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THE SYNTHESIS AND REDOX PROPERTIES OF NEW 1,3-DITHIOLE SYSTEMS

by

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Department of Chemistry
University of Durham

A thesis submitted for the degree of Doctor of Philosophy at the
University of Durham

October 1992

DECLARATION

The work described in this thesis was carried out by the author, in the Department of Chemistry, University of Durham, between October 1989 and September 1992. It has not been submitted previously for a degree at this, or any other, University.

MEMORANDUM

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The members of Lab. 29 who have made the duration of my Ph.D. an enjoyable time.

ABSTRACT

The Synthesis and Redox Properties of New 1,3-Dithiole Systems

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The theory of conductivity in organic metals and a review of organic π-electron donors is introduced in Chapter One, outlining some of the many variations that have been made to the tetrathiafulvalene (TTF) molecule, the donor component in the first true organic metal.

A range of new alkylseleno-substituted ethanediylidene-2,2'-bis(1,3-dithiole) donors have been efficiently synthesised. These compounds form semi-conducting charge-transfer complexes with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ). The synthesis, electrochemistry, *X*-ray crystal structure and magnetic properties are presented (Chapter Two).

Various 1,3-dithiolium cations and 1,3-dithiole anions have been used in the synthesis of compounds targeted as high-spin systems (Chapter Three). The theory of organic ferromagnetism is discussed, and various compounds with interesting magnetic and redox properties have been prepared.

Chapter Four deals with the synthesis of a series of conjugated, multi-1,3-dithiole, multi-chalcogen, π-electron donors. These compounds are members of the dendralene family of hydrocarbons and the crystal structure of a tricyclic [3]-dendralene is presented. The formation of semi-conducting charge-transfer salts is also discussed.

Multistage redox behaviour of a new anthraquinodimethane derivative of TTF has been observed (Chapter Five), and cyclic voltammetic data and *X*-ray crystal structures of such systems are presented.

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Chapter Five Anthraquinodimethane Derivatives of Tetrathiafulvalene 74

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CHAPTER ONE

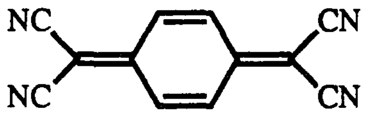
INTRODUCTION

1.1 ORGANIC METALS

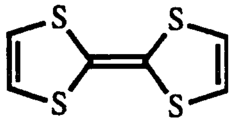
The majority of organic materials are electrical insulators (room temperature conductivity, $\sigma_{rt} = 10^{-9}$-10^{-14} Scm^{-1}) and one of the most exciting and challenging areas of research for today's organic chemist is the development of new organic materials that have interesting electrical, magnetic and/or optical properties. The possibility that organic solids might exhibit the characteristics of a metal was suggested over seventy-five years ago[1,2], and research in the last two decades in particular has given rise to three classes of 'organic metals'. Of these three, which are charge-transfer (C-T) salts and ion-radical salts, organometallic species[3] and conjugated polymers[4], it is in the area of charge-transfer salts that this thesis will concentrate.

1.2 HISTORICAL PERSPECTIVE

In 1954 the first conducting organic compound was discovered. This was an unstable perylene - bromine salt[5] reported by Japanese workers to have $\sigma_{rt} = 1$ Scm^{-1}. However, it was not until after the synthesis by workers at DuPont of a new powerful electron accepter, tetracyanoquinodimethane (TCNQ) (1)[6], that the early 1960's produced a flow of semi-conducting charge-transfer salts[7]. Complexes of TCNQ with a wide range of π-electron donors and closed-shell cations produced C-T salts with conductivities in the range $\sigma_{rt} = 10^{-2}$ - 10^{-5} Scm^{-1}, and quinolinium TCNQ was the best of the bunch at that time with $\sigma_{rt} = 100$ Scm^{-1}.



(1) - TCNQ



(2) - TTF

It was almost a decade later, however, before the first true 'organic metal' was synthesised. This compound was a stable, crystalline, 1:1 C-T complex[8] formed from the donor tetrathiafulvalene (TTF) (2)[9] and the acceptor TCNQ (1). The room temperature conductivity of $\sigma_{rt} = 500$ Scm^{-1} rises to a maximum of $\sigma = 1\times10^{4}$ Scm^{-1} at 59K, and it was the revelation of these metallic properties that was the founding stone for the growing science of organic conductors. To put these values of conductivity into context, the best insulators such as PTFE have room temperature conductivities in the range 10^{-16}- 10^{-20} Scm^{-1}, whereas semiconductors such as silicon have conductivities of about 10^{-2}- 10^{-8} Scm^{-1}, and metals such as copper and silver have conductivities that approach 10^{6} Scm^{-1}.

1.3 PHYSICAL CONCEPTS [10]

1.3.1 Charge-Transfer Complexes

Such complexes have been studied in detail since the beginning of the century[11]. A stable charge-transfer complex is usually the result of the transfer of an electron from a donor to an acceptor molecule forming an ionic crystal where the donor and acceptor molecules stack alternately face to face within the crystal lattice of the complex. In such complexes that contain mixed donor-acceptor stacks there will always be filled HOMO's (highest occupied molecular orbitals) and empty LUMO's (lowest unoccupied molecular orbitals), regardless of charge transfer, resulting in an insulating C-T salt. Conducting C-T salts require the presence of highly ordered arrays of donor and acceptor molecules forming segregated stacks, with the transfer of electrons from the donor to the acceptor stack. In the case of a 1:1 donor-acceptor complex there must be partial charge transfer from donor to acceptor, and in the case of non-stochiometric complexes complete charge transfer may also result in an organic metal (e.g. $D^{+}(TCNQ)_2^{\cdot-}$). Both cases (Figure 1.1) result in a partially filled HOMO and require the presence of thermodynamically stable radical ions. There is considerable π-electron overlap and delocalisation along these one-dimensional stacks and, consequently, the conductivity is anisotropic. Many organic metals are, therefore, termed 'one-dimensional' metals. The key to understanding why certain organic materials behave like metals lies in the basic concepts of band theory.

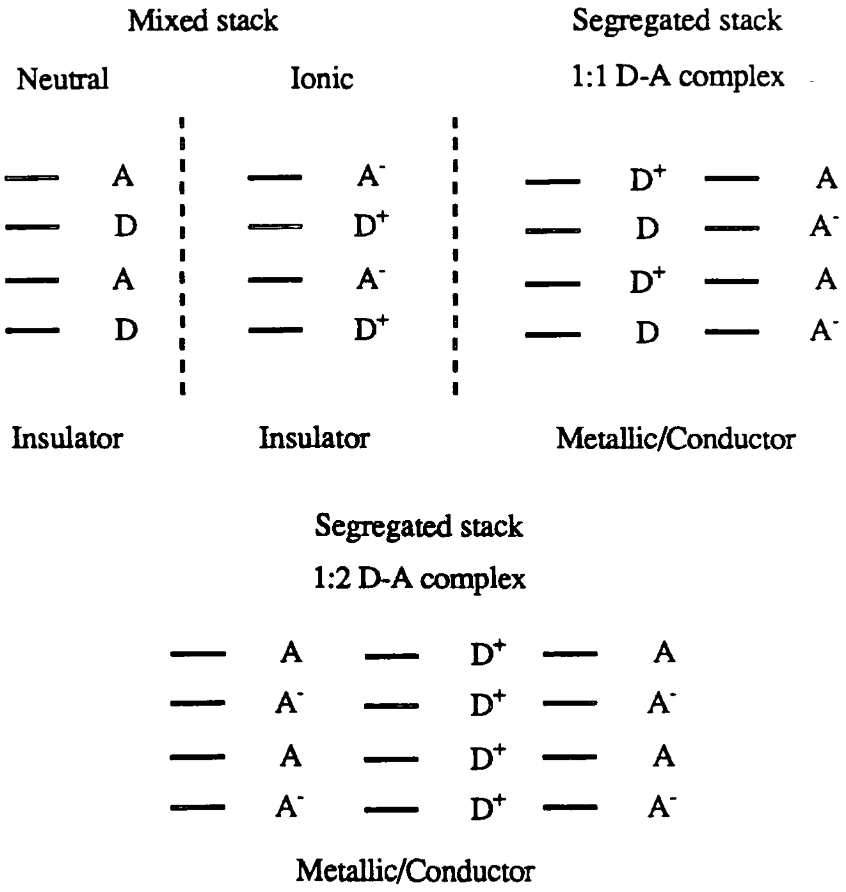


Figure 1.1 - Classification of C-T Complexes

1.3.2 Band Theory [22]

When a large number of atoms or molecules are brought together in a crystalline solid, the electronic states (the atomic and molecular orbitals) can mix so as to form bands (a continuum of energy states). A simple model of this behaviour is the formation of electronic bands from a stack of ethylene molecules (Figure 1.2). On bringing together the two atomic p-orbitals of the adjacent carbon atoms a π-bonding and a π^*-anti-bonding set of molecular orbitals are formed, the lower energy π-bonding level containing (and filled by) the two electrons from the two p-orbitals. The higher energy π^* level is empty. On bringing together two of these ethylene molecules in a stack, the energy levels are split once more, resulting in two π-bonding levels (molecular orbitals) and two π^*-anti-bonding levels (molecular orbitals) of higher energy. Since there are two electrons per bonding π orbital both of the new π levels are filled and the π* levels remain empty.

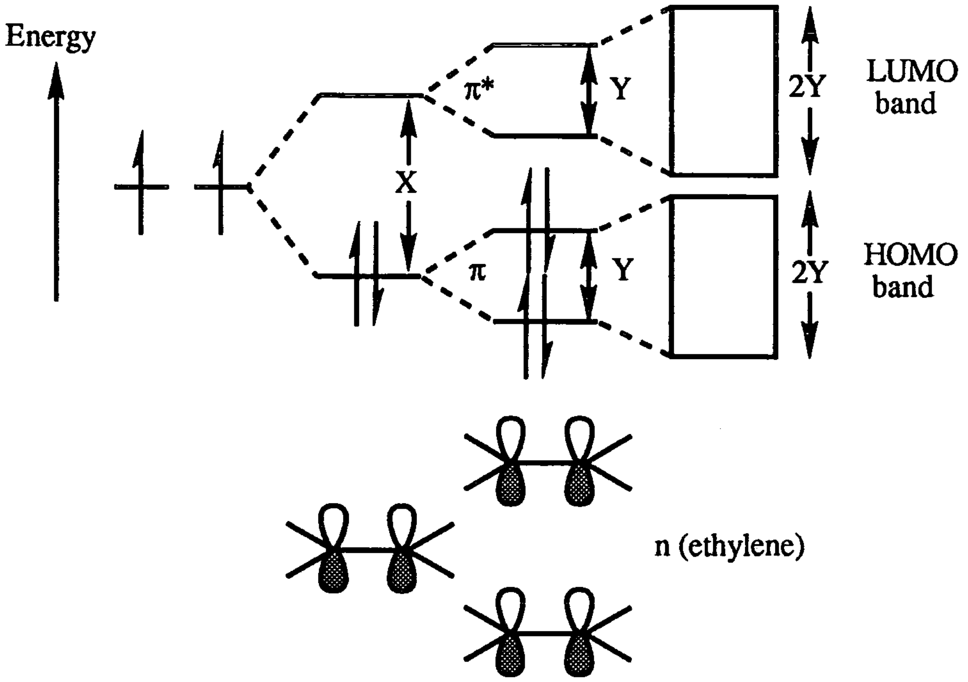


Figure 1.2 - Formation of electronic bands from a stack of ethylene molecules. The band width is given by the value 2Y and is approximately twice the value of the dimer splitting, Y.

This stacking of molecules can be continued until we have n molecules stacked in a crystal, the π-bonding levels continually splitting into n levels (with infinitesimally different energies) and creating one band (the HOMO band), with the π*-anti-bonding levels also splitting into n levels creating another band (the LUMO band) of higher energy. The lower HOMO band is completely filled with 2n electrons and the higher LUMO band is empty. The width of the bands is determined by the extent to which the molecular orbitals overlap. However, the extensive interaction of molecular orbitals is not the only requirement to produce metallic properties. It is the occupancy of these energy bands that dictates the physical characteristics. The energy states that are near in energy to the highest occupied state within a band are readily accessible and can, therefore, influence the physical properties. They are termed the Fermi Level.

When the energy gap, E_g, between the highest occupied band (the valence band, derived from the HOMO's of the molecules) and the lowest unoccupied band (the conduction band, derived from the LUMO's of the molecules) is large, electrons cannot be promoted from the valence band to the conduction band and the material is an insulator. As this gap decreases, thermal excitation of the electrons from the valence band to the conduction band becomes possible and the material is now an intrinsic semiconductor (Figure 1.3).

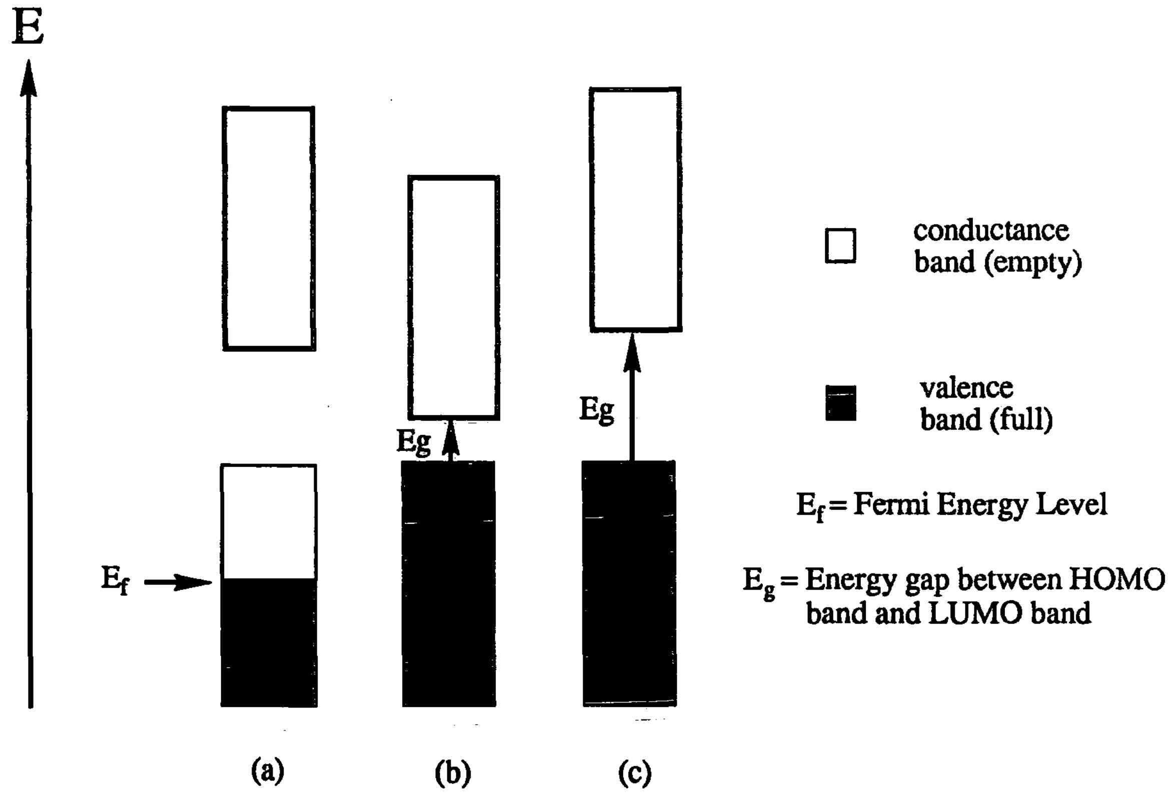


Figure 1.3 - Band structures of (a) a metal, (b) a semi-conductor, and (c) an insulator.

When the gap between the bands becomes vanishingly small, the material behaves as a metal. In this case there is a partially filled band in which it is possible for a large number of electrons to move easily into the infinitesimally higher energy states within the whole band. In charge-transfer complexes these states (at the Fermi Level) are derived from the HOMO's of the donor species and the LUMO's of the acceptor species. In semi-conductors the conductivity decreases as the temperature is lowered, because there is less energy to promote electrons across the band gap E_g. In metals this energy gap, E_g, is unimportant because we already have partially filled bands. Here the temperature dependance of conductivity is governed by the mobility of the charge carriers and is thus dominated by the scattering of the conducting electrons by interactions with vibrations of the atomic lattice (phonons). As the temperature is lowered the lattice vibrations are of a lower amplitude and decreased frequency, no longer hindering the mobility of the electrons to such an extent and, therefore, the conductivity increases.

From this description it is obvious that to form either a semi-metal or metal we need incompletely filled bands, which gives us the requirement for stable organic radicals.

1.3.3 Conductivity in One-Dimensional Metals and the Peierls Distortion

The band theory described above holds for organic and inorganic metals, and explains the conductivity of both three-dimensional metals and one-dimensional metals. However, the physics of a one-dimensional system can be dramatically different from that of a three-dimensional system. The behaviour of such organic systems was considered in the mid-1950's by Fröhlich[12] and Peierls[13] who argued that at low temperature a quasi one-dimensional metal (e.g. TTF-TCNQ) could not sustain long range order but would be unstable with respect to lattice distortions (analogous to the well-known Jahn-Teller distortion).

The degree of instability is determined by the nature of the partially filled bands. A half-filled band provides the simplest example (Figure 1.4). In this case each molecule in the stack is a radical ion and these unpaired spins provide an electronic driving force for spin pairing. When molecules dimerise in this way the half-filled conduction band is split into a fully occupied band of lower energy and an empty band of higher energy, with the concomitant creation of an energy gap between these bonding and anti-bonding levels. The size of this energy gap results in a transition from a metallic into a semi-conducting or insulating ground state.

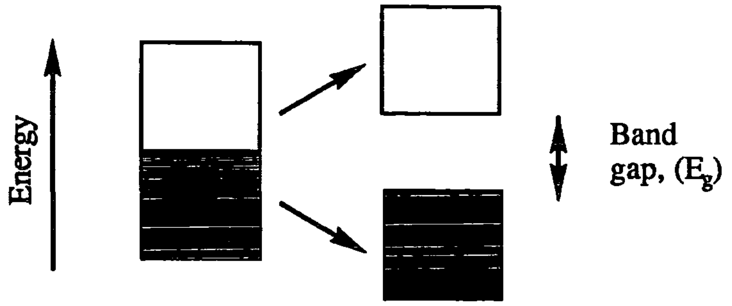


Figure 1.4 - Band splitting: The effect of Peierls distortion on energy levels

This is known as the Peierls distortion and it leads to a localisation of the previously conducting electrons and the formation of an associated charge-density wave (CDW) between the areas of high charge density and low charge density. Conductivity resulting from translation of the CDW is prevented by the potential energy gap E_g. Lattice defects and impurities can also lead to random electrostatic potentials that will tend to pin the CDW to the underlying lattice and favour the Peierls distortion. If a mechanism can be provided to free the CDW to act as a charge carrier then high conductivity and even superconductivity is possible.

A far more detailed and comprehensive discussion of the theory of conductivity in organic metals can be found in various review articles[14].

1.4 TTF - TCNQ

TTF-TCNQ was the forerunner of many hundreds of similar organic metals and it remains one of the most extensively studied. Both the donor and the acceptor molecules are planar molecules (of D_{2h} symmetry), of similar size and with a conjugated π–system.

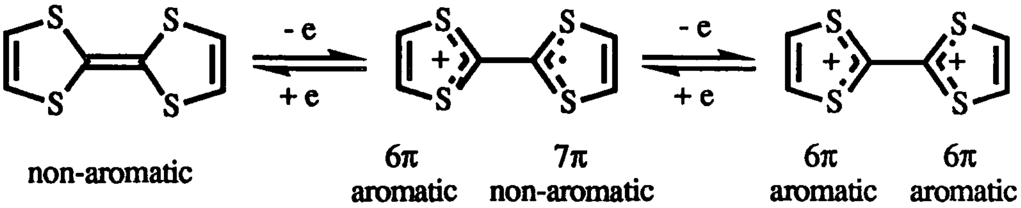


Figure 1.5 - The redox behaviour of TTF

The radical species must be thermodynamically stable and/or kinetically stable. In the case of TTF-TCNQ this is achieved by much of the spin-density residing on heteroatoms. In the TTF molecules, oxidation to the radical cation produces a resonance stabilised 6π-electron structure, and further oxidation to the dication produces two linked 6π-electron moieties (Figure 1.5). TCNQ also has resonance stabilised radical anion and dianion states. In the TTF radical cation more than 50% of the spin resides on the sulphur atoms, and in the TCNQ radical anion approximately 25% of the spin resides on nitrogen atoms (Figure 1.6).

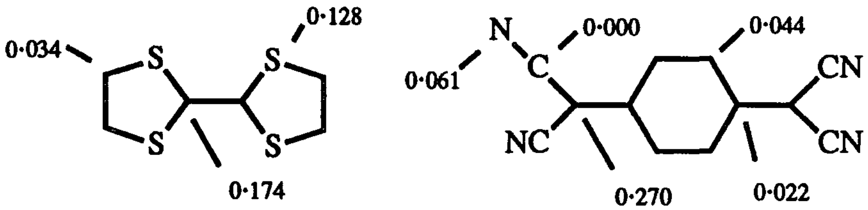


Figure 1.6 - Spin distribution of TTF and TCNQ radicals

The crystal structure of TTF-TCNQ[15] consists of TTF and TCNQ molecules uniformally spaced along the b-axis (the stacking axis) in interlocking, segregated stacks. The planes within which the molecules lie are tilted with respect to the stacking axis, the tilt of the donor molecules being in an opposite direction to the tilt of the acceptor molecules. This gives rise to the so-called 'herringbone structure' (Figure 1.7)[151]. Within these segregated donor and acceptor columns, the molecules do not lie directly on top of one another. There is a lateral displacement so that the exocyclic carbon-carbon double bond of one molecule lies over the ring of the molecule adjacent to it in the stack: so-called 'ring over bond' overlap (Figure 1.8).

This structure results in strong intra-stack interaction and electron delocalisation, and only weak inter-stack interactions. Thus, conductivity along the stacking axis is over 500 times greater than that along the crystallographic a or c axes. The conductivity of TTF-TCNQ rises twenty-fold from 500 Scm^{-1} at 293K to $>10^4$ Scm^{-1} at 59K but on further cooling three successive phase transitions occur at 53, 47 and 38K (Figure 1.9) leading eventually to an insulating state with three-dimensional order. This is due to Peierls distortions.

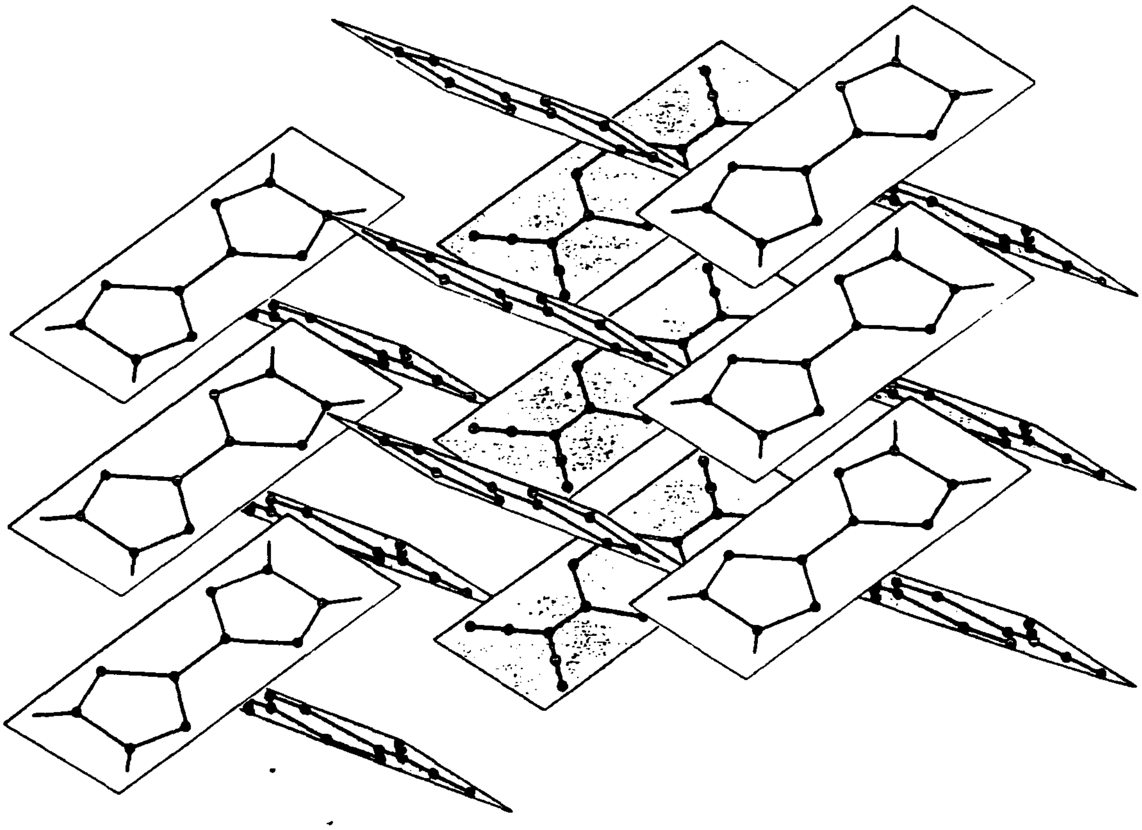


Figure 1.7 - "Herringbone" stacking in crystals of TTF-TCNQ

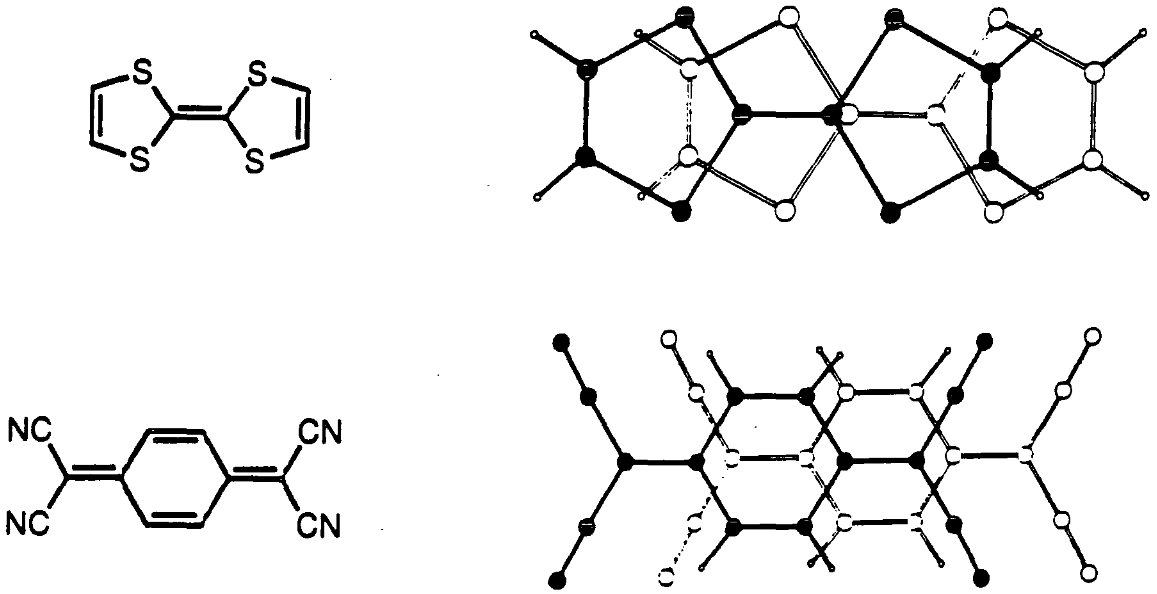


Figure 1.8 - Ring-over-bond overlap in crystals of TTF-TCNQ

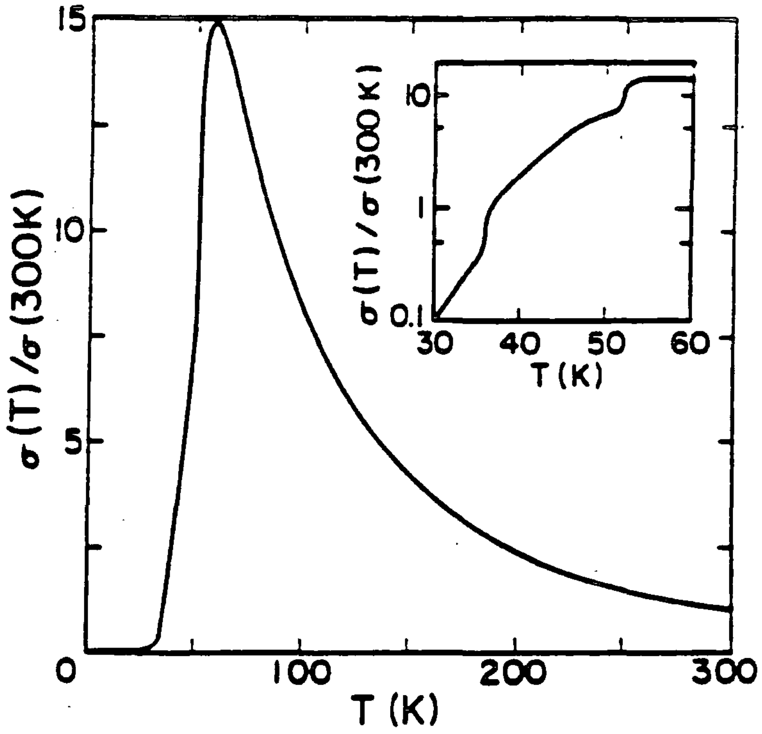


Figure 1.9 - Conductivity of TTF-TCNQ as a function of temperature;
Inset: phase transitions observed between 60 and 30K

Infra-red spectroscopy[16] and diffuse *X*-ray scattering techniques[17] have ascertained the degree of charge-transfer (ρ) from TTF to TCNQ to be 0.59 electrons per molecule. So, with both bands partially filled, both stacks contribute to the metallic conductivity. The actual mechanism of conductivity is ~~of some~~ a matter of conjecture. Possible mechanisms involve a sliding charge density wave[18], or single particle conductivity[19], or perhaps a combination of both mechanisms[20].

The partial transfer of electrons is crucially important for this system to be an organic metal. Where ρ = 1 (e.g. TTF-Br[21]), $\sigma_{rt} < 1\text{x}10^{-11}$ Scm^{-1} compared to TTF-Br$_{0.71}$ (ρ = 0.71), where σ_{rt} = 200 Scm^{-1}. The partial charge transfer in TTF-TCNQ results from the delicate balance of the ionisation potential of TTF with the electron affinity of the TCNQ.

1.5 THE DESIGN OF NEW CONDUCTING C-T COMPLEXES

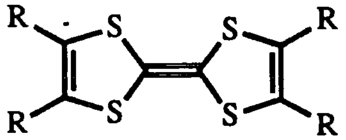
What makes TTF-TCNQ stand out over traditional complexes of donors and acceptors? The key features have been mentioned above and are all-important. In 1982 Cowan and Kini published a set of design constraints for the preparation of good organic conductors[22]:

1) Stable open-shell (free radical) species in order to form a partially filled band.
2) Planar molecules with delocalised π-molecular orbitals so that effective overlap of HOMO and/or LUMO can occur.
3) Inhomogenous charge and spin distribution to reduce the intramolecular Coulombic repulsion when like charged molecules are stacked.
4) Segregated stacks of radical species - regardless of charge transfer, a mixed stack will always have a completely filled band.
5) No periodic distortion which opens a gap at the Fermi level (uniform stacks).
6) Little or no disorder (symmetrical radicals and/or radical anions and cations) - disorder tends to produce a potential which localises the wave function.
7) Molecular components of similar size (though this has since been demonstrated to be not always the case).
8) Fractional charge (mixed-valence); by adjusting the charge, it is possible to minimise the on-site Coulombic repulsion, which should be small compared to the band width.
9) Relatively strong interchain coupling to suppress phase transitions.
10) Cation and/or anion nominally divalent ; unless the molecular components can support doubly charged species, only a correlated type of conductivity is possible.
11) Polarisable species.

It is really beyond our ability to induce molecules to pack within a crystal lattice in the desired manner, so it becomes a matter of tuning certain factors (*i.e.* those specified above) until a particular combination of structural modifications gives the desired properties of an organic metal. Considerable research effort has been expended in synthesising new donors and acceptors, following these guidelines, and the last few years have resulted in a large increase in the number of organic compounds with high conductivity. Major advances are the stabilisation of the metallic state down to lower temperatures and the attainment of organic superconductivity.

1.6 NEW ELECTRON DONORS

A host of new TTF analogues exist, various synthetic routes to which are regularly updated[23], and a brief overview will be given here. Synthetic chemists have given much attention to new donors containing the 1,3-dithiole ring system of TTF. The first modifications of the TTF molecule involved extending the σ–bond framework, for example tetramethyl-TTF (TMTTF)[24] (3) and hexamethylene-TTF (HMTTF)[25] (4), and extending the π–orbital system, e.g. di-benzo TTF (DBTTF)[26] (5).



(3) R = Me
(4) R-R = $(CH_2)_3$
(5) R-R = $(CH{=}CH)_2$

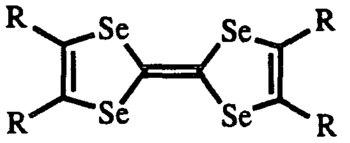
The effect of alkyl substituting the TTF was to lower the oxidation potential of the donor, relative to that of unsubstituted TTF. The TCNQ salt conductivities of (3) and (4) at room temperature are of the same order of magnitude as for TTF-TCNQ. However, the metal-insulator transition temperature ($T_{M\text{-}I}$) is raised somewhat, due to a slight reduction of (already small) inter-stack interactions, increasing the one dimensionality. The π-extended system (DBTTF) shows an increased oxidation potential, as do TTF's bearing electron withdrawing groups, such as -CN and $-CF_3$[23a]. TCNQ salts of these donors tend to have conductivities several orders of magnitude less than TTF-TCNQ.

Because it is known that an increase in dimensionality will help to suppress the Peierls distortion, work was directed towards extending the dimensionality. This can be encouraged in two ways;

1) by the use of additional polarisable heteroatoms in and around the donor framework. This can lead to an increase in intra-stack π-interactions and induce inter-stack interactions.

2) by screening various inorganic counter ions for subsequent C-T salt formation.

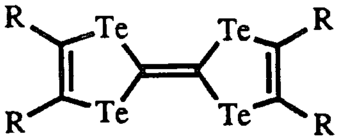
Thus, the sulphur atoms in TTF were replaced by selenium to produce tetraselenafulvalene (TSeF)[27] (6), tetramethyl-TSeF (TMTSeF)[28] (7), hexamethylene-TSeF (HMTSeF)[29] (8) and dibenzo-TSeF (DBTSeF)[30] (9). [For the synthesis of organic conductors containing selenium and tellurium see ref.22]



(6) R = H
(7) R = Me
(8) R-R = $(CH_2)_3$
(9) R-R = $(CH=CH)_2$

In general, the TCNQ complexes of the tetraselenafulvalenes do have an increased stabilisation of the metallic state relative to TTF-TCNQ. The d-orbitals of the selenium atoms increase the conductivity along the donor stacks compared to the acceptor stacks due to increased intra-stack interactions. For example, TSeF-TCNQ has a room temperature conductivity of $\sigma_{rt} = 800$ Scm^{-1} and the metallic state is stabilised down to 40K[31]. In the case of HMTSeF-TCNQ[32] $\sigma_{rt} = 1500$ Scm^{-1}, and although the conductivity reaches a maximum on cooling down to 45-70K, the complex remains metallic down to 1K. This demonstrates the beneficial effect of increasing the dimensionality, and the crystal structure reveals strong Se··N contacts between donor and acceptor stacks. It should also be noted here that inorganic salts of TMTSeF provided the first generation of organic superconductors[33] and these will briefly be mentioned later (Chapter 1.7.1).

Tetratellurafulvalenes are significantly harder to synthesise. The first to be synthesised, in 1982, were hexamethylene-TTeF (HMTTeF)[34] (10) and dibenzo-TTeF (DBTTeF)[35] (11), and it was not until 1987 that the parent TTeF (12) was reported in the literature[36].



(10) R-R = $(CH_2)_3$
(11) R-R = $(CH=CH)_2$
(12) R = H

The 1:1 TCNQ salt conductivities show an increase in the room temperature conductivities and a stabilisation of the metallic state due to significantly increased dimensionality [Table 1.1].

COMPLEX	σ_{rt} (Scm^{-1})	ρ	T_{M-I} (K)
TTF-TCNQ	500	0.59	59
TSeF-TCNQ	800	0.63	40
TTeF-TCNQ	*ca.* 2000	0.71	-

Table 1.1 - Data for tetraheterofulvalene-TCNQ complexes.

In TTeF-TCNQ there is no Peierls distortion and the conductivity increases down to 2K[37]. The *X*-ray crystal structure shows the donor molecules to be in layers (*c.f.* TTF-TCNQ and TSeF-TCNQ) with close inter- and intra-stack interactions. TTeF-TCNQ can, therefore, be considered to be a two dimensional metal.

1.7 ORGANIC SUPERCONDUCTIVITY

1.7.1 Bechgaard Salts $(TMTSeF)_2X$

An amazing discovery in 1980, reported by Bechgaard, Jérome and workers, was that a cooled and pressurised sample of $(TMTSeF)_2PF_6$ [0.9K, 12kbar][33a] completely lost its electrical resistance. This first superconducting organic material stimulated research into the synthesis of many similar salts with various inorganic counter-anions. These are the so called Bechgaard Salts. For the salts where X = PF_6^-, AsF_6^-, SbF_6^- and ReO_4^- [38], there appears to be an insulating ground state. When single crystals of these salts are subjected to a certain external pressure this insulating state is suppressed and the salt becomes metallic, and eventually superconducting on cooling. The salt where X = ClO_4^-[39] is the only ambient pressure superconductor in the TMTSeF series. It should be noted that isostructural $(TMTTF)_2X$ salts are not superconducting. *X*-Ray crystallography shows the essentially planar TMTSeF molecules stacking in a 'ring-over-bond' fashion forming a one-dimensional chain, this being the direction of highest conductivity. The Se··Se interactions are similar for both inter- and intra-stack distances, resulting in a two-dimensional network, with the supporting anions separating adjacent sheets and preventing three-dimensionality (Figure 1.10).

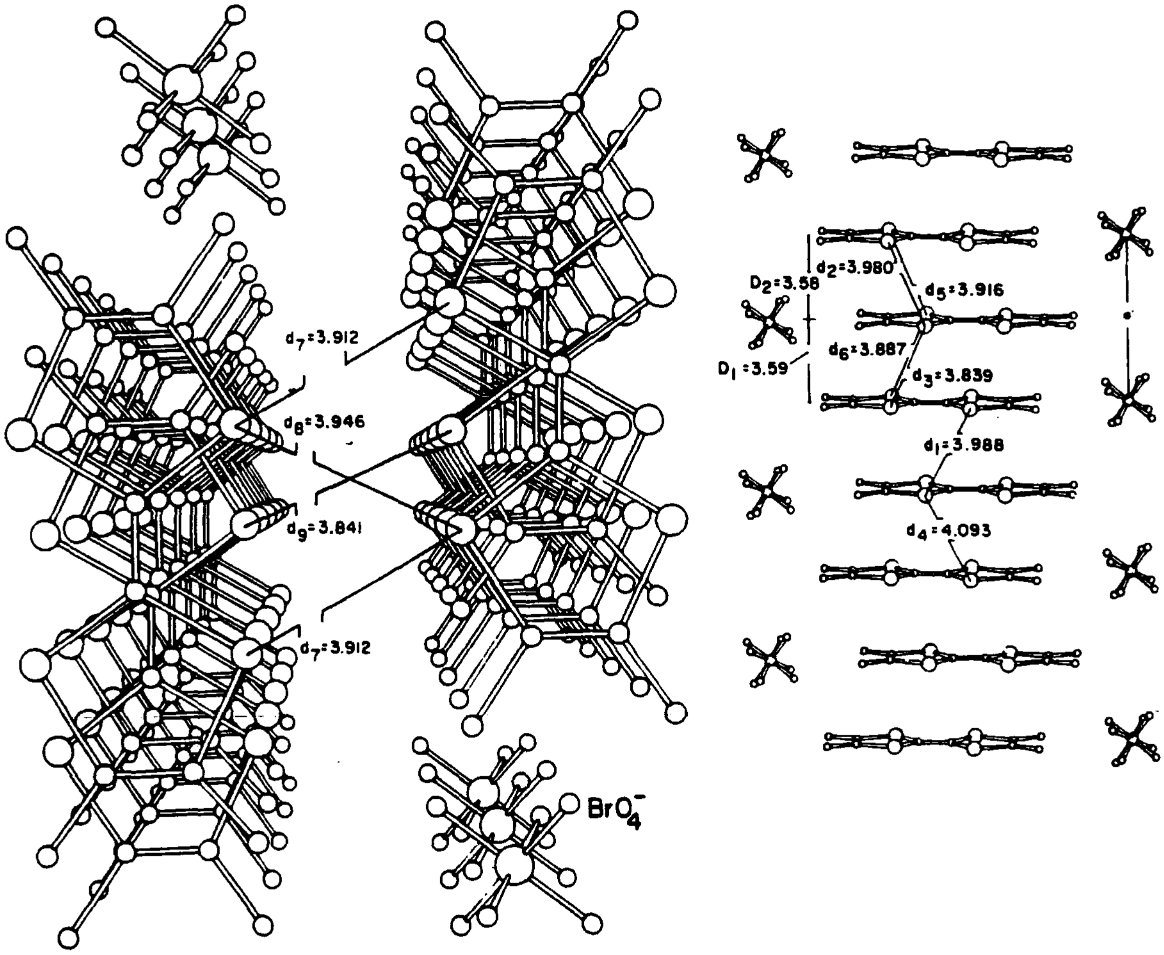


Figure 1.10 - Crystal structure of $(TMTSeF)_2BrO_4$, looking down the stacks along the $\underline{a}$ axis (left) and perpendicular to the same stacks (right). The Se··Se contact distances (d's) are indicated.

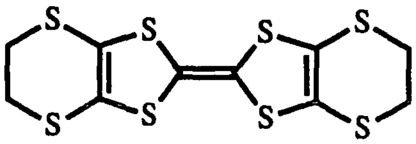
The anions play little, if any, part in the conduction process, this being dominated by the selenium-selenium interactions. However, the position of the anions in the lattice is all-important. At room temperature they are fairly disordered and provide a means for electron scattering. On cooling they order, and this fact in conjunction with the external pressure squeezing the selenium atoms closer together, leads to the onset of superconductivity.

For inorganic materials theory states that the charge carriers for superconductivity are pairs of electrons (Cooper Pairs)[40], as distinct from single electrons in metallic conductivity. This electron pairing can be driven by phonons below a certain critical temperature (T_c), if a strict set of structural and electronic energy conditions are fulfilled. The electron pairs are dissociated by thermal energy above T_c and superconductivity is lost. Whether or not this theory is adequate for organic materials is a matter of some conjecture[41].

