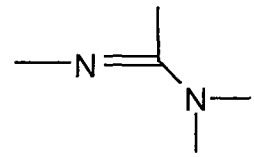
Chapter 3

Syntheses of some amıdine derivatives of 2,2-(isoindolin-1,3-diylidene)-bıspropanedınıtrile.

3.1 Introduction

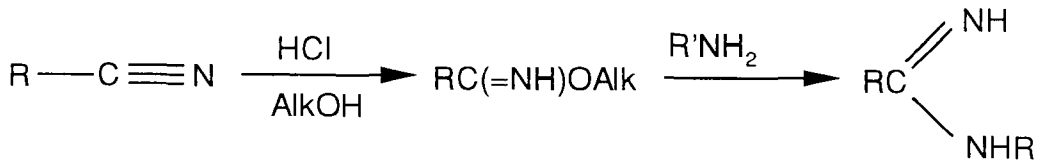
Previously, the reaction of 2,2-(isoindolin-1,3-diylidene)bispropanedinitrile [65] with a variety of amines had been investigated [44] This yielded new compounds containing an amidine group The reaction with the amine had resulted in attack at the nitrile functionality In this introduction, there will be a short review of amidine synthesis, with special emphasis on amidine formation from nitriles

Amidines [RC(NR'$_2$)=NR''] can be considered as the nitrogen analogues of carboxylic acids They consist of a carbon to nitrogen double bond with the same carbon also singly bonded to a second nitrogen atom The amidine moiety [96] may be included in cyclic or acyclic systems giving rise to important structural parts of many compounds of biological and medicinal interest



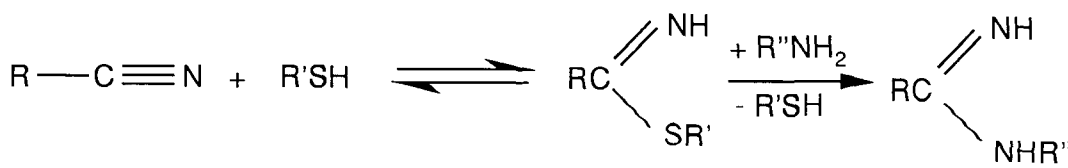
[96]

Their traditional synthesis has been through the use of nitriles, involving the formation of an intermediate imino ester via the Pinner synthesis [64] This reaction proceeds by reaction of the nitrile with an alcohol under acid conditions The intermediate is then reacted with an amine to produce the desired substituted amidine, scheme 3 01



Scheme 3 01

This reaction has also been carried out via[65] a thioimidate intermediate, scheme 3 02



Scheme 3 02

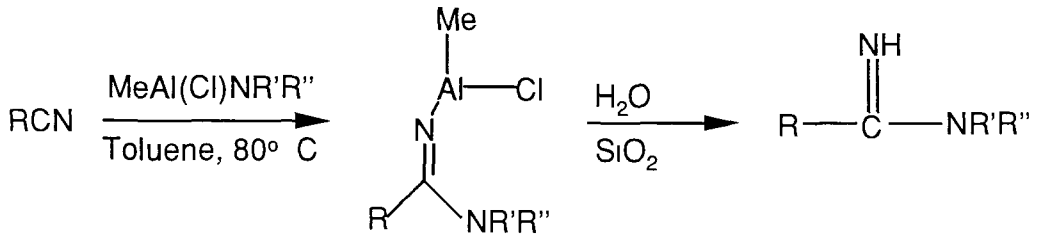
This modified Pinner synthesis usually requires a buffered acidic medium to ensure ready formation of alkyl amidines If more basic aliphatic amines are used, the first step of the reaction is reversed and the nitriles are recovered

The Pinner synthesis can utilise a large variety of nitriles, however, two cases exist whereby the reaction does not proceed

- the nitrile is severely hindered
- the nitrile has powerful electron-withdrawing substituents

In the second case, imidates are formed, however there is immediate decomposition to the amide Another disadvantage of the Pinner synthesis is that only unsubstituted imidates can be formed directly by it

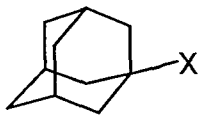
The first limitation of the Pinner synthesis has been overcome recently Garigipati has reported[66] the direct conversion of sterically-hindered nitriles to amidines in high yields, scheme 3 03



Scheme 3 03

The reaction involves addition of methylchloroaluminium amides,[67] generated from trimethyl aluminum and ammonium chloride, to nitriles It is found that alkyl, benzyl and aryl amidines can be prepared from the corresponding nitriles while mono- and di-substituted amidines can be prepared by addition of the appropriately N-substituted methyl chloroaluminium amide

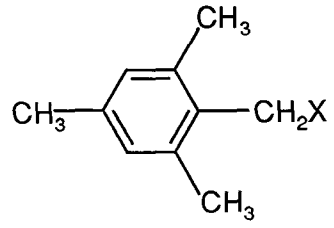
Some examples of sterically hindered nitriles that are inert to the standard Pinner imidate procedure but which react using Garigipati's method are given below [97-100] [68]



[97]

$(CH_3)_3CCH_2X$

[98]

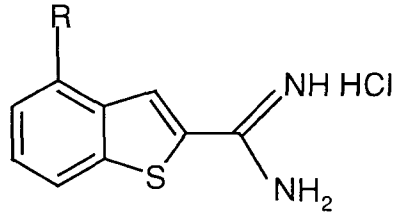


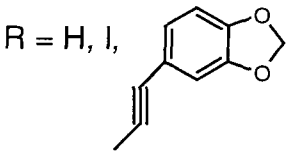
[99]

$CH_3(Ph)_2CX$

[100]

Garigipati's reaction has also been applied to producing amidines of biological importance [69] These included the selective urokinase inhibitors, 4-substituted benzo[b]thiophene-2-carboxamidines [101]

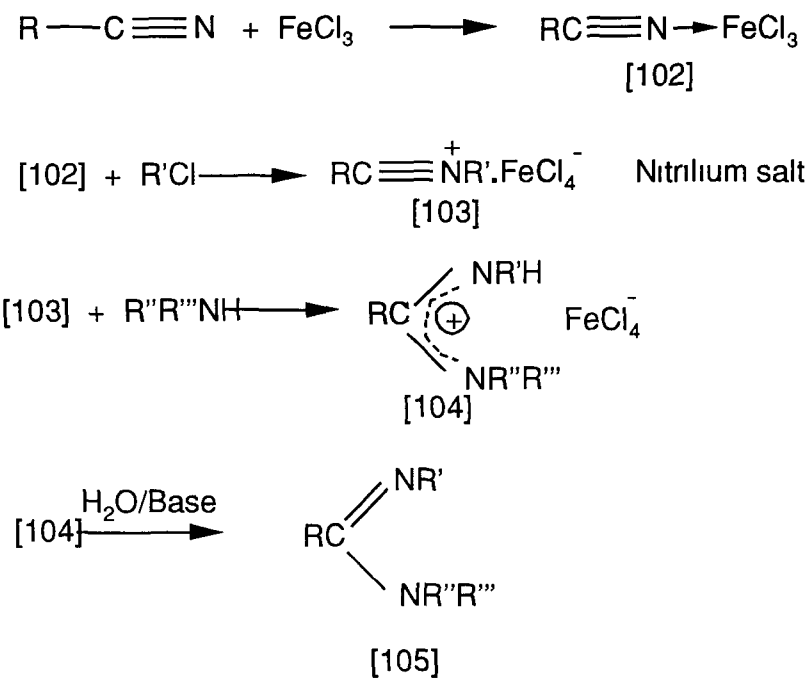




[101]

The second limitation of the Pinner synthesis, that of inertness when there are powerful electron-withdrawing substituents on the nitrile, has been overcome[70] by the use of a base-catalysed reaction of the nitrile group with alcohols It was actually found[71] that intermediate imidate formation was enhanced by the presence of the electron-withdrawing group This base catalysed reaction has been applied to a broad range of nitriles by reaction with a lower alcohol This simple base-catalysed conversion of nitriles to imidates is a very attractive method for synthesis of amidines, and nitriles unsuitable for use in this reaction usually gave excellent results in the Pinner synthesis

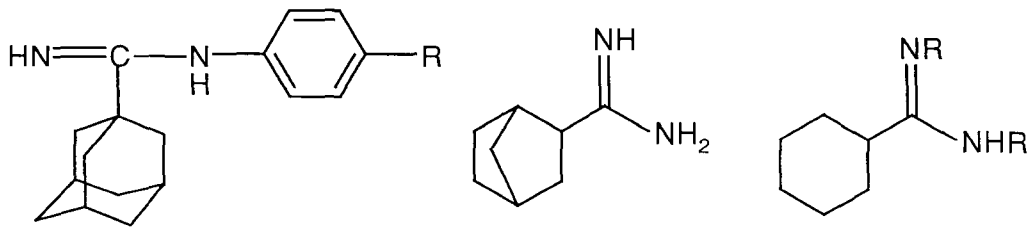
Another general method[72] for the preparation of amidines from unactivated nitriles has been through the reaction with Lewis acids This reaction consists of four steps involving a nitrile, an alkyl halide, a Lewis acid and an amine [73] It is a one-pot synthesis and it is illustrated in scheme 3 04 below



Scheme 3 04

In the first step, a nitrile-Lewis acid complex [102] is formed N-Alkylation of the complex results in a nitrilium salt [103] The amidinium salt [104] is then formed by aminolysis of the nitrilium salt [103] Compound [104] is then neutralised with a base yielding a substituted amidine [105] This reaction has proved to be a convenient method for preparation of mono-, di- and tri-substituted amidines

A range of amidines [106-108] have been synthesised in this way [74] They have been shown to be effective against a range of viruses including influenza A2, vaccinia and herpes



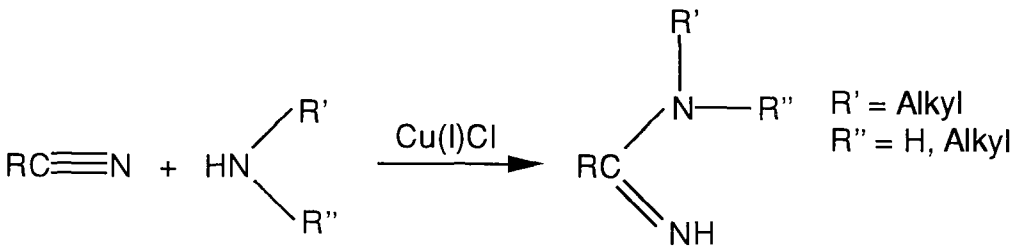
[106] [107] [108]

[106] 1-Adamantanecarbamidines, [107] 2-Norbornanecarboxamidine, [108] Cyclohexanecarboxamidine

Lanthanide (III) ions have been used[75] as catalysts for the reactions of amines with nitriles They readily result in a condensation reaction with primary amines and

primary diamines [$H_2N(CH_2)_nNH_2$] to yield N,N'-disubstituted and cyclic amidines respectively If excess nitrile is used, symmetrically substituted triazines are often seen as side products

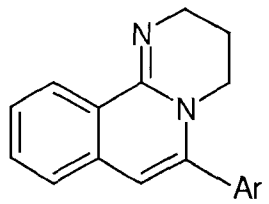
A disadvantage of Garigipati's method, the lanthanide (III) triflate catalysed condensation reaction and the reaction with the Lewis acids is that monosubstituted amidines cannot be exclusively obtained from primary amines N,N'-disubstituted amidines are readily obtained as single products from secondary amines However, primary amines generally give rise to a mixture of mono- and N,N'-disubstituted amidines This has resulted in the report of a copper-induced addition of amines to unactivated nitriles [76] In the first general one-step synthesis of alkylamidines reported, the copper (I) chloride catalyst is used under mild conditions, scheme 3 05, coordination with Cu(I) activating the nitrile towards nucleophilic attack of amine



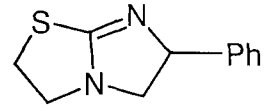
Scheme 3 05

Selective synthesis of the mono- or di-substituted amidines can be achieved by variations between the stoichiometry of the amine and copper catalyst

Many methods of amidine synthesis from compounds other than nitriles have been reported[77] in the literature A general route[78] to cyclic amidines from aminoheterocycles has yielded biologically active compounds [79] Two examples are given below



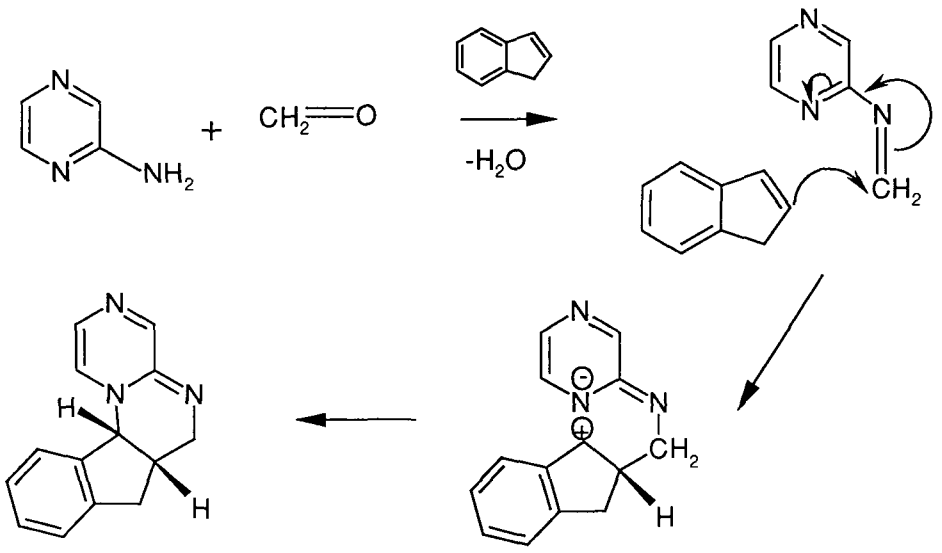
[109]



