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SYNTHESIS AND CHARACTERISATION OF CHARGE TRANSFER  
COMPLEXES OF NEW ELECTRON ACCEPTORS.

by

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A Thesis submitted for the degree of  
Doctor of Philosophy at the University of Durham.

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### DECLARATION

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## ABSTRACT

### SYNTHESIS AND CHARACTERISATION OF CHARGE TRANSFER COMPLEXES OF NEW ELECTRON ACCEPTORS.

New electron acceptors, possessing various skeletal frameworks have been prepared and characterised. Complexation with a range of metal and organic cations reveal the suitability of the electron acceptors in the field of conducting charge-transfer complexes.

Unsuccessful attempts to synthesise sterically demanding TCNQ derivatives, directly from the corresponding p-benzoquinone in the presence of titanium tetrachloride, provided a convenient route to a range of mono(dicyanomethylated)alkyl-p-benzoquinones, which were converted into N,7,7-tricyanoquinomethaneimine derivatives. Semi-conducting charge-transfer salts of these new acceptors are described.

Reduction of 2-dicyanomethylene-1,3-indandione (DCID) with cationic iodides, initiated a fascinating rearrangement to afford crystalline salts of the isomeric 2,3-dicyano-1,4-naphthoquinone (DCNQ), as confirmed by X-ray analysis.

1,3-Metadinitrobenzene and 1,3,5-trinitrobenzene both form neutral, insulating, diamagnetic complexes with tetrathiafulvalene. The crystal structure of each complex is characterised by mixed stacks of alternate donor and acceptor molecules.

The study of tetrachloro-DCID and 1,3-bis(dicyanomethylene)indane further establishes that a wide range of electron acceptors belong in the development of organic metals.

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CHAPTER ONE

INTRODUCTION TO ORGANIC METALS



## 1.1 WHY STUDY ORGANIC METALS ?

Organic materials are traditionally considered to be electrical insulators with room temperature conductivity ( $\sigma_{rt}$ ) in the range  $10^{-9}$  -  $10^{-14}$  S cm<sup>-1</sup>. Consequently, the possibility of high electrical conductivity in organic solids is very exciting, and when eventually realised in the 1960's, paved the way for extensive research into the field of organic metals. Fruitful interplay between organic chemists, solid state physicists and material scientists has resulted in the preparation and characterisation of highly conducting and superconducting materials, which offer great technological potential. Also the study of quasi one-dimensional (1-D) systems has enabled physicists to test and adapt previous theoretical predictions based upon hypothetical 1-D systems.

The ultimate goal of much research on organic conductors is the attainment of high temperature superconductivity. However, it is important not to neglect the study of organic insulators and semiconductors, as these materials offer further valuable insights into the chemistry and physics that underpins the organic solid state, thus aiding the development of systems possessing the more glamorous properties<sup>1</sup>.

Although highly conducting polymeric systems constitute an important area of organic metals, this thesis will focus solely upon the area of charge transfer (CT) complexes.

## 1.2 ELECTRICAL CONDUCTION IN QUASI 1-D METALS

Before concentrating on electrical conduction in a 1-D system, we will briefly review the band theory of traditional 3-D metals.

Consider an atom which provides a valence s-orbital at energy level,  $E$ . Combination of two atoms, with the corresponding overlap of the s-orbitals, forms a bonding and an antibonding molecular orbital at energies  $E_1$  and  $E_1^*$  respectively ( $E_1 < E$ ;  $E_1^* > E$ ). Combination of  $N$  atoms, in a linear array, results in the formation of  $N$  molecular orbitals, covering a band of finite width. When  $N$  becomes sufficiently large, the energy gap between the molecular orbitals is reduced such that a virtually continuous band results. The band formed from the overlap of s-orbitals is called the s-band. P-orbitals interacting in a similar manner, give rise to a p-band (Figure 1.1).

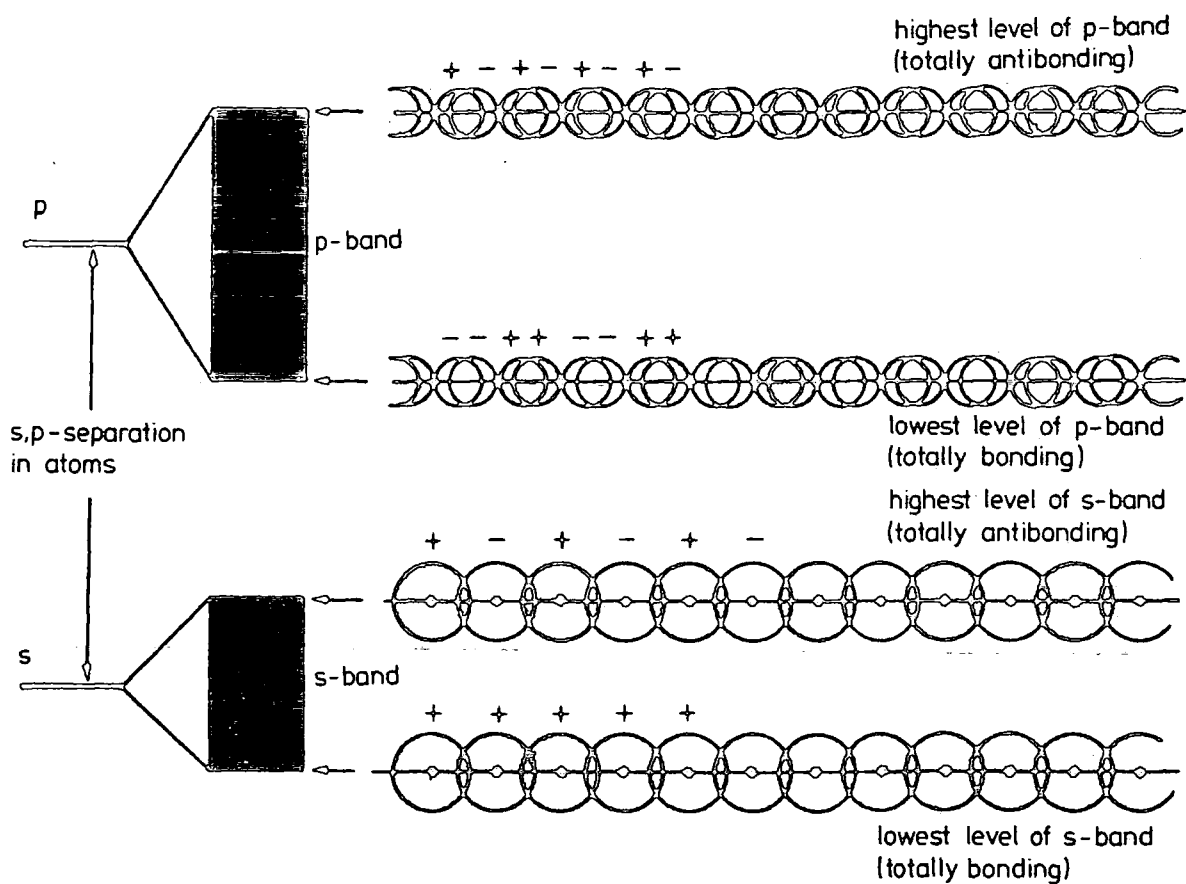
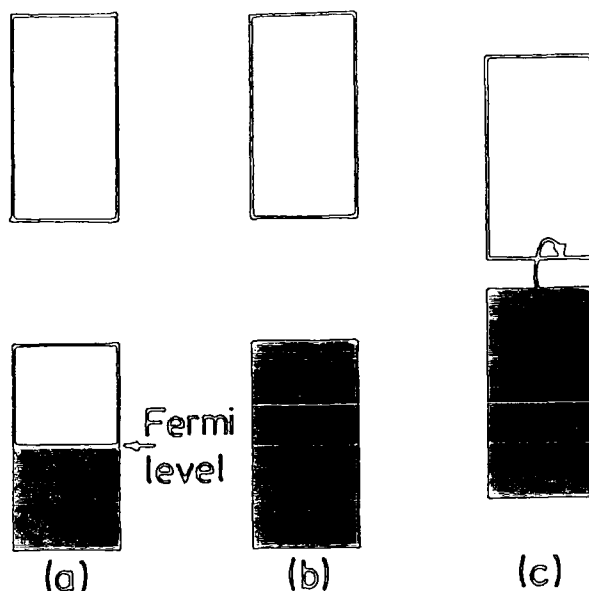


Figure 1.1 *Metal Molecular Orbitals: s and p-Band Structures;* (reproduced from P.W. Atkins, "Physical Chemistry", Oxford University Press, 1982).

Consider a situation in which each atom contributes one electron to the s-band (eg. an alkali metal). According to the Aufbau principle, this provides a half-filled band (Figure 1.2a).



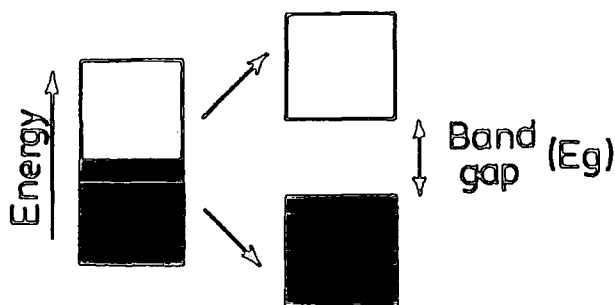
**Figure 1.2** *Band Filling Leads to a) Metal; b) Insulator; c) semiconductor; (reproduced from P.H. Atkins, "Physical Chemistry", Oxford University Press, 1982).*

Consequently, empty, higher energy orbitals lie very close to the uppermost filled orbitals (the Fermi level) and subsequent promotion of electrons, an essential requirement for conduction, is attained with the appliance of a small potential difference. Hence, metallic conductivity is a property characteristic of a partially filled band.

If each atom provides two electrons, the lower band will be full (Figure 1.2b). The energy level between the Fermi level and the empty conduction band corresponds to the very large potential difference required to promote the electrons, and hence the material is an insulator. In some materials this energy gap is sufficiently small to allow thermal excitation of the electrons into the upper conduction band, leaving positive "holes" in the valence band (Figure 1.2c). In such circumstances, both electrons and holes contribute to the

conductivity. This corresponds to semiconductor behaviour, which is characterised by an increase in conductivity with increasing temperature, *ie.* as the number of charge carriers increases. Introducing impurities into a system is another, well established, method of providing charge carriers in semiconductors.

Electrical conductivity in 1-D metals can be understood in terms of the band theory described above. However, the physics of a 1-D system differs dramatically from that found in three dimensions, this difference being at the heart of the study of organic metals. A 1-D array of atoms/molecules is inherently unstable towards periodic displacement along the 1-D chain<sup>2</sup>. This so-called Peierls distortion is analogous to the familiar Jahn-Teller distortion. The driving force towards such distortion is the electronic stability gained from the splitting of the band into a fully occupied band of lower energy and an empty band of higher energy (Figure 1.3).

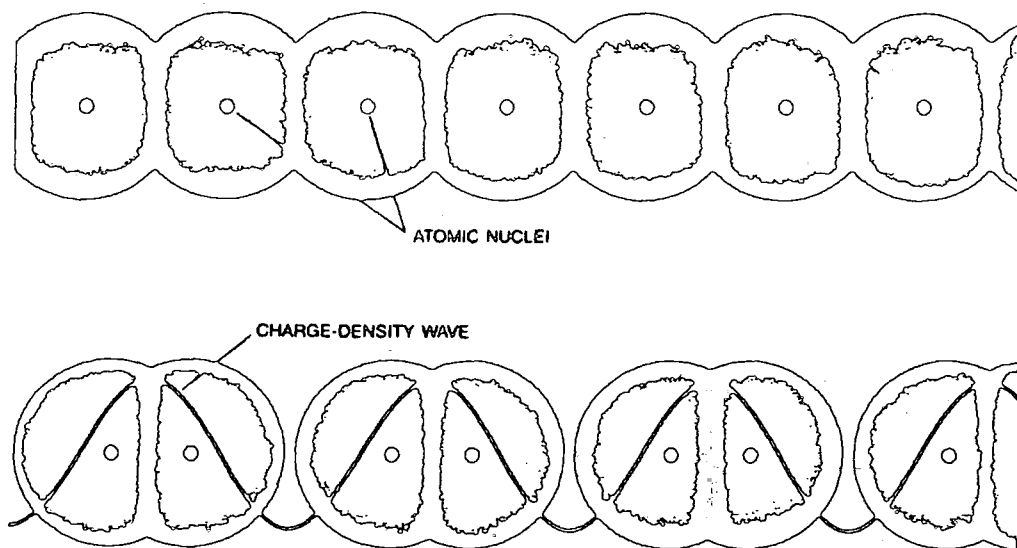


**Figure 1.3** *Band Splitting - the Driving Force Behind the Peierls Distortion.*

In the example of a half-filled band, the singly charged atoms/molecules within the chain, dimerise, giving rise to a new cell dimension double that of the original and an associated charge density wave (CDW) (Figure 1.4).

In the dimerised state, the period of the CDW is commensurate with the period of the underlying lattice. Conductivity resulting from

translational motion of the CDW is prevented by a potential energy barrier, represented by the band gap,  $E_g$ .



**Figure 1.4** *Peierls Distortion within a Linear Array of Atoms, and the Associated Charge Density Wave (CDW) (Ref.3a).*

Consequently, the CDW is "pinned" to the underlying lattice, giving rise to an insulator. In an incommensurate system, *ie.* one in which the number of electrons is not a simple fraction of the number of atoms/molecules, translation of the CDW through the 1-D lattices does not affect the energetics of the system and hence translation occurs freely, giving rise to metallic behaviour. Theory states that in an impurity free, truly incommensurate state, the CDW will be superconducting.

In a truly 1-D system, the distortions mentioned above, only occur at  $T = 0$  K. However, in 'real' quasi 1-D systems, interchain interactions giving rise to 3-D ordering, force the phase transitions to occur at a finite temperature above  $T = 0$  K. Consequently, the incommensurate state will undergo a phase transition at a finite temperature. However, the energy gained upon distortion is less favourable than in the commensurate state and consequently the phase

transition occurs at lower temperatures. Both states exhibit phase transitions at low temperatures (typically 20 - 100 K).

The reader should be aware that the theory of conduction in organic materials is continually being updated, and that the picture presented here is relatively simplistic. A far more comprehensive discussion of this topic can be found in the numerous review articles related to organic metals, as well as specific papers devoted to the conduction process<sup>1,3,4</sup>.

### 1.3 TTF-TCNQ AND ITS CENTRAL ROLE IN CONDUCTING CT COMPLEXES

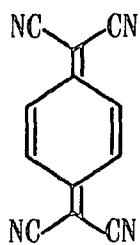
The possibility of CT complexes exhibiting metallic properties was suggested as long ago as 1913. However, it wasn't until the early 1960's, when workers at Dupont prepared the powerful electron acceptor 7,7,8,8-tetracyano-p-quinodimethane, (TCNQ) (1), that this suggestion became reality<sup>5</sup>.

A plethora of TCNQ salts were subsequently prepared, generating three distinct classes, namely:

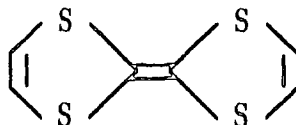
- 1)  $\pi$ -Complexes with aromatic hydrocarbons, amines and polyhydric alcohols.
- 2) Simple salts of formula  $M^{n+}(TCNQ^-)_n$ , where  $M^{n+}$  is a metallic or organic cation.
- 3) Complex salts of formula  $M^+(TCNQ^-)(TCNQ)$ , where  $M^+$  is an alkyl or aryl substituted ammonium, phosphonium, arsonium, stibonium, sulphonium or oxonium cation.

A comprehensive review of the three classes is given by Melby *et al*<sup>6</sup>. The complex salts received the most attention, as they displayed markedly anisotropic conductivities in the semiconducting regime ( $\sigma_{rt} \sim 10^{-2} - 10^{-5} \text{ S cm}^{-1}$ ). Particularly exciting was quinolinium

(TCNQ)<sub>2</sub>, which exhibits high conductivity [ $\sigma_{rt}(\text{single crystal}) = 100 \text{ S cm}^{-1}$ ], indicative of metallic behaviour.



TCNQ (1)



TTF (2)

The attainment of semiconducting complexes, together with Little's proposal at about this time, that high temperature superconductivity was possible along a linear hydrocarbon chain surrounded by polarisable dyes<sup>7</sup>, prompted further research into the field of organic metals, concentrating mainly upon the salts of TCNQ.

In 1970, the highly symmetric ( $D_{2h}$ ) and polarisable electron donor, tetrathiafulvalene (TTF) (2) was prepared, with a view to preventing build up of random potentials, associated with asymmetric cations, and reducing the Coulombic repulsion between electrons on neighbouring TCNQ anions<sup>8</sup>. High conductivity in the chloride salt of TTF ( $\sigma_{rt} = 0.2 \text{ S cm}^{-1}$ ) indicated that the TTF radical cation was not only capable of enhancing the conductivity along the TCNQ stacks, but could also contribute directly to the conduction process. In 1973, complexation of TCNQ with N-methylphenazinium<sup>9</sup> ion and TTF<sup>10,11</sup>, provided the first truly metallic CT complexes, displaying  $\sigma_{rt}$  values of 200 and 500  $\text{S cm}^{-1}$  respectively.

Since its discovery, TTF-TCNQ has been extensively studied, aided by the ease with which crystals of good size and quality are prepared<sup>12</sup>. The complex exhibits most of the electrical, magnetic, optical and structural properties characteristic of an organic metal. Consequently, this archetypal organic metal, is a reference point for all conducting

CT complexes made thereafter, and hence is central to the development of the whole field of organic metals<sup>1,13</sup>.

TTF-TCNQ is a 1:1 complex which exhibits highly anisotropic electrical and optical properties, indicative of a quasi 1-D system. For example, the conductivity ( $\sigma_{rt}$ ) along the crystallographic b-axis is 500 times greater than that along the a or c axes. Also, at wavelengths corresponding to electron transfer, only light polarised parallel to the conducting axis is absorbed. At wavelengths corresponding to intra-molecular transitions, only light polarised in the plane of TCNQ molecules is absorbed.

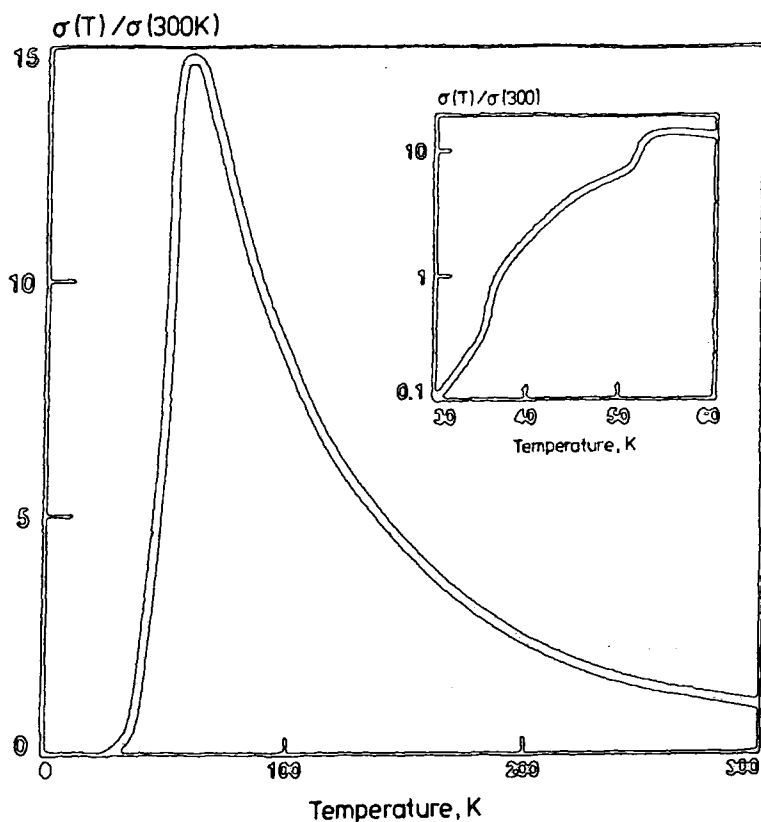


Figure 1.5 *Conductivity of TTF-TCNQ - Variation with Temperature (Ref.1).*

The temperature dependence of the conductivity (Figure 1.5) shows metallic behaviour (*ie.* increasing  $\sigma$  with decreasing temperature) down to 59 K, where the conductivity peaks with a value greater than  $10^4$  S

$\text{cm}^{-1}$ . On further cooling, the complex undergoes three phase transitions at 53, 47 and 38 K leading to an insulating state.

X-ray crystallographic studies, show the structure of TTF-TCNQ to be dominated by segregated stacks of donor and acceptor moieties, each running parallel to the crystallographic b-axis<sup>14</sup>. The normals of both TTF and TCNQ are tilted by differing degrees ( $24.5^\circ$  and  $34.0^\circ$  respectively) and in opposite directions, giving rise to the so-called "herringbone" structure (Figure 1.6).

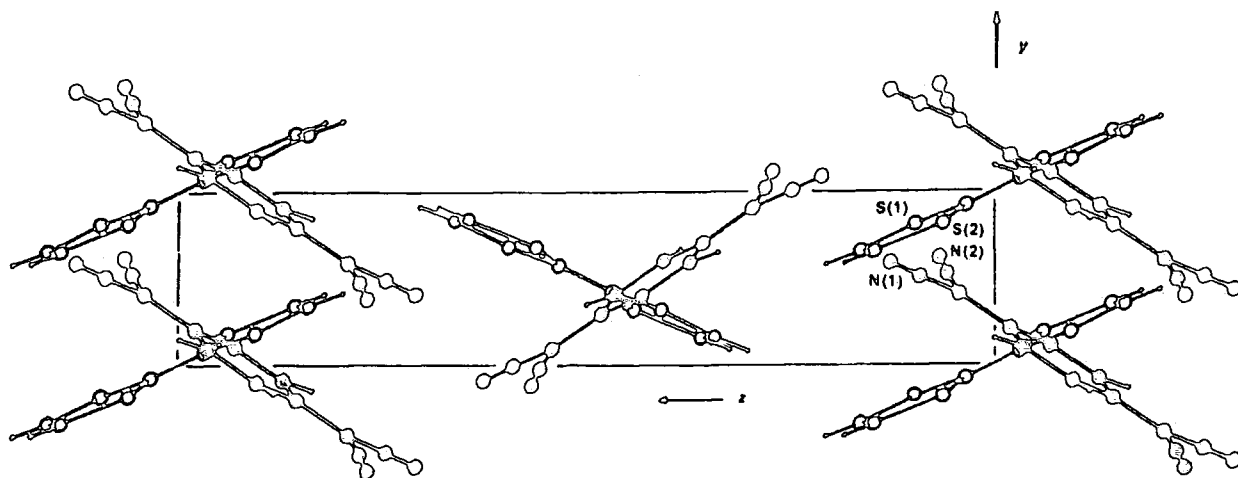


Figure 1.6 *Crystal Packing in TTF-TCNQ (Ref.14).*

Within a stack, adjacent molecules do not lie directly above one another, but exhibit a lateral displacement, such that the exocyclic double bond of one molecule, lies over the ring of its neighbours. Based on molecular dimensions from X-ray analysis, infrared spectroscopy and diffuse X-ray scattering techniques, the degree of charge transfer,  $\rho$ , from TTF to TCNQ has been estimated to be 0.59 electrons per molecule, *ie.* 59 electrons are distributed over 100 TCNQ molecules.

Close structural examination of the low temperature phase transitions, using diffuse X-ray and neutron scattering, reveals distortions along the longitudinal (b) axis, at 54 and 38 K. Between 49 and 38 K, a structural modification is observed in the transverse

direction, along the a-axis. The overall result of these transitions is the formation of a 3-D, insulating phase. Although decreasing, the conductivity between 54 and 38 K remains high ( $\sigma > 10^3 \text{ S cm}^{-1}$ ) thus delaying entry into the insulating phase until below 38 K. Such behaviour suggests that the donor and acceptor stacks undergo independent transitions at 54 and 38 K. Thermoelectric power (TEP) measurements reveal that conduction in the metallic regime is dominated by the TCNQ stacks, and that the transition at 54 K occurs primarily on these, whereas the transition at 38 K is driven by the TTF stacks.

What structural aspects of TTF-TCNQ determine its high conductivity and the phase transitions at lower temperatures? Comparison with earlier synthesised TCNQ salts provides an adequate model for the highly conducting CT complex. The TCNQ salts chosen for comparison, namely TMPD-TCNQ, NMP-TCNQ, NNDB-TCNQ and DMPH-TCNQ<sup>†</sup> are similar to TTF-TCNQ in that they are all 1:1 complexes, the donor is organic and nominally planar and the ground state of the salt is at least partially ionic.

Table 1.1 clearly shows that insulating (or at best semiconducting) properties arise from a mixed stacking mode, whereas high conductivity is favoured by segregated stacks of donor and acceptor. Direct comparison between NMP-TCNQ and TTF-TCNQ, infers that the smaller stacking distance between TCNQ molecules in the latter complex provides greater interaction of the  $\pi$ -orbitals and hence larger conductivity. Similar packing within the TTF and TCNQ stacks, indicates that unlike NMP, TTF contributes to the conductivity. This proposal has been confirmed by thermoelectric power measurements, mentioned earlier. Finally, it would appear significant that TTF-TCNQ, unlike the other TCNQ salts, does not exhibit parallel sheets of donor and acceptor

---

<sup>†</sup>TMPD  $\equiv$  N,N,N',N'-tetramethyl-p-phenylenediamine; NMP  $\equiv$  N-methylphenazinium; NNDB  $\equiv$  N,N'-dimethylbenzimidazolium; DMPH  $\equiv$  N,N'-dimethyl-dihydrophenazinium

moieties.

COMPOUND	STRUCTURAL MOTIF	STACKING DISTANCE	$\sigma(\text{rt})$ (S/cm)
TMPD-TCNQ	Parallel sheets of cations and anions.	Mixed stack of cation and anion (3.27Å).	$10^{-6}$
NMP-TCNQ	Parallel sheets of cations and anions.	Segregated stacks of cations (3.36Å) and anions (3.26Å).	200
NNDB-TCNQ	Parallel sheets of cations and anions.	Discrete dimers cations (3.50Å), anions (3.07Å).	1
DMPH-TCNQ	Parallel sheets of cations and anions.	Mixed stack of cation and anion (~3.3Å).	$10^{-5}$
TTF-TCNQ	Interleaving herringbone packing of cations and anions.	Segregated stacks of cations (3.47Å) and anions (3.17Å).	500

Table 1.1 *Structural Characteristics and Room Temperature Conductivities of Several Organic Cation-TCNQ Structures; (Ref.14).*

In quasi 1-D systems, the degree of charge transfer is a crucial factor in influencing the conductivity. Transfer of 0.59 electrons from TTF to TCNQ gives rise to a CDW which is incommensurate with the underlying lattice and hence allows for the observed high conductivity. The phase transitions are attributed to Peierls distortions in the individual stacks, which eventually lead to a fully three-dimensional system through interstack interactions.

It must be pointed out that partial charge transfer may be achieved in one of two ways: either by delicately balancing the ionisation potential of the donor with the electron affinity of the acceptor, as seen for TTF-TCNQ, or by formation of a salt of stoichiometry other than 1:1 (*eg.* TTF-Br<sub>0.71-0.76</sub>).

In summary, design of a highly conducting CT complex has the

following constraints. Both donor and acceptor should be planar or nearly planar, with delocalised  $\pi$ -orbitals. Highly symmetrical donors and acceptors of similar size to each other favour ordered crystal structures, and the free radical salt of one or both components should be stable. Segregated stacking is imperative, providing bands through the overlap of  $\pi$ -orbitals. Combined with partial charge transfer and the associated incommensurate CDW's, a metallic state is attainable.

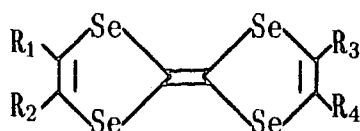
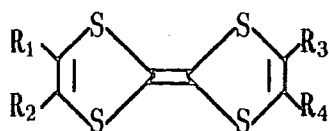
## 1.4 NEW ELECTRON DONORS

### 1.4.1 The Design of Organic Metals

Chemical modification of the TTF-TCNQ system provides an outstanding opportunity to study systematic changes in electronic and crystallographic structure, and to examine the effect of these factors upon solid state properties. The quest for new, highly conducting materials, and major advances in synthetic methodology<sup>15,16</sup> towards TTF-type systems, have gone hand-in-hand to provide a phenomenal number of new electron donors. The major rewards for such extensive research have been the stabilisation of the metallic state and the attainment of organic superconductivity. Although an extensive review of new electron donors is beyond the scope of this thesis, we wish to use a few specific examples which have made significant contributions to our understanding of the features controlling electron transport in CT complexes.

Original modifications of TTF concentrated on extending the  $\sigma$ -framework. Replacement of the hydrogens with, for example, methyl groups, reduces the ionisation potential of the donor and hence affects the electronic band structure of the CT complex. Similar to TTF-TCNQ, TCNQ salts of dimethyl-TTF (*cis,trans*)<sup>11</sup>, tetramethyl-TTF (TMTTF)<sup>17</sup> and

hexamethylene-TTF (HMTTF)<sup>18</sup>, structures (3), (4) and (5) respectively, exhibit  $\sigma_{rt}$  values in the range 200 - 1500 S cm<sup>-1</sup>. The metallic behaviour observed on lowering the temperature is disrupted by a metal-insulator (M-I) phase transition occurring below 100 K. Unfortunately, subtle crystallographic differences, compared to TTF-TCNQ, obscure the electronic effect of the substituents on the solid state properties. TMTTF-TCNQ, for example, displays reduced interchain coupling thus increasing the 1-D character of the complex.



- (3)  $R_1=R_3=Me; R_2=R_4=H$  (*cis*)  
 $R_1=R_4=Me; R_2=R_3=H$  (*trans*)  
 (4)  $R_1=R_2=R_3=R_4=Me$   
 (5)  $R_1-R_2=R_3-R_4=-(CH_2)_3-$

- (6)  $R_1=R_2=R_3=R_4=H$   
 (7)  $R_1=R_2=R_3=R_4=Me$   
 (8)  $R_1-R_2=R_3-R_4=-(CH_2)_3-$

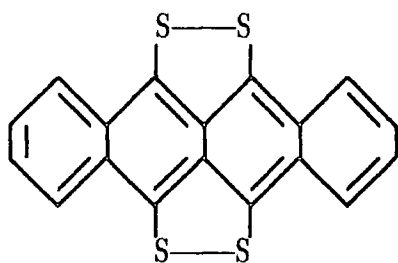
Substitution of sulphur by selenium was the next logical, but chemically demanding, step. The larger, more polarisable selenium atoms were expected to reduce Coulombic repulsions and to increase the conductivity, due to the larger bandwidth associated with greater intrastack overlap between cation radicals. Tetraselenafulvalene (TSeF) (6)-TCNQ<sup>19</sup>, having an isomorphous crystal structure to TTF-TCNQ, is an ideal candidate to assess the effect of selenium on the transport properties. TSeF-TCNQ exhibits a conductivity value ( $\sigma_{rt} \sim 800$  S cm<sup>-1</sup>) nearly double that of TTF-TCNQ and the metallic state is stabilised down to 29 K<sup>20</sup>, some 29 K below the M-I transition found in TTF-TCNQ. Hence, selenium would appear to have the desired effect upon the conductivity.

As demonstrated by the following example, increased dimensionality, through interchain Se interactions has a profound effect upon the transport properties. Consider tetramethyl-tetraselenafulvalene (TMTSeF) (7)<sup>21</sup> and hexamethylene-tetraselenafulvalene (HMTSeF) (8)<sup>22</sup>, which from

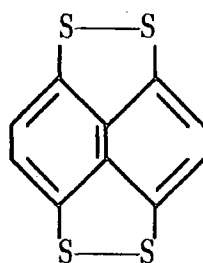
spectroscopic, electrochemical and magnetic studies are electronically indistinguishable. However, their respective TCNQ salts display very different transport properties at lower temperatures ( $< 100$  K). TMTSeF-TCNQ exists in two phases, a red insulating and a black conducting phase, of which only the latter is of relevance here. The black conducting phase exhibits a  $\sigma_{rt}$  value of  $\sim 800 \text{ S cm}^{-1}$ , which increases seven-fold on cooling, reaching a maximum at 57 K. On further cooling, the material undergoes a single M-I phase transition. X-ray crystal data show the TMTSeF cations and TCNQ anions exist in separate, homologous stacks with interplanar spacings of  $3.60\text{\AA}$  and  $3.26\text{\AA}$ , respectively, consistent with the structure expected for a highly conducting CT complex, susceptible to a M-I phase transition at lower temperatures. By comparison, HMTSeF-TCNQ has a  $\sigma_{rt}$  value ranging from  $1400 - 2200 \text{ S cm}^{-1}$ . On cooling the conductivity rises three-four fold to a broad maximum between  $70 - 45$  K. On further cooling, the conductivity decreases, but remains in the metallic regime down to 1.1 K. Intrastack interactions within the donor and acceptor stacks, were found to be very similar in both complexes, indicating that the profound difference in the transport properties of the two complexes, results from differing interstack interactions. HMTSeF-TCNQ displays four strong ( $3.10\text{\AA}$ ) Se-N contacts (*cf.* Se-N sum of Van der Waals radii =  $3.50\text{\AA}$ ), whereas interstack interactions in TMTSeF-TCNQ consist of two Se-Se contacts ( $3.98\text{\AA}$  and  $4.04\text{\AA}$ ; *cf.* Van der Waals radii of Se =  $2.00\text{\AA}$ ) and two Se-N contacts ( $3.36\text{\AA}$ ) which are slightly less than the sum of the Van der Waals radii ( $3.50\text{\AA}$ ). This comparison points to the fact that increased dimensionality in quasi 1-D systems stabilises the metallic state. Inevitably the question arose as to how this was actually occurring. Present theories predict the introduction of energy states into the band gap and/or disruption of the 3-D coupling between

chains, as possible mechanisms for the smearing of the Peierls transition in these quasi 1-D metals.

In view of this profound effect of increased dimensionality, planar, aromatic donors were synthesised with S or Se atoms, and their associated spins, at the periphery of the molecules. High conductivity in tetrathiatetracene (TTT) (9)-I<sub>1.5</sub> ( $\sigma_{rt} = 600 - 1200 \text{ S cm}^{-1}$ )<sup>23</sup>, prompted research into other TTT-halides, and analogous to the TTF-halides, these compounds enabled studies of electron transport solely in the donor stacks. Also, with the TTT-halides existing in a range of stoichiometries, it was possible to probe the subtle effects the donor/acceptor ratio has upon the observed properties<sup>24</sup>. Disadvantages associated with TTT, namely inhibition of intermolecular S-S interactions by the peri hydrogens, insolubility and size incompatibility with TCNQ, prompted the synthesis of tetrathianaphthalene (TTN) (10)<sup>25</sup>.



TTT (9)

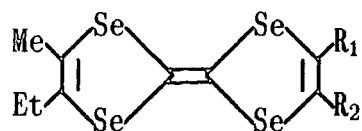


TTN (10)

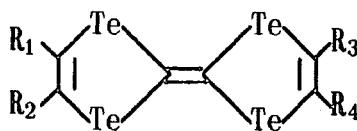
It was found that TTN is a poorer donor than TTT and TTF and that TTN-TCNQ is metallic over only a narrow temperature range. Tetraselenatetracene salts (TSeT)<sub>2</sub>X (X = Br, Cl)<sup>26</sup> both show high conductivities ( $\sigma_{rt} = 10^3 \text{ S cm}^{-1}$ ), and upon cooling undergo a metal-semimetal transition at *ca.* 20 K. The absence of a M-I transition is explained by the development of substantial 2-D character arising from significant Se-Cl<sup>-</sup> ion interactions.

Introduction of disorder is another technique by which the uniform,

periodic distortions, associated with 1-D metals can be prevented. Although beneficial in this respect, it must be noted that random disorder generates random potentials which hinder electron transport. However, the unsymmetrical donor complex dimethyl-diethyl-tetraselenafulvalene (DMDETSeF)-TCNQ provides an interesting study through two effects<sup>27</sup>. The bulky ethyl groups significantly reduce intermolecular overlap and the *cis/trans* isomers (11) provide static disorder. The conductivity as a function of temperature, reflects metallic behaviour with a gradual progression into the insulating regime at lower temperatures. Anomalies in thermoelectric power (TEP) measurements point towards a smeared phase transition at 28 K, which is otherwise unobservable from conductivity measurements alone.



(11)  $R_1 = \text{Me}; R_2 = \text{Et}$  (*cis*)  
 $R_1 = \text{Et}; R_2 = \text{Me}$  (*trans*)



(12)  $R_1 = R_2 = R_3 = R_4 = -(\text{CH}_2)_3-$   
 (13)  $R_1 = R_2 = R_3 = R_4 = \text{H}$

The technique of alloying is another method by which disorder is introduced to a system. For example, introducing 10% methyl-TCNQ, MTCNQ (15), (*vide infra*) into TSeF-TCNQ, "blurs" the phase transition at 28 K<sub>c</sub> and increases the conductivity at 4 K by four orders of magnitude<sup>28</sup>. Interestingly, doping with TTF has very little influence on the conductivity as a function of temperature. This is attributed to the fact that, although the presence of TTF introduces disorder to the system, the TTF molecule has a significant effect upon the band structure, which counteracts the effect of disorder. The apparent absence of this phenomenon, when doping with MTCNQ, implies donor stack dominance in the transport properties. Similar results are obtained, with similar conclusions from doping TMTSeF-DMTCNQ with 25% MTCNQ<sup>27</sup>

(DMTCNQ = 2,5-dimethyl-TCNQ; (16) *vide infra*).

Introduction of tellurium into the fulvalene skeleton has proved very difficult and consequently only a few TTeF derivatives exist. The anticipated effects of this change were enhanced conductivities in the salts, due to increased bandwidths, a more polarisable donor and a stabilisation of the metallic state due to increased dimensionality. Hexamethylene-tetratellurafulvalene (HMTTeF) (12) provided an encouraging start, forming a 1:1 complex with  $\sigma_{rt}$  (powdered sample) *ca.*  $1 \text{ S cm}^{-1}$ <sup>29</sup>. Since then the most significant advance has been the recent preparation of tetratellurafulvalene (TTeF) (13) which enables a comparison with the sulphur and selenium analogues<sup>30</sup>. Although TTeF-TCNQ possesses a higher  $\sigma_{rt}$  value ( $1800 \pm 300 \text{ S cm}^{-1}$ ) than its TTF and TSeF analogues, a detailed analysis of the transport properties of TTeF-TCNQ at lower temperatures, is hampered by poor quality crystals<sup>31</sup>.

In summary, the phenomenal number of TTF derivatives which have emerged over the past two decades provide a better understanding of the factors governing electron transport in these quasi 1-D, CT complexes. A few useful guidelines for the design of new materials can be drawn up:

- 1) Substitution of sulphur by selenium increases  $\sigma(rt)$  and lowers the M-I phase transition temperature. Also the selenium donor stacks dominate the transport properties.
- 2) Bulky substituents tend to increase the anisotropy of the system.
- 3) Introducing disorder into a system results in a "smearing" of the phase transition.
- 4) Increased dimensionality tends to eliminate the M-I transition.

It should be stressed that these are only guidelines and that the crystal structure is also critically important in determining the observed properties. The control of crystal packing has so far eluded the chemist, and thus our ability to design materials is still poorly developed.

## 1.4.2 Organic Superconductors

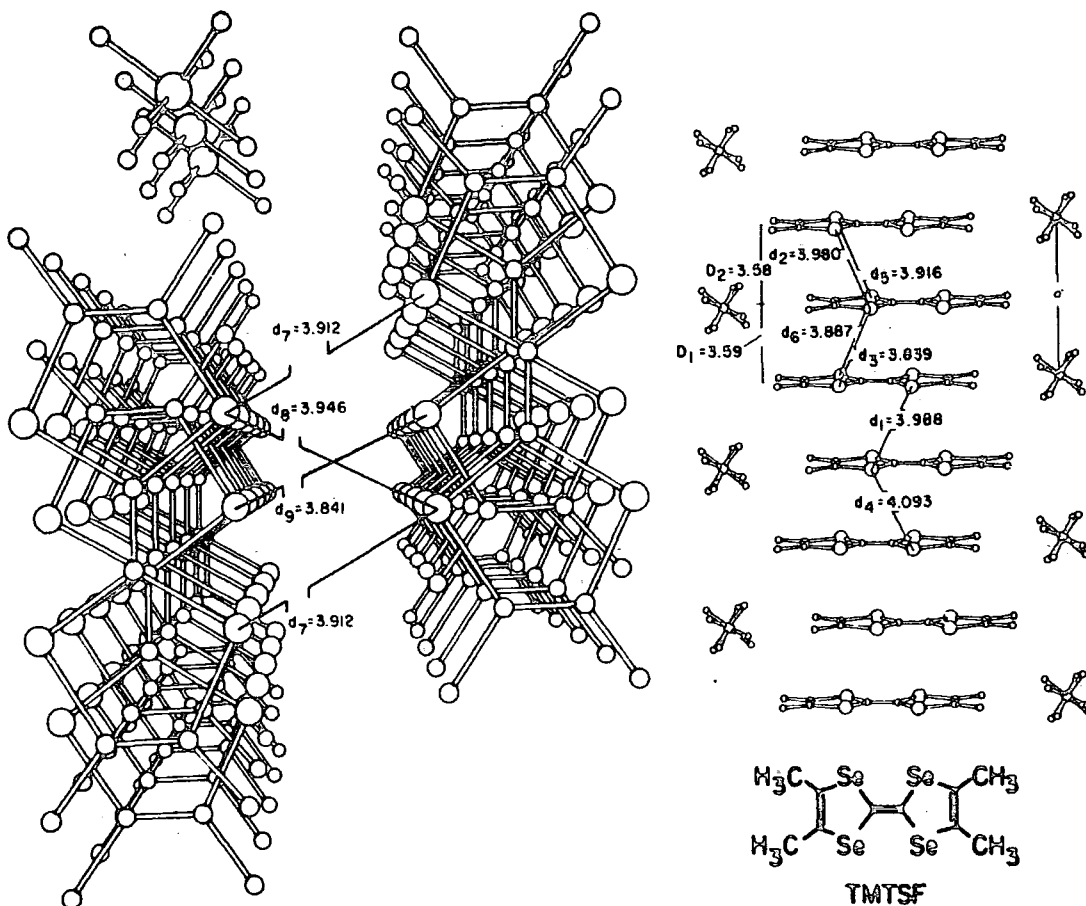
To complete this section on new electron donors, we wish to briefly review the organic materials which have exhibited superconductivity, pointing out key features relating to their behaviour. The more enthusiastic reader is referred to excellent reviews on this topic by Williams<sup>32-34</sup> and Wudl<sup>3c</sup>.

Arguably the most exciting discovery in the field of organic metals, was superconductivity displayed by the Bechgaard salts. Prior to this, TMTSeF-DMTCNQ at ambient pressure, displayed a sharp M-I transition at 42 K<sup>35</sup>. However, under pressure (13 kbar), the conductivity rose to  $10^5 \text{ S cm}^{-1}$  at 10 K, continuing to rise down to 1 K. This was the first organic salt in which a truly metallic state was stabilised, by pressure, down to 1 K. Surprisingly, the driving force for the M-I transition resided solely within the TMTSeF donor stacks.

These intriguing results prompted Bechgaard to prepare a range of cation radical salts,  $(\text{TMTSeF})_2\text{X}$ , with inorganic anions ( $\text{X} = \text{NO}_3^-, \text{BF}_4^-, \text{PF}_6^-, \text{AsF}_6^-, \text{SbF}_6^-, \text{TaF}_6^-, \text{ClO}_4^-$  etc), the so-called "Bechgaard salts". The salts  $(\text{TMTSeF})_2\text{X}$  ( $\text{X} = \text{NO}_3^-, \text{BF}_4^-, \text{PF}_6^-, \text{AsF}_6^-$ ) displayed unusually high conductivities at low temperatures ( $\sigma_{\text{rt}} \text{ ca. } 10^5 \text{ S cm}^{-1}$ ), as well as the anticipated M-I transition<sup>36</sup>. In a bid to suppress the Peierls distortion, pressure was applied to  $(\text{TMTSeF})_2 \text{PF}_6$ , providing the first organic superconductor (conduction with zero resistance) with a critical temperature ( $T_c$ ) of 0.9 K<sup>37</sup>. Shortly afterwards superconductivity at ambient pressure was observed in  $(\text{TMTSeF})_2 \text{ClO}_4$  ( $T_c = 1.3 \text{ K}$ )<sup>38</sup>. Subsequently, superconductivity under pressure has been observed and independently verified in  $(\text{TMTSeF})_2\text{X}$  ( $\text{X} = \text{AsF}_6^-, \text{SbF}_6^-, \text{TaF}_6^-, \text{ReO}_4^-$ )<sup>31,39</sup>.

Inevitably, the important features related to superconductivity in these materials are reflected in the crystal structure. An unusual

feature of all these salts is that they are all isostructural, belonging to the triclinic class (space group  $P\bar{1}$ ). The essentially planar TMTSeF molecules arrange themselves in zig-zag fashion, forming a quasi 1-D chain, which parallels the axis of highest conductivity. This feature is observed in  $(\text{TMTSeF})_2\text{BrO}_4$ , whose crystal structure is representative of the whole series of salts (Figure 1.7).