More recently, many salts of sulphur based TTF systems have been shown to exhibit superconductivity. The most important family are inorganic salts of bis(ethylenedithiolato)-TTF (BEDT-TTF).

1.7.2 (BEDT-TTF)$_2$X Salts and (DMET)$_2$X Salts

As an alternative to replacing the sulphur atoms in the core of the TTF structure with other chalcogen atoms, another possibility is to add more chalcogens to the periphery of the TTF molecule. This led to the formation of BEDT-TTF (*a.k.a.* 'ET') (13)[42], synthesised in 1978, which has contributed to more than half of today's ambient pressure superconductors[14a].



(13)

While the properties of the complex of TCNQ and ET are quite unremarkable, crystals of inorganic cation-radical salts of ET grown electrochemically are superconducting. (ET)$_2$ReO$_4$ was the first to exhibit pressure induced superconductivity

(T_c = 1.5K, 7kbar)[43]. If the anions are I_3^-, $Cu(SCN)_2^-$ or $Cu[N(CN)_2]Cl^-$, ambient pressure superconductivity is observed.

In the crystal structures the cations are non-planar, with the peripheral ethylene bridges twisted. This prevents close π-overlap face to face and inhibits columnar stacking. Short S··S 'inter-stack' interactions lead to an increase in dimensionality. Some of these salts can crystallise in up to four crystallographically unique phases. For example, $(ET)_2I_3$ has an α-phase ($T_{M\text{-}I}$ =135K)[44] and three superconducting phases β, θ and κ[45] (Figure 1.11). Salts with the highest T_c values are kappa phase structures. Here there are no stacks or sheets but instead there are interacting dimers which are positioned orthogonally to each other forming a conducting two-dimensional S··S network. The anions form insulating V-shaped polymeric chains. The T_c for ET salts increases as the linear length of the anion increases[46].

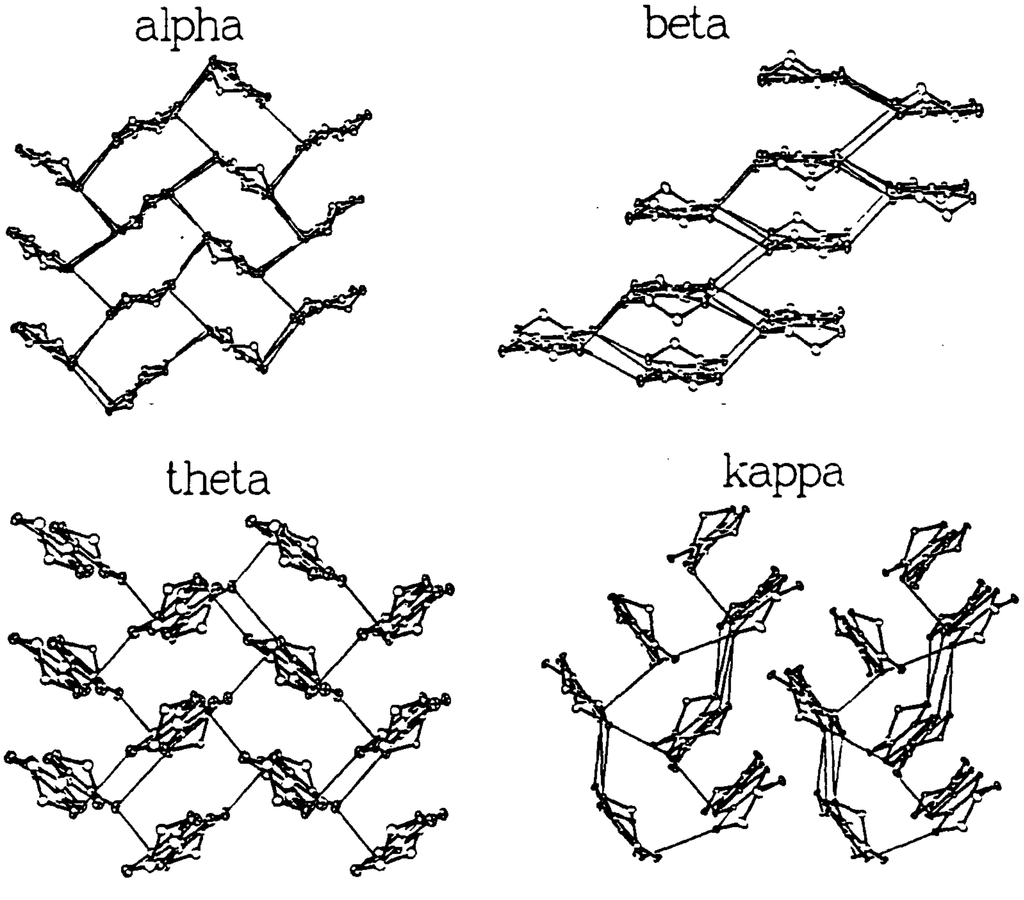
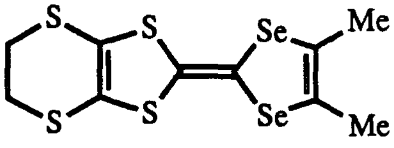


Figure 1.11 - Packing schemes of ET molecules, viewed along the long molecular axis, in α, β, θ and κ phases of $(ET)_2I_3$[150].

Presently the highest T_c organic superconductor is κ-$ET_2Cu[N(CN)_2]Br$[47] with T_c = 11.6K at ambient pressure. Superconductivity has not been found in (BEDSe-TTF)$_2$X salts or (BEDSe-TSeF)$_2$X salts.

Of the many mixed S,Se donors that have been synthesised[48], only dimethyl (ethylenedithio)-diselenadithiafulvalene (DMET)[49] (14) has formed superconducting salts.



(14)

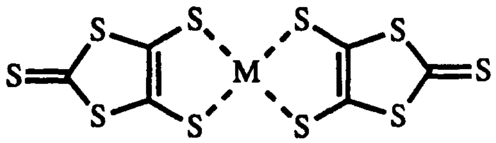
This asymmetrical molecule is a hybrid of TMTSeF and ET and the $(DMET)_2AuBr_2$ salt has the highest T_c of 1.9K at ambient pressure[50]. Again, different crystal phases are exhibited, and in all cases there are close intermolecular S··S contacts, giving rise to a high degree of dimensionality.

1.7.3 Metal (dmit)2 Acceptors

Superconductivity has also been exhibited by complexes of $M(dmit)_2^{n-}$ (where M = Ni, Pd, Pt and dmit = 4,5-dimercapto-1,3-dithiole-2-thione) (15). These are the only examples of superconductivity in π-acceptor compounds, for example;

1) $TTF[Ni(dmit)_2]_2$ T_c = 1.6K, 7kbar[51].

2) α'-$TTF[Pd(dmit)_2]_2$ T_c = 6K, 19kbar[52].

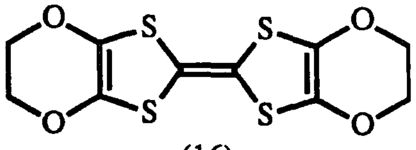


(15)

The $M(dmit)_2$ system is essentially planar and, again, there is a high degree of dimensionality with many short S··S contacts.

1.7.4 Oxygen Containing Systems

Replacement of the four central sulphur atoms of the TTF molecule by oxygen has not been accomplished, but attaching oxygen atoms to the periphery of TTF has been achieved. Bis(ethylenedioxalato)-TTF (BEDO-TTF), (BO) (16) was reported in 1989[53]. The effect on the redox properties is shown in Table 1.2.


(16)

DONOR	$E_1^{1/2}$ (mv)*	$E_2^{1/2}$ (mv)*	E_2-E_1 (mv)
TTF (2)	367	748	381
ET (13)	567	829	262
BO (16)	435	699	264

Table 1.2[53] - Redox properties of TTF donors *Ag/AgCl ref. electrode.

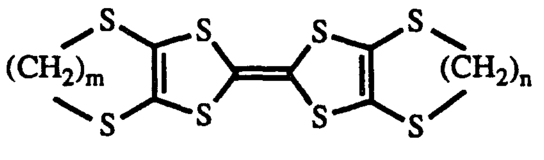
The reasoning behind this substitution by oxygen was that in superconductivity theory T_c varies inversely with the square root of the mass of the ions in the lattice, *i.e.* T_c for BEDO-TTF salts should be higher than for ET. One superconducting salt of BEDO-TTF has been discovered. This is (BEDO-TTF)$_3$Cu$_2$(NCS)$_3$ (T_c = 1.06K)[54].

1.8 ADAPTATIONS TO BEDT-TTF

Due to the fact that it has formed so many superconducting salts, ET has attracted considerable attention. Thus, various modifications have been made to the ET structure to investigate the effect of these changes. Examples include:

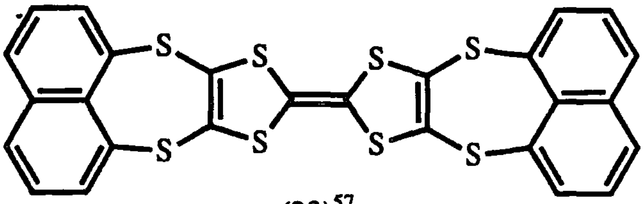
1) Modifying the peripheral bridging groups whilst keeping the C_6S_8 core intact. In ET salts the anions reside in cavities formed by the buckled ethylene bridges,

(weakly hydrogen-bonding to the -CH_2- groups) and this relative orientation of the anions to the donor molecules plays an important part in the properties of the complex. Therefore, the outer ring has been modified to form -CH_2- cavities of various size and shape [compounds (16)-(23)].



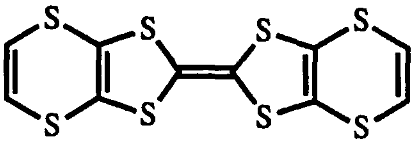
(16) m=n=1[55], (20) m=1, n=2[58]
(17) m=n=2[42], (21) m=1, n=3[59]
(18) m=n=3[56], (22) m=2, n=3[60]
(19) m=n=4[57]

Electrocrystallisation experiments[61] have shown that these relatively small structural modifications of the ET molecule lead, in some cases, to new structure types, rather than simple expansions or contractions of the $(ET)_2X$ structure, where X is a linear triatomic anion.



(23)[57]

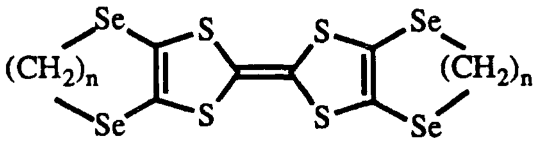
In order to increase the planarity of the ET structure donor (24)[62] was synthesised having vinylene units in place of the ethylene bridges. The cyclic voltammetry of this donor reveals one, two-electron, irreversible oxidation ($E^{1/2}$ = 0.83V vs S.C.E.). However, no crystal structure or conductivity measurements of TCNQ-salt have been reported.



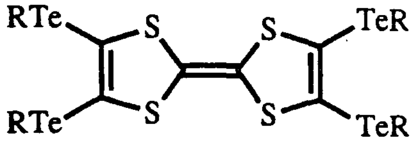
(24)

2) Replacing the outer sulphur atoms in ET with larger selenium and

tellurium atoms (this has proved relatively trivial to achieve by reacting lithiated TTF with elemental Se or Te) and/or enlarging the periphery of ET by adding yet more chalcogen atoms.



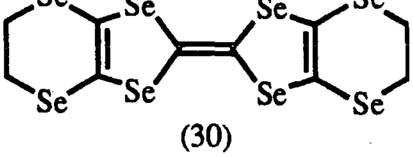
(25) n = 1
(26) n = 2
(27) n = 3



(28) R = Me
(29) R = Et

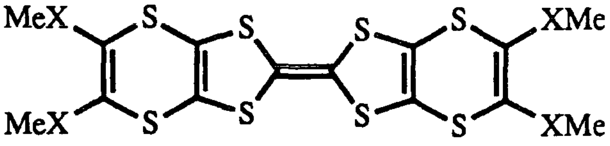
Compounds (25)-(27), analogous to compounds (16)-(18), have been synthesised with selenium atoms in the peripheral chalcogen positions[63]. [BEDSe-TTF(26)]$_2$IBr$_2$ is isostructural to β(ET)$_2$ICl$_2$ yet it is semiconducting (σ_{rt} = 3.5 x 10^{-3} Scm^{-1})[63d], not superconducting. Similarly the tellurium compounds (28) and (29) have also been made[64,65]. Compound (28) forms a 1:1 complex with TCNQ with a conductivity of $\sigma_{rt} = 1\times10^{-2}$ Scm^{-1} [66]. The effect on redox potentials on going from S to Se to Te substituents on the TTF moiety is to slightly lower both $E_1{}^{1/2}$ and $E_2{}^{1/2}$ values.

The all-selenium equivalent of ET (BEDSe-TSeF) (30)[67] has been found to have a crystal structure isostructural to the neutral ET structure. However, (BEDSe-TSeF)$_2$AuBr$_2$ is only semiconducting[68], not superconducting like its sulphur analogue.



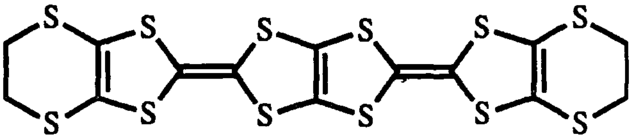
(30)

It is possible to increase the number of chalcogen atoms in ET by further extending the periphery of the molecule, for example donors (31) and (32) have been synthesised by Japanese workers[69]. As for donor (24), both these donors show a single irreversible oxidation to the dication. $E^{1/2}$ = 0.83V for (31) and $E^{1/2}$ = 0.86V for (32). (Both values *vs* S.C.E.- $E_2^{1/2}$ for ET = 0.82V).



(31) X = S
(32) X = Se

3) Enlarging the internal core in ET whilst retaining the external features. Attempts to synthesise a compound such as compound (33) have so far been unsuccessful.



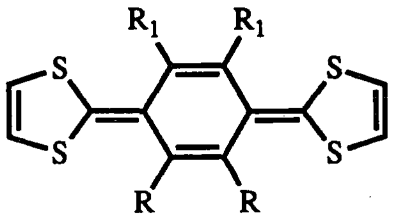
(33)

1.9 EXTENDED π-SYSTEMS

As an alternative to placing different substituents around the periphery of the TTF unit, it is also possible to synthesise new donors by changing the basic skeletal structure. Thus, a whole range of new 1,3-dithiole-2-ylidene electron donors have been prepared, in the hope of discovering properties either different or superior to those previously obtained. Extending the conjugation between the 1,3-dithiole rings should achieve the following:

1) Stabilised dication states due to reduced intra-molecular Coulombic repulsion.
2) The radical cation should also be stabilised by extended conjugation and greater delocalisation.
3) Due to rotation about the units linking the dithiole rings, these new derivatives may no longer be planar. This may induce novel inter- and intra-stack interactions but major distortions may well be a hindrance to such interactions.

The initial research in this area concerned the insertion of aromatic spacer units, such that the neutral donors are in a quinoid form [compounds (34)-(36)], with the oxidised radical cation and dication species affording aromatisation on the system. This obviously stabilises the oxidised states, resulting in lower oxidation potentials, in some cases low enough to air-oxidise the donor (Table 1.3). In fact many donors of this form only show one single two-electron oxidation directly yielding the dication. Donors of the type (36) will be discussed in Chapter 5.

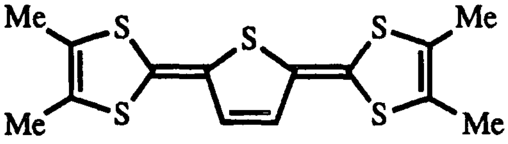


(34) $R = R_1 = H$
(35) $R = H, R_1\text{-}R_1 = (CH{=}CH)_2$
(36) $R\text{-}R = R_1\text{-}R_1 = (CH{=}CH)_2$

DONOR	$E_1^{1/2}$ (V)*	$E_2^{1/2}$ (V)*	ΔE(V)	D:TCNQ	$\sigma_{rt}(Scm^{-1})^b$
(34)[71]	-0.11	-0.04	0.07	3:4	5.3×10^{-4}
(35)[71]	0.00	-	0.00	2:3	2.9×10^{-2}
(36)[72]	0.40[a]	-	-	1:4	4×10^{-3}
(37)[70]	0.04	0.31	0.27	1:2	80

Table 1.3 - Redox properties of extended donors
**vs* S.C.E., [a]Ag/AgCl ref. electrode, [b]compressed pellet.

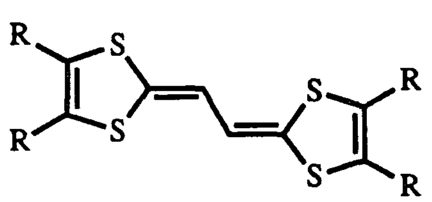
In order to increase inter-stack interactions another sulphur atom can be introduced by using thiophene as the aromatic spacer unit (37)[70].



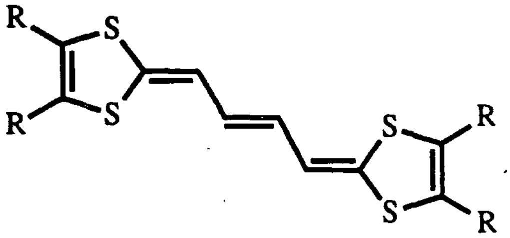
(37)

In this case two, well-defined, one-electron, reversible oxidations are observed, *i.e.* the radical cation and the dication species both exist. The dication state is again stabilised as indicated by the small difference between the two oxidation potentials (E_2-E_1 = 0.27V) compared to that value for TTF (E_2-E_1 = 0.36V).

Another group of extended donors is that with a polyene spacer unit between the dithiole rings. Yoshida's group in particular has contributed a large number of donors to this family (38-43).



(38) R = H
(39) R = Me
(40) R-R = $(CH=CH)_2$



(41) R = H
(42) R = Me
(43) R-R = $(CH=CH)_2$

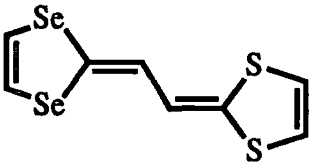
The simplest case is to have one extra carbon-carbon bond separating the end units (38-40)[73]. The effect of this conjugation on the oxidation potentials (Table 1.4) of these

DONOR	$E_1^{1/2}$ (V)*	$E_2^{1/2}$ (V)*	ΔE(V)	D:TCNQ	σ_{rt}(Scm^{-1})^a
(38)	0.20	0.36	0.16	1:1	0.79
(39)	0.19	0.34	0.15	1:1	3.7×10^{-8}
(40)	0.47	0.64	0.15	1:1	~5[78]
(41)	0.22	-	0.00	not isolated	-
(42)	0.21	-	0.00	1:1	not reported
(43)	0.47	-	0.00	1:1	not reported
(44)	0.26	0.40	0.14	2:3	0.07
(45)	0.33	0.47	0.14	2:3	0.24
TTF	0.34	0.71	0.37	1:1	2.5

Table 1.4 - Redox properties and conductivity data for extended donors (38)-(45)
*Ag/AgCl ref. electrode, ^{a}compressed pellet

vinylogues is to lower E_1 (compared to TTF) and to decrease the separation of the two oxidation potentials (*i.e.* smaller E_2-E_1, compared to TTF).

If the conjugation is further increased by an extra carbon-carbon double bond [compounds (41)-(43)[74]] the separation between E_1 and E_2 is eliminated and a single two-electron oxidation is observed. The effect of chalcogen substituents on the periphery of these vinylogues will be discussed in detail in Chapter 2.



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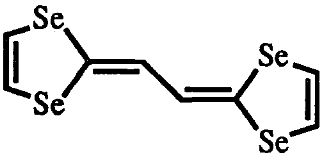
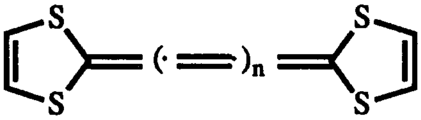


(45)

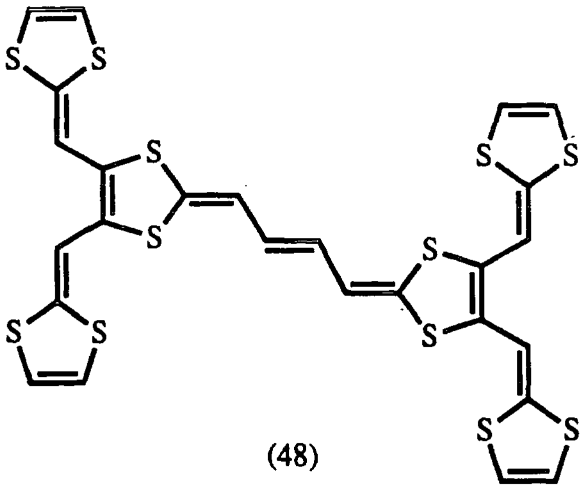
Derivatives of vinylogues of TTF substituted with two or four selenium atoms in place of the central sulphur atoms have also been prepared [compounds (44) and (45)[75]]. Redox behavior and conductivities of complexes for donors (38)-(45) are summarised in Table 1.4[76], sequential selenium incorporation [(38), (44) and (45)] increasing the redox potentials.

Attempts to synthesise donors with allene spacer units between the dithiole rings was thwarted by the molecules' extreme instabilities, and the neutral compounds (46) and (47) were not isolated, being characterised as their dication salts[77].



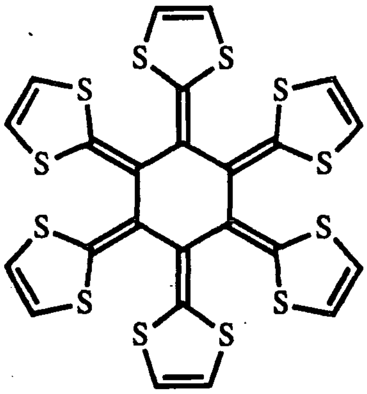
(46) n = 1
(47) n = 3

Another example of a stretched TTF system (48)[79] is that synthesised by Gorgues *et al.* Unfortunately, this compound is easily air-oxidised (E_1 = 0.12, E_2 = 0.47 *vs.* S.C.E.), is fairly insoluble and no TCNQ salt data is given.



(48)

In the last five years in particular, interest has been focussed on radialene-type structures[148] that exhibit a high degree of symmetry, and compounds such as (49)[80] and (50)[81] have been synthesised by Japanese workers. Molecules of this type with D_{3h} symmetry had previously been predicted by theory to be possible sources of organic ferromagnetism and this topic will be discussed further in Chapter 3.



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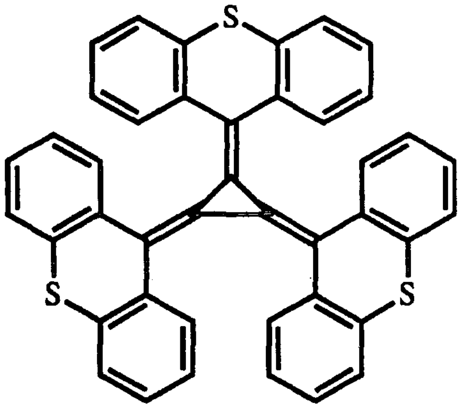

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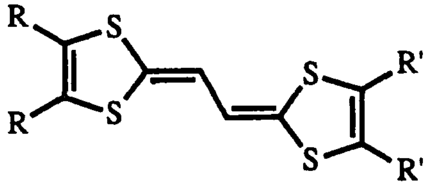
CHAPTER TWO

NEW VINYLOGOUS TETRATHIAFULVALENE π-ELECTRON DONORS WITH PERIPHERAL ALKYLSELENO SUBSTITUTION

2.1 BACKGROUND

An exciting new class of stretched-TTF derivatives, first reported in 1983, included the parent TTF-'vinylogue', ethanediylidene-2,2'-bis(1,3-dithiole) (38)[76,82]. This molecule was designed on the basis that the dication species (formed on oxidation of the donor) should be significantly stabilised due to the increased separation of the 1,3-dithiole rings, reducing the intramolecular Coulombic repulsion between positive charges.

Much research has centred on the synthesis of new multichalcogen π-electron donors based on TTF[83] and, following this theme, three research groups (including our own) have independently synthesised the ET vinylogue (51)[84-86] that had previously been identified as a desirable target by Japanese workers[87].



(38) R = R' = H
(51) R-R = R'-R' = SCH_2CH_2S
(52) R-R = SCH_2CH_2S, R' = Me
(53) R = R' = SMe

The solution redox behaviour of the extended donors (38) and (51) has been observed by cyclic voltammetry and this shows that they both undergo two, reversible, single-electron oxidations (similar to TTF and ET). Two important consequences of 'stretching' the 1,3-dithiole rings apart from one another by the introduction of two sp^2 carbon atoms can be noted:

1) Both the first and second oxidation potentials of (51) are substantially lowered compared to the parent system, ET, *i.e.* molecule (51) is a stronger donor than ET [and similarly molecule (38) is a stronger donor than TTF], and $E_2^{1/2}$ (the radical cation-dication redox wave) for (51) is seen at a very similar potential to that value for TTF (Figure 2.1)[85] .

2) The difference between the two redox waves, $\Delta E^{1/2}$, is also significantly reduced in the vinylogous materials relative to the 'parent' materials, reflecting the reduced intramolecular Coulombic repulsion in the dication states.

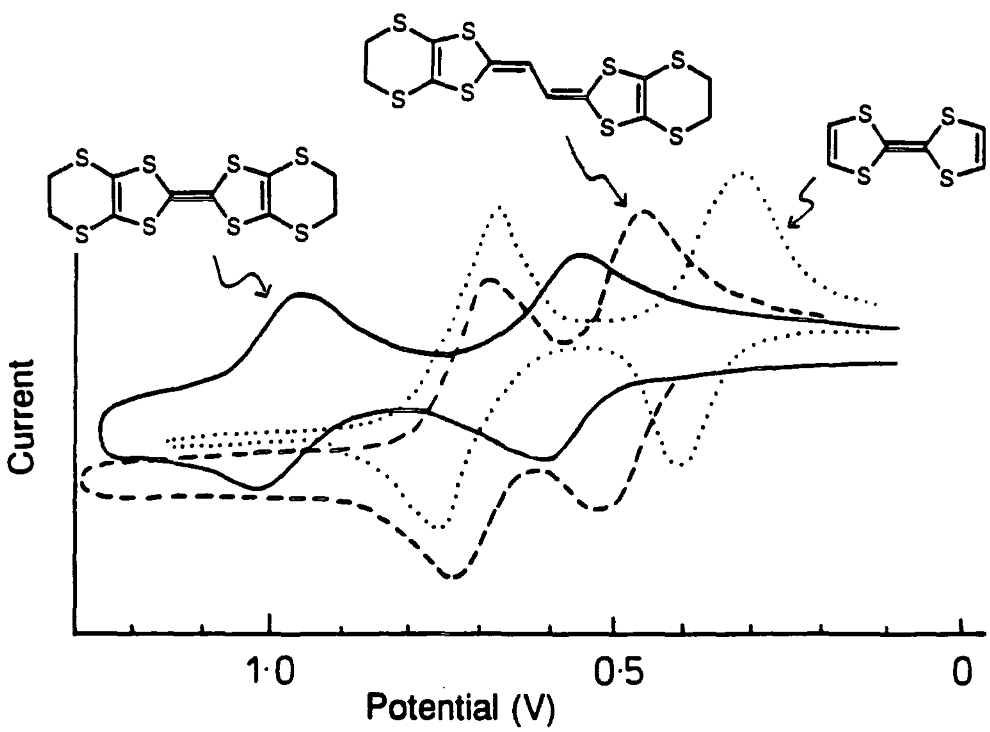


Figure 2.1 - Cyclic voltammetric data for TTF (2), ET (13) and vinylogous ET derivative (51) (Pt electrode *vs.* Ag/AgCl; electrolyte $EtN_4^+PF_6^-$ in CH_2Cl_2)

Due to this different redox behaviour, and the altered solid-state structure, salts of extended donors may show electronic and magnetic properties that are quite different from salts of TTF or ET. Thus, a series of symmetrical and unsymmetrical vinylogues has been synthesised in our laboratory[88] and *X*-ray crystal structures of two of these neutral compounds, donors (52) and (53), have been solved.

Molecule (52) is almost completely planar, in contrast to the neutral ET molecule which has a marked deviation from planarity (Figure 2.2), though the planarity, in this case, does not lead to any short (< 4.0 Å), non-bonded sulphur-sulphur contacts. In the case of donor (53) the central C_8S_4 core is also planar with the peripheral SMe groups bent out of the plane (Figure 2.3). The TCNQ salts of these sulphur substituted vinylogues have room temperature powder conductivity values in the range $\sigma_{rt} = 5x10^{-4}$ - $6x10^{-8}$ Scm^{-1}, which is a significant decrease from the value for the TCNQ salt of unsubstituted vinylogue (38). A crystal structure of the TCNQ complex of donor (53), obtained in our work, reveals a mixed stack structure (Figure 2.4)[89]. Such a structure does not fulfill the criteria for high conductivity, which explains the poor conductivity values of the TCNQ salts of these donors. Why mixed stacks should form with these stretched donors is not easily explained.

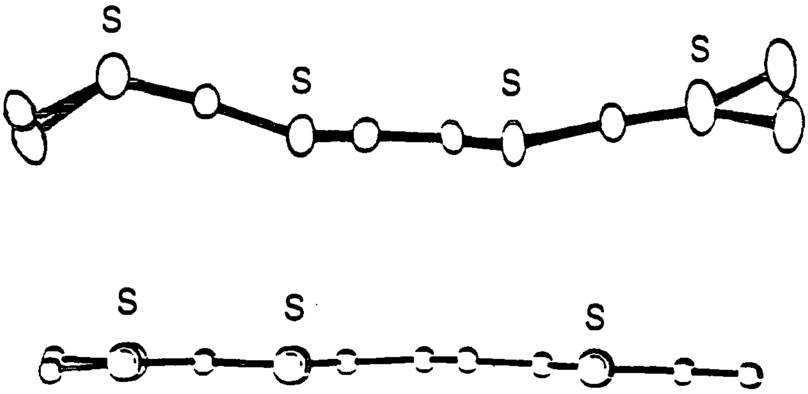


Figure 2.2 - Molecular structures of the neutral donors ET (above) and compound (52) (below), as determined by single crystal *X*-ray analysis: viewed along the best plane formed by the sulphur atoms.

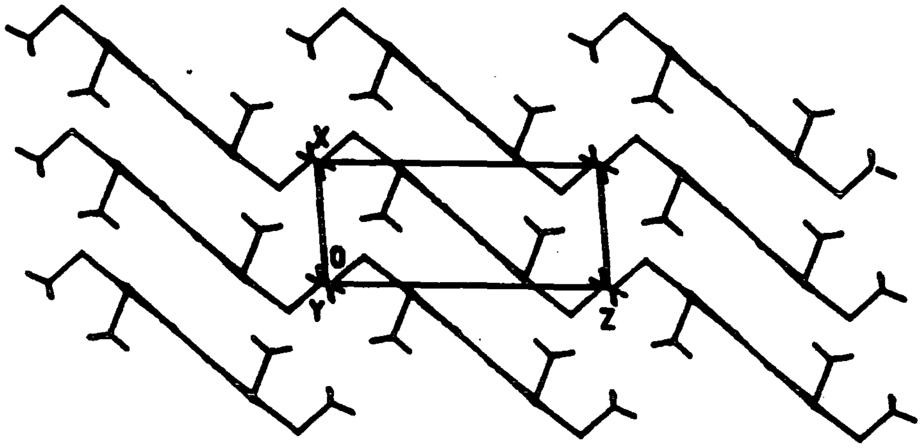


Figure 2.3 - Packing diagram for neutral donor (53)

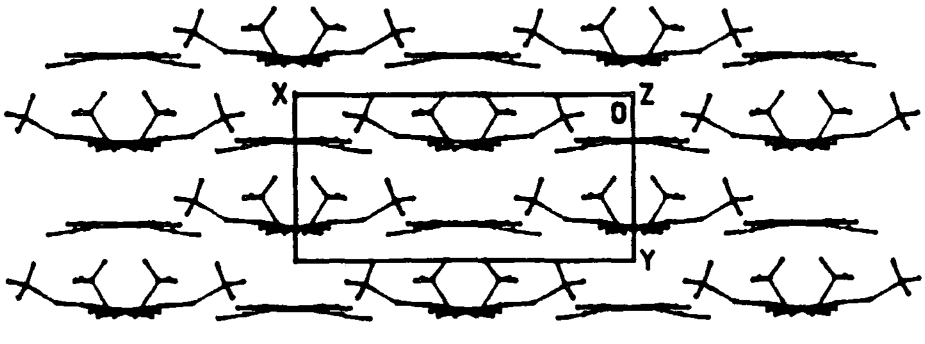


Figure 2.4 - *X*-Ray crystal structure of a 1:1 complex of donor (53) with TCNQ

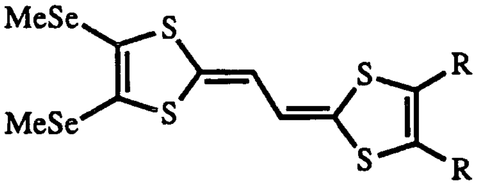
Work in the mid-1970's established that the substitution of the sulphur atoms of TTF with selenium generally had beneficial effects on the properties of the TCNQ salt. The room temperature conductivity is increased and the metal-insulator transition temperature is lowered. Also, the more diffuse p- and d- orbitals of Se lead to the transport properties being dominated by the donor stack[27-32]. However, in comparison with the number of sulphur containing systems known, there has been comparatively little research on selenium containing systems. Reasons for this are that they are invariably harder to synthesise[22], are insoluble, and the oxidation potential is raised by sequential selenium incorporation[90]. Not withstanding this, Yoshida's group have synthesised the donors with both two and four selenium atoms incorporated into the structure, compounds (44) and (45)[75]. Redox potentials and TCNQ salt conductivities of some of these vinylogous donors are given in Table 2.1.

DONOR	$E_1^{1/2}(V)^a$	$E_2^{1/2}(V)^a$	$\Delta E^{1/2}(V)$	D:TCNQ	$\sigma_{rt}(Scm^{-1})^b$
(38)	0.20	0.36	0.16	1:1	0.79
(51)	0.48	0.71	0.23	1:1	3×10^{-5}
(52)	0.36	0.62	0.26	1:1	2×10^{-3}
(53)	0.43	0.59	0.16	1:1	7×10^{-8}
(44)	0.26	0.40	0.14	2:3	0.072
(45)	0.33	0.47	0.14	2:3	0.24
TTF(2)	0.34	0.71	0.37	1:1	2.5

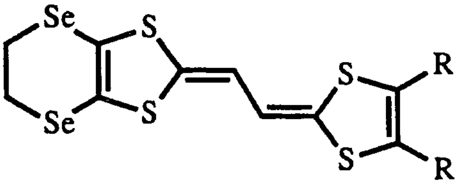
Table 2.1 - Redox properties for vinylogous TTF's and conductivity data for their TCNQ salts. [a] *vs.* Ag/AgCl ref. electrode, [b] compressed pellet

2.2 SYNTHESIS, X-RAY CRYSTAL STRUCTURE AND REDOX BEHAVIOUR OF NEW ALKYLSELENO SUBSTITUTED VINYLOGUES

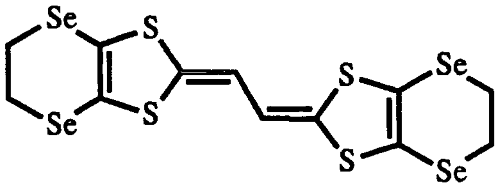
This chapter is concerned with the synthesis and solution redox behaviour of new vinylogues, (54)-(58), which are the first derivatives of system (38) that have selenium atoms attached to the periphery of the framework. The formation of semiconducting TCNQ complexes of these donors will also be discussed.



(54) R = SMe
(55) R = SeMe



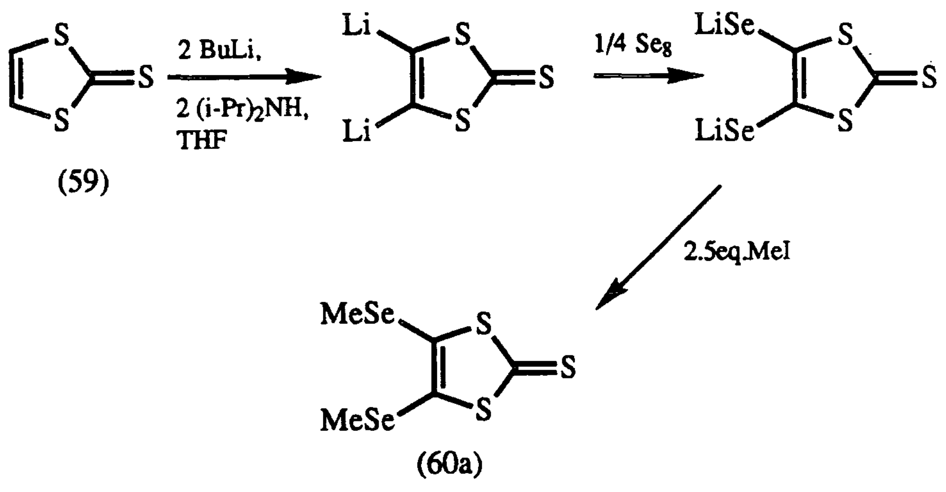
(56) R = Me
(57) R = SeMe



(58)

2.2.1 Synthesis

The syntheses are presented in Schemes 2.1 and 2.2. The key step in assembling the vinylogous TTF skeleton is Wittig-Horner reaction of a vinylogous aldehyde (66) with a phosphonate anion (68) (Scheme 2.2), as described previously for other vinylogues[82,84-86]. Starting materials were thiones (60). Thiones (60b)-(60d) were synthesised using the appropriate literature procedures[24,91-93]. Thione (60a) has been mentioned previously[94] but neither synthetic details nor characterisation data were given. Details for (60a) are, therefore, presented here (Scheme 2.1). 1,3-Dithiole-2-thione (59) was lithiated at the 4,5-positions and reacted with elemental selenium in THF. The addition of methyl iodide to the resulting diselenate at 0°C yielded the required thione (60a) [40 % yield from (59)].

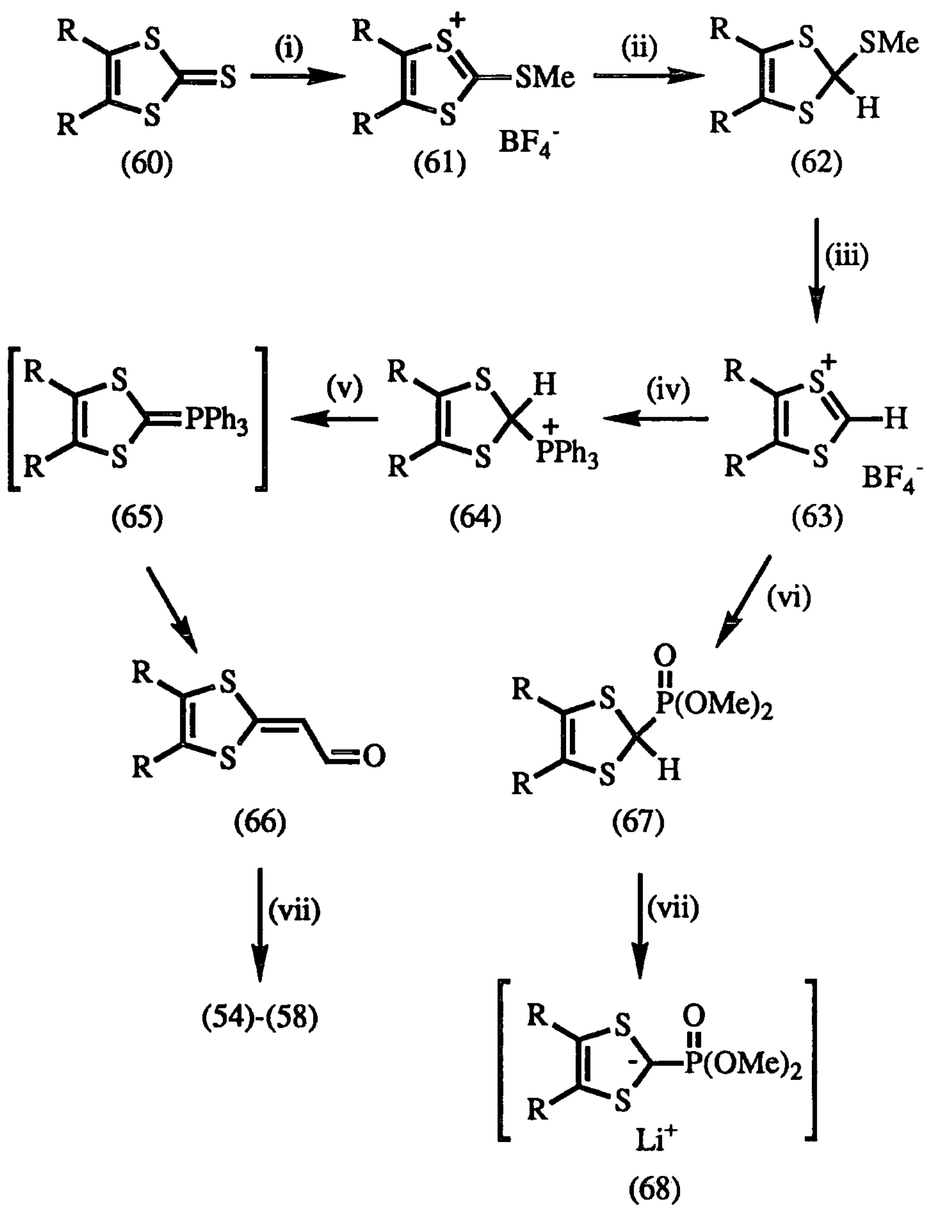


Scheme 2.1

S-Methylation of (60), using neat dimethyl sulphate, yielded the dithiolium cation which was isolated as the crystalline tetrafluoroborate salt (61) in high yield. [An analytically pure sample of thione (60) was essential for clean conversion into salt (61)]. Cation salt (61) was reduced by sodium borohydride to yield thioether (62) as a red oil which could be purified by column chromatography. Conversion of compound (62) into dithiolium cation (63) was achieved by treatment with acetic anhydride followed by addition of tetrafluoroboric acid. The overall yield for the three step sequence (60) → (63) is typically > 65%. Salts (63a) and (63b) are both white solids which are notably more air- and moisture-sensitive than the analogous bis(methylthio)-[88] and ethylenedithio- analogues[85b].

Cation salt (63), on reaction with triphenylphosphine, yielded phosphonium salt (64) which was not isolated; deprotonation with triethylamine *in situ* gave the transient ylid (65) which was intercepted with glyoxal to afford the desired vinylogous aldehyde (66) (59-80% yield). Alternatively, cation salt (63) reacted with trimethylphosphite to yield phosphonate ester (67) in high yield. Compound (67) could be stored for several weeks under vacuum at 20°C, but rapidly decomposed on exposure to air.

The generation of carbanion (68) from ester (67) was achieved by treatment of the latter compound with *n*-butyllithium at -78°C; subsequent addition of the appropriate aldehyde (66) gave new vinylogous TTF derivatives (54)-(58) in 60-80% yields.