[110]

These reactions were originally considered as single-step Diels-Alder reactions, but have been shown to proceed by a multi-step pathway [80] This reaction involves the

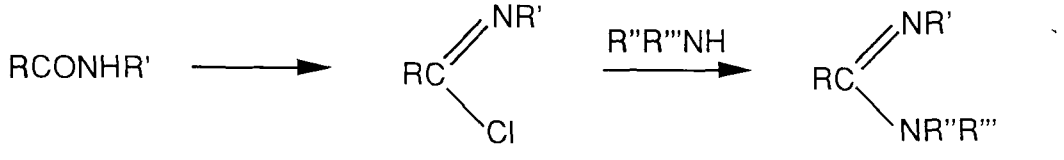
formation of an imine at the primary amine site giving regioselective addition to the electron-rich alkene and, following cyclisation, yielding a single amidine, scheme 3 06



Scheme 3 06

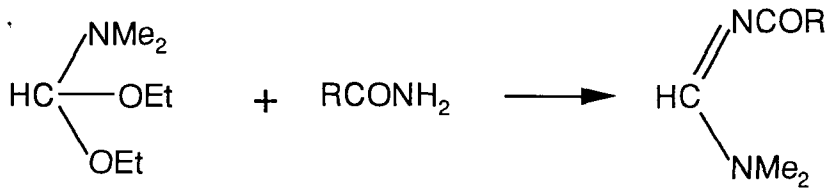
The choice of amine is important Best results are achieved with amines which on one hand give relatively electrophilic imines to permit reaction with the alkene, yet on the other hand are sufficiently nucleophilic to permit the final cyclisation to the desired product

Amidines have also been prepared from amides and thioamides [77] The reaction proceeds by activation of the starting material by modification of the carbonyl or thiocarbonyl group An example is reaction of imidoyl chlorides with ammonia or primary or secondary amines to yield amidines, scheme 3 07 Imidoyl chlorides are prepared by action of phosphorous pentachloride, phosphorous oxychloride or thionyl chloride on secondary amides



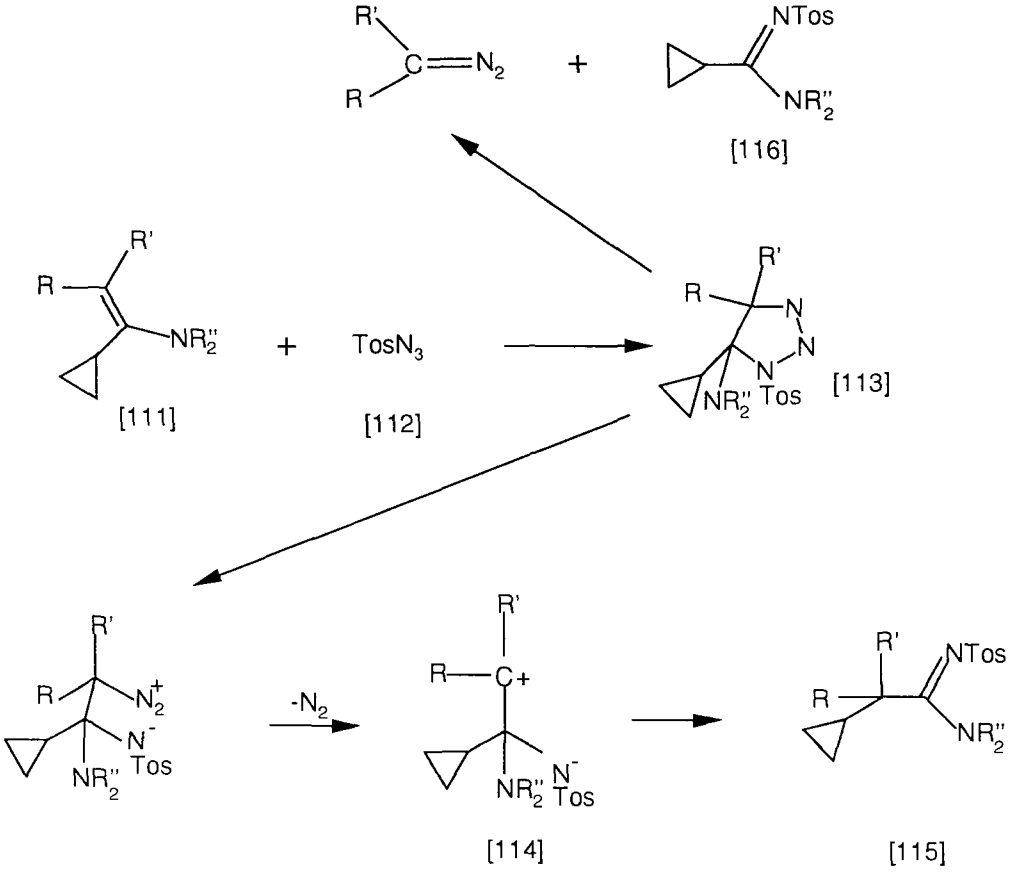
Scheme 3 07

Primary amides and thioamides can also be converted to acylamidines[81,82] on treatment with dimethylformamide diethyl acetal, scheme 3 08



Scheme 3 08

An example of an amidine preparation involving a heterocyclic intermediate has been reported[83] by Pocar and Trimarco In their reaction, α-cyclopropylenamines [111] react with tosylazide [112] via a 1,3-dipolar cycloaddition, scheme 3 09

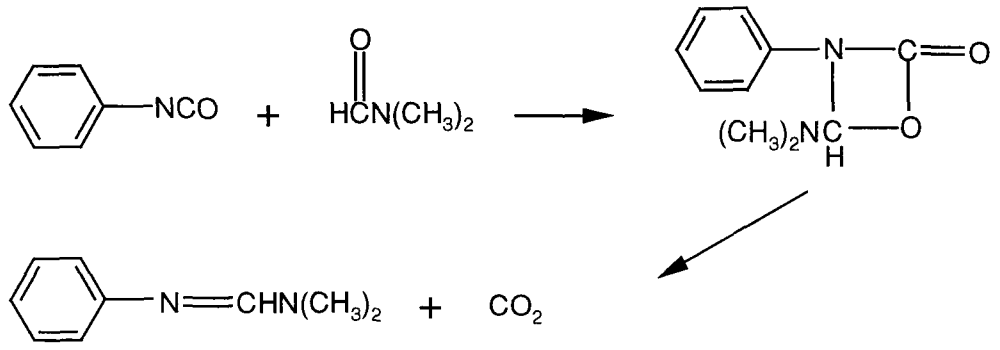


Scheme 3 09

The intermediate triazolines [113] decompose by two different pathways, in each case producing amidines as products An increase in alkyl substitution in the enamine favoured formation of the rearranged product [115], believed to be due to increased stabilisation of the carbocation intermediate [114]

Another route for amidine synthesis involves the reaction of an isocyanate[84] with amide The reaction proceeds via a [2+2] cycloaddition of the isocyanate to the

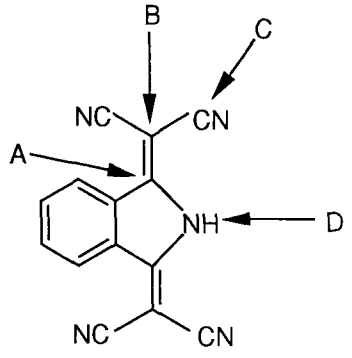
amide yielding a 4-membered ring, which then readily converts to an amidine and carbon dioxide, scheme 3 10



Scheme 3 10

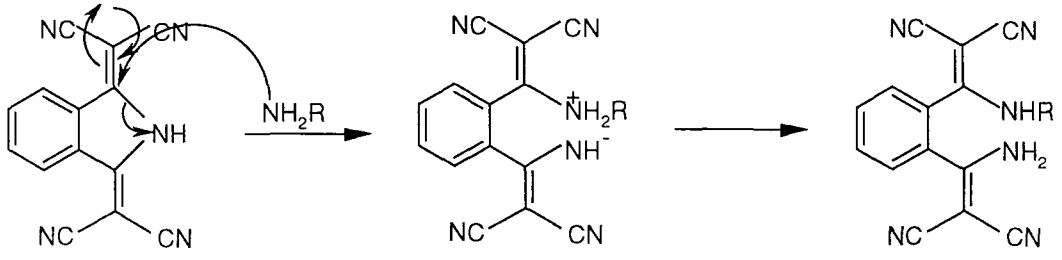
3.2 Synthesis of the amidine derivatives of the heterocyclic analogue of benzo-TCNQ

It had been previously postulated[44] that there were four prime sites in [65] at which amines might attack



[65]

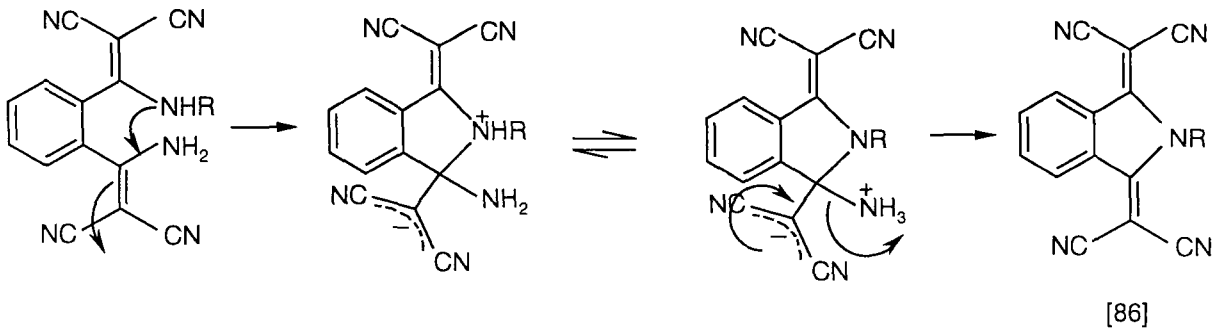
Attack at site A by a nucleophile, such as an amine, might lead to ring opening giving the intermediate [117], scheme 3 11



[65] [117]

Scheme 3 11

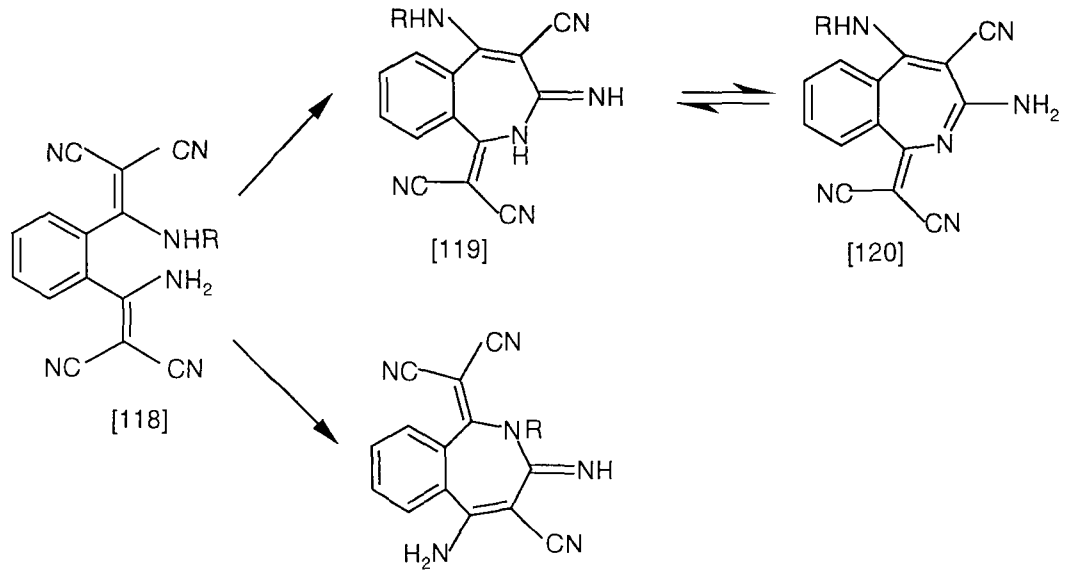
This intermediate [117] might then be subjected to ring closure (scheme 3 12) with an elimination of ammonia or possibly the amine yielding the N-substituted compound [86] or [65] respectively



[86]

Scheme 3 12

Alternatively, given that there is free rotation around the carbon to carbon single bond at both the 1- and 2- positions of the aromatic ring of [117], a 7-membered ring system could possibly form by addition of either nucleophilic amino group to a cyano on the adjacent dicyanoethenylamino group, scheme 3 13

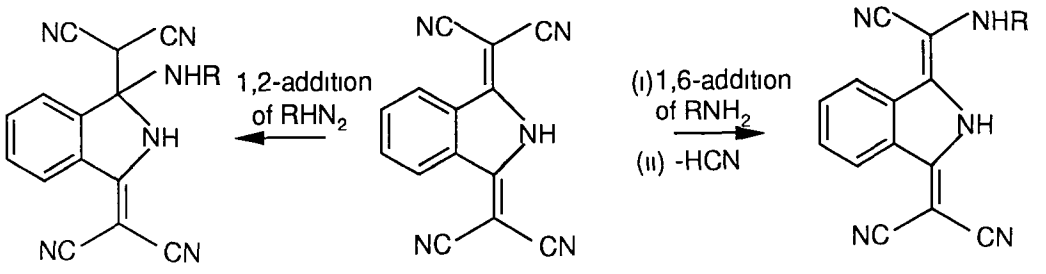


Scheme 3 13

An attack at site A could also result in a 1,2 addition across the carbon-carbon double bond producing compound [122], scheme 3 18

An attack at site B might lead to a 1, 6-addition-elimination reaction, scheme 3 14