**Figure 1.7** *Crystal Structure of  $(\text{TMTSeF})_2\text{BrO}_4$  Viewed Down the Stacking Direction (left) and Showing the Zig-Zag Stacking of the TMTSeF Molecules (right side view) (Ref.32).*

Unusually short ( $d < 4.00\text{\AA}$ ) Se-Se interstack interactions give rise to an "infinite sheet network", with associated 2-D character. Separation of the "sheets" by the supporting anions prevents the establishment of a 3-D network. On cooling (298 - 125 K), the "sheet

network" contracts in a quite remarkable manner. X-ray crystallographic studies reveal that the "vertical chain" separation decreases, on average, by twice as much as the intrastack distances, and considerable bonding interactions and electronic delocalisation through the Se...Se network result. Consequently, the anions appear to play no direct role in the conduction process, although they do, indirectly, significantly modify the electrical properties.

Unlike previously studied CT complexes, the M-I transition, in the salts of centrosymmetric anions,  $(\text{TMTSeF})_2\text{X}$  ( $\text{X} = \text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{SbF}_6^-$  and  $\text{TaF}_6^-$ ), is driven by an antiferromagnetic spin density wave (SDW) ground state. This transition does not involve electron-phonon coupling, and consequently structural changes are not observed. Under applied pressure the SDW state is suppressed giving rise to a superconducting ground state. In contrast, the  $(\text{TMTSeF})_2\text{X}$  salts containing non-centrosymmetric anions ( $\text{X} = \text{ClO}_4^-$ ,  $\text{BrO}_4^-$ ,  $\text{ReO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{FSO}_3^-$  and  $\text{H}_2\text{F}_2^-$ ) show structural phase transitions at higher temperatures than those associated with magnetic (SDW) transitions. These transitions are associated with anion ordering phenomena and the formation of Se...O interactions. Wudl correlated the temperature of the phase transition to the nucleophilicity of the anion and, consequently, provided an explanation for the absence of a M-I transition in the  $\text{ClO}_4^-$  salt<sup>3c</sup>. The relatively "non-nucleophilic"  $\text{ClO}_4^-$  ion undergoes a "softer" transition which does not obliterate the metallic state, allowing a superconducting state to develop at ambient pressure.

The anions are also found to play a crucial role in the development of the superconducting state. It was noted that as the size of the anion is varied, there are systematic changes in both the observed unit cell volume,  $V_c$ , and the average interstack Se...Se distances,  $d_{\text{av}}$ <sup>40</sup>. Significantly, the minimum values of  $V_c$  and  $d_{\text{av}}$  centre around those

observed for the  $\text{ClO}_4^-$  salt, from which it was concluded that the application of pressure to the other TMTSeF anion salts produces a contraction of the Se-Se network, yielding a crystal structure similar to that of  $(\text{TMTSeF})_2\text{ClO}_4$ , and hence one in which a superconducting transition is structurally favoured.

Finally, the onset of superconductivity is probably associated with anion ordering, due to weak anion-methyl group interactions. Comparison of the anion environment in  $(\text{TMTSeF})_2\text{AsF}_6$ <sup>41</sup> and  $(\text{TMTSeF})_2\text{ClO}_4$ <sup>42,43</sup>, shows the distorted  $\text{AsF}_6^-$  ion existing in an isotropic sea of hydrogen atoms, with no short H-F separations, whereas the tetrahedral  $\text{ClO}_4^-$  ion "sees" an asymmetric hydrogen atom environment, with numerous short H-O contacts. Such contacts tend to pin the anion, giving rise to a sluggish anion ordering transition at 24 K, an apparent prerequisite for superconductivity. Further evidence for this phenomena is provided by quickly cooled samples, which retain their "disordered" anion configuration, resulting in complete loss of superconductivity or a severely depressed  $T_c$ .

Another donor, whose salts exhibit superconductivity, is the sulphur based bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF or simply ET) (14). The potential of ET was soon realised when  $\text{ET}_2\text{ClO}_4$ (1,1,2-trichloroethane)<sub>0.5</sub><sup>44</sup> remained metallic between 298 - 1.4 K. Following this,  $\text{ET}_2\text{ReO}_4$  under >4 kbar pressure, displayed superconductivity at 2 K<sup>45</sup>. In the absence of pressure, an M-I transition developed at 81 K. The structure of  $\text{ET}_2\text{ReO}_4$  was ascertained from the isostructural  $\text{ET}_2\text{BrO}_4$ <sup>46</sup>, and was found to differ from the Bechgaard salts in many ways. Firstly, the ET cations are decidedly non-planar, with the  $\text{CH}_2$  groups protruding out of the molecular plane. Secondly, the  $\text{ReO}_4^-$  anion is ordered at room temperature, which, by analogy with  $(\text{TMTSeF})_2\text{ClO}_4$ , appears to be a prerequisite for superconductivity. Thirdly, there is

an apparent lack of columnar stacking, the structure of ET salts being dominated by 2-D sheets arising from short S-S "interstack" interactions. This anisotropy is highlighted by  $\text{ET}_2\text{ClO}_4(\text{TCE})_{0.5}$  in which the conductivity is  $10^2 - 10^3$  times greater along the sheets than in the "columnar" direction. Further, short interstack S-S interactions give rise to the so-called "corrugated sheet network" (Figure 1.8), which by analogy with the Bechgaard salts, provides the main pathway for electrical conduction.

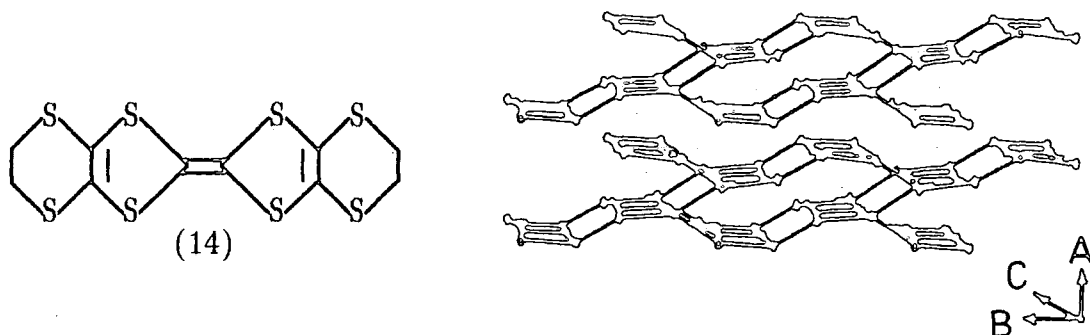


Figure 1.8 Structure of ET (14) and Two-Dimensional "Corrugated Sheet Network" Observed in  $(\text{ET})_2\text{ReO}_4$  and  $(\text{ET})_2\text{BrO}_4$  (Ref.46).

The first example of ambient pressure superconductivity in an  $\text{ET}_2\text{X}$  salt was found in  $\beta\text{-ET}_2\text{I}_3$  ( $T_c = 1.5 \text{ K}$ )<sup>47</sup> (the  $\alpha$ -phase undergoes an M-I transition at 135 K).  $\beta\text{-ET}_2\text{I}_3$  also consists of a "corrugated sheet network" structure, separated by linear, symmetric  $\text{I}_3^-$  anions, which are encapsulated by the hydrogen atoms of the  $\text{CH}_2$  groups. Predictions that the "interstack" separations are dependent on anion size, led to the substitution of  $\text{I}_3^-$  for the shorter, isostructural  $\text{IBr}_2^-$  and the subsequent rise of  $T_c$  to 2.7 K<sup>48</sup>. Use of the asymmetric, crystallographically disordered  $\text{I}_2\text{Br}^-$  anion, suppressed the onset of superconductivity even at 5 kbar pressure<sup>49</sup>. An increased critical temperature ( $T_c = 7 - 8 \text{ K}$ ) was reported for  $\beta\text{-ET}_2\text{I}_3$ , when a pressure of 1.3 kbar was applied<sup>50</sup>; the pressure is believed to prevent a structural

modification arising from  $\text{CH}_2$  group disorder, related to  $\text{CH}_2$ -I interactions. From these, and other data, Williams concluded that the optimum anion for ambient pressure superconductivity with increased  $T_c$ , is a linear, symmetrical chain, with a length intermediate between  $\text{IBr}_2$  and  $\text{I}_3$ .  $\text{AuI}_2$  fits these criteria and when incorporated into an ET salt, ambient pressure superconductivity occurs at 5 K<sup>51</sup>. More recently the thiocyanate salt  $(\text{ET})_2\text{CuNCS}$  has exhibited superconductivity at 10.4 K<sup>52</sup>.

Considering the Bechgaard and ET salts together, it seems clear that superconductivity is associated with the 2-D, chalcogen atom network, the control of which is finely tuned by the supporting anions. Consequently, in the quest for higher  $T_c$ 's, particularly in the  $\text{ET}_2\text{X}$  salts, it is essential to eliminate molecular and anionic disorder and avoid structural modification: this is a very challenging task!

## 1.5 NEW ELECTRON ACCEPTORS

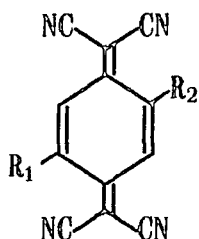
### 1.5.1 TCNQ Derivatives

In this section we shall review the area of new electron acceptors for organic metals, highlighting the important advances that have been made since the discovery of TCNQ. It must be borne in mind that far fewer publications have been concerned with new acceptors than new donors. Consequently, our knowledge of the role of the acceptor in determining solid state properties is still rather limited, leaving considerable scope for new studies. Without doubt a major factor contributing to the lack of acceptors is the difficulty of synthesis.

The initial step forward was the preparation and characterisation of twenty one substituted TCNQ derivatives in 1975<sup>53</sup>. Complexes with TTF (2), TTT (9), and various other donors, displayed a whole range of

conductivities, none of which were an improvement upon the corresponding TCNQ salts<sup>54</sup>. TCNQ's, substituted at the 2,5 positions with halogens, alkyl and alkoxy groups offered a range of electron affinities, steric factors and heavy atom effects which were correlated with the observed conductivities<sup>55</sup>. Comparing  $\sigma_{rt}$  with the degree of charge transfer ( $\rho$ ), revealed the former rising to a maximum with increasing  $\rho$  (TTF-TCNQ:  $\sigma_{rt} = 500 \text{ S cm}^{-1}$ ,  $\rho = 0.59$ ). Further increase in  $\rho$  *ie.* towards simple salt formation resulted in a decrease in  $\sigma_{rt}$ . Using redox potentials to gauge the degree of charge transfer, it became apparent that high conductivity was associated with moderate donors and acceptors, in which the redox potentials were closely matched [*ie.*  $\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}D}^1 - E_{\frac{1}{2}A}^1 \leq 0.25 \text{ V}$ ]. However, it is essential to bear in mind that other important factors must be taken into account. For instance, although the electron affinities of 2,5-diethyl-TCNQ (DETCNQ) (17) and 2,5-diisopropyl-TCNQ (DiPrTCNQ) (18) are very similar, their respective TTF salts display conductivities differing by seven orders of magnitude (TTF-DETCNQ  $\sigma_{rt} = 10 \text{ S cm}^{-1}$ ; *cf.* TTF-DiPrTCNQ  $\sigma_{rt} = 10^{-6} \text{ S cm}^{-1}$ ) this reflects the effect of bulky substituents upon the crystal structure and the corresponding transport properties. The effect of bulky substituents is also highlighted by TCNQ(OMe)(O-iPr) (19) which does not complex with TTF (9), whereas the TTF complex of TCNQ(OMe)(OEt) has a  $\sigma_{rt}$  value of *ca.*  $1 \text{ S cm}^{-1}$ . As a general guideline it was concluded that favourable crystallographic packing for high conductivity requires: i) the absence of bulky substituents and ii) a combination of donor and acceptor with similar dimensions. It was also suggested that replacement of chlorine substituents by the more polarisable bromine and iodine atoms had a favourable effect upon the conductivity (TTF-TCNQCl<sub>2</sub>  $\sigma_{rt} = 3.4 \times 10^{-4} \text{ S cm}^{-1}$ ; TTF-TCNQBr<sub>2</sub>  $\sigma_{rt} = 5 \text{ S cm}^{-1}$ ; TTF-TCNQI<sub>2</sub>  $\sigma_{rt} = 2.2 \times 10^{-2} \text{ S cm}^{-1}$ ). However, the intermediate value observed for TTF-TCNQI<sub>2</sub> indicates that

the polarisability is offset by other factors, the size of the iodine atom for instance.



- (15)  $R_1 = \text{Me}; R_2 = \text{H}$     (18)  $R_1 = R_2 = \text{iPr}$   
 (16)  $R_1 = R_2 = \text{Me}$         (19)  $R_1 = \text{MeO}; R_2 = \text{iPrO}$   
 (17)  $R_1 = R_2 = \text{Et}$

Of all substituted TCNQ's, the alkyl derivatives, methyl-TCNQ (MTCNQ) (15), 2,5-dimethyl-TCNQ (DMTCNQ) (16) and (DETCNQ) (17), have received the most attention. Study of the alkyl derivatives was considered important for several reasons. Firstly, although the presence of the alkyl groups will reduce the electron affinity, as confirmed by cyclic voltammetry (CV), the effect upon band filling and the corresponding transport properties should not be too dramatic. Secondly, the alkyl groups act as "spacers", thus isolating the donor and acceptor stacks and hence increasing the one-dimensionality of the system. Finally, there is interest in the intrastack arrangement of the adjacent acceptor molecules. For instance, will each molecule be inverted with respect to its neighbours, thus reducing steric interactions between alkyl groups, or will a randomised arrangement exist, thus introducing disorder into the lattice?

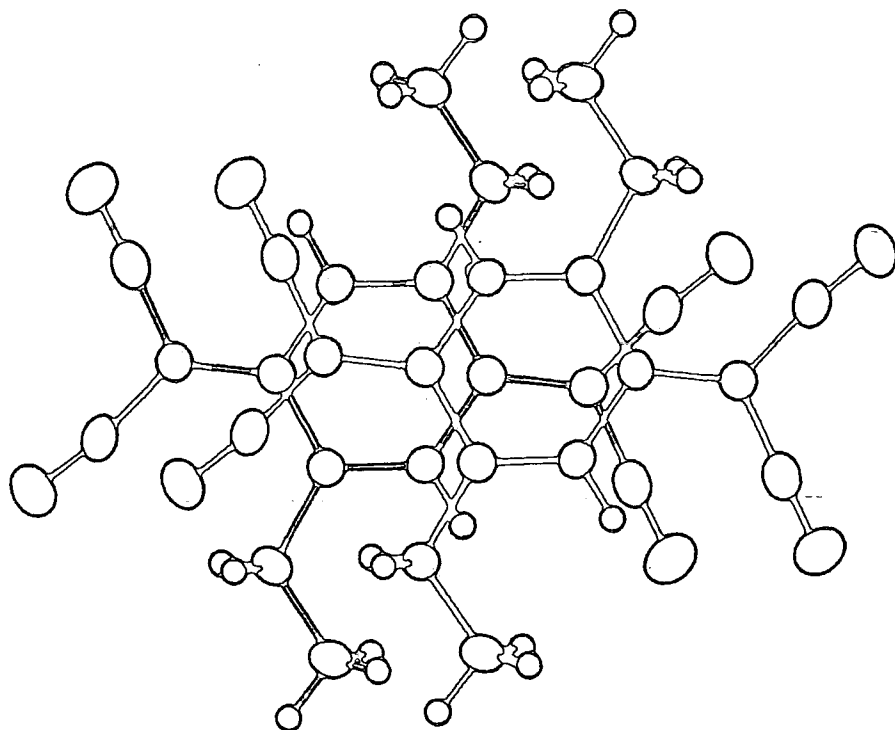
TTF-MTCNQ exhibited metallic behaviour ( $\sigma_{rt} = 200 - 500 \text{ S cm}^{-1}$ ) reaching a broad conductivity maximum ( $\sigma_{max}/\sigma_{rt} = 1.2$ ) at 210 K<sup>56</sup>. Plots of  $\log \sigma$  vs T did not reveal a well-defined transition. However, below 100 K, the complex became semiconducting. Use of electrochemical half-wave potentials ( $E_{1/2}^1$ ) as a measure of electron affinity, showed MTCNQ and TCNQ to be virtually identical, which may account for the remarkably similar  $\sigma_{rt}$  values of the corresponding TTF salts. The methyl group, as well as providing a modified crystal structure and

stacking pattern, also gives the acceptor molecule a small dipole moment. The influence of this dipole moment was clearly seen by the absence of a sharp maximum in  $\sigma(T)$ , which was explained by a pinning of the CDW above the transition temperature. Methyl group inhibition of the 3-D ordering process, was also considered to contribute to the broadening of the phase transition. In conclusion, the presence of the methyl group appeared to affect the solid state properties in a well-defined manner.

Within the alkyl derivatives, DMTCNQ (16) provided the most interesting study. The 1:1 complex of DMTCNQ with TMTSeF (7) exhibited high ambient pressure conductivity ( $\sigma_{rt} = 300 \text{ S cm}^{-1}$ ), rising to a maximum value of *ca.*  $3000 \text{ S cm}^{-1}$  at 50 K, below which the complex underwent an M-I transition<sup>57</sup>. Comparison with TMTSeF-TCNQ revealed similar crystal structures and conductivity data, although the M-I transition occurred at 20 K lower in the DMTCNQ salt. To explain these results, possible disorder effects were considered, resulting from the stacking arrangement of the acceptor. A contribution to the metallic state was provided by the 10% increase in unit cell volume, observed in the DMTCNQ salt, thereby reducing the interchain coupling interaction. However, it has already been noted (section 1.4.2), that the driving force for the phase transition in TMTSeF salts, resides solely upon the donor stacks and can be removed by the appliance of pressure.

Substituting hydrogen atoms for the bulkier methyl/ethyl groups in the acceptor (or donor), not only affects the interstack interactions, but also, inevitably, the intrastack separations and the associated bandwidths. The separation of TTF's in many 1-D systems is comparable with the Van der Waals separations, whereas, for example, the separation of TCNQ in TTF-TCNQ being  $3.17\text{\AA}$  is less than the sum of the Van der Waals radii for aromatic carbon atoms ( $3.34\text{\AA}$ ), and hence maintaining

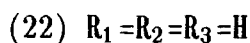
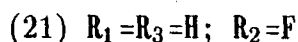
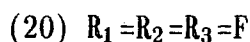
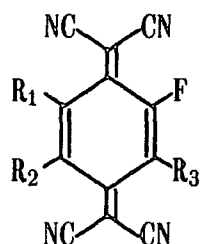
close packing and metallic behaviour in substituted TCNQ's is not an easy task. TTF-DETCNQ, displays a segregated stacking motif in which the perpendicular interplanar spacing of TTF and DETCNQ is 3.59Å and 3.25Å respectively<sup>58</sup>. These values, being greater than those observed in TTF-TCNQ (3.47Å and 3.17Å respectively)<sup>14</sup>, almost certainly contribute to the lower conductivity observed for the DETCNQ salt ( $\sigma_{rt} = 10 \text{ S cm}^{-1}$ )<sup>54</sup>. Projections perpendicular to the planes of the donor and acceptor reveal the overlap of the TTF's to be identical to that found in TTF-TCNQ: in contrast, the DETCNQ molecules overlap in a slightly less symmetric manner, due to the steric requirements of the ethyl groups (Figure 1.9)<sup>58</sup>.



**Figure 1.9** *Projection of the Overlap Between Neighbouring DETCNQ Molecules Viewed Perpendicular to the Molecular Planes (Ref.58).*

X-ray data concerning the stacking mode of DETCNQ indicate that close stacking in tri- and tetra-substituted TCNQ, would be virtually impossible due to steric interactions.

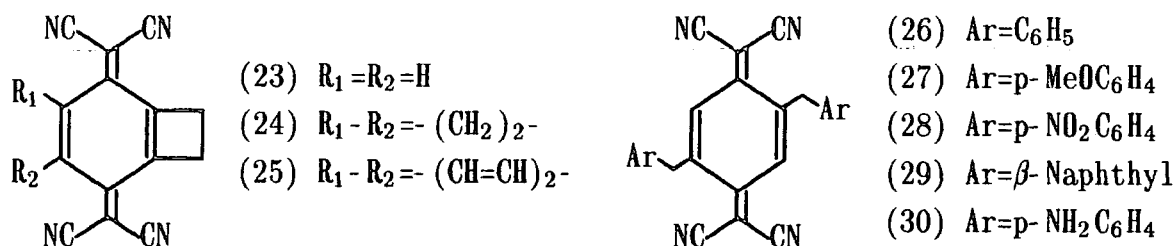
Substitution of hydrogens in the TCNQ skeleton by fluorine provided an excellent way of studying the effects of increased electron affinity while retaining planarity, similar molecular dimensions and favourable intrastack interactions within a complex. Comparing the HMTTF (5) salts of TCNQ and tetrafluoro-TCNQ (TCNQF<sub>4</sub>) (20) showed the former salt to be metallic at high temperatures, with a metal-semiconductor transition at 48 K, whereas the latter salt exhibited semiconductor behaviour at all temperatures; their respective  $\sigma_{rt}$  values differed by six orders of magnitude<sup>59</sup>. These two acceptors also formed isostructural salts with HMTSeF (8), whose transport properties compared in a similar manner<sup>60</sup>. To explain such phenomena, two models were proposed. Either the fluorine atoms draw electron density into the ring (*ie.* away from the dicyanomethylene groups) thus increasing the intermolecular Coulomb repulsion energy (U) of the dianion; or alternatively the fluorines resulted in complete charge transfer from donor to acceptor, giving rise to a Mott-Hubbard insulator. Of these models, the second is the accepted one.



A logical way to reduce the possibility of complete charge transfer, was to prepare the difluoro analogue (21). The TTF complex of 2,5-difluoro-TCNQ (TCNQF<sub>2</sub>) was found to be semiconducting ( $\sigma_{rt} = 2 \times 10^{-5} \text{ S cm}^{-1}$ )<sup>61</sup>. In terms of electron affinity, fluoro-TCNQ (TCNQF) (22), would appear to be far more attractive acceptor; moreover the single fluorine atom imparts an asymmetric electronic perturbation to the acceptor ion, which by analogy with N-methylphenazinium (NMP)-TCNQ,

could suppress the Peierls distortion. TCNQF (22) complexed with a range of TTF-type donors (*eg.* TTF, TMTTF, TMTSeF, HMTTF and HMTSeF)<sup>62</sup>; all complexes displayed  $\sigma_{rt}$  (compaction) values which compare favourably with the corresponding TCNQ salts. However, the Peierls distortion in these complexes was not suppressed.

In the synthesis of cyclobutane-fused TCNQ (23), Japanese workers prepared the first disubstituted TCNQ, whose substituents were not in the 2,5 positions<sup>63</sup>. The role of the cyclobutane ring, as with other alkyl substituents, was to affect both the intra and interstack interactions, while having the minimum effect upon the electronic state of the parent TCNQ. The electronic similarity between cyclobutane-TCNQ and TCNQ was confirmed by cyclic voltammetry. A 1:1 complex of (23) with TTF, exhibited conductivity in the metallic regime [ $\sigma_{rt}$ (compaction) = 0.3 S cm<sup>-1</sup>]. TCNQ substituted with two cyclobutane rings (24) also formed a TTF complex, whose  $\sigma_{rt}$  value was five orders of magnitude lower<sup>63</sup>. Considering the small effect the ethane group has upon the electronic state of the parent TCNQ, this significant difference in conductivity must be due to steric factors affecting the crystal structure. Steric arguments also explained why the tetra-substituted TCNQ derivative (25) failed to complex with TTF.



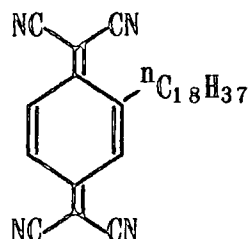
It has become increasingly clear that the multi-parameter optimisation required for high conductivity in CT complexes is not easily attainable. Possibly, of all parameters, the problem of segregated, rather than mixed stacking, is the most acute. In an

attempt to combat this problem, a range of molecules containing both donor and acceptor moieties ( $D_m-A_n$ ) connected by alkyl bridges was prepared. With a fixed stoichiometric ratio of donor and acceptor, and the ability to vary donor and acceptor strengths, it was possible to design molecules with predetermined degrees of charge transfer. Also, it was hoped that the structural packing of such molecules would force a segregated stacking motif, or at least provide a new insight into factors controlling this phenomenon. The X-ray crystal structure of 2,5-dibenzyl-TCNQ (26) showed some tendency for segregated stacks of the acceptor moiety and this prompted the characterisation of a range of derivatives (27)-(30) displaying variable donor ability *ie.* substituted benzyl groups<sup>64,65</sup>. However, to date this approach has not led to significant advances, other than to establish that crystal packing forces largely control the stacking motif.

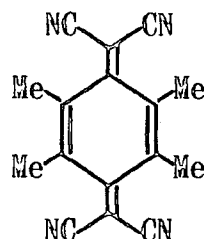
A greater control over the orientation of the donor and acceptor molecules within the solid state, has recently been achieved with the use of Langmuir-Blodgett films. This point being adequately demonstrated by TMTTF-octadecyl-TCNQ (31), which as a 4 nm thick monolayer film has a conductivity ( $\sigma_{rt} = 1 \text{ S cm}^{-1}$ ) two orders of magnitude greater than the corresponding compaction value<sup>66</sup>. Such high conductivity implies an ordered structure within the film, with close segregated stacks of the CT complex, despite the presence of long insulating alkyl chains. With the ability to manipulate the solid state structure in such a manner, the Langmuir-Blodgett technique will undoubtedly be extensively exploited in future research on organic metals.

Continued research into new TCNQ derivatives, led to the synthesis of tetramethyl-TCNQ (TMTCNQ) (32)<sup>67,68</sup>. TMTCNQ, which was prepared in order to probe the forementioned effects of methyl group substitution, suffered from a significant loss of planarity due to the steric

interaction between the dicyanomethylene groups and the substituents.



(31)



(32)

Electrochemical studies showed TMTCNQ to be a significantly poorer acceptor than TCNQ, as expected. Interestingly, the molecule underwent a simple, reversible, two-electron reduction rather than the more familiar two, reversible, one-electron reductions observed with TCNQ, MTCNQ and DMTCNQ. The fact that diethano-TCNQ (24) undergoes two, one-electron reductions, indicates that the redox characteristics are a result of steric rather than electronic effects. The X-ray crystal structure of TMTCNQ shows a very strong deformation of the TCNQ skeleton into a boat conformation<sup>68</sup>; this explains the unsuccessful attempts to complex TMTCNQ with TTF, TMTTF and TMTSeF.

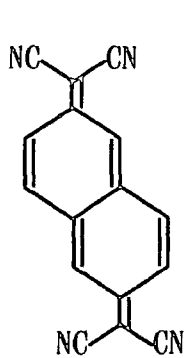
Finally, with the aim of obtaining rigid, bulky modifications with small electronic perturbations on TCNQ, Japanese workers prepared and characterised the complexes of a series of barreleno-TCNQ derivatives<sup>69</sup>. Such bulky substituents were expected to have a prolific effect upon the stacking mode of the component molecules and intra/interstack interactions. The highest conductivities were found in the TTF salts of tetrahydrobarreleno-TCNQ and dihydrobarreleno-TCNQ; these complexes are best described as small bandgap semiconductors. Unfortunately, X-ray quality crystals are not formed, but high  $\sigma_{\text{rt}}$  values ( $40 \text{ S cm}^{-1}$ ) for TTF-tetrahydrobarreleno-TCNQ suggest a segregated stack structure.

### 1.5.2 TCNQ Derivatives With Extended $\pi$ -Systems

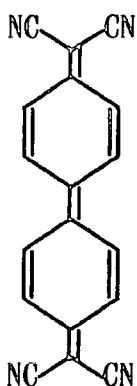
Early work by Berlinsky *et al.*<sup>70</sup>, and Lowe<sup>71</sup>, using MO calculations on TCNQ<sup>-</sup> dimers, established that maximum overlap of the HOMO's (and hence, maximum bandwidth) occurred at exactly the geometry observed in TTF-TCNQ. Hence the slipped configuration within each TCNQ stack makes its maximum contribution to the conductivity. In contrast, calculations concerning TTF<sup>+</sup> dimers, showed that overlap of the HOMO's was poor for the geometry found in TTF-TCNQ<sup>14</sup>. The most stable configuration was computed to occur when TTF molecules are stacked directly on top of each other, *ie.* the exact geometry observed in the conducting TTF-halides<sup>72</sup>. In the light of this, acceptors were sought with a different size and shape to TCNQ, in a bid to force the TTF molecules to stack directly on top of one another, thus enhancing the donor stack contribution to the conductivity.

Accordingly, TNAP (33) was synthesised, whose complexes with TTF<sup>73</sup> and HMTSeF<sup>74</sup> were both found to be segregated stack structures ( $\sigma_{rt} = 40 \text{ S cm}^{-1}$  and  $2500 \text{ S cm}^{-1}$  respectively). The TTF salt underwent a sharp M-I transition at 185 K, whereas the HMTSeF salt exhibited a conductivity maximum at 47 K, before entering a semi-metallic regime ( $\sigma < 47 \text{ K} = 250 - 3000 \text{ S cm}^{-1}$ ). For TTF-TNAP, the interplanar cationic and anionic spacing, 3.4Å and 3.1Å respectively, is very close to that observed for TTF-TCNQ. Significantly greater penetration of the TTF ions into the TNAP layers, and vice versa, compared to TTF-TCNQ, points towards greater interstack interaction and enhanced stabilisation of the metallic state, in the TNAP complex. However, it should be noted that the M-I transition occurs at 185 K in TTF-TNAP, compared to 54 K for TTF-TCNQ. For HMTSeF-TNAP, two relatively short Se...N contacts per molecule and Se...Se interactions contribute to the transition into a

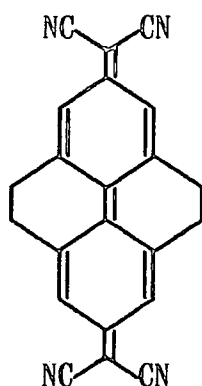
semi-metal rather than an insulator. In general, although it was encouraging that TNAP salts exhibited metallic behaviour, success has been hampered by poor quality crystals.



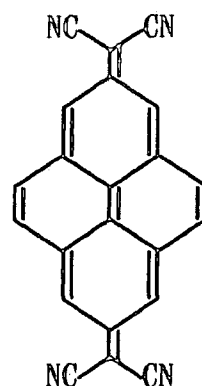
(33)



(34)



(35)



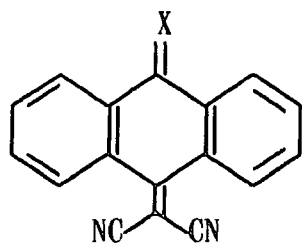
(36)

Extended symmetrical analogues of TCNQ *viz* TCNDQ (34), TCNTHPQ (35) and TCNPQ (36), were sought because the scope for reduced Coulombic repulsions within the dianion, and greater overlap of the extended  $\pi$  system, could give rise to larger bandwidths. Unfortunately, initial attempts to synthesise neutral TCNDQ failed, leading only to polymeric material. However, the radical anion and dianion were isolated as their alkali metal and tetraalkylammonium salts<sup>75</sup>. The radical anion was readily identified in solution by its complex ESR spectrum: in the solid state the alkali metal salts,  $M^+TCNDQ^-$ , have a single, strong ESR signal reminiscent of  $M^+TCNQ^-$  salts. The key feature to emerge from the electrochemical studies on  $TCNDQ^{2-}$  was the small difference between the first and second redox potentials of the dianion, due to increased electron delocalisation within the system. A TTF complex of TCNDQ was prepared by metathesis reaction between  $Na_2(TCNDQ^{2-})$  and  $(TTF^{2+})Br_2$ , but very little solid state data have been reported<sup>76</sup>. Neutral TCNDQ was eventually obtained by controlled-potential electrolysis of the dianion<sup>76</sup>.

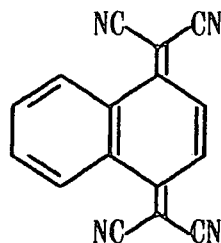
Pyrene derivatives TCNTHPQ (35) and TCNPQ (36) were the next

targets, with the aim of retaining the favourable electronic properties of TCNDQ, while suppressing its propensity to polymerise. Also the ethano and etheno bridges eliminate steric interactions between hydrogen atoms which cause a twist about the central double bond of neutral TCNDQ (34). TCNTHPQ, like TCNDQ, underwent two one-electron reversible reductions, the small  $\Delta E$  values pointed towards reduced Coulombic repulsions in the dianion compared to TCNQ<sup>77</sup>. The suitability of TCNTHPQ as an acceptor was confirmed by formation of a complex with TMTTF, which displayed a reasonably large conductivity value ( $\sigma_{rt} = 0.2 \text{ S cm}^{-1}$ ). Attempts to isolate neutral TCNPQ (36) were less fruitful: chemical oxidation of pyrene-2,7-dimalononitrile provided a purple solid which was considered to be polymeric. Electrochemistry of the pyrene-2,7-dimalononitrile dianion showed a reversible, one-electron oxidation followed by an irreversible oxidation, suggesting an unstable neutral compound which undergoes further reactions at room temperature<sup>78</sup>. Attempts to prepare TTF salts of TCNPQ (36) by metathesis reaction with  $(\text{TTF})_3(\text{BF}_4)_2$  and  $(\text{TTF})\text{Br}_2$  with the n-butylammonium salt of the dianion failed<sup>78</sup>.

Research into TCNQ's with extended  $\pi$  systems continued with the synthesis of TCAQ (37)<sup>79-81</sup>.



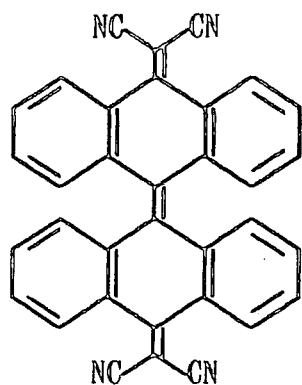
(37)  $\text{X}=\text{C}(\text{CN})_2$   
 (38)  $\text{X}=\text{O}$



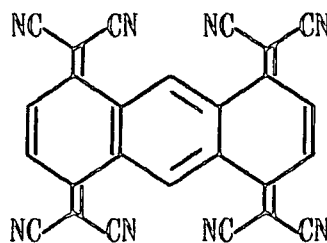
(39)

UV spectra of the neutral species, suggested the molecule is highly distorted. This was verified by the X-ray crystal structure which showed the central ring bent into a boat form and the two non-coplanar

benzene rings buckling to form a butterfly conformation. This relieves steric interactions between the dicyanomethylene groups and the peri hydrogens. Similar boat-shaped quinonoid moieties are also exhibited, to a lesser extent, by 9-dicyanomethylene anthrone (38)<sup>81</sup> and benzo-TCNQ (39)<sup>82</sup>. Electrochemical studies<sup>79</sup> show TCAQ to be a poorer acceptor than TCNQ, but more significantly, the first redox wave corresponds to a reversible, two-electron reduction, as observed with TMTCNQ (32)<sup>68</sup>. Comparison with cyclic voltammetric data for TCNQ and benzo-TCNQ shows an increasing coalescence of the first and second reduction potentials with increasing benzo-substitution. To explain the two-electron reduction it has been suggested that the molecular distortion in TCAQ (37) causes the first reduction potential ( $E_{\frac{1}{2}}^1$ ) to shift to a more negative range, while not affecting the second reduction potential ( $E_{\frac{1}{2}}^2$ ), all steric interactions being relieved in the dianion. Alternatively, TCAQ (37) may be considered as two independent electron sinks (two distorted diphenyldicyanomethylene units). A second, reversible, redox wave attributed to trianion formation, and a further irreversible redox wave due to tetraanion formation, are very similar to those observed for anthracene; these data suggest that in the TCAQ dianion, the negative charges localise upon the dicyanomethylene units, which subsequently twist out of the plane of the ring, thus "isolating" the anthracene ring. In the light of the severe distortion exhibited by TCAQ (37), it is not surprising that all attempts to form solid salts with various TTF-type donors, alkali metals *etc.*, have failed. Continuing on this theme, TBAQ (40) was synthesised and the X-ray structure determined<sup>83</sup>. Steric interactions between two sets of peri hydrogens in TBAQ, as well as with the dicyanomethylene groups, result in possibly the most sterically crowded TCNQ derivative prepared so far.

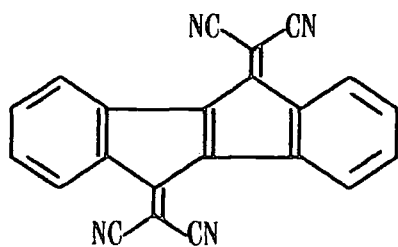


(40)

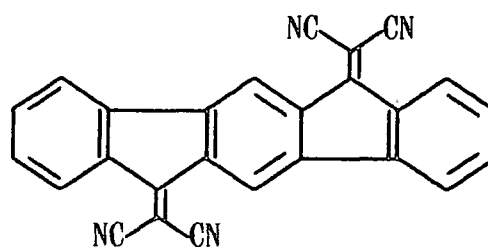


(41)

OCNAQ (41) provided the first example of a coupled TCNQ<sup>84</sup>. OCNAQ was found to be a stronger acceptor than TCNQ, with a reduced on-site Coulomb repulsion in the dianion. X-ray structural data on  $\text{Et}_4\text{N}^+$  (OCNAQ<sup>-</sup>) show that the quinonoid structure is maintained in the monoanion, which is inevitably related to the ease with which a second electron is accepted. The central ring of OCNAQ is essentially planar, while steric interactions force the TCNQ nuclei into distorted boat forms, the bows and sterns of each boat pointing in opposite directions. The conductivity ( $\sigma_{\text{rt}}$  single crystal =  $4 \times 10^{-4} \text{ S cm}^{-1}$ ) is larger than the corresponding compaction value of the TCNQ salt ( $\sigma_{\text{rt}} \leq 10^{-6} \text{ S cm}^{-1}$ ), which has been attributed to the reduction of on-site Coulombic repulsion in OCNAQ. However, such deductions from a comparison of single crystal and compaction conductivities, differing by only two orders of magnitude, is certainly open to criticism. The TTF salt of OCNAQ, possesses an unusual stoichiometry ( $\text{TTF}_{1.15}\text{-OCNAQ}$ ) and exhibits semiconductor behaviour ( $\sigma_{\text{rt}} = 10^{-2} \text{ S cm}^{-1}$ ).



(42)

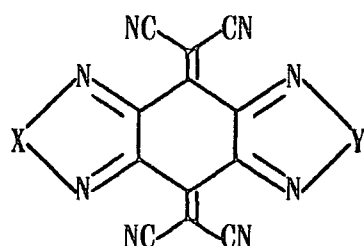


(43)

Two recently prepared electron acceptors (42) and (43), from electrochemical studies, appear to be promising candidates for conducting CT complexes<sup>86,87</sup>. However, salts of these acceptors have yet to be reported. So, overall, the results of some extensive synthetic work directed towards extended TCNQ derivatives have been disappointing and early hopes that this approach would afford highly conducting complexes has not been realised.

### 1.5.3 Heterocyclic TCNQ Derivatives

In order to overcome the steric problems in TCAQ, the benzo substituents were replaced by heterocycles, to yield BTDA-TCNQ (44)<sup>88</sup>.



(44) X=Y=S

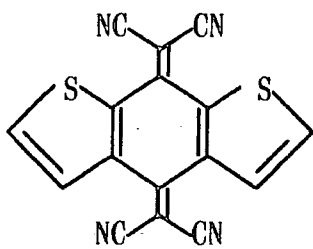
(45) X=S; Y=Se

(46) X=Y=Se

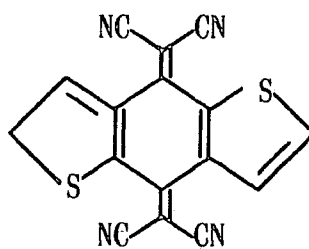
In line with predictions, the crystal structure of neutral BTDA-TCNQ (44) shows the molecule to be essentially planar, with bond lengths indicating resonance stabilisation of the thiadiazole rings<sup>89</sup>. A columnar stacking arrangement involving only the thiadiazole rings and extensive, transverse S-NC interactions forming a two-dimensional network, suggests that the heteroatoms could increase intra- and interstack interactions, thus stabilising the metallic state of salts. Electrochemical data showed that BTDA-TCNQ (44) is a weaker acceptor than TCNQ, but the thermodynamic stability of the radical anions are very similar. BTDA-TCNQ interacts with a range of donors to form 1:1 complexes, TTT-(BTDA-TCNQ) being the most highly conducting ( $\sigma_{rt} = 6 \text{ S cm}^{-1}$ )<sup>90</sup>. TTF-(BTDA-TCNQ) is a neutral insulating ( $\sigma_{rt} = 4 \times 10^{-8} \text{ S}$

$\text{cm}^{-1}$ ) complex. TTF-(BTDA-TCNQ) exhibits the expected 2-D network resulting from strong heteroatom interactions. However, in contrast to the expected effect, the network provides cavities in which the TTF molecules reside, thus leading to a mixed stack motif<sup>91</sup>. TTT (9) being a larger donor, with lower oxidation potential, will not fit into the cavity and hence a highly conducting TTT complex results, presumably due to a segregated stack motif. The selenium analogues (45) and (46) were prepared and X-ray data show enhanced inter-heteroatom interactions (*cf.* TMTSeF)<sup>92</sup>. To date, complexes of (45) and (46) have not been reported.

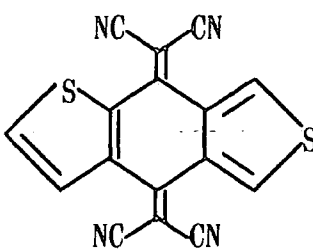
The enhanced interstack interactions and reduction of the intramolecular Coulombic repulsion in BTDA-TCNQ (44), prompted research towards other heterocyclic fused TCNQ's. The preparation of TCNQ fused thiophenes provided four isomers (47)-(50)<sup>93</sup>.



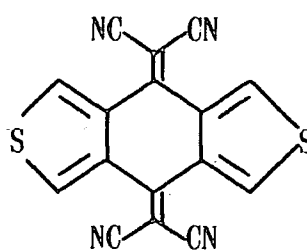
(47)



(48)



(49)

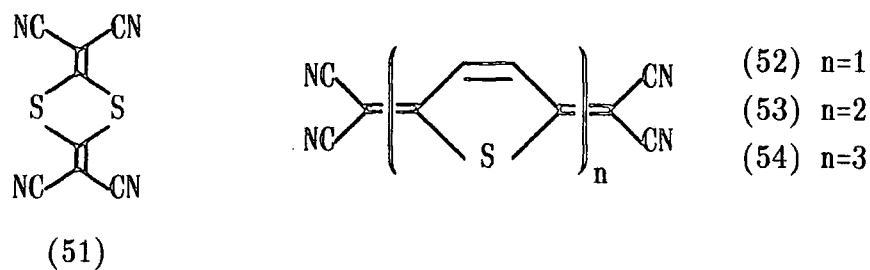


(50)

Isomers (49) and (50) were found to be weak acceptors that failed to yield any complexes. This poor acceptor ability was attributed to the formation of an unstable tetravalent sulphur species, upon reduction. In contrast, the remaining two isomers (47) and (48) gain

aromatic stability upon reduction and hence are stronger acceptors than (49) and (50). Consequently isomers (47) and (48) do form 1:1 complexes with TTF which display  $\sigma_{rt}$  (compaction) values of 0.89 - 4.8 S cm<sup>-1</sup>.

Several thiophene acceptors have been studied recently by Japanese workers. In the 1970's, 2,4-bis(dicyanomethylene)-1,3-dithietan (51) was prepared<sup>94</sup>. Although this molecule is isoelectronic with TCNQ, it is a very poor acceptor and consequently forms an insulating complex with TTF. The thiophene ring analogue (52) has the added advantage that the molecule can form an aromatic sextet upon reduction to the radical anion. The stability of the radical anion was established by the isolation of the lithium salt of compound (52)<sup>95</sup>.



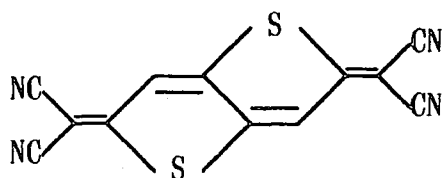
Increasing the number of thiophene units to two or three, forming compounds (53) and (54), reduces the electron affinity of the acceptor, as well as the effective Coulombic repulsion in the dianion. Molecules (53) and (54) are interesting analogues of TCNDQ (34): in the *trans* conformation there is a reduction of the steric interactions found in TCNDQ. The room temperature conductivities of complexes of acceptors (52)-(54) are given in Table 1.2<sup>96</sup>.

This general trend that increasing the conjugation of the acceptor provides an increase in the conductivity, points to the fact that conjugated acceptors with weak electron affinities are capable of forming conductive CT complexes, because of increased overlap of the extended  $\pi$  systems and effective diminution of the on-site Coulombic repulsions.

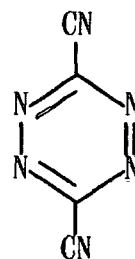
ACCEPTOR	$\sigma(\text{rt})/\text{S cm}^{-1}$ <sup>a</sup>	
	TTF	TTN
52	$6.7 \times 10^{-9}$	----
53	$2.2 \times 10^{-4}$	$3.3 \times 10^{-4}$
54	$3.3 \times 10^{-3}$	$7.2 \times 10^{-1}$

Table 1.2 Conductivity Data for TTF and TTN Complexes of the Thiophene Based Acceptors (52)-(54); a=Compaction, four-probe measurements (Ref.96).