For (59) to (68):
a) R = SeMe
b) R-R = $SeCH_2CH_2Se$

Additionally for formulae (60)-(63), (67) and (68):
c) R = Me
d) R = SMe

Scheme 2.2

<u>Scheme 2.2 - Reagents and Conditions</u>

(i) Dimethylsulphate, 70°C, then HBF_4, 20°C, (ii) sodium borohydride, acetonitrile, 20°C, (iii) acetic anhydride, HBF_4, ether, 0°C, (iv) triphenylphosphine, acetonitrile, 20°C, (v) glyoxal, triethylamine, acetonitrile, 20°C, (vi) trimethylphosphite, sodium iodide, acetonitrile, 20°C, (vii) *n*-butyllithium, compound (67), THF, -78°C → 20°C.

Compound (58) has very low solubility in common organic solvents, although solutions can be obtained in carbon disulphide and boiling 1,1,2-trichloroethane. Vinylogues (54)-(57) are soluble in many organic solvents, *e.g.* dichloromethane.

2.2.2 *X*-Ray Crystal Structure of Compound (54)

The molecular structure of compound (54), determined by single crystal *X*-ray analysis, is shown in Figure 2.5.

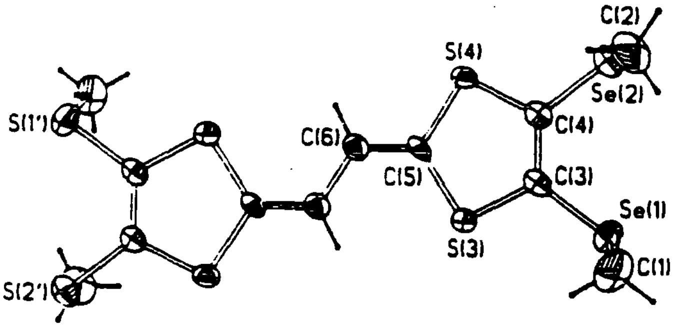


Figure 2.5 - Molecular structure of compound (54)

This compound, which is isostructural with molecule (53), is disordered over a centre of symmetry, so that the terminal methylseleno and methylthio groups are indistinguishable; these heteroatoms were refined as 50% S and 50% Se.

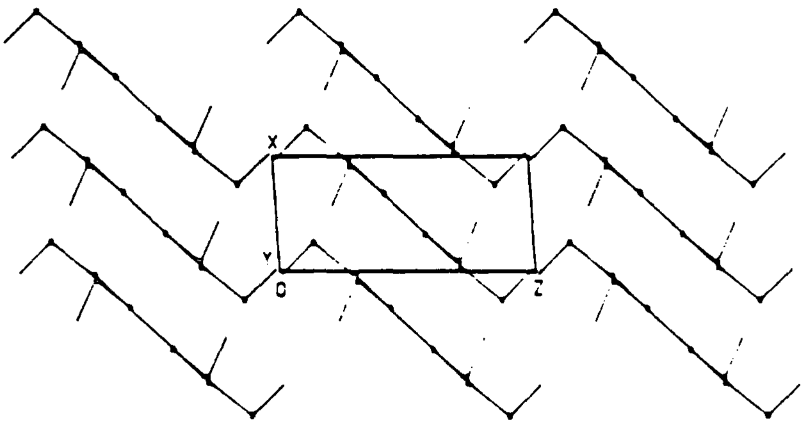


Figure 2.6 - Parallel projection along the *b* axis showing the packing of the molecules of (54). Intermolecular S··S contacts < 4.0 Å are a) 3.963 Å [S(1)··S(3')], b) 3.688 Å [S(1)··S(4')], c) 3.805 Å [S(2)··S(4')], d) 3.918 Å [S(3)··S(3')] and e) 3.812 Å [S(3)··S(4')].

The ethanediylidene-2,2'-bis(1,3-dithiole) framework in compound (54) is planar. This is in marked contrast to the non-planar tetrathiafulvalene framework of analogous tetra(alkylchalcogeno)TTF systems[95], where planarity of the C_6S_8 core is achieved only by attachment of long chains[95] or medium sized rings[57] at the periphery of the molecule.

The molecules of compound (54) stack uniformly with several intermolecular S··S(Se) contacts close to the sum of the Van der Waals radii (Figure 2.6). [The accepted literature value for S··S Van der Waals distance is 3.7 Å].

2.2.3 Redox Behaviour of Donors (54)-(58)

The solution redox properties of donors (54)-(58) have been studied by cyclic voltammetry in dichloromethane solutions and the results are collated in Table 2.2.

DONOR	$E_1^{1/2}$(V)[a]	$E_2^{1/2}$(V)[a]	$\Delta E^{1/2}$(V)	D:TCNQ[b]	σ_{rt}(Scm^{-1})[c]
(54)	0.394	0.571	0.177	1:1	10^{-5}
(55)	0.392	0.593	0.201	1:1	10^{-2}
(56)	0.286	0.544	0.258	1:1	10^{-5}
(57)	0.346	0.562	0.216	1:2	10^{-6}
(58)	0.407[d]	0.631[d]	0.224[d]	1:1	10^{-2}
TTF (2)	0.340	0.710	0.370	1:1	2.5

Table 2.2 - Redox properties and conductivity data for vinylogous TTF's

[a] Experimental conditions: donor (*ca.* 1×10^{-5} mol dm^{-3}), electrolyte $Et_4N^+PF_6^-$ (*ca.* 1×10^{-1} mol dm^{-3}) in dry dichloromethane under nitrogen, 20°C, *vs.* Ag/AgCl, Pt electrode, scan rate 100 mV s^{-1} using a BAS Electrochemical Analyser.

[b] CHN analyses were all within acceptable limits (See Chapter Six - Experimental).

[c] Two-probe compressed pellet measurement.

[d] Data for oxidative scan, see text for discussion.

All the compounds undergo two, separate, one-electron oxidations (*i.e.* sequential formation of the radical cation and the dication species). The redox waves are reversible for all the compounds except donor (58) for which the reductive scan shows a single two-electron reduction (dication $\longrightarrow$ neutral species) at $E^{1/2} = +0.34$ V. This behaviour for donor (58) is reproducible on repeated recycling of the solution between 0.0 and 1.0V. Previous work has established that 'stretching' the TTF or ET systems by insertion of a vinyl group [*viz.* molecules (38)[76,82] and (51)[85,86]] lowers the potential of both the first and second redox waves, $E_1{}^{1/2}$ and $E_2{}^{1/2}$, respectively, as well as significantly reducing the difference between them, $\Delta E^{1/2}$. Similar behaviour is observed for the new systems described herein. Compound (56) is the best donor in the series (lowest value of $E_1{}^{1/2}$): this is because two methyl substituents are in place of the alkylthio or alkylseleno groups of the other donors (54)-(58).

Donors (54)-(58) all form charge-transfer complexes with TCNQ with stoichiometries (donor : acceptor) of 1:1 [for donors (54)-(56), and (58)] or 1:2 [for donor (57)]. The highest room temperature conductivity values (two probe, compressed pellet data) are $\sigma_{rt} = 10^{-2}$ Scm^{-1} for the 1:1 complexes of the symmetrical donors (55) and (58) (Table 2.2). This clearly implies that there is segregated stacking and partial charge-transfer from donor to acceptor in these complexes. The infra-red stretching frequency of the nitrile group of TCNQ is often used to estimate the degree of charge carried by the acceptor molecule in a complex[16]; however this method is not reliable for the complexes in Table 2.2 For example, for complex (56):(TCNQ), $\nu_{max} = 2150$ cm^{-1}, which is well outside the usual range of anionic TCNQ.

2.2.4 Magnetic Susceptibility Data for the Complex (58):(TCNQ)

For the TCNQ complex of donor (58), variable temperature magnetic susceptibility data (χ_M) have been obtained. For a paramagnetic material susceptibilities depend inversely on temperature and often follow, or closely approximate, the behaviour required by the simple equation (The Curie Law),

$$\chi_M{}^{corr} = C/T$$

where T = absolute temperature, C = a constant known as the Curie Constant

$\chi_M{}^{corr}$ = Molar Susceptibility corrected for diamagnetic contributions and any temperature independent paramagnetism (TIP).

Thus a plot of $1/\chi_M^{corr}$ *vs*. T should be a straight line through the origin. In fact many substances show a plot that cuts the T-axis at a temperature, θ, other than 0 K. In this case the Curie Law can be modified to become the Curie-Wiess Law, explained by the equation,

$$\chi_M^{corr} = C/(T-\theta)$$

where θ = Weiss Constant.

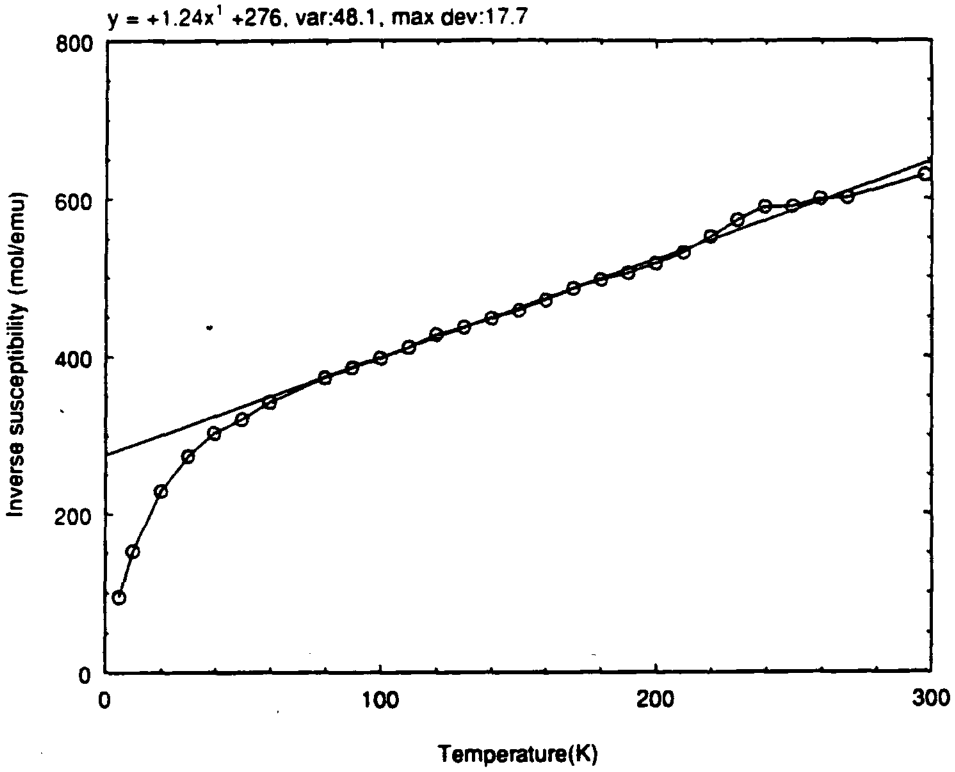


Figure 2.7 - Variable temperature magnetic susceptibility data for the TCNQ complex of donor (58)

For the TCNQ complex of donor (58) a plot of $1/\chi_M^{corr}$ *vs*. T (Figure 2.7) shows a straight line (above 80 K) that, when extrapolated, cuts the T-axis at θ = -222.6 K. Below 80 K a marked deviation from Curie-Weiss behaviour is observed. This is illustrated better on a plot of χ_M^{corr} (T-θ) *vs*. T (Figure 2.8) which should be a straight line of zero gradient in the region of the graph where the Curie-Weiss Law is obeyed.

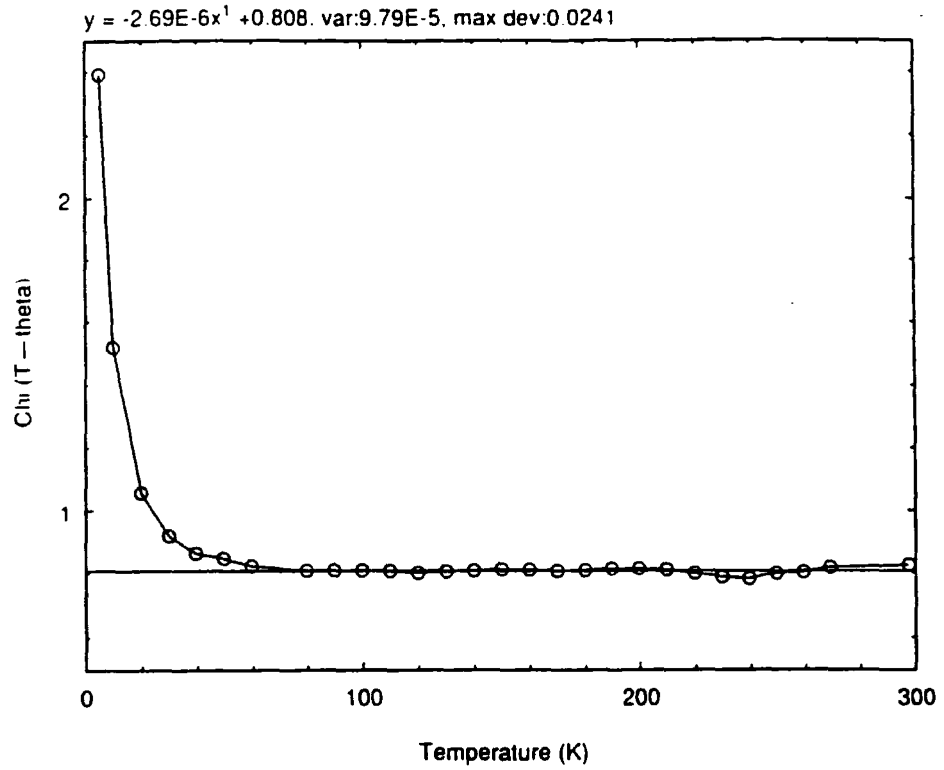


Figure 2.8 - Plot of χ_M^{corr} (T-θ) *vs.* T for the TCNQ complex of donor (58)

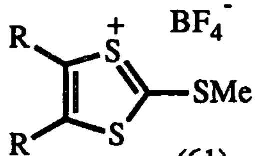
The upward deviation observed at *ca.* 80 K is indicative of ferromagnetic inter-ionic interactions which have magnitudes comparable to the thermal energy at this temperature (80 K) and which become progressively greater as the temperature is further lowered. The moments of the separate ions are aligning themselves parallel to one another, thus reinforcing one another. Above 80 K, thermal energies randomise these orientations; below 80 K, the tendency to alignment becomes controlling and the susceptibility increases much more rapidly with decreasing temperature than it would if the ion moments behaved independently of one another.

CHAPTER THREE

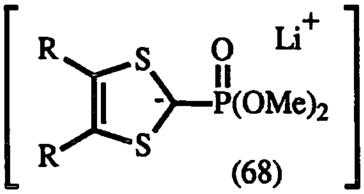
NEW REACTIONS OF 1,3-DITHIOLIUM CATIONS AND 1,3-DITHIOLE ANIONS DIRECTED TOWARDS HIGH-SPIN SYSTEMS

3.1 INTRODUCTION

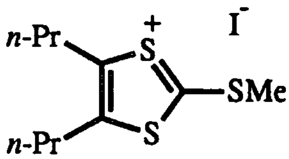
As part of a continuing program of research in our laboratory on the synthesis of new electron donors related to TTF[10c], the present work involves the preparation and reactions of the aromatic cations (61) and the 8π (formally anti-aromatic) anions (68). The syntheses of these systems are well established[9a, 72, 96] and various reactions have been studied previously in our laboratory (see Chapter 2).



(61)



(68)

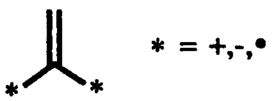


(61) & (68): a) R =SeMe, b) R-R = $SeCH_2CH_2Se$,
c) R = Me, d) R = SMe, e) R = H,
f) R-R = SCH_2CH_2S

(69)

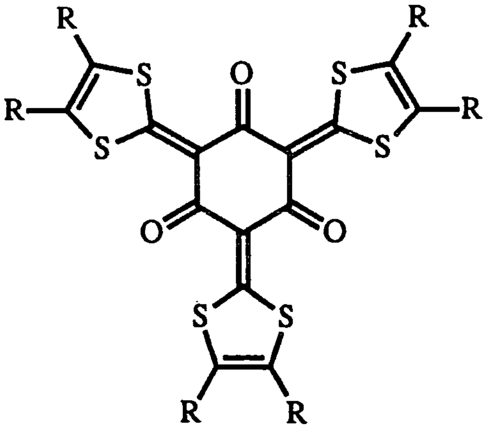
The dipropyl analogue (69), however, was unknown at the outset of the present work. Two separate themes have engaged our attention:

(1) Nucleophiles are known to react at the C(2) carbon atom on the 1,3-dithiolium cation. We aimed to exploit this characteristic reaction in the synthesis of novel multisulphur heterocyclic systems, for example trimethylenemethane (TMM) derivatives.



TMM

(2) The unknown propyl system (69) was of interest from the viewpoint that the propyl substituents should increase the solubility of a range of 1,3-dithiole systems, e.g. (70), the study of which had previously been hampered by extreme insolubility [97,137].



(70) R = *n*-propyl

3.2 ORGANIC FERROMAGNETISM

A major contemporary challenge facing the organic chemist is the synthesis of high-spin systems exhibiting ferromagnetism. This very interesting physical property (achieved by spin alignment throughout the bulk of a particular material) has only rarely been achieved in organic materials. Various theoretical models for obtaining ferromagnetically interacting spins in organic solids have been proposed by McConnell[98], Breslow[99], Wudl[100], and Torrance[101] (Figure 3.1)[100].

The basic premise behind McConnell's idea [Figures 3.1(a) and 3.1(b)] is to prepare ionic charge-transfer salts D^+A^- in which the D^+A^- pair, through back charge-transfer excitation to a neutral triplet state, would also be a triplet, due to mixing of the charge-transfer state with the ground state. If this mixing of a high-spin arrangement is present between adjacent donors and acceptors in a multidimensional array in a solid, macroscopic parallel alignment, and thus ferromagnetic behaviour of the solid, are possible. Candidates for this model include hexaaminobenzene dication salts[102] and cyclopentadienyl cations[103], both of these being antiaromatic ions.

The Breslow approach to organic ferromagnets [3.1(c)] relies on a careful match of the redox potentials of the donor-derived monocation and the acceptor-derived monoanion. Further charge-transfer (if the cation is a strong enough donor) can mix the diionic states of the molecules. If the dication is a ground state triplet then this charge transfer interaction should promote a ferromagnetic alignment of the two unpaired spins

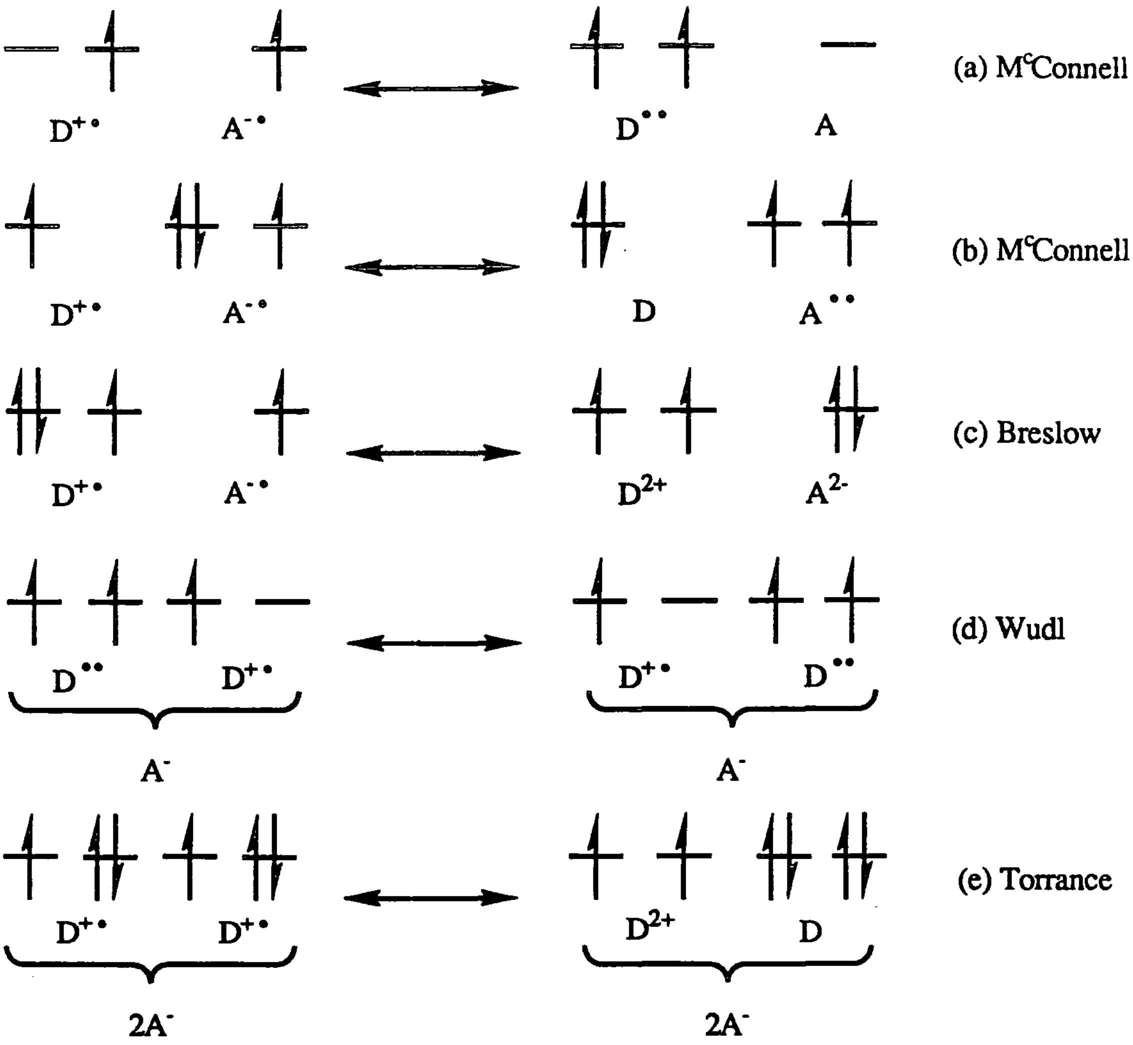
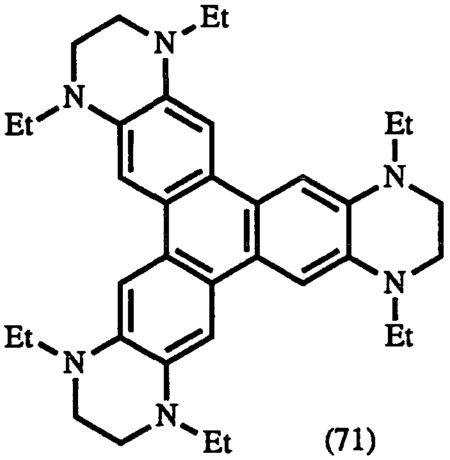


Figure 3.1 - Theoretical models to explain organic ferromagnetism involving charge transfer mixing.

on the donor and the acceptor. Breslow and LePage have thus concentrated on the synthesis of donors that can support stable antiaromatic triplet dications, for example compound (71)[99d]. However, C-T salts with acceptors of the desired electron affinity have yielded only antiferromagnetic materials.

Figure 3.1(d) indicates a ferromagnetic organic material consisting of donors with ground-state triplets and radical cations derived from the same donors, plus closed-shell counteranions (A^-) at a nearby site in the lattice. A further variation by Torrance proposes a disproportionation of two radical cations resulting in a D^{2+}/D^0 pair, the dication existing as a triplet diradical (this species being the lowest excited state). Admixing of this excited triplet state with the triplet ground state (no mixing, of course, being possible between the excited triplet state and the singlet ground state), will stabilise the triplet ground state relative to the singlet ground state. This would remove the triplet-singlet degeneracy, leaving the total spin state for the pair of molecules as a triplet. Based on this model Torrance reacted triaminobenzene with iodine, and claimed an organic ferromagnetic polymer[101]. These results are, however, extremely irreproducible[99d,101]. For further variations on these models see references 104-107.



(71)

The chemical system that we are concerned with is trimethylenemethane (TMM). Derivatives of TMM are of considerable interest[108-114] because a TMM dication on complexation with a dianionic donor has the possibility to form a CT complex containing a neutral TMM with a ground state triplet (following M^cConnell's hypothesis). Thus, reactions of compound (61) and (69) have been directed toward such derivatives.

3.3 TRIPLET TRIMETHYLENEMETHANES

Trimethylenemethanes are notoriously unstable 4π-electron 'Y-anti-aromatic' systems (for the background to Y-aromaticity see references 115 and 116). Fortunately, however, the judicious use of certain substituents can lend a degree of stability to such systems. Theoretical calculations (INDO-CI and MNDO-CI)[117] have shown that a planar trimethylenemethane species is more stable as a triplet than as a singlet state (Table 3.1)[113]. Unfortunately, in an isolated parent TMM, the singlet methylenecyclopropane, formed on ring-closure of the diradical species, is even more thermodynamically stable.

We thus need to design a molecule in which the triplet character of the parent TMM is preserved and ring closure to methylenecyclopropane is prevented.

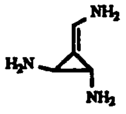
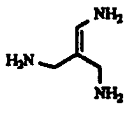
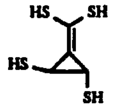
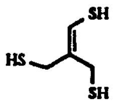
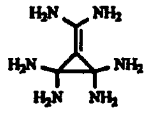
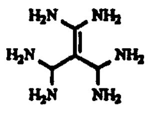
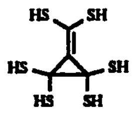
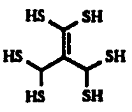
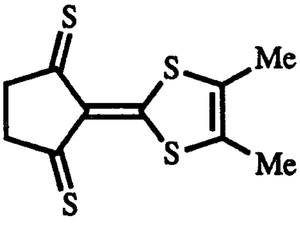
SINGLET			SINGLET	TRIPLET
39.6			88.6	53.3
72.0			92.3	63.3
55.5			89.0	57.0
104.7			175.0	151.3
83.0			127.5	98.1

Table 3.1 - Heats of formation of TMM's and methylenecyclopropanes (MNDO/CI), H_f (kcal/mol)

It is known that the thermal stability of TMM is enhanced by its incorporation into a five-membered ring (*i.e.* a 2-alkylidene-1,3-cyclopentadiyl derivative)[108,109], and further calculations show that alkylthio- and dialkylamino- substituents stabilise triplet TMM relative to both the singlet TMM and the singlet methylenecyclopropane[111]. For a comparison of the thermal stability of various TMM's and methylenecyclopropanes see Table 3.1. The presence of sulphur atoms in the molecular framework will also maximise inter-molecular and inter-stack interactions, consequently leading to the possibility of a three dimensional inter-connected solid, a pre-requisite for observing bulk ferromagnetism. This knowledge suggested to us that heterocycle (72) would be an interesting compound to synthesise. Here the TMM framework is both incorporated into a five-membered ring and is tetrathio-substituted. Gompper *et al.* have previously prepared the TMM dication (73)[113], cyclic voltammetry of which shows reversible redox behaviour, indicating the formation of a TMM rather than a methylenecyclopropane.



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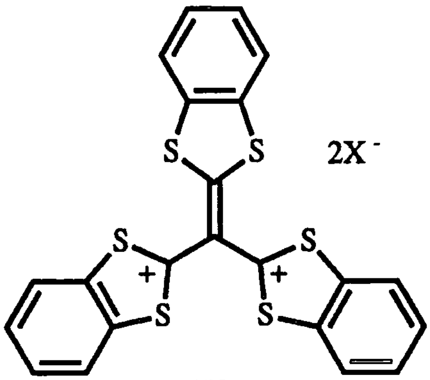
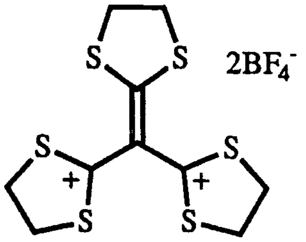


(73)



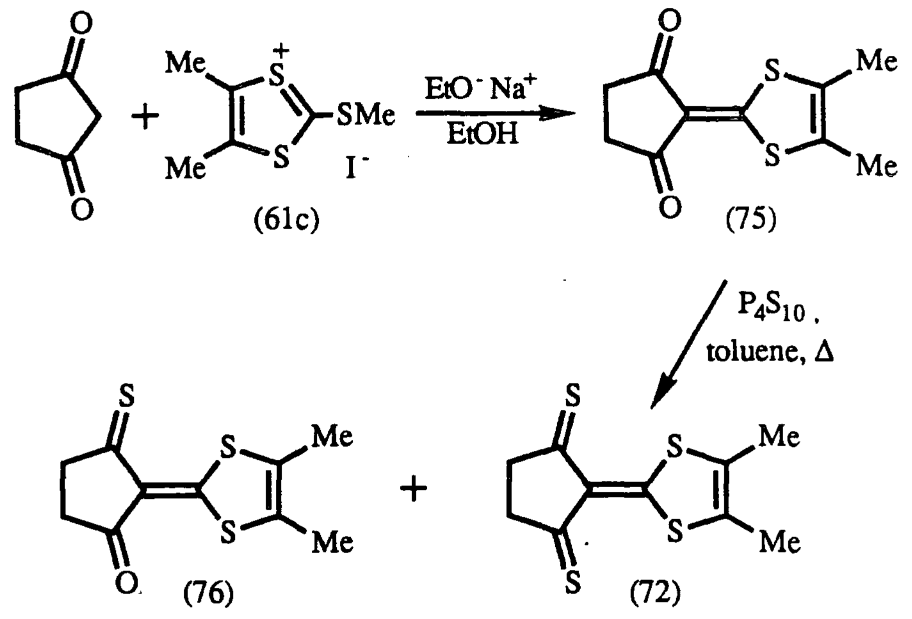
(74)

ESR data on the dication (73) have been reported by Sugimoto *et al.*[118]. A frozen acetonitrile solution of (73, X = $CF_3SO_3^-$), when electrochemically reduced, showed the characteristics of randomly orientated triplet species, with some delocalisation of the two unpaired electrons over the sulphurs. The temperature dependence of the signal intensity established the ground state triplet. Upon reduction of the related dication (74) the ESR spectrum of the diradical could not be detected because of its high reactivity, ring-closing to the methylenecyclopropane.

3.3.1 Synthesis and Crystal Structure of a Tetrathiotrimethylenemethane Derivative

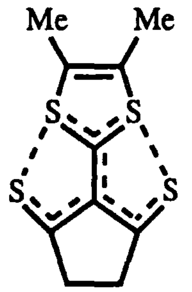
Compound (72) has been prepared (58 % yield) from thionation of the diketone (75) with phosphorus pentasulphide (Scheme 3.1), a reaction that also yielded the monothione product (76). Diketone (75) was the product of the reaction of 4,5-dimethyl-2-methylthio-1,3-dithiolium iodide[72a] (61c) and the anion of 1,3-cyclopentanedione, under conditions described previously for analogous reactions[119].

Compound (72) is, in some ways, structurally related to compound (77), which has recently been synthesised using a completely different methodology by Wudl and co-workers[112]. However, there are striking differences in the reactivity of (72) and (77).

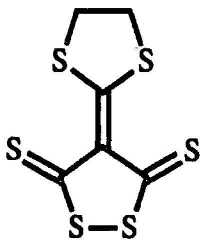


Scheme 3.1

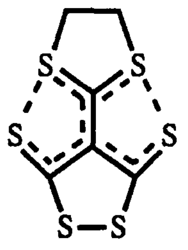
The *X*-ray crystal structure of (72) establishes that the molecule is best represented as a hybrid of dithione structure (72) and the heteroaromatic, 10π-electron 1,2-dithiolo-1,2-dithiole structure (72'). Wudl's compound (77) exhibits more pronounced 10π-electron delocalisation (77').



(72')



(77)



(77')

Intramolecular bond distances and angles for (72) are shown in Figure 3.2. Notable features are as follows:

(I) While there is considerable shortening of both the C1-C5 and C4-C5 bonds, they are significantly longer than the C5-C6 bond;

(II) The C=S bond lengths are longer (by *ca.* 0.07 Å) than the accepted literature values;

(III) The S··S distances (S1-S3 and S2-S4) are considerably shorter (by *ca.* 0.7 Å) than the sum of the Van der Waals radii of two sulphur atoms;

(IV) The C7-C9 bond length of 1.328 Å is normal for a C=C double bond, which implies that the two π electrons of this bond are not involved to any extent in the delocalised system in (72').

Molecule (72) is essentially planar but with a small amount of puckering at the ethylene bridge of the dithione ring. A packing diagram reveals that molecule (72) forms overlapping dimers in the solid state within which there are two relatively short intermolecular S··S contacts (*viz.* S3-S4'=3.912 Å and S1-S4'=3.960 Å) (Figure 3.2 right).

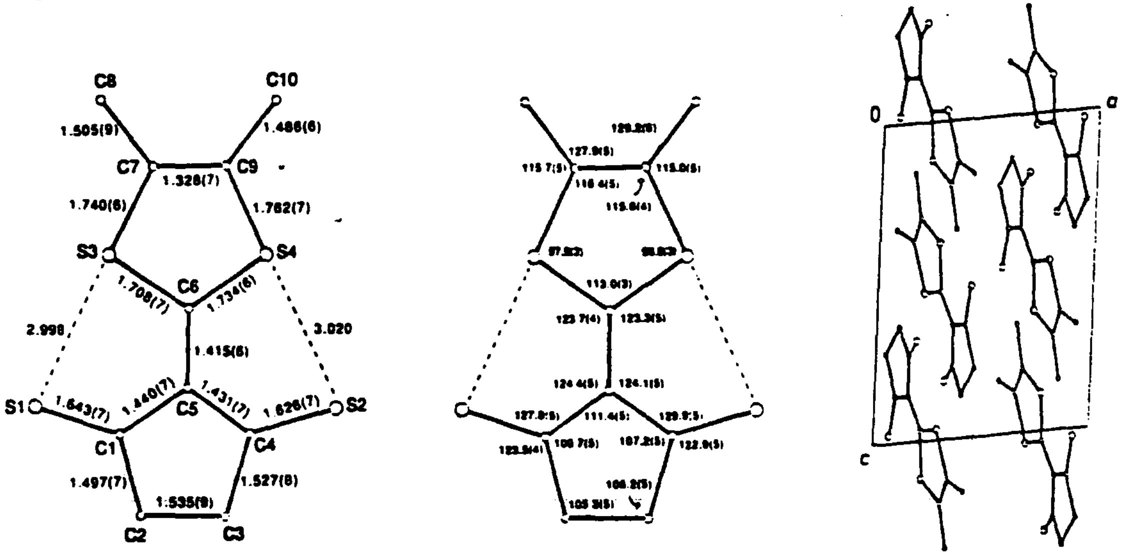
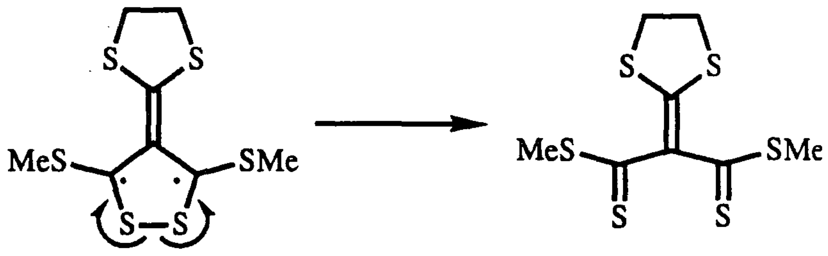
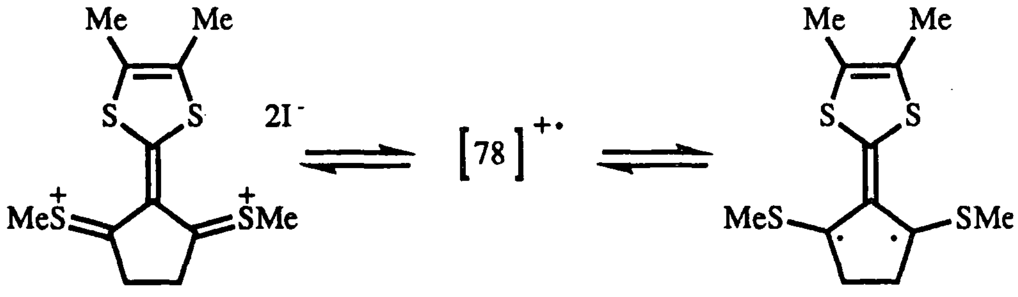


Figure 3.2 - Structure of (72) with bond lengths (left) and angles (middle). Right: Unit cell of (72) viewed along the *b* axis.

Wudl *et al.* observed that compound (77) did not react with methyl iodide, either neat at room temperature, or in refluxing acetone[112]. In marked contrast to this, both thioxo sulphur atoms of compound (72) are readily methylated by methyl iodide in dichloromethane at 20°C to yield the air-stable dication salt (78). This observation is entirely consistent with the *X*-ray data which imply that compound (72) is less aromatic than compound (77). An advantage of our compound (72) over compound (77) is that it does not contain a weak S-S bond that is liable to fracture and destroy any diradical that could be formed upon methylation to a dication and then reduction.



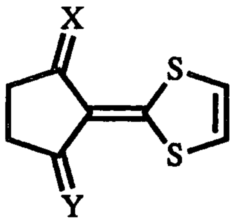
Cyclic voltammetry of dication (78) revealed two reversible, one electon reductions at $E_1^{1/2}$ = +0.34 V and $E_2^{1/2}$ = +0.61 V *vs*. Ag/AgCl. These data clearly point to the formation in solution of the tetrathiotrimethylenemethane diradical (79), for which delocalised structures comprising a 1,3-dithiolyl radical can be drawn. Attempts to detect diradical (79) by ESR spectroscopy have been unsuccessful, however. The strong ESR signal obtained in a frozen dichloromethane solution following electrochemical reduction of dication (78) is assigned to the radical cation ($78^{+\cdot}$). The spectra at 293K and 153K show no fine structure and the g value of 2.0059 is consistent with spins partially localised at the sulphur atoms. Although the cyclic voltammogram of compound (78) was promising, attempts to chemically form the diradical by reduction with Zn/Cu couple, Ph_3Sb and Li^+ $TCNQ^{-\cdot}$ proved unsuccessful.



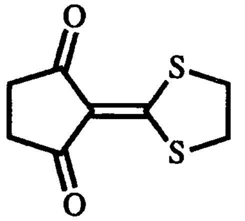
(78)

(79)

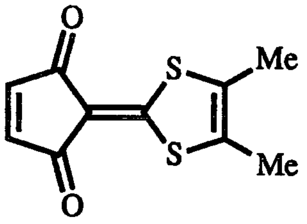
Other derivatives of this system that we have synthesised are compounds (80)-(84). In the case of (82), however, methylation stops at the mono-methylated product, this probably being the result of extreme insolubility. Compound (82), and also the monothione product (81), were obtained from diketone (80) in a manner similar to (72) and (76). Diketones (83) and (84) could not be thionated due to insufficient solubility and the polarity of the carbonyl groups. Compound (84) had been synthesised from compound (85) in a reaction previously described by Nakayama *et al* [120].



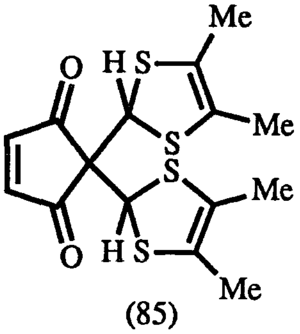
(80) X = Y = O,
(81) X = S, Y = O,
(82) X = Y = S



(83)



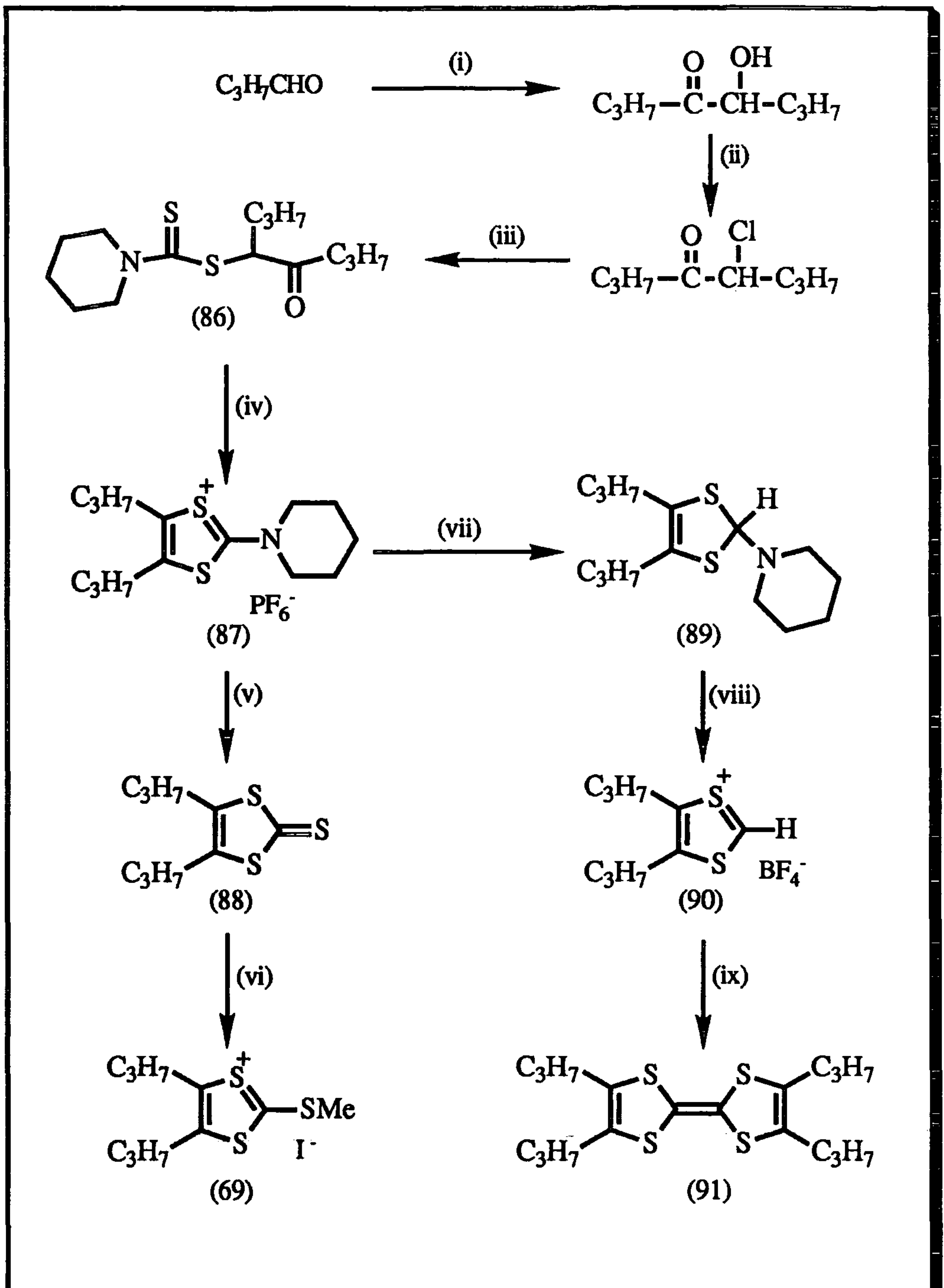
(84)



(85)

3.4 THE SYNTHESIS OF 1,3-DITHIOLIUM CATION SALT (69)

We turned our attention to dithiole reagents carrying solubilising propyl side chains, for example compound (69). The sequence of reactions involved in the preparation of the iodide salt of compound (69) is based on a route described previously for the synthesis of tetra-*n*-pentyl-TTF[121], and is outlined in Scheme 3.2. 4-Hydroxyoctan-5-one was prepared in good yield from butyraldehyde, following the literature procedure in a thiazolium catalysed reaction[122]. Originally, an acyloin condensation using molten sodium in xylene had been used[123] but a severe problem had been caused by repeated polymerisation of the reaction mixture. The alcohol functionality was chlorinated by thionyl chloride yielding 5-chloro-octan-4-one[124] which was then reacted with potassium piperidinodithiocarbamate to obtain compound (86). This could be cyclised to dithiolium cation salt (87) in concentrated sulphuric acid, which was converted into the thione (88) with sodium thiole. Subsequent methylation with methyl iodide provided the required 4,5-di-*n*-propyl-1,3-dithiole-2-thiomethyl iodide (69) in 11 % overall yield from butyraldehyde.