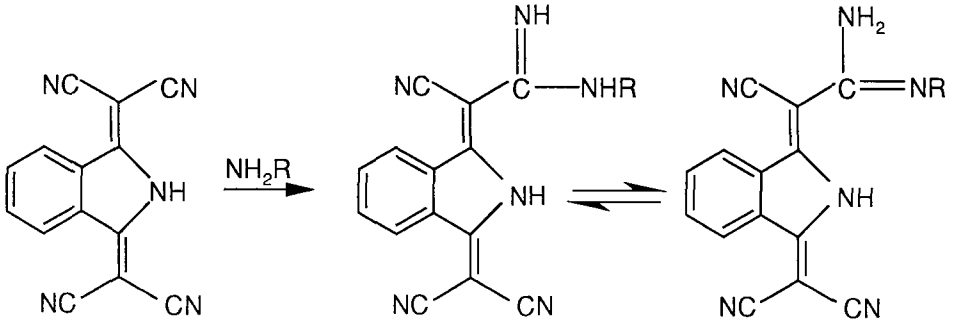
An analogous reaction has been reported for TCNQ [85]



[122] [65] [123]

Scheme 3 14

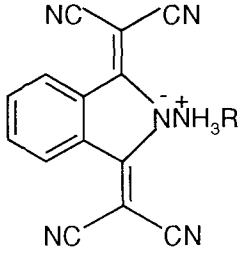
Reaction of an amine with a cyano group, for example at site C, might result in production of an amidine which might exist in either of two tautomeric forms, scheme 3 15



[124a] [124b]

Scheme 3 15

Finally, an attack at site D, the NH group, would be expected to yield an alkylammonium salt [125] of [65], involving protonation of the amine by the acidic NH group

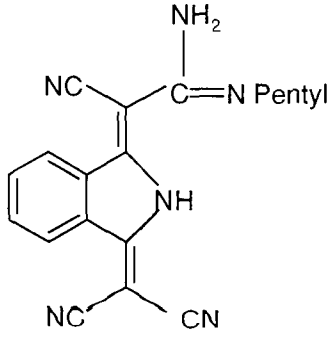


[125]

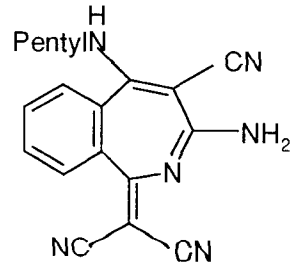
In the following section, the reactions of a number amines with the ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile are reported The ammonium salt [71] was used due to its greater solubility than [65] in common solvents

3.2.1 Reaction of the ammonium salt of 2,2'-(isoindolin-1,3-diylidene)-bispropandinitrile with 1-aminopentane.

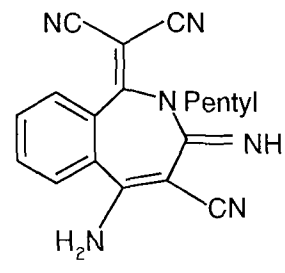
1-Aminopentane, a primary alkyl amine and [71] were reacted to give a dark orange solid product Given that there were so many possibilities for the structure of this product, microanalysis data was used initially to eliminate some of those postulated The microanalysis data was consistent with the molecular formula $C_{19}H_{18}N_6$ eliminating product [123] , which would have resulted from a 1, 6 addition-elimination reaction ^{1}H-NMR spectroscopy indicated three sets of unsymmetrical aromatic multiplets integrating in the ratio 1 1 2 at 8 17, 7 17 and 7 69 ppm respectively At 70 °C, four separate multiplets appeared in the aliphatic region integrating for a total of eleven protons and consistent with the presence of a 1-pentyl substituent The two proton triplet at 3 38 ppm, obscured by solvent absorption at room temperature, was consistent with this being attached to a nitrogen The absence of a dicyanomethyl proton signal eliminated a structure resulting from a 1, 2 addition reaction at site A, [122] and also indicated that the product of the reaction was unsymmetrical, thus eliminating two further structures, [118] and [125] The unsymmetrical structure of this product was again verified by the observation of six different aromatic absorptions between 123 55 and 138 25 ppm in the ^{13}C-NMR spectrum The presence of only three cyano carbons also excluded compound [117] as a possible product Compound [117] is non-symmetrical but contains four unique cyano groups This left only three possible structures, [126], [127] and [128]



[126]

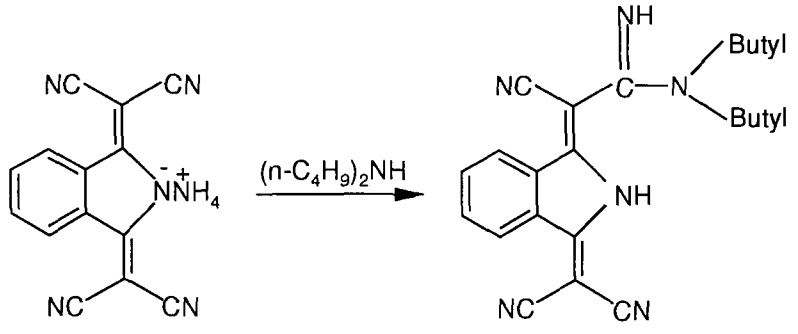


[127]



[128]

The presence of nineteen unique carbons was also consistent with these The IR spectrum showed the presence of two NH bands at 3343 and 3272 cm^{-1} with aliphatic peaks at 2928 and 2874 cm^{-1} A sharp band at 2210 cm^{-1} also indicated the cyano group presence in the compound



[71] [129]

Scheme 3 16

Comparison of these results with those for compound [129], (scheme 3 16), a product of reaction between the ammonium salt of 2,2-(isoindolin-1,3-diylidene)-bispropanedinitrile and N,N-di(n-butyl)amine[44] showed many spectral similarities Their UV/visible spectra were found to be essentially identical X-ray crystallography had confirmed that the dibutyl-derived product is the amidine [129], resulting from attack by the secondary amine at site C It seems likely, therefore, that the product from reaction of [71] with 1-aminopentane has the analogous structure, [126] This was further supported by comparison of their ^{13}C-NMR spectra in table 3 1 Each of the carbon absorptions for the 1-aminopentane product corresponds with similar chemical shift values to that of compound [129]

The combination of UV/visible and ^{13}C-NMR spectral data provides a strong confirmation that [126], an amidine, is the product of the reaction of [71] with 1-aminopentane From scheme 3 15, it is seen that compound [126] may exist as a tautomeric equilibrium between the two structures Tautomerism in amidines is very fast and according to NMR studies[86] , proton exchange can occur several times per second In the case of [126], ^{1}H-NMR data indicated that one set of CH_2 protons were only visible at higher temperatures This may be evidence to demonstrate that the position of the equilibrium changes as the temperature changes Further studies at

varying temperatures could be carried out in the future to confirm this for compound [126]

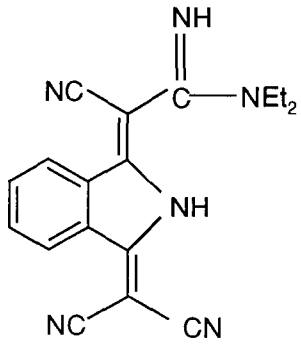
Table 3 1 Comparison of ^{13}C-NMR data of [129] with products of reaction of [71] with primary and secondary amines

Compound	**[129]** δ/**ppm**	**[126]** δ/**ppm**	**[130]** δ/**ppm**	**[133]** δ/**ppm**
Cyano C	116 80 118 20 118 50	115 36 115 99 117 29	116 41 117 64 117 76	117 21 117 74 119 71
Aromatic C	122 70 122 90 131 00 131 10 137 70 137 80	123 55 123 87 131 65 132 09 135 23 138 25	122 14 122 37 130 44 130 56 137 14 137 23	123 94 124 29 131 16 131 31 137 73 139 30
>C=C(CN)-	73 20 50 80	72 09 56 80	72 57 55 33	72 24 56 83
>C=C(CN)-	165 40 171 50	167 10 170 64	164 96 170 93	169 35 172 37
C=N	159 20	159 16	157 96	162 64
Alkyl	13 40, 13 60 19 20, 28 50	13 82, 21 67 27 34, 28 63 42 49	11 49 34 22	23 68, 25 29 50 57

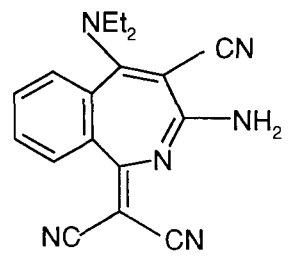
3.2.2 Reaction of the ammonium salt of 2,2'-(isoindolin-1,3-diylidene)-bispropanedinitrile with N,N-diethylamine

A bright orange solid was precipitated from reaction of [71] with N,N-diethylamine Microanalysis results were consistent with the molecular formula $C_{18}H_{16}N_6$, eliminating compound [123] as a possible product from this reaction The ^{1}H-NMR spectrum revealed the presence of a quartet and triplet at 3 68 and 1 42 ppm

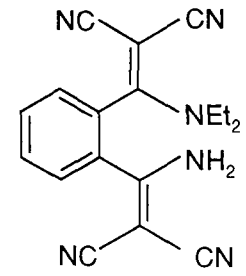
integrating for ten protons and consistent with an N,N-diethylamino group There were three aromatic multiplets between 8 50 and 7 45 ppm in the ratio of 1 1 2, implying that the structure was non-symmetrical and discounting the possibility of a product resulting from attack at site D, [125] In this case also, no dicyanomethyl proton signal was observed indicating that there had not been a 1,2 addition reaction at site A No NH proton resonances were seen in the ^{1}H-NMR spectrum, however on the IR spectrum, a band was present at 3344 cm^{-1} with a minor shoulder at 3300 cm^{-1} Three cyano bands were also present at 2220, 2203 and 2200 cm^{-1} respectively ^{13}C-NMR spectroscopy indicated a total of sixteen unique carbons consistent with structures [130], [131] and [132]



[130]



[131]



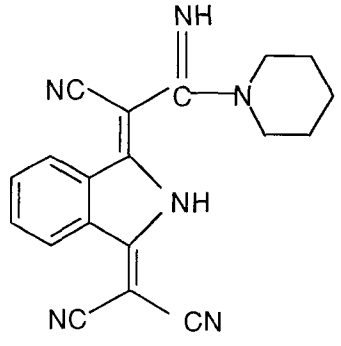
[132]

However, only three cyano peaks, between 116 41 and 117 76, were noted, eliminating structure [132], which would have had four cyano signals in the ^{13}C-NMR spectrum To distinguish conclusively between structures [130] and [131] would require X-ray crystallography but efforts to produce crystals for a study of this type were unsuccessful However, assignment of a final structure to the product could be unambigously made by comparison of UV/visible and ^{13}C-NMR spectra data with that of compound [129], whose structure (section 3 2 1) had been confirmed by X-ray crystallography The UV/visible spectrum of [130] was essentially identical to that of [129], while each non-aliphatic carbon absorption of [130] was analogous to that of compound [129], table 3 1

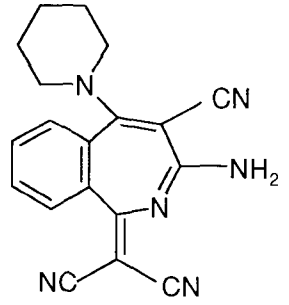
3.2.3 Reaction of the ammonium salt of 2,2'-(isoindolin-1,3-diylidene)-bispropanedimtrile with piperidine.

As in the previous reactions, the ammonium salt [71] and the secondary amine, piperidine, were heated together under reflux Microanalysis of the product indicated a molecular formula of $C_{19}H_{16}N_6$ This matched all of the postulated strucures, excluding [123] The ^{1}H-NMR spectrum indicated three multiplets in the aromatic region, integrating in the ratio 1 1 2, implying that the product was unsymmetrical Three types of aliphatic protons were observed at 3 72, 1 65 and 1 51 ppm consistent with the presence of a piperidino ring A single broad peak was observed at 10 79 ppm Addition of D_2O to the NMR sample caused this peak to disappear confirming that it belonged to an NH group Compound [122], generated from a 1,2 addition reaction, was discounted as a possible structure due to the absence of a dicyanomethyl proton signal in the ^{1}H-NMR spectrum.

Some peaks of note in the IR spectrum were the NH stretches at 3321 and 3370 cm^{-1}, a strong cyano band at 2201 cm^{-1} and an imino stretch as 1655 cm^{-1} ^{13}C-NMR spectroscopy indicated a total of seventeen unique carbons A lack of symmetry in the product was indicated by the six aromatic and three cyano carbon signals This eliminated a further structure, [118], unsymmetrical but containing four unique cyano carbons This process of elimination only left two compounds, [133] and [134] as possible products of the reaction



[133]



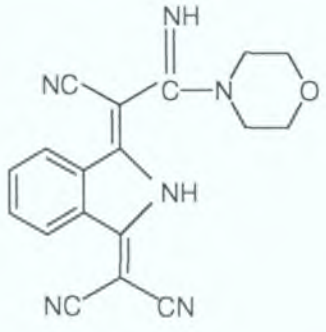
[134]

As in sections 3 2 1 and 3 2 2, the UV/visible and ^{13}C-NMR spectral data obtained was compared with that of the known structure, [129] The ^{13}C-NMR absorptions (table 3 1) were consistent with that of an amidine structure while the

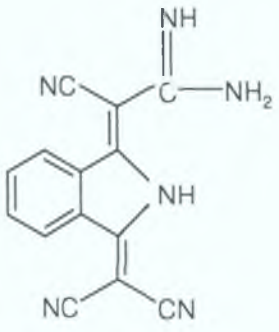
UV/visible spectra were identical. It can be concluded, therefore, that the product of this reaction is the amidine, [133].