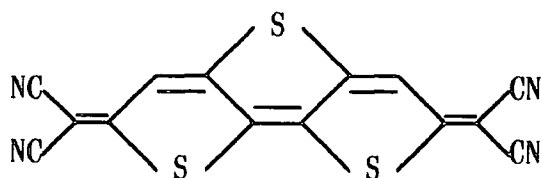
A logical extension to this particular area of research was to study acceptor molecules containing fused thiophene units. Both compounds (55) and (56), which are potentially similar to TNAP (33), form highly conducting complexes with TTF ( $\sigma_{\text{rt}} = 13$  and  $2.3 \text{ S cm}^{-1}$  respectively). Surprisingly, while (56) also forms a conducting complex with TTF ( $\sigma_{\text{rt}} = 3.0 \text{ S cm}^{-1}$ ), the corresponding complex of (55) is insulating ( $\sigma_{\text{rt}} = 10^{-8} \text{ S cm}^{-1}$ )<sup>97</sup>. A better understanding of such phenomena requires X-ray crystal data.



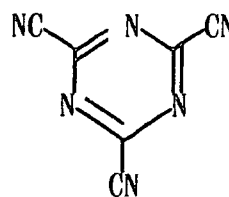
(55)



(57)



(56)

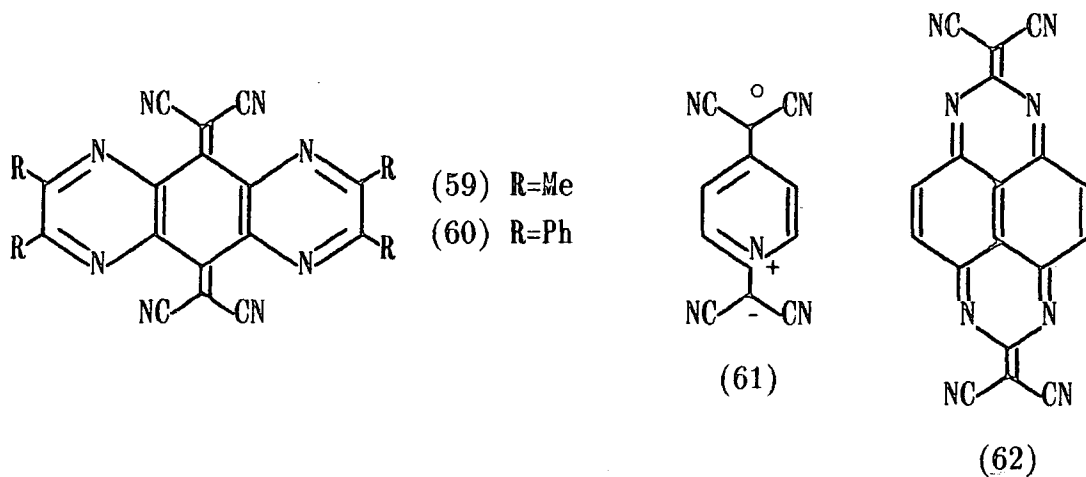


(58)

Further research into heterocyclic acceptors, led to the synthesis of 3,6-dicyano-1,2,4,5-tetrazine (57) and 2,4,6-tricyano-S-triazine

(58), the former yielding a 1:1 TTF complex with metallic conductivity ( $\sigma_{rt} = 35 \text{ S cm}^{-1}$ )<sup>98</sup>. This was an important breakthrough, being the first complex in which the attainment of aromaticity in the radical anion was not a prerequisite for high conductivity. Compound (58) forms a semiconducting TTF complex ( $\sigma_{rt} = 2 \times 10^{-4} \text{ S cm}^{-1}$ ). Unexpectedly, upon exposure to air the  $\sigma$  value for this complex increased dramatically. This was considered to be related to a cyano group being replaced by a hydroxyl group.

Introducing nitrogen atoms into the TCAQ skeleton (37) had rather disappointing results<sup>99</sup>. Tetramethyldipyrazino-TCNQ (59) forms 1:1 insulating complexes with both ET (14) and TMTTF (4). The tetraphenyl derivative (60), failed to form complexes with these donors, presumably due to steric interactions of the phenyl groups.



Aza-TCNQ (61), although possessing similar geometry to TCNQ, should exhibit very different electronic properties, the radical anion having a diamagnetic property related to the presence of C—N ylid bonding. Simple salts of (61) with a range of alkylammonium cations exhibit typical semiconductor behaviour in the temperature range 273 - 358 K, with  $\sigma_{rt}$  between  $10^{-6} - 10^{-9} \text{ S cm}^{-1}$ <sup>100</sup>. Mixed salts of the general formula  $[\text{Cation}]^+[\text{aza-TCNQ}^-]_x[\text{TCNQ}^-]_{1-x}$  ( $x \leq 0.17$ ), display higher conductivities ( $\sigma_{rt} = 10^{-4} - 10^{-6} \text{ S cm}^{-1}$ ) than the corresponding TCNQ

salts. This indicates that incorporation of aza-TCNQ into the TCNQ radical anion stacks reduces the bandgap.  $(\text{TMTSeF})_2\text{-azaTCNQ}$  ( $\sigma_{\text{rt}} \sim 0.1 \text{ S cm}^{-1}$ ) possesses an interesting crystal structure: the TMTSeF (7) molecules arrange themselves in 1-D stacks, providing the sole conduction path. The donor stacks are surrounded by aza-TCNQ's, orientated perpendicular to the donors<sup>101</sup>.

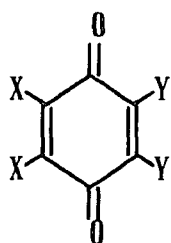
To conclude this section on heterocyclic TCNQ derivatives, TCQQ (62) is worth a mention. TCQQ was prepared because i) the synthesis was easier than the pyrene derivative (36), and ii) the presence of the nitrogen atoms will increase the electron affinity of the acceptor and also the number of available oxidation states<sup>102</sup>. Unfortunately TCQQ could only be isolated as the dianion: attempted chemical oxidation to the monoanion and neutral species failed. Electrochemistry revealed a single reversible, one-electron reduction to the trianion. All attempts to observe an oxidation of the dianion, at higher, positive potentials, were unsuccessful. Complex formation with various TTF-type donors has not yet been reported.

#### 1.5.4 Quinones and N-Cyanoimines

A different and successful approach to the choice of new acceptors was made by Torrance *et al.*, in the late 1970's<sup>103,104</sup>. Torrance confronted the problem of meeting the two essential requirements for high conductivity, namely a segregated stack motif and incomplete charge transfer. For the latter requirement, electrochemical half-wave potentials were used as a guide to the ionisation potential (IP) of the donor and the electron affinity (EA) of the acceptor, the difference ( $\Delta E_{\frac{1}{2}}$ ) (Equation 1.1) providing a guideline to the valency of the resulting complex.

$$\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}D}^1 - E_{\frac{1}{2}A}^1 = IP - EA \quad (1.1)$$

Torrance argued that  $\Delta E$  values greater than +0.25 V would give rise to a neutral complex,  $\Delta E$  values less than -0.25 V an ionic complex, and intermediate values a mixed valence complex, possibly exhibiting high conductivity. Support for this theory came from the study of two acceptors, TCNQ and DDQ (63), and two donors, dibenzo-TTF (DBTTF) (64) and TTF, whose combinations should span the range of valencies<sup>103</sup>. As predicted, combination of the weakest donor (DBTTF) and weakest acceptor (TCNQ) ( $\Delta E_{\frac{1}{2}} = +0.32$  V) gave a neutral complex<sup>‡</sup> with a  $\sigma_{rt}$  value of *ca.*  $10^{-7}$  S  $\text{cm}^{-1}$ . For DBTTF-DDQ ( $\Delta E_{\frac{1}{2}} = -0.01$  V) a mixed valence complex was predicted and confirmed by the high, room temperature conductivity value ( $\sigma_{rt} = 8$  S  $\text{cm}^{-1}$ ). Further evidence for a mixed valence, segregated stack structure, came from optical absorption spectra, a broad band at 0.4 eV being characteristic of all organic metals (*eg.* TTF-TCNQ). This complex provided an important step forward for research in the area of organic metals, as it was one of the first highly conducting complexes not to contain a TCNQ-type acceptor. The  $\Delta E$  value for TTF-DDQ ( $\Delta E_{\frac{1}{2}} = -0.27$  V) was such that combination of these two moieties afforded a fully ionic, insulating salt.

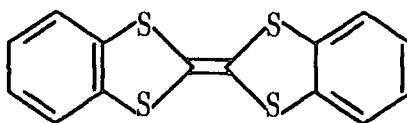


(63) X=CN; Y=Cl

(65) X=Y=F

(66) X=Y=Cl

(67) X=Y=Br



(64)

Attainment of segregated stacks is considerably more difficult; most CT complexes prefer to exist in mixed stacks. However, the idea

<sup>‡</sup>A neutral complex refers to a complex in which the constituent molecules are present as neutral species and there is no observable degree of ionisation.

was introduced that segregated stacking would be favoured when the frontier orbitals of the donors and acceptors had opposite symmetry upon inversion, as is the case with TTF-TCNQ and NMP-TCNQ. With the fore-mentioned criteria in mind, TTF and TMTTF (4) were combined with the tetrahalobenzoquinones (65)-(67), giving 1:1 complexes, existing in more than one phase<sup>104</sup>. Only the most highly conducting phases are of interest here, the compaction conductivities of which are summarised in Table 1.3.

$\sigma(300\text{ K})/S\text{ cm}^{-1}$	TETRAHALOBENZOQUINONE			TCNQ
	(65)	(66)	(67)	
TTF	10	$8 \times 10^{-4}$	$6 \times 10^{-4}$	70
TMTTF	7	20	1 (5†)	35

Table 1.3 *Conductivity Data for the Most Highly Conducting TTF and TMTTF-Tetrahalobenzoquinones Complexes (Ref.104)*  
 †Single Crystal Value.

TMTTF-bromanil (67) has been studied in detail and comparison of its X-ray crystal structure with TMTTF-TCNQ, despite obvious differences between the two acceptors, reveals remarkable similarities<sup>105</sup>. Predictably, the donor and acceptor in both complexes are essentially planar, and they form segregated stacks. The overlap and interplanar spacings of the TMTTF molecules are virtually identical in both structures, and the "ring over bond" type overlap associated with TCNQ is also observed in the bromanil stacks. The similarity of the overlap in both acceptors is ultimately related to the similar nodal properties of the LUMO's in both acceptors, the slipped arrangement providing the most favourable interaction. The most noteworthy difference between the two structures is the 0.1Å greater intra-stack separation between the bromanil molecules, compared to the TCNQ separation. This difference is surely related to the bulk of the bromine atoms and accounts for the

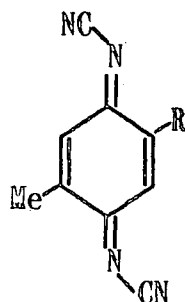
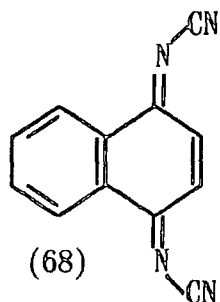
lower conductivity found in TMTTF-bromanil. Correspondingly the  $\sigma_{rt}$  value for TMTTF-chloranil is higher than that of TMTTF-bromanil.

Partial charge transfer in both the bromanil and chloranil complexes is confirmed by vibrational spectra, each having a  $\rho$  value of *ca.* 0.5 electrons per molecule<sup>106</sup>. Consequently, the two essential criteria for high conductivity have been met, as predicted. Moreover, this study established that for high conductivity in complexes, the acceptors are not restricted to TCNQ-type molecules. Although very similar in many respects, TMTTF-bromanil and TMTTF-TCNQ have one important difference. In TMTTF-TCNQ the conductivity and magnetic susceptibility become activated at the same temperature ( $T_c$  *ca.* 55 K) which is typical of organic metals undergoing a Peierls type transition. In contrast, the conductivity in TMTTF-bromanil is activated at temperatures well above the magnetic susceptibility transition temperature ( $T_c = 75$  K). Thus, above 75 K, TMTTF-bromanil is a magnetic semiconductor and not a simple quasi 1-D metal<sup>106</sup>. The immediate question arising from this study is: what causes the conductivity, but not the magnetic susceptibility to be activated? Until such questions are answered, it is premature to claim a full understanding of TTF-TCNQ type systems.

In contrast to the TMTTF salts, the TTF salts of fluoranil (65), chloranil (66)<sup>107</sup>, and bromanil (67)<sup>108</sup> exhibit a mixed stack arrangement, with uniform spacing along the stacks. Interestingly the bromanil complex has an ionic ground state, whereas the fluoranil and chloranil complexes are neutral. This suggests that the larger polarisation of bromanil must play an important role in stabilising the ionic ground state in TTF-bromanil. The mixed stacking arrangement in the TTF complexes apparently contradicts the argument<sup>104</sup>, that if the HOMO of the donor and the LUMO of the acceptor have opposite symmetry with respect to inversion, then eclipsed overlap of the two molecules

should provide zero stabilisation and hence segregated stacks form by default. Close inspection of the donor/acceptor overlap in TTF-chloranil and TTF-fluoranil indicates that orbital overlap determines the relative orientation in one case (TTF-fluoranil), but yields to larger steric interactions in the other (TTF-chloranil)<sup>107</sup>. In both cases a non-eclipsed configuration is achieved with a net positive orbital overlap, without the need for segregated stacking. This work clearly emphasises the need to direct research towards understanding the factors controlling the all-important aspect of crystal structure.

A most exciting recent development due to Hunig and coworkers, has been the use of the N-cyanoimine group in place of the dicyanomethylene group, to furnish new electron acceptors. The synthesis of a whole range of acceptors involves, without exception, a clean, one-step, high yielding reaction from the corresponding quinone<sup>109</sup>. This immediately makes the study of such compounds an attractive proposition. Another attractive property is the flexibility of the N-cyanoimine group (*cf.* the rigid C(CN)<sub>2</sub> group), thus enabling retention of planarity in sterically demanding derivatives. The potential of this class of acceptors was first realised in 1984, when the complex between N,N'-dicyano-1,4-naphthoquinonediimine (68) and TTF exhibited high ambient temperature conductivity ( $\sigma_{rt} = 25 \text{ S cm}^{-1}$ ), and remained metallic down to 140 K<sup>110</sup>. These results were particularly encouraging in light of the fact that benzo-TCNQ (39) does not complex with TTF (this being attributed to twisting within the acceptor molecule to alleviate steric strain, *vide supra*). The most notable points concerning the crystal structure of TTF-(68) are i) segregated uniform stacks of essentially planar donors and acceptors, ii) strong S-NC interactions between donor and acceptor, and iii) the *syn* configuration of the N-cyanoimine groups.



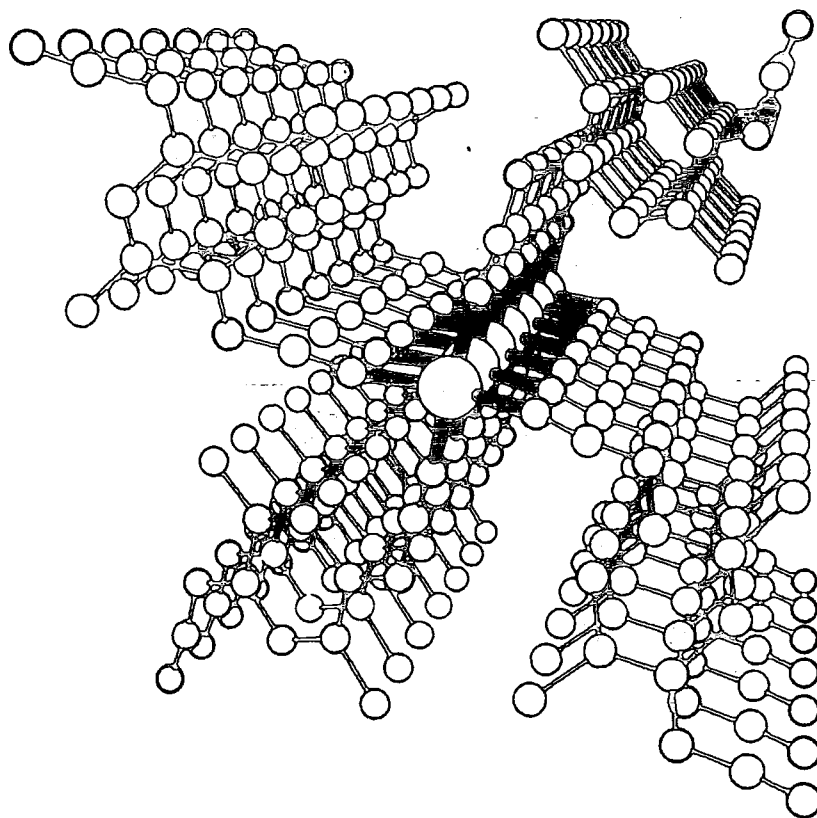
(69) R=Me

(70) R=Cl

(71) R=Br

(72) R=I

The most dramatic result, without doubt, to emerge from the study of the N,N'-dicyanoquinonediimines, has been the discovery of exceptionally high conductivity in the copper salt of the 2,5-dimethyl derivative, 2,5-DM-DCNQI (69)<sup>111</sup>.  $\text{Cu}(2,5\text{-DM-DCNQI})_2$  has a  $\sigma_{\text{rt}}$  value of  $800 \text{ S cm}^{-1}$ , which upon cooling rises to a value of  $500,000 \text{ S cm}^{-1}$  at 3.5 K. This result is quite amazing in view of the fact that  $\text{Cu}(\text{TCNQ})_2$  is a semiconductor.



**Figure 1.10** *Crystal Structure of  $\text{Cu}(2,5\text{-DM-DCNQI})_2$ ; Viewed Down the Chain of Copper Atoms, Surrounded by Four Stacks of 2,5-DM-DCNQI Molecules (Ref.111).*

The crystal structure of  $\text{Cu}(2,5\text{-DM-DCNQI})_2$  (Figure 1.10) shows the copper ions arranged in chains, each surrounded by four stacks of  $N,N'$ -dicyanoquinonediimine. Co-ordination to the copper ion through the terminal nitrogen atoms of four acceptors, gives rise to a distorted tetrahedral arrangement.

The far greater separation of the copper ions within the chain (388 pm) compared to that in copper metal ( $\text{Cu-Cu} = 256$  pm) makes it unlikely that the conduction pathway is through the copper chains. Conductivity, therefore, derives from the stacks of delocalised  $\pi$ -electron systems, with the copper ions acting as a conductivity bridge between individual stacks. This last point is supported by i) the observation of a broadened ESR signal, and ii) the absence of a phase transition; this clearly suggests multi-dimensional character. Thus, this is the first example in which the metallic state is stabilised to low temperatures, where the conduction pathway is solely through stacks of acceptor molecules.

A range of 2,5-disubstituted- $N,N'$ -dicyanoquinonediimine salts with various metal ions (Cu, Ag and alkali metals) has since been studied<sup>112,113</sup>. The copper salts of (2,5-dimethyl), (2-chloro-5-methyl) and (2-bromo-5-methyl) derivatives, compounds (69)-(71) respectively, all exhibit higher  $\sigma_{\text{rt}}$  values ( $\sigma_{\text{rt}} = 300 - 1000 \text{ S cm}^{-1}$ ) than the corresponding silver and alkali metal salts. Also, with the exception of  $\text{Cu}(2,5\text{-DM-DCNQI})_2$ , all these salts, at lower temperatures, undergo a phase transition into the semiconducting regime. Surprisingly  $\text{Cu}(2\text{-iodo-5-methyl-}N,N'\text{-dicyanoquinonediimine})_2$  (72) displays a continuous increase in conductivity down to 1.2 K. This different behaviour is attributed to the large iodine atom, increasing the strain within the crystal, thus suppressing the Peierls transition. Poor overlap of the quinonoid  $\pi$ -orbitals also explains the reduced conductivity of this salt

$$(\sigma_{rt} = 0.2 \text{ S cm}^{-1}).$$

Comparing the crystal structures of the salts of 2,5-DM-DCNQI and 2-chloro-5-methyl-DCNQI with alkali metal, ammonium, copper and silver cations, revealed various features common to them all. In the case of asymmetric acceptors, within the face-to-face stacks each molecule is superimposed upon its inverted image. The interplanar separations range from 3.15Å - 3.27Å, which compare favourably with the anion separation in TTF-TCNQ (3.17Å). Also analogous to TTF-TCNQ, is the "ring over bond" type overlap within the DCNQI columns. Surprisingly, the separation along the stacking axis is largely unaffected by differing cation radii. Finally, the geometry of co-ordination is very cation dependent.

With the large number of N,N'-dicyanoquinonediimine derivatives now available<sup>109</sup>, this class of compounds seems sure to provide further, very interesting studies and possibly a new class of organic superconductor.

## 1.6 CONCLUDING REMARKS

In summary, research over the last 20 years into new electron acceptors for conducting CT complexes has failed to establish a class of molecules which is far superior to TCNQ, in terms of room temperature conductivity and stabilisation of the metallic state. The recently synthesised DCNQI derivatives, *eg.* (69) clearly point a way forward. Study of the donors would appear to have been far more fruitful with the advent of superconducting salts. However, it must be remembered that far more attention has been focused upon the donors, and who, for example, would have predicted superconductivity in the Bechgaard salts, two decades ago!

CHAPTER TWO

NEW DERIVATIVES OF THE TCNQ AND DCNQI SYSTEMS

FROM ALKYL BENZOQUINONES

## 2.1 INTRODUCTION

From the phenomenal amount of work which has preceded this thesis (Chapter 1), it is clear that the effect of certain factors (*eg.* degree of charge transfer,  $\rho$ ) upon the conductivity of complexes is well documented and understood. Electrochemical techniques allow the value of  $\rho$  for any donor-acceptor pair to be predicted with a satisfactory degree of certainty. In contrast, many factors, particularly those concerned with the all-important crystal structure, are poorly understood and have to be explained with hindsight. For example, it is well known that a segregated stacking mode is crucial for high conductivity in these materials, however, despite the advances made by Torrance *et al.*<sup>104,105</sup> with TMTTF-bromanil, the formation of a mixed stack arrangement in TTF-fluoranil and TTF-chloranil<sup>107</sup> clearly emphasises that the controlling factors are far from predictable.

What is the optimum degree of dimensionality for highly conducting, quasi one-dimensional complexes? Work upon electron donors has firmly established that substitution of sulphur for selenium generally increases the dimensionality of the system, resulting in a lowering of the temperature of the metal-insulator (M-I) phase transition or its elimination<sup>21,22</sup>. By comparison, the presence of the methyl substituent in TTF-MTCNQ reduces the important interchain coupling compared to TTF-TCNQ, with subsequent broadening of the M-I transition<sup>56</sup>. These two examples highlight how different effects contribute to the stability of the metallic state, optimisation of which requires very fine tuning: in organic metals, bulk molecular properties are very sensitive to small structural changes. The few examples highlighted reflect the need for further research into these systems, so that one day highly conducting, or superconducting complexes may be designed with confidence. In

particular, the role of the acceptor molecule in these quasi one-dimensional materials is poorly understood.

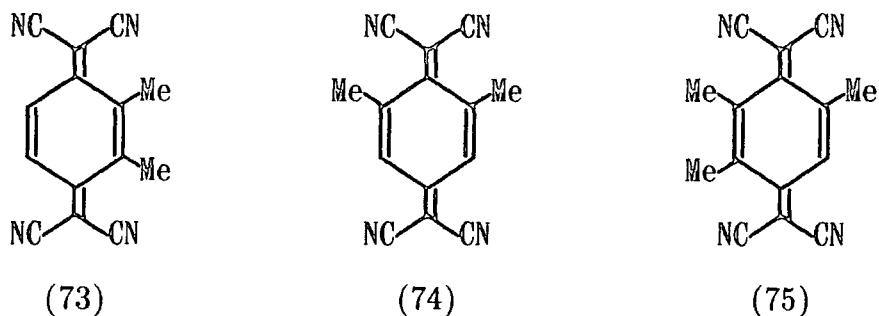
The aim of this thesis is to prepare and characterise new electron acceptors, whose CT complexes should provide valuable insight into the factors controlling conductivity and its associated phenomena. This chapter is concerned with our work on new alkylated TCNQ derivatives. Why study alkylated TCNQ's? Previous studies have shown that the alkyl substituents have the advantage that, although the electron affinity (EA) of the acceptor is reduced compared to TCNQ, this effect is not too dramatic (Table 2.1)<sup>114</sup>.

COMPOUND	$E_{\frac{1}{2}}^1$	$E_{\frac{1}{2}}^2$	$\sigma_{rt}$ (S cm <sup>-1</sup> )
TCNQ	0.19	-0.35	500 <sup>a</sup>
MTCNQ	0.17	-0.34	500 <sup>a</sup>
2,5-DMTCNQ	0.11	-0.35	1 <sup>b</sup>
2,5-DETCNQ	0.12	-0.365	500 <sup>a</sup>

**Table 2.1** *Half-Wave Reduction Potentials (V vs SCE) Determined by Cyclic Voltammetry at a Pt-Button Electrode in CH<sub>3</sub>CN-[n-Bu<sub>4</sub>N][BF<sub>4</sub>] (0.1M), and Room Temperature Conductivity (S cm<sup>-1</sup>) of the Corresponding TTF Complexes; a=single crystal measurement; b=compaction measurement (Ref.114).*

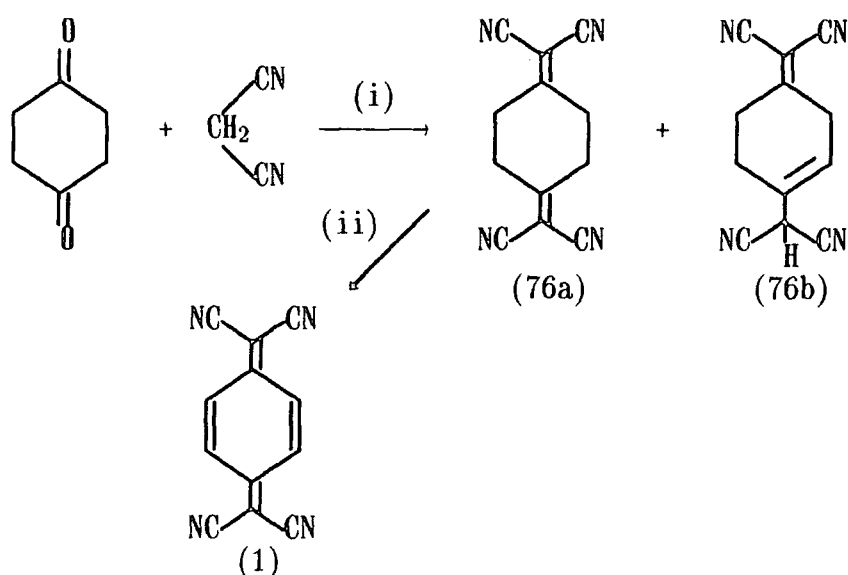
Consequently the value of  $\rho$  should not be too greatly affected, yet crystal packing is modified to accommodate the methyl substituent(s). Both intra- and inter-stack separations are affected, thus enabling the effect of changes to the bandwidth and inter-stack interactions on solid state properties to be studied. The  $\sigma_{rt}$  values of the TTF salts (Table 2.1) indicate that the effect of methyl/ethyl substitution upon the bandwidth is small, all values existing in the metallic regime. The particular TCNQ derivatives which interested us were 2,3-dimethyl-TCNQ (73), 2,6-dimethyl-TCNQ (74) and 2,3,5-trimethyl-TCNQ (75). The

preparation and characterisation of these three TCNQ derivatives would complete the range of possible methylated TCNQ's and, hence, allow the derivatives to be studied as a whole rather than individually. Although (73) was a known compound (from previous work by Bryce *et al.*<sup>115</sup>), full synthetic details and data concerning complex formation had yet to be reported.



## 2.2 SYNTHESIS OF TCNQ DERIVATIVES

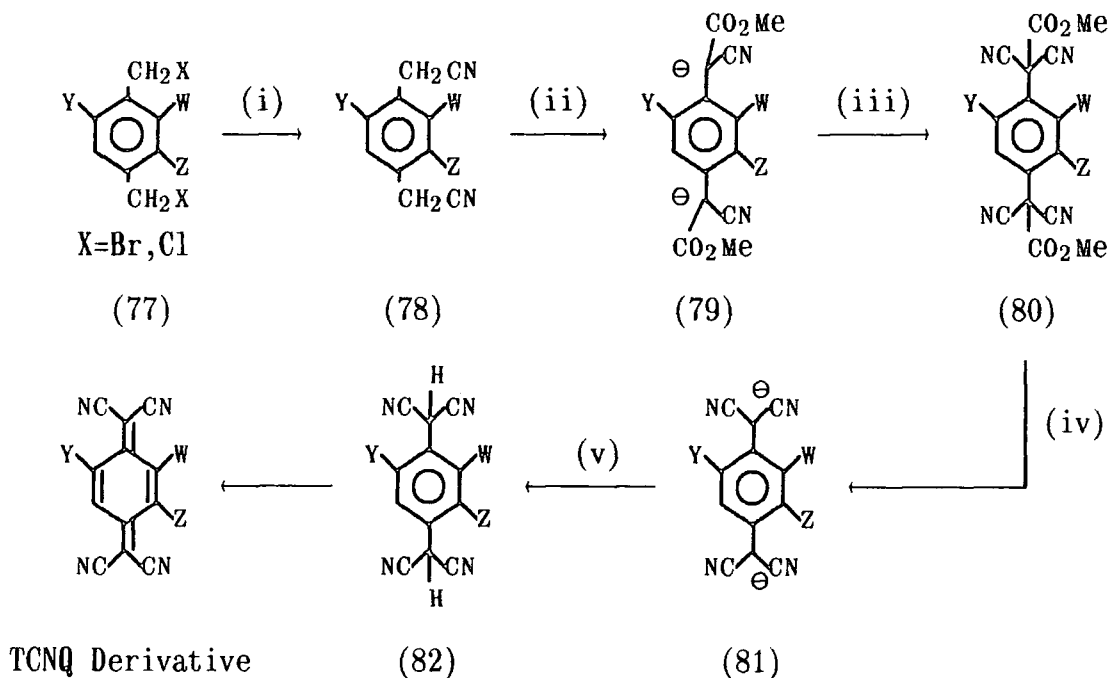
The crucial step in the synthesis of TCNQ derivatives, that frequently poses many problems is the construction of the dicyanomethylene group. Initial syntheses of TCNQ derivatives (Scheme 2.1) involved condensation of malononitrile with 1,4-cyclohexandione to give 1,4-bis(dicyanomethylene)cyclohexane (76a)<sup>116</sup>.



**Scheme 2.1** *Synthetic Steps: (i)  $\beta$ -Alanine; (ii)  $Br_2$ /Pyridine.*

Condensation in benzene solution gave a mixture of (76a) and (76b) whereas, in aqueous solution a high yield (97%) of (76a) was obtained. Oxidation of (76a) in the presence of pyridine and either N-bromosuccinimide (NBS) or bromine gave TCNQ (1) in good yield (80%). This approach also affords MTCNQ (15) and 2,5-DMTCNQ (16)<sup>116</sup>.

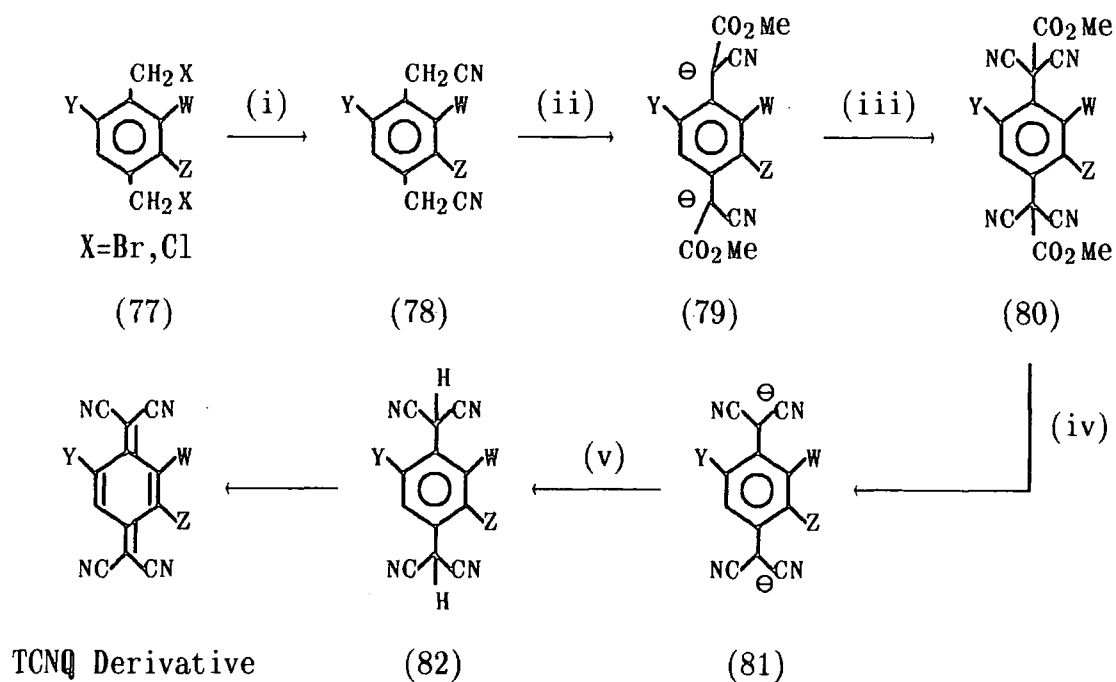
Wheland and Martin have described a versatile synthetic route (Scheme 2.2) starting with the corresponding p-xylenedihalide (77)<sup>53</sup>. Reaction of (77) with sodium cyanide gave the p-xylenedicyanide (78), which on treatment with sodium methoxide in benzene-dimethylcarbonate established an equilibrium with dianion (79). Addition of cyanogen chloride then afforded the tetracyano diacetate (80). Treatment of (80) with hydroxide ion hydrolyses the ester group and decarboxylation gives dianion (81), which is converted to the dihydro-TCNQ (p-phenylenedimalononitrile) (82) with hydrochloric acid. Finally, oxidation with bromine afforded the corresponding TCNQ.



**Scheme 2.2** Synthetic Steps: (i) NaCN; (ii) NaOMe/(MeO)<sub>2</sub>CO [-MeOH]; (iii) ClCN; (iv) KOH [-CO<sub>2</sub>]; (v) HCl.

Condensation in benzene solution gave a mixture of (76a) and (76b) whereas, in aqueous solution a high yield (97%) of (76a) was obtained. Oxidation of (76a) in the presence of pyridine and either *N*-bromosuccinimide (NBS) or bromine gave TCNQ (1) in good yield (80%). This approach also affords MTCNQ (15) and 2,5-DMTCNQ (16)<sup>116</sup>.

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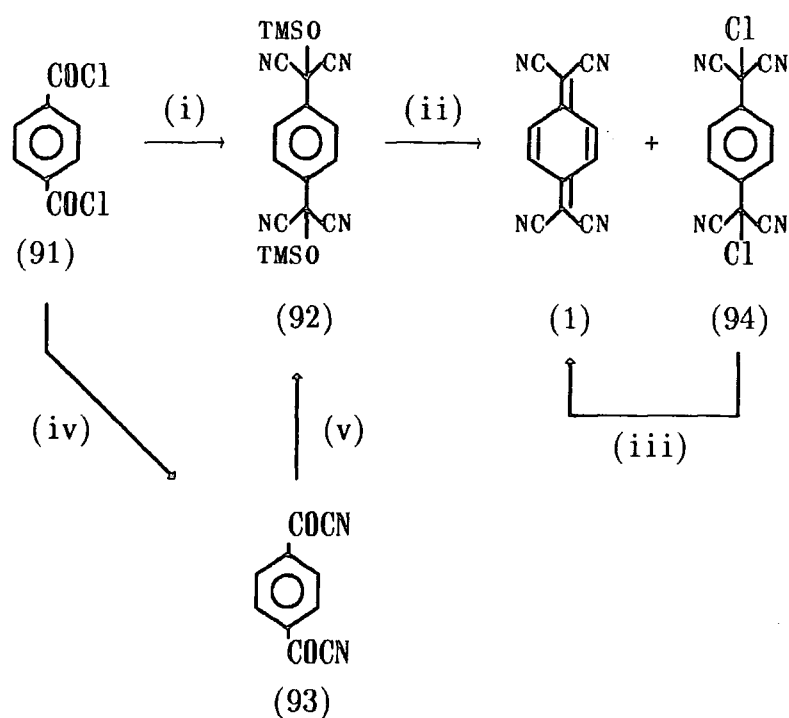


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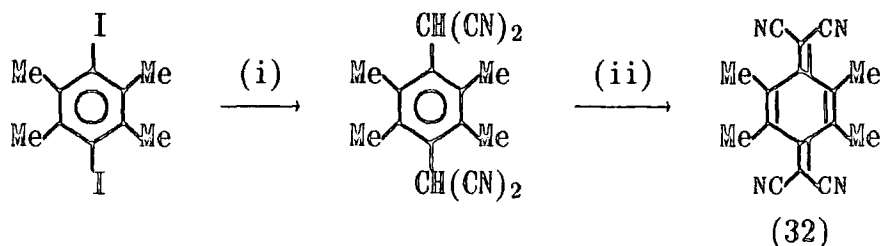
for the synthesis of several TCNQ derivatives<sup>119</sup>, but it is not applicable to our target alkyl derivatives, as the p-xylene dicyanides we would require are not readily available.

Another cyanating agent to be employed in TCNQ synthesis is cyanotrimethylsilane, TMSCN (90)<sup>120</sup>. Terephthaloyl chloride (91) treated with excess (90) in the presence of pyridine gives 1,4-bis(dicyanotrimethylsiloxymethyl)benzene (92) in good yield (70%). Compound (92) was also prepared in 62% yield by reaction of the same reagents, (90) and pyridine, with terephthaloyl cyanide (93) which was prepared from (91) and copper (I) cyanide. Compound (92), when treated with a  $\text{POCl}_3$ -pyridine mixture at room temperature, afforded TCNQ (1) and the dichloride (94), which was readily converted to TCNQ by sodium borohydride (Scheme 2.5). 2,5-Dimethyl-TCNQ (16) and 2-bromo-TCNQ were prepared by the same method, using the corresponding terephthaloyl chlorides. This methodology was utilised to prepare the sterically demanding tetramethyl-TCNQ (32), although in modest yield (28%)<sup>68</sup>.



**Scheme 2.5** Synthetic Steps: (i) and (v) TMSCN (90), Pyridine; (ii)  $\text{POCl}_3$ , Pyridine; (iii)  $\text{NaBH}_4$ ; (iv)  $\text{Cu(I)CN}$ .

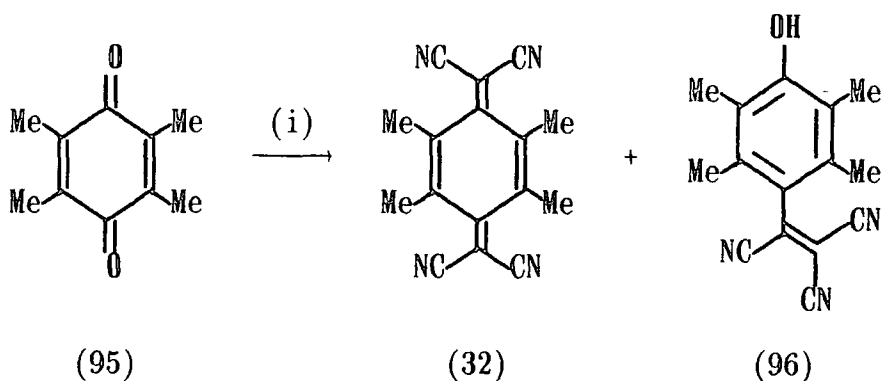
An alternative route to TMTCNQ (32) *via* the di-iodoarene has been utilised by Staab *et al.*<sup>68</sup> (Scheme 2.6).



**Scheme 2.6** *Synthetic Steps: (i) CH<sub>2</sub>(CN)<sub>2</sub>, NaOMe, CuI, HMPT, 2h, 100°C; (ii) Br.*

Similar syntheses involving nucleophilic substitution of di-iodoarenes with the malononitrile anion, in the presence of palladium catalysts, namely dichloro-bis(triphenylphosphine)palladium(II) or tetrakis(triphenylphosphine)palladium(0), have also been reported<sup>121</sup>.

Titanium tetrachloride (TiCl<sub>4</sub>) has proved a particularly useful reagent in the synthesis of TCNQ derivatives, when used to mediate Knoevenagel condensations by the procedure originally developed by Lehnert<sup>122</sup>. For example, tetramethyl-TCNQ (32) has been recently prepared in a one-step reaction from duroquinone (95) in 55% yield, in the presence of TiCl<sub>4</sub>, a side product being the phenolic compound (96) (Scheme 2.7)<sup>67</sup>.



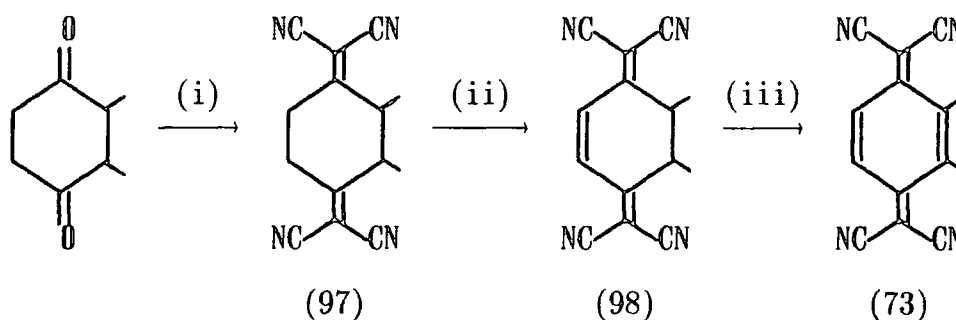
**Scheme 2.7** *Synthetic Steps: (i) CH<sub>2</sub>(CN)<sub>2</sub>, TiCl<sub>4</sub>, Pyridine, CH<sub>2</sub>Cl<sub>2</sub>, 24h, RT,.*

In the absence of TiCl<sub>4</sub>, quinones do not yield quinodimethanes when

reacted with malononitrile, but a range of phenolic and heterocyclic products arising from conjugate additions<sup>123</sup>. Another attractive feature of the  $\text{TiCl}_4$  mediated Knoevenagel condensation is that it allows the formation of sterically demanding TCNQ derivatives, TCAQ (37) being another example<sup>80</sup>.

### 2.3 SYNTHESIS OF NEW TCNQ DERIVATIVES

One aim of this section of work was to repeat the synthesis of 2,3-dimethyl-TCNQ (73)<sup>115</sup>, and hopefully to improve on the overall yield. The synthetic route of Bryce *et al.*<sup>115</sup> is outlined in Scheme 2.8.



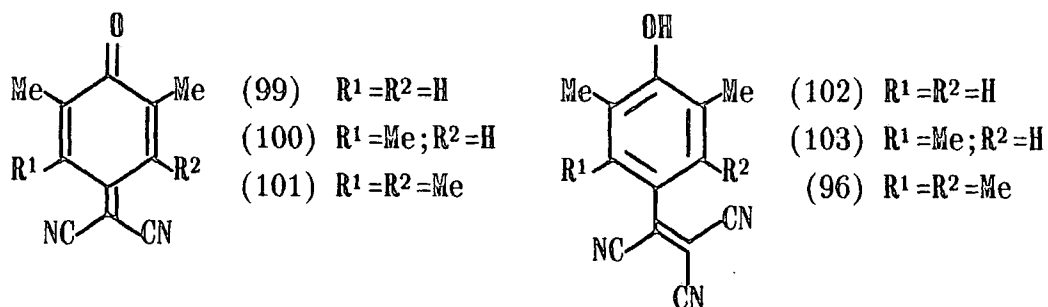
Scheme 2.8 *Synthetic Steps: (i)  $\text{CH}_2(\text{CN})_2$ ,  $\beta$ -Alanine; (ii)  $\text{Br}_2$ , Pyridine; (iii) Se, 200°C.*

The preparation of (97) and (98) were repeated according to the literature. The reproducibility of the third step, (98) to (73) however, proved to be a major problem. This was overcome by ensuring that the selenium (pellets, 99.999% from Aldrich) was ground under an atmosphere of nitrogen and the reaction temperature was increased to 220°C. Unfortunately the yield of (73) was very poor (1%). Consequently, insufficient quantities of 2,3-dimethyl-TCNQ (73) were available to enable investigations into the structural properties and complexes of this compound. Attempted oxidations of (98) to 2,3-dimethyl-TCNQ (73) using N-bromosuccinimide/pyridine, N-chlorosuccinimide/pyridine, 10%

palladium on charcoal in the presence of sulphur, and manganese dioxide, all failed. Oxidation of (97) to (98) with excess bromine (greater than two equivalents), unexpectedly introduced one rather than both double bonds. However, as revealed by  $^1\text{H}$  NMR (250 MHz), the reaction converts an isomeric mixture (*cis/trans*) of (97) to a single isomer (presumably *trans*) of (98). This conversion requires the abstraction of the methine hydrogen radical, which is returned in preference to a bromine radical, providing the least sterically hindered, *trans* isomer. From this, we conclude that entry of the bromine radical is sterically prohibited by the methyl substituent. To combat this problem, we unsuccessfully attempted to incorporate a chlorine atom, using N-chlorosuccinimide. Palladium on charcoal and sulphur are two commonly used dehydrogenation reagents, a mixture of which has been successfully used to prepare 2,3-dimethyl-TCNQ (73) in 10% yield from the dihydro-TCNQ (98)<sup>124</sup>. Our attempts to reproduce this work proved fruitless. Active manganese dioxide, which in refluxing chloroform is an effective dehydrogenating agent for electron-deficient systems<sup>125</sup>, also failed to oxidise (98) to 2,3-dimethyl-TCNQ (73).