Scheme 3.2

Scheme 3.2 - Reagents and conditions:

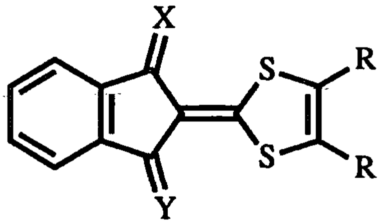
(i) 3-Benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride, triethylamine, ethanol, reflux, (ii) pyridine, thionyl chloride, dichloromethane, 20°C, (iii) N-piperidinodithiocarbamate, hexamethylphosphoric acid triamide, 90°C, (iv) concentrated sulphuric acid, hexafluorophosphoric acid, 80°C, (v) sodium thiol hydrate, 20°C, (vi) methyl iodide, nitromethane, 40°C, (vii) sodium borohydride, ethanol, 5°C, (viii) acetic anhydride, tetrafluoroboric acid, diethyl ether, 0°C, (ix) triethylamine, dichloromethane, 20°C.

The hexafluorophosphate salt (87) can be reduced by sodium borohydride to afford the 2*H*-1,3-dithiole derivative (89), which was converted into the dithiolium cation salt (90) by treatment with acetic anhydride and tetrafluoroboric acid. Reaction of this tetrafluoroborate salt with triethylamine yielded the unknown tetra-*n*-propyl-TTF (91) in 62 % yield. The cyclic voltammogram of donor (91) showed two reversible, one-electron oxidations ($E_1^{1/2}$ = 0.29 V and $E_2^{1/2}$ = 0.69 V *vs*. Ag/AgCl) and a 1:1 C-T complex (room temperature compressed pellet conductivity $\sigma_{rt} = 4 \times 10^{-5}$ Scm^{-1}) was formed on mixing boiling dichloromethane solutions of (91) and TCNQ.

3.5 DONORS DERIVED FROM INDANE-1,3-DIONE

3.5.1 Synthesis of Donors (92)-(99) and *X*-Ray Crystal Structure of Compound (99)

Further TMM derivatives [compounds (97), (98) and (99)] similar to compound (72) (Chapter 3.3.1) can be obtained from the reaction of the anion of indane-1,3-dione with cation salts (61c), (61d) and (69) [yielding diketones (92)-(94)], followed by thionation with phosphorus pentasulphide.



(92) X = Y = O, R = Me
(93) X = Y = O, R = SMe
(94) X = Y = O, R = *n*-Pr
(95) X = S, Y = O, R = SMe
(96) X = S, Y = O, R = Pr
(97) X = Y = S, R = Me
(98) X = Y = S, R = SMe
(99) X = Y = S, R = *n*-Pr

The thionation reactions also yielded the monothiones (95) and (96). Dithione (99) formed *X*-ray quality crystals from a dichloromethane / acetonitrile solution and the structure revealed intramolecular dimensions very similar to those of compound (72), e.g. S(2)··S(4) = 3.043 Å, C(7)-S(1) = 1.636 Å (Figure 3.3) [*c.f.* S(2)··S(4) = 3.020

Å, C(1)-S(1) = 1.643 Å for compound (72)]. The propyl chains which could, conceivably, prevent any close intermolecular interactions, did not force the dimers apart compared to (72) as indicated by the intermolecular distance S(4)··S(4') = 3.822 Å [*c.f.* S(3)··S(4') = 3.912 Å for compound (72)].

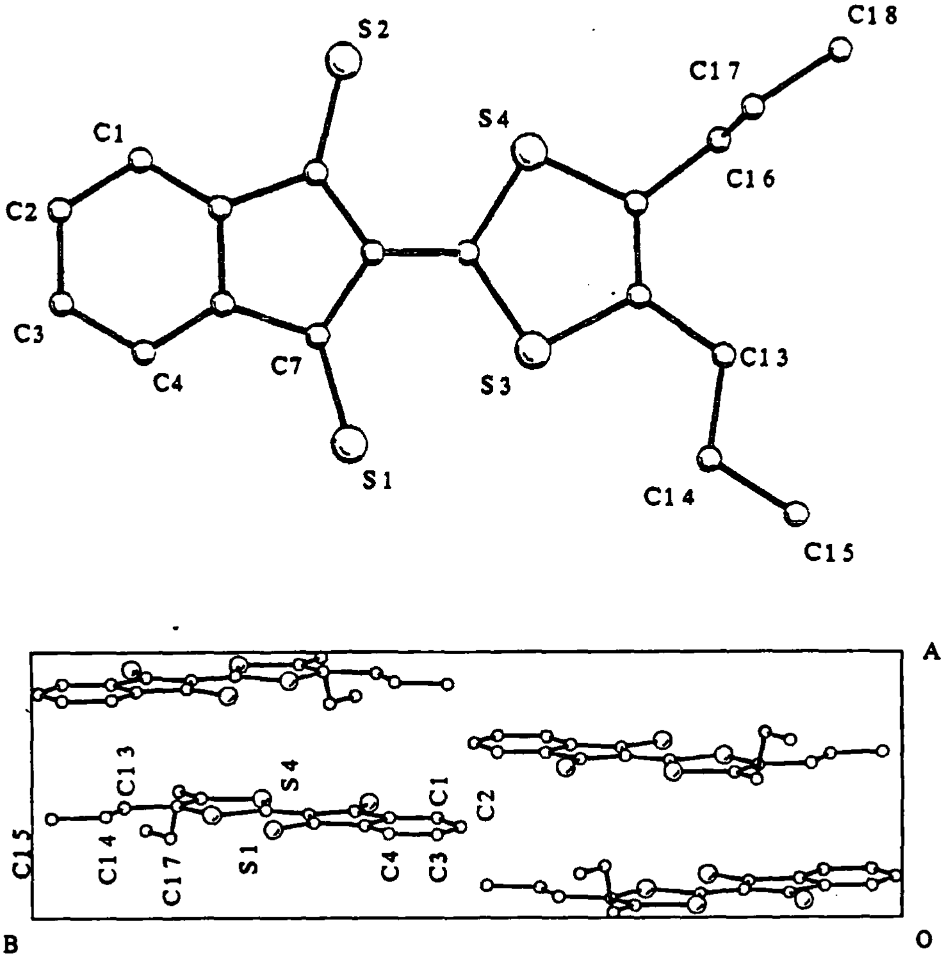
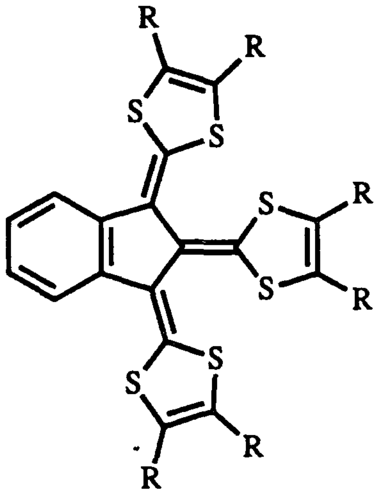


Figure 3.3 - *X*-Ray crystal structure of compound (99).
Molecular structure (above) and unit cell (below)

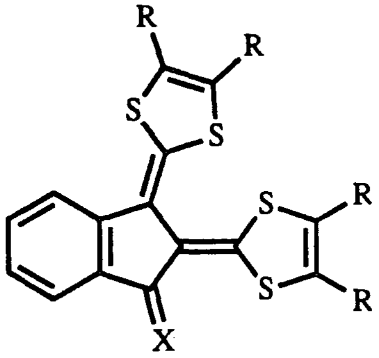
Unfortunately, attempted methylation of compounds (97)-(99) with methyl iodide only resulted in the formation of a multi-component mixture from which nothing could be isolated in pure form and characterised. [Compounds (92) and (97) had been prepared previously in our laboratory and shown to form highly crystalline complexes with TCNQ[139]].

3.5.2 Synthesis of Neutral Donors (100)-(103) and their C-T Complexes

Diketones (92)-(94) obviously have the possibility of undergoing Wittig-Horner reactions and we were thus interested in synthesising the multi-1,3-dithiole compounds (100) and (101) and investigating the solid-state properties of their C-T complexes. Wittig-Horner reactions on diketones (92) and (93) with the appropriate phosphonate esters (68c) and (68d) did, indeed, yield the required products.

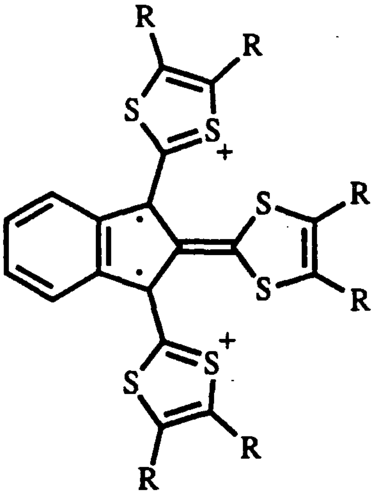


(100) R = Me
(101) R = SMe

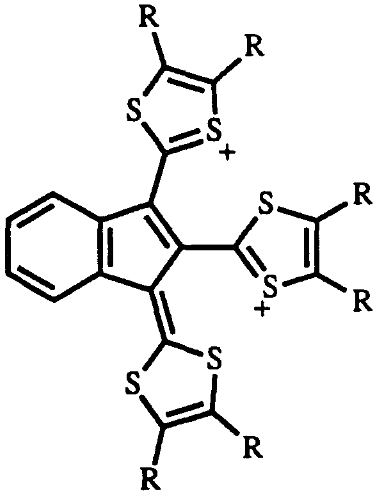


(102) R = Me, X = O
(103) R = Me, X = S

Oxidised species of donors (100) and (101), although ostensibly TMM's, would be unsuitable for a stable triplet diradical (100a) because the thermodynamically more stable dication (100b) would preferentially form on oxidation of the radical cation.



(100a)



(100b)

Nonetheless, in terms of forming conducting charge-transfer salts these donors were considered to be promising target molecules. Donor (100) did form a complex with TCNQ (100c) (1:2 stoichiometry), the resulting powder having a room temperature compressed pellet conductivity of $\sigma_{rt} = 5 \times 10^{-6}$ Scm^{-1}. Donor (101), though, did not form a complex on mixing with TCNQ. Compound (102) was formed by the reaction of compound (100) with only one equivalent of Wittig-Horner reagent (68c), and subsequent thionation with phosphorous pentasulphide yielded the donor (103). This compound also formed a complex with TCNQ (103a) (analysis indicating a 1:1.3 complex) having a compressed pellet powder conductivity of $\sigma_{rt} = 5 \times 10^{-5}$ Scm^{-1}.

3.5.3 Magnetic Susceptibility Data for Complex (100c)

Variable temperature magnetic susceptibility data have been obtained for the TCNQ complex of donor (100) [compound (100c)] and a plot of $\chi(T-\theta)$ *vs*. T shows Curie-Weiss behaviour above 80K (Figure 3.4). The upward deviation at *ca*. 80K is similar to that obtained with the TCNQ complex of donor (58) (Chapter 2.2.4), and is again indicative of significant ferromagnetic ordering below this temperature.

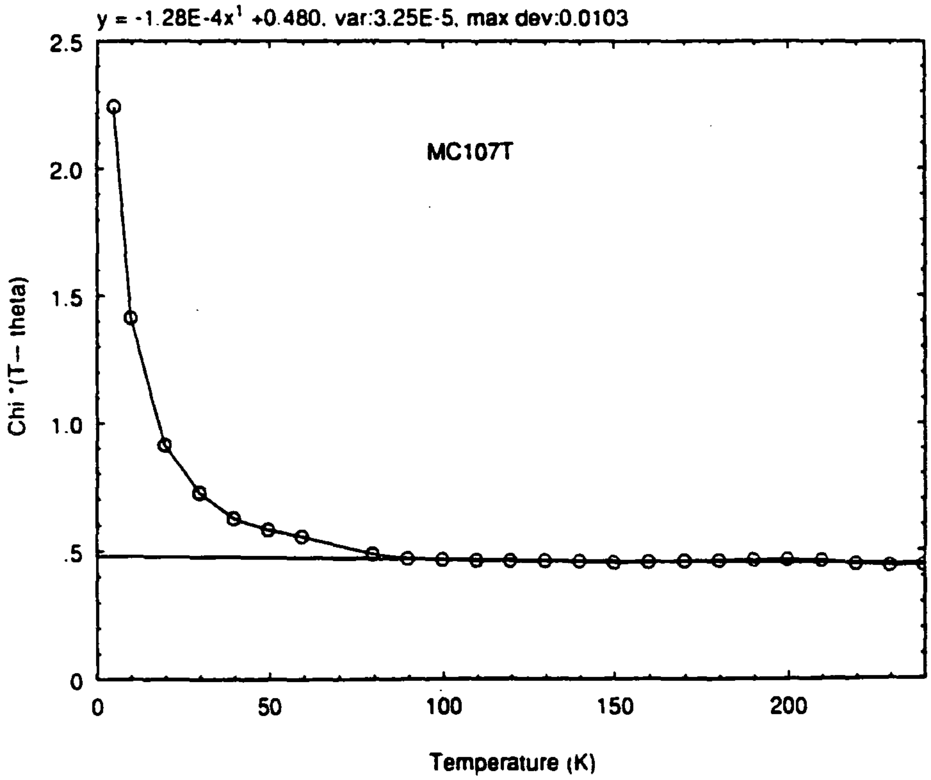


Figure 3.4 - Variable temperature magnetic susceptibility data for complex (100c)

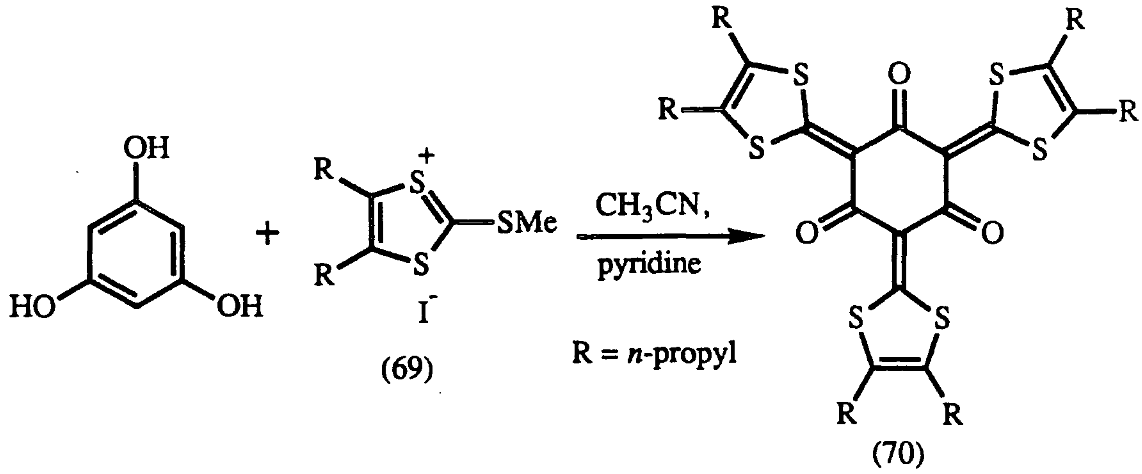
3.6 OTHER REACTIONS OF CATION SALT (69):

3.6.1 2,4,6-Tris(4,5-di-*n*-propyl-1,3-dithiole-2-ylidene)-1,3,5-cyclohexanetrione (70): Synthesis, X-Ray Crystal Structure and Amphoteric Redox Properties of a Highly-Delocalised Heterocyclic π-System

Organic molecules which possess multi-stage, amphoteric redox properties (*i.e.* the ability to undergo both anodic oxidation and cathodic reduction) within a relatively small range of potentials are rare[125]. Notable examples, all of which contain a highly delocalised π-electron framework, include cyclobuta[*b*]quinoxaline-1,2-dione[126], 9,9'-bianthryl-10,10'-dicarbonitrile[127] and extended quinones[128,129]. In these molecules both the π-donor and π-acceptor ability are enhanced by aromatic stabilisation of the charged species and by judicious choice of functional groups attached to the molecule. An extended quinone is claimed to exhibit the smallest value of E^{sum}, *viz* 0.75 V[128] [$E^{sum} = E^{ox} + (-E^{red})$].

We were attracted by system (70), for which heteroaromatic, 6π, 1,3-dithiolium cations and phenoxy anions could participate in stabilising oxidised and reduced states, respectively. Furthermore, hexasubstituted benzene derivatives that have three-fold symmetry and can be readily oxidised, are prime candidates for achieving ferromagnetic interactions in organic materials, as the dication may be a ground state triplet due to orbital degeneracy[99d,102,130-135]. (Other workers have pointed out that an appropriately substituted dianion can, theoretically, also lead to a triplet species[133]).

The reaction of 1,3,5-trihydroxybenzene (phloroglucinol dihydrate) with 2-methylthio-4,5-di-*n*-propyl-1,3-dithiolium iodide in acetonitrile with pyridine as base, afforded the target compound (70) in 30% yield (Scheme 3.3). The carbonyl absorption frequency of compound (70) occurs at 1530 cm^{-1}; this low value indicating strong S··O interactions in the structure[136]. [The unsubstituted derivative of this system (R = H)[137] and the hexamethyl analogue (R = Me) are intractable solids which could not be recrystallised. We, therefore, prepared the hexa-*n*-propyl analogue, described herein, to increase the solubility].



Scheme 3.3

Orange crystals of compound (70), grown from toluene solution, were suitable for *X*-ray analysis. The crystal structure of (70) is shown in Figure 3.5. The molecule is almost planar (with the exception of the propyl chains) with a slight deviation from D_{3h} symmetry. Analysis of the bond lengths (Appendix 1.3) reveals a fascinating electron distribution in the neutral molecule, which is best represented by the highly-delocalised structure (70b). Contributing canonical structures include (70a) and (70c), and other structures with positive charge placed on the sulphur atoms can be drawn. The central ring, which has pronounced benzenoid character, can be considered to be covalently embedded within a 24 π-electron milieu. All the C-C bonds that radiate from the 'benzene' ring are intermediate in length between single and double bonds, while the C-O distances are close to the accepted value for a carbon-oxygen double bond. The intramolecular S··O separations are all in the range 2.57-2.60 Å, which is considerably shorter than the sum of their Van der Waals radii (3.25 Å), indicating significant S··O··S bonding interactions in the structure. The peripheral C-C distances within the 1,3-dithiole rings, e.g. C(8)-C(9), are all consistent with a normal carbon-carbon double bond, which implies that these π-electrons are not delocalised to any extent.

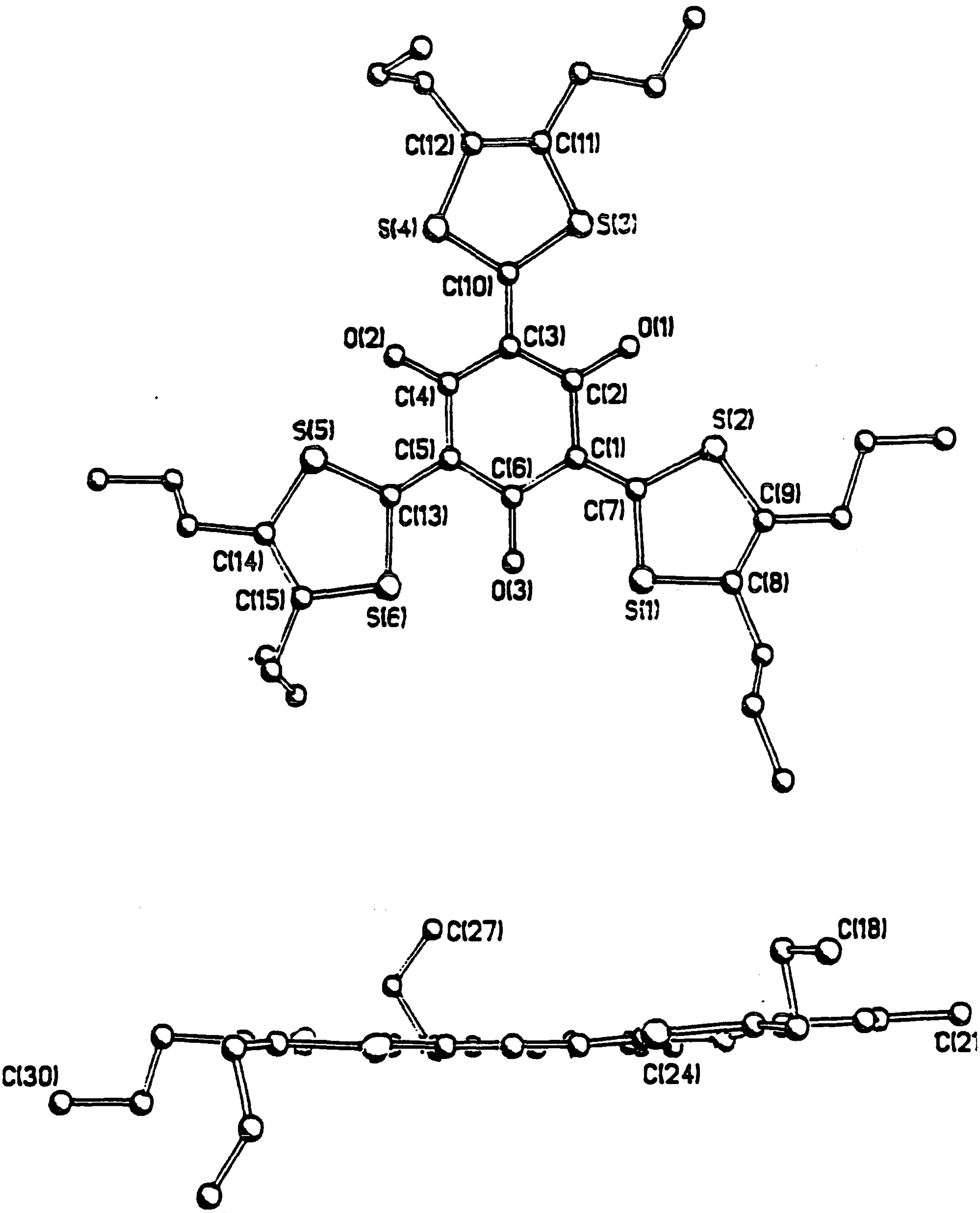
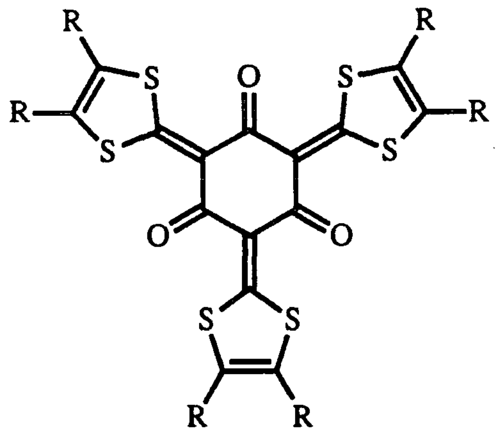
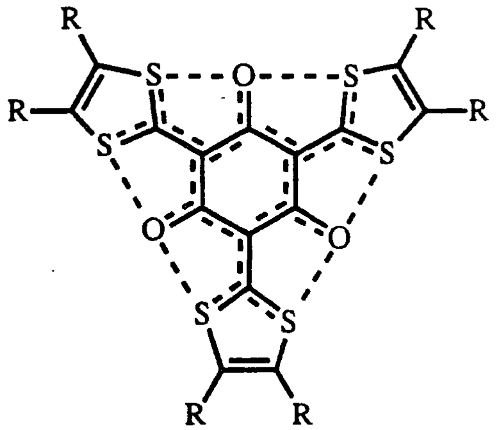


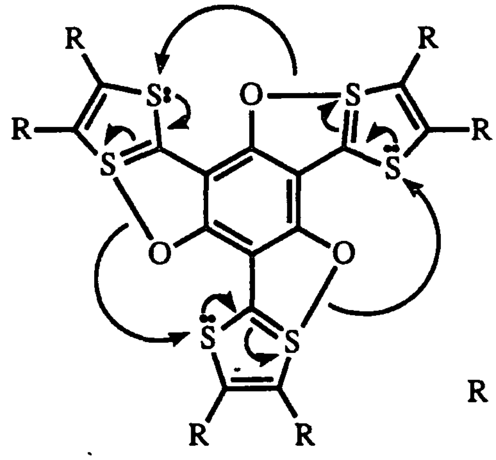
Figure 3.5 - Molecular structure of compound (70) viewed along the normal to the central C_6 ring (above) and viewed along the plane of the molecule (below).



(70a)

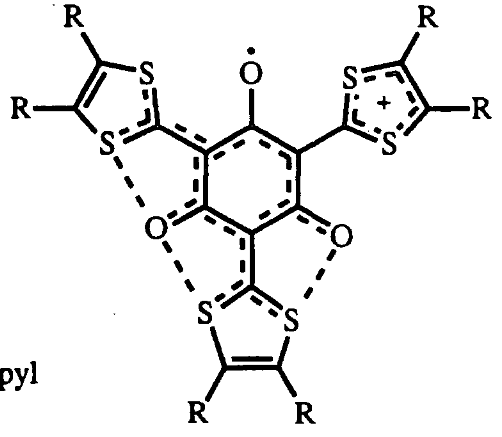


(70b)



(70c)

R = *n*-propyl



(70d)

The electrochemical behaviour of compound (70) has been studied by cyclic voltammetry [*vs*. Ag/AgCl, Pt electrode. The values of E_1^{ox}, E_2^{ox} and E_1^{red} quoted are calculated by averaging the anodic and cathodic potentials {i.e. $E = (E_p^a + E_p^c)/2$}. For E_3^{ox}, where the reduction process is not observed on the return sweep, the value quoted is for E_p^{ox}]. These experiments required rigorous exclusion of oxygen, water and other protic impurities. A variety of solvents were investigated and the best quality data were obtained in propionitrile solution at low temperatures (< 0°C), where four-stage amphoteric behaviour is observed (Figure 3.6). Compound (70) can be oxidised in three, successive, one-electron transfer steps: E_1^{ox} (*i.e.* the formation of the radical cation) and E_2^{ox} (*i.e.* the formation of the dication) occur at + 0.65 V and + 0.80 V, respectively, and both are reversible processes within the scan range 0.0 to + 1.1 V. If a higher potential range is scanned, a third irreversible oxidation is seen at + 1.25 V and

E_2^{ox} now becomes irreversible. The oxidised redox stages will, presumably, be stabilised by the involvement of 6π dithiolium cations, e.g. canonical structure $(70d)^{+\cdot}$. The π electrons of the peripheral C=C double bonds would be delocalised in this structure, which contrasts with their localisation in the neutral system (*X*-ray data discussed above). The difference, ΔE, between E_1^{ox} and E_2^{ox} (0.15 V) is significantly less than that between E_2^{ox} and E_3^{ox} (0.45 V); this is a reflection of increased Coulombic repulsion in the trication.

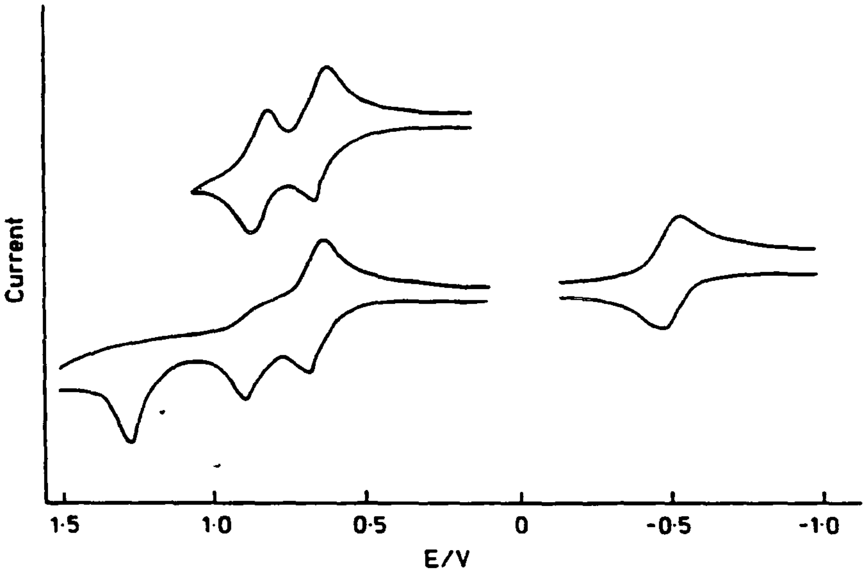


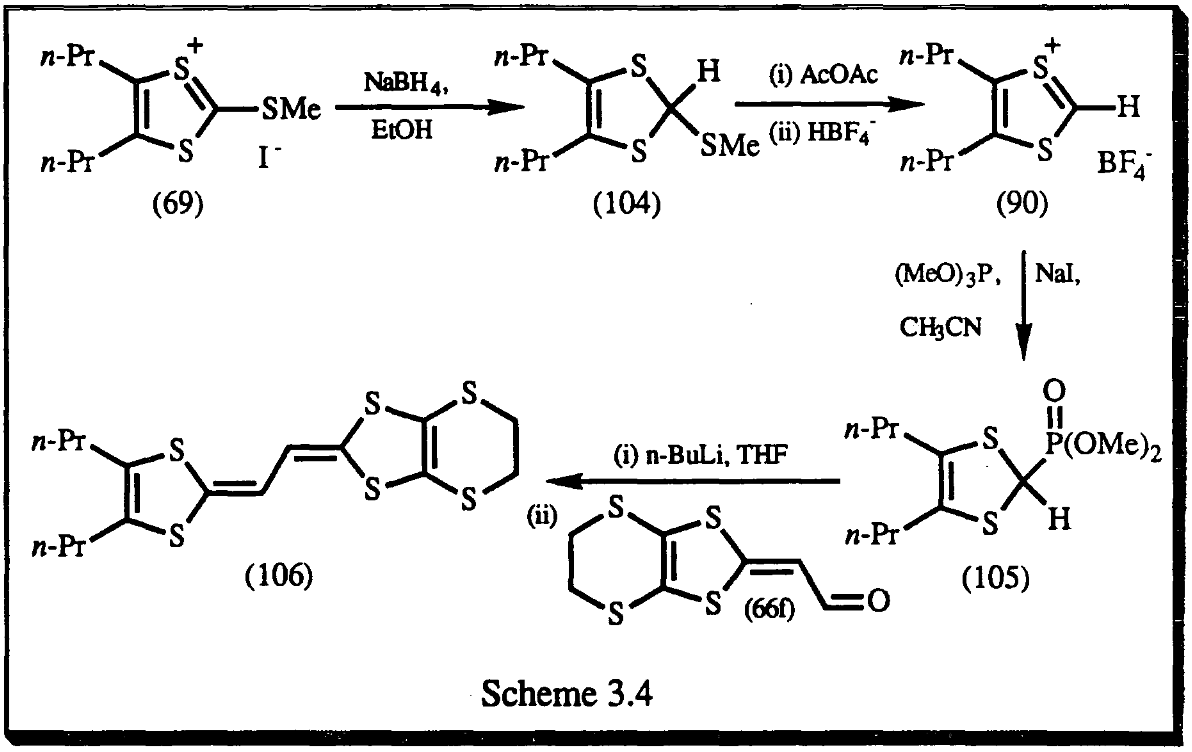
Figure 3.6 - Cyclic voltammograms of compound (70)

One reductive wave was observed for compound (70) at E^{red} = -0.51 V, which corresponds to the formation of the radical anion $(70)^{-\cdot}$. Controlled potential coulometry confirmed this to be a single electron process. This is a reversible wave, but further reduction could not be clearly identified, even upon sweeping to -2.5 V. The negative charge in reduced states of (70), will, presumably, be localised predominantly on the oxygen atoms and it seems that their close proximity inhibits dianion formation. The oxidation of compound (70) is reminiscent of 2,4,6-(4,5-dimethyl-1,3-dithiole-2-ylidene)-1,3,5-trithiane, which also forms a trication in electrochemical experiments[97], and hexakis-(1,3-dithiole-2-ylidene)-cyclohexane derivatives which display three oxidation waves leading to a tetracation[138]: however, neither of these systems undergoes electrochemical reduction. Unfortunately, due probably to a combination of steric hindrance and the fact that canonical form (70c) contributes significantly to the structure of (70), experiments to thionate the ketone functionality with phoshorus pentasulphide or hydrogen sulphide were unsuccessful. We were also unable to chemically generate TCNQ salts of this system.

In conclusion, compound (70) has been shown by *X*-ray analysis to comprise a highly-delocalised π-electron system, and four-stage, amphoteric, redox behaviour has been observed. The value of E_1^{sum} (*viz.* 1.16 V) is low by comparison with most other closed-shell organic compounds.

3.6.2 Synthesis of 4,5-Ethylenedithio-4',5'-di-*n*-propyl-2,2'-ethanediylidene-bis(1,3-dithiole) (106)

Compound (69) can be taken through the series of reactions outlined in Scheme 3.4 (see also Chapter 2) to obtain the phosphonate ester (105).



Scheme 3.4

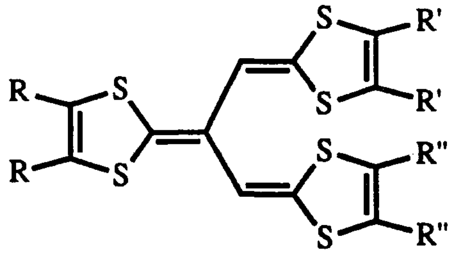
If treated with butyl lithium this Wittig-Horner reagent can then be reacted with an aldehyde such as compound (66f) to synthesise another vinylogous TTF derivative, compound (106). This was attempted in order to obtain a crystalline vinylogue for *X*-ray analysis. Although crystallinity was not the case here, a crystalline derivative was obtained with compound (54) (Chapter Two).

CHAPTER FOUR

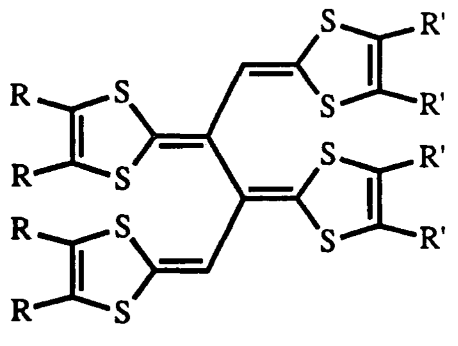
THE SYNTHESIS AND PROPERTIES OF MULTI-1,3-DITHIOLE DENDRALENE SYSTEMS

4.1 INTRODUCTION

In the continued quest for multi-dimensional organic metals with high electrical conductivity many structural variations on the TTF framework have been made. Chapter Two dealt with the separation of the two 1,3-dithiole rings by a carbon-carbon (both sp^2 hybridised) spacer unit and the attachment of peripheral chalcogen atoms. Chapter Three involved the synthesis of some novel tris-(1,3-dithiole) systems, and here we are concerned with the synthesis of a series of conjugated, multi-1,3-dithiole, multi-chalcogen, π -electron donors, (109)-(112), (119) and (120). These compounds are tricyclic and tetracyclic derivatives of the dendralene family of hydrocarbons. (Dendralenes are acyclic and cyclic cross-conjugated polyolefins derived from 3-methylene-1,4-pentadiene, relatively little being known about such substituted or unsubstituted derivatives of this system. For a comprehensive review of dendralenes see reference 147). The tetrakis-(1,3-dithiole) derivatives (119) and (120) presented here are effectively dimers (minus two hydrogen atoms) of the vinylogues synthesised in Chapter Two.



(109) R = Me
(110) R = R' = Me, R"-R" = SCH_2CH_2S
(111) R = Me, R'-R' = R"-R" = SCH_2CH_2S
(112) R = R' = R" = SMe
(113) R = R' = R" = CO_2Me
(114) R-R = R'-R' = R"-R" = $(CH=CH)_2$
(115) R = R' = R" = H

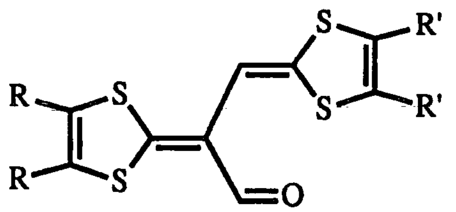


(119) R = Me, R'-R' = SCH_2CH_2S
(120) R = R' = SMe

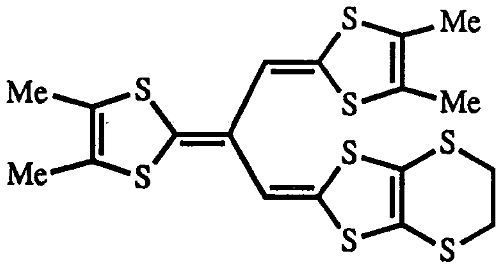
Yoshida *et al.*[140] have attempted the synthesis of 1,3-dithiole-[3]-radialene and 1,3-dithiole-[4]-radialene, for which purpose they synthesised the derivatives (113)-(115). However, these derivatives contained substituents ($-CO_2Me$, -benzo and -H) which are relatively unimportant in terms of being able to induce significant inter-molecular interactions. The synthesis of compounds (113)-(115) used the appropriately substituted vinylogues as starting materials (themselves involving lengthy and tricky syntheses), and no formation of charge-transfer salts with acceptors such as TCNQ was reported. We have now used a simplified and higher yielding synthesis to take us directly to the tris-(1,3-dithiole) systems (109)-(112), and have introduced peripheral chalcogen atoms in the hope of obtaining crystalline materials with appreciable inter-molecular interactions.

4.2 SYNTHESIS OF MULTI-1,3-DITHIOLE DENDRALENES

Our starting materials for the preparation of these multi-(1,3-dithiole) systems were the methylene-malonaldehydes (107) and (108) (Scheme 4.1). These were readily obtained by reacting the sodium salt of malonaldehyde with the 2-methylthio-1,3-dithiolium salts (61c) and (61d) in acetonitrile (following the literature procedure outlined by Gompper *et al* [113]). Wittig-Horner reactions with the appropriate phosphonate esters (67) yielded the tris-(1,3-dithiole) derivatives (109), (111) and (112) in high yield (Scheme 4.1).



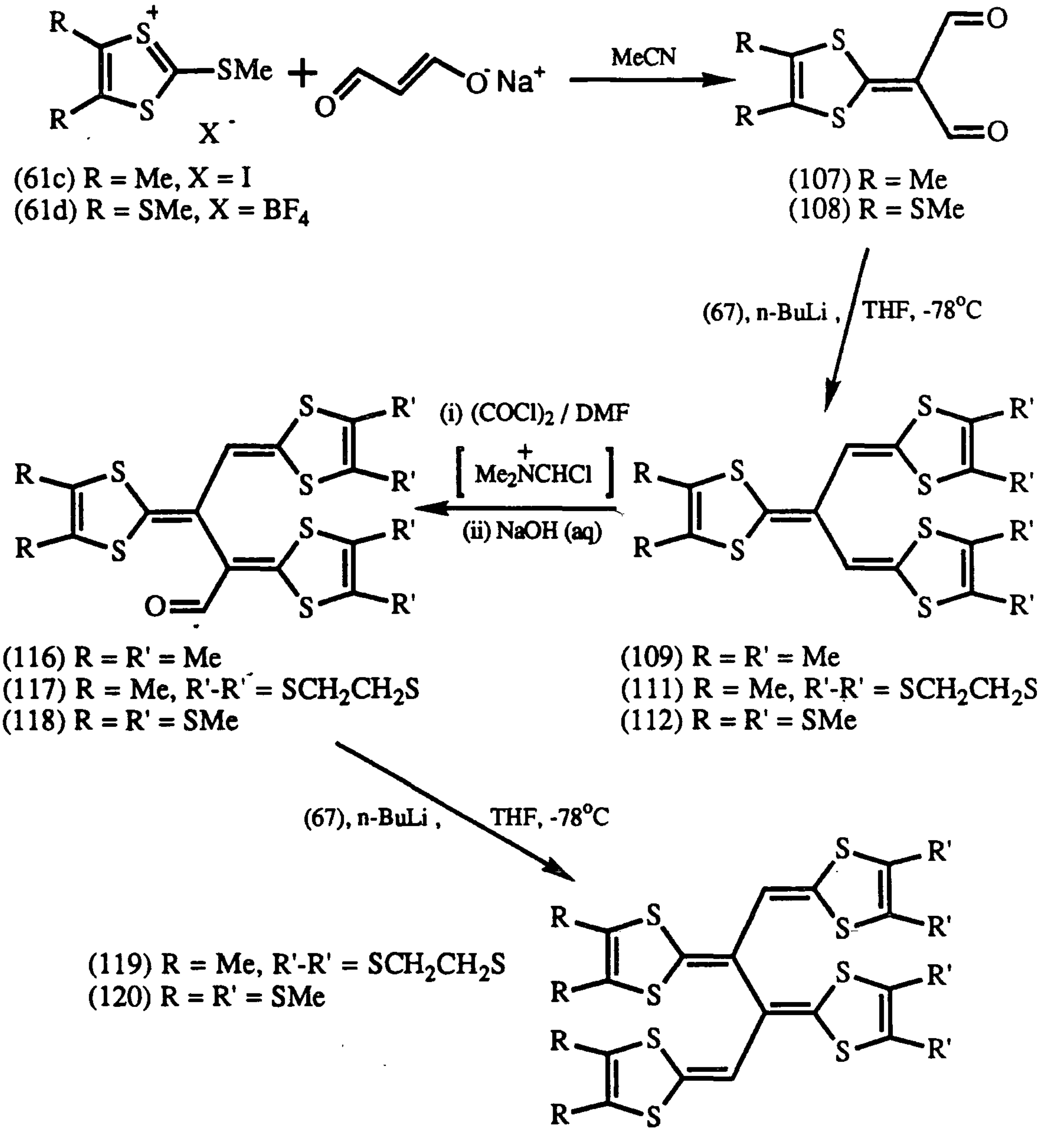
(121) R = R' = Me
(122) R = R' = SMe



(110)

Reactions of dialdehydes (107) and (108) with only one equivalent of Wittig-Horner reagent [during the reactions to make (109) and (112)] yielded the formyl-substituted vinylogues (121) and (122) in 28% and 30% yields, respectively. This allowed the synthesis of tris-(1,3-dithiole) derivatives containing dithiole rings with differing functionality, for example donor (110) which was obtained from (121) in 65% yield.