3.2.4 Reaction of the ammonium salt of 2,2'-(isoindolin-1,3-diylidene)-bispropanedinitrile with morpholine.

The reaction of morpholine with the ammonium salt [71] of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile yielded an orange solid consisting of two components with very similar R_f values. By analogy with the previous amine reactions with [71], it was anticipated that the most likely product from this reaction would be the amidine [135]. Recrystallisation of the product mixture yielded a single component whose ^{13}C-NMR spectrum indicated the presence of only fourteen unique carbons. This did not match that of compound [135] which would have contained sixteen unique carbons. The compound was unsymmetrical with six different aromatic carbon absorptions between 123.65 and 138.37 ppm.



[135]



[136]

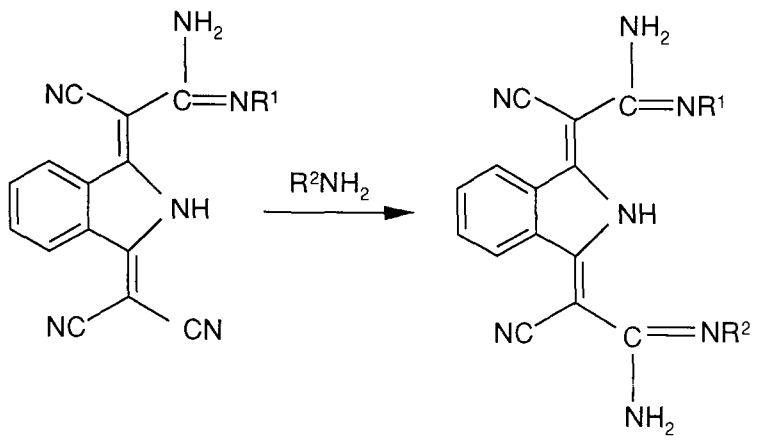
No aliphatic carbons were observed, indicating the absence of the morpholine unit from its structure. ^{1}H-NMR spectroscopy revealed the presence of three aromatic multiplets at 8.31, 8.15 and 7.71 ppm respectively integrating in the ratio 1:1:2. Two broad NH absorptions were also present, and the absence of the aliphatic protons again confirmed the absence of a morpholine unit. IR data indicated a cyano peak at 2212 cm^{-1}. On comparison of this data with that for the previous compounds synthesised, it seems apparent that this compound has structure [136], the parent amidine of this series, presumably generated from reaction of ammonia with [71] at site C, though microanalysis results for the solid were outside the normally acceptable limits for structure [136].

All attempts to separate out the other component from the mixture were unsuccessful NMR spectroscopy of the mixture indicated that the second component may have been the morpholino-amidine [135] In addition to the peaks present in the ^{13}C-NMR spectrum of the isolated component, the mixture gave rise to sixteen additional carbon resonances including two in the aliphatic region The ^{1}H-NMR spectrum included two triplets at 3.60 and 3 79 ppm, each integrating for four protons, and supporting the presence of a morpholino appendage From the ^{1}H-NMR spectrum integration values, it also appeared that both compounds were present in equal quantities

It appears that, as in all the other cases, reaction has occurred at site C, resulting in an addition across the carbon to nitrogen triple bond yielding [135] and [136] The formation of [136] would involve the addition of ammonia presumably generated from the ammonium salt [71] during the reaction Attempts to synthesise [136] directly by bubbling ammonia through an ethanolic solution of [71] were unsuccessful

3.2.5 Investigation of the synthesis of bis-amidines

It was of interest to investigate the synthesis of bis-amidines by further reaction of the mono-amidines with amines, scheme 3 17 It seemed possible that the second dicyanomethylene group might also participate in a reaction process similar to that described in the previous section, though it had been noticed that in



[137] [138]

Scheme 3 17

the amidine syntheses from the ammonium salt [71], the use of excess amine had resulted in only the mono-amidine [137] being isolated In this section, two different mono-amidine products are treated with different amines and the results reported below

In the first case, piperidine was heated with 2-cyano-N^2,butyl-2-(3-dicyanomethylene-isoindol-1-ylidene)acetamidine in THF No new products were formed On heating butylamine with 2-cyano-N',N'-dibutyl-2-(3-dicyanomethylene-isoindol-1-ylidene)acetamidine only minor amounts of product were observed on TLC These could not be isolated by recrystallisation Only starting material was recovered The reaction conditions employed may not have been vigorous enough for a reaction to proceed to produce [138] The starting material [137] is now less reactive than [65] due to the replacement of a cyano group by the amidine group

3.2.6 Conclusion

From the reaction of primary and secondary amines with the ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropandinitrile, one product was isolated in each case Microanalysis data and ^{1}H and ^{13}C-NMR spectroscopy eliminated a number of possible structures for the products from these reactions Comparison of their UV/visible and ^{13}C-NMR data with those of a known compound [129] confirmed that in each case an amidine was formed It appears, therefore, that reaction of [71] with an amine occurs by attack at site C, resulting in addition across the carbon to nitrogen triple bond, presumably preferred because it results in minimum disturbance across the π-system of the molecule

3.3 Charge-transfer studies of 2-cyano-N^2-pentyl-2-(3-dicyanomethylene-isoindolin-1-ylidene)acetamidine [126] and 2-cyano-2-(3-dicyanomethylene-isoindolin-1-ylidene)-N-(1-iminoethyl)piperidine [133] using UV spectroscopy

3.3.1 Introduction

UV/visible spectroscopy is one of the most widely used methods for the study of charge-transfer complex (CTC) formation. A charge-transfer complex or a radical-ion salt is formed when a donor (D) and an acceptor (A) interact by overlapping their π-systems in either partial or complete electron-transfer. This commonly results in an intense new electronic absorption in the visible or near UV region that is distinct from those of either the donor or acceptor, but is characteristic of a new molecular species, the CTC. These new bands in the UV or visible spectra have been explained by Mulliken.[87] He suggested that electronic excitations from the HOMO of the donor to the LUMO of the acceptor bring about these C-T bands. C-T arises, therefore, from an overlap between the HOMO of the donor and the LUMO of the acceptor, fig 3.1.

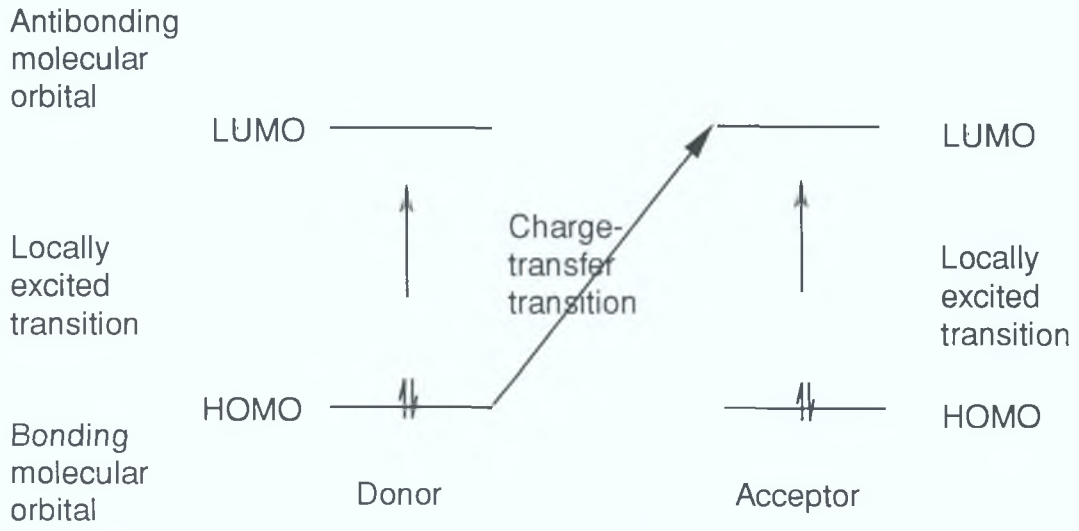
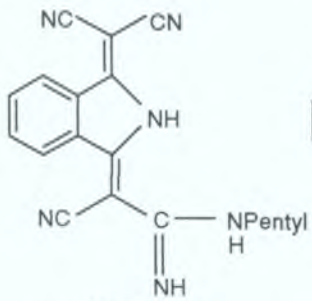


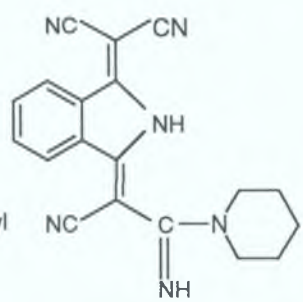
Fig 3.1 Electronic excitations in charge-transfer complexes

In this section, two potential acceptor compounds, [126] and [133], were investigated for stable C-T complex formation with the donors N,N,N',N'-tetramethylphenylenediamine (TMDA) [72] and tetrathiafulvalene (TTF) [3]. Previously, similarly structured compounds [65], [66][44] and [139][88] had interacted

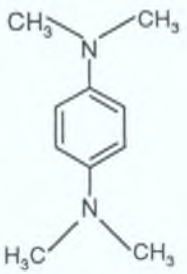
with the donors [72] and [3] to produce CTCs. It was anticipated that [126] and [133] might form related complexes.



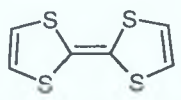
[126]



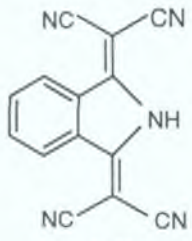
[133]



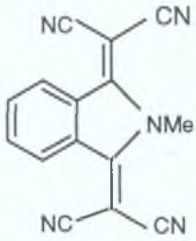
[72]



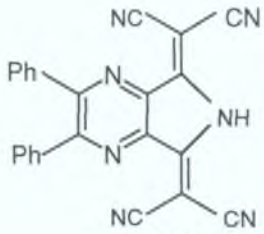
[3]



[65]



[66]



[139]

3.3.2 C-T Studies

The donors [3] and [72] were each added in turn to the amidines [126] and [133] in acetonitrile. No solid precipitated from solution and on analysis by UV/visible spectroscopy, no new spectral bands were observed. This implied that CTC formation had not occurred.

3.3.3 Discussion

The magnitude of C-T and intensity of the C-T bands is dependent on the degree of acceptor-donor overlap, the ionisation potential of the donor and the electron-affinity of the acceptor. Absorptions of weak C-T complexes are difficult to observe since their concentrations are much less than that of the donor and the acceptor and this may explain why no C-T was observed. However, C-T may just not have occurred due to the structural differences between [126] and [133] on the one hand and [66], [65] and [139] which readily formed CTCs on the other. In compounds [126] and [133], there are only three cyano groups present compared

with four cyano groups in the others This contributes to a lack of symmetry in these molecules, symmetrical structure being a prerequisite for CTC formation In addition, the amidine moiety is much less electron-withdrawing than a cyano group The pentyl group of [126] and the bulky piperidine ring of [133] may also make it more difficult for the donor to achieve parallel planarity with the acceptors, and this may be compounded by the presence of the more sterically-demanding amidino unit The degree of intermolecular interaction influences the degree of overlap which is required for strong CT interaction It has been shown recently[89] by Orti et al that steric hindrance is also introduced by lateral benzoannulation of TCNQ They investigated the molecular and electronic structures of TCNQ and its π-extended derivatives, benzo-TCNQ and 11,11,12,12-tetracyano-9,10-anthraquinodimethane (9,10-TCAQ) They found that there is loss of planarity of the TCNQ moiety for benzo-TCNQ and 9,10-TCAQ, the most stable conformation in each case corresponding to a butterfly-type structure in which the TCNQ ring adopts a boat conformation and the aromatic rings remain planar Our acceptor compounds differ from benzo-TCNQ in two ways, the replacement of a cyano group by an alkyl amidino function and the substitution of a carbon-carbon double bond by an NH group A possibility exists, therefore, that the overall structure of our compounds, excluding the bulky alkyl substituents, may also be non-planar These factors may explain why C-T formation for compounds [126] and [133] is unfavourable

Chapter 4
Cyclic VoltammetryAnalysis

4.1 Introduction

Cyclic voltammetry is an electroanalytical technique often used for the initial electrochemical studies of new systems. It is an extremely useful tool and can also be used for identification of short-lived intermediates It is a three electrode system consisting of a working electrode, counter electrode and a reference electrode In any electrochemical process the reference electrode has a fixed potential, therefore any changes in the electrochemical cell are due to the working electrode It is said that the potential of the working electrode is observed with respect to the reference which is equivalent to monitoring the energy of electrons within the working electrode As the electrode is driven to more negative potentials, the energy of the electrons is raised until they eventually reach a level high enough to occupy vacant sites on species in the electrolyte In this situation, the electron flow from the electrode to the solution results in a reduction current, figure 4 1 In the same way an oxidation current flows as the energy of the electrons is lowered by driving the electrode to more positive potential and eventually the electron on solutes in the electrolyte find more favourable energy on the electrode and transfer there The critical potentials at which these processes occur are related to the standard potential, E^0, for specific chemical substances in the system

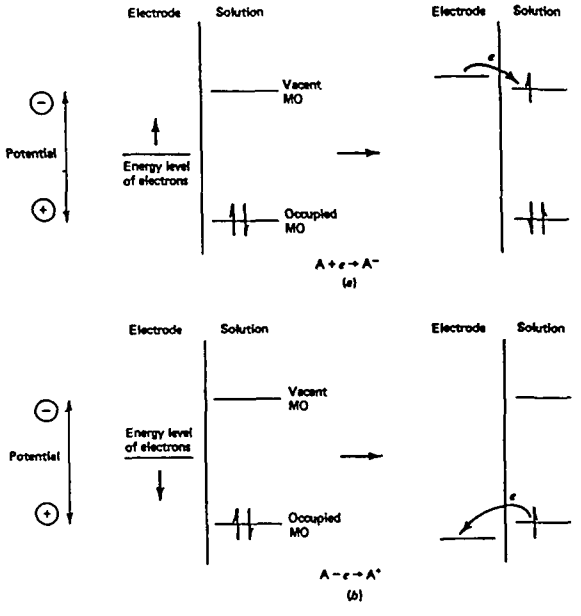
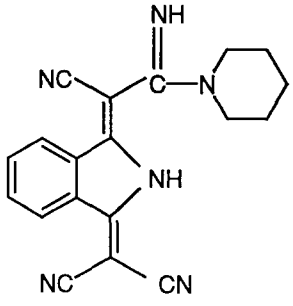
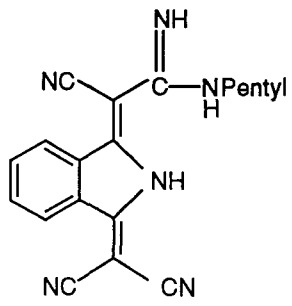