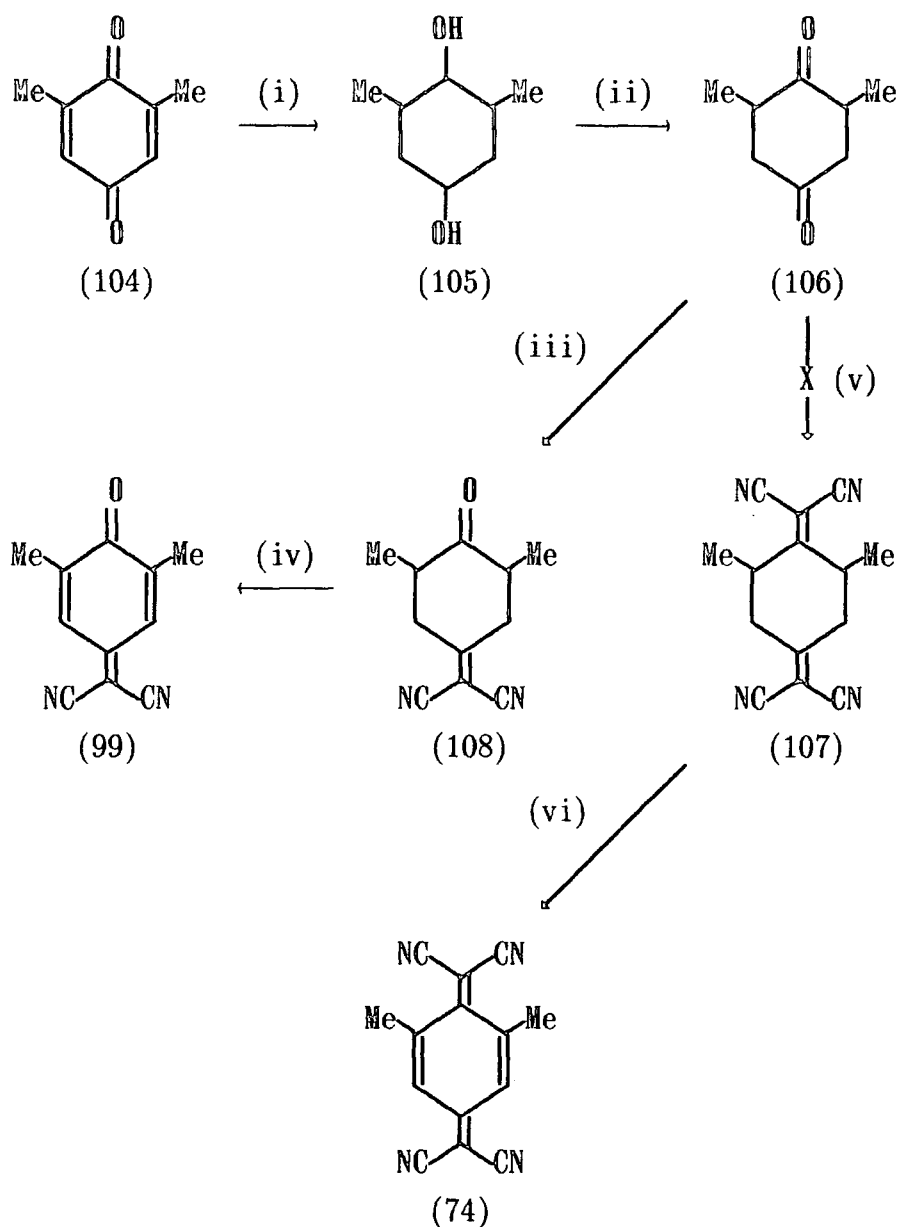
All attempts to synthesise 2,6-dimethyl-TCNQ (74) and 2,3,5-trimethyl-TCNQ (75) failed. Much time was concerned with establishing conditions for alkyl-TCNQ (74 and 75) synthesis *via* a  $\text{TiCl}_4$  mediated Knoevenagel condensation between malononitrile and the appropriate p-benzoquinone. Most reactions led to the synthesis of the mono(dicyanomethylated) products (99) and (100). In all cases, a second product was obtained, which although impure, was tentatively assigned the corresponding phenolic structures (102) and (103) from spectroscopic data. To substantiate these assignments, compound (102) was prepared from (99) and malononitrile in DMF, and the spectroscopic data of this analytically pure sample used for comparative purposes. In order to

elucidate the essential experimental details necessary for TCNQ synthesis, we attempted to repeat the preparation of tetramethyl-TCNQ (32), as reported by Cowan *et al.*<sup>67</sup> In our laboratory, this reaction provided the mono(dicyanomethylated) (101) and phenolic products (96). Although on one occasion tetramethyl-TCNQ (32) was obtained in 2% yield (*vide infra*).



Before discussing the successful work we performed with compounds (99)-(101) (Section 2.4) we will briefly consider our fruitless attempts to synthesise TCNQ derivatives (74) and (75). The initial route proposed for the synthesis of 2,6-dimethyl-TCNQ (74) and 2,3,5-trimethyl-TCNQ (75) is outlined in Scheme 2.9. Reduction of 2,6-dimethyl-*p*-benzoquinone (104), under an atmosphere of hydrogen (140 atm.), in the presence of activated nickel catalyst<sup>126</sup>, gave the corresponding diol (105) in effectively quantitative yield, as a yellow oil. A previously reported synthesis of diol (105) involving reduction of 2,6-dimethylhydroquinone with a 5% rhodium on alumina catalyst, provided the product as a mixture of isomers which could be separated and isolated as white solids<sup>127</sup>. The crude diol (105), identified by i.r. spectroscopy, was oxidised directly to dione (106) in good yield (78%), using modified Jones' reagent (CrO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O and MnSO<sub>4</sub>). Condensation of the diketone (106) with malononitrile using the procedure of Acker and Hertler<sup>116</sup> (an aqueous solution of diketone (106), malononitrile and  $\beta$ -alanine, 45 min, 100°C), afforded compound (108), rather than the desired 1,4-bis(di-

cyanomethylene)cyclohexane (107). The reaction was repeated for 3h and 24h with exactly the same outcome.



**Scheme 2.9** *Synthetic Steps: (i) Ni, H<sub>2</sub>; (ii) CrO<sub>3</sub>; (iii) and (v) CH<sub>2</sub>(CN)<sub>2</sub>, β-Alanine; (iv) and (vi) Br<sub>2</sub>, Pyridine.*

In a bid to force the second dicyanomethylene group into (108), a melt of compound (108), malononitrile and β-alanine was heated at 150°C for 5h. This resulted in decomposition and no product was obtained.

Compound (108) was also prepared from (106) and malononitrile using

benzene as solvent. Oxidation of (108) to (99) was achieved by an extension of well established methods<sup>116</sup>. In view of these results, it was considered pointless to pursue this route with the trimethyl analogues.

To overcome the apparent steric interaction between the two methyl groups in diketone (106) and malononitrile, thus preventing the formation of the bis(dicyanomethylene) compound (107), we focused our attention on other routes to TCNQ derivatives and, in particular, the use of  $\text{TiCl}_4$ .  $\text{TiCl}_4$  is an attractive reagent to use in TCNQ synthesis, providing one-step syntheses from the corresponding quinone, and more importantly, enabling introduction of the dicyanomethylene group into sterically crowded environments similar to those found in compounds (99) and (100). Tetramethyl-TCNQ (32) and TCAQ (37), both formed *via*  $\text{TiCl}_4$  mediated Knoevenagel condensations, adopt a severely distorted structure to alleviate the steric interactions between the dicyanomethylene groups and methyl substituents<sup>68,80</sup>.

In a search for the elusive conditions required for TCNQ synthesis, we found that concentration, reagent ratio, reaction temperature, reaction time and order of reactant addition had a marked effect upon the percentage yield of the mono(dicyanomethylated) products (99)-(101). We also believe that the yields of the tricyanovinylphenols (96), (102) and (103) are affected by these changes, although we lack concrete evidence to support this, due to our inability to purify these compounds. Column chromatography revealed the presence of many other unidentifiable products in all cases: but we are confident that TCNQ derivatives were not formed in any significant yield.

Both the 2,6-dimethyl (99) and 2,3,5-trimethyl (100) derivatives are prepared by adding  $\text{TiCl}_4$  (2.5 equivalents) to a mixture of quinone (1 equivalent), malononitrile (2.5 equivalents) and pyridine (5

equivalents). Compound (100) is also prepared by addition of the quinone to a mixture of malononitrile, pyridine and  $\text{TiCl}_4$ . This points to the fact that the order of addition does not adversely affect the reaction. However, when  $\text{TiCl}_4$  is added to 2,3,5-trimethylquinone (109), forming the adduct first, which is then treated with a mixture of malononitrile and pyridine, the mono(dicyanomethylated) product (100) was not isolated. Stirring at room temperature for 60h afforded the phenolic product (103) only, whereas stirring for 18h yielded a mixture of starting material and phenol (103). Incidentally, this order of addition is the one described by Cowan in the synthesis of tetramethyl-TCNQ (32)<sup>67</sup>.

Increasing the reaction temperature not only failed to yield the desired TCNQ derivatives, but also had an adverse effect on the yield of the mono(dicyanomethylated) products (99) and (100). Treating 2,6-dimethyl-p-benzoquinone (104) with a solution of malononitrile (2.5 equivalents), pyridine (5 equivalents) and  $\text{TiCl}_4$  (2.5 equivalents) in dichloromethane and then refluxing for 24h, afforded compound (99) in only 6% yield.

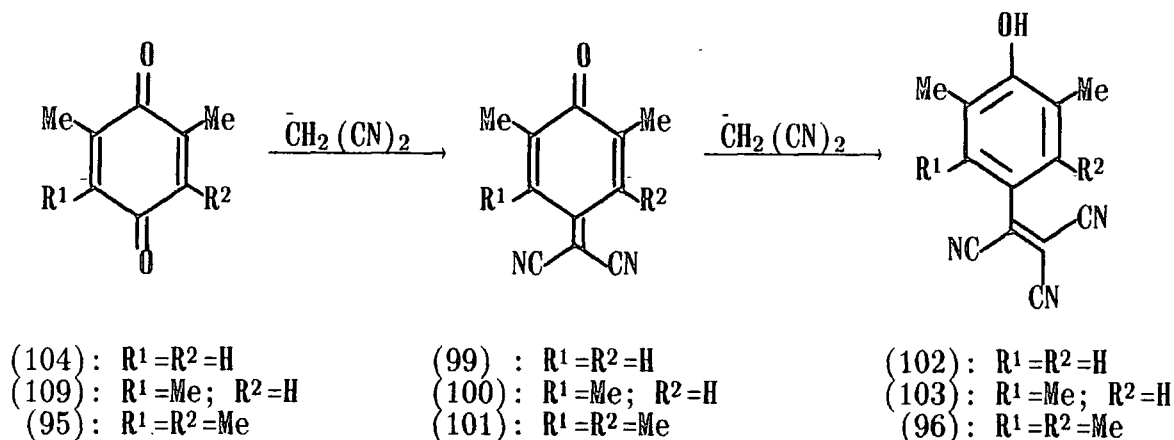
Recently, Panetta *et al.* have reported the synthesis of a range of substituted TCAQ derivatives from anthraquinones, in the presence of  $\text{TiCl}_4$ <sup>128</sup>. They note that in the absence of  $\beta$ -alanine, their experimental procedure leads to a material which was assigned the mono(dicyanomethylated) structure. Introducing  $\beta$ -alanine into our reaction mixture did not affect the formation of the mono(dicyanomethylated) product (99) which was obtained in 23% yield, but again the desired TCNQ derivative (74) was not obtained.

Increasing the concentration of the reaction solution (to ca. 5 mmol scales in 10 ml dichloromethane), significantly reduced the yield of the 2,6-dimethyl derivative (99) and afforded unidentifiable products

with 2,3,5-trimethyl-p-benzoquinone (109).

In a final bid to elucidate the conditions required for TCNQ formation, we repeated the work of Cowan *et al.*<sup>67</sup> All attempts to repeat their experimental procedure down to the finest detail, even after personal communications with the group, failed to yield the tetramethyl-TCNQ (32), giving instead the mono(dicyanomethylated) (101) and phenolic (96) products. Identical products were obtained when duroquinone (95) was added to a mixture of malononitrile, pyridine and  $\text{TiCl}_4$ , although on one occasion we did obtain tetramethyl-TCNQ (32) in 2% yield after chromatography.

To summarise, the desired TCNQ derivatives (74), (75) and (32) have proved inaccessible in our hands. We conclude that reaction of the malononitrile anion with the p-benzoquinones (95), (104) and (109) results in dicyanomethylation at the least hindered site for the 2,6-dimethyl and 2,3,5-trimethyl derivatives. Reaction with a second malononitrile anion results in the formation of the tricyanovinyl phenols (96), (102) and (103) (Scheme 2.10).



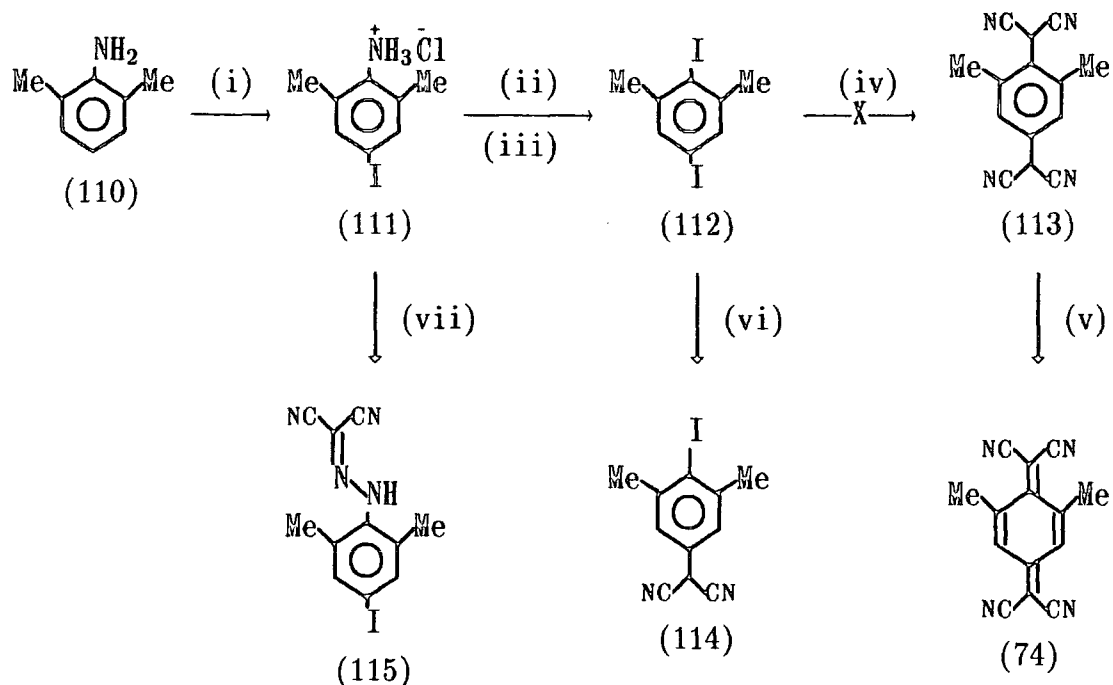
Scheme 2.10

After all the work conducted on these systems we are still unable to answer the question: Why does the second malononitrile anion attack the  $\alpha$ -carbon atom to the nitrile groups in preference to the carbonyl functionality? Steric hindrance from the methyl substituents can be

ruled out, as we have shown ourselves that a dicyanomethylene group can be introduced into such an environment [*eg.* formation of compound (101)]. Arguments that attack on the dicyanomethylene group is sterically or energetically favoured compared to attack on the sterically hindered carbonyl group (hence favouring sole formation of the phenolic product), seem unlikely in view of the synthesis of tetramethyl-TCNQ (32)<sup>67</sup>. It would appear that after mono(dicyanomethylation) there are two possible reactions: "Cowan's conditions" allow TCNQ formation as well as the phenolic by-product, whereas "our conditions", without doubt, favour sole formation of phenolic product. A difference in the purity of the titanium tetrachloride available to us is a possible explanation, as the reactions clearly depend upon titanium activation of the carbonyl group. We have used neat, commercial reagent, before and after distillation, and the commercial solution of  $TiCl_4$  in dichloromethane, all with no change in results.

Another approach towards the synthesis of sterically demanding TCNQ derivatives has been *via* the formation of phenylenedimalononitriles from the corresponding di-iodoarene: tetramethyl-TCNQ (32) once again being the leading example<sup>68</sup>. Our proposed route to 2,6-dimethyl-TCNQ (74) using this methodology is outlined in Scheme 2.11. Iodination of 2,6-dimethylaniline (110), using iodine monochloride was achieved using the synthesis described by Holland *et al.*<sup>129</sup> The product was isolated as the hydrochloride salt (111), all attempts to liberate the free base having failed. This was not inconvenient as (111) was directly converted to the diazonium salt, which in the presence of potassium iodide, afforded the diiodide (112). Attempted substitution of both iodines with malononitrile anion in the presence of copper (I) iodide, using the experimental procedure of Suzuki and co-workers<sup>130</sup>, gave the monosubstituted product (114), with complete absence of the desired

phenylenedimalononitrile (113).

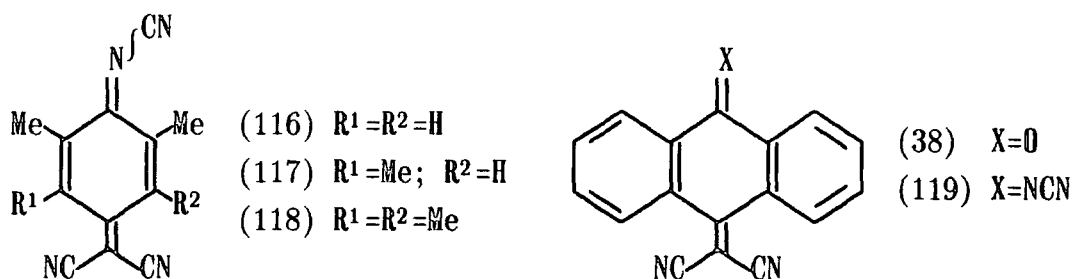


**Scheme 2.11** *Synthetic Steps: (i) ICl; (ii) NaNO<sub>2</sub>; (iii) KI; (iv) and (vi) CuI, CH<sub>2</sub>(CN)<sub>2</sub>, NaOMe, HMPT; (v) Br<sub>2</sub>, Pyridine; (vii) NaNO<sub>2</sub> followed by CH<sub>2</sub>(CN)<sub>2</sub>.*

In light of the fact that Suzuki *et al.*<sup>130</sup> point out categorically that steric congestion around the reaction site does not provide a serious problem to the substitution of the iodine atom, and that Staab *et al.*<sup>68</sup> used the same experimental procedure to synthesise tetramethyl-TCNQ (32), it is puzzling that we can only isolate the monosubstituted product (114). All attempts to introduce the second malononitrile group under an atmosphere of nitrogen and/or in the dark, failed to yield (113). Further attempts to introduce the malononitrile group, between the methyl substituents, involved direct reaction between the diazonium salt of (111) and the malononitrile anion. Unfortunately, rather than the desired substitution product, compound (115) was isolated in *ca.* 11% yield; structural assignment for (115) followed simply from micro-analytical and spectroscopic data. The reaction sequence (Scheme 2.11) was, therefore, abandoned.

2.4 4-(DICYANOMETHYLENE)-p-BENZOQUINONES AND N-7,7-TRICYANOQUINO-  
METHANEIMINES (TCNQI)

Although our studies into  $TiCl_4$  mediated Knoevenagel condensations between quinones (95), (104), (109) and malononitrile failed to yield the desired TCNQ derivatives (74), (75) and (32), we had developed a very convenient synthesis to three 4-dicyanomethylene-p-benzoquinones (99)-(101). In view of the recent advances made by Hunig *et al.* with N,N'-dicyano-p-quinonediimines (DCNQI's) and in particular the copper salt of 2,5-dimethyl-DCNQI (1:2 stoichiometry) which does not undergo a Peierls distortion, and exhibits a conductivity<sup>111</sup>  $\sigma_{3.5K} = 5 \times 10^5$  S  $cm^{-1}$ , we turned our attention to introducing the N-cyanoimine functionality into compounds (99)-(101). This would give rise to new electron acceptors, which can be considered as hybrids of TCNQ and DCNQI systems, with the potential to form highly conducting complexes. Compounds (99)-(101) being hybrids of TCNQ and p-benzoquinone systems, also possess the potential to form highly conducting CT complexes. Torrance *et al.* have already shown that the tetrahalo-p-benzoquinones are capable of forming conducting CT complexes by virtue of their quinonoid structure and electron affinity<sup>103,104</sup>. TCNQ speaks for itself.



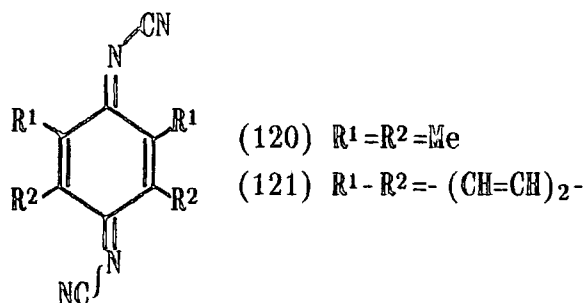
Acceptors (116)-(119) were prepared cleanly in one step from the corresponding mono(dicyanomethylated)quinones (99)-(101) and (38), by reaction with bis(trimethylsilyl)carbodiimide in the presence of  $TiCl_4$ ,

the reaction conditions being essentially those described by Aumüller and Hunig on the route to DCNQI derivatives<sup>109</sup>. Compounds (116)-(119) were isolated as air stable, orange, crystalline solids. 10-(Dicyanomethylene)anthrone (38) was prepared from anthraquinone, using similar conditions described for the synthesis of (100) and (101). The product was obtained in low yield (27%) after a difficult separation from the starting material. An alternative synthesis of (38) from anthrone which provides the product in high yield (80%) has been described by Takimoto and Krbeček<sup>131</sup>.

COMPOUND	$E_{\frac{1}{2}}^1$	$E_{\frac{1}{2}}^2$	$\Delta E$ (V)	$\lambda_{\max}$ (nm) <sup>f</sup>
(116) <sup>a</sup>	+0.11	-0.43	0.54	387.0
(117) <sup>a</sup>	+0.07	-0.41	0.48	387.5
(118) <sup>a</sup>	-0.03	-0.23	0.20	358.5
(119) <sup>b</sup>	-0.43			342.0 278.0
TMTCNQ <sup>c</sup>	-0.40(2e)			375 <sup>g</sup>
TCAQ <sup>d</sup>	-0.29(2e)			347 305 283
TMDCNQI <sup>e</sup>	+0.05	-0.39	0.44	346
DCAQI <sup>e</sup>	-0.11	-0.46	0.35	322 251

Table 2.2 *Cyclic Voltammetric and U.V. Spectroscopic Data for the Tricyanoquinomethaneimines (116)-(119); (a) This work vs Ag/AgCl, 0.02M [Bu<sub>4</sub>N][ClO<sub>4</sub>], MeCN, Pt Electrode, scan rate = 100 mV/sec; (b) As (a) except CH<sub>2</sub>Cl<sub>2</sub> solvent, scan rate = 50 mV/sec; (c) Ref.67, vs Ag/AgNO<sub>3</sub> in MeCN; (d) Ref.80, vs Ag/AgNO<sub>3</sub> in MeCN; (e) Ref.132, vs Ag/AgCl in CH<sub>2</sub>Cl<sub>2</sub>; (f) Solvent: CH<sub>2</sub>Cl<sub>2</sub> for (116)-(119) and TCAQ (Ref.79,80); MeCN for TMDCNQI and DCAQI (Ref.109); not given for TMTCNQ (Ref.67); (g) cf.  $\lambda(\max)$  TCNQ = 393 nm, 2,5-dimethyl-TCNQ = 396 nm (Ref.67).*

Table 2.2 contains cyclic voltammetric and U.V. spectroscopic data for compounds (116)-(119) along with previously reported data for TMTCNQ (32), TCAQ (37), TMDCNQI (120) and DCAQI (121), for comparison.



For the alkyl-TCNQI derivatives (116)-(118) the first reduction wave is reversible (anodic-cathodic peak separation of *ca.* 60 mV established a one-electron process), while the second reduction is fully reversible only for the tetramethyl derivative (118) (Figure 2.1). The difference,  $\Delta E$ , between the first and second reduction potentials for the tetramethyl derivative (118) (0.2 V) is significantly reduced relative to the di- and tri-methyl derivatives (0.54 V and 0.48 V respectively). This behaviour for (118) is intermediate between that for TMTCNQ (32) ( $\Delta E = 0.00$  V)<sup>67</sup> and TMDCNQI (120) ( $\Delta E = 0.44$  V)<sup>132</sup>. This comparison lends support to Cowan's assertion that the coalescence of the two reduction waves of TMTCNQ (32) occurs for steric, rather than electronic reasons, *ie.* to relieve the severe crowding in neutral (32) which has a severely distorted ring skeleton<sup>67,68</sup>. The NCN group is both smaller and more flexible than the rigid  $C(CN)_2$  group, as noted by Hunig *et al.*<sup>109</sup>, and hence steric hindrance decreases progressively along the series TMTCNQ (32), TMTCNQI (118) and TMDCNQI (120), with an associated increase in  $\Delta E$ .

Within the alkyl-TCNQI series (116)-(118) there is a predictable lowering of the electron affinity with increasing methyl substitution. The anthraquinone derivative (119) is a considerably weaker acceptor than the alkyl derivatives (116)-(118). This trend is paralleled by the N,N'-dicyanoimine series (DCNQI derivatives, Table 2.3) prepared by Hunig *et al.*<sup>132</sup>, although the trimethyl derivative slightly disrupts the

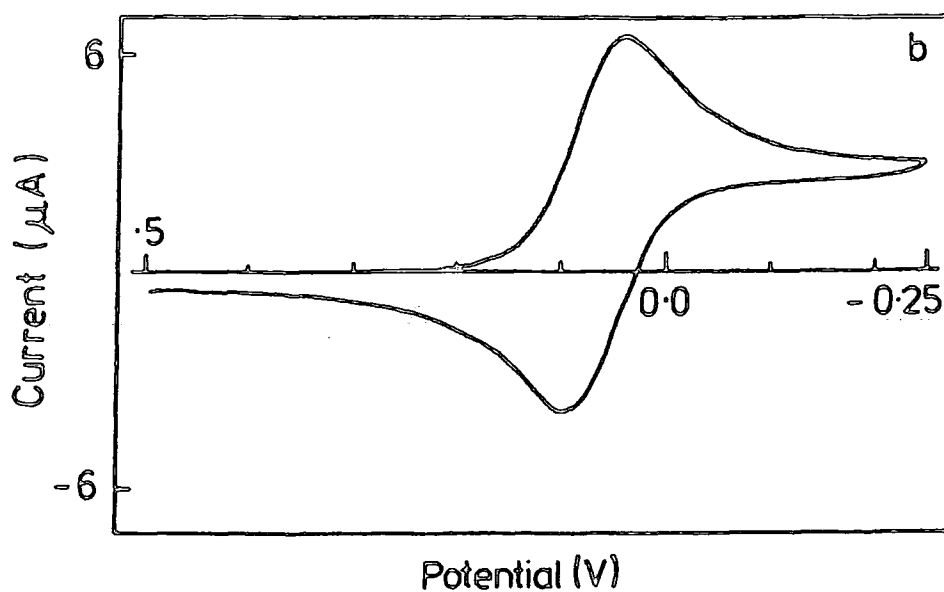
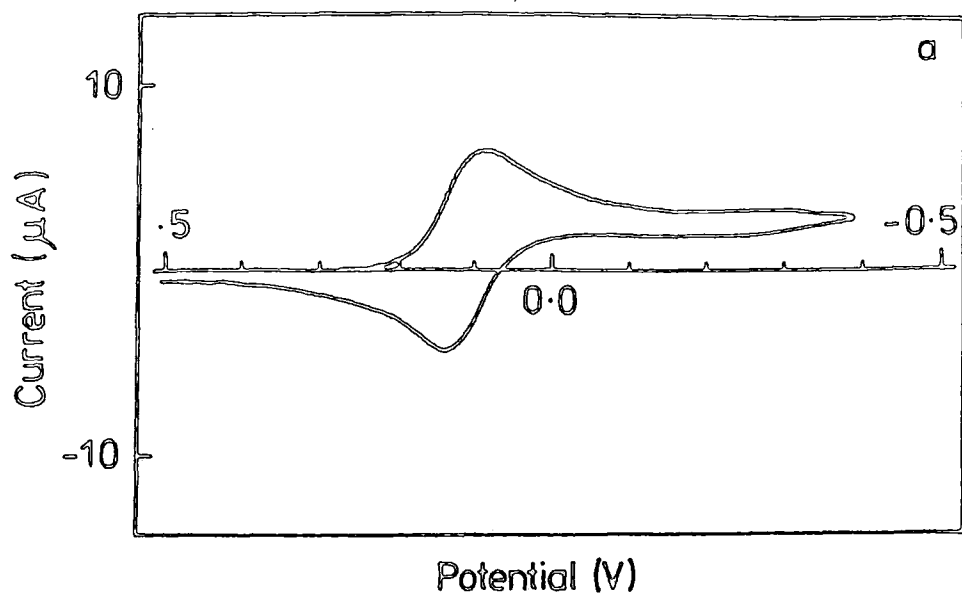


Figure 2.1 *Cyclic Voltammograms of the Tricyanoquinomethaneimines; (a) Compound (116); (b) Compound (117).*

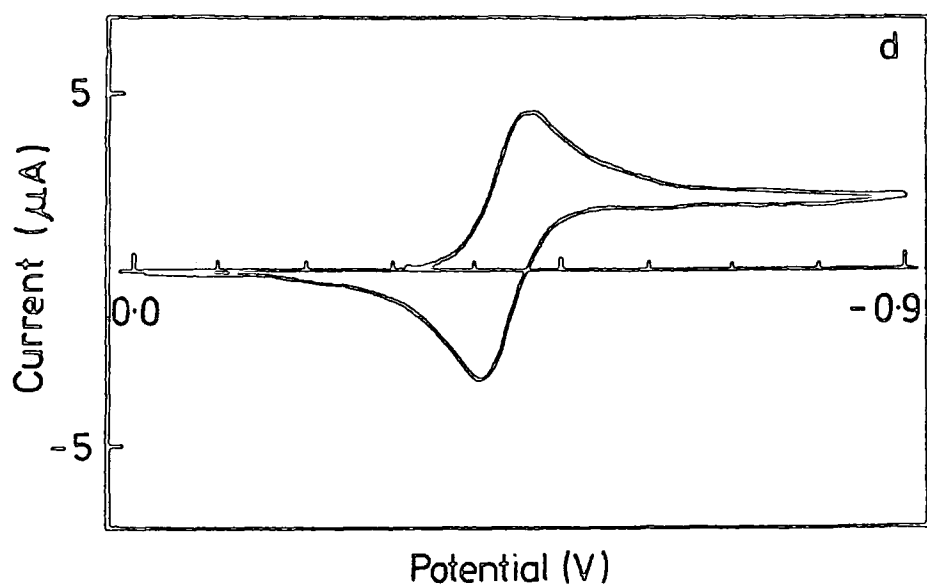
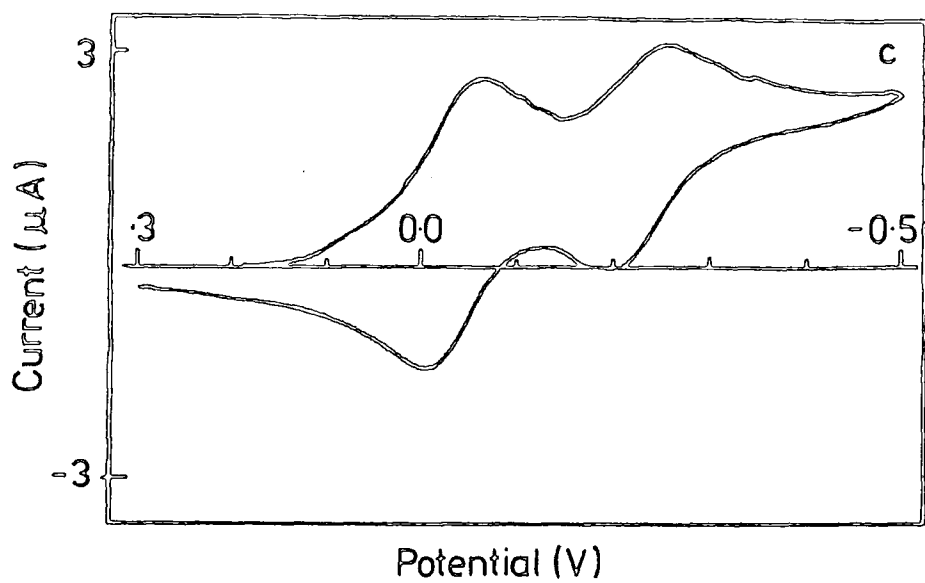
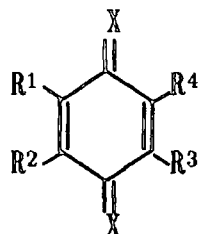


Figure 2.1 *Cyclic Voltammograms of the Tricyanoquinomethaneimines;*  
 (cont'd) (c) Compound (118); (d) Compound (119).

general trend. As noted earlier, methyl substitution [*eg.* MTCNQ (15) and 2,5-DMTCNQ (16)] upon the TCNQ skeleton reduces the electron affinity by a small, but finite amount.



SUBSTITUENTS				[X = N-CN] <sup>a</sup>		[X = C(CN) <sub>2</sub> ]	
R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	E <sub>1/2</sub> <sup>1</sup>	E <sub>1/2</sub> <sup>2</sup>	E <sub>1/2</sub> <sup>1</sup>	E <sub>1/2</sub> <sup>2</sup>
H	H	H	H	+0.39	-0.25	+0.39	-0.28 <sup>a</sup>
						+0.13	-0.29 <sup>b</sup>
						+0.17	-0.37 <sup>c</sup>
Me	H	H	H	+0.31	-0.31	+0.17	-0.34 <sup>d</sup>
Me	H	Me	H	+0.21	-0.38	+0.10	-0.38 <sup>c</sup>
Me	H	H	Me	+0.21	-0.37	Compound Unknown	
Me	Me	Me	H	+0.25	-0.38	Compound Unknown	
Me	Me	Me	Me	+0.05	-0.39	-0.40 (2e) <sup>a,e</sup>	
DCAQI (121)/				-0.11	-0.46	-0.20 (2e) <sup>a</sup>	
TCAQ (37)						-0.23 (2e) <sup>f</sup>	
						-0.28 (2e) <sup>g</sup>	

**Table 2.3** *Cyclic Voltammetric Data (V) for a Series of Methylated 1,4-Benzoquinoid Compounds; (a) Ref.132, vs Ag/AgCl in CH<sub>2</sub>Cl<sub>2</sub>; (b) Ref.116, vs SCE in MeCN; (c) Ref.54, vs SCE in MeCN; (d) Ref.114, vs SCE in MeCN; (e) Ref.67, vs Ag/AgNO<sub>3</sub> in MeCN; (f) Ref.132, vs Ag/AgCl in MeCN; (g) Ref.79, vs Ag/AgCl in MeCN.*

However, as shown in Table 2.3, the effect of tetramethyl substitution is sufficient to reduce the electron affinity of TMTCNQ (32) below that of TCAQ (37), a trend which is not observed in the TCNQI and DCNQI series. Cyclic voltammetric behaviour of the anthraquinone derivative (119) contrasts markedly with both the TCNQ analogue, TCAQ (37) and the DCNQI analogue, DCAQI (121): compound (119) undergoes a

reversible, one electron reduction and the dianion of (119) is not detected (Figure 2.1d), whereas for both TCAQ (37)<sup>79</sup> and DCAQI (121)<sup>132</sup>, dianion formation is clearly observed. As yet, we cannot provide an explanation for this anomalous behaviour of compound (119).

The U.V. spectra of compounds (118) and (119) are strikingly blue shifted and weaker compared to compounds (116) and (117). This is clearly indicative of non-planar structures for (118) and (119), but with less deviation from planarity than the respective TCNQ analogues (32)<sup>67</sup> and (37)<sup>79,80</sup> (Table 2.2).

The suitability of the tricyanoquinomethaneimines (116), (117) and (119) for the formation of crystalline charge-transfer salts has been confirmed by the formation of the corresponding copper salts. We chose to prepare and characterise the copper salts in the hope of emulating the successful work of Hunig *et al.* related to the copper salt of 2,5-DMDCNQI<sup>111</sup>. Another advantage of copper salt formation is the relatively simple preparation, involving immersion of a shiny copper wire into an acetonitrile solution of the appropriate acceptor under an atmosphere of nitrogen. This led to the copper salts of (116) and (117) as black powders [(116a) and (117a) respectively]. Microanalysis revealed an unusual stoichiometry of copper:acceptor of 4:3. The tetramethyl derivative (118) did not yield a copper salt under these conditions. This is attributed to the non-planar structure, resulting from steric interaction of the dicyanomethylene group and the two adjacent methyl substituents. However, the fact that TMTCNQ (32), which is distorted to a greater extent, forms a 2:1 salt with copper, indicates that other factors have to be taken into consideration<sup>67</sup>. In view of the fact that (118) did not form a copper salt, we were surprised to find that the anthraquinone derivative (119) did form a copper salt (119a). Unfortunately, microanalysis does not allow a

confident determination of the stoichiometry. The observation of copper salt formation with (119) implies that the anthraquinone derivative (119) is less distorted than the tetramethyl analogue (118). [Obviously, X-ray analysis of both neutral species would shed some light upon this problem].

The room temperature, compaction conductivities of (116a) and (117a) are both in the semiconducting regime with values of *ca.*  $6 \times 10^{-5}$  S  $\text{cm}^{-1}$ . Magnetic susceptibility data on both salts show each to be diamagnetic, which indicates a pairing of the acceptor radical anions, which is consistent with the relatively low  $\sigma_{\text{rt}}$  values. Comparing our copper salts with  $\text{Cu}(2,5\text{-DMDCNQI})_2$ , we felt that a higher conductivity could be attained with a salt of the "correct" stoichiometry (1:2). Preliminary experiments, preparing the salts in the presence of  $\text{CuBr}_2$ , [*ie.* the conditions used for  $\text{Cu}(2,5\text{-DMDCNQI})_2$ ], provided a copper salt of (116) with 1:1 stoichiometry. Although the conductivity of a 1:1 copper salt is expected to be semiconducting at best, these experiments provide encouragement that the stoichiometry of the salts can be controlled with careful modification of the reaction conditions.

We now wish to briefly discuss complex formation of the monocyano-methylated quinones (99)-(101) which we had available. Table 2.4 contains C.V. data for these three compounds, and TCNQ for comparison, together with the difference ( $\Delta E = E_{\frac{1}{2}}^{\text{D}} - E_{\frac{1}{2}}^{\text{A}}$ ) between the first oxidation potential of TTF (0.34 V vs Ag/AgCl) and the first reduction potential of the acceptor under the same conditions. The conductivities ( $\sigma_{\text{rt}}$ ) of the corresponding TTF complexes are also listed. Compound (99) is the only derivative to undergo a reversible one-electron reduction (Figure 2.2a). However, further reduction *viz.* radical anion to dianion, is irreversible. Both the trimethyl and tetramethyl derivatives (100) and (101) respectively, exhibit irreversible redox waves upon reduction to

the radical anion (Figures 2.2b and c). Interestingly, the cyclic voltammogram of (101) shows reduction to the radical anion upon the cathodic sweep, followed by the generation of two peaks on the reverse (anodic) sweep. The first of these anodic peaks (-0.21 V vs Ag/AgCl) is tentatively assigned as being coupled to the reduction peak (-0.39 V vs Ag/AgCl). The second anodic peak (+0.14 V) is attributed to a new species, formed *via* the radical anion of (101), which itself is electroactive. The irreversibility of the first reduction in compounds (100) and (101) reflects instability in the radical anion, a situation which does not hold well for the formation of a conducting charge transfer complex.

COMPOUND	$E_{\frac{1}{2}}^1$ (V) <sup>a</sup>	$E_{\frac{1}{2}}^2$ (V) <sup>a</sup>	$\Delta E$ (V)	$\sigma_{rt}$ (S cm <sup>-1</sup> )
(99)	-0.19	----	0.53	$2.3 \times 10^{-3}$ <sup>b</sup>
(100)	-0.22 <sup>d</sup>	----	0.56	$< 10^{-10}$ <sup>c</sup>
(101)	-0.30 <sup>d</sup>	----	0.64	No Complex
TCNQ (1)	+0.22	-0.34	0.12	500 <sup>b</sup>

Table 2.4 *Cyclic Voltammetric Data for (99)-(101); (a) vs Ag/AgCl, Pt electrode, MeCN, 0.02M [Bu<sub>4</sub>N][ClO<sub>4</sub>]; scan rate = 100 mV/sec; (b) single crystal conductivity; (c) compaction conductivity; (d) irreversible reduction.*

Comparison of the reduction potentials of compounds (99)-(101) with TCNQ, shows the former three to be far weaker acceptors. Using the guidelines set down by Torrance *et al.*, the large positive values of  $\Delta E$  indicate that acceptors (99)-(101) will form neutral, insulating complexes with TTF<sup>103</sup>. Both the 2,6-dimethyl (99) and 2,3,5-trimethyl (100) derivatives form green 1:1 complexes with TTF. The failure of the tetramethyl derivative (101) to complex with TTF is not wholly unexpected and is attributed to the loss of planarity within the acceptor, analogous to TMTCNQ<sup>68</sup>.

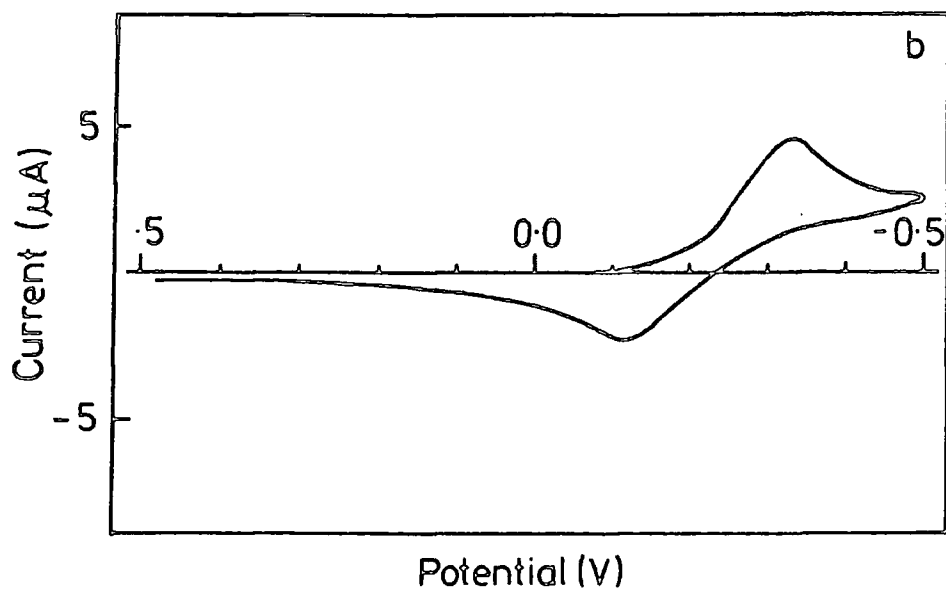
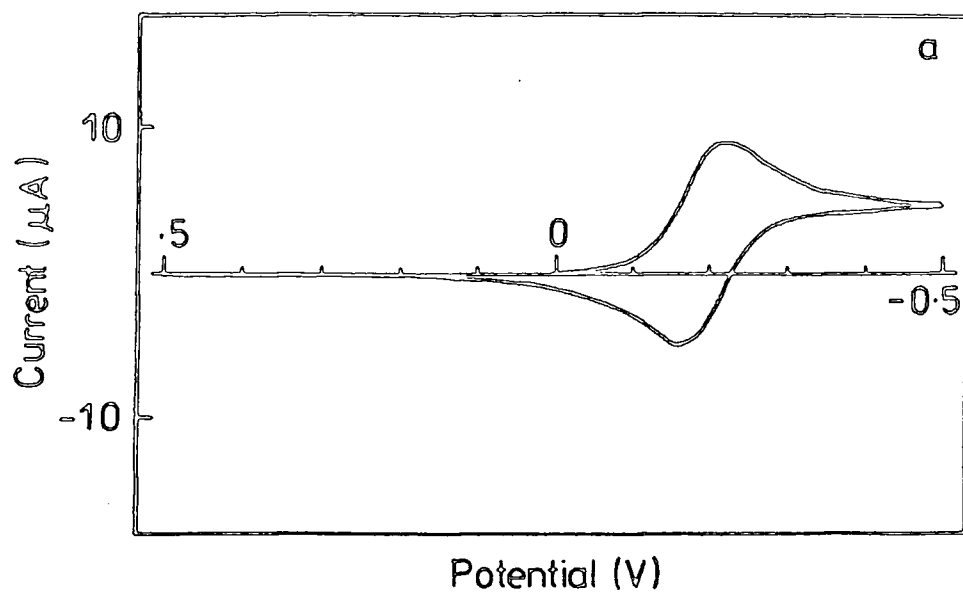


Figure 2.2 Cyclic Voltammograms of the Mono(dicyanomethylated)-*p*-benzoquinones; (a) Compound (99); (b) Compound (100).