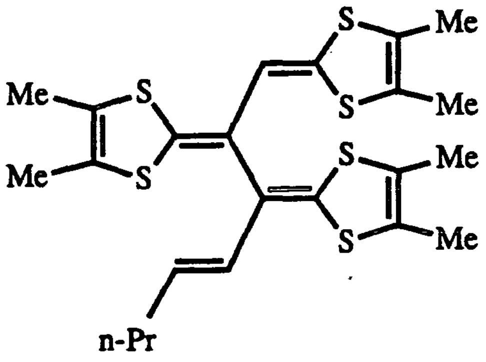
To introduce a formyl group to compounds (109), (111) and (112) we adopted Yoshida's method[140] of using a Vilsmeyer reaction. This involves formation of the



Scheme 4.1

very reactive electrophile Me_2NCHCl^+ by reacting oxalyl chloride with dimethyl formamide (DMF). Attack of this electrophile on one of the electron rich, exocyclic, carbon-carbon double bonds of the tris-(dithiole), followed by basic hydrolysis, affords the required aldehydes (116)-(118) in *ca.* 50 % yield (Scheme 4.1).

A further Wittig-Horner reaction on the aldehydes (117) and (118) afforded the [4]-dendralene derivatives (119) and (120) in *ca.* 60% yield. In the case of aldehyde (116) the expected tetrakis-(1,3-dithiole) derivative was not obtained. Instead product (123), arising from attack of butyl lithium on the carbonyl group of (116), was isolated. The coupling constant of the protons of the double bond of the pendant chain (J_{HH} = 15 Hz) are indicative of a trans configuration. (With hindsight it is obvious that the use of LDA as a base would have prevented this).



(123)

4.3 X-RAY CRYSTAL STRUCTURE OF DONOR (109)

The hexamethyl-substituted tris-(1,3-dithiole) derivative (109) formed *X*-ray quality crystals on vacuum sublimation at 220°C.

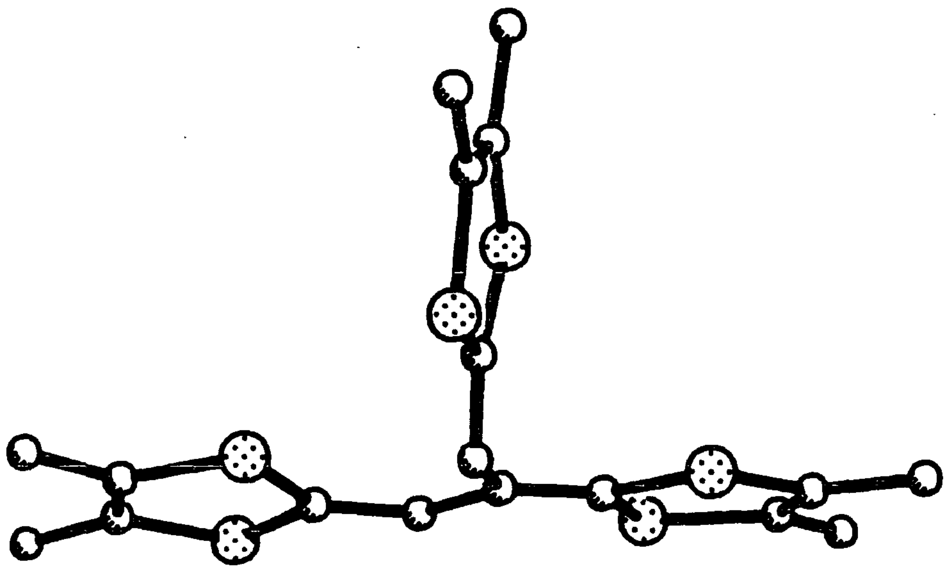


Figure 4.1 - *X*-Ray crystal structure of compound (109)

It is interesting to note that two of the dithiole rings of (109) are coplanar [*cf.* vinylogue (52)], with the third dithiole ring adopting an orientation almost perpendicular (78.2°) to the plane of the other two rings (Figure 4.1). Unfortunately, this non-planar structure inhibits any significant intermolecular interactions and prevents the formation of ordered stacks in the crystal lattice.

4.4 REDOX BEHAVIOUR AND C-T SALT FORMATION OF DONORS (109)-(112), (119)-(120), (129) AND (131)

Cyclic voltammograms of tris-1,3-dithiole compounds (109) - (112) were obtained to observe their redox behaviour (Table 4.1). All exhibited three pairs of reversible waves, each of which corresponds to a one-electron transfer. Tetrakis-1,3-dithiole compounds (119) and (120) also exhibited three pairs of reversible waves, but for these compounds the first two waves each corresponded to one-electron transfer whilst the third wave corresponded to two-electron transfer (Table 4.1).

DONOR	$E_1^{1/2}$ mV^a	$E_2^{1/2}$ mV^a	$E_3^{1/2}$ mV^a	ν_{CN} / cm^{-1}	σ_{rt}^b/Scm^{-1}
(109)	84	327	1246	2180	$< 10^{-8}$
(110)	168	411	1221	2180	$< 10^{-8}$
(111)	245	470	1244	no complex	-
(112)	360	490	1195	no complex	-
(119)	227	393	807	2180	2×10^{-6}
(120)	258	366	687	no complex	-
(129)	350	510	1207	2185	1×10^{-7}
(131)	306	506	1180	-	-

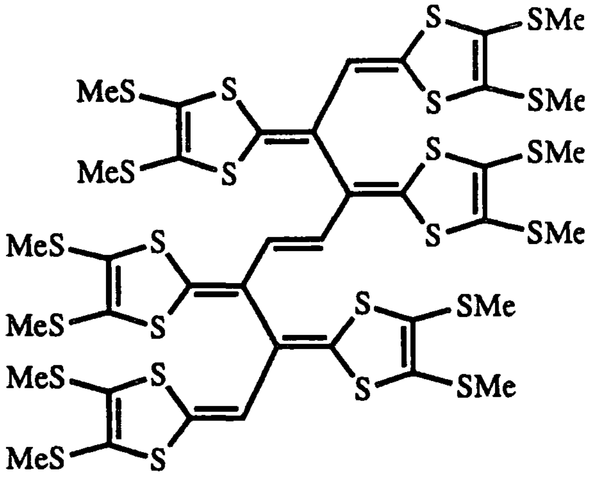
Table 4.1 - Redox behaviour for multi-1,3-dithiole systems and IR and conductivity data of their TCNQ salts.
^{a} *vs* Ag/AgCl, Pt electrode, ^{b} compressed pellet

The donors (109), (110) and (119) all formed C-T salts when boiling solutions of donor and TCNQ in dry acetonitrile were mixed together, as was indicated by the immediate formation of a dark green/blue solution. Furthermore, upon evaporation of the solution to a resulting black solid, charge transfer from donor to TCNQ was confirmed by the characteristic IR absorption (in nujol mull) of the TCNQ radical anion at 2180 cm^{-1}. However, these amorphous black powders were of irreproducible elemental analysis and recrystallisation did not enhance the purity. This suggests the possibility that a number of different complexes of varying stoichiometry formed simultaneously, as is known to occur in a number of other donor-acceptor systems[141].

The first donor we synthesised in this series was compound (109) and the CV showed that the first oxidation occurred at + 0.08V. This very low value for $E_1^{1/2}$ indicates that compound (109) is an exceptionally good donor. The consequence of this low oxidation potential is that in the complex obtained with TCNQ there is complete charge-transfer from donor to acceptor ($\nu_{CN} = 2180\ cm^{-1}$) and an insulating material is obtained. (Partial charge-transfer is required for an organic conductor - see Chapter One). We, thus, aimed to reduce the donating ability of these materials which was achieved by the replacement of methyl groups by methylthio and ethylenedithio groups on the dithiole rings (these act as electron-withdrawing groups, destabilising the radical-cation formed on oxidation). The first and second oxidation potentials of (110), (111) and (112) were raised, relative to (109), but, unfortunately, a complex of donor (110) with TCNQ was again an insulating salt with complete charge-transfer, and donors (111) and (112) did not form a complex at all!

With donor (119) the two 4,5-dimethyl substituted dithiole rings again underwent oxidation very easily (as shown by the low oxidation potentials $E_1^{1/2}$ and $E_2^{1/2}$) resulting in a charge transfer complex with near complete charge transfer and low conductivity. Donor (120) was thus synthesised and the first oxidation potential was raised by 42 mV. Again, however, no complex was formed with TCNQ. It seems, therefore, that subtle steric effects in the dithiole system determine whether or not complexes are formed with TCNQ.

Aldehydes (116)-(118), (121) and (122) are potentially interesting reagents for M^cMurray-type coupling reactions leading to multi-1,3-dithiole systems such as (124).



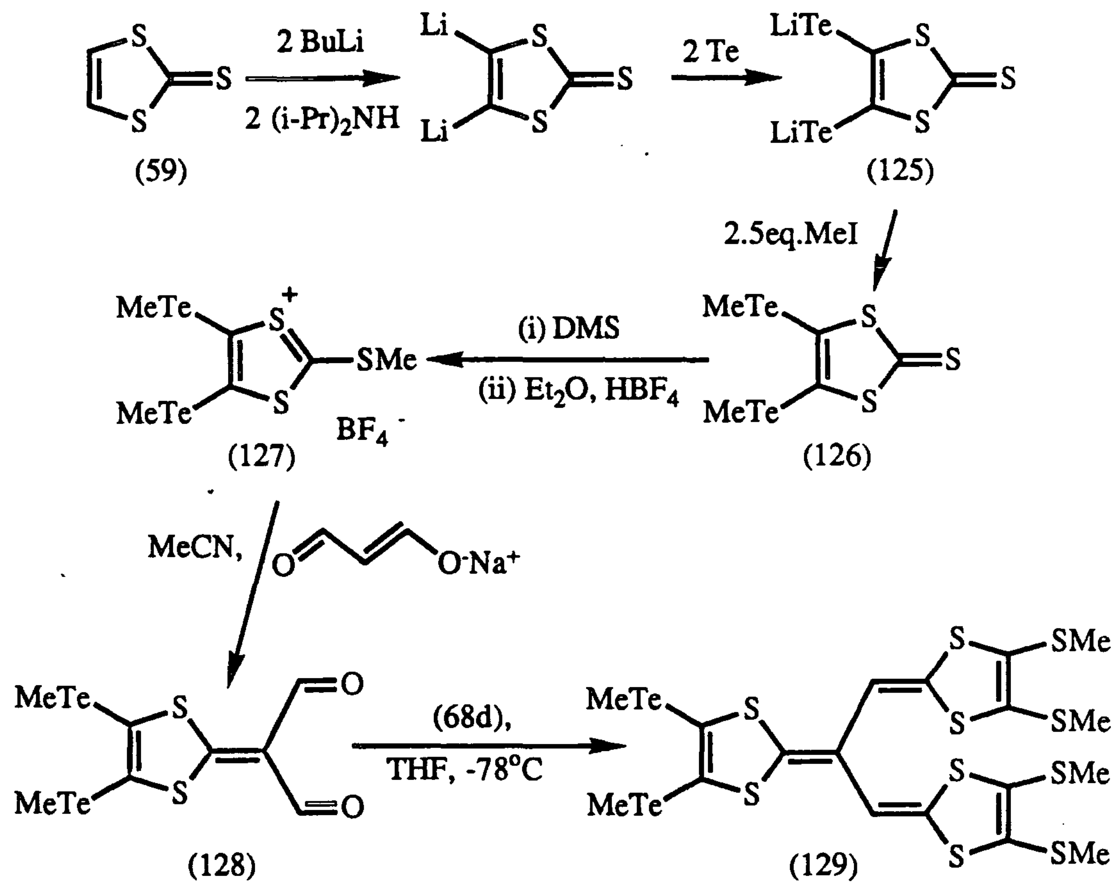
(124)

A M^{c}Murray reaction on compound (122) was tried using $TiCl_3(monoglyme)_{1.5}$ / Zn-Cu[142] and no coupled product was observed. The only isolated product was the alcohol resulting from reduction of the aldehyde. The use of different M^{c}Murray reagents is a possibility for future work.

4.5 THE SYNTHESIS OF TELLURIUM SUBSTITUTED 1,3-DITHIOLE SYSTEMS

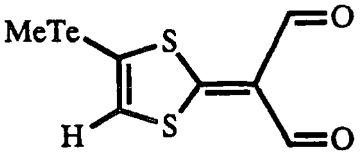
The presence of tellurium atoms in the donor framework is generally advantageous for the formation of inter- and intra- stack molecular interactions (see Chapter One). The synthesis of tetra(methyltelluro)-TTF was reported in 1985, involving tetralithiation of TTF followed by the insertion of elemental tellurium and then reaction with methyl iodide[143].

Following this same procedure, using vinylene trithiocarbonate (59) instead of TTF, we succeeded in synthesising 4,5-bis(methyltelluro)-1,3-dithiole-2-thione (126), albeit in poor yield (*ca.* 10%) (Scheme 4.2). We were unable to form the 4,5-ethyleneditelluro-1,3-dithiole-2-thione species on addition of dibromomethane to the ditellurate anion (125), isolating only black, intractable products. Methylation of thione (126) with dimethyl sulphate at 70°C yielded salt (127) as a black oil which was reacted, without isolation, with the sodium salt of malonaldehyde affording the dialdehyde (128) in 22% yield. This in turn underwent a double Wittig-Horner reaction (as for previous compounds, Scheme 4.1) to form the mixed tellurium / sulphur-substituted tris-1,3-dithiole derivative (129) (49% yield).



Scheme 4.2

A second tellurium containing tris(1,3-dithiole) derivative (131) was formed from Wittig-Horner reactions on dialdehyde (130). Compound (130) had itself been isolated in low yield during the preparation of dialdehyde (128), presumably due to the batch of thione (126) being contaminated with the mono-telluromethyl substituted thione. The cyclic voltammograms of donors (129) and (131) are similar to the other tris(1,3-dithioles), exhibiting three reversible one-electron oxidations (Table 4.1).



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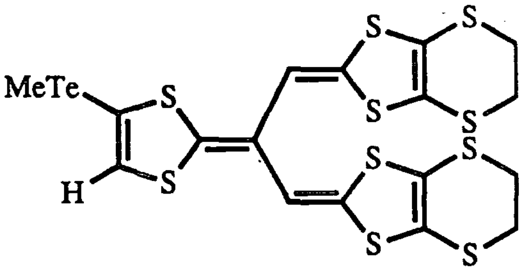


(131)

Although these two interesting new tellurium containing donors (129) and (131) were synthesised, the very poor yields precluded any further reactions to make [4]-dendralene derivatives. The complex of donor (129) with TCNQ has a room temperature compressed pellet conductivity of $\sigma_{rt} = 10^{-7}$ Scm^{-1}.

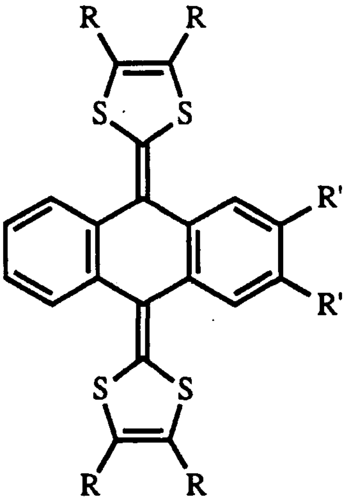
In conclusion, a series of [3]- and [4]-dendralenes with a variety of substituents in the 4,5-positions have successfully been synthesised, continuing the use of Wittig-Horner methodology from Chapters Two and Three. The crystal structure of the tricyclic [3]-dendralene (109) has been solved, showing a twisted structure, and compounds (119) and (129) were found to form semi-conducting charge-transfer complexes with TCNQ.

CHAPTER FIVE

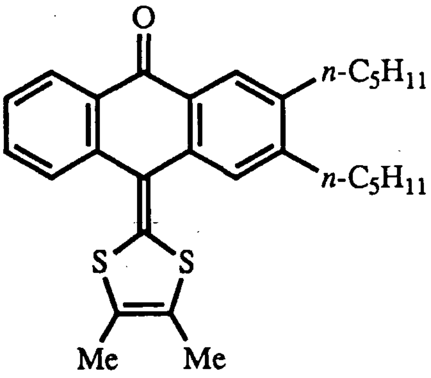
ANTHRAQUINODIMETHANE DERIVATIVES OF TETRATHIAFULVALENE

5.1 INTRODUCTION

Tetrathiafulvalene derivatives that consist of two heterocyclic rings that are separated by, and conjugated through, quinodimethane groups[72,90a,144] are currently of interest because of their novel redox chemistry which is relevant to the development of new organic metals and organic superconductors[81]. Such extended conjugation has the effect of considerably reducing the intra-molecular Coulombic repulsion between cations localised in the two dithiole rings, hence stabilising the dication state in a similar manner to the bis(1,3-dithiole) vinylogues discussed in Chapter Two. Donors must have this ability to support a stable dication, otherwise "only a correlated type of conductivity is possible"[22] in a charge-transfer complex of that donor. Such TTF analogues that are capable of sustaining higher oxidation states (over and above the dication state of TTF itself) have been identified as promising targets[81] and a few examples of this are known[140,145].



(132) R = Me, R' = H
(133) R = SMe, R' = H
(134) R = Me, R'= *n*-pentyl

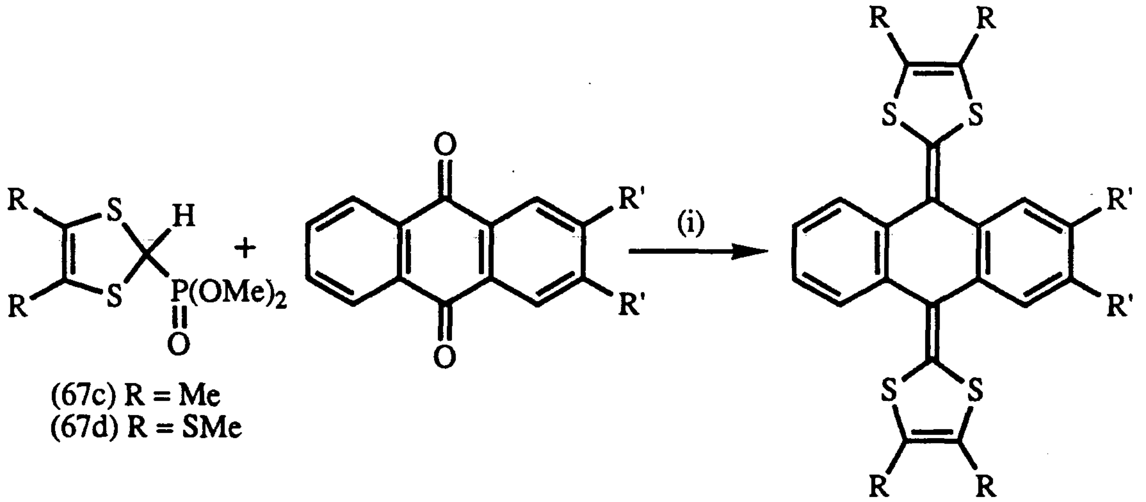


(135)

The anthraquinodimethane derivative (132) has been studied previously in our laboratory[72] and that of Yamashita *et al* [144b]. The single-crystal *X*-ray structure of donor (132) shows that the neutral molecule is butterfly shaped with the central quinonoid ring severely distorted into a boat form. According to Cowan and Kini's design constraints for the preparation of good organic conductors[22], planarity is a prerequisite. This is obviously not the case with donor (132), but nonetheless a highly conductive 1:4 complex is formed with TCNQ. The dications of (132) present in the complex show an extreme deviation from planarity, with the dithiole rings almost perpendicular to the plane of the anthracene group[146]. Such interesting behaviour lead us to synthesise the related donors (133) and (134).

5.2 SYNTHESIS OF COMPOUNDS (133) AND (134)

Both anthraquinodimethane derivatives (133) and (134) were synthesised in one step (38% and 28% yields, respectively) from the appropriately substituted anthraquinone and the required phosphonate ester (67d) or (67c) in a double Wittig-Horner reaction (Scheme 5.1). Alongside compound (134), anthrone derivative (135) (24% yield) was isolated, as the result of one Wittig-Horner reaction on the anthraquinone derivative.



(67c) R = Me
(67d) R = SMe

Reagents and conditions: (i) *n*- BuLi, 1.1 eq., THF, -78°C

(133) R = SMe, R' = H
(134) R = Me, R'= *n*-pentyl

Scheme 5.1

5.3 *X*-RAY CRYSTAL STRUCTURES OF COMPOUNDS (133) AND (134)

Compound (133) furnished *X*-ray quality crystals from an acetonitrile / dichloromethane solution and the crystal structure of this neutral molecule exhibits a very similar conformation to compound (132), adopting the back-to-back boat orientation (Figure 5.1).

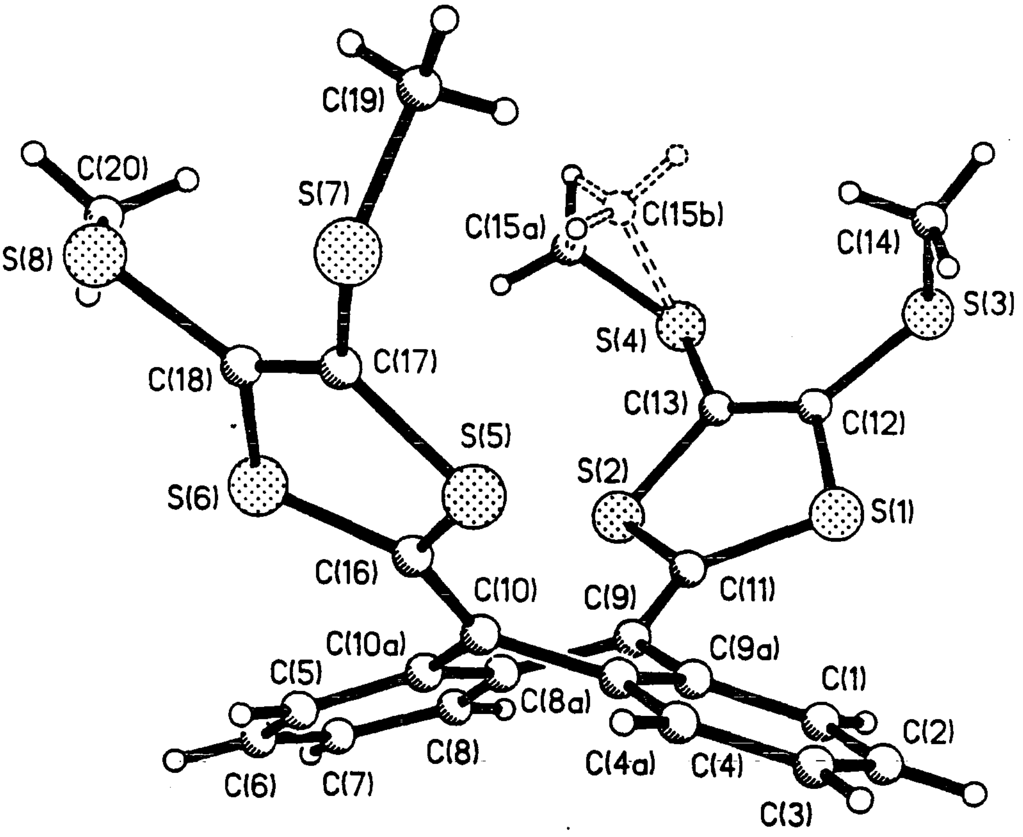


Figure 5.1 - Molecular structure of compound (133) solved by *X*-ray analysis

The distortion of the central quinonoid ring is clearly visible in Figure 5.1. The angle formed by planes 1 and 2 is 30.6° and by planes 2 and 3 is 30.8°, where plane 1 contains C(9), C(9a) and C(8a), plane 2 contains C(8a), C(10a), C(9a) and C(4a) and plane 3 contains C(10), C(10a) and C(4a). In the crystal structure the methyl groups have a 50 % probability of being in either of the two positions indicated in Figure 5.1.

The *X*-ray crystal structure of compound (134) has also been determined and there are two different molecules (A and B) in the unit cell, one of which has a partially disordered sidechain. The structure of compound (134) (molecule A) is shown in Figure 5.2. Once again the ring system is butterfly-shaped with the central quinonoid ring severely distorted into a boat form [to a slightly greater extent than in compound (133)]. The angle formed by planes 1 and 2 is 34.9° and by planes 2 and 3 is 35.0°, where plane 1 contains C(12), C(13) and C(19), plane 2 contains C(12), C(7), C(29) and C(19) and plane 3 contains C(7), C(6) and C(29). The corresponding values for molecule B are 32.8° and 32.1°.

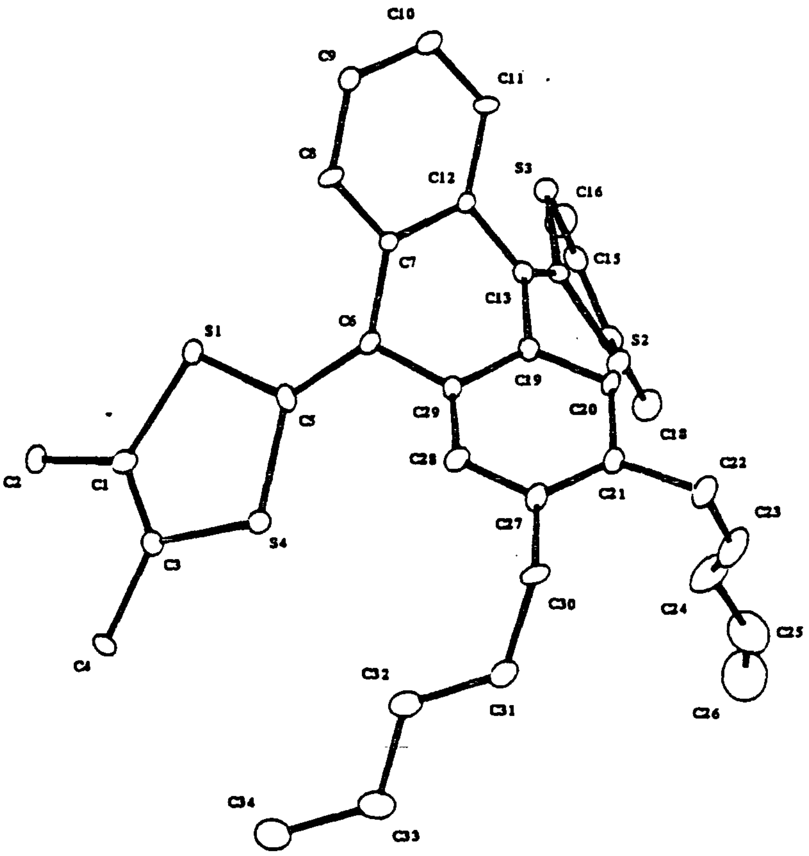


Figure 5.2 - Molecular structure of compound (134) solved by *X*-ray analysis

5.4 REDOX BEHAVIOUR OF COMPOUNDS (133) AND (134)

The neutral donors (132) and (133) both undergo a single, two-electron oxidation directly forming the dication. The cyclic voltammogram of (133) shows a reversible two-electron oxidation at +0.45 V, being slightly harder to oxidise than donor (132), which loses its two electrons at +0.42 V. The extreme insolubility of the dication salts of (132) produced either electrochemically[72,144b] or chemically[72,146], however, prevents any further examination of this interesting redox system, hence our synthesis of donor (134).

Due to the two pentyl sidechains, the solubility of compound (134) is markedly increased compared to compounds (132) and (133) and this allows us to observe, for the first time, the +3 and +4 oxidation states in a quinodimethane derivative of TTF. Compound (134) is structurally quite distinct from other TTF analogues which afford high (> +2) oxidation states (*e.g.* those considered in Chapter 4) because they consist of multiple 1,3-dithiole rings which are themselves the sites of oxidation. For compound (134) the first two oxidations involve the two dithiole rings whilst the third and fourth oxidations involve the linking group.

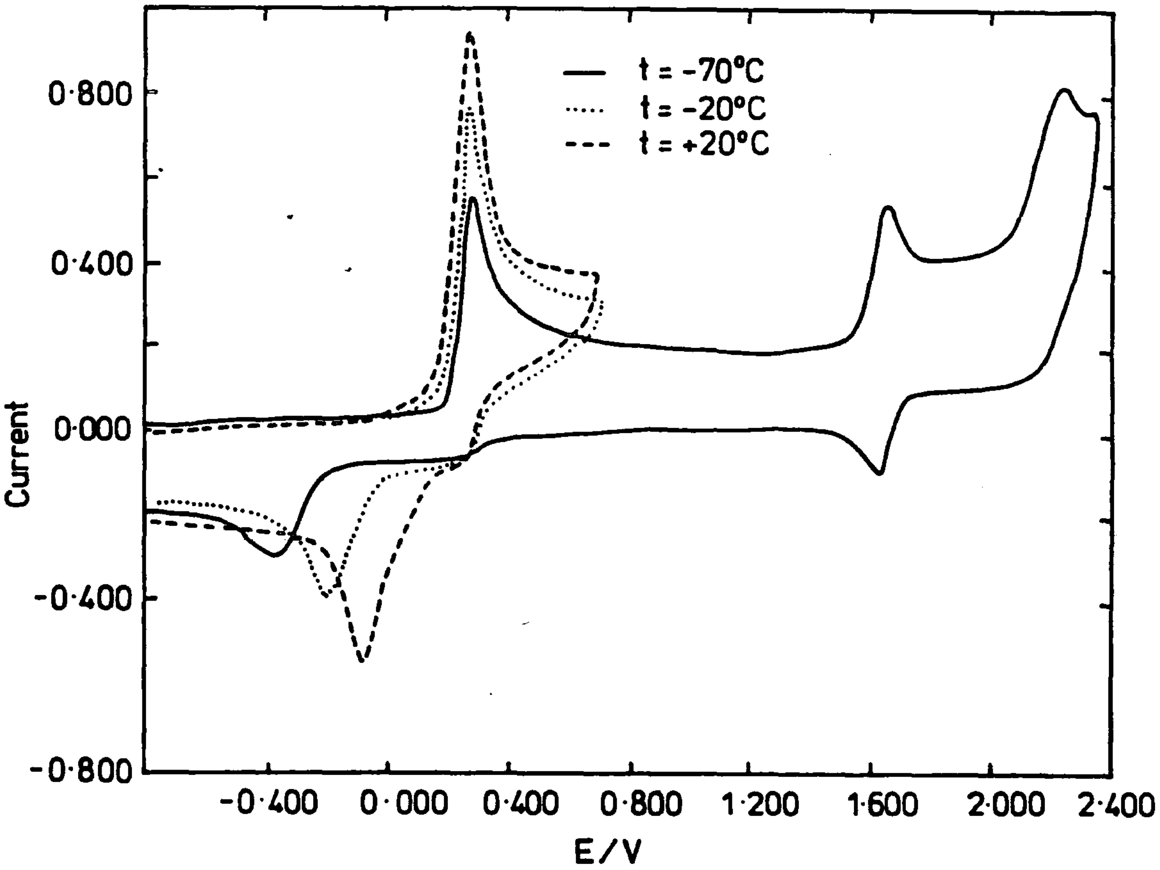
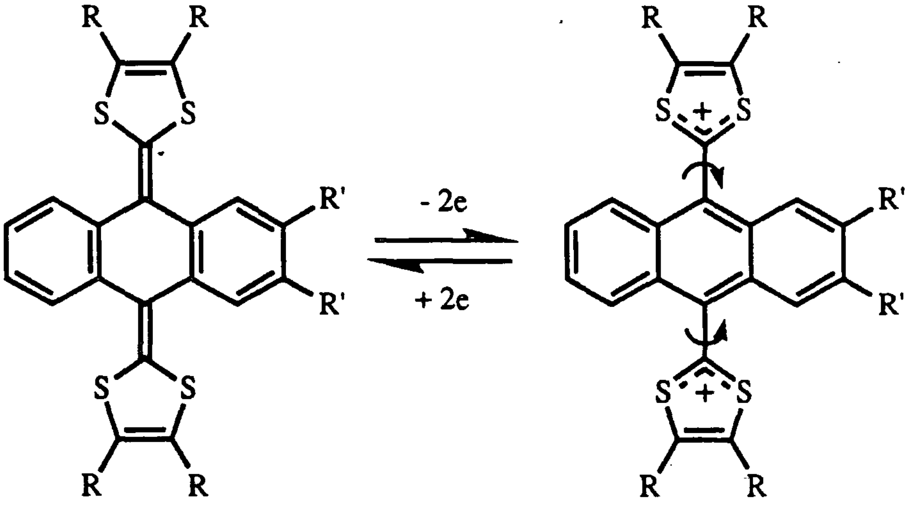


Figure 5.3 - Cyclic voltammograms of neutral donor (134) at various temperatures, Pt electrode *vs.* Ag/AgCl in CH_2Cl_2, electrolyte Bu_4NPF_6

The oxidation of compound (134) has been studied by cyclic voltammetry in three different solvents (dichloromethane, acetonitrile and propylene carbonate) under rigorously anhydrous conditions. Dichloromethane solutions provided the most informative results, and the greatly increased solubility of compound (134) over compounds (132) and (133) has allowed data to be obtained at low temperatures. At -70°C three distinct oxidation steps are clearly observed (Figure 5.3). The first redox wave (E_{OX} = + 0.28 V) is a quasi-reversible, two-electron transfer to yield the dication species $(134)^{2+}$ and is directly analogous to that described previously for donor (132) at 20°C[72,144b]. Subsequently, there are two further, sequential, one-electron oxidations of the anthracene system of $(134)^{2+}$ which were not observed for $(132)^{2+}$. These afford the novel trication and tetracation species of (134). The first anthracene oxidation ($E_3{}^{1/2}$ = + 1.64 V) is cleanly reversible, whereas the second anthracene oxidation ($E_4{}^{1/2}$ = *ca.*+2.2 V) is at the limit of the solvent "window" and is thus irreversible.



(132) R = Me, R' = H
(133) R = SMe, R' = H
(134) R = Me, R'= *n*-pentyl

$(132)^{2+}$ R = Me, R' = H
$(133)^{2+}$ R = SMe, R' = H
$(134)^{2+}$ R = Me, R'= *n*-pentyl

The first two-electron step for system (134) has been examined under various conditions in an attempt to determine experimentally the interaction energy between the radical cation and dication states. However, even at -80°C and different scan rates ranging from 20 mV - 50 mVsec^{-1}, there is still only one single oxidation peak. Simulation of the cyclic voltammogram obtained at -80°C and 100 mVsec^{-1} provides an interaction energy for E_1 and E_2 of < 50 mV. The potential of the first oxidation peak is temperature independent; however, the reduction peak of dication $(134)^{2+}$ ⟶ neutral (134) in the back sweep is shifted progressively to more negative potentials with decreasing temperature (Figure 5.3). This is undoubtedly a reflection of the aromaticity of the newly-formed anthracene system, together with the additional stabilisation within the 6π, 1,3-dithiolium rings, at the dication redox stage $(134)^{2+}$. The marked conformational change that must occur on reduction [planar anthracene $(134)^{2+}$ ⟶ buckled anthraquinodimethane (134)] accounts for the temperature dependance and the irreversibility of this step.

5.5 CHARGE-TRANSFER COMPLEX FORMATION OF DONORS (133) AND (134)

Unfortunately, when a boiling solution of compound (133) (in either dichloromethane or acetonitrile) was mixed with a boiling solution of TCNQ no formation of a charge-transfer complex was observed. Donor (134), similarly to donor (132), was found to form a 1:4 complex with TCNQ. This was isolated as a black powder from acetonitrile solution, and a two-probe, compressed-pellet conductivity measurement showed this complex to be a semi-conductor, $\sigma_{rt} = 1 \times 10^{-4}$ Scm^{-1}, containing anionic TCNQ ($\nu_{max} = 2180$ cm^{-1}).

In conclusion, multistage redox behaviour, leading to a tetracation species, albeit at high potential, has been observed in the new TTF-derived donor (134), the *X*-ray structure of which has been determined. In contrast to previously studied systems, oxidation occurs at the dithiole rings and at the central linking group. These results open the way for the synthesis of new systems with novel redox chemistry, for example bianthrone analogues which may exhibit six oxidations to yield the hexacation species.

CHAPTER SIX

EXPERIMENTAL

6.1 GENERAL METHODS

Melting points were recorded on a Kofler hot-stage microscope and are uncorrected.

Infra-red spectra were recorded on Perkin-Elmer 377 and 577 spectrophotometers; samples were either embedded in KBr discs, nujol mulls or neat (if liquid).

Proton NMR and carbon-13 NMR were recorded on a Bruker AC 250 instrument, operating at 250.133 MHz for protons and 62.896 MHz for the carbon nucleus. Chemical shifts, given in ppm, are relative to tetramethylsilane (TMS) as an internal standard.

Mass spectra were obtained on a VG 7070E spectrometer operating at 70 eV, with ionisation modes as indicated. All selenium-containing mass peaks are reported for the ^{80}Se isotope and all telurium-containing mass peaks are reported for the ^{128}Te isotope.

Elemental analyses were performed on either a Carlo-Erba Strumentazione (C, H, N) or a Perkin-Elmer HGA 500 (S) instrument.

TLC data were obtained using Merck pre-coated alumina (0.2 mm) or Merck pre-coated silica (0.2 mm) aluminium backed sheets. For column chromatography, Merck alumina (activity II to III, 70-230 mesh) or Merck silica gel (70-230 mesh) were employed as indicated. Neutral alumina refers to alumina pre-soaked in ethyl acetate overnight. All solvents were distilled prior to use in chromatography.

Solvents were dried from the following agents under a nitrogen atmosphere: diethyl ether, THF, and toluene (sodium metal); chlorocarbons (P_2O_5); acetonitrile (CaH_2); methanol (magnesium methoxide) and ethanol (magnesium ethoxide). All other reagents were reagent grade and used as supplied, unless otherwise stated.

Cyclic voltammetry (CV) experiments were performed in a one-compartment cell with platinum working and counter electrodes and a silver / silver chloride reference electrode. Measurements were made with a BAS 100 electrochemical analyser and were i.r. compensated. The cell contained a solution of donor (*ca.* 1 x 10^{-5} M) with oven dried (120°C) tetrabutylammonium hexafluorophosphate (0.01 M) as the supporting electrolyte in either dry dichloromethane or dry acetonitrile (*ca.* 10 ml); all solutions were purged with argon and retained under an inert atmosphere while the CV data were recorded.

Conductivity measurements on powdered samples were obtained using the two-probe technique; samples were manually compressed between two steel probes and the sample resistance measured with a Fluka 8000A Digital Multimeter.

Bulk magnetic susceptibility data were obtained using a Faraday balance.

All solid compounds prepared were recrystallised from dichloromethane/hexane mixtures unless otherwise stated.

6.2 EXPERIMENTAL TO CHAPTER TWO

6.2.1 Materials

General details are the same as those reported recently [82a,84-86].

4,5-(Ethylenediseleno)-1,3-dithiole-2-thione (60b) was prepared according to the literature procedure[91] from vinylene trithiocarbonate (1,3-dithiole-2-thione), selenium and dibromoethane (55 % yield). Mpt. 155-156°C (lit.[91] 156-157°C).

2-Dimethoxyphosphoryl-4,5-dimethyl-1,3-dithiole (67c) was prepared in four steps from 4,5-dimethyl-1,3-dithiole-2-thione (60c)[24] following the literature procedure (*ca.*70 % yield)[85c,57].

2-Dimethoxyphosphoryl-4,5-bis(methylthio)-1,3-dithiole (67d) was prepared in four steps from 4,5-bis(methylthio)-1,3-dithiole-2-thione (60d)[92] following the literature procedure (*ca.*75 % yield)[88].

6.2.2.1 4,5-Bis(methylseleno)-1,3-dithiole-2-thione (60a)

This material has been mentioned previously but neither synthetic details nor characterisation data were given[94]. Details for (60a) are, therefore, presented here.

1,3-Dithiole-2-thione (vinylene trithiocarbonate) (2.0 g, 15 mmol) was lithiated and reacted with elemental selenium in THF as described previously[94]. To the resulting diselenate at 0°C was added methyl iodide (6.0 g, 45 mmol) and the solution was allowed to warm to 20°C with stirring which was maintained for 12 h. The mixture was diluted with water and extracted into dichloromethane. The organic layer was separated, dried ($MgSO_4$) and evaporated to yield a red oil. Purification on a silica column [eluent hexane/dichloromethane (3:1 v/v)] yielded **compound (60a)** which after recrystallisation from dichloromethane/hexane was obtained as orange needles (1.44 g, 30%). M.Pt.: 100-101°C; MS: m/e (EI) 322 (M^+), (CI) 323 (M^++1); $\delta_H(CDCl_3)$ = 2.41(s) ppm.; Anal.: Calcd. for $C_5H_6S_3Se_2$: C, 18.7; H, 1.89; S, 30.0 %. Found: C, 18.6; H, 1.80; S, 30.1 %.

6.2.2.2 2-Methylthio-4,5-bis(methylseleno)-1,3-dithiole (62a)

A suspension of compound (60a) (1.0 g; 3.1 mmol) in dimethyl sulphate (5 ml) was heated at 70°C under nitrogen until dissolution was complete (*ca.* 1 h). The mixture was cooled to 20°C and tetrafluoroboric acid (0.6 mL, 3.3 mmol) was added dropwise, followed by dry ether (100 ml). The resulting yellow precipitate was collected, washed with dry ether and dried. **Salt (61a)** (1.21 g, 96%) thus obtained was identified by NMR spectroscopy [$\delta_H(CDCl_3)$ = 3.24 (3H, s), 2.68 (6H, s) ppm.] and then used directly in the next step. To a solution of salt (61a) (1.21 g, 2.9 mmol) in a mixture of acetonitrile (30 ml) and ethanol (30 ml) was added sodium borohydride (0.15 g, 3.9 mmol) turning the solution from yellow to colourless. After stirring for 1 h at 20°C, the solvent was evaporated and the residue extracted into dichloromethane, which was washed with water and dried ($MgSO_4$). Evaporation of the organic phase yielded an oil which was purified by chromatography on a silica column (eluent: hexane/dichloromethane, 2:1 v/v) to yield **thioether (62a)** as a red oil (0.75 g, 78%). MS: m/e (EI) 338 (M^+), (CI) 339 (M^++1); $\delta_H(CDCl_3)$ = 5.90 (1H, s), 2.29 (6H, s) and 2.21 (3H, s) ppm.