Figure 4 1 Representation of (A) reduction and (B) oxidation process of a species A in solution

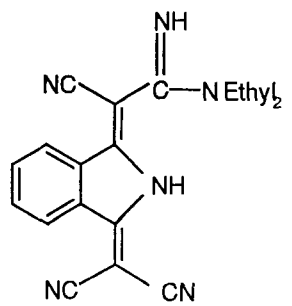
In this chapter, electrochemical studies of the acceptor molecules [133], [126], and [130] are carried out



[133]



[126]



[130]

In a typical cyclic voltammetry experiment,[90] one has an unstirred solution containing a supporting electrolyte and a redox species (in solution or on the surface) The applied potential at the working electrode is measured with respect to the reference electrode and is varied linearly with time The potential of the working electrode is swept first in one direction and then reversed This sweep rate is controlled and is usually fast, typically 20-400 mVs^{-1} Rather than presenting the current variation vs time, a current vs potential plot is normally drawn A typical CV is shown in figure 4 2 The electrode reaction consists of a species O which is reduced to species R

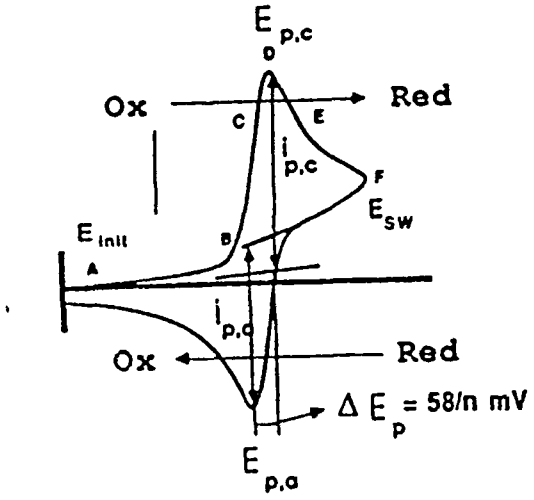


Fig 4 2 A cyclic voltammogram for a freely diffusing species

The scan is begun well positive of E^0 for the reduction (A) No current flows at this point When the electrode potential moves towards E^0 the reduction begins and current starts to flow (B) The potential continues to grow more negative, the surface concentration of the neutral species at the working electrode drops The potential moves past E^0, the surface concentration drops to near zero, mass transfer of the neutral species reaches a maximum rate (D) and then declines as the depletion effect sets in (E) At point (F), the potential is reversed and is swept in the positive direction There is a large concentration of the oxidisable anion radical in the electrode vicinity The anion becomes oxidised and an anodic current flows The reverse current has a shape essentially like that of the forward peak Repeated scanning of electroactive compounds should give a stable voltammogram if the compound contains a stable redox couple

In cyclic voltammetry, there are five main parameters involved These are $E_{p,c}$ and $E_{p,a}$ (c = cathodic, a = anodic), their difference ΔE_p, and the peak currents $i_{p,c}$ and $i_{p,a}$. These characteristics of the voltammogram indicate whether a system is reversible or not If an electrochemical system follows the Nernst equation [1] then it is said to be reversible or Nernstian

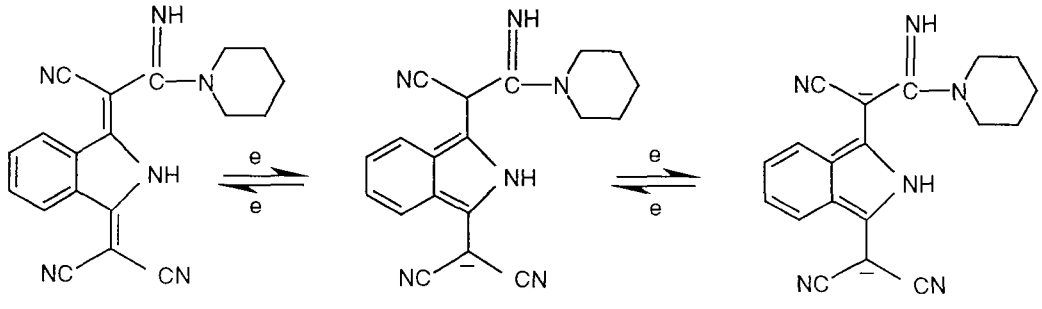
$$E = E^0 + RT/nF \ln C_O/C_R \qquad \text{Eqn [1]}$$

where E is the applied potential, E^0 is formal potential, R is the gas constant, T is 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

4.2 Electrochemical studies of new amidine derivatives of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile [65]

In this experiment a glassy carbon electrode, an Ag/AgCl electrode and a platinum electrode were employed as the working electrode, reference electrode and counter electrode respectively The supporting electrolyte was tetrabutylammonium perchlorate (TBAP) and the solvents used were acetonitrile for compounds [133] and [130], with dimethylformamide being used for [126] due to its lack of solubility in acetonitrile at room temperature In all three cases, it is apparent from figures 4 3 to 4 5 that each of the compounds can be oxidised and reduced electrochemically, each producing two redox couples

In the CV of [133], the potential was scanned between -0 3 V and -1 5 V The scan rate was 100 mVs^{-1} This rate was found to give optimum results for all samples investigated The resulting voltammogram showed the formation of a reduction peak at $E_{p,c}^{1}$ = -0 71 V and a subsequent second reduction peak at $E_{p,c}^{2}$ = -1 19 V On reversing the potential, two oxidation peaks were present at $E_{p,a}^{1}$ = -0 64 V and $E_{p,a}^{2}$ = -1 12 V respectively The scans were repeated a number of times giving a stable voltammogram indicating two stable redox couples For a reversible process $I_{p,a} = I_{p,c}$ and this indeed is evident from the graphs obtained At each reduction peak, an electron is transferred resulting firstly in the formation of anion radical [140] which is then further reduced to give the dianion [141], scheme 4 1

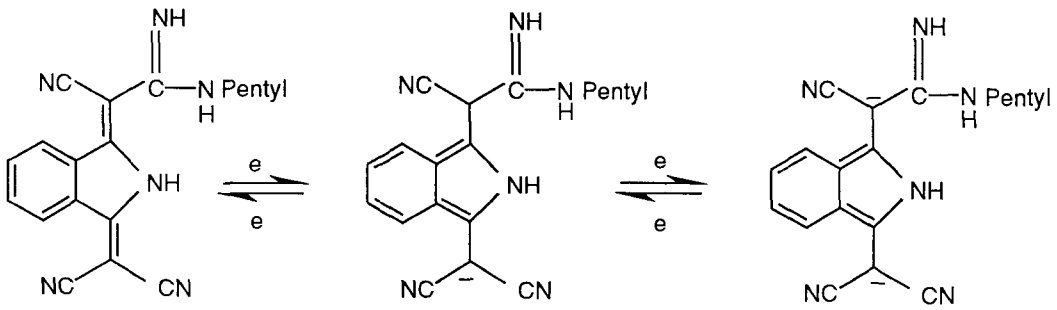


[133] [140] [141]

Scheme 4 1

For the second amidine derivative, the voltage was scanned from -0 4 V to -1 65 V and then reverse swept again at 100 mVs^{-1} The solvent used here was dimethylformamide Examination of the cyclic voltammogram of [126] indicated the

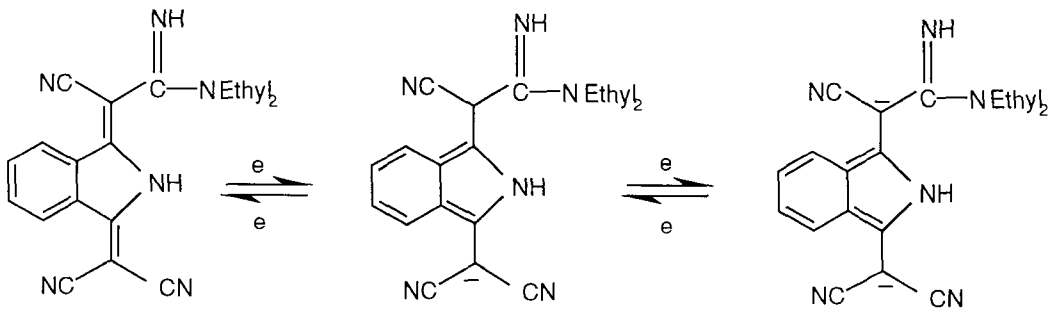
first reduction potential, $E_{p,c}^{1}$ = -0 776 V while the second appeared at $E_{p,c}^{2}$ = -1 375 V Reversing the potential again produced two oxidation peaks at $E_{p,a}^{2}$= -1 22 V and $E_{p,a}^{1}$=-0 654 V, respectively, indicating the formation of two redox couples The redox products are represented as the anion radical [142] and the dianion [143], scheme 4 2



[126] [142] [143]

Scheme 4 2

The final amidine examined [130], resulted in the cyclic voltammogram shown in figure 4 5 The voltage was scanned from -0 45 V to -1 5 V and then reversed The diethyl amidine indicated two redox couples appearing in generally the same region as the other samples The first reduction potential $E_{p,c}^{1}$ = -0 733 V while the second was at $E_{p,c}^{2}$ = -1 242 V Oxidation peaks were detected at $E_{p,a}^{1}$ = -0 656 V and $E_{p,a}^{2}$ = -1 151 V The most likely products from the reduction are the anion radical [144] and the dianion [145], scheme 4 3

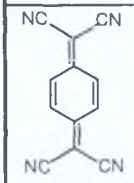
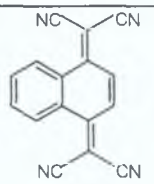
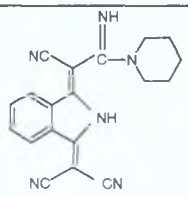
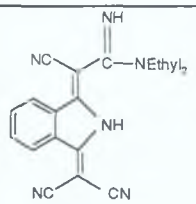
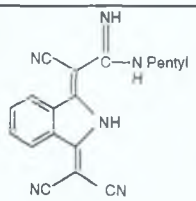


[130] [144] [145]

Scheme 4 3

A summary of the results are given in table 4 1 where $E_{1/2}(1)$ is equal to potential of the first reduction peak, $E_{1/2}(2)$ the second reduction peak and ΔE equal to the difference between them

Table 4.1 Comparison of ΔE values of the electroactive amidino derivatives of [71]

Acceptor	Solvent	$E_{1/2}(1)$/V	$E_{1/2}(2)$/V	ΔE/V
 TCNQ	DMF	-0.12	-0.72	0.60
	Acetonitrile	-0.14	-0.69	0.55
 benzo TCNQ	DMF	-0.30	-0.73	0.43
	Acetonitrile	-0.04	-0.41	0.37
 [133]	Acetonitrile	-0.71	-1.19	0.48
 [130]	Acetonitrile	-0.73	-1.24	0.51
 [126]	DMF	-0.78	-1.38	0.60

Comparison of the three samples with TCNQ and benzoTCNQ (table 4.1) allows us to predict the electron acceptor abilities of [126], [130] and [133]. $E_{1/2}(1)$ for TCNQ is at -0.12 V with $E_{1/2}(2)$ = -0.72 V. Similarly, benzo-TCNQ has its $E_{1/2}(1)$ = -0.30 V with $E_{1/2}(2)$ = -0.73 V when dimethylformamide is used as the solvent. When acetonitrile is used as solvent, $E_{1/2}(1)$ is equal to –0.14 V with $E_{1/2}(2)$ = -0.69 V for TCNQ while the corresponding values produced for benzoTCNQ occur at –0.04 V

and –0 41 V respectively $E_{1/2}(1)$ and $E_{1/2}(2)$ for amidine [133] were observed at –0 71 and –1 19 V When amidine [130] was also analysed in acetonitrile, it gave values of $E_{1/2}(1)$ = -0 73 V and $E_{1/2}(2)$ = -1 24 V The final sample [126] was run in dimethylformamide giving its $E_{1/2}$ values at –0 78 V and –1 38 V respectively

Fig 4 3 2-Cyano-2-(3-dicyanomethyleneisoindolin-1-ylidene)-N-(1-iminoethyl)-piperidine [133] in acetonitrile with 0 1 M tetrabutylammonium perchlorate

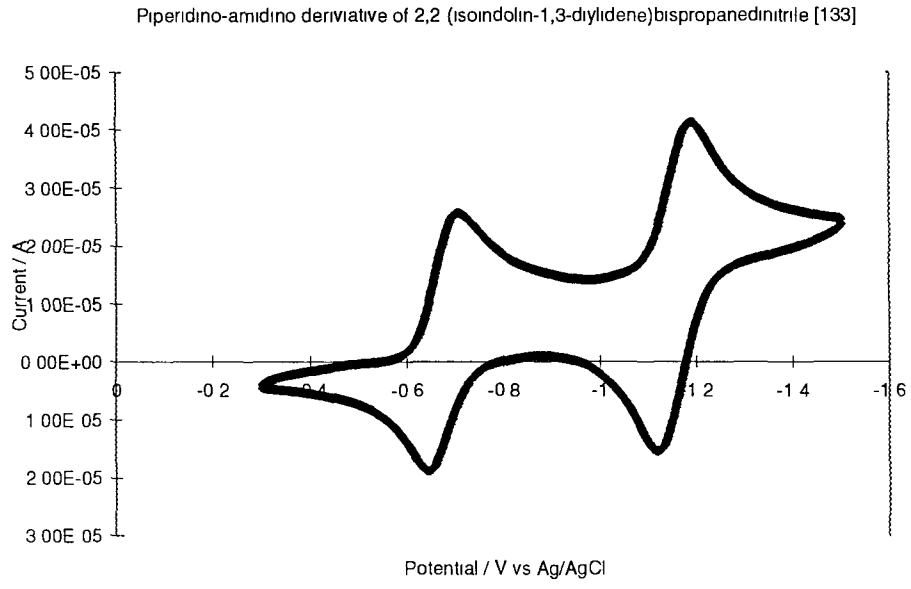


Fig 4 4 2-Cyano-N^2-pentyl-2-(3-dicyanomethyleneisoindolin-1-ylidene)-acetamidine [126] in DMF with 0 1 M tetrabutylammonium perchlorate