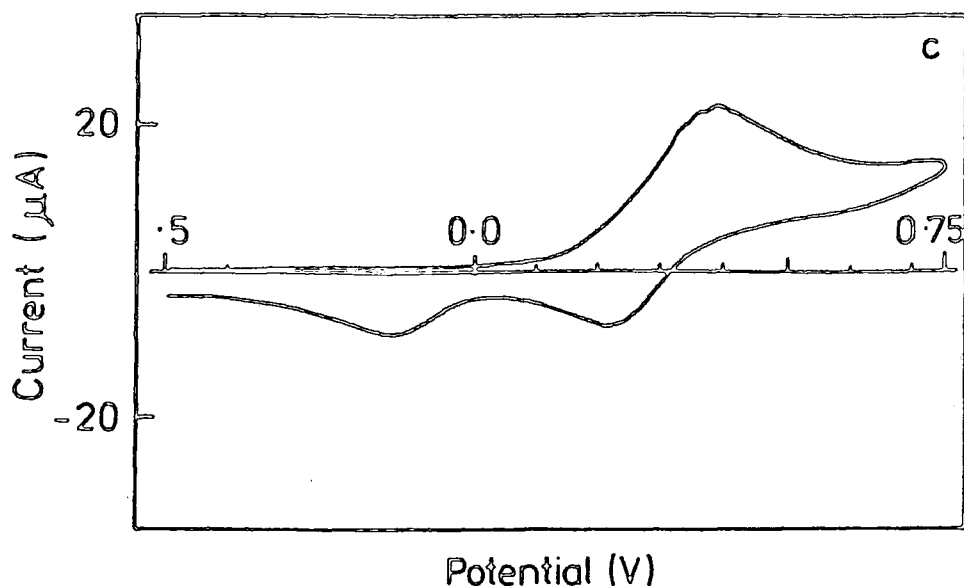


Figure 2.2 *Cyclic Voltammetry of the Mono(dicyanomethylated)-*  
(cont'd) *p*-benzoquinones; (c) *Compound (101)*.

The two TTF complexes, with (99) and (100) exhibit vastly different  $\sigma_{rt}$  values (Table 2.4). A  $\sigma_{rt}$  value in the semiconducting regime ( $2.3 \times 10^{-3} \text{ S cm}^{-1}$ ) for TTF-(99), clearly points to a segregated stack motif with partial charge transfer, thus contradicting the earlier predictions of a neutral, insulating complex. Charge transfer between the donor (TTF) and acceptor (99) is confirmed from E.S.R. measurements, which show a strong signal with a  $g$ -value of 2.0003 which is characteristic of an unpaired electron in an organic molecule. By contrast, the very low conductivity ( $\leq 10^{-10} \text{ S cm}^{-1}$ ) of the TTF complex of (100) infers zero charge transfer. This point is confirmed by an extremely weak E.S.R. signal. Combined with the small  $\sigma_{rt}$  value, the extremely weak E.S.R. signal is most likely to arise from impurities within the neutral complex. This possibility is supported by the C.V. data, which point towards (100) being a very weak acceptor whose radical anion is inherently unstable. Further support for a neutral complex requires X-ray analysis, with specific reference to the bond lengths in TTF which

vary significantly in the neutral and cationic species<sup>133</sup>.

## CONCLUSIONS

Our attempts to improve upon the reported synthesis of 2,3-dimethyl-TCNQ (73) failed<sup>115</sup>. We have also failed to synthesise the sterically demanding and unknown 2,6-dimethyl-TCNQ (74) and 2,3,5-trimethyl-TCNQ (75). Instead, we have established a convenient one-step synthesis of the mono(dicyanomethylated)-p-benzoquinones (99)-(101). These molecules, which can be considered as hybrids of p-benzoquinone and TCNQ systems, are intermediates to other acceptors (116)-(119) as well as being acceptors in their own right. This latter point is confirmed by the high conductivity exhibited by the TTF complex of (99). Low conductivity in the TTF complex of (100) is mainly attributed to zero charge transfer, which indicates that future work with molecules containing the same skeletal framework, should be directed towards acceptors with a larger electron affinity, *ie.* a reduced number of alkyl substituents and/or the presence of electron withdrawing substituents such as the halogens.

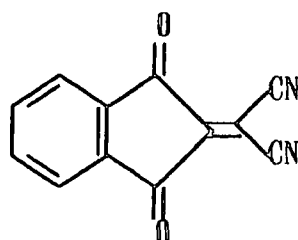
Conversion of the mono(dicyanomethylated)-p-benzoquinones (99)-(101) into the N,7,7-tricyanoquinomethaneimines (TCNQI derivatives) provided another new class of acceptors. The suitability of these molecules as electron acceptors can be seen from the formation of copper salts with 2,6-dimethyl-TCNQI (116), 2,3,5-trimethyl-TCNQI (117) and the anthraquinone derivative (119). Cyclic voltammetric data indicates that (116) has the potential to form a mixed valence complex with TTF. Consequently, future work in this area should be directed towards TTF complexes of (116) and other derivatives with increased electron affinities.

CHAPTER THREE

REARRANGEMENT OF 2-DICYANOMETHYLENE-1,3-INDANDIONE (DCID)  
TO 2,3-DICYANO-1,4-NAPHTHOQUINONE (DCNQ), AND SOLID STATE  
PROPERTIES OF RADICAL ION SALTS OF DCNQ

### 3.1 INTRODUCTION

Since the discovery of TTF-TCNQ<sup>10,11</sup>, several hundred molecular conductors have been characterised. Although significant advances have been made, it is notable that the structural variations of the component molecules are very limited; the vast majority of these materials comprise derivatives of the parent TCNQ (1) and TTF (2) skeletons (Chapter 1). In view of this, and as part of our program towards the synthesis and characterisation of new electron acceptors, we chose to study acceptors with different skeletal structures, in the search for novel organic conductors, focusing our attention upon 2-dicyanomethylene-1,3-indandione, DCID (122).



(122)

For the formation of highly conducting charge transfer (CT) complexes, two essential prerequisites must be satisfied<sup>13a</sup>. These are: i) the formation of highly-ordered, segregated stacks of donor and acceptor molecules along which there is extensive  $\pi$ -electron delocalisation - the characteristics of molecules which generally facilitate this are planarity and a high degree of symmetry; and (ii) the energy band formed from electrons responsible for conduction should be partially filled; this situation arises as a result of partial charge transfer from donor to acceptor (eg. TTF-TCNQ,  $\rho = 0.59$  electrons), or by crystallisation of a salt in a stoichiometry other than 1:1 [eg. Quinolinium(TCNQ)<sub>2</sub>]. A completely full or vacant energy (conduction)

band gives rise to an insulator.

Acceptors other than simple derivatives of TCNQ (1) that are of current interest include fused ring TCNQ derivatives [*eg.* TCAQ (37) and TBAQ (40)], Hunig's quinoneimines, cyano-substituted heteroaromatics and nitrobenzenes (Chapter 5). Recent results published on these acceptors, reviewed in Chapter 1, place the present chapter into context.

### 3.2 WHY STUDY DCID ?

We were attracted to DCID (122) as an acceptor for the formation of CT salts for the following reasons:

- (1) The molecule should be planar or very near planar, thus facilitating well ordered crystal structures of salts.
- (2) Radical anion species derived from DCID should be delocalised and stable.
- (3) Previously reported syntheses are one-step, high yielding conversions from either ninhydrin or 1,2,3-indantrione<sup>123</sup>.
- (4) Charge transfer complex formation with a range of aromatic  $\pi$ -donors in solution ( $\text{CH}_2\text{Cl}_2$ ), and the subsequent determination of the electron affinity (EA) (*ca.* 1.36 eV compared to chloranil 1.37 eV) *viz.* CT bands (450 - 750 nm) in the UV-visible spectrum and polarographic half-wave reduction potentials, provide good precedents that DCID will form conducting, solid-state CT complexes<sup>134,135</sup>.
- (5) The reported lithium salt of DCID (122)<sup>135</sup>, by analogy with TCNQ (1)<sup>6</sup>, and many other acceptors, should be a versatile precursor to a wide range of organic and metal-cation salts of DCID, formed by metathesis reaction.

Despite its obvious potential to provide a conducting CT complex with a

range of TTF-type donors, such complexes have yet to be reported.

### 3.3 PREPARATION OF DCID (122) AND SALTS (123a)-(123c)

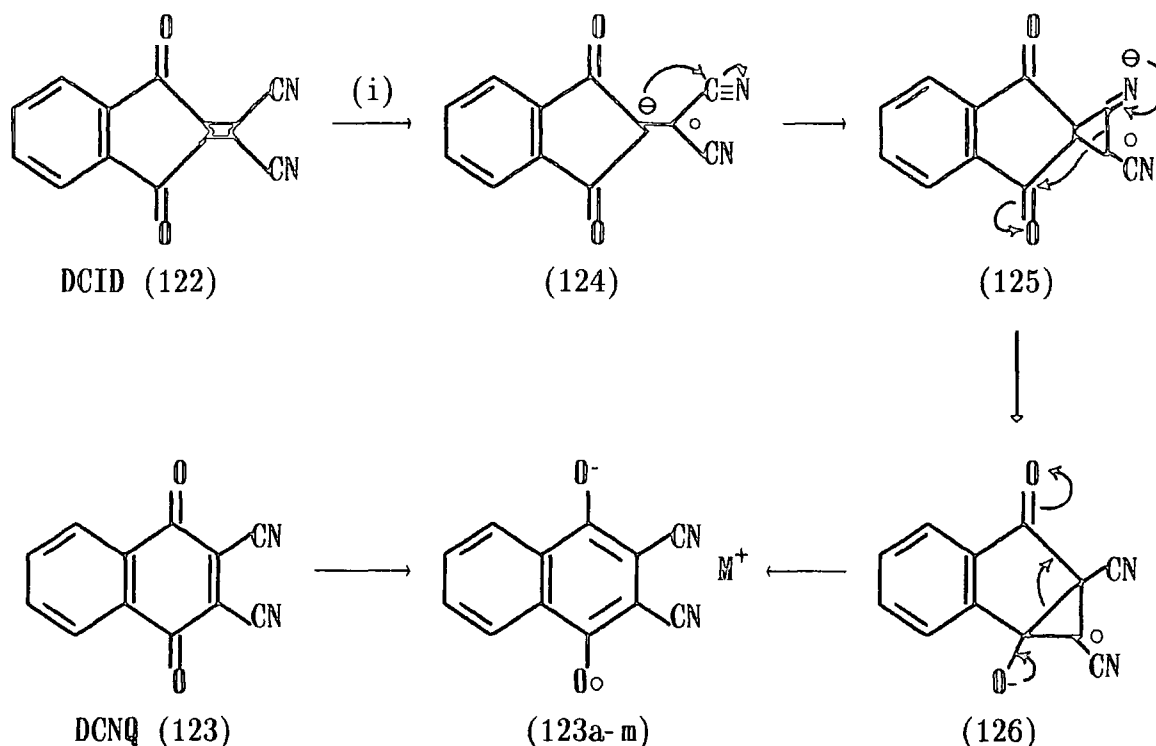
DCID (122) was prepared in good yield as yellow, air-stable crystals by reaction of ninhydrin and malononitrile in water. This method was found to be as convenient as the previously described synthesis by Junek and Sterk, from 1,3-indandione and tetracyanoethylene<sup>136</sup>.

Initial experiments established that reduction of DCID (122) by reaction with lithium iodide or methyltriphenylphosphonium iodide led to the isolation of crystalline salts in good yields. Elemental analysis established a cation:DCID ratio of 1:1. The dark green lithium salt (123a) is an insulator ( $\sigma_{rt}$  compaction =  $10^{-9}$  S cm<sup>-1</sup>), which is consistent with that found for fully ionic 1:1 cation-TCNQ salts which are Mott insulators according to the theories developed by Soos<sup>137</sup> and later stressed by Torrance<sup>13b</sup>. However, doubts that the anionic component of these salts was DCID (122) were quickly aroused by the fact that the nitrile absorption in the infrared spectrum moved to a slightly larger wavenumber on formation of the lithium salt ( $\nu_{max} = 2230$  cm<sup>-1</sup> for neutral DCID, *cf.* Li<sup>+</sup> salt = 2235 cm<sup>-1</sup>). This behaviour contrasts with the expected bathochromic shift observed with TCNQ on formation of the radical anion (*cf.* neutral TCNQ absorbs at  $\nu_{max} = 2215$  cm<sup>-1</sup> while Li<sup>+</sup> TCNQ<sup>-</sup> absorbs at  $\nu_{max} = 2180$  cm<sup>-1</sup>)<sup>138</sup>. Single crystal X-ray analysis of the methyltriphenylphosphonium salt (123b) (*vide infra*) confirmed that DCID (122) had isomerised to 2,3-dicyano-1,4-naphthoquinone (DCNQ) (123) and therefore, the salts (123a) and (123b) we had isolated were naphthoquinol (DCNQ) and not DCID salts. Identical i.r. spectra of samples prepared from DCID and the authentic quinone, DCNQ (123)<sup>139</sup>

confirmed the structure of the lithium salt. Furthermore, both lithium and phosphonium salts (123a) and (123b), prepared from DCID (122), when treated with concentrated hydrochloric acid, as described previously for authentic salt (123a)<sup>139</sup>, gave neutral 2,3-dicyanonaphthoquinone (123) in 65% and 40% yields respectively. Under identical conditions, DCID (122) was recovered unchanged in quantitative yield with no isomerisation to compound (123). Single crystal X-ray analysis of DCID (122) confirms that the structure is as stated (*vide infra*) and hence an isomerisation occurs upon salt formation. Chatterjee's earlier claim to have prepared  $\text{Li}^+ \text{DCID}^-$  is therefore considered erroneous.

The rearrangement of DCID (122) to yield salts (123a-m) outlined in Scheme 3.1 is a fascinating isomerisation which we had not anticipated would occur. The notable features are the ring expansion of the indandione skeleton into the naphthoquinone skeleton with the formal 1,2-migration of a cyanide group. At this stage it was necessary to establish whether the rearrangement is driven by nucleophilic attack of iodide ion on DCID (122) and/or single electron transfer from iodide to (122). Reaction of DCID (122) with sodium suspended in THF yielded the rearranged sodium salt (123c) in 22% yield, which was identical (I.R. comparison) with the sodium salt obtained (50% yield) by metathesis reaction of the lithium salt (123a) and sodium iodide. This provided conclusive evidence that nucleophilic attack on DCID (122) is not required for the rearrangement. In view of this, a possible mechanism for the isomerisation is suggested (Scheme 3.1). It is initiated by a single one-electron transfer to the dicyanomethylene group of DCID (122). This leads to the symmetrical radical anion (124) which is stabilised by the two adjacent ketone groups. Nucleophilic attack onto either of the nitrile groups gives rise to a spirocyclopropane intermediate (125). Rearrangement of (125), as shown, leads to formal

1,2-migration of the nitrile group and the formation of a second cyclopropane compound (126). Compound (126) can ring open to form the delocalised naphthoquinol radical anion, and hence salts (123a-m), which we isolate.



**Scheme 3.1** *Proposed Mechanism for the Rearrangement of DCID (122) to DCNQ (123); (i)  $M^+I^-$ ,  $CH_3CN$ , reflux or Na, THF, 20°C.*

The electron acceptor properties of DCID (122) have been studied by cyclic voltammetry (CV). The first one-electron reduction, *viz.* neutral to radical anion, occurs at 0.008 V; this is followed by a second one-electron reduction to the dianion at -0.98 V (vs Ag/AgCl, Pt electrode) (Figure 3.1). Under these conditions the first reduction wave is fully reversible (Figure 3.1a), with no detectable change in the voltammogram after 15 minutes of continuous cycling between +0.50 V and -0.60 V. The second reduction, *viz.* radical anion to dianion, is irreversible, and this is clearly shown in Figure 3.1b. It is interesting to note that we do not detect the presence of any anionic species derived from DCNQ

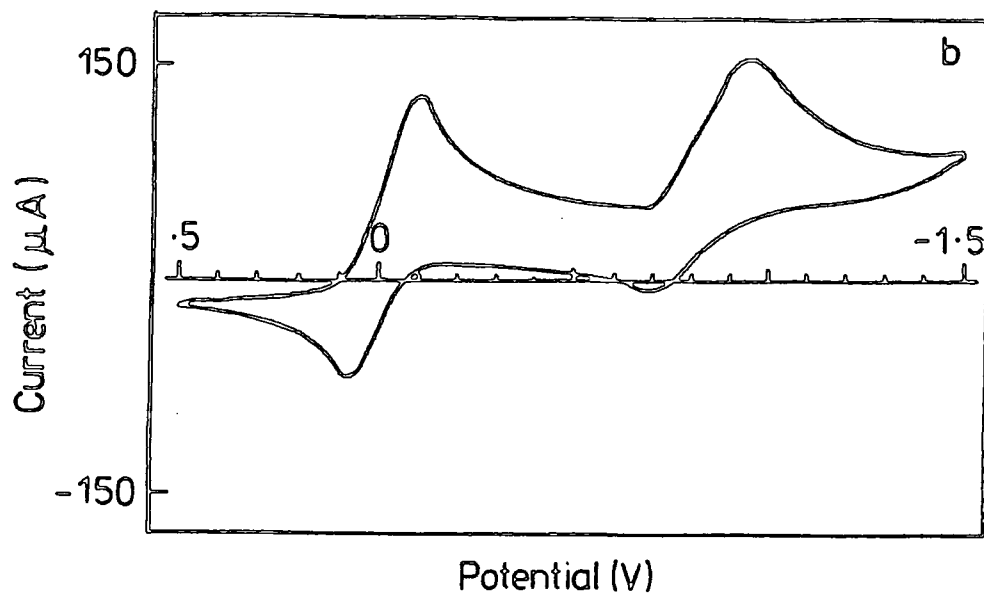
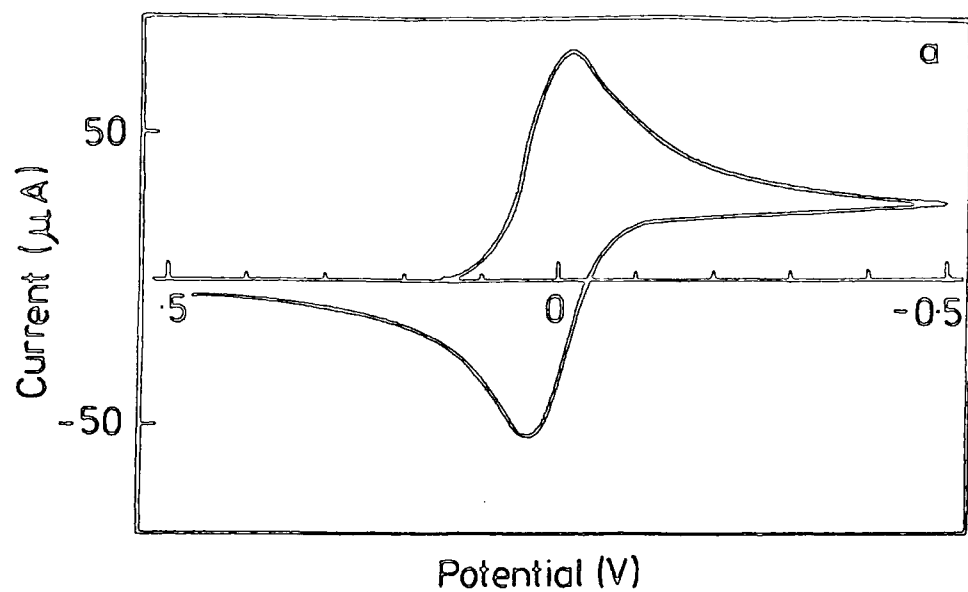


Figure 3.1 Cyclic Voltammograms of the DCID (122); (a) One-Electron Reduction viz.  $\text{DCID} \rightarrow \text{DCID}^{\cdot-}$ ; (b) Reduction to the Dianion  $\text{DCID}^{2-}$ ; V vs Ag/AgCl, Scan rate = 100 mV/sec.

(123) in the cyclic voltammogram of DCID (122). For comparison, the electrochemical reduction of DCNQ (123) is shown in Figure 3.2. DCNQ is a stronger acceptor than DCID. The first reduction,  $\text{DCNQ} \rightarrow \text{DCNQ}^{\cdot-}$ , is fully reversible occurring at +0.22 V, hence the presence of any  $\text{DCNQ}^{\cdot-}$  formed from DCID should be clearly observable (Figure 3.1). The second, one-electron reduction of  $\text{DCNQ}^{\cdot-}$  to the dianion  $\text{DCNQ}^{2-}$  is irreversible, occurring at -0.55 V [cf. TCNQ (1):  $E_{\frac{1}{2}}^1 = +0.22$  V,  $E_{\frac{1}{2}}^2 = -0.34$  V]. The electrochemical reversibility between the neutral and radical anion states of DCID (122) (Figure 3.1a) would appear to contradict the proposed mechanism for the rearrangement, which is initiated by a one-electron reduction (Scheme 3.1). To reconcile these data, it is tempting to suggest that the conversion of DCID (122) into DCNQ salts (123a-m) (Scheme 3.1) involves an intermediate DCID dianion, which could be formed by a strong reducing agent, *eg.* sodium metal. However, electrochemical reduction of  $\text{DCID}^{\cdot-}$  to the dianion does not give rise to reduction waves which are associated with DCNQ (Figure 3.1b). Furthermore, this hypothesis is not supported by the fact that rearrangement also occurs on reduction of DCID by the comparatively weak electron donor tetrathiafulvalene (2), giving salt (123l) (*vide infra*): the reduction potentials for TTF are  $E_{\frac{1}{2}}^1 = +0.34$  V,  $E_{\frac{1}{2}}^2 = +0.78$  V (vs Ag/AgCl). According to the guidelines of Torrance *et al.*, a combination of DCID and TTF should give rise to a neutral complex (*ie.*  $\Delta E > 0.25$  V)<sup>103</sup>.

With the lithium salt (123a) readily available, we have used this material in metathesis reactions with a range of cation salts to furnish a series of dicyanonaphthoquinol salts (123b-k) containing organic and metal counterions (Table 3.1). Our aim here was primarily to obtain a crystalline salt suitable for X-ray analysis to confirm beyond doubt that rearrangement from DCID to DCNQ, had occurred.

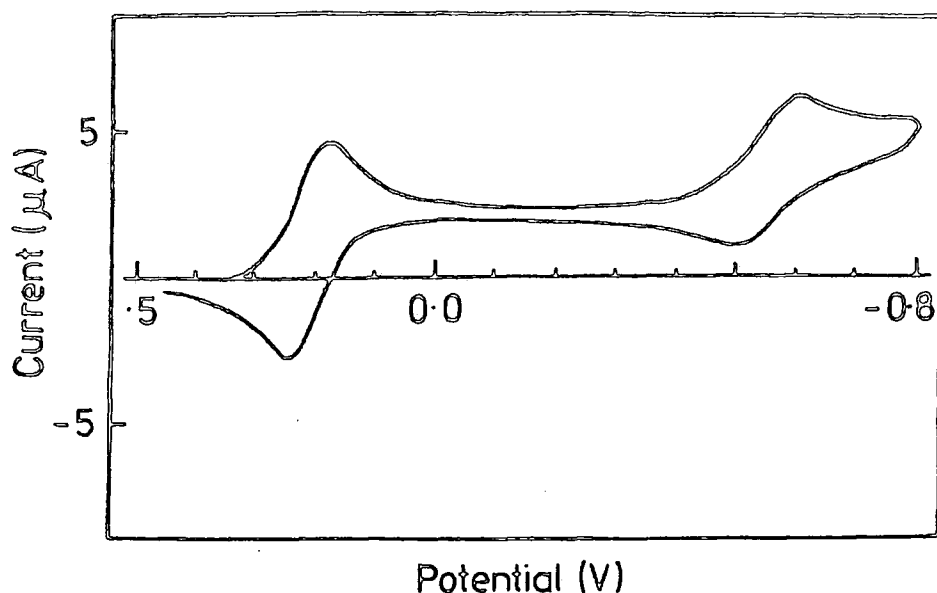


Figure 3.2 *Cyclic Voltammogram of DCNQ (123); For Conditions See Figure 3.1.*

Also, we wished to examine conductivity and magnetic properties of DCNQ radical anion salts. DCNQ salts of 1:1 stoichiometry (123a-g) are formed with lithium, methyltriphenylphosphonium, sodium, tetrabutylammonium, tetraphenylarsonium, rubidium and caesium cations, respectively, and four of these are hydrated [*viz.* (123b), (123c), (123f) and (123g)]. In contrast copper, nickel, cobalt and zinc form 1:2 salts (123h-k), three of which are hydrated. The cation:DCNQ stoichiometry was, in all cases, unambiguous from microanalysis and, where applicable, a stoichiometric amount of water was added to give a best fit to the analytical data.

The infrared spectra of all these salts (125a-k) show a very strong nitrile absorption in the range  $2180-2235\text{ cm}^{-1}$  compared to a weak nitrile absorption peak at  $2230\text{ cm}^{-1}$  for neutral DCID (122) and the absence of a nitrile absorption peak for neutral DCNQ (123). In comparison, the carbonyl absorption, which is very strong in both neutral DCID and neutral DCNQ (observed at  $1705$  and  $1680\text{ cm}^{-1}$ ,

DCNQ SALT	CATION/Source	APPEARANCE OF SALT	STOICHIOMETRY CATION:DCNQ:H <sub>2</sub> O	FORMULA	MICROANALYSIS FOUND (CALC)	% YIELD	IR (KBr) $\nu$ (CN) cm <sup>-1</sup>
(123a)	Li/ LiI	Dark Green	1:1	C <sub>12</sub> H <sub>4</sub> LiN <sub>2</sub> O <sub>2</sub>	C, 66.9 (67.0) H, 1.9 (1.9) N, 13.1 (13.0) Li, 3.3 (3.2)	94	2235
(123b)	MePh <sub>3</sub> / MePh <sub>3</sub> I	Black	1:1:(1)†	C <sub>31</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> P	C, 76.2 (76.7) H, 5.0 (4.6) N, 5.4 (5.8)	93	2197
(123c)	Na/ NaI or Na	Dark Green	1:1:3	C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub>	C, 50.0 (50.5) H, 2.9 (3.5) N, 9.2 (9.8)	50	2210
(123d)	t-Bu <sub>4</sub> N/ t-Bu <sub>4</sub> NI	Red	1:1	C <sub>28</sub> H <sub>40</sub> N <sub>3</sub> O <sub>2</sub>	C, 75.4 (74.6) H, 9.3 (9.0) N, 9.2 (9.3)	90	2200
(123e)	AsPh <sub>4</sub> / AsPh <sub>4</sub> Cl	Pale Green	1:1	C <sub>36</sub> H <sub>24</sub> AsN <sub>2</sub> O <sub>2</sub>	C, 72.7 (73.1) H, 3.9 (4.1) N, 4.5 (4.7)	35	2180
(123f)	Rb/ RbI	Dark Green	1:1:2	C <sub>12</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> Rb	C, 44.2 (43.7) H, 2.3 (2.5) N, 8.4 (8.5) Rb, 25.0 (25.9)	44	2205
(123g)	Cs/ CsI	Green	1:1:3	C <sub>12</sub> H <sub>10</sub> CsN <sub>2</sub> O <sub>5</sub>	C, 37.5 (36.8) H, 1.6 (1.8) N, 7.3 (7.1)	48	2200

Table 3.1 Spectroscopic and Microanalytical Data for DCNQ Salts (123a-m); †Salt (123b), without water of crystallisation, was obtained from reactions of DCID (122) and MePh<sub>3</sub><sup>+</sup>I<sup>-</sup> in dry acetonitrile; the analytical data given above are for this sample. Hydrated salt (123b) was obtained from salt (123a) and MePh<sub>3</sub><sup>+</sup>I<sup>-</sup> in water: found C, 74.2; H, 4.2; N, 5.4; Calc. for C<sub>31</sub>H<sub>24</sub>N<sub>2</sub>O<sub>3</sub>P: C, 73.9; H, 4.4; N, 5.6%.

DCNQ SALT	CATION/ Source	APPEARANCE OF SALT	STOICHIOMETRY CATION:DCNQ:H <sub>2</sub> O	FORMULA	MICROANALYSIS FOUND (CALC)	% YIELD	IR (KBr)§ ν(CN) cm <sup>-1</sup>
(123h)	Cu/ CuCl <sub>2</sub> ·2H <sub>2</sub> O	Black	1:2	C <sub>24</sub> H <sub>8</sub> CuN <sub>4</sub> O <sub>4</sub>	C, 60.2 (60.1) H, 1.5 (1.7) N, 11.6 (11.7) Cu, 13.5 (13.2)	78	2215
(123i)	Ni Ni(NO <sub>3</sub> )·6H <sub>2</sub> O	Green	1:2:11	C <sub>24</sub> H <sub>30</sub> N <sub>4</sub> NiO <sub>15</sub>	C, 43.4 (42.8) H, 4.2 (4.5) N, 8.4 (8.3) Ni, 8.5 (8.7)	60	2220
(123j)	Co/ CoCl <sub>2</sub> ·6H <sub>2</sub> O	Green	1:2:10	C <sub>24</sub> H <sub>28</sub> CoN <sub>4</sub> O <sub>14</sub>	C, 43.9 (44.0) H, 4.3 (4.3) N, 8.4 (8.5)	50	2218
(123k)	Zn/ Zn(NO <sub>3</sub> ) <sub>2</sub>	Green	1:2:11	C <sub>24</sub> H <sub>28</sub> N <sub>4</sub> O <sub>14</sub> Zn	C, 42.5 (42.4) H, 3.9 (4.4) N, 7.8 (8.2) Zn, 9.6 (9.6)	50	2215
(123l)	TTF/ TTF	Black	3:2	C <sub>42</sub> H <sub>20</sub> N <sub>4</sub> O <sub>4</sub> S <sub>12</sub>	C, 48.9 (49.0) H, 1.9 (1.9) N, 5.4 (5.5)	79	2190
(123m)	TWTF/ TWTF	Black	3:2	C <sub>54</sub> H <sub>55</sub> N <sub>4</sub> O <sub>4</sub> S <sub>12</sub>	C, 53.9 (54.2) H, 3.5 (3.7) N, 4.3 (4.7)	75	2195 ?*

Table 3.1 Spectroscopic and Microanalytical Data for DCNQ Salts (123a-m); §The position of cyanide absorption was the only peak to vary significantly between the different salts (123a-k). The remainder of the spectrum of the DCNQ radical anion was superimposable ( $\pm 5$  cm<sup>-1</sup>) in all the salts (123a-m) viz: 1545, 1500, 1270, 1114, 915, 882, 750, 742, 720, 680, 508, 500 and 490 cm<sup>-1</sup>. \*Tentative assignment, as the peak is largely obscured by a broad charge-transfer band.

respectively) is absent in the 1:1 quinol salts (123a-g), although it is present in the 1:2 salts (125h-k), albeit in reduced intensity relative to (123). From this we infer that neutral DCNQ is present in the 1:2 salts along with the DCNQ<sup>-</sup> radical anion. The hydrated salts all show the expected OH stretch in the I.R. spectrum.

We have considered the possibility that these salts are not hydrated, but instead, one of the nitrile groups has been replaced by a hydroxyl group derived from water during the metal exchange reaction (a process which could be promoted by complexation to the cation). There are early precedents for CN substitution by OH during reaction of DCNQ with sodium hydroxide<sup>139</sup> and recently, during complexation of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) with amidopyridines in solvents containing water<sup>140</sup>. However, microanalytical data for our hydrated DCNQ salts (especially the metal and nitrogen analyses) are clearly inconsistent with nitrile displacement having occurred to any significant extent.

Slow cooling of an equimolar mixture of TTF (2) and DCID (122) in acetonitrile leads to formation of the complex (TTF)<sub>3</sub>(DCNQ)<sub>2</sub> (1231) as a black, crystalline solid in 94% yield. The 3:2 stoichiometry of the complex has been established from microanalytical data and is most unusual for a charge transfer complex of TTF. A 3:2 salt formed by TTF (2) and tetrafluoroborate anions provides another example of this rare stoichiometry<sup>141</sup>. Rearrangement of DCID to DCNQ upon complexation is confirmed by isolation of the same 3:2 complex (1231), obtained from TTF (2) and DCNQ (123) (identical i.r. spectra). This result shows that TTF is a sufficiently strong reducing agent to effect the isomerisation of DCID (122) into DCNQ (123). Conductivity data for the complex (TTF)<sub>3</sub>(DCNQ)<sub>2</sub> were obtained for compressed pellet samples using standard four probe techniques. At room temperature the material is a good

conductor,  $\sigma_{rt}$  ca.  $1.0 \text{ S cm}^{-1}$ . This result is significant as it is among the highest values reported for the conductivity of a TTF complex that is not a derivative of TCNQ. Tetramethyl-TTF (4) which is a stronger electron donor than TTF also forms a 3:2 complex (123m) when mixed with DCID. The room temperature conductivity of complex (123m) is  $4 \times 10^{-3} \text{ S cm}^{-1}$ . These conductivity values clearly imply crystal structures for the TTF and TMTTF complexes with segregated stacks of donor and DCNQ molecules; however, we have been unable to obtain single crystals of (1231) or (123m) suitable for X-ray analysis.

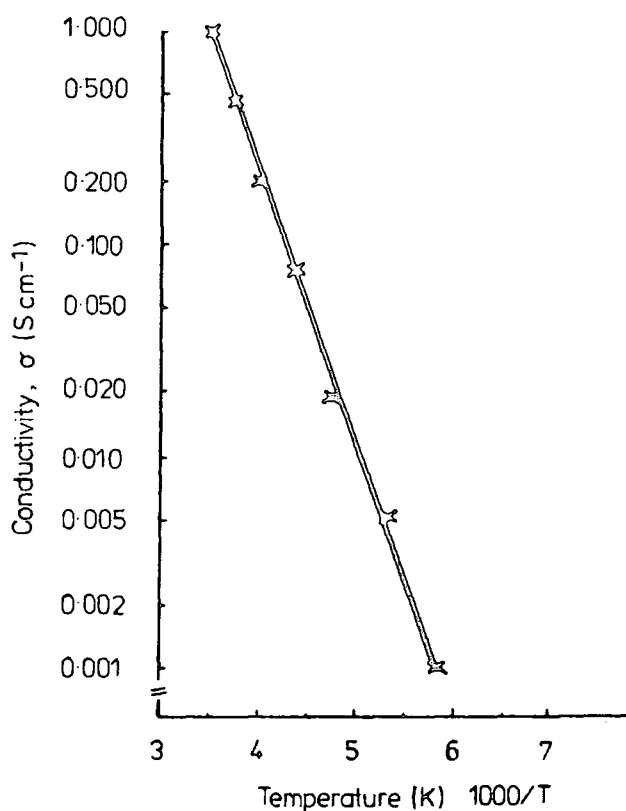


Figure 3.3 Variable Temperature Conductivity Plot for  $\text{TTF}_3\text{DCNQ}_2$  (1231).

Variable temperature conductivity measurements on (1231) were performed over the temperature range 300 - 160K and the exponential temperature dependence characteristic of a semiconductor is observed with activation energy  $E_a = 0.25 \text{ eV}$  (Figure 3.3). This activation energy value is high when compared with the values for many organic salts with similar

conductivities. However, it must be emphasised that the activation energy value is less reliable when obtained from data on compressed pellets than on single crystals, since the former samples are subject to the effects of electrical resistance associated with imperfect interparticle contact<sup>142</sup>. Conductivity measurements were performed on compressed pellets of DCNQ salts (123a), (123b), (123d) and (123h), and they are all insulators.

### 3.4 MAGNETIC PROPERTIES OF DCNQ SALTS

Magnetic properties of a selection of these salts (123) have been studied by Dr. G. Ashwell's group, using a Faraday balance and the results are presented in Table 3.2. Methyltriphenylphosphonium-DCNQ salt (123b) is diamagnetic and this is consistent with strongly interacting spins within the  $(\text{DCNQ}^-)_2$  dimer unit, as indicated by the relatively short intermolecular spacing observed in the X-ray structure. The magnetic susceptibilities of (123a), (123b), (123e) and (123l) are temperature independent and the values are consistent with those calculated from Pascal's constants.

SALT	$\chi_{300\text{K}}$ (total) emu mol <sup>-1</sup>	$\chi$ (diamag) <sup>a</sup> emu mol <sup>-1</sup>	$\chi_{300\text{K}}$ (paramag) emu mol <sup>-1</sup>	C <sup>b</sup>	$\mu_{\text{eff}}$
(123a)	-1.0(3)x10 <sup>-4</sup>	-1.0x10 <sup>-4</sup>			
(123b)	-2.9(3)x10 <sup>-4</sup>	-2.9x10 <sup>-4</sup>			
(123d)	+8.5(3)x10 <sup>-4</sup>	-3.0x10 <sup>-4</sup>	+11.5(3)x10 <sup>-4</sup>	0.35	1.68
(123e)	-3.2(3)x10 <sup>-4</sup>	-3.2x10 <sup>-4</sup>			
(123h)	-0.6(3)x10 <sup>-4</sup>	-2.0x10 <sup>-4</sup>	+ 1.4(3)x10 <sup>-4</sup>	0.043	0.58
(123l)	-4.7(3)x10 <sup>-4</sup>	-4.6x10 <sup>-4</sup>			

Table 3.2 *Magnetic Susceptibility Data for DCNQ Salts; (a) Calculated from Pascal's Constants; (b) Units are emu mol<sup>-1</sup> K.*

In contrast, the susceptibilities of the tetrabutylammonium and copper salts, (123d) and (123h), respectively have paramagnetic contributions which obey the Curie law (Figure 3.4). Their susceptibilities vary as  $\chi = C/T$  where  $C = 0.35$  and  $0.043 \text{ emu mol}^{-1} \text{ K}$ , which corresponds to effective Bohr magneton numbers ( $\mu_{\text{eff}} = 2.83 C^{1/2}$ ) of  $1.68$  and  $0.58 \mu_{\text{B}}$  respectively. For the tetrabutylammonium salt (123d) this value is in close agreement with  $\mu_{\text{eff}} = 1.73 \mu_{\text{B}}$  calculated for a well developed spin-1/2 system, whereas for the copper salt (123h), the data correspond to only *ca.* 0.16 spins per molecule. This weak paramagnetism suggests that the DCNQ $\cdot^-$  spins of (123h) couple antiferromagnetically, in which case the Curie Law behaviour probably arises from the presence of some paramagnetic  $\text{Cu}^{2+}$  in the host lattice, as the species  $\text{Cu}^{2+}(\text{DCNQ})_2^{2-}$ .

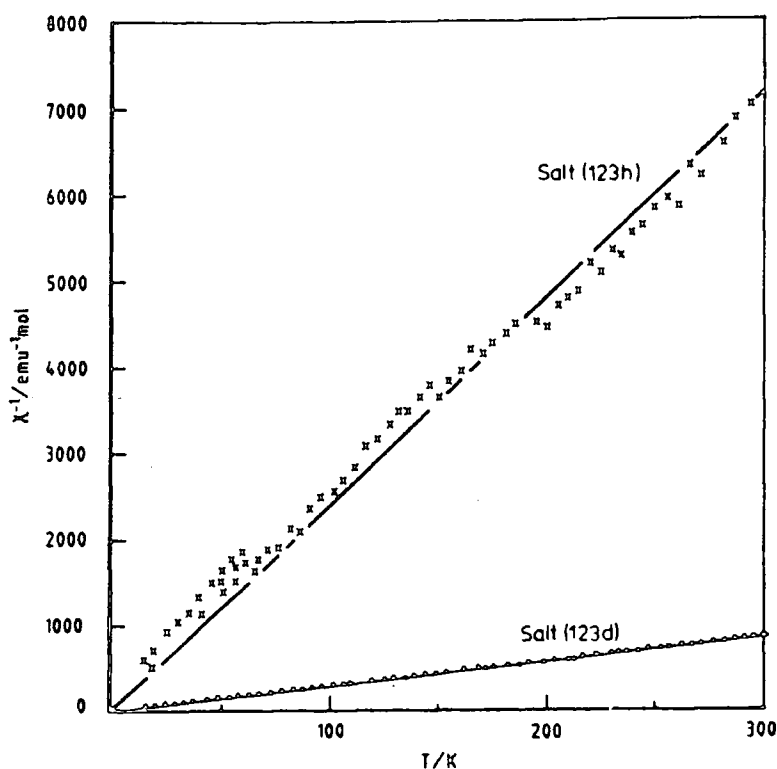


Figure 3.4 *Temperature Dependence of the Reciprocal Susceptibility for Salts (123d) and (123h) Corrected for Core Diamagnetism.*

### 3.5 X-RAY STRUCTURE OF SALT (123b).H<sub>2</sub>O

Crystals of salt (123b) were weakly diffracting, but nevertheless the data obtained confirm beyond doubt that the ionic component is DCNQ not DCID, which was the prime objective of the X-ray study. The X-ray crystal structure of (123b) was determined by Dr. M. Hasan and Dr. M. Drew at the University of Reading and is shown in Figure 3.5. The cation has the expected dimensions with the P-Me bond somewhat shorter than the P-Ph bond lengths. The dimensions of the anion are difficult to interpret, partly due to the inadequate data resulting from the weakly diffracting crystal. There is no clear indication that the negative charge on DCNQ is localised, and it seems likely that the charge is delocalised over several positions as would be expected for the naphthoquinol system. There is only one intermolecular contact of note [*viz.* O(10)-O(100) = 2.760(3)Å] which is indicative of a hydrogen bond. Remaining contacts between the cation, anion and water molecule are consistent with Van der Waals radii.

Figure 3.5 shows that the anions pack together in pairs across a centre of symmetry. The closest interatomic distance between the rings is C(5)-C(11) = 3.25Å.

### 3.6 X-RAY STRUCTURE OF DCID

The X-ray crystal structure of DCID (122) was determined by R. Short and Prof. M.B. Hursthouse at Queen Mary College, and a packing diagram is shown in Figure 3.6. The data obtained confirm that DCID has been assigned the correct structure<sup>136</sup>. A mean plane calculation reveals that the two cyanide groups deviate slightly from the plane formed by all the ring carbon atoms.