6.2.2.3 2-Methylthio-5,6-dihydro-1,3-dithiolo[4,5-b][1,4]diselenin (62b)

This was prepared from compound (60b) (1.0 g, 3.1 mmol) following the procedure described for compound (62a) (Chapter 6.2.2.2) and isolated by column chromatography on silica gel (eluent hexane : dichloromethane 1:1 v/v) as a red oil (0.80

g, 83%). MS: m/e (EI) 336 (M^+), (CI) 337 (M^++1); $\delta_H(CDCl_3)$ = 5.86 (1H, s), 3.30 (4H, m) and 2.22 (3H, s) ppm.

6.2.2.4 2-Formylmethylene-4,5-bis(methylseleno)-1,3-dithiole (66a)

Diethyl ether-tetrafluoroboric acid (0.4 ml, 2.78 mmol) was added dropwise over 15 min to a stirred solution of compound (62a) (0.75 g, 2.23 mmol) in a mixture of acetic anhydride (5 mL) and ether (20 ml) at 0°C under nitrogen. After stirring for a further 15 min, ether (100 ml) was added and the white solid which had precipitated was removed by filtration, washed with ether and dried. The air- and moisture- sensitive **salt (63a)** (0.75 g, 89%) thus obtained was used directly in the next step.

Dithiolium salt (63a) (0.75 g, 2.00 mmol) was dissolved in dry acetonitrile (50 ml) under nitrogen, to which was added triphenylphosphine (0.53 g, 2.02 mmol). After 0.5 h at 20°C, excess glyoxal (10 ml, 40% solution in water) was added, followed by excess triethylamine (*ca.* 5 ml) and stirring was then continued at 20°C for 3 h. The solvent was then removed *in vacuo* and the residue extracted into dichloromethane, which was then washed with water. The organic layer was dried ($MgSO_4$) and evaporated to yield a viscous oil which was purified by chromatography on a silica column (eluent initially hexane/dichloromethane, 1:1 v/v, followed by neat dichloromethane) to afford **compound (66a)** as a viscous yellow oil (0.47 g, 71%). MS: m/e (EI) 332 (M^+), (CI) 333 (M^++1); $\delta_H(CDCl_3)$ = 9.27 (1H, d, J = 1.8 Hz), 6.59 (1H, d, J = 1.8 Hz), 2.44 (3H, s), 2.38 (3H, s) ppm.

6.2.2.5 2-Formylmethylene-5,6-dihydro-1,3-dithiolo[4,5-b][1,4]-diselenin (66b)

This was prepared analogously to compound (66a) (Chapter 6.2.2.4) from compound (62b) (0.80 g) and isolated as a yellow solid (0.55 g, 78%). M.Pt: 102-104°C; MS: m/e (EI) 330 (M^+), (CI) 331 (M^++1); $\delta_H(CDCl_3)$ = 9.36 (1H, d, J = 1.5 Hz), 6.68 (1H, d, J = 1.5 Hz), 3.40 (4H, s) ppm.; Anal.: Calcd. for $C_7H_6OS_2Se_2$: C, 25.6; H, 1.84 %. Found: C, 25.5; H, 1.90 %.

6.2.2.6 2-Dimethoxyphosphoryl-4,5-bis(methylseleno)-1,3-dithiole (67a)

A mixture of dithiolium salt (63a) (0.45 g, 1.20 mmol), trimethylphosphite (0.15 g, 1.21 mmol) and sodium iodide (0.18 g, 1.2 mmol) in dry acetonitrile (50 ml) was stirred at 20°C overnight under dry nitrogen. The solvent was evaporated and the residue extracted into dichloromethane which was washed with water, the organic layer was then dried ($MgSO_4$) and the solvent removed. The resulting oil was passed down a neutral alumina column eluting with hexane:dichloromethane (1:1 v/v) to yield **compound (67a)** as a red oil (0.38 g, 80%). $\delta_H(CDCl_3)$ = 4.81 (1H, d, J = 4.4 Hz), 3.88 (6H, d, J = 11.0 Hz), 2.34 (6H, s) ppm.

6.2.2.7 2-Dimethoxyphosphoryl-5,6-dihydro-1,3-dithiolo[4,5-b][1,4]-diselenin (67b)

This was prepared analogously to compound (67a) (Chapter 6.2.2.6) from salt (63b) (0.50 g). Recrystallisation from dichloromethane/hexane gave **compound (67b)** as a white solid, which rapidly turned black on exposure to air (0.31 g, 59%). M.Pt 100-102°C; MS: m/e (EI) 398 (M^+), (CI) 399 (M^++1); $\delta_H(CDCl_3)$ = 4.83 (1H, d, J = 6.2 Hz), 3.86 (6H, d, J = 10.6 Hz), 3.30 (4H, m) ppm.; Anal.: Calcd. for $C_7H_{11}O_3PS_2Se_2$: C, 21.2; H, 2.80 %. Found: C, 21.8; H, 2.83 %.

6.2.2.8 Vinylogous TTF Derivatives (54)-(58) General Procedure

A solution of phosphonate ester (67) (1.0 mmol) in dry tetrahydrofuran (THF) (30 mL) was cooled to -78°C under nitrogen and treated with *n*-butyl lithium (1.6 M, 1.1 mmol) causing an immediate colour change from red to yellow. After 0.5 h, a solution of aldehyde (66) (0.9 mmol) in THF (10 ml) was added by syringe into the reaction mixture which was allowed to warm to 20°C over 16 h. The solvent was then evaporated, and the residue dissolved in dichloromethane (50 ml) which was washed with water, dried ($MgSO_4$) and evaporated to yield the crude product which was purified by elution through an alumina column (eluent hexane-dichloromethane *ca.* 2:1 v/v). The product was recrystallised from hexane-dichloromethane.

6.2.2.9 4,5-Bis(methylseleno)-4',5'-bis(methylthio)-2,2'-ethanediylidenebis(1,3-dithiole) (54)

This was obtained from ester (67d)[88] and aldehyde (66a) and isolated as large orange plates in 76% yield. M.Pt: 120-122°C; MS: m/e 510 (M^+); $\delta_H(CDCl_3)$ = 5.76 (2H, s), 2.40 (3H, s), 2.39 (3H, s), 2.31 (3H, s), 2.30 (3H, s) ppm.; Anal.: Calcd. for $C_{12}H_{14}S_6Se_2$: C, 28.3; H, 2.77 %. Found: C, 28.4; H, 2.78 %.

6.2.2.10 4,4',5,5'-Tetrakis(methylseleno)-2,2'-ethanediylidenebis(1,3-dithole) (55)

This was obtained from ester (67a) and aldehyde (66a) and isolated as a orange solid in 58% yield. M.Pt: 132-134°C; MS: m/e 605 (M^+); $\delta_H(CDCl_3)$ = 5.78 (2H, s), 2.32 (12H, m) ppm.; Anal.: Calcd. for $C_{12}H_{14}S_4Se_4$: C, 23.9; H, 2.34 %. Found: C, 23.8; H, 2.40 %.

6.2.2.11 4,5-Ethylenediseleno-4',5'-dimethyl-2,2'-ethanediylidenebis(1,3-dithiole) (56)

This was obtained from ester (67c)[95] and aldehyde (66b) and isolated as a yellow solid in 62% yield. M.Pt: 198-200°C; MS: m/e (EI) 444, (CI) 445 (M^++1); $\delta_H(CDCl_3)$ = 5.80 (2H, dd), 3.33 (4H, s), 1.90 (3H, s), 1.89 (3H, s) ppm.; Anal.: Calcd. for $C_{12}H_{12}S_4Se_2$: C, 32.6; H, 2.73 %. Found: C, 32.8; H, 2.75 %.

6.2.2.12 4,5-Ethylenediseleno-4',5'-bis(methylseleno)-2,2'-ethanediylidenebis(1,3-dithiole) (57)

This was obtained from ester (67a) and aldehyde (66b) and isolated as an orange solid in 65% yield. M.Pt: 123-125°C; MS: m/e 604 (M^+); $\delta_H(CDCl_3)$ = 5.81 (2H, s), 3.33 (4H, s), 2.31 (3H, s), 2.30 (3H, s); Anal.: Calc. for $C_{12}H_{12}S_4Se_4$: C, 24.0; H, 2.01 %. Found: C, 23.8; H, 1.94 %.

6.2.2.13 4,5-Ethylenediseleno-4',5'-ethylenediseleno-2,2'-ethanediylidenebis(1,3-dithiole) (58)

This was obtained from ester (67b) and aldehyde (66b) and isolated as a yellow solid in 55% yield. M.Pt: > 340°C after recrystallisation from carbon disulphide / methanol; $\delta_H(CS_2)$ = 5.71 (2H, s) and 3.31 (8H, s) ppm.; Anal.: Calcd. for $C_{12}H_{10}S_4Se_4$: C, 24.1; H, 1.68; S, 21.4 %. Found: C, 23.9; H, 1.65; S, 21.3 %. The compound was too involatile to give a mass spectrum (EI, CI or DCI modes).

Complex	Formula	Anal: Found	Anal: Required	σ_{rt} / Scm^{-1}
(54):(TCNQ)$_1$	$C_{24}H_{18}N_4S_6Se_2$	C, 40.5 H, 2.49 N, 7.87	C, 40.5 H, 2.55 N, 7.86	10^{-5}
(55):(TCNQ)$_1$	$C_{24}H_{18}N_4S_4Se_4$	C, 36.4 H, 2.28 N, 7.45	C, 35.7 H, 2.25 N, 6.95	10^{-2}
(56):(TCNQ)$_1$	$C_{24}H_{16}N_4S_4Se_2$	C, 44.4 H, 2.30 N, 9.48	C, 44.6 H, 2.49 N, 8.67	10^{-5}
(57):(TCNQ)$_2$	$C_{36}H_{20}N_8S_4Se_4$	C, 43.1 H, 2.04 N, 11.01	C, 42.9 H, 2.00 N, 11.11	10^{-6}
(58):(TCNQ)$_1$	$C_{24}H_{14}N_4S_4Se_4$	C, 35.6 H, 1.77 N, 6.75	C, 35.9 H, 1.76 N, 6.98	10^{-2}

Table 6.1 - Analytical and Conductivity Data[a] for Complexes of Donors (54)-(58) with TCNQ.

[a] Two probe, compressed pellet measurement.

6.2.2.14 Complexes of donors (54)-(58) with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ)

Donors (54)-(57) were dissolved in boiling dichloromethane [1,1,2-trichloroethane for donor (58)] and added to an equimolar dichloromethane solution of TCNQ. The resultant dark green/black solutions were refluxed for 15 min and then allowed to cool to room temperature. The precipitated complexes (30-50% yield) were removed by filtration. Data for the complexes are collated in Table 6.1.

6.3 EXPERIMENTAL TO CHAPTER THREE

6.3.1 Materials

4,5-Dimethyl-2-methylthio-1,3-dithiolium iodide (61c) was prepared in one step from 4,5-dimethyl-1,3-dithiole-2-thione (60c)[24] following the literature procedure (*ca.* 85 % yield)[9a].

4,5-Dihydro-2-methylthio-1,3-dithiolium iodide (61e) was prepared in one step from vinylene trithiocarbonate following the literature procedure (*ca.* 80 % yield)[149].

2-Formylmethylene-4,5-ethylenedithio-1,3-dithiole (66f) was prepared in five steps from 4,5-(ethylenedithio)-1,3-dithiole-2-thione[42] following the literature procedure (*ca.*70 % yield)[88].

4-Hydroxyoctan-5-one was prepared according to the literature procedure [122] from butryaldehyde in *ca.* 70 % yield. B.Pt: 80-85 °C, at *ca.* 12 mm Hg (lit. 90-92 °C, at 13-14 mm Hg).

4-Chloro-octan-5-one. This known compound was prepared in a manner different from that in the literature[124]. A mixture of 4-hydroxyoctan-5-one (8.8 g, 60 mmol) and pyridine (2 ml) dissolved in dichloromethane (50 ml) was added dropwise at

10°C over a period of 1 h to a stirred solution of thionyl chloride (4.4 ml, 70 mmol) and pyridine (2 ml), dissolved in dichloromethane (250 ml). The mixture was then stirred at room temperature overnight and quenched with ice-water (100 ml). The organic layer was separated, washed with water (4 x 100 ml), dried ($MgSO_4$) and evaporated to leave a red oil (9.0 g, 90 %) which was used directly in the next step without further purification. MS: m/e 163, 165 (EI) (M^+); $\delta_H(CDCl_3)$ = 4.21 (1H, dd, J = 5.7 and 5.2 Hz), 2.59 (2H, t, J = 7.3 Hz), 1.8-0.8 (12H, m) ppm.; $\nu_{c=o}$(neat) = 1720 cm^{-1}

2-(4,5-Dimethyl-1,3-dithiole-2-ylidene)-1,3-indanedione (92) was prepared in one step from 4,5-dimethyl-1,3-dithiole-2-thione (60c)[24], 1,3-indanedione and sodium ethoxide following the literature procedure[140].

6.3.2.1 4,5-Dimethyl-2-(1,3-cyclopentanedione-2-ylidene)-1,3-dithiole (75)

Cyclopentanedione (1.0 g, 10 mmol) was added to a solution of sodium ethoxide (Na, 0.23 g, 10 mmol) in dry ethanol (100 ml) and stirred at room temperature under nitrogen. After 15 min the iodide salt of cation (61d) (4.65 g, 15 mmol) was added and the resulting mixture refluxed for 3 h under nitrogen. The solvent was then evaporated *in vacuo* and water (50 ml) added to the residue. The mixture was extracted into dichloromethane (3 x 25 ml), dried ($MgSO_4$), filtered and evaporated to yield a red solid. Purification by chromatography on a silica column (eluent: dichloromethane) afforded **compound** (75) as a yellow solid (1.1 g, 48 %). M.Pt: 216-218°C; $\delta_H(CDCl_3)$ = 2.65 (4H, s), 2.31 (6H, s) ppm.; MS: m/e (EI) 226 (M^+); ν_{max}(nujol) = 1620, 1290, 1270 cm^{-1}; Anal.: Calc. for $C_{10}H_{10}O_2S_2$: C, 53.1; H, 4.45 %. Found: C, 53.0; H, 4.31 %.

6.3.2.2 4,5-Dimethyl-2-(1,3-cyclopentanedithione-2-ylidene)-1,3-dithiole (72)

Diketone (75) (0.60 g, 2.7 mmol) was dissolved in dry toluene (50 ml) and to this solution was added an excess of phoshorus pentasulphide (0.75 g, 1.8 mmol). Stirring was continued for 2 h at 50°C under a nitrogen atmosphere. The solvent was then carefully decanted off and the remaining mixture was further extracted into hot toluene (3 x 50 ml). The combined extracts were washed sequentially with 5M sodium hydroxide solution (3 x 50 ml), sodium chloride solution (2 x 50 ml), distilled water (2 x 50 ml), and then dried ($MgSO_4$), filtered and evaporated *in vacuo* to yield a red oil. This was chromatographed on a silica column (eluent: dichloromethane/hexane 1:1v/v) to yield **compound (72)** (0.55 g, 58 %) as a dark red cystalline solid. *X*-Ray quality crystals were grown from a chloroform/methanol (1:1 v/v) solution. M.Pt: > 340°C; MS: (EI) 358 (M^+); $\delta_H(CDCl_3)$ = 3.31 (4H, s), 2.49 (6H, s) ppm.; $\delta_C(CDCl_3)$ = 205.0, 171.7, 143.2, 131.4, 47.8, 13.3 ppm.; λ_{max} (CH_2Cl_2) = 262, 370, 464 nm ; Anal.: Calc. for $C_{10}H_{10}S_4$: C, 46.5; H, 3.88 %. Found: C, 46.3; H, 3.80 %. Continued elution of the column with dichloromethane yielded the mono-thionated product, **compound (76)** (0.19 g, 30 %) as an orange/red solid. M.Pt: 212-215°C; MS: (EI) 242 (M^+); $\delta_H(CDCl_3)$ = 3.16 (2H, m), 2.81 (2H, m), 2.46 (3H, s), 2.43 (3H, s) ppm.; ν_{max} (nujol) = 1660 cm^{-1}; Anal.: Calc. for $C_{10}H_{10}OS_3$: C, 49.6; H, 4.10 %. Found: C, 49.5; H, 4.13 %.

6.3.2.3 4,5-Dimethyl-2-[cyclopentane-1,3-bis(methylthio)-2-ylidene]-1,3-dithiole diiodide salt (78)

Compound (72) (0.2 g, 0.78 mmol) was dissolved in dichloromethane (10 ml) and excess methyl iodide (5 ml) was added to this deep red solution. After stirring at room temperature under nitrogen for 3 h dry ether (150 ml) was added to the resulting black solution, and the precipitated black solid was stirred in ether overnight. This solid was filtered and washed with ether (2 x 50 ml) to yield the **diiodide salt (78)** (0.38 g, 90%) as a black solid. M.Pt: 119-125°C (decomp.); MS: 288 (EI) (M^+); λ_{max}

(CH_2Cl_2) = 295, 461 nm ; Anal.: Calc. for $C_{12}H_{16}I_2S_4$: C, 26.6; H, 2.97 %. Found: C, 27.0; H, 2.85 %.

6.3.2.4 4,5-Dihydro-2-(1,3-cyclopentanedione-2-ylidene)-1,3-dithiole (80)

Following the procedure for compound (75) the iodide salt (61e) (1.0 g, 3.6 mmol) was added to an ethanol solution (100 ml) of cyclopentanedione (0.35 g, 3.6 mmol) and sodium ethoxide (3.6 mmol). After refluxing for 2 h the resulting insoluble precipitate was filtered and washed with ethanol (3 x 50 ml) and dichloromethane (2 x 50 ml) to yield **compound (80)** as a light brown solid (0.56 g, 79 %). MS: m/e (EI) 198 (M^+), (CI) 199 (M^++1); Anal.: Calc. for $C_8H_6O_2S_2$: C, 48.5; H, 3.05 %. Found: C, 48.8; H, 3.20 %.

6.3.2.5 4,5-Dihydro-2-(1,3-cyclopentanedithione-2-ylidene)-1,3-dithiole (82) and 4,5-dihydro-2-(3-thiocyclopentane-1-one-2-ylidene)-1,3-dithiole (81)

Following the procedure outlined for compound (72) (Chapter 6.3.2.2), a suspension of diketone (80) (0.2 g, 1mmol) in toluene (50 ml) was reacted with phosphorus pentasulphide (0.31 g, 0.7 mmol) to yield a red solid. Purification on a silica column (eluent: dichloromethane) produced **compound (82)** as a deep red solid after recrystallisation from dichloromethane/hexane (0.09 g, 39 %). M.Pt: 195-196°C; MS: m/e 230 (EI) (M^+); $\delta_H(CDCl_3)$ = 7.71 (2H, s), 3.35 (4H, s) ppm.; Anal.: Calc. for $C_8H_6S_4$: C, 41.7; H, 2.61. Found: C, 41.6; H, 2.54 %. Continued elution of the column with dichloromethane yielded **compound (81)** as a red solid after recystallisation from dichloromethane/hexane (0.06 g, 28 %). M.Pt: 209-210°C; MS: m/e 214 (EI) (M^+); Anal.: Calc. for $C_8H_6OS_3$: C, 44.9; H, 2.80 %. Found: C, 45.2; H, 2.89 %.

6.3.2.6 2-(1,3-Cyclopentanedione-2-ylidene)-1,3-dithiolan (83)

2-Methylthio-1,3-dithiolanylium iodide[119] (1.6 g, 6.7 mmol) was added to a solution of cyclopentanedione (0.46 g, 4.7 mmol) and sodium ethoxide (5 mmol) in ethanol (50 ml). After 2 h at 60°C and cooling to room temperature an insoluble solid was filtered off and washed sequentially with ethanol (2 x 50 ml) and dichloromethane (2 x 50 ml) to yield **compound (83)** as a white/cream solid (0.82 g, 87 %). MS: m/e 200 (EI) (M^+), 201(CI) (M^++1); δ_H(d_6-DMSO) = 3.88 (4H, s), 2.78 (4H, s) ppm.; ν_{max} (nujol) = 1660 cm^{-1}; Anal.: Calc. for $C_8H_8O_2S_2$: C, 48.0; H, 4.00 %. Found: C, 47.3; H, 4.27 %.

6.3.2.7 2,2'-Bis(4,5-dimethyl-1,3-dithiole-2-yl)-4-cyclopentene-1,3-dione (85)

This was prepared analogously to the bis(4,5-dihydro-1,3-dithiole-2-yl) derivative synthesised by Nakayama *et al* [120]. 4,5-Dimethyl-1,3-dithiole-2-ylium tetrafluoroborate (63c) (2.38 g, 11 mmol) was added to a solution of cyclopentanedione (0.52 g, 5 mmol) in ethanol (50 ml) and stirred at room temperature for 3 h. The resultant red precipitate was filtered off and washed with ethanol (2 x 50 ml) to yield **compound (85)** as a red solid (1.35 g, 71 %). M.Pt: 163-165°C; MS: m/e 356 (EI) (M^+); $\delta_H(CDCl_3)$ = 7.48 (2H, s), 5.31 (2H, s), 1.74 (12H, s) ppm.; $\nu_{C=O}$(nujol) = 1695 cm^{-1}; Anal.: Calc. for $C_{15}H_{16}O_2S_4$: C, 50.5; H, 4.49 %. Found: C, 50.7; H, 4.10 %.

6.3.2.8 4,5-Dimethyl-2-(1,3-cyclopentenedione-2-ylidene)-1,3-dithiole (84)

This also was prepared analogously to the 4,5-dihydro-1,3-dithiole-2-ylidene derivative synthesised by Nakayama *et al* [120]. To DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) (0.7 g, 3.1 mmol) dissolved in dioxane (50 ml) was added compound (85) (1.0 g, 2.8 mmol), turning the yellow solution black. This solution was stirred at room temperature for 3 h and then the solvent was evaporated *in vacuo*. The resultant black solid was extracted into dichloromethane (100 ml), washed with water (3 x 50 ml), dried ($MgSO_4$), evaporated and columned on a silica column (eluent: chloroform) to yield **compound (84)** as a red solid (0.45 g, 72 %). Crystals could be grown from dichloromethane/methanol. M.Pt: 192-195°C (sub.); MS: m/e 224 (EI) (M^+), 225 (CI) (M^++1); $\delta_H(CDCl_3)$ = 6.88 (2H, s), 2.27 (6H, s) ppm.; $\nu_{C=O}$(nujol) = 1650 cm^{-1}; Anal.: Calc. for $C_{10}H_8O_2S_2$: C, 53.5; H, 3.59 %. Found: C, 53.0; H, 3.62 %.

6.3.2.9 4-(Piperidinodithiocarbamoyl)octan-5-one (86)

To a solution of potassium piperidinodithiocarbamate (2.83 g, 14 mmol) in hexamethylphoshoric triamide (HMPA) (20 ml) was added crude 4-chloro-octan-5-one (Chapter 6.3.1) (1.51 g, 9.3 mmol) over a period of 5 min, and the mixture was heated at 90°C overnight. Aqueous work-up and extraction with toluene (4 x 20 ml) afforded a red oil, a hexane solution of which was eluted through a silica column (eluent: hexane) to yield **compound (86)** as a yellow oil (1.05 g, 40 %). MS: m/e 288 (CI) (M^++1); $\delta_H(CDCl_3)$ = 4.94 (1H, t, J = 6.8Hz), 4.5-4.1 (4H, broad m), 2.7-2.5 (2H, m), 1.7-0.8 (18H, m) ppm.; ν_{max} (neat) = 1710, 1428, 1240, 1230, 850 cm^{-1}.

6.3.2.10 2-Piperidino-4,5-di-*n*-propyl-1,3-dithiolium hexafluorophosphate salt (87)

A mixture of compound (86) (1.0 g, 3.5 mmol) and concentrated sulphuric acid (10 ml) was heated at 80°C for 2 h with vigorous stirring. After dilution with cold water, hexafluorophosphoric acid was added dropwise in excess. The mixture was extracted into dichloromethane, dried ($MgSO_4$) and evaporated to yield **compound (87)** as a brown oil (1.3 g, 90 %). MS: m/e 270 (EI) (M^+); $\delta_H(CDCl_3)$ = 3.79 (4H, broad, s), 2.63 (4H, t, J = 5.7Hz), 1.8-1.5 (10 H, m), 0.89 (6H, t, J = 7Hz) ppm.; ν_{max} (neat) = 1610, 1540, 1445, 1000, 850, 730 cm^{-1}.

6.3.2.11 4,5-Di-*n*-propyl-1,3-dithiole-2-thione (88)

Sodium thiol hydrate (1.43 g, 25 mmol) was added to a stirred solution of compound (87) (5.3 g, 12 mmol) in a mixture of ethanol and acetic acid (3:1 v/v, 100 ml), and stirred at room temperature overnight. Aqueous work-up and extraction into dichloromethane, followed by sequential washing with aqueous potassium carbonate (50 ml) and sodium hydroxide (50 ml), and drying with $MgSO_4$ yielded compound **(88)** as a yellow oil (1.8 g, 65%) which was used directly in the next step without further purification. MS: m/e 219 (CI) (M^++1); $\delta_H(CDCl_3)$ = 2.47 (4H, t, J = 7.4Hz), 1.54 (4H, sextet, J = 7.5Hz), 0.90 (6H, t, J = 7.3Hz) ppm.

6.3.2.12 4,5-Di-*n*-propyl-1,3-dithiole-2-thiomethyl iodide (69)

Thione (88) (1.0 g, 4.8 mmol) was stirred under nitrogen with methyl iodide (2 g, 13 mmol) and nitromethane (15 ml) at 40°C overnight. Ether (100 ml) was added and the yellow precipitate was filtered off and recrystallised from ethanol to yield **compound (69)** as a yellow solid (1.32 g, 81 %). $\delta_H(CDCl_3)$ = 3.34 (3H, s), 3.02 (4H, t, J = 7.6 Hz), 1.82 (4H, sextet), 1.07 (6H, t, J = 7.2 Hz) ppm.; Anal.: Calc. for $C_{10}H_{17}IS_3$: C, 33.3; H, 4.75 %. Found: C, 32.9; H, 4.63 %.

6.3.2.13 2-Piperidino-4,5-di-*n*-propyl-2H-1,3-dithiole (89)

Sodium borohydride (0.35 g, 9.2 mmol) was added over a period of 5 min to a stirred solution of compound (87) (2.27 g, 6.15 mmol) in methanol (100 ml) at 5°C. After stirring for 1 h, the solvent was evaporated in *vacuo* and the residue extracted into dichloromethane and washed with water (2 x 100 ml). Drying ($MgSO_4$) and purification on a silica column (eluent: dichloromethane/hexane 1:1 v/v) afforded **compound (89)** as a pale yellow oil (1.4 g, 84 %). MS: m/e 271 (EI) (M^+); $\delta_H(CDCl_3)$ = 5.79 (1H, s), 2.40 (4H, m), 2.20 (4H, m), 1.5-1.4 (10 H, m), 0.83 (6H, t, J = 3.8 Hz) ppm.; ν_{max} (neat) = 1610, 1450, 1380, 1310, 1090, 990 cm^{-1}.

6.3.2.14 4,5-Di-*n*-propyl-1,3-dithiolium tetrafluoroborate (90)

Compound (92) (1.0 g, 4.2 mmol) was stirred in acetic anhydride (10 ml) under nitrogen for 15 min. Fluoroboric acid (diethyl ether complex, 2.0 ml) was then added dropwise and stirring continued at room temperature for a further 30 min. Upon addition of dry diethyl ether (100 ml) an oil separated. The ether was decanted off and the oil was twice washed with more ether, adding, stirring and decanting both times. The oil was dissolved in dichloromethane (100 ml), dried ($MgSO_4$) and evaporated to yield

compound (90) as a red oil (960 mg, 82 %). $\delta_H(CDCl_3)$ = 11.04 (1H, s), 3.14 (4H, t, J = 7.8 Hz), 1.85 (4H, sextet), 1.07 (6H, t, J = 7.1 Hz).

6.3.2.15 4,5-Tetra-*n*-propyl-tetrathiafulvalene (91)

To a solution of salt (90) in toluene (10 ml) was added triethylamine (0.5 ml) and this solution was stirred at room temperature overnight under nitrogen. The whole reaction mixture was directly purified on a silica column (eluent: toluene). The orange oil thus obtained was crystallised by dissolving in pentane and evaporating rapidly on a vacuum line to afford **compound (91)** as an orange solid (84 mg, 62 %). MPt: 38°C; MS: m/e 372 (EI) (M^+); $\delta_H(CDCl_3)$ = 2.27 (2H, m), 1.53 (2H, sextet), 0.93 (3H, t, J = 7.2 Hz); Anal.: Calcd. for $C_{18}H_{28}S_4$: C, 58.0; H, 7.57 %. Found: C, 57.5; H, 7.11%.

6.3.2.16 4,5-Tetra-*n*-propyl-tetrathiafulvalene - 7,7,8,8-tetracyano-*p*-quinodimethane complex (91a)

A boiling solution of compound (91) (50 mg, 0.13 mmol) in dry dichloromethane (10 ml) was added to a solution of TCNQ (1) (30 mg, 0.15 mmol) in dry dichloromethane (10 ml) and the resultant dark green solution was refluxed for 15 min. After cooling to room temperature the precipitated solid was collected by filtration and washed with ice-cold dichloromethane (2 x 10 ml) to yield **complex (91a)** as a black solid (28 mg, 38 %). Anal.: Calc. for $C_{30}H_{32}N_4S_4$ (1:1 complex): C, 62.4; H, 5.6; N, 9.5 %. Found: C, 61.7; H, 5.1; N, 9.6 %; Compressed pellet powder conductivity: $\sigma_{rt} = 4 \times 10^{-5}$ Scm^{-1}.

6.3.2.17 2-[4,5-Bis(methylthio)-1,3-dithiole-2-ylidene]-1,3-indanedione (93)

Diketone (93) was prepared analogously to diketone (92) (Chapter 6.3.1). Compound (61d) (3.0 g, 9.1 mmol) was added to a stirred solution of 1,3-indanedione (1.2 g, 8.2 mmol) and sodium ethoxide (8.4 mmol) in ethanol (100 ml). After refluxing for 4 h, work-up and purification on a silica column (eluent: dichloromethane/hexane 1:1

v/v), followed by recrystallisation from dichloromethane/hexane, yielded **compound (93)** as a yellow solid (1.8 g, 65 %). M.Pt: 183-185°C; MS: m/e 338 (EI) (M^+), 339 (CI) (M^++1); $\delta_H(CDCl_3)$ = 7.8-7.6 (4H, m), 2.58 (6H, s) ppm.; Anal.: Calc. for $C_{14}H_{10}O_2S_4$: C, 49.7; H, 2.98 %. Found: C, 49.8; H, 2.94 %.

6.3.2.18 2-(4,5-Di-*n*-propyl-1,3-dithiole-2-ylidene)-1,3-indanedione (94)

Diketone (94) was prepared analogously to diketone (92) (Chapter 6.3.1). Compound (69) (0.6 g, 1.7 mmol) was added to a stirred solution of 1,3-indanedione (0.24 g, 1.6 mmol) and sodium ethoxide (1.6 mmol) in ethanol. This mixture was refluxed for 3h under nitrogen and then the solvent was evaporated *in vacuo* to leave a green oily solid which was extracted into dichloromethane (50 ml) and washed with water (2 x 50 ml). The dichloromethane solution was dried ($MgSO_4$) and evaporated to yield a green solid which was purified on a silica column (eluent: cyclohexane/dichloromethane 1:1 v/v) to obtain **compound (94)** as a yellow solid recrystallised from ethanol (0.41 g, 76 %). M.Pt: 102-104°C; MS: m/e 330 (EI) (M^+); ν_{max} (nujol) = 1655, 1595 cm^{-1}; Anal.: Calc. for $C_{18}H_{18}O_2S_2$: C, 65.4; H, 5.49; S, 19.4 %. Found: C, 65.2; H, 5.20; S, 18.9 %.

6.3.2.19 2-[4,5-Bis(methylthio)-1,3-dithiole-2-ylidene]-indan-1-one-3-thione (95) and 2-[4,5-bis(methylthio)-1,3-dithiole-2-ylidene]-indan-1,3-dithione (98)

These mono-thionated and di-thionated compounds were prepared analogously to compounds (76) and (72) (Chapter 6.3.2.2). Diketone (93) (0.45 g, 1.33 mmol) was reacted with phosphorus pentasulphide (0.6 g, 1.34 mmol) in toluene (100 ml) to provide, after work-up and silica column chromatography (eluent: dichloromethane / hexane 1:1 v/v), compounds (95) and (98). The first fraction eluted from the column yielded **compound (98)** as a green/black solid, recrystallised from dichloromethane/hexane (0.14 g, 28 %). M.Pt: 207-210°C; MS: m/e 370 (EI) (M^+), 371 (CI) (M^++1); $\delta_H(CDCl_3)$ = 7.68 (2H, m), 7.49 (2H, m), 2.62 (6H, s) ppm.;

Anal.: Calc. for $C_{14}H_{10}S_6$: C, 45.4; H, 2.72 %. Found: C, 45.5; H, 2.67 %. Continued elution with dichloromethane yielded **compound (95)** as a red solid which was recrystallised from dichloromethane/hexane (0.19 g, 41 %). M.Pt: 175-176°C; MS: m/e 354 (EI) (M^+), 355 (CI) (M^++1); $\delta_H(CDCl_3)$ = 7.9-7.5 (4H, m), 2.63 (3H, s), 2.58 (3H, s) ppm.; Anal.: Calc. for $C_{14}H_{10}OS_5$: C, 47.4; H, 2.84 %. Found: C, 47.1; H, 2.74 %.

6.3.2.20 2-(4,5-Di-*n*-propyl-1,3-dithiole-2-ylidene)-indan-1-one-3-thione (96) and 2-(4,5-di-*n*-propyl-1,3-dithiole-2-ylidene)-1,3-indandithione (99)

These mono-thionated and di-thionated compounds were prepared analogously to compounds (76) and (72) (Chapter 6.3.2.2). Diketone (94) (0.22 g, 0.67 mmol) and phosphorus pentasulphide (0.2 g, 0.45 mmol) were refluxed in toluene for 3 h to yield compound (99) and then compound (96) after column chromatography on silica (eluent: cyclohexane/dichloromethane, 1:1 v/v). **Compound (96)**, red solid (0.09 g, 39 %), recrystallised from dichloromethane/methanol. M.Pt: 95-98°C; MS: m/e 347 (CI) (M^++1); $\delta_H(CDCl_3)$ = 7.86-7.5 (4H, m), 2.72 (4H, m), 1.73 (4H, m), 1.02 (6H, t, J = 7.3 Hz) ppm.; Anal.: Calc. for $C_{18}H_{18}OS_3$: C, 62.4; H, 5.24 %. Found: C, 62.2; H, 5.21 %. **Compound (99)**, red solid (0.15 g, 63 %), *X*-ray quality crystals of which were grown from dichloromethane/acetonitrile solution. M.Pt: 134°C; MS: m/e 362 (EI) (M^+); $\delta_H(CDCl_3)$ = 7.62 (2H, m), 7.45 (2H, m), 2.66 (4H, t, J = 7.5 Hz), 1.70 (4H, sextet), 1.00 (6H, t, J = 7.1 Hz) ppm.; Anal.: Calc. for $C_{18}H_{18}S_4$: C, 59.6; H, 5.00; S, 35.4 %. Found: C, 59.5; H, 4.95; S, 35.5 %.

6.3.2.21 1,2,3-(4,5-Dimethyl-1,3-dithiole-2-ylidene)-1,3-dihydro-1,3-indanedione (100) and 1,2-(4,5-dimethyl-1,3-dithiole-2-ylidene)-1-dihydro-1,3-indanedione (102)

Phosphonate ester (67c) (0.56 g, 2.3 mmol) was dissolved in anhydrous THF (100 ml) and the Wittig-Horner reagent (68c) was formed by the addition of *n*-BuLi (1.4 ml, 2.3 mmol) at -78°C under nitrogen. After stirring for 30 min a solution of compound

(92) (0.3 g, 1.1 mmol) in THF (20 ml) was added. The temperature was maintained at -78°C for 2 h and then allowed to warm to room temperature overnight. The solvent was evaporated *in vacuo* to yield a red solid. This was extracted into dichloromethane (100 ml), washed with water (2 x 50 ml), dried ($MgSO_4$), evaporated and then chromatographed on a neutral alumina column (eluent: hexane/dichloromethane 2:1 v/v) to yield **compound (100)** as a yellow solid (0.11 g, 20 %) that slowly darkens on exposure to air. M.Pt: >230°C; MS: m/e 502 (EI) (M^+), 503 (CI) (M^++1); $\delta_H(CDCl_3)$ = 7.38 (2H, m), 7.19 (2H, m), 2.06 (12H, s), 2.04 (6H, s) ppm.; Anal.: Calc. for $C_{24}H_{22}S_6$: C, 57.3; H, 4.41 %. Found: C, 56.9; H, 4.25 %. Continued elution with hexane/dichloromethane (1:1 v/v) yielded **compound (102)** as a red solid (0.3 g, 71 %). M.Pt: >230°C; MS: m/e 388 (EI) (M^+), 389 (CI) (M^++1); $\delta_H(CDCl_3)$ = 7.71-7.18 (4H, m), 2.25 (3H, s), 2.18 (3H, s), 2.12 (3H, s), 2.10 (3H, s) ppm.; Anal.: Calc. for $C_{19}H_{16}OS_4$: C, 58.7; H, 4.15. Found: C, 58.9; H, 4.10 %.

6.3.2.22 1,2,3-(4,5-Dimethyl-1,3-dithiole-2-ylidene)-1,3-dihydro-1,3-indanedione - 7,7,8,8-tetracyano-*p*-quinodimethane complex (100c)

A boiling solution of compound (100) (20 mg, 0.04 mmol) in dry dichloromethane (10 ml) was added to a solution of TCNQ (1) (10 mg, 0.05 mmol) in dry dichloromethane (10 ml) and the resultant dark green solution was refluxed for 15 min. After cooling to room temperature the precipitated solid was collected by filtration and washed with ice-cold dichloromethane (2 x 10 ml) to yield **complex (100c)** as a black solid (11 mg, 47 %). Anal.: Calc. for $C_{48}H_{30}N_8S_6$ (1:2 complex): C, 63.3; H, 3.32; N, 12.3 %. Found: C, 62.4; H, 3.34; N, 12.6 %; ν_{CN}(nujol) = 2175 cm^{-1}; Compressed pellet conductivity: $\sigma_{rt} = 5 \times 10^{-6}$ Scm^{-1}.

6.3.2.23 1,2,3-[4,5-Bis(methylthio)-1,3-dithiole-2-ylidene]-1,3-dihydro-1,3-indanedione (101)

This compound was prepared analogously to compound (100) (Chapter 6.3.2.21). Phosphonate ester (67d) (0.56 g, 1.8 mmol), *n*-BuLi (1.6M, 1.25 ml, 2 mmol) and compound (93) (0.25 g, 0.74 mmol) yielded **compound (101)** as a yellow solid (0.44

g, 85 %) that was purified on a neutral alumina column (eluent: hexane/dichloromethane 2:1 v/v) and recrystallised from dichloromethane/hexane. M.Pt: 140-142°C; MS: m/e 695 (CI) (M^{+}+1); $\delta_H(CDCl_3)$ = 7.38-7.24 (4H, m), 2.48 (6H, s), 2.46 (12H, s) ppm.; Anal.: Calc. for $C_{24}H_{22}S_{12}$: C, 41.5; H, 3.19 %. Found: C, 41.4; H, 3.20 %.

6.3.2.24 1,2-(4,5-Dimethyl-1,3-dithiole-2-ylidene)-1-dihydro-1,3-indanedithione (103)

Compound (102) (50 mg, 0.13 mmol) and phosphorus pentasulphide (30 mg, 0.067 mmol) were refluxed in toluene (100 ml) under nitrogen for 3 h. The solid was then filtered off and extracted with toluene (2 x 50 ml). The resulting black solution was washed sequentially with 2M sodium hydroxide solution (2 x 100 ml), water (2 x 100 ml), dried ($MgSO_4$) and evaporated to yield a black solid that was purified by column chromatography on silica (eluent: dichloromethane/hexane 1:1 v/v) to obtain **compound (103)** as a dark green/black solid (45 mg, 87 %). M.Pt: 229-231°C; MS: m/e 405 (CI) (M^{+}+1); $\delta_H(CDCl_3)$ = 7.97-7.18 (4H, m), 2.31 (6H, s), 2.11 (6H, s) ppm.; Anal.: Calc. for $C_{19}H_{16}S_5$: C, 56.4; H, 3.99 %. Found: C, 55.8; H, 4.12 %.

6.3.2.25 1,2-[4,5-Bis(methylthio)-1,3-dithiole-2-ylidene]-1-dihydro-1,3-indan-dithione - 7,7,8,8-tetracyano-*p*-quinodimethane complex (103a)

This was prepared analogously to complex (100c) (Chapter 6.3.2.22) from compound (103) (15 mg, 0.037 mmol) and TCNQ (1) (8 mg, 0.039 mmol) in dichloromethane (20 ml) and isolated as a black solid (8 mg, 35 %). Anal.: Calc. for $C_{31}H_{20}N_4S_5$ (1:1 complex): C, 61.2; H, 3.31; N, 9.20 %. Found: C, 60.8; H, 3.12; N, 10.7. Anal.: Calc. for 1:1.3 complex: C, 62.0; H, 3.19; N, 10.9 % suggesting that the initial product is either a slightly impure 1:1 complex or a non-stoichiometric complex]. ν_{CN}(nujol) = 2175 cm^{-1} (no neutral TCNQ-2220 cm^{-1}); Compressed pellet conductivity: $\sigma_{rt} = 5 \times 10^{-5}$ Scm^{-1}.

6.3.2.26 2,4,6-Tris(4,5-di-*n*-propyl-1,3-dithiol-2-ylidene)-1,3,5-cyclohexanetrione (70)

Pyridine (0.35 ml) was added to a solution of trihydroxybenzene (phloroglucinol dihydrate) (0.1 g, 0.6 mmol) in dry acetonitrile (20 ml) and stirred at room temperature under nitrogen for 15 min. Compound (69) (0.65 g, 1.8 mmol) was then added and the mixture heated at reflux for 3 h. Work-up and silica gel column chromatography (eluent: dichloromethane/cyclohexane 1:1 v/v) yielded **compound (70)** as a yellow solid that was recrystallised from ethanol (0.11 g, 26 %). Crystals suitable for *X*-ray crystallography were grown from toluene. M.Pt: 312-315°C (sub.); MS: m/e 678 (EI) (M^+); $\delta_H(CDCl_3)$ = 2.61 (2H, t, J = 7.4 Hz), 1.65 (2H, m), 0.90 (3H, t, J = 7.2 Hz) ppm.; $\nu_{C=O}$(nujol) = 1530 cm^{-1}; Anal.: Calc. for $C_{33}H_{42}O_3S_6$: C, 58.4; H, 6.23; S, 28.3 %. Found: C, 58.0; H, 6.12; S, 27.5 %.