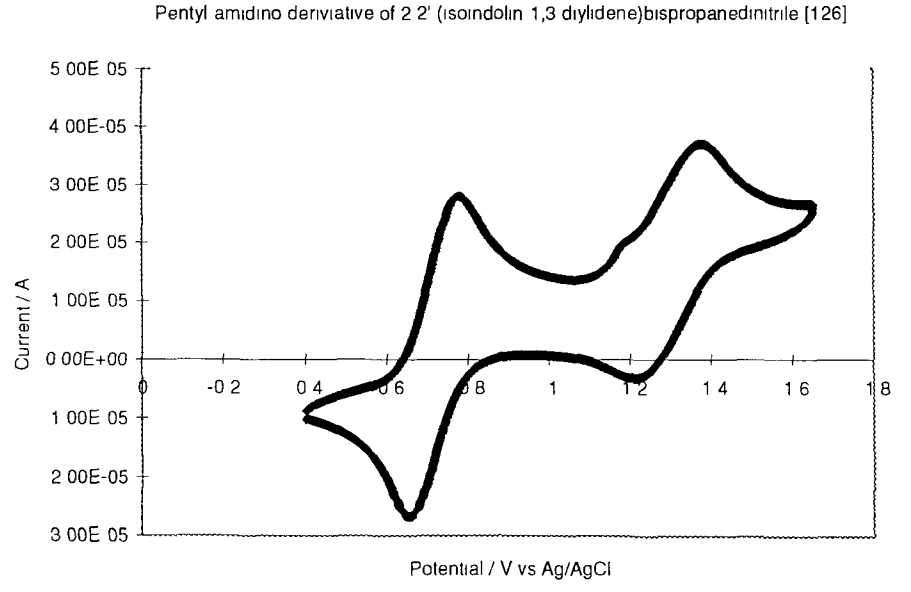
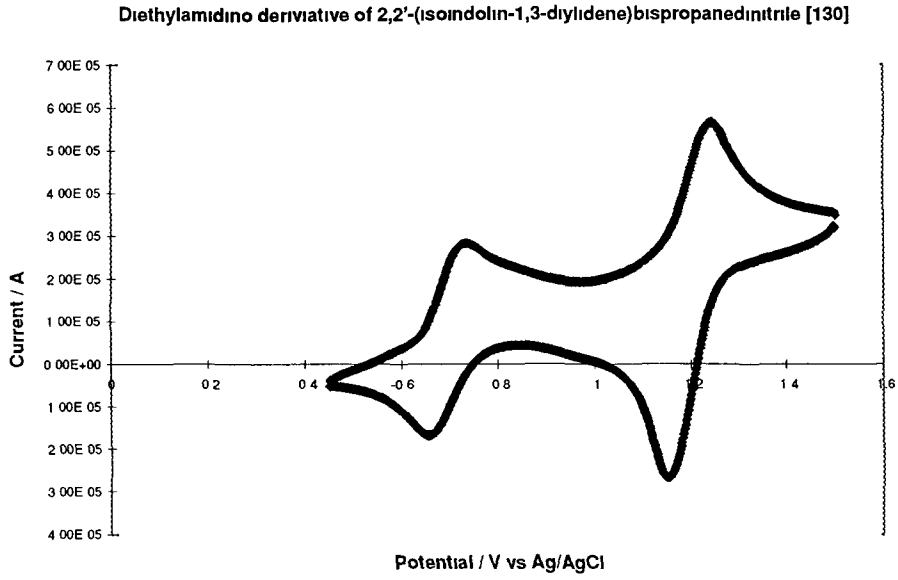


Fig 4 5 2-Cyano-N',N'-diethyl-2-(3-dicyanomethyleneisoindol-1-ylidene)-acetamidine [130] in acetonitrile with 0 1 M tetrabutylammonium perchlorate



It is the absolute values of $E_{1/2}$ which predict the electron acceptor properties of compounds In the case of amidines [133], [130] and [126], there was a significant difference between the absolute $E_{1/2}$ values recorded and that of TCNQ, the values for the amidines being significantly more negative Compounds having more negative $E_{1/2}$ values than TCNQ are less likely to participate in charge-transfer formation This was seen when attempts to synthesise charge-transfer complexes with [133] and [126] using the donors TTF and TMDA were unsuccessful

4.3 Conclusion

The three amidines studied using CV have shown electrochemical activity Each resulted in two redox couples, each with reversible characteristics Each was also very stable in its anion radical and dianion forms and repeated cycling of the current resulted in reproducible current versus potential profiles

Chapter 5

Experimental Section

General

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ACF 400 instrument operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR The following abbreviations are used s = singlet, t = triplet, q = quartet, qn = quintet, st = sextet, m = multiplet, bs = broad singlet

Infra-red (IR) spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectophotometer using KBr pellets

Elemental analyses were carried out by the Microanalytical Laboratory at University College Dublin

Melting point determinations were recorded using a Griffin melting point apparatus and are uncorrected

Ultra-violet (UV) spectra were recorded on a Shimadzu UV 3100 UV-VIS recording spectrophotometer The units for ε are $dm^{3}mol^{-1}cm^{-1}$ Spectrograde acetonitrile was used as solvent unless otherwise stated

Thin layer chromatography (TLC) was carried out using silica gel TLC plates containing a fluorescent indicator (Riedel De Haen, DC cards SiF, layer thickness 0 2 mm)

Synthesis of 3-phenylimino-1-iminoisoindoline (67a)[44]

Sodium methoxide (1.68 g, 3.10 x 10^{-2} moles) was added to a solution of phthalonitrile (20.02 g, 1.56 x 10^{-1} moles) in methanol (400 cm^3). Aniline (14.57 g, 1.56 x 10^{-1} moles) was added and the mixture heated under reflux for 2.5 hours. The hot solution was filtered through a bed of silica gel to remove a small amount of navy blue solid (phthalocyanines). Rotary evaporation of the solution yielded a solid which was recrystallised from ethanol to give [67b] (17.26 g, 50%); mp 203 °C (lit,[44] 203 °C); IR : υ_{max} 3031, 1692, 1604, 1594 ,1530 ,1432, 1332, 1290, 1215, 1128, 1100, 999, 908, 780, 743, 720, 697 and 644 cm^{-1}; UV (CH_3OH) : λ_{max} 372 (ε = 4,585), 348 (4,538), and 232 (12,866) nm; ^{1}H-NMR (DMSO-d_6) : δ 8.72 (bs, 1H, NH), 8.51 (bs, 1H, NH) 6.99-7.94 ppm (m, 9H, aromatic); ^{13}C-NMR (DMSO-d_6) δ 120.65, 121.34, 123.09, 126.62, 128.04, 130.03, 130.85, 135.09, 140.46, 150.27 (aromatic), 164.94 and 171.43 ppm (C=N).

Ammonium salt of 2, 2'-(isoindolin-1,3-diylidene)bispropanedinitrile [71][44]

To a stirring solution of 3-phenylimino-1-iminoisoindoline [67b] (15.00 g, 6.78 x 10^{-2} moles) in dimethylformamide (130 cm^3), malononitrile (9.42 g, 1.43 x 10^{-1} moles, 10% excess) was added dropwise at room temperature. The solution changed from yellow to a dark red colour with evolution of ammonia gas confirmed by litmus paper. Addition of chloroform precipitated the salt. The solid was filtered off and recrystallised from methanol to yield dark red needle-like crystals of [71] (15.00 g, 85%); mp 348-349°C (dec)[44]; IR : υ_{max} 3181, 3091, 2211, 1612, 1577, 1501, 1450, 1432, 1307, 1259, 1195, 1164, 1096, 920, 770, 749 and 704 cm^{-1}; UV (CH_3CN) : λ_{max} 496 (ε = 25,905), 466 (27,120), 360 (9,612), 344 (12,359) and 240 (9,331) nm; ^{1}H-NMR (DMSO-d_6): δ 8.08 (m, 2H, aromatic), 7.64 (m, 2H, aromatic) and 7.07 ppm (1:1:1 t, J_{N-H} = 51 Hz, 4H, NH); ^{13}C-NMR (DMSO-d_6): δ 53.44 [C=C(CN)$_2$], 115.74, 116.74 (CN), 122.40, 130.90 (aromatic), 136.91 (quaternary), 171.48 [C = C(CN)$_2$] ppm.

Synthesis of the tetramethylammonium salt of 2,2'-(isoindolin-1,3-diylidene)-bispropanedinitrile [73].[44]

The ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile [71] (2.02 g, 7.76 x 10^{-3} moles) was added to tetramethylammonium chloride (0.85 g, 7.76 x 10^{-3} moles) in methanol (100cm^3) and stirred at room temperature overnight. Orange crystals precipitated and were recrystallised from ethanol yielding [73] (12.16 g, 88%); mp 250-251 °C (lit,[44] 251-252 °C); IR : υ_{max} 3029, 2205, 1653, 1598, 1577, 1498, 1577, 1496, 1309, 1256, 1098, 947, 917, 778, 767, 745, 711 and 703 cm^{-1}; UV (CH_3CN) : λ_{max} 496 (ε = 83,340), 466 (87,132), 342 (40,692), 238 (84,840) nm; ^{1}H-NMR (DMSO-d_6) : δ 8.10 (m, 2H, aromatic) 7.66 (m, 2H, aromatic), 3.08 ppm (s, 12H, Me); ^{13}C-NMR (DMSO-d_6) : δ 172.02 [$\underline{C}$=C(CN)$_2$], 137.42 (quaternary C), 131.36, 122.88 (aromatic C), 117.23, 116.28 (CN), 59.73 [C=$\underline{C}$(CN)$_2$], 54.34 (1:1:1 t, $J_{N\text{-}C}$ = 15 Hz, Me) ppm.

Synthesis of the tetraethylammonium salt of 2,2'-(isoindolin-1,3-diylidene)-bispropanedinitrile [74]

The ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile [71] (6.00 g, 2.3 x 10^{-2} moles) and tetraethylammonium bromide (4.8 g, 2.3 x 10^{-2} moles) were dissolved in methanol (150 cm^3) and stirred overnight. Orange crystals precipitated from solution and were collected using vacuum filtration. Recrystallisation from ethanol yielded [74] (5.99 g, 71%), mp 130 °C; IR : υ_{max} 2979, 2919, 2206, 1488, 1474, 1310, 1260, 1095, 999, 783 and 709 cm^{-1}; UV (CH_3CN) : λ_{max} 496 (ε = 58,892), 465 (58,312) 358 (18,292), 342 (24,666), 279 (6,084), 241 (57,029) nm; ^{1}H-NMR (acetone-d_6) : δ 7.63 (m, 2H, aromatic) 7.17 (m, 2H, aromatic), 2.72 (q, 8H, CH_2), 0.67 ppm (t, 12H, CH_3); ^{13}C-NMR (DMSO-d_6) : δ 7.09 (CH_3), 51.34 [1:1:1 t, $J_{N\text{-}C}$ = 2.8 Hz (CH_2)], 54.01 [C=$\underline{C}$(CN)$_2$], 117.28, 116.31 (CN), 122.94, 131.46, (aromatic), 137.45 (quaternary), 172.06 [$\underline{C}$ = C(CN)$_2$] ppm; Microanalysis : Found C, 70.89; H, 6.61; N, 22.55; $C_{22}H_{24}N_6$ requires C, 70.94; H, 6.49 ; N, 22.56 %.

Synthesis of the tetrabutylammonium salt of 2,2'-(isoindolin-1,3-diylidene)-bispropanedinitrile [75]

The ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile [71] (7.10 g, 2.73 x 10^{-2} moles) was dissolved in methanol (200 cm^3) and tetrabutylammonium iodide (10.08 g, 2.73 x 10^{-2} moles) was added. The solution was allowed to stir overnight at room temperature. The orange crystals which precipitated were filtered off and recrystallised from ethanol to give the tetrabutylammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile [75], (7.01 g, 53%), mp 50-52°C; IR : ν_{max} 2967, 2931, 2871, 2205, 1492, 1482, 1312, 1257, 1097, 916, 880 and 705 cm^{-1}; UV (CH_3CN) : λ_{max} 496 (ε = 30,341), 456 (29,982), 342 (12,729), 279 (3,950), 268 (4,255), 241 (32,154), 236 (32,280) nm; ^{1}H-NMR (DMSO-d_6) : δ 8.09 (m, 2H, aromatic), 7.64 (m, 2H, aromatic), 3.15 (t, 8H, NCH_2), 1.53 (qn, 8H, CH_2), 1.29 (st, 8H, CH_2), 0.90 (t, 12H, CH_3) ppm; ^{13}C-NMR (DMSO-d_6) : δ 13.45, 19.19, 23.05, 57.53 (aliphatic), 53.92 [C=<u>C</u>$(CN)_2$], 116.22, 117.22 (CN), 122.88, 131.34 (aromatic), 137.44 (quaternary), 172.00 [<u>C</u>=C$(CN)_2$] ppm; Microanalysis : Found C, 74.51; H, 8.35; N, 17.50; $C_{30}H_{40}N_6$ requires C,74.34; H, 8.32; N, 17.34 %.