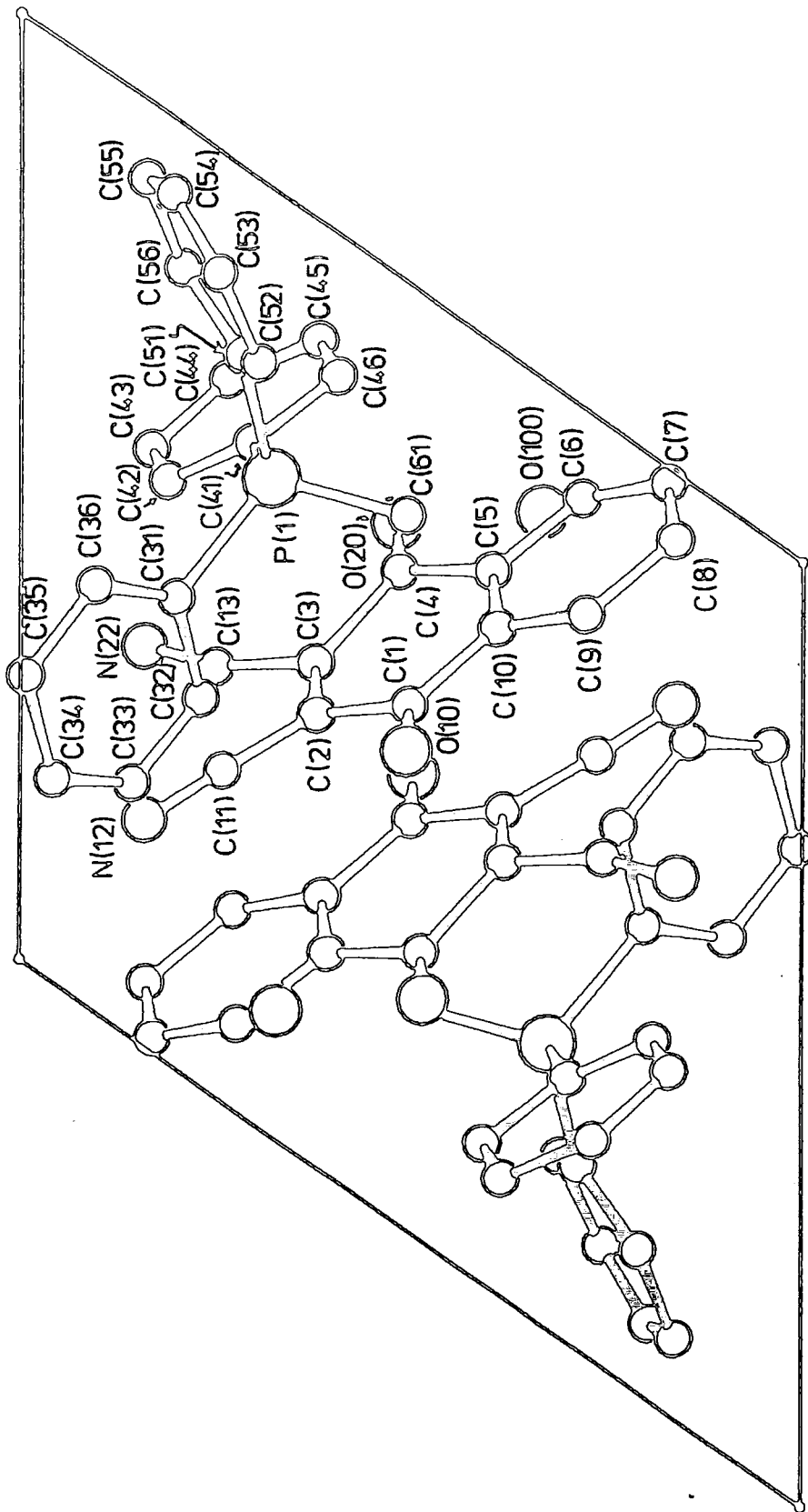


Figure 3.5 *Single Crystal X-Ray Structure of Salt (123b).H<sub>2</sub>O; the Unit Cell in the *a* Projection and the Atom Numbering Scheme.*

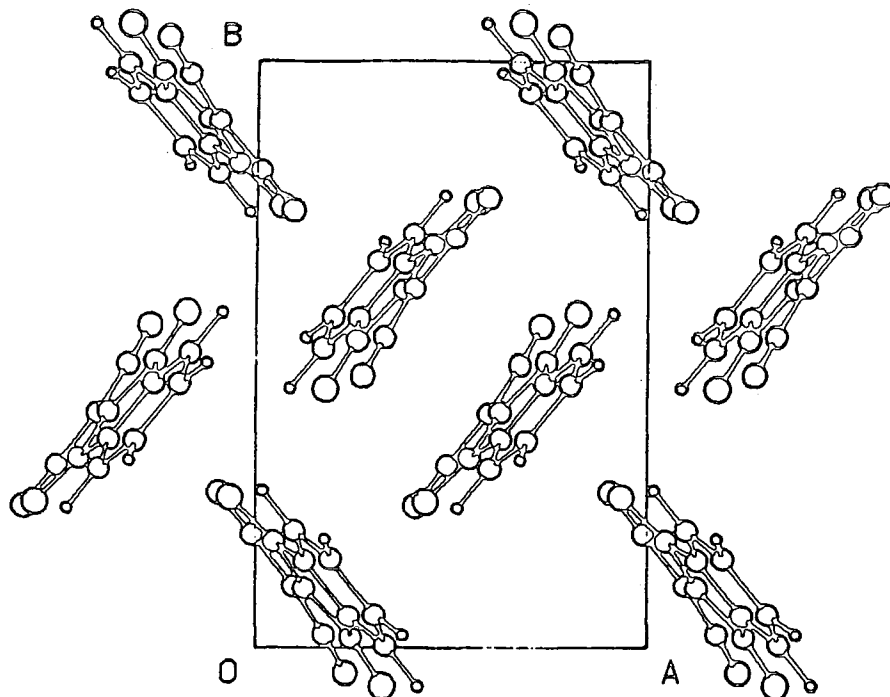


Figure 3.6 *Single Crystal X-Ray Structure of DCID (122): the Unit Cell in the  $c$  Projection.*

### 3.7 CONCLUSIONS

We have been unable to isolate the radical anion salts of the acceptor molecule DCID (122) due to a fascinating rearrangement of the radical anion derived from (122) to yield isomeric DCNQ salts (123a-m). The X-ray crystal structures of neutral DCID (122) and one of the "rearranged salts" *viz.* the hydrated methyltriphenylphosphonium-DCNQ salt (123b) have been determined. A range of DCNQ radical anion salts, with organic and inorganic counterions, have been isolated, and variable temperature magnetic susceptibility data for a selection of these salts have been discussed. The complexes of DCNQ with tetrathiafulvalene (TTF, (2)) and tetramethyl-TTF (4) are both semiconductors. The high  $\sigma_{rt}$  values exhibited by both complexes, particularly  $(TTF)_3(DCNQ)_2$ , reaffirm that conducting CT complexes can be prepared with acceptor molecules which possess a different skeletal structure to TCNQ (1).

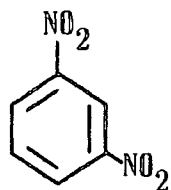
CHAPTER FOUR

NITROBENZENES AS ELECTRON ACCEPTORS

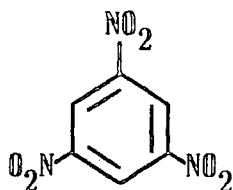
## 4.1 INTRODUCTION

Since the discovery of the remarkably high conductivity exhibited by TTF-TCNQ<sup>10</sup>, the vast majority of work conducted in the field of organic metals has focused upon the most highly conducting materials (Chapter 1). However, the investigations into insulating salts *eg.* HMTTF-TCNQF<sub>4</sub><sup>59</sup>, TTF-halobenzoquinones<sup>107,108</sup> and dibenzo-TTF-TCNQ<sup>103</sup>, have also added greatly to our understanding of the physics and chemistry of intermolecular interactions in the organic solid state. Cowan and Wiygul have recently emphasised that in order to refine the principles that should be applied to the design of new materials, it is important to fully characterise complexes with a range of electrical properties<sup>1</sup>.

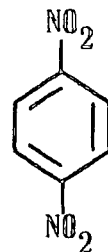
Continuing with our theme of developing the solid state chemistry of electron acceptors that possess a different skeleton to TCNQ, we chose to study 1,3-dinitrobenzene, *m*-DNB (127) and 1,3,5-trinitrobenzene, TNB (128). These two molecules differ from the huge majority of previously reported acceptors (Chapter 1, section 1.5), in that they possess an aromatic ground state, rather than the quinonoid ground state of TCNQ and the halobenzoquinones. The importance of the quinonoid ground state has been stressed by Torrance and co-workers<sup>104,105</sup>. However, while our work was in progress, a report from an Italian group demonstrated that acceptors with an aromatic ground state, *viz.* 1,4-dicyanotetrazine (57) and 1,3,5-tricyanotriazine (58), form moderately conducting complexes with TTF [*eg.* TTF-(57),  $\sigma_{rt} = 35 \text{ S cm}^{-1}$ ]<sup>98</sup>. This result was important as it showed that the attainment of aromaticity at the radical anion stage, is not a prerequisite for conductivity in a donor-acceptor pair.



(127)



(128)



(129)

Our study of m-DNB (127) and TNB (128) is an extension of the work performed by Bryce *et al.*, with p-dinitrobenzene, p-DNB (129)<sup>143</sup>. We believe that comparison of a wide range of acceptors, and their complexes, is far more beneficial than studying individual molecules in the hope of elucidating the crucial factors controlling the solid state properties. Bryce *et al.* chose p-DNB (129) as an acceptor as it resembled TCNQ in two important ways. Firstly, both molecules are of similar size; probably the failure of some larger acceptors to form complexes with TTF, *eg.* TCNPQ (36)<sup>78</sup> is a result of incompatible molecular dimensions. Secondly, p-DNB (129) has the same high degree of symmetry as TCNQ ( $D_{2h}$ ). The key role of the symmetry of the TCNQ radical anion in dictating the stacking arrangement in TTF-TCNQ has been shown independently by Berlinsky *et al.*<sup>70</sup> and Lowe<sup>71</sup>. Finally, electron spin resonance studies of the radical anions of aromatic compounds show that the electronegativity of the nitro group is very similar to that of the dicyanomethylene group<sup>144</sup>. Hence, the two acceptors, TCNQ and p-DNB, should have similar spin and charge distributions in the radical anion. TTF-pDNB was, however, found to be a neutral 1:1 complex which is an insulator at room temperature ( $\sigma_{rt} = 2.5 \times 10^{-7} \text{ S cm}^{-1}$ ). The crystal structure of TTF-pDNB consists of mixed stacks of alternating TTF and p-DNB (129) molecules. The lack of significant intermolecular contacts, and the interplanar spacing of 3.64Å (larger than in even the weak CT complexes TTF-X, where X is chloranil or fluoranil<sup>107</sup>), are

consistent with a neutral complex.† Interestingly, the projection of the TTF molecule onto the plane of the p-DNB (129) ring, reveals that the angle between the long molecular axes of each molecule is  $126^{\circ}$  (Figure 4.1). This contrasts with an earlier suggestion by Torrance *et al.*<sup>107</sup>, that if the donor and acceptor have long molecular axes, they tend to align. Consequently, this work suggested that orbital overlap was playing a greater role in determining the relative molecular orientation in donor-acceptor complexes, than was originally thought. In the light of these results we studied m-DNB (127) and TNB (128) as acceptors.

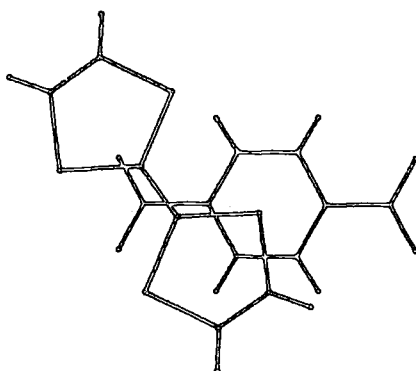


Figure 4.1 *Projection of the TTF Molecule onto the Plane of the p-DNB Ring (Ref 143).*

#### 4.2 TETRATHIAFULVALENE-META-DINITROBENZENE

A black, highly crystalline 1:1 complex was obtained in good yield (84%) by slowly cooling a toluene solution of TTF and m-DNB, present in equimolar amounts. All the data obtained agree and show that TTF-mDNB (127a) is a neutral, insulating complex. The i.r spectrum of TTF-mDNB (127a) consists of sharp peaks, typical of an insulating complex and it

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†Neutral complex refers to a complex in which there is no intermolecular charge transfer, and the component molecules are present in their neutral states.

does not display a charge-transfer absorption band (*ca.*  $5000\text{ cm}^{-1}$ )<sup>13b</sup> or the broad bands in the i.r region that are typical of conducting complexes. These i.r data are supported by optical measurements; the UV spectrum of a powdered sample of TTF-mDNB does not show an absorption characteristic of the TTF radical cation (2.1 - 2.8 eV)<sup>145</sup>. Furthermore, the solid state e.s.r signal is vanishingly weak and the bulk magnetic susceptibility of the complex ( $\chi = -162.1 \times 10^{-6}\text{ emu mol}^{-1}$ ) is constant over the temperature range 20 - 300K, in agreement with the calculated value ( $\chi = -159.5 \times 10^{-6}\text{ emu mol}^{-1}$ ) from Pascal's constants for TTF and m-DNB (127). These data clearly point to a diamagnetic complex. Consistent with these data, the single crystal conductivity (four probe d.c. measurement) resides in the insulating regime ( $\sigma_{\text{rt}} = 2.7 \times 10^{-9}\text{ S cm}^{-1}$ ).

The single crystal X-ray structure of TTF-mDNB was determined by Dr. M. Motevalli and Prof. M. Hursthouse. There are mixed stacks of TTF and m-DNB (127) molecules arranged in alternating donor-acceptor fashion along the a-axis (Figure 4.2). The TTF molecules lie on centres of symmetry and the m-DNB molecules on two-fold axes. A projection onto the molecular plane of a TTF molecule shows that there is no face to face overlap between the TTF molecule and the neighbouring m-DNB molecules. This is in marked contrast to the eclipsed donor-acceptor packing of the neutral TTF complexes in which the acceptor is of similar dimensions to m-DNB (127) *viz.* TTF-chloranil<sup>107</sup>, TTF-fluoranil<sup>107</sup>, TTF-pDNB<sup>143</sup> and TTF-TNB (*vide infra*). The tilt angle between the planes of the TTF and m-DNB molecules is  $8.2^{\circ}$ . The relative molecular orientation of the component molecules in this complex accounts for the neutral, insulating properties observed in the solid state measurements described above. All intermolecular distances in the TTF-mDNB complex are greater than the sum of the Van der Waals radii for the appropriate

atoms. There are no close inter-stack sulphur-sulphur contacts in TTF-mDNB. This is noteworthy in light of the growing number of organic materials based on TTF derivatives that show inter-stack sulphur-sulphur interactions<sup>3c,13a</sup>.

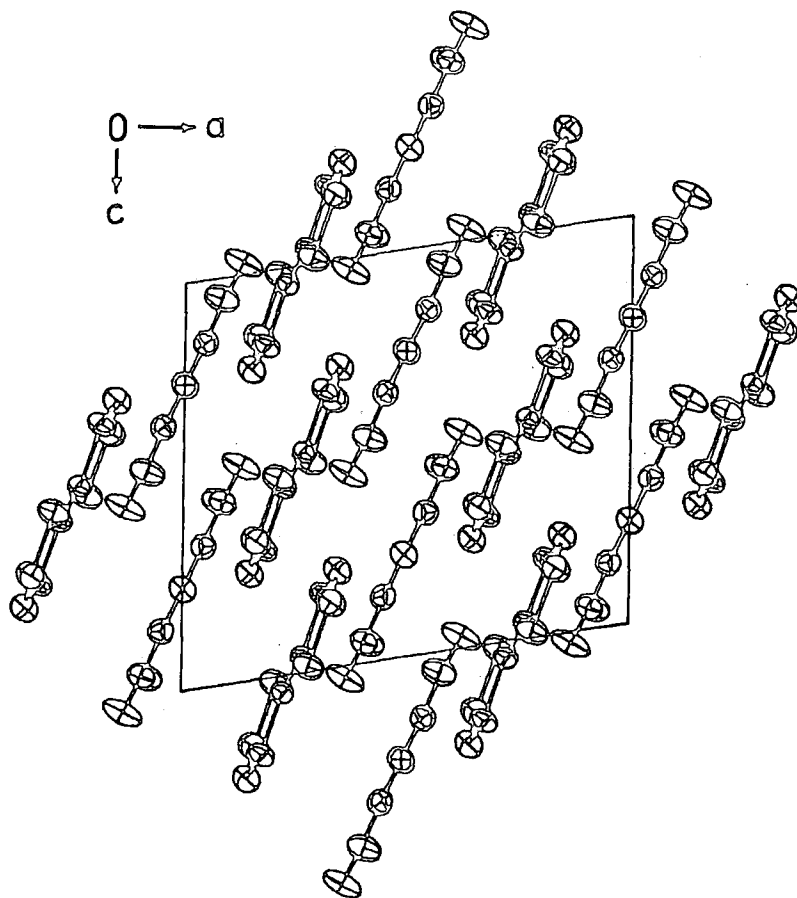


Figure 4.2 X-Ray Crystal Structure of TTF-mDNB Viewed Along the *b*-Axis.

Analysis of the bond lengths of the tetrathiafulvalene moiety in TTF complexes is a commonly employed technique for determining the degree of charge transfer,  $\rho$ , as neutral TTF has significantly different bond lengths from that of the cationic TTF species<sup>133</sup>. However, too much emphasis should not be placed on these data as the bond lengths reported in the literature for many TTF salts have large standard deviations, often resulting from partially disordered structures (eg. TTF-TCNQF<sub>4</sub>)<sup>146</sup>. The bond lengths which are most sensitive to  $\rho$  are the central and (to a lesser extent) the ring C=C double bonds [*viz.* C(1)-

C(1') and C(2)-C(3) respectively in structure (2)].

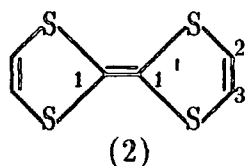


Table 4.1 compares these lengths for TTF-mDNB with those of neutral TTF<sup>147</sup>, three neutral complexes, *viz.* TTF-chloranil<sup>107</sup>, TTF-pDNB<sup>143</sup> and TTF-benzo[1,2-*c*:4,5-*c'*]bis[1,2,5-thiadiazole]-4,8-dione<sup>148</sup> and two partially ionic complexes, *viz.* TTF-TCNQ ( $\rho = 0.59$ )<sup>14</sup> and TTF-Cl<sub>0.67</sub><sup>4b</sup> ( $\rho = 0.67$ ), and one fully ionic complex *viz.* TTF-HgCl<sub>3</sub> ( $\rho = 1.0$ )<sup>149</sup>. These data clearly support the other solid-state data for TTF-mDNB and strongly suggest that TTF is present as a neutral species in the complex.

COMPOUND	$\rho$	Ring C=C (Å)	Central C=C (Å)
TTF- mDNB	0	1.314(5)	1.342(5)
TTF	0	1.314(3)	1.349(3)
TTF- pDNB	0	1.317(4)	1.349(3)
TTF- chloranil	0	1.314(5)	1.354(5)
TTF- X ‡	0	1.315(4)	1.342(3)
TTF- TCNQ	0.59	1.323(3)	1.369(3)
TTF- Cl <sub>0.67</sub>	0.67	1.32(1)	1.38(1)
TTF- HgCl <sub>3</sub>	1.0	1.31(1)	1.41(1)

Table 4.1 *Variation in Tetrathiafulvalene Bond Lengths With Degree of Charge Transfer,  $\rho$ ; ‡X=Benzo[1,2-*c*:4,5-*c'*]bis[1,2,5-thiadiazole]-4,8-dione.*

The difference in redox potentials of the constituent molecules provides a useful guideline to the degree of charge transfer expected for a donor-acceptor pair<sup>103</sup>. Based upon the calculated electron affinity of m-DNB, from charge transfer energies and half-wave reduction potentials<sup>150</sup>, the formation of a neutral complex between TTF (2) and

m-DNB (127) is to be expected, in line with Torrance's theories<sup>103</sup>.

This study clearly emphasises that the role of crystal packing forces in influencing the donor-acceptor overlap (or lack of it in TTF-mDNB) in mixed stack TTF complexes cannot be predicted at the present time. In this respect the present structure is markedly different from the isomeric TTF-pDNB complex<sup>143</sup>. It must be noted that TTF-mDNB is one of the first complexes formed by TTF (or a TTF derivative) which does not exhibit eclipsed stacking in a projection perpendicular to the TTF plane, either with itself (segregated stacks) or with the acceptor (mixed stack).

#### 4.3 TETRATHIAFULVALENE-TRINITROBENZENE

A key feature of this material is that it provides one of the first examples of an acceptor that has  $D_{3h}$  symmetry forming a complex with TTF. While many of the structural and electronic features of acceptors (eg. planarity and electron affinity) that influence TTF complexation have been studied in depth (Chapter 1), the role of the symmetry of the acceptor is virtually unexplored.‡

A black 1:1 complex of tetrathiafulvalene (2) and 1,3,5-trinitrobenzene, TNB (128) was prepared in a manner directly analogous to the preparation of TTF-mDNB (*vide supra*). In line with predictions, all the solid state data suggest that TTF-TNB (128a) is a neutral complex. The magnetic susceptibility of the complex ( $\chi = -191 \times 10^{-6} \text{ emu mol}^{-1}$ ) between 22K and 296K is constant (the calculated value from Pascal's constants for TTF and TNB (128) is  $\chi = -195 \times 10^{-6} \text{ emu mol}^{-1}$ ). The lack of charge transfer is evident from the absence of the peak assigned to

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‡It is noteworthy that CT-complexes incorporating acceptors with  $C_3$  symmetry or higher, have potential in the field of organic ferromagnets (Reference 151).

the TTF radical cation in the solid state UV-visible spectrum (*ca.* 2.8 eV)<sup>145</sup> and from the non existent solid state e.s.r signal obtained for the complex. Consistent with a neutral complex, this material is an insulator,  $\sigma_{rt} = 5 \times 10^{-10} \text{ S cm}^{-1}$  for single crystals.

X-ray analysis of TTF-TNB (performed by Drs. J.A.K. Howard and O. Johnson) shows the presence of a mixed donor-acceptor stack regime, of alternating TTF (2) and TNB (128) molecules (Figure 4.3).

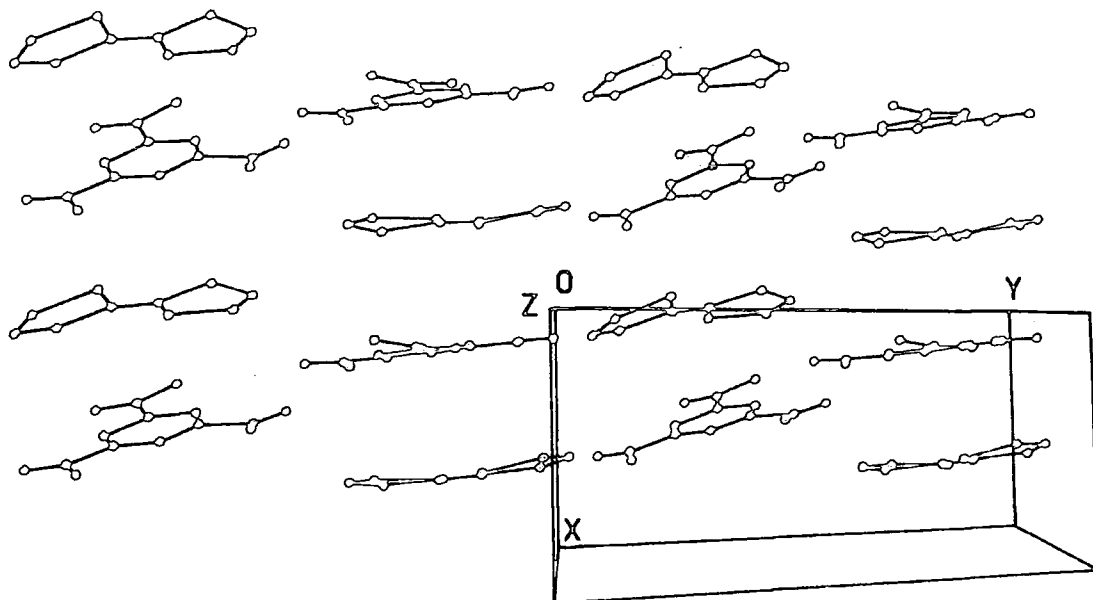


Figure 4.3 *Alternate Mixed Stacking Arrangement in TTF-TNB.*

A projection onto the molecular plane of several TTF molecules shows the existence of two distinct modes of overlap between the TTF molecule and its neighbouring TNB (128), each mode being retained within a stack [Figures 4.4(a) and 4.4(b)]. This is, to our knowledge, the first example of such a phenomenon (*ie.* two types of mixed stack) in a TTF complex, and this indicates that crystal packing forces dictate the relative orientation of the TTF and TNB rather than orbital overlap. Interestingly, the TNB-centroid to sulphur-plane distances are different in the two environments [3.43Å separation for the environment represented in Figure 4.4(b), compared to 3.51Å for the corresponding

environment in Figure 4.4(a)], although it must be noted that both values are greater than the sum of the Van der Waals radii for aromatic carbon atoms (3.34Å).

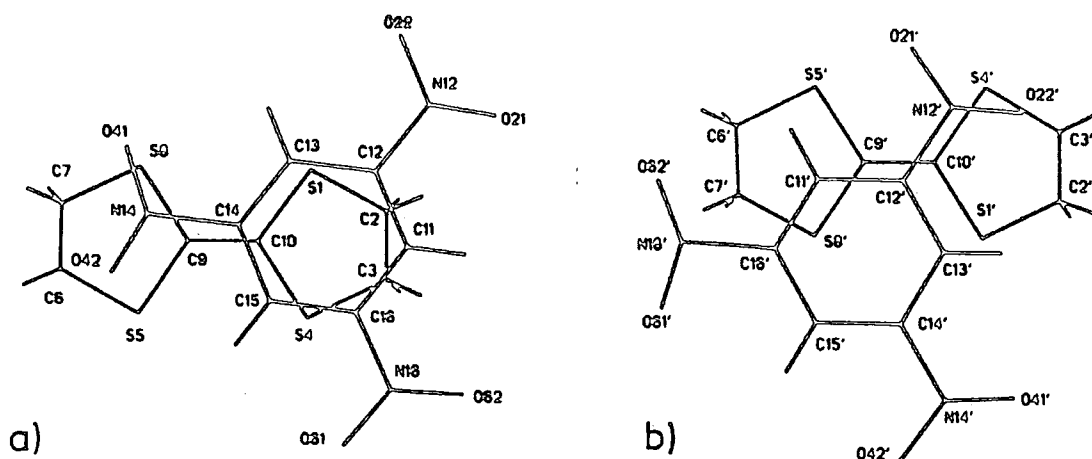
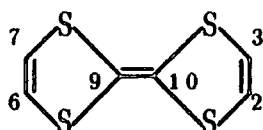


Figure 4.4 *Projection onto the Molecular Plane of Crystallographically Distinct TTF Molecules, in TTF-TNB.*

Despite the relatively poor refinement ( $R_w = 0.0984$ ) of the structure, the bond lengths of the TTF molecules, although different in each environment, lend support to the forementioned solid-state data and are consistent with TTF-TNB being a neutral complex (Table 4.2).



BOND	Figure 4.4(a) (Å)	Figure 4.4(b) (Å)
C(2)-C(3)	1.347(30)	1.353(29)
C(6)-C(7)	1.307(34)	1.344(31)
C(9)-C(10)	1.335(40)	1.346(37)

Table 4.2 *Bond Lengths of the Two Crystallographically Distinct TTF Molecules Found in TTF-TNB.*

The ring C=C bond lengths, with the exception of C(6)-C(7) represented in Figure 4.4(a), are all greater than the bond lengths found for the neutral TTF complexes listed in Table 4.1, which is

indicative of charge transfer between the donor (TTF) and acceptor (TNB). However, the central C=C bond lengths (*cf.* Table 4.1), which display greater sensitivity to  $\rho$ , of the two crystallographically distinct TTF molecules, point towards a neutral complex.

#### 4.4 CONCLUSIONS

Earlier work with p-dinitrobenzene (129)<sup>143</sup> prompted us to prepare and characterise the TTF complexes of meta-dinitrobenzene (127) and trinitrobenzene (128). In accord with the electron affinities of each acceptor, both complexes were neutral and insulating. This class of material, despite its high resistivity, is nonetheless worthy of study, providing valuable insight into the factors controlling the range of observed solid state properties. Both complexes provided crystal structures that exhibited novel features within this class of material. To put these results in perspective: Torrance *et al.*<sup>107</sup> concluded from their studies of the TTF-tetrahalobenzoquinones, that the role of orbital overlap can be undermined by steric interactions, particularly if the latter provides an alignment of the long axes of the donor and acceptor. In contrast, from the work conducted upon TTF-pDNB, it was concluded that far greater emphasis should be stressed upon the role of orbital overlap. Our results suggest these conclusions were premature and that neither of these factors necessarily controls the relative orientation of donor and acceptor.

Whether our results are specific to our systems or are relevant to the structures of other TTF complexes cannot be determined at present. All in all, our understanding of the factors controlling the crystal packing is far from complete, thus leaving plenty of scope for further research into related systems.

CHAPTER FIVE

MISCELLANEOUS ACCEPTORS CONTAINING

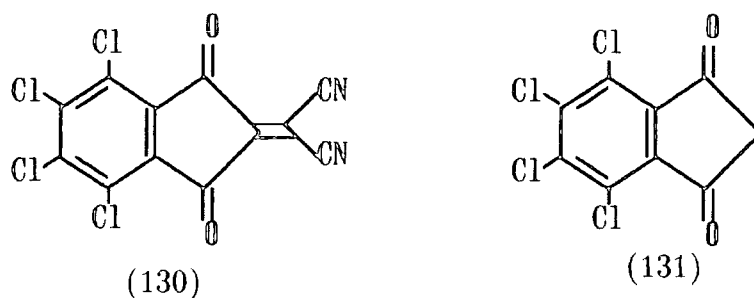
DICYANOMETHYLENE GROUPS

## 5.1 INTRODUCTION

This chapter describes, briefly, our more exploratory studies with a range of acceptors containing the dicyanomethylene group; in particular we sought to modify the electron affinity by incorporating halogen atoms.

## 5.2 4,5,6,7-TETRACHLORO-2-DICYANOMETHYLENE-1,3-INDANDIONE

In the light of the interesting results obtained with DCID (122) (Chapter 3) we chose to study tetrachloro-DCID (130). The presence of the chlorine atoms would not only increase the electron affinity of the acceptor relative to DCID (122), but also, we considered that the radical anion of (130) might be sufficiently stabilised not to rearrange to the dicyanonaphthoquinone skeleton (*cf.* Chapter 3), thus enabling complexes of (130) to be studied.



Tetrachloro-1,3-indandione (131) was prepared as described in the literature<sup>152</sup> (18% overall yield; two steps starting from tetrachlorophthalic anhydride), and then reacted with tetracyanoethylene to afford tetrachloro-DCID (130) (76% yield), using the conditions of Junek and Sterk<sup>136</sup>. Cyclic voltammetry of (130) shows a reversible one-electron reduction at potential = +0.21 V vs Ag/AgCl, confirming that the tetrachloro derivative (130) is a significantly stronger acceptor than

DCID (122) (*cf.* Chapter 3;  $E_{\frac{1}{2}}^1 = +0.008$  V vs Ag/AgCl), as predicted (Figure 5.1). Attempts to form the dianion of (130) electrochemically resulted in a completely irreversible, second reduction wave.

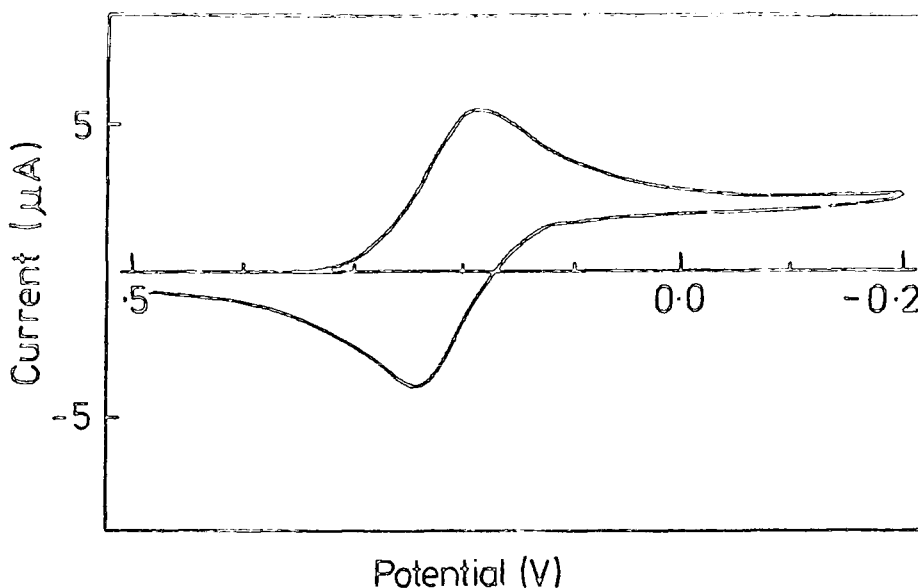


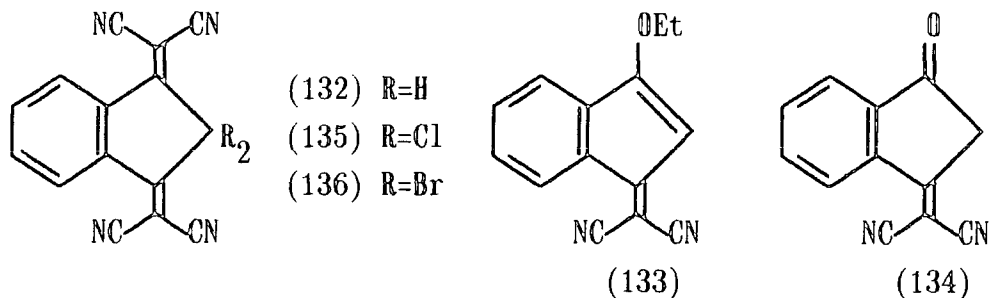
Figure 5.1 *Cyclic Voltammogram of Tetrachloro-DCID (130).*

The increased electron affinity of (130) compared to DCID (122), indicated that salt formation (*eg.* with lithium or methyltriphenylphosphonium cations) should be facile. On mixing neutral (130) with either lithium iodide or methyltriphenylphosphonium iodide in acetonitrile, a colour change was observed which clearly indicated salt formation in solution. However, in both cases a solid salt could not be isolated. By comparison, on mixing equimolar quantities of TTF (2) and tetrachloro-DCID (130) in acetonitrile, a black precipitate formed immediately. Microanalysis of the complex (130a) gave a 1:1 ratio of TTF:tetrachloro-DCID. This complex exhibits a relatively low, compaction room temperature conductivity value of *ca.*  $2 \times 10^{-5}$  S cm<sup>-1</sup>. Although in the semiconducting regime, a conductivity of this magnitude does not necessarily confirm segregated stacks of donor and acceptor, and partial charge transfer, which would be predicted from the half-wave reduction

potential for tetrachloro-DCIQ. Due to the low conductivity value we were discouraged from studying this complex further and we have, therefore, not established whether or not rearrangement of (130) has occurred to tetrachloro-2,3-dicyanonaphthoquinone.

### 5.3 DICYANOMETHYLATED 1,3-INDANDIONES

To extend our series of new electron acceptors possessing a different skeletal shape to TCNQ (1) we chose to study 1,3-bis(dicyanomethylene)indane (132) which was prepared as described in the literature<sup>153</sup>, from 1,3-indandione and malononitrile in ethanol with ammonium acetate as catalytic base. Early attempts to synthesise (132) yielded a new compound (133) in 4% yield. The mechanism of formation of (133) presumably involves substitution with ethoxide (produced *in situ*) at the carbonyl carbon of intermediate (134), followed by elimination.



Cyclic voltammetry of (132) showed an irreversible reduction wave at -0.55 V vs Ag/AgCl, inferring that (132) is a very poor acceptor which, therefore, seemed likely to yield a neutral, insulating complex with TTF (Table 5.1). Surprisingly, a 1:1 complex (132a) with TTF exhibits a conductivity value of  $\sigma_{rt} = 3 \times 10^{-4} \text{ S cm}^{-1}$ , which points towards a segregated stack structure and partial charge transfer. Comparison of (132) with benzo-TCNQ (39)<sup>82</sup> and TCAQ (37)<sup>79,80</sup>, which do not form TTF complexes, indicates that the steric interaction between

the dicyanomethylene group and the peri hydrogens is significantly reduced in compound (132), giving rise to a more planar structure. X-ray crystal data on the neutral species (132) would obviously shed more light upon the situation.

To increase the electron affinity of compound (132), the known 2,2-dichloro and 2,2-dibromo derivatives (135) and (136) were prepared<sup>153</sup>. Cyclic voltammetry data are collated in Table 5.1.

COMPOUND	$E_{\frac{1}{2}}^1$ (V) <sup>a</sup>
(132)	-0.55
(135)	-0.14
(136)	+0.07

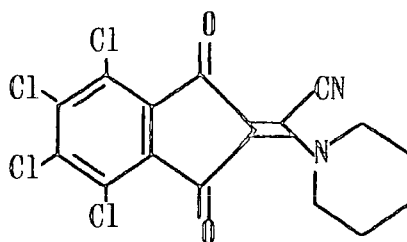
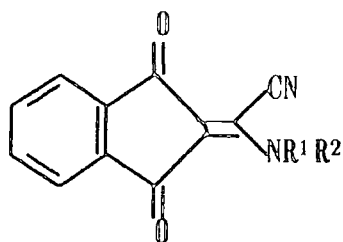
Table 5.1 *Cyclic Voltammetric Data for 1,3-Bis(dicyanomethylated) indanes (132), (135) and (136); (a) vs Ag/AgCl; [Bu<sub>4</sub>N][ClO<sub>4</sub>] electrolyte (0.02M); MeCN solvent; Pt working electrode; scan rate=100 mV/sec; irreversible reduction.*

As predicted, both the dichloro (135) and dibromo (136) derivatives are significantly stronger electron acceptors than (132). However, from the relative electronegativity of chlorine and bromine alone, the dibromo derivative (136) was not expected to be a stronger acceptor than the dichloro derivative (135). Reference to earlier work by Torrance *et al.*<sup>107,108</sup> shows that while the TTF salts of fluoranil and chloranil are neutral, TTF-bromanil has an ionic ground state. This phenomenon was attributed to the larger polarisation of the bromanil molecule, playing an important role in stabilising the ionic ground state. It appears likely that a similar phenomenon could explain the observed reduction potentials (Table 5.1). It must be noted that the reduction waves for all three 1,3-bis(dicyanomethylene)indanes (132), (135) and (136) are not reversible. All attempts to complex both the dichloro (135) and the dibromo (136) derivatives with TTF, in a range of solvents

(acetonitrile, 1,1,1-trichloroethane and benzene), failed.

#### 5.4 AMINE-SUBSTITUTED DCID DERIVATIVES

With DCID (122) and tetrachloro-DCID (130) in hand we sought to synthesise amine substituted derivatives which might hold promise as materials for non-linear optics, by virtue of the presence of both donor (amine) and acceptor (cyanide and carbonyl) moieties in the same molecule<sup>154</sup>. Previous work<sup>155</sup> had shown that one cyano group of DCID (122) could be substituted with a range of anilines. We have extended this and shown that aliphatic amines react similarly, *eg.* piperidine, *n*-butylamine, benzylamine and *n*-octadecylamine derivatives, (137)-(140) respectively, have been prepared (40-65% yields). Tetrachloro-DCID (130) reacts similarly with piperidine to yield (141) (53%).

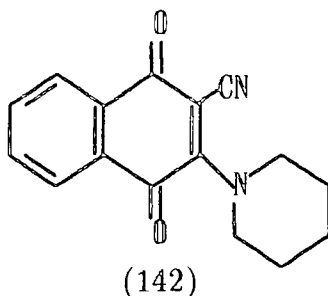


- (137) R<sup>1</sup>-R<sup>2</sup>=-(CH<sub>2</sub>)<sub>5</sub>-  
(138) R<sup>1</sup>=H; R<sup>2</sup>=nC<sub>4</sub>H<sub>9</sub>  
(139) R<sup>1</sup>=H; R<sup>2</sup>=CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>  
(140) R<sup>1</sup>=H; R<sup>2</sup>=nC<sub>18</sub>H<sub>37</sub>

For all these compounds (137)-(141), two carbonyl stretching frequencies were observed at *ca.* 1700 cm<sup>-1</sup> and 1650 cm<sup>-1</sup>, which indicates significant interaction between the donor moiety (amine) and one of the carbonyl functionalities (acceptor), thus confirming the potential of this class of material in the field of non-linear optics<sup>154</sup>. To probe this possibility further, we attempted to lay Langmuir-Blodgett (LB) films of the octadecylamine derivative (140), which were then to be tested for non-linear optical properties.

Preliminary attempts to lay a film of (140) were successful, but this was not reproducible. One possible explanation may lie with the fact that the sample could not, despite all our efforts, be obtained analytically pure. Consequently this line of research was abandoned.

In view of the DCID (122) to DCNQ (123) rearrangement, which is considered to be initiated by single electron transfer (Chapter 3), we needed to establish that the amines were not initiating this same rearrangement. We thus reacted DCNQ (123) with piperidine to obtain (142). This compound (142) was clearly different from (137) ( $^1\text{H}$  NMR, IR and melting point comparisons), thus demonstrating that structures (137)-(141) are correctly assigned and that rearrangement had not occurred.



## 5.5 CONCLUSIONS

Miscellaneous dicyanomethylene-containing acceptors with skeletal structures markedly different from TCNQ (1) have been synthesised. The presence of halogen atoms increases the electron affinity of these acceptors, as judged by cyclic voltammetry. Some of these acceptors complex with TTF to form semiconducting materials. This study further extends the range of acceptors to be employed in this context.

CHAPTER SIX

EXPERIMENTAL

## 6.1 GENERAL METHODS

Melting points were recorded on a Kofler hot-stage microscope apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer 577 and 457 spectrophotometers. Proton NMR were recorded on a Bruker AC 250 instrument, operating at 250.133 MHz, and a Perkin-Elmer R-24B instrument, operating at 60 MHz. Chemical shifts, given in ppm, are relative to tetramethylsilane (TMS) as internal standard. Mass spectra were obtained on a VG 7070E instrument, operating at 70 eV, with ionisation modes as indicated.

For column chromatography, Merck silica gel (70-230 mesh) and Merck alumina (activity II to III, 70-230 mesh) were employed as indicated. The alumina was soaked in ethyl acetate for at least 30 minutes prior to use.

The term "dry" in this thesis refers to solvents dried, under an atmosphere of nitrogen, in the following ways: tetrahydrofuran (THF) was dried over sodium. Dichloromethane and carbon tetrachloride were distilled from phosphorus pentoxide. Acetonitrile was distilled from calcium hydride. Pyridine (Aldrich HPLC grade) was stored over activated molecular sieve (4Å).

Conductivity measurements on powdered samples were obtained by manually compressing the sample between two steel probes, and monitoring the resistance with a Fluka 8000A Digital Multimeter. To obtain single crystal conductivity measurements, two pressure contacts were made using silver paste, and a Keithley 228 voltage/current source was used. Conductivity values of the nitrobenzene complexes (Chapter 4) were obtained using the four-probe technique. Bulk magnetic susceptibility data were obtained using a Faraday balance.

Cyclic voltammograms (CV) were recorded on a BAS100 electrochemical analyser. The cell (unless otherwise stated) consisted of dry acetonitrile solvent, Ag/AgCl reference electrode, platinum working electrode and tetrabutylammonium perchlorate, TBAP (0.02 M) electrolyte. All solutions were purged with nitrogen and retained under this inert atmosphere while the CV data were recorded.

## 6.2 EXPERIMENTAL TO CHAPTER 2

### 6.2.1 2,3-Dimethyl-1,4-bis(dicyanomethylene)cyclohexane (97)

To 2,3-dimethyl-1,4-cyclohexanedione (335 mg, 2.39 mmol) was added a mixture of malononitrile (347 mg, 5.25 mmol) and a catalytic amount of  $\beta$ -alanine (30 mg) in water (10 ml). The reaction mixture was heated at reflux for 3.5h. The product was isolated by filtration and washed with water. Recrystallisation from acetonitrile yielded compound (97) (379 mg, 67%) as a white solid. Mpt. 186-189°C; EI m/e: 236 ( $M^+$ ); CI m/e: 237; Analysis found: C, 71.3; H, 5.2; N, 24.0. Calculated for  $C_{14}H_{12}N_4$ : C, 71.2; H, 5.1; N, 23.7%; IR  $\nu_{max}$  (KBr): 2980, 2940, 2915, 2250 ( $C\equiv N$ ), 1600, 1460, 1445, 1385, 1365, 1314, 1177, 1085, 1058, 1035, 968, 945, 775 and 580  $cm^{-1}$ ;  $\delta H(60MHz, d^6\text{-acetone})$ : 3.33(q,2H), 3.10(s,4H) and 1.30(d, J=7Hz,6H) ppm.

### 6.2.2 5,6-Dimethyl-1,4-bis(dicyanomethylene)-2-cyclohexene (98)

A solution of compound (97) (900 mg, 3.9 mmol) and bromine (0.44 g, 8.5 mmol) in dry acetonitrile was cooled to 0°C and stirred under an atmosphere of nitrogen. Pyridine (1.6 g, 20 mmol) was syringed dropwise into the reaction vessel over a period of 10 min. The mixture was then

stirred at 0°C for 30 min and at room temperature for a further 2h. Cold water was added and the mixture stirred for about 15 min. The resultant precipitate was collected by filtration, washed with water and recrystallised from acetonitrile, yielding compound (98) (774 mg, 86%) as a white solid. MPt. 203-205°C; EI m/e: 234 (M<sup>+</sup>); CI m/e: 234; Analysis found: C, 71.9; H, 4.2; N, 23.8. Calculated for C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>: C, 71.8; H, 4.3; N, 23.9%; IR  $\nu_{\max}$  (KBr): 2980, 2235 (C≡N) and 1570 (conjugated C=C) cm<sup>-1</sup>;  $\delta$ H(250MHz, CD<sub>3</sub>CN): 7.16(s, 2H), 3.21(q, J=7Hz, 2H) and 1.17(d, J=7Hz, 6H) ppm.

### 6.2.3 2,3-Dimethyl-7,7,8,8-tetracyanoquinodimethane (73)

A mixture of compound (98) (440 mg, 1.9 mmol) and elemental selenium (pellets) (300 mg, 3.8 mmol) was ground up under an atmosphere of nitrogen. The mixture was transferred to a dry carius tube, which was evacuated and sealed, and then heated at 220°C for 2h. The reaction mixture was extracted with boiling dichloromethane and the extract dried and evaporated. Purification was achieved by silica column chromatography using dichloromethane as eluent. The two main components isolated from this chromatography were, in order of elution, starting material (98) and compound (73). Preparative t.l.c on a silica coated plate, using dichloromethane eluent, provided a spectroscopically pure sample of (73) (5 mg, 1%). 2,3-Dimethyl-7,7,8,8-tetracyanoquinodimethane (73) was identified by its <sup>1</sup>H NMR spectrum<sup>115</sup>.  $\delta$ H(250MHz, CDCl<sub>3</sub>): 7.56 (s, 2H), 2.46(s, 6H) ppm.