6.3.2.27 2-Methylthio-4,5-di-*n*-propyl-1,3-dithiole (104)

To a solution of salt (69) (2.5 g, 7 mmol) in ethanol (75 ml) was added sodium borohydride (6.25 g, 14 mmol) and the mixture was stirred at room temperature overnight. The solvent was then evaporated *in vacuo*, water added (100 ml), the product extracted into dichloromethane (3 x 50 ml) and then dried ($MgSO_4$). Evaporation of the organic phase gave a red oil, which was purified by chromatography on a silica column (eluent: cyclohexane/dichloromethane 1:1 v/v) to yield **thioether (104)** as a red oil. $\delta_H(CDCl_3)$ = 5.75 (1H, s), 2.27 (4H, m), 2.21 (3H, s), 1.51 (4H, sextet), 0.91 (6H, d. of t., J = 7.3 Hz) ppm.

6.3.2.28 2-Dimethoxyphosphoryl-4,5-di-*n*-propyl-1,3-dithiole (105)

To a solution of salt (90) (500 mg, 2 mmol) in dry acetonitrile (30 ml) was added trimethylphoshite (0.21 ml, 2 mmol) and sodium iodide (0.3 g, 0.2 mmol). The resulting mixture was stirred at room temperature overnight before evaporation of the solvent, extraction into dichloromethane, washing with water, drying ($MgSO_4$), and evaporating the organic phase afforded an orange oil. This was purified on a neutral alumina column (eluent: cyclohexane/chloroform 1:1 v/v) to yield **phosphonate ester**

(**105**) as an orange oil (450 mg, 84 %). $\delta_H(CDCl_3)$ = 4.61 (1H, d, J = 4.0Hz), 3.77 (3H, s), 3.73 (3H, s), 2.09 (4H, m), 1.37 (4H, sextet), 0.81 (6H, t, J = 7.3 Hz) ppm.

6.3.2.29 4,5-Ethylenedithio-4',5'-di-*n*-propyl-2,2'-ethanediylidene-bis(1,3-dithiole) (106)

This was prepared following the general procedure outlined in Chapter 6.2.2.8 from compound (105) (400 mg, 1.3 mmol), *n*-BuLi (1.6M, 0.9 ml, 1.35 mmol) and compound (66f) (332 mg, 1.35 mmol) in dry THF. Purification was achieved through a silica column (eluent: hexane/dichloromethane 3:1 v/v) to obtain **compound (106)** as a yellow solid (370 mg, 68 %). MPt: 98-99°C; MS: m/e 404 (EI) (M^+), 405 (CI) (M^++1); $\delta_H(CDCl_3)$ = 5.78 (2H, d of d, J = 12 Hz), 3.28 (4H, s), 2.28 (4H, m), 1.50 (4H, m), 0.93 (6H, t, J = 7.3 Hz) ppm.; Anal.: Calc. for $C_{16}H_{20}S_6$: C, 47.5; H, 4.98 %. Found: C, 47.4; H, 5.03 %.

6.4 EXPERIMENTAL TO CHAPTER FOUR

6.4.1 Materials

1,3-Propanedial-2-[4,5-bis(methylthio)-1,3-dithiole-2-ylidene] (108) was prepared following the literature procedure[113] from the sodium salt of malonaldehyde and 4,5-bis(methylthio)-1,3-dithiole-2-thiomethyl tetrafluoroborate (61d) in 51 % yield. MPt: 172°C (Lit. 166-167°C)[113]; $\delta_H(CDCl_3)$ = 9.76 (2H, s), 2.62 (6H, s).

2-Dimethoxyphosphoryl-4,5-ethylenedithio-1,3-dithiole (67f) was prepared in four steps from 4,5-ethylenedithio-1,3-dithiole-2-thione[42] following the literature procedure (*ca.*70 % yield)[88].

6.4.2.1 1,3-Propanedial-2-(4,5-dimethyl-1,3-dithiole-2-ylidene) (107)

This was prepared following the literature procedure described for compound (108)[113]. 4,5-Dimethyl-1,3-dithiole-2-thio-methyl iodide (61c) (0.9 g, 3 mmol) was added to a suspension of the sodium salt of malonaldehyde (0.3 g, 3.2 mmol) in acetonitrile (100 ml) and stirred at room temperature overnight. The solvent was evaporated *in vacuo* , dichloromethane added (100 ml), the solution was washed with water (2 x 50 ml), dried ($MgSO_4$) and evaporated to afford a yellow solid that was purified on a neutral alumina column (eluent: dichloromethane/hexane 1:1 v/v) yielding **dialdehyde (107)** as a pale yellow solid (0.20 g, 34 %). MPt: 150°C (sub.); MS: m/e 200 (EI) (M^+), 201 (CI) (M^++1); $\delta_H(CDCl_3)$ = 9.74 (2H, s), 2.42 (6H, s) ppm.; $\nu_{C=O}$(nujol) = 1620 cm^{-1}; Anal.: Calc. for $C_8H_8O_2S_2$: C,48.0; H, 4.03 %. Found: C, 47.7; H, 3.90 %.

6.4.2.2 Propane-1,2,3-tris(4,5-dimethyl-1,3-dithiole-2-ylidene) (109) and propane-1,2-bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-3-al (121)

To a solution of 2-dimethoxyphosphoryl-4,5-dimethyl-1,3-dithiole (67c) (0.36g, 1.5 mmol) in THF (50 ml) at -78°C under nitrogen was added *n*-BuLi (1.6M, 1 ml, 1.6 mmol). After 1 h compound (107) (0.15 g, 0.75 mmol) in THF (10 ml) was added and the solution was stirred at -78°C for 2 h. The solution was then allowed to warm to room temperature overnight at which point the solvent was evaporated and the residue extracted into dichloromethane (100 ml), which was washed with water (2 x 100 ml) and dried ($MgSO_4$). Evaporation of the organic phase yielded an orange solid which was purified on a neutral alumina column (eluent: hexane/dichloromethane 2:1 v/v) to yield **compound (109)** as a yellow solid (0.20 g, 62 %). MPt: >230 °C ; MS: m/e 428 (EI) (M^+), 429 (CI) (M^++1); $\delta_H(CDCl_3)$ = 5.72 (2H, s), 1.92 (6H, s), 1.89 (12H, s) ppm.; Anal.: Calc. for $C_{18}H_{20}S_6$: C, 50.4; H, 4.70 %. Found: C, 50.6; H, 5.01 %. Continued elution with hexane/dichloro-methane (1:1 v/v) afforded **compound (121)** as an orange solid (65 mg, 28 %). MPt: 211-214 °C ; MS: m/e 314 (EI) (M^+), 315 (CI) (M^++1); $\delta_H(CDCl_3)$ = 9.43 (1H, s), 5.94 (1H, s), 2.17 (3H, s), 2.16 (3H, s), 1.92 (3H, s), 1.88 (3H, s) ppm.; $\nu_{C=O}$(nujol) = 1610 cm^{-1}; Anal.: Calc. for $C_{13}H_{14}OS_4$: C, 49.6; H, 4.49 %. Found: C, 49.6; H, 4.70 %.

6.4.2.3 Propane-1,2-bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-3-(4,5-ethylenedithio-1,3-dithiole-2-ylidene) (110)

To a solution of 2-dimethoxyphosphoryl-4,5-ethylenedithio-1,3-dithiole (67f) (64 mg, 0.21 mmol) in THF (50 ml) at -78°C under nitrogen was added *n*-BuLi (0.14 ml 1.6M, 0.22 mmol). After 1 hr aldehyde (121) (55 mg, 0.18 mmol) was added and the solution was stirred at -78°C for 2 h. The solution was then allowed to warm to room temperature overnight before work-up (as above, 6.4.2.2) and purification down an alumina column (eluent: hexane/dichloromethane 1:1 v/v) yielded **compound (110)** as a yellow solid (55 mg, 65 %). MPt: 225-226 °C; MS: m/e 491 (DCI) ($M^{+}+1$); $\delta_H(CDCl_3)$ = 5.84 (1H, s), 5.67 (1H, s), 3.27 (4H, s), 1.93 (6H, s), 1.90 (6H, s) ppm.; Anal.: Calc. for $C_{18}H_{18}S_8$: C, 44.1; H, 3.70 %. Found: C, 44.2; H, 3.56 %.

6.4.2.4 Propane-1,3-bis(4,5-ethylenedithio-1,3-dithiole-2-ylidene)-2-(4,5-dimethyl-1,3-dithiole-2-ylidene) (111)

This was prepared following the procedure outlined for propane-1,2,3-tris(4,5-dimethyl-1,3-dithiole-2-ylidene) (109) (Chapter 6.4.2.2) from phosphonate ester (67f) (180 mg, 0.6 mmol) and 1,3-propanedial-2-(4,5-dimethyl-1,3-dithiole-2-ylidene) (107) (60 mg, 0.3 mmol) in THF (50 ml). Purification was achieved on a silica column (eluent: dichloromethane/hexane 1:1 v/v) to yield **compound (111)** as a yellow solid (135 mg, 82 %). MPt: 232 °C ; MS: m/e 552 (DEI) (M^{+}); $\delta_H(CDCl_3)$ = 5.80 (2H, s), 3.28 (8H, s), 1.93 (6H, s) ppm.; Anal.: Calc. for $C_{18}H_{16}S_{10}$: C, 39.1; H, 2.92 %. Found: C, 38.8; H, 2.77 %.

6.4.2.5 Propane-1,2,3-tris[4,5-bis(methylthio)-1,3-dithiole-2-ylidene] (112) and propane-1,2-bis[4,5-bis(methylthio)-1,3-dithiole-2-ylidene]-3-al (122)

These compounds were prepared following the procedure outlined for compound (109) (Chapter 6.4.2.2) from phosphonate ester (67d) (0.70 g, 2.3 mmol) and compound (108) (0.30 g, 1.1 mmol) in THF (50 ml). Purification was achieved on a neutral alumina column (eluent: dichloromethane/hexane 1:2 v/v) to yield **compound**

(**112**) as a yellow oil (0.47 g, 67 %). MS: m/e 621 (DCI) (M^{+}+1); $\delta_H(CDCl_3)$ = 5.65 (2H, s), 2.35 (6H, s), 2.34 (6H, s), 2.33 (6H, s) ppm.; Anal.: Calc. for $C_{18}H_{20}S_{12}$: C, 34.8; H, 3.25 %. Found: C, 34.4; H, 3.57 %. Continued elution with hexane/ dichloro-methane (1:1 v/v) afforded **compound (122)** as a red solid (0.15 g, 30 %). MPt: 126-127 °C ; MS: m/e 443 (DCI) (M^{+}+1); $\delta_H(CDCl_3)$ = 9.42 (1H, s), 5.98 (1H, s), 2.54 (3H, s), 2.49 (3H, s), 2.43 (3H, s), 2.37 (3H, s) ppm.; Anal.: Calc. for $C_{13}H_{14}OS_8$: C, 35.3; H, 3.19 %. Found: C, 35.2; H, 3.22 %.

6.4.2.6 Butane-1,2,3-tris(4,5-dimethyl-1,3-dithiole-2-ylidene)-4-al (116)

Oxalyl chloride (0.1 ml) was added to anhydrous dimethylformamide (DMF) (5 ml) at -5°C and the mixture stirred at room temperature for 0.5 h under nitrogen. A solution of compound (109) (0.20 g, 0.47 mmol) in anhydrous DMF (2 ml) was then added and after 3 h the solution was hydrolysed with 5M NaOH (2 ml), slowly turning the colour from brown to red. Dichloromethane (50 ml) was added and the organic phase was washed with water (3 x 100 ml), dried ($MgSO_4$) and evaporated. The resulting red solid was purified on a neutral alumina column (eluent: hexane/dichloromethane 1:1 v/v) to yield **compound (116)** as a red solid (0.14 g, 65 %). MPt: 208-210 °C ; MS: m/e 457 (DCI) (M^{+}+1); $\delta_H(CDCl_3)$ = 9.06 (1H, s), 5.92 (1H, s), 2.18 (3H, s), 2.14 (3H, s), 1.95 (3H, s), 1.85 (3H, s), 1.82 (3H, s), 1.77 (3H, s) ppm.; Anal.: Calc. for $C_{19}H_{20}OS_6$: C, 50.0; H, 4.41 %. Found: C, 50.0; H, 4.44 %.

6.4.2.7 Butane-1,3-bis(4,5-ethylenedithio-1,3-dithiole-2-ylidene)-2-(4,5-dimethyl-1,3-dithiole-2-ylidene)-4-al (117)

This was prepared analogously to compound (116) (Chapter 6.4.2.6) by the addition of compound (111) (50 mg, 0.1 mmol) in anhydrous dichloromethane (10 ml) to oxalyl chloride (0.1 ml) in anhydrous DMF (10 ml), followed by hydrolysis with 5M NaOH. Purification on a neutral alumina column (eluent: hexane/dichloromethane 1:1 v/v) yielded **aldehyde (117)** as a red solid (29 mg, 55 %). MPt: 204-207 °C ; MS: m/e 581 (DCI) (M^{+}+1); $\delta_H(CS_2)$ = 8.89 (1H, s), 5.78 (1H, s), 3.35 (4H, s), 3.20 (4H, s), 1.96 (3H, s), 1.89 (3H, s) ppm.; Anal.: Calc. for $C_{19}H_{16}OS_{10}$: C, 39.3; H, 2.78 %. Found: C, 38.8; H, 2.85 %.

6.4.2.8 Butane-1,2,3-tris[4,5-bis(thiomethylthio)-1,3-dithiole-2-ylidene]-4-al (118)

This was prepared analogously to compound (116) (Chapter 6.4.2.6) by the addition of compound (112) (200 mg, 0.32 mmol) in anhydrous DMF (5 ml) to oxalyl chloride (0.1 ml) in anhydrous DMF (10 ml), followed by hydrolysis with 5M NaOH. Purification on a neutral alumina column (eluent: hexane/dichloromethane 2:1 v/v) yielded **aldehyde (118)** as a red solid (110 mg, 53 %). MPt: 172-174 °C ; MS: m/e 649 (DCI) ($M^{+}+1$); $\delta_H(CDCl_3)$ = 9.08 (1H, s), 5.90 (1H, s), 2.55 (3H, s), 2.48 (3H, s), 2.43 (3H, s), 2.36 (3H, s), 2.34 (3H, s), 2.27 (3H, s) ppm.; Anal.: Calc. for $C_{19}H_{20}OS_{10}$: C, 35.2; H, 3.11 %. Found: C, 35.3; H, 3.23 %.

6.4.2.9 Butane-1,3-bis(4,5-ethylenedithio-1,3-dithiole-2-ylidene)-2,4-bis(4,5-dimethyl-1,3-dithiole-2-ylidene) (119)

To a solution of phoshonate ester (67c) (80 mg, 0.33 mmol) in dry THF (50 ml) under nitrogen at -78 °C was added *n*-BuLi (1.6M, 0.22 ml, 0.35 mmol). After 1 h a solution of compound (117) (160 mg, 0.28 mmol) in dry THF (10 ml) was added and the mixture stirred at -78 °C for 1 h before being allowed to warm to room temperature overnight. The solvent was then evaporated, water added (100 ml) and the product extracted into dichloromethane (3 x 50 ml). Drying ($MgSO_4$), evaporation and column chromatography on neutral alumina (eluent: cyclohexane/dichloromethane 3:1 v/v) yielded **compound (119)** as a yellow solid (120 mg, 63 %). MPt: 192-195 °C ; MS: m/e ($M^{+}+1$) not observed (DCI); $\delta_H(CS_2)$ = 5.55 (1H, s), 5.43 (1H, s), 3.24 (4H, s), 3.21 (4H, s), 1.95 (3H, s), 1.90 (3H, s), 1.85 (6H, s) ppm.; Anal.: Calc. for $C_{24}H_{22}S_{12}$: C, 41.5; H, 3.19 %. Found: C, 42.0; H, 2.56 %.

6.4.2.10 Butane-1,2,3,4-tetrakis[4,5-bis(methylthio)-1,3-dithiole-2-ylidene] (120)

This was prepared following the procedure described for compound (119) (Chapter 6.4.2.9) from phosphonate ester (67d) (150 mg, 0.5 mmol) and compound (118) (260 mg, 0.4 mmol). Purification on a neutral alumina column (eluent: hexane/dichloromethane 2:1 v/v) yielded **compound (120)** as a yellow solid (190 mg, 57 %). MPt: 87-92 °C ; MS: m/e 827 (DCI) (M^{+}+1); $\delta_H(CDCl_3)$ = 5.68 (1H, s), 3.47 (3H, s), 3.45 (3H, s), 3.43 (3H, s), 3.40 (3H, s) ppm.; Anal.: Calc. for $C_{24}H_{26}S_{16}$: C, 34.8; H, 3.17 %. Found: C, 34.9; H, 3.23 %.

6.4.2.11 Octan-1,2,3-tris(4,5-dimethyl-1,3-dithiole-2-ylidene)-4-ene (123)

This was prepared following the procedure described for compound (119) (Chapter 6.4.2.9) from phosphonate ester (67c) (300 mg, 1.25 mmol), 1.6M *n*-BuLi (1.4 ml, 2.2 mmol) and compound (116) (160 mg, 0.4 mmol). Purification on a neutral alumina column (eluent: hexane/dichloromethane 3:1 v/v) yielded **compound (123)** as a yellow solid (50 mg, 30 %). MPt: 210-212 °C ; MS: m/e 496 (EI) (M^{+}), 497 (DCI) (M^{+}+1); $\delta_H(CDCl_3)$ = 5.60 (1H, d, J = 15Hz), 5.54 (1H, s), 5.14 (1H, m), 2.02 (2H, m), 1.93 (3H, s), 1.89 (6H, s), 1.82 (6H, s), 1.79 (3H, s), 1.35 (2H, sextet), 0.87 (3H, s) ppm.; Anal.: Calc. for $C_{23}H_{28}S_6$: C, 55.6; H, 5.69 %. Found: C, 55.2; H, 5.61 %.

6.4.2.12 4,5-Bis(methyltelluro)-1,3-dithiole-2-thione (126)

To a solution of lithium diisopropylamine (55 mmol) in anhydrous THF (50 ml) at -78 °C was added vinylene trithiocarbonate (59) (3.56 g, 26 mmol). After 2 h powdered elemental tellurium (6.85 g, 54 mmol) was added and the mixture allowed to warm to room temperature overnight. The resulting deep purple solution of the ditellurate anion (125) was then cooled to -40 °C and methyl iodide (8.2 g, 58 mmol) added. After warming to room temperature unreacted tellurium was filtered off, water (200 ml) was added and the residue was extracted into dichloromethane (3 x 100 ml), dried ($MgSO_4$) and evaporated to yield an orange solid. Purification was achieved by chromatography on a silica column (eluent: hexane/dichloromethane 3:1 v/v) and recrystallisation from hexane/dichloromethane, affording **thione (126)** as a yellow crystalline solid (0.95 g, 9 %). MPt: 120-123 °C; MS: m/e 418 (EI) (M^+), 419 (CI) ($M+1^+$); $\delta_H(CDCl_3)$ = 2.29 (6H, s) ppm.; Anal.: Calc. for $C_5H_6S_3Te_2$: C, 14.4; H, 1.45; S, 23.0 %. Found: C, 14.7; H, 1.41; S, 23.5 %.

6.4.2.13 1,3-Propanedial-2-[4,5-bis(methyltelluro)-1,3-dithiole-2-ylidene] (128) and 1,3-propanedial-2-(4-methyltelluro-5-hydro-1,3-dithiole-2-ylidene) (130)

A suspension of thione (126) (210 mg, 0.5 mmol) in dimethyl sulphate (DMS) (10 ml) was heated under nitrogen at 70 °C for 2 h until the solid went into solution. Upon cooling to 0 °C tetrafluoroboric acid (excess) was added dropwise, followed by dry ether (200 ml) which separated out a black oil. The ether was decanted off and the oil was washed with dry ether (3 x 50 ml). The addition of acetonitrile to the oil (127) produced a red solution to which was added the sodium salt of malonaldehyde (0.10 g, 1.1 mmol) and the mixture was stirred at room temperature overnight. The yellow solution was evaporated, extracted into dichloromethane (50 ml), washed with water (2 x 100 ml), dried ($MgSO_4$), evaporated and chromatographed (neutral alumina column, eluent: cyclohexane/dichloromethane 1:1 v/v) to yield **compound (128)** as a yellow solid (50 mg, 22 %). MPt: 160-162 °C; MS: m/e 313 (EI) (M^+-MeTe); $\delta_H(CDCl_3)$ = 9.74 (2H, s), 2.52 (6H, s) ppm.; Anal.: Calc. for $C_8H_8O_2S_2Te_2$: C, 21.1; H, 1.77 %. Found: C, 21.5; H, 1.72 %. Continued elution with cyclohexane/dichloromethane (1:1 v/v) afforded **compound (130)** as a yellow solid (35 mg). MPt: 120-124 °C; MS: m/e 314 (EI) (M^+), 315 (CI) (M^++1); $\delta_H(CDCl_3)$ = 9.79 (1H, s), 9.74 (1H, s), 7.69 (1H, s), 2.36 (3H, s) ppm.; Anal.: Calc. for $C_7H_6O_2S_2Te$: C, 26.8; H, 1.93 %. Found: C, 26.2; H, 1.79 %.

6.4.2.14 Propane-1,3-bis[4,5-bis(methylthio)-1,3-dithiole-2-ylidene]-2-[4,5-bis(methyltelluro)-1,3-dithiole-2-ylidene] (129)

This was prepared following the procedure outlined for compound (109) (Chapter 6.4.2.2) from phosphonate ester (67d) (120 mg, 0.4 mmol), *n*-BuLi (1.6M, 0.3 ml, 0.5 mmol) and compound (128) (80 mg, 0.18 mmol) in THF (50 ml). Purification was achieved on a silica column (eluent: dichloromethane/hexane 1:3 v/v) to yield **compound (129)** as a yellow oil (68 mg, 49 %). MS: m/e M^+ not observed (DEI); $\delta_H(CDCl_3)$ = 5.71 (2H, s), 2.41 (6H, s), 2.40 (6H, s), 2.33 (6H, s) ppm.; Anal.: Calc. for $C_{18}H_{20}S_{10}Te_2$: C, 26.6; H, 2.48 %. Found: C, 25.9; H, 2.87 %.

6.4.2.15 Propane-1,3-bis(4,5-ethylenedithio-1,3-dithiole-2-ylidene)-2-(4-methyltelluro-5-hydro-1,3-dithiole-2-ylidene) (131)

This was prepared following the procedure outlined for compound (109) (Chapter 6.4.2.2) from phosphonate ester (67f) (55 mg, 0.18 mmol), *n*-BuLi (1.6M, 0.12 ml, 0.19 mmol) and compound (124) (28 mg, 0.09 mmol) in THF (50 ml). Purification was achieved on a silica column (eluent: dichloromethane/hexane 1:1 v/v) to yield **compound (131)** as an orange solid (26 mg, 43 %). MPt: 96-100°C; MS: m/e M^+ not observed (DEI); $\delta_H(CDCl_3)$ = 6.48 (1H, s), 5.60 (1H, s), 5.57 (1H, s), 3.28 (8H, s), 2.21 (3H, s) ppm.; Anal.: Calc. for $C_{17}H_{14}S_{10}Te$: C, 30.6; H, 2.12 %. Found: C, 30.9; H, 2.26 %.

6.5 EXPERIMENTAL TO CHAPTER FIVE

6.5.1 Materials

6.5.2.1 9,10-Bis[4,5-bis(methylthio)-1,3-dithiole-2-ylidene]-9,10-dihydroanthracene (133)

To a solution of phosphonate ester (67d) (0.9 g, 3 mmol) in anhydrous THF (20 ml) at -78°C under nitrogen was added *n*-BuLi (1.6M, 2 ml, 3.2 mmol). After 30 min at -78°C a solution of anthraquinone (0.3 g, 1.4 mmol) in dry THF (10 ml) was added and the mixture stirred at -78°C for 1 h before warming to room temperature overnight. The solvent was then evaporated *in vacuo*, dichloromethane (100 ml) added, the organic phase washed with water (2 x 100 ml), dried ($MgSO_4$) and evaporated to afford a yellow solid. This solid was purified on a silica column (eluent: hexane/dichloromethane 2:1 v/v) to yield **compound (133)** as a yellow solid (0.31 g, 38 %). *X*-Ray quality crystals were grown from an acetonitrile/dichloromethane solution. MPt: >230°C; MS: m/e 564 (EI) (M^+); $\delta_H(CDCl_3)$ = 7.57 (4H, m), 7.32 (4H, m), 2.40 (12H, s) ppm.; Anal.: Calc. for $C_{24}H_{20}S_8$: C, 51.0; H, 3.57 %. Found: C, 50.9; H, 3.54 %.

6.5.2.2 2,3-Dipentyl-9,10-bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-9,10-dihydroanthracene (134) and 2,3-dipentyl-9-oxo-10-(4,5-dimethyl-1,3-dithiole-2-ylidene)-9,10-dihydroanthracene (135)

These compounds were prepared follwing the procedure detailed for compound (133) (Chapter 6.5.2.1) from phosphonate ester (67c) (1 g, 4 mmol), *n*-BuLi 2.5M (1.8 ml, 4.5 mmol) and 2,3-dipentylanthraquinone (0.78 g, 2.2 mmol) [kindly supplied by Prof. K.Müllen (Mainz)] in anhydrous THF (50 ml). Work-up followed by column chromatography on silica (eluent: toluene/cyclohexane 1:3 v/v) yielded **compound (134)** as a yellow solid (0.36 g, 28 %). MPt: 199-202°C; MS: m/e 576 (EI) (M^+), 577 (CI) (M^++1); $\delta_H(CDCl_3)$ = 7.52 (2H, m), 7.30 (2H, s), 7.15 (2H, m), 2.56 (4H, m), 1.80 (12H, s), 1.55 (4H, m), 1.31 (8H, m), 0.84 (6H, t, J = 6.7 Hz) ppm.; Anal.: Calc. for $C_{34}H_{40}S_4$: C, 70.8; H, 6.99 %. Found: C, 71.0; H, 7.24 %. Continued elution with dichloromethane yielded unreacted anthraquinone and **compound (135)** as a red solid (0.25 g, 24 %). MPt: 80-83°C; MS: m/e 462 (EI) (M^+); $\delta_H(CDCl_3)$ = 8.19-7.17 (6H, m), 2.64 (4H, m), 1.87 (6H, s), 1.62 (4H, m), 1.31 (8H, m), 0.85 (6H, m) ppm.

6.5.2.3 2,3-Dipentyl-9,10-bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-9,10-dihydroanthracene-7,7,8,8-tetracyano-*p*-quinodimethane complex (134a)

A boiling solution of donor (134) (50 mg, 0.09 mmol) in dry acetonitrile (15 ml) was added to a boiling solution of TCNQ (36 mg, 0.18 mmol) in dry acetonitrile (15 ml). After cooling and evaporation to 5 ml the resultant dark green precipitate was recrystallised from dichloromethane to afford a green/black solid, **complex (134a)** (18 mg, 30 %). Anal.: Calc. for $C_{82}H_{56}N_{16}S_4$ (i.e. a 1:4 complex): C, 70.7; H, 4.05; N, 16.1 %. Found: C, 70.6; H, 3.88; N, 16.5 %.

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APPENDIX ONE

X-RAY CRYSTAL DATA

A.1.1 Crystal Data for 4,5-Bis(methylseleno)-4',5'-bis(methylthio)-2,2'-ethanediylidenebis(1,3-dithiole) (54)

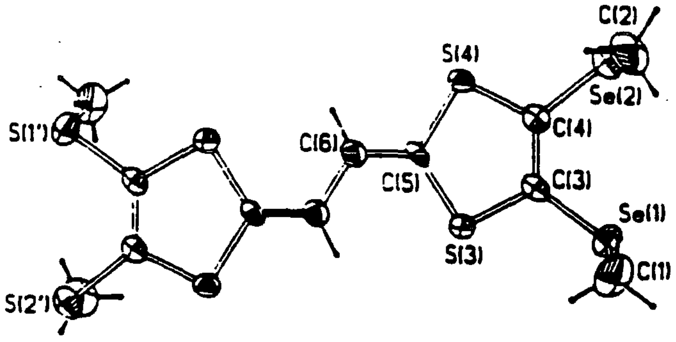

Figure A.1 - Molecular structure of compound (54) showing atom labelling.

CRYSTAL DATA

Empirical Formula:	$C_{10}H_{14}S_6Se_2$
Colour, size:	Orange, 0.48 x 0.26 x 0.04 mm
Crystal System:	Triclinic
Space Group:	P1bar
Unit Cell Dimensions:	a = 5.152(1) Å, b = 8.110(2) Å, c = 11.285(3) Å $\alpha = 90.0$, $\beta = 96.53(3)^\circ$, $\gamma = 90.0^\circ$
Z:	1
Formula Weight:	508.5
Density (calc):	1.886 g/cm^3
F(000):	250

DATA COLLECTION

Radiation:	CuKα (λ = 1.54184 Å)
Temperature:	240 K
Reflections Collected:	2981
Unique Reflections:	1355
Observed Reflections:	1351 [$F > 4\sigma(F)$]

SOLUTION AND REFINEMENT

System Used:	Siemens SHELXTL
Solution:	Direct Methods
Refinement Methods:	Blocked-cascade least-squares
Number of Parameters Refined:	92
R Indices (full data):	R = 5.30 %,wR = 3.04 %

The molecule is disordered over a centre of symmetry, so that the terminal SMe and SeMe groups are indistinguishable; these heteroatoms were refined as 50% S and 50% Se.

BOND LENGTHS (Å)

Se(1)-C(1)	1.881(7)	Se(1)-C(3)	1.840(5)
Se(2)-C(2)	1.869(8)	Se(2)-C(4)	1.828(6)
S(3)-C(3)	1.743(6)	S(3)-C(5)	1.747(5)
S(4)-C(4)	1.749(5)	S(4)-C(5)	1.763(5)
C(3)-C(4)	1.381(7)	C(5)-C(6)	1.350(8)
C(6)-C(6')	1.445(11)		

SELECTED INTERMOLECULAR NON-BONDED DISTANCES (Å)

S(1)-S(3')	3.963	S(2)-S(4')	3.805
S(1)-S(4')	3.688	S(3)-S(3')	3.918
S(2)-S(3')	4.040	S(3)-S(4')	3.812

BOND ANGLES (°)

C(1)-Se(1)-C(3)	96.9(2)	C(2)-Se(2)-C(4)	97.2(3)
C(3)-S(3)-C(5)	96.6(3)	C(4)-S(4)-C(5)	97.2(2)
Se(1)-C(3)-S(3)	117.5(3)	Se(1)-C(3)-C(4)	124.9(4)
S(3)-C(3)-C(4)	117.6(4)	Se(2)-C(4)-S(4)	117.2(3)
Se(2)-C(4)-C(3)	127.6(4)	S(4)-C(4)-C(3)	115.2(4)
S(3)-C(5)-S(4)	113.3(3)	S(3)-C(5)-C(6)	124.6(4)
S(4)-C(5)-C(6)	122.1(4)	C(5)-C(6)-C(6')	123.3(6)

A.1.2 Crystal Data for 4,5-Dimethyl-2-(1,3-cyclopentanedithione-2-ylidene)-1,3-dithiole (72)

CRYSTAL DATA

Empirical Formula:	$C_{10}H_{10}S_4$
Crystal System:	Monoclinic
Space Group:	P21/n
Unit Cell Dimensions:	a = 7.634(3) Å, b = 14.018(3) Å, c = 10.561(3) Å $\alpha = 90.0$, $\beta = 96.53(3)°$, $\gamma = 90.0°$
Z:	4

Formula Weight: 258.45
Density (calc): 1.53 g/cm^3
F(000): 536

DATA COLLECTION

Radiation: MoKα (λ = 0.71069 Å)
Temperature: 293 K
Reflections Collected: 5401
Unique Reflections: 3665
Observed Reflections: 2156 [$F > 4\sigma(F)$]

SOLUTION AND REFINEMENT

System Used: Siemens SHELXTL
Solution: Direct Methods
Refinement Methods: Full-matrix least-squares
Number of Parameters Refined: 137
R Indices (full data): R = 5.6 %, wR = 4.8 %

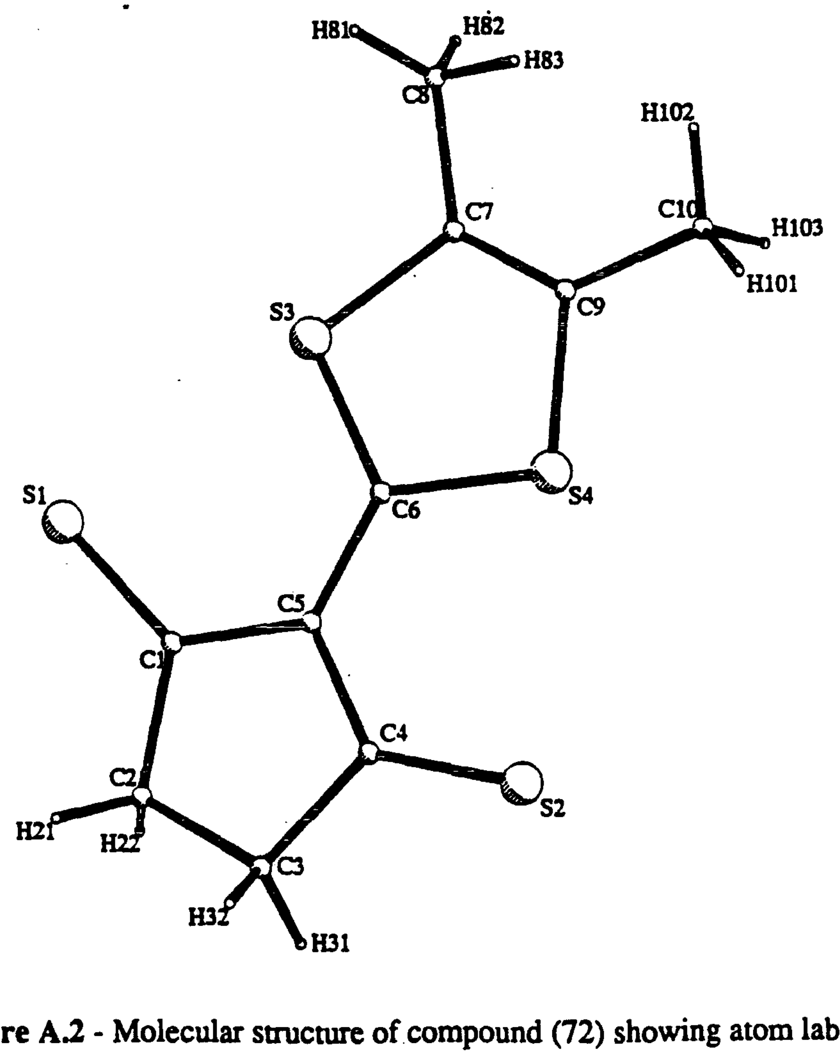

Figure A.2 - Molecular structure of compound (72) showing atom labelling.

BOND LENGTHS (Å)

C(1)-S(1)	1.643(7)	C(2)-C(1)	1.497(7)
C(5)-C(1)	1.440(7)	C(3)-C(2)	1.535(9)
C(4)-C(3)	1.527(8)	S(2)-C(4)	1.626(7)
C(5)-C(4)	1.431(7)	C(6)-C(5)	1.415(6)
S(3)-C(6)	1.708(7)	S(4)-C(6)	1.734(6)
C(7)-S(3)	1.740(6)	C(8)-C(7)	1.505(9)
C(9)-C(7)	1.328(7)	C(10)-C(9)	1.486(6)
S(4)-C(9)	1.762(7)		

SELECTED INTRAMOLECULAR NON-BONDED DISTANCES (Å)

S(4)-S(2)	3.020	S(3)-S(1)	2.998

SELECTED INTERMOLECULAR NON-BONDED DISTANCES (Å)

S(3)-S(2b)	3.760	S(4)-S(3a)	3.912
S(4)-S(1b)	3.960	S(2)-S(1c)	3.710
S(3)-S(3a)	3.958		

Key to symmetry operations relating designated atoms to reference atoms at (x, y, z)

a) 1.0-x, 2.0-y, -z

b) -x, 2.0-y, -z

c) 0.5-x, -0.5+y, -0.5-z

BOND ANGLES (°)

C(2)-C(1)-S(1)	123.5(4)	C(5)-C(1)-S(1)	127.8(5)
C(5)-C(1)-C(2)	108.7(5)	C(3)-C(2)-C(1)	105.3(5)
C(4)-C(3)-C(2)	106.2(5)	S(2)-C(4)-C(3)	122.9(5)
C(5)-C(4)-C(3)	107.2(5)	C(5)-C(4)-S(2)	129.9(5)
C(4)-C(5)-C(1)	111.4(5)	C(6)-C(5)-C(1)	124.4(5)
C(6)-C(5)-C(4)	124.1(5)	S(3)-C(6)-C(5)	123.7(4)
S(4)-C(6)-C(5)	123.3(5)	S(4)-C(6)-S(3)	113.0(3)
C(7)-S(3)-C(6)	97.9(3)	C(8)-C(7)-S(3)	115.7(5)
C(9)-C(7)-S(3)	116.4(5)	C(9)-C(7)-C(8)	127.9(5)
C(10)-C(9)-C(7)	129.2(6)	S(4)-C(9)-C(7)	115.8(4)
S(4)-C(9)-C(10)	115.0(5)	C(9)-S(4)-C(6)	96.8(3)

A.1.3 Crystal Data for 2,4,6-Tris(4,5-di-*n*-propyl-1,3-dithiole-2-ylidene)-1,3,5-cyclohexanetrione (70):

CRYSTAL DATA

Empirical Formula:	$C_{33}H_{42}S_6O_3$
Colour; Habit; Size:	Orange-red crystal, 0.14 x 0.18 x 0.44 mm
Crystal System:	Triclinic
Space Group:	P1bar
Unit Cell Dimensions:	a = 8.878(2) Å, b = 12.914(2) Å, c = 15.175(2) Å α = 82.96(1)°, β = 86.70(1)°, γ = 87.20(1)°
Z:	2
Formula Weight:	679.1
Density (calc):	1.309 g/cm^3
F(000):	720

DATA COLLECTION

Diffractometer Used:	Stoe-Siemens
Radiation:	CuKα (λ = 1.54184 Å)
Temperature:	295 K
Unique Reflections:	5097
Observed Reflections:	3554 [$F > 4\sigma(F)$]

SOLUTION AND REFINEMENT

System Used:	Siemens SHELXTL
Solution:	Direct Methods
Refinement Methods:	Blocked-cascade least-squares
Number of Parameters Refined:	390
R Indices (full data):	R = 6.07 %,wR = 7.57 %
Goodness-of-Fit:	1.04

BOND LENGTHS (Å)

S(1)-C(7)	1.718(5)	S(1)-C(8)	1.744(5)
S(2)-C(7)	1.718(5)	S(2)-C(9)	1.746(5)
S(3)-C(10)	1.718(5)	S(3)-C(11)	1.753(5)
S(4)-C(10)	1.717(4)	S(4)-C(12)	1.738(5)
S(5)-C(13)	1.726(5)	S(5)-C(14)	1.756(5)
S(6)-C(13)	1.729(5)	S(6)-C(15)	1.748(5)
O(1)-C(2)	1.240(6)	O(2)-C(4)	1.257(5)

O(3)-C(6)	1.257(6)	C(1)-C(2)	1.442(6)
C(1)-C(6)	1.445(6)	C(1)-C(7)	1.399(6)
C(2)-C(3)	1.456(6)	C(3)-C(4)	1.439(6)
C(3)-C(10)	1.397(6)	C(4)-C(5)	1.452(6)
C(5)-C(6)	1.444(6)	C(5)-C(13)	1.389(6)
C(8)-C(9)	1.321(7)	C(8)-C(16)	1.504(8)
C(9)-C(19)	1.511(7)	C(11)-C(12)	1.335(7)
C(11)-C(22)	1.501(9)	C(12)-C(25)	1.503(7)
C(14)-C(15)	1.324(7)	C(14)-C(28)	1.518(8)
C(15)-C(31)	1.508(8)	C(16)-C(17)	1.336(12)
C(17)-C(18)	1.525(15)	C(19)-C(20)	1.467(8)
C(20)-C(21)	1.519(8)	C(22)-C(23)	1.360(13)
C(23)-C(24)	1.483(12)	C(25)-C(26)	1.489(12)
C(26)-C(27)	1.254(20)	C(28)-C(29)	1.496(15)
C(29)-C(30x)	1.372(27)	C(29)-C(30y)	1.347(23)
C(31)-C(32)	1.526(11)	C(32)-C(33)	1.447(14)

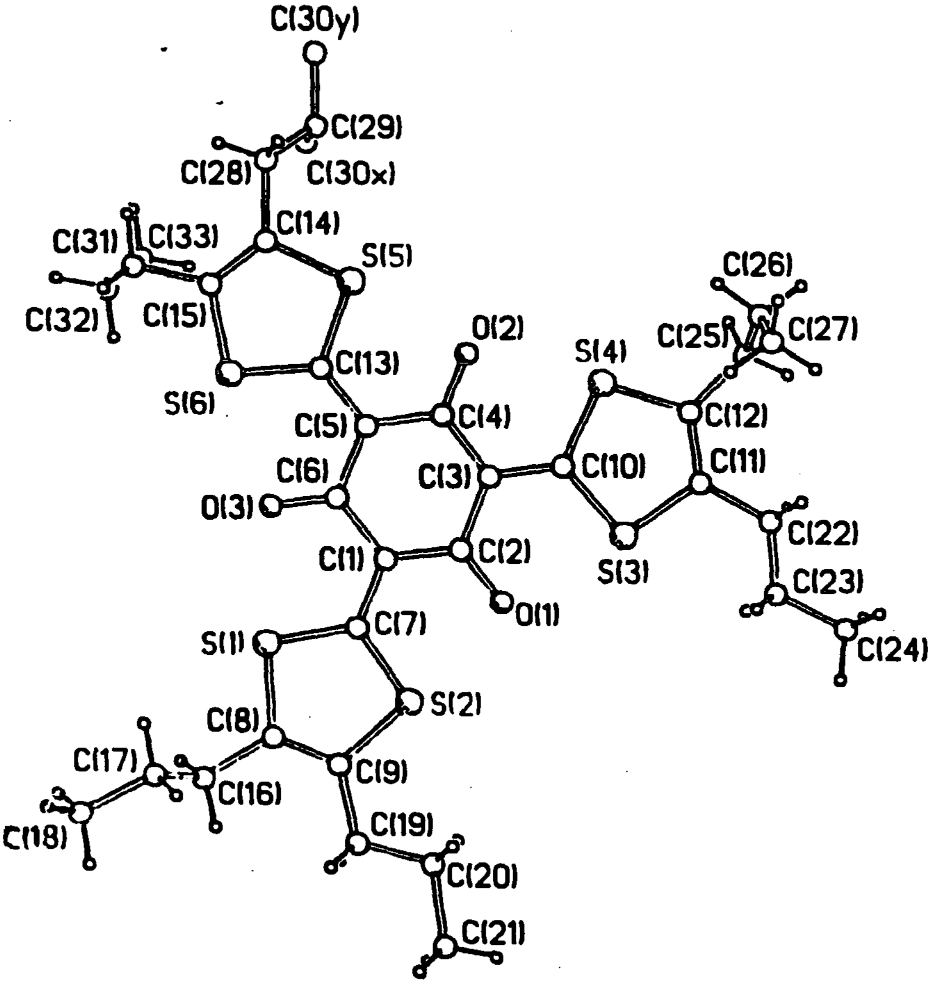

Figure A.3 - Molecular structure of compound (70) showing atom labelling.