Synthesis of the tetrapentylammonium salt of 2,2'-(isoindolin-1,3-diylidene)-bispropanedinitrile [76]

The ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile [71] (5.50 g, 2.11 x 10^{-2} moles) and tetrapentylammonium iodide (8.92 g, 2.10 x 10^{-2} moles) were dissolved in methanol (200 cm^3) and the solution allowed to stir overnight at room temperature. The orange solid which precipitated from solution was recrystallised from ethanol to yield large needles of [76] (7.42 g, 65%); mp 198-199 °C; IR : ν_{max} 2931, 2874, 2516, 2203, 1491, 1478, 1379, 1312, 1258, 1096, 916, 779 and 709 cm^{-1}; UV (CH_3CN) : λ_{max} 496 (ε = 36,682), 465 (36,470), 359 (11,647), 343 (15,647), 279 (3,529), 267 (4,118), 241 (35,600) nm; ^{1}H-NMR (DMSO-d_6) : δ 8.09 (m, 2H, aromatic), 7.65 (m, 2H, aromatic), 3.14 (m, 8H, NCH_2), 1.58 (qn, 8H, CH_2), 1.29, (qn, 8H, CH_2), 1.21 (st, 8H, CH_2), 0.91 ppm (t, 12H, CH_3); ^{13}C-NMR

(DMSO-d_6) δ 13 92, 20 94, 21 77, 28 13, 57 84 (aliphatic), 54 14 [C=<u>C</u>$(CN)_2$], 116 44, 117 44 (CN), 123 04, 131 57 (aromatic), 137 65 (quaternary), 172 21 ppm [<u>C</u>=C$(CN)_2$], Microanalysis Found C, 75 77, H, 9 10, N, 15 59, $C_{34}H_{48}N_6$ requires C, 75 51, H, 8 95, N, 15 54%

Pyrolysis of the tetramethylammonium salt of 2,2'-(isoindolin-1,3-diylidene)-bispropanedinitrile [73]

The tetramethyl ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropane-dinitrile [73] (2 00 g, 6 32 $x10^{-3}$ moles) was heated under reflux for 24 hours in 1,2,4-trichlorobenzene (25 cm^3) During this time the solution changed from dark orange to black and TLC showed the formation of a new fast-running product that increased in concentration as the reaction proceeded The solvent was removed under reduced pressure and the resulting mixture purified by column chromatography on silica gel [60 40 ethyl acetate light petroleum (bp 40-60°C) to afford 2,2'-(2-methylisoindol-1,3-diylidene)bispropanedinitrile [66] Recrystallisation from acetonitrile yielded [66] (0 41 g, 25%), mp 264 °C (lit,[44] 264 °C) , IR υ_{max} 3121, 2224, 1598, 1557, 1471, 1446, 1318, 1225, 1109, 785 and 690 cm^{-1}, UV (CH_3CN) λ_{max} 416 (ε = 25,247), 394 (25,017), 294, 280 and 244 (10,868) nm, ^{1}H-NMR (acetone-d_6) δ 8 65 (m, 2H, aromatic), 7 98 (m, 2H, aromatic), 4 10 (s, 3H, Me) ppm, ^{13}C-NMR (acetone-d_6) δ 160 92 [<u>C</u>=C$(CN)_2$], 135 30 (quaternary), 125 70, 132 10 (aromatic), 113 76, 114 52 (CN), 61 90 [C=<u>C</u>$(CN)_2$], 37 59 (Me) ppm

Pyrolysis of the tetraethylammonium salt of 2,2'-(2-isoindolin-1,3-diylidene)-bispropanedinitrile [74]

The salt [74] (2 00 g, 5 37 x 10^{-3} moles) was heated under reflux in 1,2,4-trichlorobenzene (25 cm^3) for 36 hours The reaction was maintained under a blanket of nitrogen with constant monitoring by TLC using 70 30 ethyl acetate light petroleum (bp 40-60 °C) A faint yellow band appeared as a fast running component

similar to that seen in the synthesis of [66] However increased reaction times did not appear to increase its concentration, only producing a more complex mixture of products Separation on column chromatography using a silica gel stationary phase and similar mobile phase to TLC proved unsuccessful

Pyrolysis of the tetrabutylammonium salt of 2,2'-(isoindolin-1,3-diylidene)-bispropanedinitrile [75]

The tetrabutylammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile [75] (2 05 g, 4 23 x 10^{-3} moles) was heated under reflux in 1,2,4-trichlorobenzene (25 cm^3) The solution changed from red to black after 2 hours reflux The reaction was monitored by TLC using 70 30 ethyl acetate light petroleum (bp 40-60°C) as the mobile phase A complex mixture of products were observed The reaction was heated for 30 hours in total On evaporation of the solvent, attempts to separate the mixture of products on column chromatography (mobile phase as for TLC) proved ineffective

Pyrolysis of the tetrapentylammonium salt of 2,2'-(isoindolin-1,3-diylidene)-bispropanedinitrile [76]

The tetrapentylammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile [76] (1 00 g, 1 85 x10^{-3} moles) was added to 1,2,4-trichlorobenzene (15 cm^3) The mixture was heated under reflux for 24 hours under a blanket of nitrogen gas The solution was monitored by TLC using 70 30 ethyl acetate light petroleum (bp 40-60°C) showing a complex mixture of products Removal of the solvent and subsequent column chromatography using 60 40 ethyl acetate light petroleum (bp 40-60°C) was unproductive in separation of the mixture

Attempted synthesis of 2,2'-(2-N-succinimidomethylisoindolin-1,3-diylidene)bispropanedinitrile [77] from the ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile [71], formaldehyde and succinimide.

The ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile [71] (0 65 g, 2 50 x 10^{-3} moles) and succinimide (0 29 g, 2 93 x 10^{-3} moles, ~20% excess) were dissolved in hot ethanol (60 cm^3) The solution was allowed to cool to 45 ^{0}C Formaldehyde (37 % aqueous solution, 0 49 cm^3, 2 equiv , 6 23 x 10^{-3} moles) was added slowly An orange precipitate formed The reaction was heated under reflux for 1 5 hours until the precipitate dissolved The mixture was allowed to cool and the resulting orange precipitate was then filtered off and recrystallised from DMF ethanol (20 80) IR and melting point were identical with those of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile [65]

Attempted synthesis of 2,2'-(N-succinimidomethylisoindolin-1,3-diylidene)-bispropanedinitrile [77] from 2,2'-(isoindolin-1,3-diylidene)bispropane-dinitrile [65], formaldehyde and succinimide.

2, 2'-(Isoindolin-1,3-diylidene)bispropanedinitrile [65], (0 80 g, 3 29 x 10^{-3} moles) and succinimide (0 39 g, 3 95 x 10^{-3}moles, 20% excess) were dissolved in hot methanol (25 cm^3) After cooling the mixture to 45°C, formaldehyde (37% aqueous solution, 0 27 cm^3, 3 equiv , 9 87 x 10^{3} moles) was added slowly and the reaction was heated under reflux for 1 5 hours On cooling, a solid precipitated from solution Filtration and recrystallisation from ethanol yielded [65], confirmed from IR and mp data

Attempted synthesis of 2,2'-(N-methylanilinomethylisoindolin-1,3-diylidene)bispropanedinitrile [78] from 2,2'-(isoindolin-1,3-diylidene)-bispropanedinitrile [65], formaldehyde and N-methylaniline.

2,2'-(Isoindolin-1,3-diylidene)bispropanedinitrile [65] (1 00 g, 4 11 x 10^{-3}moles) was dissolved in methanol (40 cm^3) by heating N-Methylaniline (0 51 g, 4 93 x 10^{-3}

moles, 20% excess) was added giving an orange solution Cooling this solution to 45°C, formaldehyde (37% aqueous solution, 0 94 cm^3, 3 equiv) was added slowly The solution was heated under reflux for 1 5 hours Removal of solvent yielded a yellow solid which again proved to be (65)

Synthesis of N-methylphthalimide[58]

Phthalic anhydride (10 g, 6 80 x 10^{-2} moles) was dissolved in glacial acetic acid (100 cm^3) Methylamine (40% ethanolic solution, 5 28 g, 6 80 x 10^{-2} moles) was added and heated under reflux for 20-30 mins A solid precipitated on cooling Recrystallisation from ethanol yielded white crystals of [14], (8 22 g, 75 %), mp 129-130 °C (lit,[58] 131-132 °C), IR ν_{max} 3455, 3150, 2960, 1723, 1609, 1606, 1536, 1470, 1343, 1295, 1250 and 717 cm^{-1}, ^{1}H-NMR ($CDCl_3$) δ, 7 78 (m, 2H, aromatic), 7 65 (m, 2H, aromatic), 3 12 (s, 3H, methyl) ppm, ^{13}C-NMR ($CDCl_3$) δ 168 18 (carbonyl), 131 56 (quaternary), 131 86, 122 85 (aromatic), 23 62 (Me) ppm.

Synthesis of bromomalononitrile[60]

A suspension of malononitrile (13 2 g, 1 99 x 10^{-1} moles) in water (150 cm^3) was stirred and kept ice-cold This was then transferred in small amounts to bromine (3 2 g, 4 00 x 10^{-1} moles) The reaction was maintained at 0 °C for 4 hours, stirring throughout this time The suspension of almost colourless crystals was filtered and washed with ice-water They were then dried in vacuo over sulphuric acid to yield bromomalonitrile (1 23 g, 43%), mp 64-65 °C (lit,[60] 64-65 °C), IR ν_{max} 2369, 2262, 1280, 1014, 919, 897 and 684 cm^{-1}, ^{1}H-NMR (acetone-d_6) δ 4 22 (s, CH) ppm, ^{13}C-NMR (acetone-d_6) δ 112 20 (CN), 8 55 (CH) ppm

Attempted reaction of bromomalononitrile with N-methylphthalimide in the presence of zinc.

A three-necked round bottomed flask was equipped with a 100 cm^3 dropping funnel, a mechanical stirrer and a double surface condenser to which calcium chloride guard tubes were attached. Zinc powder (10.00 g, 1.53 x 10^{-1} moles) which had been dried at 100 °C, was placed in the flask and a solution of bromomalononitrile (18.00 g, 1.25 x 10^{-1} moles) and N-methylphthalimide (24.78 g, 1.54 x 10^{-1} moles) in toluene (20 cm^3) and dried diethyl ether (5 cm^3) was placed in the dropping funnel. About 5 cm^3 of the solution was added to the zinc and the mixture was heated under reflux. No immediate reaction was observed. Heating was continued and the remainder of the solution was added. The mixture was heated on a water bath at a moderate reflux for 1.5 hours. The flask was cooled in an ice bath and 12.5 cm^3 of 10% sulphuric acid added with vigorous stirring. The solution was then transferred to a separatory funnel, the aqueous layer removed and the toluene layer then washed twice with 5% sulphuric acid (4 cm^3), once with 10% sodium carbonate (2 cm^3) and finally with water (2 cm^3). The organic layer was then reduced to a smaller volume by removal of the toluene and a white solid precipitated. Recrystallisation of the solid followed by mp and IR analyses indicated N-methylphthalimide (22.34 g, 90%) was recovered.

Synthesis of 1,3-diiminoisoindoline [67a][47]

Phthalonitrile (4.50 g, 3.51 x 10^{-2} moles) and sodium methoxide (1.90 g, 3.51 x 10^{-2} moles) were stirred together at room temperature in a methanolic solution (100 cm^3) for 1 hour while a rapid stream of anhydrous ammonia was bubbled through the system. The reaction was then heated under reflux for a further 3 hours while maintaining the ammonia flow. The solution was filtered hot through a bed of silica gel to remove a tiny amount of a grey solid. Rotary evaporation to remove the solvent gave a viscous green oil which on scratching with a glass rod yielded a yellow solid. Recrystallisation from 70:30 methanol:diethyl ether using decolourising charcoal gave [67a] (2.14 g, 42%), mp 195-196 °C (lit,[47] 196 °C); IR ν_{max} 3241,

3255, 2984 (C=NH), 1693, 1530, 1468, 1312, 1276, 1177, 1158, 1136, 1081, 1015, 950, 891, 776, 745, 708 and 695 cm^{-1}; ^{1}H-NMR (DMSO-d_6) : δ 8.80 (bs, 2H, NH), 7.85 (m, 2H, aromatic), 7.55 (m, 2H, aromatic), 3.85 (bs,1H, NH) ppm; ^{13}C-NMR (DMSO-d_6) : δ 119.98, 129.94 (aromatic), 134.36 (quaternary), 169.75 (C=NH) ppm.

Attempted benzylation of 1,3-diiminoisoindoline [67a]

Sodium hydride (0.14 g, 3.44 x 10^{-3} moles, 60% dispersion in oil) was added to a small quantity of light petroleum (bp 40-60 °C) to dissolve the oil. The liquid was decanted off and a solution of 1,3-diiminoisoindoline [67a] (0.50 g, 3.44 x 10^{-3} moles) in dimethylformamide (50 cm^3) was added. Hydrogen gas was evolved. When this subsided, benzyl chloride (0.48 g, 3.75 x 10^{-3} moles) was added and the reaction heated under reflux for one hour. After this time, TLC [90:10 ethyl acetate:light petroleum (bp 40-60 °C)] of the reaction solution was run. This showed a complex mixture of products. Isolation of these products by column chromatography was attempted but without success.