## 6.2.4 One-Step Conversion of *p*-benzoquinones to mono(dicyanomethylated)-*p*-benzoquinones

### 6.2.4.1 General Procedure

In all reactions, every possible precaution to eliminate moisture was taken. All solutions were prepared, and all reactions performed, under an atmosphere of nitrogen. The work-up procedure was as follows: the reaction mixture was washed with water, and the organic phase separated and dried over anhydrous  $\text{Na}_2\text{CO}_3$ . The solvent was then removed *in vacuo*. Silica column chromatography of the residue yielded pure product.

### 6.2.4.2 1-Oxo-2,6-dimethyl-4-dicyanomethylene-2,5-cyclohexadiene (99)

To a solution of 2,6-dimethyl-*p*-benzoquinone (104) (366 mg, 2.7 mmol), malononitrile (444 mg, 6.75 mmol) and dry pyridine (1.06 g, 13.5 mmol) dissolved in dry dichloromethane (25 ml) was added a solution of titanium tetrachloride (1.28 g, 6.75 mmol) dissolved in dry dichloromethane (25 ml) at 0-5°C. The reaction mixture was stirred at room temperature for 15h. Column chromatography, eluting with dichloromethane, yielded compound (99) (142 mg, 28%) as an orange solid. Mpt. 134-138°C; EI m/e: 184 ( $\text{M}^+$ ); CI m/e: 185; Analysis found: C, 71.8; H, 4.3; N, 15.5. Calculated for  $\text{C}_{11}\text{H}_8\text{N}_2\text{O}$ : C, 71.7; H, 4.3; N, 15.2%; IR  $\nu_{\text{max}}$  (KBr): 2220 (C≡N, weak), 1635 (C=O, strong), 1580, 1430, 1380, 1240, 1200, 1040, 1030, 950, 930, 910, 900 and 780  $\text{cm}^{-1}$ ;  $\delta\text{H}$ (60MHz,  $\text{CDCl}_3$ ): 7.26(s,2H) and 2.06(s,6H) ppm.

A second component which eluted from the column, was not obtained analytically pure, but was tentatively identified from spectroscopic data as compound (102). EI m/e: 223 ( $M^+$ ); CI m/e: 234; IR  $\nu_{\max}$  (KBr): 3400, 2230, 1598, 1522, 1480, 1310, 1290, 1210, 1170, 935, 890 and 745  $\text{cm}^{-1}$ ;  $\delta\text{H}(250\text{MHz}, \text{CDCl}_3)$ : 7.80(s, 2H) and 2.33(s, 6H) ppm.

#### 6.2.4.3 1-Oxo-2,3,6-trimethyl-4-dicyanomethylene-2,5-cyclohexadiene (100)

2,3,5-Trimethyl-p-benzoquinone (109) (867 mg, 5.8 mmol), dissolved in dichloromethane (15 ml) was added to a solution of malononitrile (420 mg, 6.4 mmol), dry pyridine (1.0 g, 12.7 mmol) and titanium tetrachloride (1.2 g, 6.4 mmol) dissolved in dry dichloromethane (25 ml) at 0-5°C. The solution was stirred at room temperature for 96h. Column chromatography, eluting with toluene-hexane (1:1 v/v) yielded compound (100) (500 mg, 43%) as an orange solid. MPt. 102-106°C; EI m/e: 198 ( $M^+$ ); CI m/e: 199; Analysis found: C, 72.4; H, 4.8; N, 14.0. Calculated for  $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}$ : C, 72.7; H, 5.1; N, 14.1%; IR  $\nu_{\max}$  (KBr): 2225, 1630, 1575, 1500, 1435, 1400, 1375, 1345, 1290, 1260, 1220, 1170, 1125, 1105, 1035, 930, 900, 875, 780, 670, 620, 580, 515 and 495  $\text{cm}^{-1}$ ;  $\delta\text{H}(250\text{MHz}, \text{CDCl}_3)$ : 7.46(s, 1H), 2.52(s, 3H) and 2.12(s, 6H) ppm.

A second component which eluted from the column, was not obtained analytically pure, but was tentatively identified from spectroscopic data as compound (103). EI m/e: 237 ( $M^+$ ); CI m/e: 238; IR  $\nu_{\max}$  (KBr): 3550, 2970, 2920, 2850, 2240, 1600, 1570, 1550, 1477, 1380, 1330, 1320, 1265, 1240, 1210, 1100, 1025, 935, 895, 862, 805, 740, 700, 685, 550, 520 and 400  $\text{cm}^{-1}$ ;  $\delta\text{H}(60\text{MHz}, \text{CDCl}_3)$ : 7.06(s, 1H), 2.30(s, 6H) and 2.16(s, 3H) ppm.

#### 6.2.4.4 1-Oxo-2,3,5,6-tetraethyl-4-dicyanomethylene-2,5-cyclohexadiene (101)

2,3,5,6-Tetramethyl-p-benzoquinone (95) (400 mg, 2.4 mmol), dissolved in dichloromethane (25 ml) was added to a solution of malononitrile (402 mg, 6.1 mmol), dry pyridine (948 mg, 12 mmol) and titanium tetrachloride (1.16 g, 6.1 mmol) dissolved in dry dichloromethane (20 ml) at 0-5°C. The reaction mixture was stirred at room temperature for 24h. Column chromatography, eluting with dichloromethane-hexane (7:3 v/v) yielded compound (101) (132 mg, 26%) as a yellow solid. MPt. 124-128°C; EI m/e: 212 (M<sup>+</sup>); CI m/e: 213; Analysis found: C, 73.0; H, 5.7; N, 12.7. Calculated for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O: C, 73.5; H, 5.7; N, 13.2%; IR  $\nu_{\max}$  (KBr): 2220, 1635, 1580, 1510, 1460, 1440, 1385, 1370, 1355, 1330, 1310, 1265, 1220, 1160, 1130, 1100, 1030, 1010, 860, 775, 690 and 600 cm<sup>-1</sup>;  $\delta$ H(250MHz,CDCl<sub>3</sub>): 2.44(s,6H) and 2.02(s,6H) ppm.

A second component which eluted from the column, was not obtained analytically pure, but was tentatively identified from i.r spectroscopic data as compound (96). IR  $\nu_{\max}$  (KBr): 3570, 2920, 2220, 1630, 1570, 1450, 1385, 1333, 1300, 1220, 1132, 1100 and 1030 cm<sup>-1</sup>.

#### 6.2.4.5 9-Oxo-10-dicyanomethylene-9,10-dihydroanthracene (38)

Anthraquinone (1.99 g, 9.5 mmol) followed by dichloromethane (150 ml) was added to a solution of malononitrile (1.57 g, 24 mmol), dry pyridine (3.78 g, 47 mmol) and titanium tetrachloride (4.54 g, 24 mmol) dissolved in dichloromethane (50 ml) at 0-5°C. The reaction mixture was heated at reflux for 5 days. Column chromatography, eluting with toluene-cyclohexane (1:1 v/v) yielded unreacted anthraquinone (ca. 1g,

50%) followed by compound (38) (650 mg, 27%) as a yellow solid. MPt. 250°C (dec) (*cf.* Lit. 289°C)<sup>131</sup>; EI m/e: 256 (M<sup>+</sup>); CI m/e: 257; Analysis found: C, 79.9; H, 3.1; N, 10.6. Calculated for C<sub>17</sub>H<sub>8</sub>N<sub>2</sub>O: C, 79.6; H, 3.1; N, 10.9%; IR  $\nu_{\max}$  (Nujol): 2218, 1675, 1597, 1585, 1540, 1528, 1340, 1325, 1315, 1290, 1175, 980, 930, 815, 790, 760, 740 and 700 cm<sup>-1</sup>;  $\delta$ H(250MHz, CDCl<sub>3</sub>): 8.32-8.28(m,4H) and 7.79-7.75(m,4H) ppm.

#### 6.2.4.6 2,6-Dimethyl-4-(tricyanoethene)phenol (102)

A solution of compound (99) (304 mg, 1.6 mmol), malononitrile (163 mg, 2.4 mmol) and  $\beta$ -alanine (30 mg, 0.3 mmol) dissolved in dry DMF, under an atmosphere of nitrogen, was heated at 80°C for 18h. After cooling, water was added to the solution until precipitation of the product ceased. The precipitate was filtered off and washed with water. The product was taken up into dichloromethane and precipitated by addition of hexane, yielding compound (102) (168 mg, 47%) as an orange-red solid. MPt. 174-176°C; EI m/e: 223 (M<sup>+</sup>); CI m/e: 224; Analysis found: C, 70.3; H, 4.0; N, 18.8. Calculated for C<sub>13</sub>H<sub>9</sub>N<sub>3</sub>O: C, 70.0; H, 4.0; N, 18.8%; IR  $\nu_{\max}$  (Nujol): 3400, 2230, 1598, 1522, 1480, 1310, 1290, 1210, 1170, 935, 890 and 745 cm<sup>-1</sup>;  $\delta$ H(250MHz, CDCl<sub>3</sub>): 7.80(s,2H) and 2.33(s,6H) ppm.

#### 6.2.5 Preparation of N-Cyano-4-dicyanomethylene-cyclohexa-2,5-dienylideneamine Derivatives

##### 6.2.5.1 General Procedure

The reactions were performed in dry dichloromethane and under an atmosphere of nitrogen. The TiCl<sub>4</sub> was freshly distilled and stirred

under nitrogen.

A stirred solution of the 4-dicyanomethylene-p-benzoquinone derivative dissolved in dichloromethane at 0-5°C was treated with  $\text{TiCl}_4$ . An orange-brown precipitate formed immediately, and the solution was stirred for 30 mins at 0-5°C. Bis(trimethylsilyl)carbodiimide<sup>156</sup> was added rapidly and the reaction mixture stirred at room temperature. Upon completion of reaction, further dichloromethane was added to the mixture until all the precipitate had dissolved. The solution was then washed with water and dried ( $\text{MgSO}_4$ ). The dichloromethane was removed *in vacuo*. Elution of the residue through a short silica column, with dichloromethane as eluent, yielded the product. Further purification, if needed, could be achieved by recrystallisation from dichloromethane-hexane.

#### 6.2.5.2 N-Cyano-2,6-dimethyl-4-dicyanomethylene-cyclohexa-2,5-dienylideneamine (116)

A solution of compound (99) (424 mg, 2.3 mmol),  $\text{TiCl}_4$  (547 mg, 2.9 mmol) and bis(trimethylsilyl)carbodiimide (534 mg, 2.9 mmol) in dichloromethane (20 ml) was stirred at room temperature for 40h. Dissolving the chromatographed material in dichloromethane (10 ml) and adding hexane (50 ml), yielded compound (116) (373 mg, 78%) as an orange-yellow solid. Mpt. ca. 260°C (dec); EI m/e: 208 ( $\text{M}^+$ ); CI m/e: 209; Analysis found: C, 69.3; H, 3.7; N, 26.9. Calculated for  $\text{C}_{12}\text{H}_8\text{N}_4$ : C, 69.2; H, 3.8; N, 26.9%; IR  $\nu_{\text{max}}$  (Nujol): 2235, 2150, 1625, 1570, 1550, 1495, 1385, 1260, 1210, 1043, 970, 945, 915, 762, 725, 655, 550 and 465  $\text{cm}^{-1}$ ;  $\delta\text{H}$ (250MHz,  $\text{CDCl}_3$ ): 7.37(s, br, 2H) and 2.50(s, vbr, 6H) ppm.

6.2.5.3 N-Cyano-2,3,6-trimethyl-4-dicyanoethylene-cyclohexa-2,5-dienylideneamine (117)

A solution of compound (100) (257 mg, 1.3 mmol),  $\text{TiCl}_4$  (308 mg, 1.6 mmol) and bis(trimethylsilyl)carbodiimide (297 mg, 1.6 mmol) in dichloromethane (12 ml) was stirred at room temperature for 40h. This yielded compound (117) (255 mg, 88%) as a dark-red solid. MPt.  $136^\circ\text{C}$  (dec); EI m/e: 236 ( $\text{M}^+$ ); Analysis found: C, 70.6; H, 4.4; N, 25.3. Calculated for  $\text{C}_{13}\text{H}_{10}\text{N}_4$ : C, 70.2; H, 4.5; N, 25.2%; IR  $\nu_{\text{max}}$  (KBr): 2220, 2160, 2140, 1630, 1540, 1445, 1408, 1380, 1310, 1230, 1130, 1040, 1015, 935, 890, 755, 665 and  $545\text{ cm}^{-1}$ ;  $\delta\text{H}(250\text{MHz}, \text{CDCl}_3)$ : 7.45(s, 1H), 2.58(s, 6H) and 2.33(s, 3H) ppm.

6.2.5.4 N-Cyano-2,3,5,6-tetramethyl-4-dicyanoethylene-cyclohexa-2,5-dienylideneamine (118)

A solution of compound (101) (100 mg, 0.47 mmol),  $\text{TiCl}_4$  (134 mg, 0.7 mmol) and bis(trimethylsilyl)carbodiimide (131 mg, 0.7 mmol) in dichloromethane (10 ml) was stirred at room temperature for 60h. This yielded compound (118) (97 mg, 87%) as a yellow solid. MPt.  $192^\circ\text{C}$  (dec); EI m/e: 222 ( $\text{M}^+$ ); CI m/e: 223; Analysis found: C, 71.3; H, 5.1; N, 23.8. Calculated for  $\text{C}_{14}\text{H}_{12}\text{N}_4$ : C, 71.2; H, 5.1; N, 23.7%; IR  $\nu_{\text{max}}$  (KBr): 2220, 2160, 1560 and  $1383\text{ cm}^{-1}$ ;  $\delta\text{H}(250\text{MHz}, \text{CDCl}_3)$ : 2.40(s, br, 6H) and 2.21(s, br, 6H) ppm.

#### 6.2.5.5 N-Cyano-10-dicyanomethylene-9,10-dihydroanthracene-9-ylideneamine (119)

10-Dicyanomethyleneanthrone (38) (144 mg, 0.56 mmol),  $\text{TiCl}_4$  (133 mg, 0.7 mmol) and bis(trimethylsilyl)carbodiimide (130 mg, 0.7 mmol) dissolved in dichloromethane (25 ml) was stirred at room temperature for 72h. Silica column chromatography, eluting with toluene yielded unreacted starting material (38) followed by compound (119) (60 mg, 38%) as a yellow solid. Mpt.  $242^\circ\text{C}$  (dec); EI m/e: 280 ( $\text{M}^+$ ); CI m/e: 281; Analysis found: C, 77.3; H, 2.5; N, 19.9. Calculated for  $\text{C}_{18}\text{H}_8\text{N}_4$ : C, 77.1; H, 2.9; N, 20.0%; IR  $\nu_{\text{max}}$  (KBr): 2230, 2180, 1610, 1590, 1565, 1465, 1338, 1300, 1288, 800, 790 and  $690\text{ cm}^{-1}$ ;  $\delta\text{H}$ (250MHz,  $\text{CDCl}_3$ ): 8.90(m, br, 1H), 8.32-8.29(m, 3H) and 7.82-7.80(m, 5H) ppm.

#### 6.2.6 2,6-Dimethyl-1,4-cyclohexanediol (105)

2,6-Dimethyl-p-benzoquinone (104) (2 g, 14.7 mmol), activated nickel (1 level teaspoon) and ethanol (25 ml) were placed in a bomb (150 ml capacity). Air was evacuated and the bomb flushed with hydrogen several times. The reduction was then carried out at  $150^\circ\text{C}$  at an initial hydrogen pressure of 140 atms, over 24h. After cooling, the catalyst was removed by filtration and the solvent was removed *in vacuo* from the filtrate. The resultant pale yellow oil (2.1 g, 100%), identified as compound (105) by i.r. spectroscopy, was not purified but was used directly in the following oxidation step. IR  $\nu_{\text{max}}$  (Neat): 3320 (broad, OH), 2900, 1445, 1360, 1300, 1220, 1175, 1112, 1090, 1030, 968, 930, 880, 830, 813, 800 and  $600\text{ cm}^{-1}$  *cf.* Lit.<sup>127</sup>.

### 6.2.7 2,6-Dimethyl-1,4-cyclohexanedione (106)

A solution of chromium trioxide (26.72 g, 0.27 mol), water (77 ml), concentrated sulphuric acid (23 ml) and manganese sulphate (0.2g) was added slowly to a stirred solution of crude 2,6-dimethyl-1,4-cyclohexanediol (105) (635 mg, 4.4 mmol) in chloroform (18 ml) at 5°C. The addition was stopped after 3 equivalents (5 ml) of chromium trioxide had been introduced (30 mins). Stirring at 20°C was continued for 4h and then the chloroform layer was separated. The aqueous layer was extracted with chloroform (3 x 50 ml) and the combined extracts were washed with an aqueous solution of concentrated ammonium hydroxide (1 ml) in saturated sodium chloride (10 ml). The chloroform layers were combined, dried (MgSO<sub>4</sub>) and the solvent removed *in vacuo*. Vacuum sublimation of the residue at *ca.* 80°C (0.001 mbar Hg) yielded the diketone (106) (479 mg, 78%) as a white solid. MPt. 88-90°C (*cf.* Lit. 87-88°C)<sup>127</sup>; EI m/e: 140 (M<sup>+</sup>); CI m/e: 141; Analysis found: C, 68.3; H, 8.8. Calculated for C<sub>8</sub>H<sub>12</sub>O<sub>2</sub>: C, 68.6; H, 8.6%; IR  $\nu_{\max}$  (KBr): 2980, 2960, 2935, 2900, 2880, 1710(strong), 1450, 1420, 1375, 1290, 1270, 1145, 1000, 925, 850, 760, 735 and 510 cm<sup>-1</sup>;  $\delta$ H(250MHz, CDCl<sub>3</sub>): 2.82(m, 2H), 2.75(m, 2H), 2.36(m, 2H) and 1.05(m, 6H) ppm.

### 6.2.8 2,6-Dimethyl-4-dicyanomethylene-cyclohexanone (108)

A solution of diketone (106) (2.04g, 14.5 mmol), malononitrile (1.44 g, 22 mmol) and  $\beta$ -alanine (170 mg, 1.9 mmol) dissolved in water (22 ml) was heated at reflux for 1h. On cooling, the aqueous solution was extracted with chloroform (3 x 50 ml). The organic layer was separated, dried (MgSO<sub>4</sub>) and the solvent removed *in vacuo*. Silica column chromatography of the resulting yellow, thick oil, eluting with

dichloromethane-toluene (2:1 v/v) yielded compound (108) (2.3 g, 84%) as an off-white solid, which was not obtained as an analytically pure sample. MPt. 55-57°C; EI m/e: 188 (M<sup>+</sup>); CI m/e: 189; Analysis found: C, 68.4; H, 6.3; N, 14.6. Calculated for C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>O: C, 70.2; H, 6.4; N, 14.9%; IR  $\nu_{\max}$  (KBr): 2970, 2930, 2870, 2238, 1720, 1605, 1450, 1375, 1245, 1145, 1128, 1095, 1045, 1008, 987, 880 and 750 cm<sup>-1</sup>;  $\delta$ H(250MHz, CDCl<sub>3</sub>): 3.26(m,2H), 2.63(m,2H), 2.46(m,2H) and 1.10(m,6H) ppm.

#### 6.2.9 1-Oxo-2,6-dimethyl-4-dicyanomethylene-2,5-cyclohexadiene (99)

A stirred solution of compound (108) (86 mg, 0.46 mmol) and bromine (154 mg, 0.96 mmol) in dry acetonitrile (5 ml) under an atmosphere of nitrogen was cooled to 0-5°C. Pyridine (145 mg, 1.84 mmol) was slowly syringed into the reaction vessel over a period of 15 mins. The mixture was then stirred at room temperature for a further 15h. Water (10 ml) was added and the aqueous solution extracted with chloroform (50 ml). The organic layer was separated, dried (MgSO<sub>4</sub>) and the solvent removed *in vacuo*. Vacuum sublimation of the resulting brown solid (*ca.* 100°C, 0.001 mbar Hg) yielded compound (99) (50 mg, 59%) as an orange solid. MPt. 134-138°C; Analysis found: C, 71.5; H, 4.4; N, 15.1. Calculated for C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>O: C, 71.7; H, 4.3; N, 15.2%; Spectroscopic data were identical with the material described earlier (Section 6.2.4.2).

## 6.2.10 Preparation of Copper Salts of N-Cyano-4-dicyanomethylene-cyclohexa-2,5-dienylideneamine Derivatives

### 6.2.10.1 General Procedure

Shiny copper wire was immersed into a solution of the N-Cyano-4-dicyanomethylene-cyclohexa-2,5-dienylideneamine derivative, dissolved in dry acetonitrile, under an atmosphere of nitrogen. When the solution had become colourless, the dark purple powder was scraped off the copper wire and dried *in vacuo*.

### 6.2.10.2 Copper Salt of 2,6-dimethyl-TCNQI (116a)

Compound (116) (22 mg, 0.1 mmol) dissolved in dry acetonitrile (5 ml) yielded the dark purple copper salt (17 mg, 58%). MPt. >240°C; Analysis found: C, 49.0; H, 2.6; N, 18.6. Calculated for  $\text{Cu}_4(2,6\text{-DMTCNQI})_3$ : C, 49.2; H, 2.7; N, 19.1%; IR  $\nu_{\text{max}}$  (KBr): 2210, 2150, 1590, 1485, 1390, 1290 and 1210  $\text{cm}^{-1}$ .

### 6.2.10.3 Copper Salt of 2,3,6-trimethyl-TCNQI (117a)

Compound (117) (20 mg, 0.09 mmol) dissolved in dry acetonitrile (5 ml) yielded the dark copper salt (14 mg, 51%). MPt. >240°C; Analysis found: C, 50.8; H, 3.4; N, 18.0. Calculated for  $\text{Cu}_4(2,3,6\text{-TMTCNQI})_3$ : C, 50.9; H, 3.3; N, 18.3%; IR  $\nu_{\text{max}}$  (KBr): 2200, 2130, 2040, 1580, 1470, 1385, 1320, 1290 and 1160  $\text{cm}^{-1}$ .

#### 6.2.10.4 Copper Salt of TCNAQI (119a)

Compound (119) (20 mg, 0.07 mmol) dissolved in dry acetonitrile yielded the black copper salt (12 mg). MPt.  $>240^{\circ}\text{C}$ ; Analysis found: C, 65.1; H, 2.2; N, 18.2. Calculated for  $\text{Cu}_3[\text{TCNAQI}]_4 \cdot \text{CH}_3\text{CN}$ : C, 65.7; H, 2.6; N, 17.6%; IR  $\nu_{\text{max}}$  (KBr): very broad spectra ( $250\text{-}4000\text{ cm}^{-1}$ ) with no definable peaks.

#### 6.2.11 Tetrathiafulvalene Complex with (99)

A hot saturated solution of TTF (40 mg, 0.2 mmol) dissolved in absolute ethanol was added to a hot, saturated solution of compound (99) (36 mg, 0.2 mmol) dissolved in absolute ethanol. The solution was slowly cooled to room temperature and then placed in a freezer at  $-20^{\circ}\text{C}$ . After 168h the dark green, crystalline complex was filtered, and dried *in vacuo* (35 mg, 46%). MPt.  $128\text{-}132^{\circ}\text{C}$ ; Analysis found: C, 52.1; H, 3.0; N, 6.0. Calculated for TTF-(99) (1:1): C, 52.5; H, 3.1; N, 7.2%; IR  $\nu_{\text{max}}$  (KBr): 3065, 2225, 1630, 1590, 1365, 1200, 890, 800, 780, 775, 735, 680, 660 and  $440\text{ cm}^{-1}$ .

#### 6.2.12 Tetrathiafulvalene Complex with (100)

Complexation of TTF (10 mg, 0.049 mmol) and compound (100) (10 mg, 0.05 mmol) was achieved by the procedure described above (Section 6.2.11). This yielded a dark green, crystalline complex (5 mg, 25%). MPt.  $124\text{-}125^{\circ}\text{C}$ ; Analysis found: C, 54.4; H, 3.5; N, 6.9. Calculated for TTF-(100) (1:1): C, 53.7; H, 3.5; N, 6.9%; IR  $\nu_{\text{max}}$  (KBr): 3060, 2920, 2220, 1625, 1580 (very weak), 1385, 1375, 1290, 1220, 865, 800, 735, 675 and  $660\text{ cm}^{-1}$ .

### 6.2.13 4-Iodo-2,6-dimethylaniline hydrochloride (111)<sup>129</sup>

Redistilled iodine monochloride (8.15 g, 50 mmol) dissolved in glacial acetic acid (50 ml) was added slowly to a cooled (<10°C) solution of dimethylaniline (110) (8.4 g, 69 mmol) in glacial acetic acid (50 ml). The colour of the ICl disappeared and white crystals separated. The reaction mixture was set aside at 0°C for 12h, the amine hydrochloride was filtered off, washed with ether and dried. This yielded crude amine hydrochloride (8 g) as a dark green powder. The product was not purified but used directly in the synthesis of (112).

### 6.2.14 1,4-Diiodo-2,6-dimethylbenzene (112)

Crude hydrochloride (111) (1 g) was dissolved in boiling water (15 ml) and the hot solution was filtered. Sodium nitrite (220 mg, 3.2 mmol) dissolved in water (1.5 ml) was added dropwise to the cooled filtrate (0-5°C) and the mixture was stirred for 30 mins, with the temperature being maintained at 0-5°C. Potassium iodide (3.5 g, 21 mmol) in water (8 ml) was added slowly (10 mins) to the reaction mixture, and the solution was stirred at 0-5°C for 1h. The reaction mixture was then heated to reflux. After cooling, the aqueous solution was extracted with dichloromethane. The organic layer was separated, dried (MgSO<sub>4</sub>) and the solvent removed *in vacuo*. Silica column chromatography, eluting with hexane, yielded compound (112) [308 mg, 10% based on 2,6-dimethylaniline (110)] as a white solid. MPt. 61-64°C; EI m/e: 358 (M<sup>+</sup>); CI m/e: 359; Analysis found: C, 26.5; H, 2.2. Calculated for C<sub>8</sub>H<sub>8</sub>I<sub>2</sub>: C, 26.8; H, 2.2%; IR  $\nu_{\max}$  (Nujol): 1560, 1545, 1260, 1130, 1055, 1026, 1008, 850, 811, 688 and 530 cm<sup>-1</sup>;  $\delta$ H(250MHz, CDCl<sub>3</sub>): 7.23 (s, 2H) and 2.20(s, 6H) ppm.

#### 6.2.15 2-Iodo-5-dicyanomethyl-1,3-dimethylbenzene (114)

Sodium hydride dispersion (60% in paraffin; 160 mg, 4 mmol) was placed in a 20 ml flask and the paraffin oil removed by washing with dry hexane (3 x 1 ml). HMPA (1 ml) was added to the remaining solid and a solution of malononitrile (238 mg, 3.6 mmol) dissolved in HMPA (2.5 ml) was added with stirring. After 15 mins, compound (112) (324 mg, 0.9 mmol) dissolved in HMPA (1 ml) was added, followed by copper iodide (689 mg, 3.6 mmol), and the mixture was gradually heated to 120°C and maintained at this temperature for 3h. The black mixture was quenched with dilute hydrochloric acid, and the organic phase extracted with ether, and the extract washed with aqueous sodium sulphite to remove any free iodine. The solvent was evaporated *in vacuo* to leave a brown residue. Silica column chromatography, with dichloromethane eluent, gave unchanged diiodide (112), followed by compound (114) (38 mg, 14%) as a white solid. Compound (114) was identified by i.r. and <sup>1</sup>H NMR spectroscopy. MPt. 85-90°C; EI m/e: 296 (M<sup>+</sup>); IR  $\nu_{\max}$  (Nujol): 2260, 1283, 1265, 1031, 1019, 1005, 970, 892, 850 and 746 cm<sup>-1</sup>;  $\delta$ H(60MHz, CDCl<sub>3</sub>): 7.06(s,2H), 4.80(s,1H) and 2.46(s,6H) ppm.

#### 6.2.16 Dicyanomethylene-(2,6-dimethyl-4-iodophenyl)hydrazone) (115)

Crude amine hydrochloride (111) (500 mg) was dissolved in boiling water (10 ml) and the solution filtered. After cooling to 0-5°C, sodium nitrite (110 mg, 1.6 mmol) dissolved in water (1 ml) was slowly added (10 mins). The reaction mixture (at 0-5°C) was then stirred for a further 45 mins. Malononitrile (115 mg, 5.2 mmol) was added and the mixture stirred at room temperature for 15h. The aqueous layer was extracted with chloroform. The organic phase was then separated, dried

( $\text{MgSO}_4$ ) and the solvent removed *in vacuo*, leaving a dark-brown residue. Silica column chromatography, eluting with hexane, yielded compound (115) [150 mg, 11% based on 2,6-dimethylaniline (110)] as a yellow solid. Recrystallisation from water, afforded an analytically pure sample. MPt. 140-143°C; EI m/e: 324 ( $\text{M}^+$ ); Analysis found: C, 40.9; H, 2.6; N, 17.5. Calculated for  $\text{C}_{11}\text{H}_9\text{N}_4\text{I}$ : C, 40.7; H, 2.8; N, 17.3%; IR  $\nu_{\text{max}}$  (KBr): 3210, 2235, 2220, 1540, 1455, 1290, 1270, 1244, 880, 852 and 645  $\text{cm}^{-1}$ ;  $\delta\text{H}$ (250MHz,  $\text{CDCl}_3$ ): 9.39(s,br,1H), 7.47(s,2H) and 2.29(s,6H) ppm.

### 6.3 EXPERIMENTAL TO CHAPTER 3

#### 6.3.1 2-Dicyanonethylene-1,3-indandione, DCID (122)

To a mechanically stirred solution of malononitrile (32.0 g, 0.48 mol) dissolved in hot water (500 ml) was added a solution of ninhydrin (32.0 g, 0.18 mol) dissolved in hot water (800 ml). A yellow precipitate formed almost immediately and the mixture was heated at reflux for 5 min. After cooling, the product was filtered, dried in air and then recrystallised from acetonitrile to yield compound (122) (26.0 g, 70%) as shiny yellow plates. MPt. 260-267°C (dec) (Lit. 281°C)<sup>136</sup>; EI m/e: 208 ( $\text{M}^+$ ); CI m/e: 209; Analysis found: C, 69.6; H, 1.9; N, 13.4. Calculated for  $\text{C}_{12}\text{H}_4\text{N}_2\text{O}_2$ : C, 69.2; H, 1.9; N, 13.5%; IR  $\nu_{\text{max}}$  (Nujol): 2230 ( $\text{C}\equiv\text{N}$ , very weak), 1749, 1705 ( $\text{C}=\text{O}$ , very strong), 1678, 1610, 1580, 1357, 1326, 1280, 1250, 1235, 1222, 1068, 810, 748, 665 and 628  $\text{cm}^{-1}$ ;  $\delta\text{H}$ (250MHz,  $\text{d}^6$ -acetone): 8.16(s,4H) ppm. This material was identical to that reported in the literature from reaction of 1,3-indandione and tetracyanoethylene<sup>136</sup>.

### 6.3.2 Lithium Salt of 2,3-dicyanonaphthoquinone (123a)

DCID (122) (1.0 g, 4.8 mmol) and lithium iodide (0.96 g, 7.2 mmol) were mixed together in dry acetonitrile (30 ml). The solution, which instantly turned dark, was heated at reflux for 1h, then cooled to room temperature and filtered. The precipitate was washed with ether and dried in air to yield salt (123a) (0.97 g, 94%) as a dark green powder. Analysis found: C, 66.6; H, 2.0; N, 13.1; Li, 3.0. Calculated for  $\text{LiC}_{12}\text{H}_4\text{N}_2\text{O}_2$ : C, 67.0; H, 1.9; N, 13.0; Li, 3.3%; IR  $\nu_{\text{max}}$  (KBr): 2250 (strong), 1615, 1575, 1515, 1450, 1385, 1322, 1282, 1200, 1180, 1150, 900, 793, 705, 660, 600, 540, 455, 385 and  $320\text{ cm}^{-1}$ . This material was identical (i.r. spectrum) to a sample prepared (45% yield) from lithium iodide and authentic 2,3-dicyanonaphthoquinone which was prepared, in turn, from 2,3-dichloronaphthoquinone<sup>139</sup>.

### 6.3.3 Metal and Organic Cation Salts of 2,3-dicyanonaphthoquinone (123b)-(123k)

These salts were prepared by metathesis reaction of the lithium salt (123a) and the appropriate metal or organic cation salt in water, as shown in Table 3.1 (Chapter 3). The product precipitated very rapidly and was collected by filtration and then dried *in vacuo*. Salt (123b) was also prepared by direct reaction of DCID (122) with methyl-triphenylphosphonium iodide in acetonitrile, in 45% yield.

Crystals of salt (123b) suitable for x-ray analysis were grown as follows. Salt (123b) (500 mg) was dissolved in a boiling mixture of ethanol (10 ml) and petroleum ether (bpt.  $100\text{-}120^\circ\text{C}$ ; 80 ml) and the mixture was allowed to cool slowly to room temperature to give salt (123b) as shiny black crystals which were dried in air.

#### 6.3.4 Sodium Salt of 2,3-dicyanonaphthoquinone (123c)

DCID (122) (300 mg, 1.5 mmol) was dissolved in dry tetrahydrofuran (5 ml) under an atmosphere of nitrogen, and finely cut sodium metal (33 mg, 1.5 mmol) was added. The mixture was stirred at room temperature for 48h. The precipitate was filtered, washed with ether and dried *in vacuo*, to afford salt (123c) as a green solid (75 mg, 22%). Salt (123c) prepared by this route, was identical with a sample prepared from lithium salt (123a) and sodium iodide in water (50%).

#### 6.3.5 Tetrathiafulvalene Complex with 2,3-dicyanonaphthoquinone (123l)

A hot solution of TTF (40 mg, 0.19 mmol) dissolved in dry acetonitrile (5 ml) was added to a hot solution of DCID (122) (40 mg, 0.19 mmol) in dry acetonitrile (*ca.* 5 ml) and the mixture cooled slowly to 0°C. The black crystalline complex was filtered and dried *in vacuo* (63 mg, 94%). The identical complex (123l) was prepared from TTF and 2,3-dicyanonaphthoquinone (123) in 75% yield. Analysis found: C, 48.9; H, 1.9; N, 5.4. Calculated for  $C_{42}H_{20}N_4O_4S_{12}$  *ie.* (TTF)<sub>3</sub>(DCNQ)<sub>2</sub>: C, 49.0; H, 1.9; N, 5.5%; IR  $\nu_{max}$  (KBr): 2190, 1542, 1490, 1435, 1370, 1272, 1095, 885, 732, 700, 675, 660 and 460  $cm^{-1}$ .

#### 6.3.6 Tetramethyltetrathiafulvalene (TMTTF) Complex with 2,3-dicyanonaphthoquinone (123m)

This complex was prepared in exactly the same manner as the TTF complex (123l). DCID (122) (20 mg, 0.096 mmol) and TMTTF (4) (25 mg, 0.096 mmol) yielded complex (123m) as shiny black crystals (28 mg, 73%). Analysis found: C, 53.9; H, 3.5; N, 4.3. Calculated for  $C_{54}H_{44}N_4O_4S_{12}$

ie.  $(\text{TTF})_3(\text{DCNQ})_2$ : C, 54.1; H, 3.7; N, 4.7%; IR  $\nu_{\text{max}}$  (KBr): C≡N stretching frequencies, if present are obscured by a broad charge transfer band; 1580, 1553, 1522, 1427, 1300 (very broad), 1080, 920, 880, 782, 692 and  $455 \text{ cm}^{-1}$ .

## 6.4 EXPERIMENTAL TO CHAPTER 4

### 6.4.1 Preparation of Tetrathiafulvalene-1,3-Dinitrobenzene Complex (127a)

A solution of TTF (80 mg, 0.39 mmol) in hot toluene (3 ml) was added to a solution of m-dinitrobenzene (127) (66 mg, 0.39 mmol) in hot toluene (2 ml). The solution instantly turned very dark and was cooled slowly to  $0^\circ\text{C}$ . The resulting black crystals were recovered by filtration, washed with cold hexane (3 ml) and dried *in vacuo* to afford a 1:1 complex (123 mg, 84%). Mpt.  $105\text{-}108^\circ\text{C}$ ; Analysis found: C, 38.4; H, 2.0; N, 7.3. Calculated for  $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_4\text{S}_4$ : C, 38.7; H, 2.2; N, 7.5%; IR  $\nu_{\text{max}}$  (KBr): 3077, 1597, 1525, 1335, 1252, 900, 797, 725, 707 and  $662 \text{ cm}^{-1}$ .

### 6.4.2 Preparation of Tetrathiafulvalene-1,3,5-Trinitrobenzene Complex (128a)

Equimolar amounts of TTF (40 mg, 0.20 mmol) and 1,3,5-trinitrobenzene (128) (42 mg) were dissolved in toluene and the solutions mixed together. Slow evaporation of the toluene, under nitrogen, afforded the (1:1) complex (82 mg, 100%) as black needles. Mpt.  $149\text{-}153^\circ\text{C}$ ; Analysis found: C, 34.5; H, 1.3; N, 9.7. Calculated for  $\text{C}_{12}\text{H}_7\text{N}_3\text{O}_6\text{S}_4$ : C, 34.5; H, 1.7; N, 10.1%; IR  $\nu_{\text{max}}$  (Nujol): 1613, 1530, 1337, 1250, 1070, 925, 920,

900, 800, 782, 731, 713, 680, 658 and 642  $\text{cm}^{-1}$ .

## 6.5 EXPERIMENTAL TO CHAPTER 5

### 6.5.1 4,5,6,7-Tetrachloro-2-dicyanomethylene-1,3-indandione (130)

Tetracyanoethylene (428 mg, 3.3 mmol) was added to a warm solution of 4,5,6,7-tetrachloro-1,3-indandione (131) (427 mg, 1.5 mmol) dissolved in absolute ethanol (80 ml). The mixture was then stirred at room temperature for 30 min. The resulting yellow precipitate was filtered, washed with cold ethanol and dried *in vacuo*, to afford compound (130) (410 mg, 79%). Mpt. 250°C (dec); EI m/e:  $\text{M}^+$  absent; Analysis found: C, 41.4; H, 8.4. Calculated for  $\text{C}_{12}\text{N}_2\text{O}_2\text{Cl}_4$ : C, 41.6; H, 8.1%; IR  $\nu_{\text{max}}$  (KBr): 1750, 1710, 1628, 1540, 1382, 1372, 1295, 1210, 1182, 1138, 935, 800, 741, 640 and 340  $\text{cm}^{-1}$ .

### 6.5.2 Tetrathiafulvalene Complex with Tetrachloro-DCID (130a)

Hot saturated solutions of (130) (20 mg,  $5.8 \times 10^{-5}$  mol) and TTF (12 mg,  $5.8 \times 10^{-5}$  mol) in dry acetonitrile, were mixed and allowed to cool to room temperature. The resulting black precipitate was filtered and dried in a desiccator (over silica gel), yielding complex (130a) (6.5 mg, 21%). Mpt. >250°C (dec); Analysis found: C, 39.0; H, 0.6; N, 5.0. Calculated for  $\text{C}_{18}\text{H}_4\text{N}_2\text{O}_2\text{S}_4\text{Cl}_4$  (1:1 complex): C, 39.3; H, 0.7; N, 5.1%; IR  $\nu_{\text{max}}$  (KBr): 3090, 2190, 2160, 1655, 1637, 1535, 1493, 1470, 1435, 1342, 1320, 1300, 1250, 1183, 1128, 1087, 830, 760, 750, 735, 690 and 490  $\text{cm}^{-1}$ .

### 6.5.3 1,3-Bis(dicyanoethylene)indane (132)

A solution of 1,3-indandione (2.4 g, 16 mmol), malononitrile (2.7 g, 41 mmol) and ammonium acetate (1.25 g, 16 mmol) dissolved in absolute ethanol (30 ml) was heated at reflux for 30 min. After cooling to room temperature, water (25 ml) was added and the solution acidified with concentrated hydrochloric acid. The brown precipitate was filtered and washed with water. Recrystallisation from glacial acetic acid afforded compound (132) (1.6 g, 41%) as a yellow-brown solid. MPt. 249-253°C; EI m/e: 242 ( $M^+$ ); CI (i-Bu) m/e: 243; Analysis found: C, 74.1; H, 2.4; N, 23.1. Calculated for  $C_{15}H_6N_4$ : C, 74.4; H, 2.5; N, 23.1%; IR  $\nu_{\max}$  (KBr): 2920, 2895, 2870, 2230 ( $C\equiv N$ , very strong), 1595, 1575, 1475, 1455, 1385, 1340, 1315, 1280, 1275, 1220, 1195, 1160, 1070, 905, 785, 620 and 390  $cm^{-1}$ ;  $\delta H(250MHz, CDCl_3)$ : 8.64-8.60(m,  $J_{AB}=6Hz, J_{AB'}=3Hz, 2H$ ), 7.90-7.86(m,  $J_{BA}=6Hz, J_{BA'}=3Hz, 2H$ ) and 4.27(s, 2H) ppm.

### 6.5.4 2,2-Dibromo-1,3-bis(dicyanoethylene)indane (136)

Compound (132) (300 mg, 1.24 mmol), N-bromosuccinimide (441 mg, 2.48 mmol) and AIBN (10 mg) in dry carbon tetrachloride were heated at reflux for 1h. After cooling to room temperature, the precipitate was filtered and washed with water. Recrystallisation from glacial acetic acid afforded compound (136) (304 mg, 61%) as pale yellow needles. MPt. 270°C (dec); EI m/e:  $M^+$  absent; CI (i-Bu) m/e: 399(60), 400(13) 401(100), 402(22), 403(59), 404(11); Analysis found: C, 45.3; H, 1.0; N, 14.0. Calculated for  $C_{15}H_4N_4Br_2$ : C, 45.0; H, 1.0; N, 14.0%; IR  $\nu_{\max}$  (KBr): 2230, 1595, 1560, 1460, 1320, 1273, 1200, 1175, 800, 785, 710, 633 and 526  $cm^{-1}$ ;  $\delta H(250MHz, CDCl_3)$ : 8.79-8.78(dd,  $J_{AB}=6.0Hz, J_{AB'}=3.1Hz, 2H$ ) and 8.03-7.99(dd,  $J_{BA}=6.0Hz, J_{BA'}=3.1Hz, 2H$ ) ppm.

### 6.5.5 2,2-Dichloro-1,3-bis(dicyanomethylene)indane (135)

Compound (132) (267 mg, 1.1 mmol), N-chlorosuccinimide (294 mg, 2.2 mmol), benzoyl peroxide (10 mg) and dry carbon tetrachloride (25 ml) under an atmosphere of nitrogen were heated at reflux for 4h. The workup was as previously described for the dibromo compound (136) (Section 6.5.4). This procedure yielded compound (135) (239 mg, 70%) as pale green needles. MPt. 265°C (dec); DCI m/e: 311; Analysis found: C, 57.6; H, 1.1; N, 18.3. Calculated for  $C_{15}H_4N_4Cl_2$ : C, 57.9; H, 1.3; N, 18.0%; IR  $\nu_{max}$  (KBr): 2230, 1605, 1570, 1325, 1275, 1225, 1200, 1100, 824, 807, 758 and 655  $cm^{-1}$ ;  $\delta H(250MHz, CDCl_3)$ : 8.79-8.75(dd,  $J_{AB}=6.0Hz$ ,  $J_{AB'}=3.0Hz, 2H$ ) and 8.07-8.04(dd,  $J_{BA}=6.0Hz$ ,  $J_{BA'}=3.0Hz, 2H$ ) ppm.

### 6.5.6 1-Ethoxy-3-dicyanomethylene-indan-1-ene (133)

A solution of 1,3-indandione (2.0 g, 13.7 mmol), malononitrile (2.25 g, 34 mmol) and ammonium acetate (300 mg, 3.9 mmol) dissolved in absolute ethanol (100 ml) was heated at reflux for 24h. The solvent was removed *in vacuo*, leaving a purple solid. The red product was extracted from the solid with boiling petroleum ether (Bpt. 40-60°C). Eluting the extract with chloroform, through a short alumina column, followed by vacuum sublimation (*ca.* 120°C, 0.001 mbar Hg) afforded compound (133) (134 mg, 4%) as a red powder. MPt. 140-143°C; EI m/e: 222 ( $M^+$ ); CI (i-Bu) m/e: 223; Analysis found: C, 75.7; H, 4.2; N, 12.8. Calculated for  $C_{14}H_{10}N_2O$ : C, 75.7; H, 4.5; N, 12.6%; IR  $\nu_{max}$  (KBr): 3100, 2225, 1610, 1545, 1455, 1400, 1382, 1360, 1300, 1265, 1230, 1138, 1100, 1085, 1018, 1005, 875, 805, 755, 676 and 640  $cm^{-1}$ ;  $\delta H(60MHz, CDCl_3)$ : 8.00(m, 1H), 7.2(m, 3H), 5.6(s, 1H), 4.2(q,  $J=7.1Hz, 2H$ ) and 1.5(t,  $J=7.1Hz, 3H$ ) ppm.