BOND ANGLES (°)

C(7)-S(1)-C(8)	96.5(2)	C(7)-S(2)-C(9)	96.9(2)
C(10)-S(3)-C(11)	96.6(2)	C(10)-S(4)-C(12)	97.4(2)
C(13)-S(5)-C(14)	96.6(2)	C(13)-S(6)-C(15)	96.7(2)
C(2)-C(1)-C(6)	121.6(4)	C(2)-C(1)-C(7)	119.3(4)
C(6)-C(1)-C(7)	119.1(4)	O(1)-C(2)-C(1)	121.1(4)
O(1)-C(2)-C(3)	120.4(4)	C(1)-C(2)-C(3)	118.5(4)
C(2)-C(3)-C(4)	121.0(4)	C(2)-C(3)-C(10)	119.7(4)
C(4)-C(3)-C(10)	119.2(4)	O(2)-C(4)-C(3)	120.8(4)
O(2)-C(4)-C(5)	120.1(4)	C(3)-C(4)-C(5)	119.2(4)
C(4)-C(5)-C(6)	120.9(4)	C(4)-C(5)-C(13)	119.3(4)
C(6)-C(5)-C(13)	119.8(4)	O(3)-C(6)-C(1)	121.0(4)
O(3)-C(6)-C(5)	120.3(4)	C(1)-C(6)-C(5)	118.8(4)
S(1)-C(7)-S(2)	113.7(2)	S(1)-C(7)-C(1)	123.1(3)
S(2)-C(7)-C(1)	123.2(3)	S(1)-C(8)-C(9)	116.9(4)
S(1)-C(8)-C(16)	116.3(4)	C(9)-C(8)-C(16)	126.8(4)
S(2)-C(9)-C(8)	116.0(3)	S(2)-C(9)-C(19)	118.7(4)
C(8)-C(9)-C(19)	125.3(4)	S(3)-C(10)-S(4)	113.7(3)
S(3)-C(10)-C(3)	123.0(3)	S(4)-C(10)-C(3)	123.3(3)
S(3)-C(11)-C(12)	116.4(4)	S(3)-C(11)-C(22)	116.9(4)
C(12)-C(11)-C(22)	126.6(5)	S(4)-C(12)-C(11)	115.9(4)
S(4)-C(12)-C(25)	115.5(4)	C(11)-C(12)-C(25)	128.5(5)
S(5)-C(13)-S(6)	113.6(3)	S(5)-C(13)-C(5)	123.2(4)
S(6)-C(13)-C(5)	123.2(3)	S(5)-C(14)-C(15)	116.5(4)
S(5)-C(14)-C(28)	114.8(4)	C(15)-C(14)-C(28)	128.7(5)
S(6)-C(15)-C(14)	116.6(4)	S(6)-C(15)-C(31)	114.6(4)
C(14)-C(15)-C(31)	128.8(5)	C(8)-C(16)-C(17)	118.8(7)
C(16)-C(17)-C(18)	117.7(9)	C(9)-C(19)-C(20)	117.4(4)
C(19)-C(20)-C(21)	112.9(5)	C(11)-C(22)-C(23)	122.3(7)
C(22)-C(23)-C(24)	120.7(9)	C(12-C(25)-C(26)	114.1(5)
C(25)-C(26)-C(27)	127.9(10)	C(14)-C(28)-C(29)	117.1(6)
C(28)-C(29)-C(30x)	117.0(11)	C(28)-C(29)-C(30y)	116.8(15)
C(15)-C(31)-C(32)	113.4(5)	C(31)-C(32)-C(33)	115.1(8)

A.1.4 Crystal Data for 2-(4,5-Di-*n*-propyl-1,3-dithiole-2-ylidene)-1,3-indanedithione (99)

CRYSTAL DATA

Empirical Formula:	$C_{18}H_{18}S_4$
Crystal System:	Monoclinic
Space Group:	P21/a
Unit Cell Dimensions:	a = 7.532(1) Å, b = 24.658(3) Å, c = 9.445(1) Å
	$\alpha = 90°$, $\beta = 93.43(1)°$, $\gamma = 90°$
Z:	4
Formula Weight:	362.61
Density (calc):	1.38 g/cm^3
F(000):	760

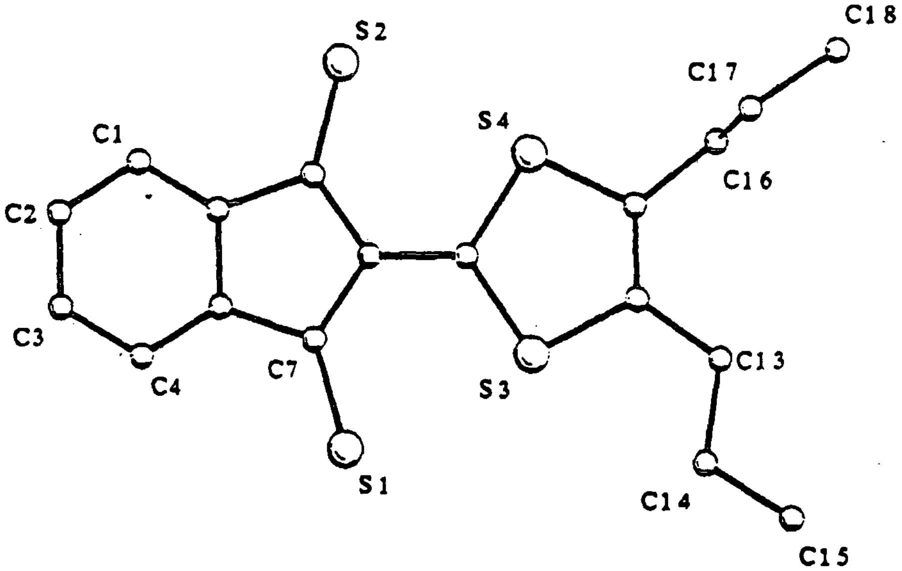

Figure A.4 - Molecular structure of compound (99) showing atom labelling.

DATA COLLECTION

Radiation:	MoKα (λ = 0.710693 Å)
Temperature:	293 K
Reflections Collected:	7971
Unique Reflections:	2979
Observed Reflections:	1337 [F > 3σ (F)]

SOLUTION AND REFINEMENT

System Used:	Siemens SHELXTL
Solution:	Direct Methods

Refinement Methods:	Full-Matrix Least-Squares
Number of Parameters Refined:	224
R Indices (full data):	R = 4.2 %,wR = 4.2 %

BOND LENGTHS (Å)

C(1)-C(2)	1.382(11)	C(6)-C(1)	1.361(10)
C(2)-C(3)	1.354(13)	C(4)-C(3)	1.383(12)
C(4)-C(5)	1.373(10)	C(6)-C(5)	1.392(9)
C(5)-C(7)	1.463(9)	C(9)-C(6)	1.492(9)
S(1)-C(7)	1.636(8)	C(8)-C(7)	1.444(8)
C(8)-C(9)	1.421(8)	C(10)-C(8)	1.415(8)
S(2)-C(9)	1.647(8)	S(3)-C(10)	1.704(8)
S(4)-C(10)	1.723(7)	C(11)-S(3)	1.744(7)
C(11)-C(12)	1.338(8)	C(13)-C(11)	1.504(9)
S(4)-C(12)	1.724(8)	C(16)-C(12)	1.509(8)
C(13)-C(14)	1.505(9)	C(15)-C(14)	1.508(10)
C(16)-C(17)	1.522(9)	C(18)-C(17)	1.510(9)

SELECTED INTRAMOLECULAR NON-BONDED DISTANCES (Å)

S(2)-S(4)	3.043	S(1)-S(3)	3.048

SELECTED INTERMOLECULAR NON-BONDED DISTANCES (Å)

S(3)-S(1a)	4.061	S(4)-S(3a)	4.059
S(1)-S(1b)	3.973	S(4)-S(4b)	3.822

Key to symmetry operations relating designated atoms to reference atoms at (x, y, z)
a) 0.5+x, 1.5-y, z
b) -0.5+x, 1.5-y, z

BOND ANGLES (°)

C(6)-C(1)-C(2)	118.1(8)	C(3)-C(2)-C(1)	121.0(9)
C(4)-C(3)-C(2)	121.3(8)	C(5)-C(4)-C(3)	118.4(8)
C(6)-C(5)-C(4)	119.7(8)	C(7)-C(5)-C(4)	130.6(7)
C(7)-C(5)-C(6)	109.7(7)	C(5)-C(6)-C(1)	121.5(7)
C(9)-C(6)-C(1)	130.5(6)	C(9)-C(6)-C(5)	108.0(7)
S(1)-C(7)-C(5)	124.3(6)	C(8)-C(7)-C(5)	106.0(6)
C(8)-C(7)-S(1)	129.7(6)	C(9)-C(8)-C(7)	110.0(6)
C(10)-C(8)-C(7)	124.6(6)	C(10)-C(8)-C(9)	125.4(6)

C(8)-C(9)-C(6)	106.3(6)	S(2)-C(9)-C(6)	123.8(6)
S(2)-C(9)-C(8)	129.9(5)	S(3)-C(10)-C(8)	123.7(5)
S(4)-C(10)-C(8)	122.6(5)	S(4)-C(10)-S(3)	113.7(4)
C(11)-S(3)-C(10)	97.2(4)	C(12)-C(11)-S(3)	115.4(6)
C(13)-C(11)-S(3)	118.0(5)	C(13)-C(11)-C(12)	126.6(6)
S(4)-C(12)-C(11)	117.0(5)	C(16)-C(12)-C(11)	125.2(6)
C(16)-C(12)-S(4)	117.8(5)	C(12)-S(4)-C(10)	96.7(4)
C(14)-C(13)-C(11)	116.6(6)	C(15)-C(14)-C(13)	113.4(6)
C(17)-C(16)-C(12)	112.1(5)	C(18)-C(17)-C(16)	111.6(6)

A.1.5 Crystal Data for Propane-1,2,3-tris(4,5-dimethyl-1,3-dithiole-2-ylidene) (109)

CRYSTAL DATA	
Empirical Formula:	$C_{18}H_{20}S_6$
Colour; Habit; Size:	Yellow Plate, 0.13 x 0.32 x 0.50 mm
Crystal System:	Triclinic
Space Group:	P1bar
Unit Cell Dimensions:	a = 9.968(3) Å, b = 10.636(5) Å, c = 12.085(5) Å α = 65.89(3)°, β = 67.07(3)°, γ = 67.52(4)°
Z:	2
Formula Weight:	428.7
Density (calc):	1.371 g/cm^3
F(000):	448
DATA COLLECTION	
Diffractometer Used:	Siemens R3m/v
Radiation:	MoKα (λ = 0.71073 Å)
Temperature:	293 K
Monochromator:	Highly oriented graphite crystal
Reflections Collected:	2899
Independent Reflections:	2710 (R_{int} = 2.20 %)
Observed Reflections:	1977 [F > 4.0σ (F)]
SOLUTION AND REFINEMENT	
System Used:	Siemens SHELXTL PLUS (VMS)
Solution:	Direct Methods
Refinement Methods:	Full-Matrix Least-Squares

Number of Parameters Refined: 217
R Indices (full data): R = 8.32 %,wR = 7.38 %
Goodness-of-Fit: 2.02

BOND LENGTHS (Å)

S(1)-C(2)	1.772(10)	S(1)-C(3)	1.744(5)
S(2)-C(2)	1.714(6)	S(2)-C(4)	1.751(9)
S(3)-C(8)	1.731(6)	S(3)-C(9)	1.758(10)
S(4)-C(8)	1.755(9)	S(4)-C(10)	1.759(6)
S(5)-C(14)	1.739(8)	S(5)-C(15)	1.741(6)
S(6)-C(14)	1.750(5)	S(6)-C(16)	1.753(9)
C(1)-C(2)	1.365(10)	C(1)-C(7)	1.409(18)
C(3)-C(4)	1.311(12)	C(3)-C(5)	1.508(13)
C(4)-C(6)	1.486(9)	C(7)-C(8)	1.381(10)
C(7)-C(13)	1.499(12)	C(9)-C(10)	1.319(12)
C(9)-C(11)	1.490(8)	C(10)-C(12)	1.513(15)
C(13)-C(14)	1.334(10)	C(15)-C(16)	1.328(11)
C(15)-C(17)	1.485(14)	C(16)-C(18)	1.502(9)

SELECTED INTERMOLECULAR NON-BONDED DISTANCES (Å)

S(3)-S(5')	4.00	S(1)-S(1')	3.96

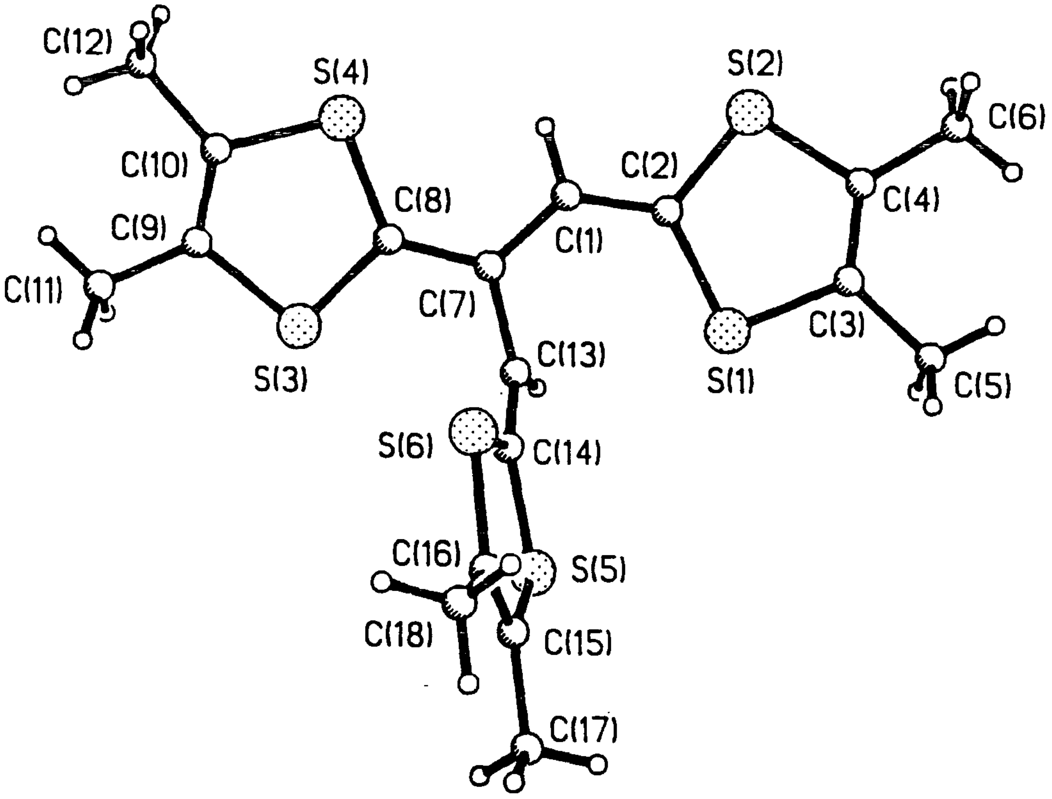

Figure A.5 - Molecular structure of compound (109) showing atom labelling.

BOND ANGLES (°)

C(2)-S(1)-C(3)	95.3(4)	C(2)-S(2)-C(4)	97.4(4)
C(8)-S(3)-C(9)	97.0(4)	C(8)-S(4)-C(10)	95.7(4)
C(14)-S(5)-C(15)	96.9(4)	C(14)-S(6)-C(16)	95.9(4)
C(2)-C(1)-C(7)	128.5(9)	S(1)-C(2)-S(2)	112.9(4)
S(1)-C(2)-C(1)	126.3(6)	S(2)-C(2)-C(1)	120.8(7)
S(1)-C(3)-C(4)	118.4(6)	S(1)-C(3)-C(5)	115.1(5)
C(4)-C(3)-C(5)	126.5(5)	S(2)-C(4)-C(3)	115.9(5)
S(2)-C(4)-C(6)	117.2(8)	C(3)-C(4)-C(6)	126.8(9)
C(1)-C(7)-C(8)	122.2(8)	C(1)-C(7)-C(13)	119.8(7)
C(8)-C(7)-C(13)	117.9(5)	S(3)-C(8)-S(4)	113.3(4)
S(3)-C(8)-C(7)	121.7(6)	S(4)-C(8)-C(7)	124.9(5)
S(3)-C(9)-C(10)	116.1(5)	S(3)-C(9)-C(11)	116.6(7)
C(10)-C(9)-C(11)	127.3(9)	S(4)-C(10)-C(9)	117.7(7)
S(4)-C(10)-C(12)	115.4(6)	C(9)-C(10)-C(12)	126.8(6)
C(7)-C(13)-C(14)	122.6(5)	S(5)-C(14)-S(6)	113.2(4)
S(5)-C(14)-C(13)	123.4(5)	S(6)-C(14)-C(13)	123.4(6)
S(5)-C(15)-C(16)	116.7(7)	S(5)-C(15)-C(17)	115.9(6)
C(16)-C(15)-C(17)	127.4(6)	S(6)-C(16)-C(15)	117.3(5)
S(6)-C(16)-C(18)	115.3(7)	C(15)-C(16)-C(18)	127.5(8)

A.1.6 Crystal Data for 9,10-Bis[4,5-bis(methylthio)-1,3-dithiole-2-ylidene]-9,10-dihydroanthracene (133)

CRYSTAL DATA
Empirical Formula: $C_{24}H_{20}S_8$
Crystal System: Triclinic
Space Group: P1bar
Unit Cell Dimensions: a = 8.771(1) Å, b = 9.993(1) Å, c = 15.375(1) Å
α = 86.93(1)°, β = 78.69(1)°, γ = 75.24(1)°
Z: 2
Formula Weight: 564.90

DATA COLLECTION
Diffractometer Used: Rigalcu AFC6S
Radiation: MoKα (μ = 7.1 cm^{-1})
Temperature: 293 K

Monochromator: Highly oriented graphite crystal
Unique Reflections: 4966
Observed Reflections: 3056 [I > 2σ (I)]

SOLUTION AND REFINEMENT

System Used: Siemens SHELX PLUS
Solution: Direct Methods
Refinement Methods: Full-Matrix Least-Squares
Number of Parameters Refined: 301
R Indices (full data): R = 4.0 %,wR = 4.7 %

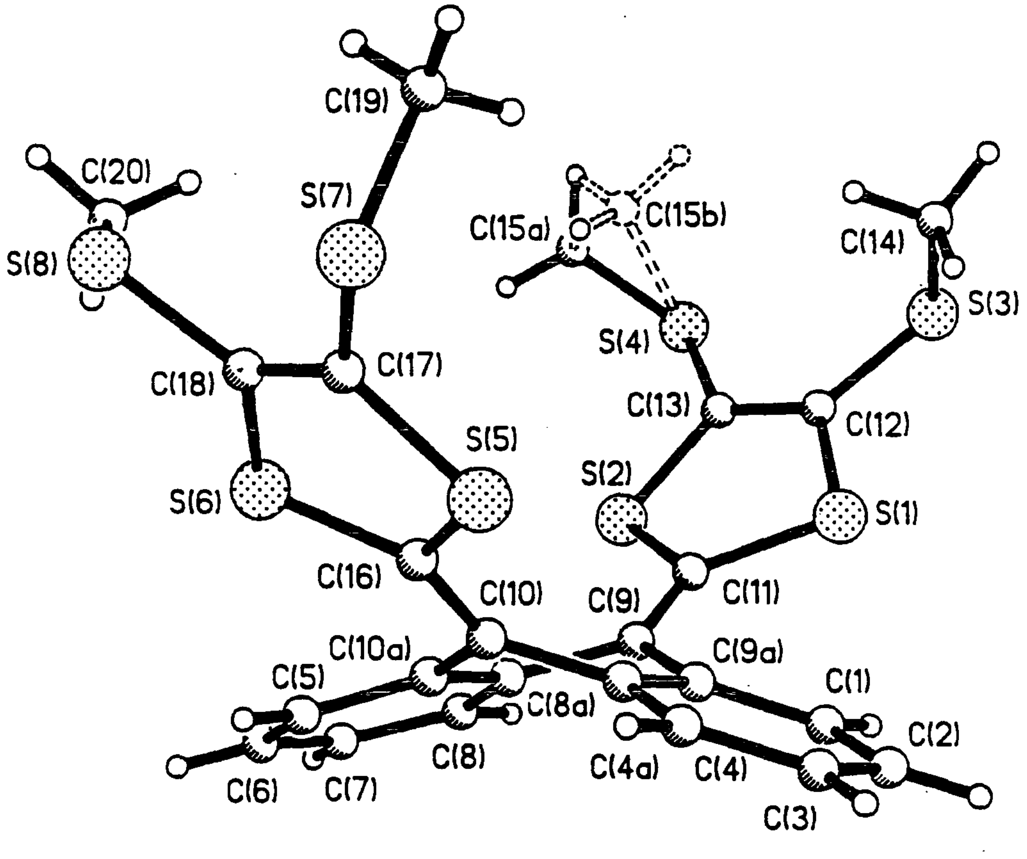

Figure A.6 - Molecular structure of compound (133) showing atom labelling.

BOND LENGTHS (Å)

S(1)-C(11)	1.769(3)	S(1)-C(12)	1.758(5)
S(2)-C(11)	1.770(4)	S(2)-C(13)	1.766(4)
S(3)-C(12)	1.757(4)	S(3)-C(14)	1.774(6)
S(4)-C(13)	1.750(5)	S(4)-C(15A)	1.763(33)
S(4)-C(15B)	1.784(29)	S(5)-C(16)	1.766(3)
S(5)-C(17)	1.758(4)	S(6)-C(16)	1.763(4)

S(6)-C(18)	1.754(4)	S(7)-C(17)	1.760(4)
S(7)-C(19)	1.799(6)	S(8)-C(18)	1.755(4)
S(8)-C(20)	1.800(5)	C(1)-C(2)	1.388(6)
C(1)-C(9A)	1.410(6)	C(2)-C(3)	1.380(6)
C(3)-C(4)	1.381(6)	C(4)-C(4A)	1.399(5)
C(4A)-C(9A)	1.409(5)	C(4A)-C(10)	1.474(5)
C(5)-C(6)	1.374(5)	C(5)-C(10A)	1.405(5)
C(6)-C(7)	1.403(6)	C(7)-C(8)	1.384(5)
C(8)-C(8A)	1.404(5)	C(8A)-C(9)	1.486(5)
C(8A)-C(10A)	1.407(5)	C(9)-C(9A)	1.484(5)
C(9)-C(11)	1.352(5)	C(10)-C(10A)	1.476(4)
C(10)-C(16)	1.367(5)	C(12)-C(13)	1.335(6)
C(17)-C(18)	1.332(5)		

BOND ANGLES (°)

C(11)-S(1)-C(12)	96.1(2)	C(11)-S(2)-C(13)	96.1(2)
C(12)-S(3)-C(14)	101.1(2)	C(13)-S(4)-C(15A)	103.3(12)
C(13)-S(4)-C(15B)	102.1(10)	C(16)-S(5)-C(17)	96.7(2)
C(16)-S(6)-C(18)	96.9(2)	C(17)-S(7)-C(19)	101.0(2)
C(18)-S(8)-C(20)	101.2(2)	C(2)-C(1)-C(9A)	120.4(4)
C(1)-C(2)-C(3)	120.1(4)	C(2)-C(3)-C(4)	120.4(4)
C(3)-C(4)-C(4A)	120.9(4)	C(4)-C(4A)-C(9A)	119.1(3)
C(4)-C(4A)-C(10)	123.5(3)	C(9A)-C(4A)-C(10)	117.3(3)
C(6)-C(5)-C(10A)	121.6(4)	C(5)-C(6)-C(7)	119.6(3)
C(6)-C(7)-C(8)	120.0(3)	C(7)-C(8)-C(8A)	120.5(4)
C(8)-C(8A)-C(9)	122.6(3)	C(8)-C(8A)-C(10A)	119.7(3)
C(9)-C(8A)-C(10A)	117.7(3)	C(8A)-C(9)-C(9A)	113.5(3)
C(8A)-C(9)-C(11)	123.0(4)	C(9A)-C(9)-C(11)	123.1(3)
C(1)-C(9A)-C(4A)	119.1(4)	C(1)-C(9A)-C(9)	122.5(3)
C(4A)-C(9A)-C(9)	118.5(3)	C(4A)-C(10)-C(10A)	114.7(3)
C(4A)-C(10)-C(16)	123.5(3)	C(10A)-C(10)-C(16)	121.7(3)
C(5)-C(10A)-C(8A)	118.6(3)	C(5)-C(10A)-C(10)	123.3(3)
C(8A)-C(10A)-C(10)	118.0(3)	S(1)-C(11)-S(2)	111.5(2)
S(1)-C(11)-C(9)	124.3(3)	S(2)-C(11)-C(9)	124.1(3)
S(1)-C(12)-S(3)	116.9(3)	S(1)-C(12)-C(13)	117.3(3)
S(3)-C(12)-C(13)	125.8(4)	S(2)-C(13)-S(4)	116.6(2)
S(2)-C(13)-C(12)	116.3(4)	S(4)-C(13)-C(12)	126.9(3)
S(5)-C(16)-S(6)	111.9(2)	S(5)-C(16)-C(10)	125.5(3)
S(6)-C(16)-C(10)	122.4(3)	S(5)-C(17)-S(7)	116.6(2)

S(5)-C(17)-C(18)	116.9(3)	S(7)-C(17)-C(18)	126.4(3)
S(6)-C(18)-S(8)	117.3(2)	S(6)-C(18)-C(17)	117.0(3)
S(8)-C(18)-C(17)	125.6(3)		

A.1.7 Crystal Data for 2,3-Dipentyl-9,10-bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-9,10-dihydroanthracene (134)

CRYSTAL DATA

Empirical Formula: $C_{34}H_{20}S_4$

Crystal System: Triclinic

Space Group: P1bar

Unit Cell Dimensions: a = 14.659(4) Å, b = 15.174(8) Å, c = 15.171(4) Å
α = 69.77(1)°, β = 84.81(1)°, γ = 82.82(1)°

Z: 1

Formula Weight: 556.77

DATA COLLECTION

Diffractometer Used: Enraf-Nonius FAST TV area detector

Radiation: MoKα (λ = 0.71069 Å)

Temperature: 293 K

Monochromator: Highly oriented graphite crystal

Reflections Collected: 11768

Unique Reflections: 4865

Observed Reflections: 3504 [F > 5σ (F)]

SOLUTION AND REFINEMENT

System Used: Siemens SHELX-S 86

Solution: Direct Methods

Refinement Methods: Full-Matrix Least-Squares

Number of Parameters Refined: 698

R Indices (full data): R = 6.40 %,wR = 6.47 %

BOND LENGTHS (Å)

C(1)-S(1)	1.897(21)	C(5)-S(1)	1.615(18)
C(14)-S(2)	1.694(18)	C(17)-S(2)	1.768(24)
C(14)-S(3)	1.698(21)	C(15)-S(3)	1.785(23)
C(3)-S(4)	1.790(19)	C(5)-S(4)	1.823(20)

C(2)-C(1)	1.472(26)	C(3)-C(1)	1.295(28)
C(4)-C(3)	1.616(27)	C(6)-C(5)	1.436(22)
C(7)-C(6)	1.488(25)		

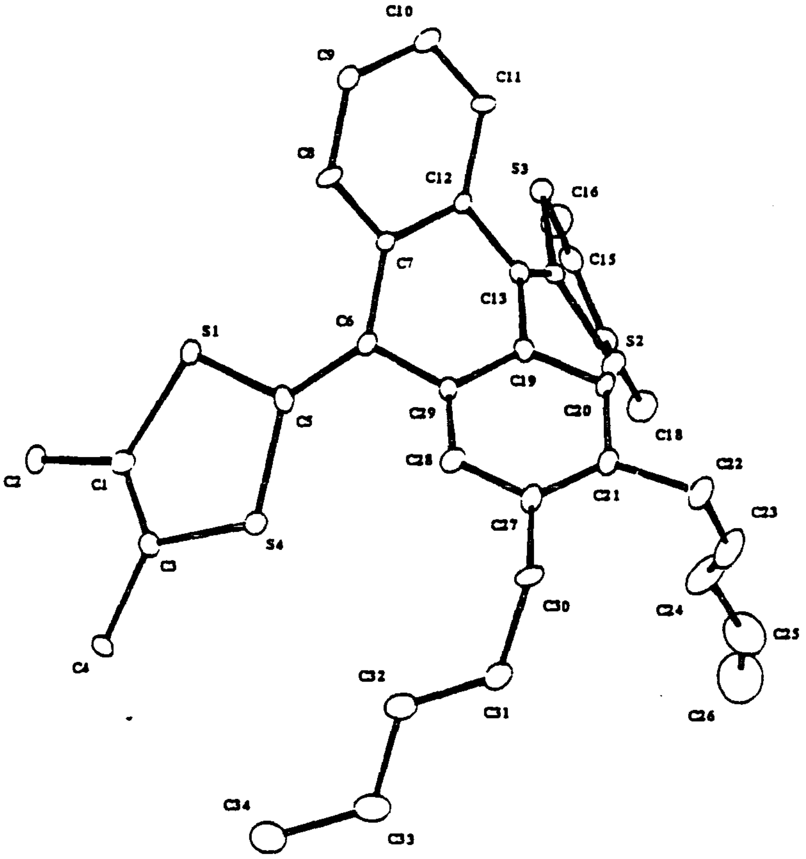

Figure A.7 - Molecular structure of compound (134) showing atom labelling.

BOND ANGLES (°)

C(5)-S(1)-C(1)	101.1(9)	C(17)-S(2)-C(14)	102.9(10)
C(15)-S(3)-C(14)	98.5(11)	C(5)-S(4)-C(3)	107.1(9)
C(2)-C(1)-S(1)	123.0(14)	C(3)-C(6)-S(1)	120.2(15)
C(3)-C(1)-C(2)	116.7(18)	C(1)-C(3)-S(4)	105.3(15)
C(4)-C(3)-S(4)	124.6(14)	C(4)-C(3)-C(1)	130.1(16)
S(4)-C(5)-S(1)	104.7(9)	C(6)-C(5)-C(1)	121.3(14)
C(6)-C(5)-S(4)	134.0(12)	C(7)-C(6)-C(5)	131.8(14)

APPENDIX TWO

COLLOQUIA, LECTURES, AND SEMINARS FROM INVITED SPEAKERS

The Board of Studies in Chemistry requires that each postgraduate research thesis contain an appendix listing:

1) All research colloquia, research seminars and lectures arranged by the Department of Chemistry and the Chemical Society during the period of residence as a postgraduate student.
2) All research conferences attended, and papers/posters presented by the authors, during the period when the research for the thesis was carried out.

A.2.1 RESEARCH COLLOQUIA, RESEARCH SEMINARS AND LECTURES

1989 - 1990 August 1 - July 31

1989

October	17	Dr. F.Palmer, Nottingham University Thunder and lightning	√
October	25	Prof. C.Floriani, University of Lausanne, Switzerland Molecular aggregates - a bridge between homogenous and heterogenous systems	√
November	1	Dr. J.P.S.Badyal, Durham University Breakthroughs in heterogenous catalysis	
November	9	Prof. N.N.Greenwood, University of Leeds Novel cluster geometries in metalloborane chemistry	
November	10	Prof. J.E.Bercaw, California Institute of Technology Synthetic and mechanistic approaches to Ziegler-Natta polymerisation of olefins	√
November	13	Dr. J.Becher, Odense University Synthesis of new macrocyclic systems using heterocyclic building blocks	√
November	16	Dr. D.Parker, Durham University Macrocycles, drugs and rock'n'roll	√

November	29	Prof. D.G.Cole-Hamilton, St. Andrews University New polymers from homogenous catalysis	√
November	30	Dr. M.N.Hughes, King's College London A bug's eye view of the periodic table	√
December	4	Dr. D.Graham, B.P.Research Centre How proteins absorb to interfaces	√
December	6	Dr. R.L.Powell, ICI The development of CFC replacements	√
December	7	Dr. A.Butler, St. Andrews University The discovery of penicillin - facts and fancies	√
December	13	Dr. J.Klinowski, Cambridge University Solid state nmr studies of zeolite catalysts	
December	15	Prof. R.Huisgen, University of Munich Recent mechanistic studies of [2+2] additions	

<u>1990</u>

January	24	Dr. R.N.Perutz, York University Plotting the course of C-H activations with organometallics	
January	31	Dr. U.Dyer, Glaxo Synthesis and conformation of c-glycosides	√
February	1	Prof. J.H.Holloway, University of Leicester Noble gas chemistry	
February	7	Dr. D.P.Thompson, Newcastle The role of nitrogen in extending silicate crystal chemistry	
February	8	Rev. R.Lancaster, Kimbolton Fireworks Fireworks - principles and practice	√

February	12	Prof. L.Lunazzi, University of Bologne Applications of dynamic nmr to the study of conformational enantiomerism	
February	14	Prof. D.Sutton, Simon Fraser University - Vancouver B.C Synthesis and applications of dinitrogen and diazo compounds of rhenium and iridium	
February	15	Prof. L.Crombie, Nottingham University The chemistry of cannabis and khat	√
February	21	Dr. C.Bleasedale, Newcastle University The mode of action of some anti-tumour agents	√
February	22	Prof. D.T.Clark, ICI Wilton Spatially resolved chemistry (using Nature's paradigm in the advanced material arena)	√
February	28	Dr. R.K.Thomas, Oxford University Neutron reflectrometry from surfaces	
March	1	Dr. J.F.Stoddart, Sheffield University Molecular lego	√
March	8	Dr. A.K.Cheetham, Oxford University Chemistry of zeolite cages	
March	21	Dr. I.Powis, Nottingham University Spinning off in a huff - photodiscossiation of methyl iodide	
March	23	Prof. J.M.Bowman Fitting experiment with theory in Ar-OH	
July	9	Prof. I.N.Rozhkov, USSR Academy of Sciences - Moscow Reactivity of perfluoroalkyl bromides	
July	9	Prof. V.E.Platonov, USSR Academy of Sciences - Novosibirsk Polyfluoroindanes - synthesis and transformation	

July	9	Prof. L.S.German, USSR Academy of Sciences - Moscow New syntheses in fluoroaliphatic chemistry - recent advances in the chemistry of fluorinated oxiranes	

1990 - 1991 August 1 - July 31

1990

October	11	Dr. W.A.MacDonald, ICI Wilton Materials for the space age	√
October	24	Dr. M.Bochmann*, University of East Anglia Synthesis, reactions and catalytic activity of cationic titanium alkyls	√
October	26	Prof. R.Soulen*, South Western University, Texas Preparation and reactions of bicycloalkenes	√
October	31	Dr. R.Jackson*, Newcastle University New synthetic methods - α-amino acids and small rings	√
November	1	Dr. N.Logan, Nottingham University Rocket propellants	√
November	6	Dr. P.Kocovosky*, Uppsala University Stereo-controlled reactions mediated by transition and non-transition metals	
November	7	Dr. D.Gerrard*, British Petroleum Raman spectroscopy for industrial analysis	
November	8	Dr. S.K.Scott, Leeds University Clocks, oscillations and chaos	
November	14	Prof. T.Bell*, SUNY, Stoney Brook, U.S.A Functional molecular architecture and molecular recognition	√
November	21	Prof. J.Pritchard, Queen Mary and Westfield College, London Copper surfaces and catalysts	

November	28	Dr. B.J.Whitaker*, Leeds University Two-dimensional velocity imaging of state-selected reaction products	
November	29	Prof. D.Crout, Warwick University Enzymes in organic synthesis	√
December	5	Dr. P.G.Pringle*, Bristol University Metal complexes with functionalised phosphines	√
December	13	Prof. A.H.Cowley, University of Texas New organometallic routes to electronic materials	√

1991

January	15	Dr. B.J.Alder, Lawrence Livermore Labs., California Hydrogen in all its glory	
January	17	Dr. P.Sarre, Nottingham University Comet chemistry	√
January	24	Dr. P.J.Sadler, Birkbeck College, London Design of inorganic drugs - precious metals, hypertension and HIV	√
January	30	Prof. E.Sinn*, Hull University Coupling of little electrons in big molecules. Implications for the active sites of (metalloproteins and other) macromolecules	
January	31	Dr. D.Lacey, Hull University Liquid crystals	√
February	6	Dr. R.Bushby*, Leeds University Biradicals and organic magnets	√
February	14	Dr. M.C.Petty, Durham University Molecular electronics	√
February	20	Prof. B.L.Shaw*, Leeds University Synthesis with coordinated, unsaturated phosphine ligands	√

February	28	Dr. J.Brown, Oxford University Can chemistry provide catalysts superior to enzymes	√
March	6	Dr. C.M.Dobson*, Oxford University NMR studies of dynamics in molecular crystals	
March	7	Dr. J.Markam, ICI Pharmaceuticals DNA fingerprinting	√
April	24	Prof. R.R.Schrock, Massachusetts Institute of Technology Metal-ligand multiple bonds and metathesis initiators	√
April	25	Prof. T.Hudlicky, Virginia Polytechnic Institute Biocatalysis and symmetry based approaches to the efficient synthesis of complex natural products	√
June	20	Prof. M.S.Brookhart, University of North Carolina Olefin polymerisations, oligomerisations and dimerisations using electrophilic late transition metal catalysts	√
July	29	Dr. M.A.Brimble, Massey University, New Zealand Synthetic studies towards the antibiotic Griseusin-A	√

1991 - 1992 August 1 - July 31

1991

October	17	Dr. J.A Salthouse, University of Manchester Son et Lumiere - a demonstration lecture	√
October	31	Dr. R.Keeley, Metropolitan Police Forensic Science Modern Forensic Science	√
November	6	Prof. B.F.G.Johnson*, Edinburgh University Cluster-surface analogies	
November	7	Dr. A.R.Butler, St. Andrews University Traditional Chinese herbal drugs - a different way of treating disease	√

November	13	Prof. D.Gani*, St. Andrews University The chemistry of PLP-dependent enzymes	√
November	20	Dr. R.More O'Ferrall*, University College Dublin Some acid-catalysed rearrangements in organic chemistry	√
November	28	Prof. I.M.Ward, IRC in Polymer Science, University of Leeds The SCI lecture: the science and technology of orientated polymers	√
December	4	Prof. R.Grigg*, Leeds University Palladium-catalysed cyclisation and ion-capture processes	
December	5	Prof. A.L.Smith, ex Unilever Soap, detergents and black puddings	√
December	11	Dr. W.D.Cooper*, Shell Research Colloid science: theory and practice	√

1992

January	22	Dr. K.D.M.Harris*, St. Andrews University Understanding the properties of solid inclusion compounds	
January	29	Dr. A.Holmes*, Cambridge University Cycloaddition reactions in the service of the synthesis of piperidine and indolizidine natural products	√
January	30	Dr. M.Anderson, Sittingbourne Research Centre, Shell Research Recent advances in the safe and selective chemical control of insect pests	√
February	12	Prof. D.E.Fenton*, Sheffield University Polynuclear complexes of molecular clefts as models for copper biosites	√
February	13	Dr. J.Saunders, Glaxo Group Research Limited Molecular modelling in drug research	√
February	19	Prof. E.J.Thomas*, Manchester University Applications of organostannanes to organic synthesis	√

February	20	Prof. E.Vogel, University of Cologne *The Musgrave Lecture* : Porphyrins - molecules of inter-disciplinary interest	√
February	25	Prof. J.F.Nixon, University of Sussex *The Tilden Lecture* : Phosphaalkynes - new building blocks in inorganic and organometallic chemistry	√
February	26	Prof. M.L.Hitchman*, Strathclyde University Chemical vapour deposition	
March	5	Dr. N.C.Billingham, University of Sussex Degradable plastics - myth or magic?	√
March	11	Dr. S.E.Thomas*, Imperial College Recent advances in organoiron chemistry	√
March	12	Dr. R.A.Hann, ICI Imagedata Electronic photography - an image of the future	√
March	18	Dr. H.Maskill*, Newcastle University Concerted or stepwise fragmentation in a deamination-type reaction	√
April	7	Prof. D.M.Knight, Philosophy Department, University of Durham Interpreting experiments - the beginning of electrochemistry	
May	13	Dr. J-C.Gehret, Ciba Geigy, Basel Some aspects of industrial agrochemical research	√

* Invited specially for the postgraduate training programme.

√ Those colloquia attended by the author.

A.2.2 RESEARCH CONFERENCES ATTENDED BY THE AUTHOR DURING THE PERIOD OCTOBER 1989 - SEPTEMBER 1992

1) The R.S.C. 150 th Aniversary Annual Chemical Congress, Imperial College London, 8-11 April 1991.

2) Autumn Meeting of R.S.C., University of York, 24-26 September 1991. A poster was presented entitled "Synthesis, Redox Properties and *X*-Ray Crystal Structures of New Multi-Sulphur Heterocycles".

3) Workshop on the Design and Synthesis of New Materials with Unconventional Electronic, Optical and Magnetic Properties, University of Durham, 12-15 April 1992.

4) 15th International Symposium on the Organic Chemistry of Sulphur, Caen, France, 28 June-3 July 1992. A poster was presented entitled "New Vinylogous TTF and BEDT-TTF Derivatives".

APPENDIX THREE

PUBLICATIONS

Some of the work presented in this thesis has been published in the following journals:

1) "A Tetrathiotrimethylenemethane Derivative" M.R.Bryce, M.A.Coffin, M.B.Hursthouse and M.Mazid, *Angew. Chem. Int. Ed. Eng.*, 30, 871, (1991).

2) "Synthesis, *X*-Ray Crystal Structure and Multistage Redox Properties of a Severely Distorted Tetrathiafulvalene Donor". M.R.Bryce, M.A.Coffin, M.B.Hursthouse, A.Karaulov, K.Müllen and H.Scheich, *Tet. Lett.*, 42, 6029, (1991).

3) "2,4,6-Tris(4,5-di-*n*-propyl-1,3-dithiole-2-ylidene)-1,3,5-cyclohexanetrione: Synthesis, *X*-Ray Crystal Structure and Amphoteric Redox Properties of a Highly Delocalised Heterocyclic π-System". M.A.Coffin, M.R.Bryce and W.Clegg, *J. Chem. Soc. Chem. Comm.*, 5, 401, (1992).

4) "New Vinylogous Tetrathiafulvalene π-Electron Donors with Peripheral Alkylseleno Substitution". M.R.Bryce, M.A.Coffin and W.Clegg, *J. Org. Chem.*, 57, 1696, (1992).