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

2-Cyano-N^2-pentyl-2-(3-dicyanomethyleneisoindol-1-ylidene)acetamidine [126]

The ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile [71] (0.55 g, 2.11 x 10^{-3} moles) and 1-aminopentane (0.37 g, 4.25 x 10^{-3} moles) were heated under reflux in ethanol (35cm^3) for 3.5 hrs. On standing overnight, an orange solid precipitated. Two recrystallisations from acetonitrile yielded [126], (0.15 g, 22%), mp 301-303 °C; IR : υ_{max} 3427, 3343, 3272, 2928, 2874, 2210, 1654, 1465, 1448, 1312, 1256, 1147, 1092, 908, 779 and 665 cm^{-1}; UV (CH_3CN) : λ_{max} 487 (ε = 14,331), 457.5 (12,987), 346.5 (5,818), 242.5 (13,031) nm; ^{1}H-NMR (DMSO-d_6) (70 °C) : δ 8.66 (bs, 1H, NH), 8.33 (m, 1H, aromatic), 8.17 (m, 1H, aromatic), 7.69 (m,

2H, aromatic), 3 38 (t, 2H, NCH_2), 1 71 (qn, 2H, CH_2), 1 37 (m, 4H, CH_2), 0 89 (t, 3H, Me) ppm, ^{13}C-NMR (DMSO-d_6) : δ 13 82, 21 67, 27 34, 28 63, 42 49 (pentyl CH), 56 80 [C=C(CN)$_2$], 72.09 [C=C(CN)], 115 36, 115 99, 117 29 (CN), 123 55, 123 87, 131 65, 132 09, 135 23, 138 25 (aromatic), 159 16, 167 10 and 170 64 [C=C(CN) and (C=N)] ppm, Microanalysis Found, C, 68 77, H, 5 53, N, 25 28%, $C_{19}H_{18}N_6$ requires C, 68 99, H, 5 49, N, 25 52%

2-Cyano-N',N'-diethyl-2-(3-dicyanomethyleneisoindol-1-ylidene)acetamidine [130]

N,N-Diethylamine (0 34 g, 4 6 x 10^{-3} moles) was added to an ethanolic solution (25 cm^3) of the ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile [71] (0 61 g, 2 34 x 10^{-3}moles) and heated under reflux for 5 5 hours The solution changed from orange to a dark red The reaction was allowed to cool and overnight a solid precipitated Recrystallisation from acetonitrile yielded a bright orange compound [130], (0 34 g, 47%), mp 196-198 ^{0}C, IR υ_{max} 3345, 2972, 2927, 2220, 2203, 1654, 1602, 1583, 1560, 1484, 1458, 1438, 1389, 1359, 1312, 1254, 1266, 1164, 1091, 910 and 720 cm^{-1}, UV (CH_3CN) λ_{max} 492 (ε = 52,438), 465 (51,226), 346 (20,010), 240 (39,704) nm, ^{1}H-NMR ($CDCl_3$) δ 8 50 (m, 1H, aromatic), 8 29 (m, 1H, aromatic), 7 45 (m, 2H, aromatic), 6 40 (bs, 1H, NH), 3 68 (q, 4H, CH_2), 1 42 (t, 6H, CH_3) ppm, ^{13}C-NMR (DMSO-d_6) : δ 11 49, 34 22, (ethyl CH), 55 33 [C=C(CN)$_2$], 72 57 [C=C(CN)], 116 41, 117 64, 117 76 (CN), 122 14, 122 37, 130 44, 130 56, 137 14, 137 23 (aromatic), 157 96, 164 96 and 170 93 [C=C(CN) and (C=N)] ppm, Microanalysis Found , C, 68 22, H, 5 09, N, 26 46 %, $C_{18}H_{16}N_6$ requires C, 68 35, H, 5 09, N, 26 56%

2-Cyano-2-(3-dicyanomethyleneisoindol-1-ylidene)-N-(1-iminoethyl)-piperidine [133]

The ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile [71] (0 80 g, 3 07 x 10^{-3} moles) and piperidine (0 52 g, 6 14 x 10^{-3} moles) were heated together in ethanol (40 cm^3) under reflux for 1 5 hrs The solution changed from bright orange to dark red and an orange solid precipitated This was filtered off and dried in vacuo

Recrystallisation from acetonitrile yielded [133] (0 40 g, 40%), mp 238-239 °C, IR υ_{max} 3321, 3270, 2935, 2898, 2201, 1648, 1602, 1582, 1556, 1492, 1474, 1438, 1374, 1308, 1261, 1181, 1106, 1090, 1022, 1004, 793 and 732 cm^{-1}, UV (CH_3CN) λ_{max} 496 (ε = 32,186), 467 (30,213), 347 (12,205), 241 (21,025) nm, ^{1}H-NMR (pyridine-d_5) δ 10 79 (bs, 1H, NH), 8 59 (m, 1H, aromatic), 8 41 (m, 1H, aromatic), 7 40 (m, 2H, aromatic), 3 72 (t, 4H, CH_2), 1 65 (m, 4H, CH_2), 1 51 (m, 2H, CH_2) ppm, ^{13}C-NMR (pyridine-d_5) δ 23 68, 25 59, 50 27 (piperidino Cs), 56 83 [C=C(CN)$_2$], 72 24 [C=C(CN)], 117 21, 117 74, 119 71 (CN), 123 94, 124 29, 131 16, 131 31, 137 73, 139 30 (aromatic), 162 64, 169 35, 172 35, [C=C(CN) and (C=N)] ppm, Microanalysis Found C, 69 21, H, 4 62, N, 25 68%, $C_{19}H_{16}N_6$ requires C, 69 50, H, 4 91, N, 25 59%

Reaction of the ammonium salt of 2,2'-(isoindolin-1,3-diylidene)-bispropanedinitrile [71] with morpholine

Morpholine (0 60 g, 6 89 x 10^{-3} moles) and the ammonium salt [71] of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile [71] (0 90 g, 3 45 x 10^{-3} moles) were heated under reflux in ethanol (45 cm^3) for 2 5 hours The solution changed to dark red and on cooling an orange solid precipitated from the solution Analysis of the solid by tlc showed two new components, present in the approximate ratio 1 1, estimated from the ^{1}H-NMR spectrum Several recrystallisations from acetonitrile yielded one component (0 27 g), mp 264-265 °C, IR ν_{max} 3410, 3338, 3234, 2212, 1664, 1670, 1654, 1499, 1477, 1311, 1269, 1091, 907 and 731 cm^{-1} , ^{1}H-NMR (DMSO-d_6) δ 9 41 (bs, 1H, NH), 8 52 (bs, 1H, NH), 8 31 (m, 1H, aromatic), 8 15 (m, 1H, aromatic), 7 71 (m, 2H, aromatic) ppm, ^{13}C-NMR (DMSO-d_6) δ 57 61 [C=C(CN)$_2$], 71 32 [C=C(CN)], 115 33, 115 92, 117 39 (CN), 123 65, 123 97, 131 78, 132 22, 135 41, 138 37 (aromatic), 162 09 (C=N), 168 30 and 170 94 ppm [C=C(CN)], Microanalysis Found C, 63 60, 63 36, H, 3 15, 3 14, N, 31 09, 30 96%, $C_{14}H_8N_6$ [136] requires C, 64 61, H, 3 10, N, 32 29% , $C_{18}H_{14}N_6O$ [135] requires C, 65 45, H, 4 27, N, 25 44% Extensive efforts to separate out the second component using recrystallisation and column chromatography were unsuccessful The main peaks observed in the NMR spectrum of the mixture (in addition to those

reported above for the isolated component) are ^{1}H-NMR (DMSO-d_6) δ 9 59 (bs, 1H, NH), 9 03 (bs, 1H, NH), 8 25 (m, 1H, aromatic), 8 15 (m, 1H, aromatic), 7 67 (m, 2H,aromatic), 3 79 (t, 4H, aliphatic), 3 60 (t, 4H, aliphatic) ppm, ^{13}C-NMR (DMSO-d_6) δ 48 68, 65 05 (morpholino Cs), 52 20 [C=C(CN)$_2$], , 72 20 [C=C(CN)], 116 85, 117 28, 118 67 (CN), 123 20, 122 87, 131 37, 131 27, 137 95, 137 36 (aromatic), 159 25 (C=N), 166 57 and 171 73 ppm [C=C(CN)]

2-Cyano-N^2-butyl-2-(3-dicyanomethyleneisoindol-1-ylidene)acetamidine [146][44]

The ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile [71] (1 50 g, 5 76 x 10^{-3} moles) and n-butylamine (0 43 g, 5 76 x 10^{-3} moles) were heated under reflux for 6 hours in ethanol (45 cm^3) On standing overnight, an orange solid precipitated Recrystallisation from acetonitrile yielded [146] (1 19 g, 65%), mp 290 °C (lit,[44] 290 °C), IR ν_{max} 3326, 3270, 2959, 2872, 2211, 1654, 1611, 1587, 1568, 1516, 1463, 1313, 1252, 1149, 1091, 910, 781, 775 765, 733 and 630 cm^{-1}, ^{1}H-NMR (DMSO-d_6) δ 10 83 (bs, 1H, NH), 8 70 (bs, 2H, NH), 8 17 (m, 1H, aromatic), 8 03 (m, 1H, aromatic), 7 62 (m, 2H, aromatic), 3 30 (m, 2H, NCH_2), 1 63 (m, 2H, CH_2), 1 38 (m, 2H, CH_2), 0 91 (t, 3H, CH_3) ppm, ^{13}C-NMR (DMSO-d_6) δ 13 4 (methyl), 19 8, 29 5, 42 3 (CH_2), 56 9 [C=C(CN)$_2$], 71 9 [C=C(CN)], 115 1, 115 9, 117 1 (CN), 123 2, 123 5, 131 1, 131 5 (aromatic), 134 9, 137 9 (quaternary), 158 9, 166 7, 170 1 [C=C(CN) and (C=N)] ppm

2-Cyano-N',N'-dibutyl-2-(3-dicyanomethyleneisoindol-1-ylidene)acetamidine [129][44]

The ammonium salt of 2,2'-(isoindolin-1,3-diylidene)bispropanedinitrile [71] (1 00 g, 3 81 x 10^{-3} moles) and N,N-dibutylamine (0 51 g, 3 81 x 10^{-3} moles) were heated under reflux for 6 hours in ethanol (35 cm^3) The solvent was removed using rotary evaporation and recrystallisation of the solid yielded [129] (1 24 g, 87%), mp 212-213 °C (lit,[44] 213 °C),, IR ν_{max} 3340, 2950, 2867, 2218, 2195, 1648, 1604, 1584, 1561, 1478, 1370, 1314, 1258, 1234, 1116, 1057, 752, 734 and 650 cm^{-1}, ^{1}H-NMR (DMSO-d_6) δ 9 6 (bs, 1H, NH), 9 0 (bs, 1H, NH), 8 3 (m, 1H, aromatic), 8 2 (m, 1H, aromatic), 7 7 (m, 2H, aromatic), 3 6 (m, 4H, CH_2), 1 7 (m, 4H, CH_2), 1 4 (m,

4H, CH_2), 0.9 (t, 6H, CH_3) ppm; ^{13}C-NMR (DMSO-d_6) : δ 13.4 (methyl), 13.6, 19.2, 28.5 (CH_2), 50.8 [C=C(CN)$_2$], 73.2 [C=C(CN)], 116.8, 118.2, 118.5 (CN), 122.7, 122.9, 131.0, 131.1 (aromatic), 137.7, 137.8 (quaternary C), 159.2, 165.4, 171.5 [C=C(CN) and (C=N)] ppm.

Attempted reaction of 2-cyano-N^2-butyl-2-(3-dicyanomethyleneisoindol-1-ylidene)acetamidine with piperidine

2-Cyano-N^2-butyl-2-(3-dicyanomethyleneisoindol-1-ylidene)acetamidine [146] (0.13 g, 4.11 x 10^{-4} moles) was dissolved in THF (15mls). Piperidine (0.07 g, 8.22 x 10^{-4} moles) was added and the solution heated under reflux for 18 hrs. No new product was observed on TLC. Removal of the solvent by rotary evaporation and recrystallisation from acetonitrile yielded [146], (0.10 g, 77%), confirmed by NMR, IR and mp data.

Attempted reaction of 2-Cyano-N',N'-dibutyl-2-(3-dicyanomethylene-isoindol-1-ylidene)acetamidine [129] with n-butylamine

2-Cyano-N',N'-dibutyl-2-(3-dicyanomethyleneisoindol-1-ylidene)acetamidine [129] (0.20 g, 5.37 x 10^{-4} moles) and n-butylamine (0.06 g, 8.20 x 10^{-4} moles, 50% excess) were refluxed together in ethanol (15cm^3) for 14 hours. TLC [70:30 ethyl acetate:light petroleum (bp 40-60 °C)] indicated one fast moving component near the solvent front with other minor components moving at a slower rate. Recrystallisation of the solid gave [129], the starting material, confirmed by NMR, IR and mp.

Investigation of C-T complex formation using ultra-violet spectroscopy

C-T interactions were studied using a Shimadzu UV 3100 UV-VIS recording spectrophotometer. To detect for C-T absorption bands, one equivalent of a donor was added to a solution of the acceptor or else increasing amounts of donor were added to a fixed concentration of the acceptor. Spectra were then recorded and

compared with individual spectra for both the acceptor and the donor to detect for the appearance of any new C-T bands The solvent used was acetonitrile (Labscan-HPLC grade) Tetrathiafulvalene (TTF) and N,N,N',N'-tetramethyl-p-phenylenediamine (TMDA) were commerically available samples

Cyclic voltammetry

Cyclic voltammetry measurements were made using a CH Instruments model 660 electrochemical workstation which was interfaced with a personal computer Solutions were made up in HPLC grade dimethylformamide or HPLC grade acetonitrile each containing 0 1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte The sample solutions were degassed for 30 minutes using nitrogen and were maintained under a blanket of nitrogen while the voltage was cycled The potentials are quoted with respect to a BAS Ag/AgCl reference electrode with platinum wire as the counter electrode The working electrode used was glassy carbon

Chapter 6

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