### 6.5.7 Tetrathiafulvalene Complex with 1,3-bis(dicyanomethylene)indane (132a)

A hot, saturated solution of compound (132) (25 mg, 0.1 mmol) dissolved in dry acetonitrile, was added to a hot, saturated solution of TTF (21 mg, 0.1 mmol) in dry acetonitrile. The mixture was cooled to room temperature and the solvent allowed to partially evaporate. The resulting precipitate was filtered and dried *in vacuo*, yielding a black complex (132a) (30 mg, 65%). MPt. >260°C; Analysis found: C, 56.4; H, 2.2; N, 12.5. Calculated for C<sub>21</sub>H<sub>10</sub>N<sub>4</sub>S<sub>4</sub> (1:1 complex): C, 56.5; H, 2.2; N, 12.6%; IR  $\nu_{\max}$  (KBr): 2230, 1600, 1572, 1485, 800, 795, 780, 760, 660, 650, 620, 438 and 390 cm<sup>-1</sup>.

### 6.5.8 Amine Substituted 2-Dicyanomethylene-1,3-indandiones

#### 6.5.8.1 General Procedure

A mixture of DCID (122), amine (1 equivalent) and dry tetrahydrofuran (THF) was heated at reflux for 1-1.5h. The reaction mixture was then stirred at room temperature for 20h. The solvent was removed *in vacuo*, and column chromatography on alumina of the resulting solid, eluting with chloroform, yielded the desired product (as the first fraction). Recrystallisation afforded analytically pure samples.

#### 6.5.8.2 N-Piperidino-(1,3-dioxo-2-indanylidene)acetonitrile (137)

DCID (122) (342 mg, 1.6 mmol) and piperidine (136 mg) in THF (15 ml) yielded compound (137) (224 mg, 52%) as an orange solid. Recrystallisation from toluene-hexane (1:1 v/v) afforded an analytically

pure sample. MPt. 125-129<sup>o</sup>C; EI m/e: M<sup>+</sup> absent; CI m/e: 267; Analysis found: C, 72.6; H, 5.4; N, 10.2. Calculated for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.2; H, 5.3; N, 10.5%; IR  $\nu_{\max}$  (KBr): 2950, 2900, 2850, 2230 (C≡N, extremely weak), 1690, 1655, 1590, 1540, 1470, 1435, 1365, 1350, 1333, 1290, 1267, 1250, 1203, 1170, 1155, 1130, 1100, 1070, 1050, 1015, 1005, 920, 895, 860, 830, 805, 788, 740, 710, 670, 660, 565, 553, 530, 430 and 345 cm<sup>-1</sup>;  $\delta$ H(250MHz, CDCl<sub>3</sub>): 7.78-7.60(m,4H), 3.94(s,br,4H) and 1.90-1.79(m,6H) ppm.

#### 6.5.8.3 N-Butylamino-(1,3-dioxo-2-indanylidene)acetonitrile (138)

DCID (122) (250 mg, 1.2 mmol) and n-butylamine (88 mg) in dry THF (20 ml) yielded compound (138) (193 mg, 63%) as a light yellow solid. Recrystallisation from hexane afforded an analytically pure sample. MPt. 110-111<sup>o</sup>C; EI m/e: M<sup>+</sup> absent; CI (i-Bu) m/e: 255; Analysis found: C, 70.9; H, 5.7; N, 10.8. Calculated for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: C, 70.9; H, 5.5; N, 11.0%; IR  $\nu_{\max}$  (KBr): 3190, 2955, 2860, 2240 (C≡N, weak), 1700, 1650, 1540(broad), 1465, 1383, 1350, 1327, 1305, 1250, 1210, 1182, 1165, 1145, 1110, 1080, 1030, 990, 872, 810, 735, 710, 690, 665, 530, 400 and 350 cm<sup>-1</sup>;  $\delta$ H(60MHz, CDCl<sub>3</sub>): 7.7(m,4H), 3.6(t, J=6.5Hz, 2H), 2.0-1.4(m,4H) and 0.95(t, 3H) ppm.

#### 6.5.8.4 N-Benzylamino-(1,3-dioxo-2-indanylidene)acetonitrile (139)

DCID (122) (353 mg, 1.7 mmol) and benzylamine (181 mg) in THF (20 ml) yielded compound (139) (272 mg, 55%) as a golden yellow solid. Recrystallisation from toluene-hexane (1:1 v/v) afforded an analytically pure sample. MPt. 163-166<sup>o</sup>C; EI m/e: 288 (M<sup>+</sup>); CI m/e: 289; Analysis found: C, 74.9; H, 4.3; N, 9.5. Calculated for C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: C, 75.0; H,

4.2; N, 9.7%; IR  $\nu_{\max}$  (KBr): 1705, 1660, 1575, 1480, 1455, 1365, 1335, 1260, 1212, 1155, 1025, 1012, 875, 815, 760, 705, 660, 600 and 540  $\text{cm}^{-1}$ ;  $\delta\text{H}$ (60MHz,  $\text{CDCl}_3$ ): 7.58(m, 4H), 7.26(s, 5H) and 4.73(s, 2H) ppm.

#### 6.5.8.5 N-Octadecylamino-(1,3-dioxo-2-indanylidene)acetonitrile (140)

DCID (122) (396 mg, 1.9 mmol) and n-octadecylamine (511 mg) in THF (20 ml) were heated at reflux for 5h, and then stirred at room temperature for 18h. The workup procedure was as previously described (Section 6.5.8.1). Further purification using silica column chromatography, eluting with ether-hexane (4:1 v/v) provided a T.l.c pure but not analytically pure sample of compound (140) (389 mg, 45%) as a pale yellow solid. MPt. 90-94 $^{\circ}\text{C}$ ; EI m/e:  $\text{M}^+$  absent. Repeated chromatography and recrystallisation from acetonitrile, ethanol, toluene and hexane did not increase the purity. Analysis found: C, 78.1; H, 10.0; N, 5.4. Calculated for  $\text{C}_{29}\text{H}_{42}\text{N}_2\text{O}_2$ : C, 77.3; H, 9.3; N, 6.2%; IR  $\nu_{\max}$  (KBr): 3200, 2915, 2850, 1700, 1655, 1570, 1465, 1350, 1329, 1200, 1150 and 733  $\text{cm}^{-1}$ ;  $\delta\text{H}$ (250MHz,  $\text{CDCl}_3$ ): 9.85(s, br, 1H), 7.87-7.67(m, 4H), 3.66(q, J=6.8Hz, 2H), 1.74(quintet, J=7.0Hz, 2H), 1.25(m, 30H) and 0.88(t, J=6.5Hz, 3H) ppm.

#### 6.5.8.6 N-Piperidino-(4,5,6,7-tetrachloro-1,3-dioxo-2-indanylidene)acetonitrile (141)

Piperidine (51 mg, 0.6 mmol) was added to a mixture of tetrachloro-DCID (130) (209 mg, 0.6 mmol) partially dissolved in dry THF (20 ml). After heating at reflux for 2h the reaction mixture was cooled to room temperature and the resultant precipitate filtered. Drying the yellow precipitate in a desiccator yielded compound (141) (128 mg, 53%). MPt. 240-244 $^{\circ}\text{C}$  (dec); EI m/e: 404 ( $\text{M}^+$ ); Analysis found: C, 47.6; H, 2.4; N,

6.9. Calculated for  $C_{16}H_{10}N_2O_2Cl_4$ : C, 47.5; H, 2.5; N, 6.9%; IR  $\nu_{max}$  (KBr): 2940, 2860, 1705, 1663, 1565, 1550, 1453, 1440, 1360, 1300, 1270, 1255, 1200, 1190, 965, 777 and 733  $cm^{-1}$ ;  $\delta H(250MHz, CDCl_3)$ : 4.03(s, br, 2H), 3.86(s, br, 2H), 1.92(m, 4H) and 1.82(m, 2H) ppm.

#### 6.5.8.7 2-Cyano-3-(N-piperidino)-1,4-dioxo-1,4-dihydro-naphthalene (142)

A mixture of 2,3-dicyano-1,4-naphthoquinone (123) (140 mg, 0.67 mmol), piperidine (57 mg, 0.67 mmol) and dry THF (10 ml) was heated at reflux for 3h. The solvent was then removed *in vacuo*. Purification of the solid residue by alumina column chromatography, eluting with chloroform-hexane (4:1 v/v), followed by recrystallisation from methanol yielded compound (142) (16 mg, 9%) as an orange-red solid which was not analytically pure. Mpt. 106-114<sup>0</sup>C (dec); EI m/e: 266 ( $M^+$ ); CI m/e: 267; Analysis found: C, 71.3; H, 5.7; N, 9.8. Calculated for  $C_{16}H_{14}N_2O_2$ : C, 72.2; H, 5.3; N, 10.5%; IR  $\nu_{max}$  (KBr): 2920, 2850, 2210, 1680, 1625, 1590, 1550, 1413, 1405, 1340, 1338, 1315, 1290, 1260, 1210, 1172, 1020, 930, 737 and 715  $cm^{-1}$ ;  $\delta H(60MHz, CDCl_3)$ : 8.2-7.5(m, 4H), 4.06-3.66(m, 4H), and 2.06-1.43(m, 6H) ppm.

## APPENDICES

APPENDIX I - X-RAY CRYSTAL DATA

A. CRYSTAL DATA FOR SALT (123b).H<sub>2</sub>O

Chemical Formula: C<sub>31</sub>N<sub>2</sub>H<sub>22</sub>O<sub>2</sub>P; M = 485.1; Z = 2; triclinic; a = 11.92(1); b = 11.49(1); c = 11.81(1); α = 125.1(1); β = 85.1(1); γ = 83.1(1); V = 1290.1 Å<sup>3</sup>; dc = 1.28 g cm<sup>-3</sup>; dm = 1.28 g cm<sup>-3</sup>; F(000) = 506; MoKα radiation; λ = 0.7107 Å; μ = 1.45 cm<sup>-1</sup>; Spacegroup = Pī.

C(1)-C(2)	1.469(16)	C(2)-C(1)-C(10)	115.6(10)
C(1)-C(10)	1.506(15)	C(2)-C(1)-O(10)	121.7(10)
C(1)-O(10)	1.178(13)	C(10)-C(1)-O(10)	122.5(10)
C(2)-C(3)	1.404(18)	C(1)-C(2)-C(3)	124.6(11)
C(2)-C(11)	1.423(16)	C(1)-C(2)-C(11)	116.5(10)
C(3)-C(4)	1.526(16)	C(3)-C(2)-C(11)	118.3(11)
C(3)-C(13)	1.426(22)	C(2)-C(3)-C(4)	123.7(12)
C(4)-C(5)	1.508(15)	C(2)-C(3)-C(13)	120.7(13)
C(4)-O(20)	1.157(13)	C(4)-C(3)-C(13)	114.5(12)
C(5)-C(6)	1.425(15)	C(3)-C(4)-C(5)	111.3(9)
C(5)-C(10)	1.484(16)	C(3)-C(4)-O(20)	126.8(11)
C(6)-C(7)	1.317(16)	C(5)-C(4)-O(20)	121.2(10)
C(7)-C(8)	1.361(17)	C(4)-C(5)-C(6)	119.3(10)
C(8)-C(9)	1.456(16)	C(4)-C(5)-C(10)	125.1(10)
C(9)-C(10)	1.375(15)	C(6)-C(5)-C(10)	115.5(10)
C(11)-N(12)	1.178(15)	C(5)-C(6)-C(7)	123.9(11)
C(13)-N(12)	1.151(18)	C(6)-C(7)-C(8)	120.7(12)
		C(7)-C(8)-C(9)	121.6(11)
		C(8)-C(9)-C(10)	117.7(10)
		C(1)-C(10)-C(5)	119.1(9)
		C(1)-C(10)-C(9)	120.0(10)
		C(5)-C(10)-C(9)	120.6(10)
		C(2)-C(11)-N(12)	176.9(14)
		C(3)-C(13)-N(22)	174.6(18)

Table A.1 Bond Lengths (Å) and Angles (°) in the Anion of Salt (123b).H<sub>2</sub>O; See Figure 3.5 For Numbering Scheme

A crystal of approximate size 0.35 x 0.3 x 0.3 mm was set up to rotate about the a-axis on a Stoe Stadi2 diffractometer and data were collected *via* variable width ω scan. Background counts were for 20 s and a scan rate of 0.0333°/sec was applied to a width of (1.5 + sin μ/tan Θ): 3216 independent reflections were measured of which 1302 with I > 2σ(I) were used in subsequent refinement. The structure was

determined by statistical methods. The phosphorus atom was refined anisotropically and remaining atoms isotropically. Hydrogen atoms were included in calculated positions although the methyl hydrogen atoms were refined as a rigid group. The water hydrogen atoms were located in a difference Fourier and refined independently apart from a distance constraint ( $O-H = 0.95\text{\AA}$ ).

The structure was given a weighting scheme in the form  $w = 1/[\sigma^2(F) + 0.003F^2]$ . The final R values were 0.094 ( $R_w = 0.097$ ). Calculations were carried out using SHELX76<sup>157</sup> and some of the programs on the Amdahl V7 at the University of Reading. Molecular dimensions in the anion and cation are given in Tables A.1 and A.2 respectively.

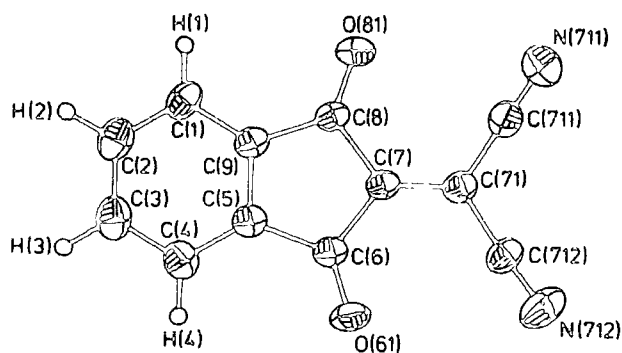
P(1)-C(31)	1.851(9)	C(31)-P(1)-C(41)	111.5(5)
P(1)-C(41)	1.784(14)	C(31)-P(1)-C(51)	109.3(5)
P(1)-C(51)	1.852(12)	C(41)-P(1)-C(51)	106.6(6)
P(1)-C(61)	1.727(13)	C(31)-P(1)-C(61)	107.5(5)
C(31)-C(32)	1.385(16)	C(41)-P(1)-C(61)	112.3(6)
C(31)-C(36)	1.387(15)	C(51)-P(1)-C(61)	109.6(5)
C(32)-C(33)	1.406(18)	P(1)-C(31)-C(32)	122.4(8)
C(33)-C(34)	1.372(16)	P(1)-C(31)-C(36)	118.3(7)
C(34)-C(35)	1.371(16)	C(32)-C(31)-C(36)	119.4(10)
C(35)-C(36)	1.394(17)	C(31)-C(32)-C(33)	120.3(13)
C(41)-C(42)	1.395(18)	C(32)-C(33)-C(34)	118.9(13)
C(41)-C(46)	1.398(20)	C(33)-C(34)-C(35)	121.5(11)
C(42)-C(43)	1.353(18)	C(34)-C(35)-C(36)	119.5(12)
C(43)-C(44)	1.368(19)	C(31)-C(36)-C(35)	120.3(11)
C(44)-C(45)	1.375(21)	P(1)-C(41)-C(42)	122.0(10)
C(45)-C(46)	1.360(22)	P(1)-C(41)-C(46)	119.0(11)
C(51)-C(52)	1.369(17)	C(42)-C(41)-C(46)	119.0(13)
C(51)-C(56)	1.348(16)	C(41)-C(42)-C(43)	122.7(13)
C(52)-C(53)	1.392(19)	C(42)-C(43)-C(44)	117.2(14)
C(53)-C(54)	1.399(19)	C(43)-C(44)-C(45)	121.6(16)
C(54)-C(55)	1.348(20)	C(44)-C(45)-C(46)	121.7(18)
C(55)-C(56)	1.367(19)	C(41)-C(46)-C(45)	117.7(16)
		P(1)-C(51)-C(52)	116.4(10)
		P(1)-C(51)-C(56)	123.8(9)
		C(52)-C(51)-C(56)	119.6(12)
		C(51)-C(52)-C(53)	120.3(14)
		C(52)-C(53)-C(54)	118.2(14)
		C(53)-C(54)-C(55)	120.4(15)
		C(54)-C(55)-C(56)	119.9(16)
		C(51)-C(56)-C(55)	121.6(12)

Table A.2 Bond Lengths ( $\text{\AA}$ ) and Angles ( $^\circ$ ) in the Cation of Salt (123b). $H_2O$ ; See Figure 3.5 For Numbering Scheme.

B. CRYSTAL DATA, INTENSITY DATA, COLLECTION PARAMETERS AND DETAILS OF REFINEMENT FOR DC10 (122)

Chemical Formula:  $C_{12}H_4O_2N_2$ ;  $M_r = 208.176$ ; crystal system monoclinic;  $a = 7.735(1) \text{ \AA}$ ;  $b = 11.551(3) \text{ \AA}$ ;  $c = 10.708(2) \text{ \AA}$ ;  $\alpha = \gamma = 90.0^\circ$ ;  $\beta = 101.39(1)^\circ$ ;  $V = 937.89 \text{ \AA}^3$ ; space group  $P21/c$ ;  $D_c = 1.47 \text{ g cm}^{-3}$ ;  $Z = 4$ ;  $F(000) = 424$ ; Cu-K $\alpha$  radiation;  $\lambda = 1.5419$ ;  $\mu = 8.234 \text{ cm}^{-1}$ ;  $\Theta$  min/max = 3, 69; T = 279 K; Total data measured = 2041; Total data unique = 1740; Total data observed = 1537; significant test  $F_o > 3\sigma(F_o)$ ; No. of parameters = 161; Absorption correction psi-scan; weighting scheme =  $1/[\sigma^2(F_o) + 0.00001F_o^2]$ ; final  $R = (F)/(F_o) = 0.0406$ ; final  $R_g = 0.0479$ .

Data were collected on a CAD 4 diffractometer following previously described procedures<sup>158</sup>. The structure was solved by direct methods (SHELX86)<sup>159</sup> and developed and refined using standard Fourier and least-squares procedures (SHELX80)<sup>160</sup>. Non-hydrogen atoms were refined anisotropically, hydrogens isotropically. Bond lengths and angles are given in Table A.3.



Atom Numbering Scheme for DCID (122)

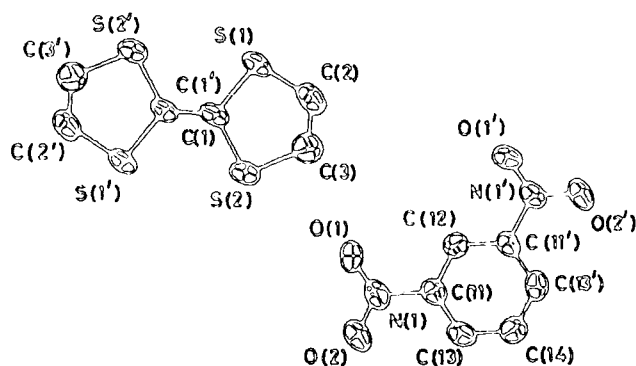
C(2)-C(1)	1.381(4)	C(9)-C(1)-C(2)	117.5(3)
H(1)-C(1)	0.951(21)	C(9)-C(1)-H(1)	122.0(13)
H(2)-C(2)	0.992(20)	H(2)-C(2)-C(1)	117.4(13)
H(3)-C(3)	0.961(22)	C(4)-C(3)-C(2)	121.5(3)
H(4)-C(4)	0.939(22)	C(4)-C(3)-H(3)	119.4(14)
C(9)-C(5)	1.398(3)	H(4)-C(4)-C(3)	121.5(13)
C(7)-C(6)	1.503(4)	C(6)-C(5)-C(4)	128.8(3)
C(8)-C(7)	1.500(4)	C(9)-C(5)-C(6)	110.2(2)
C(712)-C(71)	1.438(3)	C(7)-C(6)-C(5)	106.1(2)
N(712)-C(712)	1.133(3)	C(71)-C(7)-C(6)	126.3(2)
C(9)-C(8)	1.478(3)	C(8)-C(7)-C(71)	126.3(2)
C(9)-C(1)	1.389(3)	C(712)-C(71)-C(7)	121.9(3)
C(3)-C(2)	1.392(4)	N(711)-C(711)-C(71)	177.1(2)
C(4)-C(3)	1.378(4)	O(81)-C(8)-C(7)	125.9(2)
C(5)-C(4)	1.390(3)	C(9)-C(8)-O(81)	128.3(3)
C(6)-C(5)	1.473(3)	C(8)-C(9)-C(1)	128.6(3)
O(61)-C(6)	1.214(3)	C(2)-C(1)-H(1)	120.6(13)
C(71)-C(7)	1.341(3)	C(3)-C(2)-C(1)	121.4(3)
C(711)-C(71)	1.441(3)	C(3)-C(2)-H(2)	121.2(13)
N(711)-C(711)	1.139(3)	H(3)-C(3)-C(2)	119.1(14)
O(81)-C(8)	1.208(3)	C(5)-C(4)-C(3)	117.5(3)
		C(5)-C(4)-H(4)	121.0(13)
		C(9)-C(5)-C(4)	121.0(3)
		O(61)-C(6)-C(5)	128.6(2)
		C(7)-C(6)-O(61)	125.3(2)
		C(8)-C(7)-C(6)	107.5(2)
		C(711)-C(71)-C(7)	122.8(3)
		C(712)-C(71)-C(711)	115.3(2)
		N(712)-C(712)-C(71)	178.1(2)
		C(9)-C(8)-C(7)	105.8(2)
		C(5)-C(9)-C(1)	121.1(3)
		C(8)-C(9)-C(5)	110.4(2)

Table A.3 Bond Lengths (Å) and Angles (°) For DCID (122).

G. CRYSTAL DATA, INTENSITY DATA, COLLECTION PARAMETERS AND DETAILS OF REFINEMENT FOR TTF-DNB

Chemical Formula:  $C_{12}H_{12}O_4N_2S_4$ ;  $M = 376.478$ ; crystal system monoclinic;  $a = 11.6290(1) \text{ \AA}$ ;  $b = 12.674(2) \text{ \AA}$ ;  $c = 10.389(2) \text{ \AA}$ ;  $\alpha = \gamma = 90.0^\circ$ ;  $\beta = 99.27(1)^\circ$ ;  $V = 1511.21 \text{ \AA}^3$ ; space group P;  $D_c = 1.65 \text{ g cm}^{-3}$ ;  $Z = 4$ ;  $F(000) = 776$ ; Mo-K $\alpha$  radiation;  $\lambda = 0.71069$ ;  $\mu = 6.205 \text{ cm}^{-1}$ ;  $\Theta$  min/max = 1.5, 25; T = R.T.; Total data measured = 1524; Total data unique = 1323; Total data observed = 1055; significant test  $F_o > 3\sigma(F_o)$ ; No. of parameters = 118; Absorption correction psi-scan; weighting scheme =  $1/[\sigma^2(F_o) + 0.0000496F_o^2]$ ; final R =  $(F)/(F_o) = 0.0323$ ; final  $R_g = 0.0343$ .

Data were collected on a CAD 4 diffractometer following previously described procedures<sup>158</sup>. The structure was solved by direct methods (SHELX86)<sup>159</sup> and developed and refined using standard Fourier and least-squares procedures (SHELX80)<sup>160</sup>. Non-hydrogen atoms were refined anisotropically, hydrogens isotropically. Bond lengths and angles are given in Table A.4.



Atom Numbering Scheme for TTF and mDNB Molecules

C(1)-S(1)	1.759(4)	C(2)-S(1)-C(1)	94.8(2)
C(1)-S(1)	1.753(4)	S(2)-C(1)-S(1)	114.2(2)
C(1)-C(1a)	1.342(5)	C(2)-C(3)-S(2)	118.3(3)
C(12)-C(11)	1.375(4)	N(1)-C(11)-C(12)	118.5(3)
N(1)-C(11)	1.469(4)	C(11)-C(12)-C(11)	116.7(4)
O(1)-N(1)	1.216(4)	C(13)-C(14)-C(13)	120.0(4)
C(2)-S(1)	1.728(5)	O(2)-N(1)-C(11)	117.5(3)
C(3)-S(2)	1.734(5)	C(3)-S(2)-C(1)	94.6(2)
C(3)-C(2)	1.314(5)	C(3)-C(2)-S(1)	118.1(3)
C(13)-C(11)	1.374(4)	C(13)-C(11)-C(12)	122.6(3)
C(14)-C(13)	1.379(4)	N(1)-C(11)-C(13)	118.8(3)
C(2)-N(1)	1.224(3)	C(14)-C(13)-C(11)	119.0(3)
		O(1)-N(1)-C(11)	118.7(3)
		O(2)-N(1)-O(1)	123.8(3)

Table A.4 Selected Bond Lengths (Å) and Angles (°) in TTF-mDNB.

#### D. CRYSTAL DATA FOR TTF-TNB

Data were collected on a Nonius CAD 4 diffractometer with  $\text{CuK}\alpha$  radiation. Refinement was by full-matrix least-squares on a Digital MicroVax II using the SHELXTL plus package<sup>160</sup>. The final  $R$ -value for 177 l.s. parameters refined against 1617 data [ $I > 3\sigma(I)$ ] was 0.0963 ( $R_w = 0.0984$ ).

Chemical Formula:  $\text{C}_{12}\text{H}_7\text{N}_3\text{O}_6\text{S}_4$ ;  $M_r = 416.922$ ; crystal system triclinic;  $a = 7.087(1)$ ;  $b = 18.197(3)$ ;  $c = 15.930(2)$  Å;  $\alpha = 125.14(1)$ ;  $\beta = 83.33(1)^\circ$ ;  $\gamma = 92.73(1)^\circ$ ; space group  $P\bar{1}$ .

S(1)-C(2)	1.703(23)	C(11)-C(12)-N(12)	118.9(9)
C(2)-C(3)	1.347(30)	C(13)-C(14)-N(14)	121.0(10)
S(4)-C(10)	1.806(16)	C(11)-C(16)-N(16)	118.3(14)
S(5)-C(9)	1.738(30)	C(12)-N(12)-O(21)	120.3(16)
C(7)-S(8)	1.702(38)	O(21)-N(12)-O(22)	122.3(27)
C(9)-C(10)	1.335(40)	C(14)-N(14)-O(42)	113.5(16)
C(14)-N(14)	1.498(30)	C(16)-N(16)-O(61)	115.4(22)
N(12)-O(21)	1.198(37)	O(61)-N(16)-O(62)	126.6(18)
N(14)-O(41)	1.200(23)	S(1')-C(2')-C(3')	116.5(24)
N(16)-O(61)	1.222(39)	C(3')-S(4')-C(10')	94.7(11)
S(1')-C(2')	1.733(24)	S(5')-C(6')-C(7')	115.5(24)
C(2')-C(3')	1.353(29)	C(7')-S(8')-C(9')	94.3(11)
S(4')-C(10')	1.754(16)	S(5')-C(9')-C(10')	122.2(13)
S(5')-C(9')	1.741(28)	S(1')-C(10')-S(4')	113.9(15)
C(7')-S(8')	1.710(33)	S(4')-C(10')-C(9')	124.4(18)
C(9')-C(10')	1.346(37)	C(13')-C(12')-N(12')	117.3(14)
C(14')-N(14')	1.457(34)	C(15')-C(14')-N(14')	121.4(11)
N(12')-O(21')	1.238(35)	C(15')-C(16')-N(16')	122.4(12)
N(14')-O(41')	1.154(40)	C(12')-N(12')-O(22')	118.8(21)
N(16')-O(61')	1.172(32)	C(14')-N(14')-O(41')	118.9(17)
S(1)-C(10)	1.759(28)	O(41')-N(14')-O(42')	128.4(30)
C(3)-S(4)	1.730(33)	C(16')-N(16')-O(62')	111.3(22)
S(5)-C(6)	1.739(25)	S(1)-C(2)-C(3)	119.1(24)
C(6)-C(7)	1.307(34)	C(3)-S(4)-C(10)	94.9(11)
S(8)-C(9)	1.732(17)	S(5)-C(6)-C(7)	117.0(27)
C(12)-N(12)	1.419(33)	C(7)-S(8)-C(9)	93.8(13)
C(16)-N(16)	1.429(18)	S(5)-C(9)-C(10)	122.7(14)
N(12)-O(22)	1.250(21)	S(1)-C(10)-S(4)	112.4(15)
N(14)-O(42)	1.166(39)	S(4)-C(10)-C(9)	122.2(19)
N(16)-O(62)	1.209(37)	C(13)-C(12)-N(12)	121.1(9)
S(1')-C(10')	1.774(27)	C(15)-C(14)-N(14)	119.0(10)
C(3')-S(4')	1.721(32)	C(15)-C(16)-N(16)	121.7(14)
S(5')-C(6')	1.753(23)	C(12)-N(12)-O(22)	117.2(24)
C(6')-C(7')	1.344(31)	C(14)-N(14)-O(41)	112.7(27)
S(8')-C(9')	1.752(16)	O(41)-N(14)-O(42)	133.8(29)
C(12')-N(12')	1.473(18)	C(16)-N(16)-O(62)	117.9(23)
C(16')-N(16')	1.577(45)	C(2')-S(1')-C(10')	95.0(11)
N(12')-O(22')	1.173(35)	C(2')-C(3')-S(4')	118.8(19)
N(14')-O(42')	1.240(25)	C(6')-S(5')-C(9')	95.0(12)
N(16')-O(62')	1.132(51)	C(6')-C(7')-S(8')	119.6(19)
		S(5')-C(9')-S(8')	115.0(15)
		S(8')-C(9')-C(10')	122.8(19)
		S(1')-C(10')-C(9')	121.7(13)
		C(11')-C(12')-N(12')	122.7(14)
		C(13')-C(14')-N(14')	118.5(11)
		C(11')-C(16')-N(16')	117.3(12)
		C(12')-N(12')-O(21')	113.0(21)
		O(21')-N(12')-O(22')	128.0(16)
		C(14')-N(14')-O(42')	112.7(28)
		C(16')-N(16')-O(61')	104.3(35)
		O(61')-N(16')-O(62')	142.7(44)
C(2)-S(1)-C(10)	95.9(12)		
C(2)-C(3)-S(4)	117.0(19)		
C(6)-S(5)-C(9)	93.5(13)		
C(6)-C(7)-S(8)	119.5(22)		
S(5)-C(9)-S(8)	115.7(17)		
S(8)-C(9)-C(10)	121.5(20)		
S(1)-C(10)-C(9)	125.4(14)		

Table A.5 Bond Lengths (Å) and Angles (°) In TTF-TNB;  
See Figures 4.4(a) and (b) for Numbering Scheme.

APPENDIX II - RESEARCH COLLOQUIA, SEMINARS, LECTURES AND CONFERENCES  
ORGANISED BY THE DEPARTMENT OF CHEMISTRY DURING THE PERIOD: 1985-1986

\* - Indicates Colloquia attended by the author.

- BARNARD, Dr. C.J.F. (Johnson Matthey Group) 20th February 1986  
"Platinum Anti-Cancer Drug Development"
- BROWN, Dr. J.M. (University of Oxford) 12th March 1986  
"Chelate Control in Homogeneous Catalysis"
- CLARK, Dr. B.A.J. (Kodak Ltd.) 28th November 1985  
"Chemistry & Principles of Colour Photography"
- CLARK, Dr. J.H. (University of York) 29th January 1986  
"Novel Fluoride Ion Reagents"
- \* DAVIES, Dr. S.G. (University of Oxford) 14th November 1985  
"Chirality Control and Molecular Recognition"
- DEWING, Dr. J. (U.M.I.S.T.) 24th October 1985  
"Zeolites - Small Holes, Big Opportunities"
- ERTL, Prof. G. (University of Munich) 7th November 1985  
"Heterogeneous Catalysis"
- \* GRIGG, Prof. R. (Queen's University, Belfast) 13th February 1986  
"Thermal Generation of 1,3-Dipoles"
- HARRIS, Prof. R.K. (University of Durham) 27th February 1986  
"The Magic of Solid State NMR"
- HATHWAY, Dr. D. (University of Durham) 5th March 1986  
"Herbicide Selectivity"
- IDDON, Dr. B. (University of Salford) 6th March 1986  
"The Magic of Chemistry"
- JACK, Prof. K.H. (University of Newcastle) 21st November 1985  
"Chemistry of Si-Al-O-N Engineering Ceramics"
- LANGRIDGE-SMITH, Dr.P.R.R. (Edinburgh University) 14th May 1986  
"Naked Metal Clusters- Synthesis,  
Characterisation and Chemistry"
- LEWIS, Prof. Sir Jack (University of Cambridge) 23rd January 1986  
"Some more Recent Aspects in the Cluster  
Chemistry of Ruthenium and Osmium Carbonyls"
- LUDMAN, Dr. C.J. (University of Durham) 17th October 1985  
"Some Thermochemical Aspects of Explosions"
- \* MACBRIDE, Dr. J.A.H. (Sunderland Polytechnic) 20th November 1985  
"A Heterocyclic Tour on a Distorted Tricycle  
- Biphenylene"

- O'DONNELL, Prof. M.J. (Indiana-Purdue University) 5th November 1985  
 "New Methodology for the Synthesis of  
 Amino Acids"
- PARMAR, Dr. V.S. (University of Delhi) 13th September 1985  
 "Enzyme Assisted ERC Synthesis"
- \* PHILLIPS, Dr. N.J. (University of Technology,  
 Loughborough) 30th January 1986  
 "Laser Holography"
- PROCTOR, Prof. G. (University of Salford) 19th February 1986  
 "Approaches to the Synthesis of some  
 Natural Products"
- SCHMUTZLER, Prof. R. (University of Braunschweig) 9th June 1986  
 "Mixed Valence Diphosphorus Compounds"
- SCHRODER, Dr. M. (University of Edinburgh) 5th March 1986  
 "Studies on Macrocyclic Complexes"
- SHEPPARD, Prof. N. (University of East Anglia) 15th January 1986  
 "Vibrational and Spectroscopic Determinations  
 of the Structures of Molecules Chemisorbed on  
 Metal Surfaces"
- TEE, Prof. O.S. (Concordia University, Montreal) 12th February 1986  
 "Bromination of Phenols"
- TILL, Miss C. (University of Durham) 26th February 1986  
 "ESCA and Optical Emission Studies of the  
 Plasma Polymerisation of Perfluoroaromatics"
- \* TIMMS, Dr. P. (University of Bristol) 31st October 1985  
 "Some Chemistry of Fireworks"
- WADDINGTON, Prof. D.J. (University of York) 28th November 1985  
 "Resources for the Chemistry Teacher"
- WHITTLETON, Dr. S.N. (University of Durham) 30th October 1985  
 "An Investigation of a Reaction Window"
- WILDE, Prof. R.E. (Texas Technical University) 23rd June 1986  
 "Molecule Dynamic Processes from Vibrational  
 Bandshapes"
- YARWOOD, Dr. J. (University of Durham) 12th February 1986  
 "The Structure of Water in Liquid Crystals"

DURING THE PERIOD: 1986-1987

- \* ALLEN, Prof. Sir G. (Unilever Research) 13th November 1986  
 "Biotechnology and the Future of the  
 Chemical Industry"
- BARTSCH, Dr. B. (University of Sussex) 6th May 1987  
 "Low Co-ordinated Phosphorus Compounds"

- BLACKBURN, Dr. M. (University of Sheffield) 27th May 1987  
 "Phosphonates as Analogues of Biological Phosphate Esters"
- BORDWELL, Prof. F.G. (Northeastern University, USA) 9th March 1987  
 "Carbon Anions, Radicals, Radical Anions and Radical Cations"
- CANNING, Dr. N.D.S. (University of Durham) 26th November 1986  
 "Surface Adsorption Studies of Relevance to Heterogeneous Ammonia Synthesis"
- CANNON, Dr. R.D. (University of East Anglia) 11th March 1987  
 "Electron Transfer in Polynuclear Complexes"
- CLEGG, Dr. W. (University of Newcastle-upon-Tyne) 28th January 1987  
 "Carboxylate Complexes of Zinc; Charting a Structural Jungle"
- DÖPP, Prof. D. (University of Duisburg) 5th November 1986  
 "Cyclo-additions and Cyclo-reversions Involving Captodative Alkenes"
- DORFMÜLLER, Prof. T. (University of Bielefeld) 8th December 1986  
 "Rotational Dynamics in Liquids and Polymers"
- GOODGER, Dr. E.M. (Cranfield Inst. Technology) 12th March 1987  
 "Alternative Fuels for Transport"
- \* GREENWOOD, Prof. N.N. (University of Leeds) 16th October 1986  
 "Glorious Gaffes in Chemistry"
- HARMER, Dr. M. (I.C.I. Chemicals & Polymer Group) 7th May 1987  
 "The Role of Organometallics in Advanced Materials"
- \* HUBBERSTEY, Dr. P. (University of Nottingham) 5th February 1987  
 "Demonstration Lecture on Various Aspects of Alkali Metal Chemistry"
- HUDSON, Prof. R.F. (University of Kent) 17th March 1987  
 "Aspects of Organophosphorus Chemistry"
- HUDSON, Prof. R.F. (University of Kent) 18th March 1987  
 "Homolytic Rearrangements of Free Radical Stability"
- JARMAN, Dr. M. (Institute of Cancer Research) 19th February 1987  
 "The Design of Anti Cancer Drugs"
- KRESPAN, Dr. C. (E.I. Dupont de Nemours) 26th June 1987  
 "Nickel(0) and Iron(0) as Reagents in Organofluorine Chemistry"
- \* KROTO, Prof. H.W. (University of Sussex) 23rd October 1986  
 "Chemistry in Stars, between Stars and in the Laboratory"

- LEY, Prof. S.V. (Imperial College) 5th March 1987  
 "Fact and Fantasy in Organic Synthesis"
- MILLER, Dr. J. (Dupont Central Research, USA) 3rd December 1986  
 "Molecular Ferromagnets; Chemistry and Physical Properties"
- MILNE/CHRISTIE, Dr.A./Mr.S. (International Paints) 20th November 1986  
 "Chemical Serendipity: A Real Life Case Study"
- NEWMAN, Dr. R. (University of Oxford) 4th March 1987  
 "Change and Decay: A Carbon-13 CP/MAS NMR Study of humification and Coalification Processes"
- OTTEWILL, Prof. R.H. (University of Bristol) 22nd January 1987  
 "Colloid Science a Challenging Subject"
- PASYNKIEWICZ, Prof. S. (Technical Univ., Warsaw) 11th May 1987  
 "Thermal Decomposition of Methyl Copper and its Reactions with Trialkylaluminium"
- ROBERTS, Prof. S.M. (University of Exeter) 24th June 1987  
 "Synthesis of Novel Antiviral Agents"
- \* RODGERS, Dr. P.J. (I.C.I. Billingham) 12th February 1987  
 "Industrial Polymers from Bacteria"
- \* SCROWSTON, Dr. R.M. (University of Hull) 6th November 1986  
 "From Myth and Magic to Modern Medicine"
- SHEPHERD, Dr. T. (University of Durham) 11th February 1987  
 "Pteridine Natural Products; Synthesis and Use in Chemotherapy"
- THOMSON, Prof. A. (University of East Anglia) 4th February 1987  
 "Metalloproteins and Magneto-optics"
- WILLIAMS, Prof. R.L. (Metropolitan Police Forensic Science) 27th November 1987  
 "Science and Crime"
- WONG, Prof.E.H. (University of New Hampshire, USA) 29th October 1986  
 "Coordination Chemistry of P-O-P Ligands"
- WONG, Prof.E.H. (University of New Hampshire, USA) 17th February 1987  
 "Symmetrical Shapes from Molecules to Art and Nature"

DURING THE PERIOD: 1987- 1988

- BIRCHALL, Prof. D. (I.C.I. Advanced Materials) 25th April 1988  
 "Environment Chemistry of Aluminium"
- \* BORER, Dr. K. (University of Durham Industrial Research Laboratories) 18th February 1988  
 "The Brighton Bomb - A Forensic Science View"

<u>BOSSONS</u> , L. (Durham Chemistry Teachers' Centre) "GCSE Practical Assessment"	16th March 1988
<u>BUTLER</u> , Dr. A.R. (University of St. Andrews) "Chinese Alchemy"	5th November 1987
<u>CAIRNS-SMITH</u> , Dr. A. (Glasgow University) "Clay Minerals and the Origin of Life"	28th January 1988
<u>DAVIDSON</u> , Dr. J. (Herriot-Watt University) "Metal Promoted Oligomerisation Reactions of Alkynes"	November 1987
<u>GRAHAM</u> , Prof. W.A.G. (University of Alberta, Canada) "Rhodium and Iridium Complexes in the Activation of Carbon-Hydrogen Bonds"	3rd March 1988
<u>GRAY</u> , Prof. G.W. (University of Hull) "Liquid Crystals and their Applications"	22nd October 1987
<u>HARTSHORN</u> , Prof. M.P. (University of Canterbury, New Zealand) "Aspects of Ipso-Nitration"	7th April 1988
<u>HOWARD</u> , Dr. J. (I.C.I. Wilton) "Chemistry of Non-Equilibrium Processes"	3rd December 1987
<u>JONES</u> , Dr. M.E. (Durham Chemistry Teachers' Centre) "GCSE Chemistry Post-mortem"	29th June 1988
<u>JONES</u> , Dr. M.E. (Durham Chemistry Teachers' Centre) "GCE Chemistry A-Level Post-mortem"	6th July 1988
<u>KOCH</u> , Prof. H.F. (Ithaca College, U.S.A.) "Does the E2 Mechanism Occur in Solution"	7th March 1988
<u>LACEY</u> , Mr. (Durham Chemistry Teacher's Centre) "Double Award Science"	9th February 1988
<u>LUDMAN</u> , Dr. C.J. (Durham University) "Explosives"	10th December 1987
<u>MCDONALD</u> , Dr. W.A. (I.C.I. Wilton) "Liquid Crystal Polymers"	11th May 1988
<u>MAJORAL</u> , Prof. J.-P. (Université Paul Sabatier) "Stabilisation by Complexation of Short-Lived Phosphorus Species"	8th June 1988
<u>MAPLETOFT</u> , Mrs. M. (Durham Chemistry Teachers' Centre) "Salters' Chemistry"	4th November 1987

- NIETO DE CASTRO, Prof. C.A. (University of Lisbon  
and Imperial College) 18th April 1988  
"Transport Properties of Non-Polar Fluids"
- OLAH, Prof. G.A. (University of Southern  
California) 29th June 1988  
"New Aspects of Hydrocarbon Chemistry"
- PALMER, Dr. F. (University of Nottingham) 21st January 1988  
"Luminescence (Demonstration Lecture)"
- PINES, Prof. A. (University of California,  
Berkeley, U.S.A.) 28th April 1988  
"Some Magnetic Moments"
- RICHARDSON, Dr. R. (University of Bristol) 27th April 1988  
"X-Ray Diffraction from Spread Monolayers"
- ROBERTS, Mrs. E. (SATRO Officer for Sunderland) 13th April 1988  
Talk - Durham Chemistry Teachers' Centre  
"Links between Industry and Schools"
- ROBINSON, Dr. J.A. (University of Southampton) 27th April 1988  
"Aspects of Antibiotic Biosynthesis"
- \* ROSE, van Mrs. S. (Geological Museum) 29th October 1987  
"Chemistry of Volcanoes"
- SAMMES, Prof. P.G. (Smith, Kline and French) 19th December 1987  
"Chemical Aspects of Drug Development"
- SEEBACH, Prof. D. (E.T.H. Zurich) 12th November 1987  
"From Synthetic Methods to Mechanistic Insight"
- SODEAU, Dr. J. (University of East Anglia) 11th May 1988  
Durham Chemistry Teachers' Centre: "Spray  
Cans, Smog and Society"
- SWART, Mr. R.M. (I.C.I.) 16th December 1987  
"The Interaction of Chemicals with  
Lipid Bilayers"
- TURNER, Prof. J.J. (University of Nottingham) 11th February 1988  
"Catching Organometallic Intermediates"
- \* UNDERHILL, Prof. A.E. (University of Bangor) 25th February 1988  
"Molecular Electronics"
- WILLIAMS, Dr. D.H. (University of Cambridge) 26th November 1987  
"Molecular Recognition"
- WINTER, Dr. M.J. (University of Sheffield) 15th October 1987  
"Pyrotechnics (Demonstration Lecture)"

FIRST YEAR INDUCTION COURSE  
OCTOBER 1985

This course consists of a series of one hour lectures in the services available in the department.

1. Departmental Organisation.
2. Safety Matters.
3. Electrical appliances and infrared spectroscopy.
4. Chromatography and Microanalysis.
5. Atomic absorption and inorganic analysis.
6. Library facilities.
7. Mass spectroscopy.
8. Nuclear Magnetic Resonance.
9. Glass blowing techniques.

RESEARCH CONFERENCES ATTENDED

1. GRADUATE SYMPOSIUM, Durham University, 16th April, 1986.
2. GRADUATE SYMPOSIUM, Durham University, 19th April, 1988.
3. INTERNATIONAL CONFERENCE ON SCIENCE AND TECHNOLOGY OF SYNTHETIC METALS (ICSM '88), Santa Fe, New Mexico, U.S.A., June 26th - July 2nd, 1988. A poster was presented by the author, entitled "*Solid State Characterisation of Charge-Transfer Salts of 2,3-Dicyano-naphthoquinone (DCNQ)*".

APPENDIX III - REFERENCES

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