Functionalised tetraheterofulvalenes for conducting landmuir-blodgett films and charge-transfer complexes

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FUNCTIONALISED TETRAHETEROFULVALENES FOR CONDUCTING LANGMUIR-BLODGETT FILMS AND CHARGE-TRANSFER COMPLEXES.

by

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

September 1992.

DECLARATION.

The work described in this thesis was carried out by the author, in the Department of Chemistry and School of Engineering and Computer Science, 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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ABSTRACT.

The tetrathiafulvalene (TTF) mono-anion route to functionalised derivatives has been extended to lead to new materials for charge-transfer (CT) complexes. New improved routes have been established towards halogenated and chalcogenated TTF derivatives from the TTF anion (23). Highly conducting complexes with TCNQ (1) have been obtained from 4-chloro- (30) and 4-bromotetrathiafulvalene (32). X-Ray studies of ethylenediseleno-TTF (44) and bis(tetrathiafulvalenyl)sulphide (59) have revealed novel structural features.

New long chain TTF materials have also been synthesised, suitable for Langmuir-Blodgett (LB) films, using TTF anion and 1,3-dithiole cross-coupling methodologies. Amphiphiles bearing highly functionalised groups, both adjacent to the TTF ring and in the side chain, have been synthesised, and LB films have been formed from some of these materials. Iodine doping of the films has provided conducting mixed-valence systems.

Monofunctionalised tetraselenafulvalenes (TSF) have been synthesised from the TSF tetra-anion (118) and a range of acid chlorides, to yield the corresponding ketones. X-Ray crystal structure analysis of 4-acetyltetraselenafulvalene (123), has unequivocally proven that under these reaction conditions the TSF unit stays intact.

Graeme Cooke (September 1992).

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CHAPTER ONE.

INTRODUCTION.

1.1 ORGANIC CONDUCTORS.

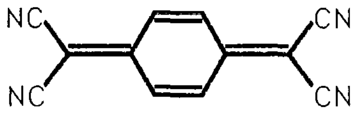
1.1.1 Introduction.

Although the majority of organic materials are electrical insulators, it was suggested early this century that certain organic materials may exhibit high conductivity[1]. Today, the study of organic conductors is at the forefront of academic attention and is providing valuable insights into the organic solid state, as well as materials that could revolutionise the electronics industry.

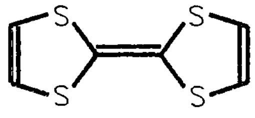
1.1.2 Historical aspects.

The first breakthrough occurred in 1954 when an unstable perylene bromine salt was found to be conducting[2]. Melby and co-workers, in the early 1960's, synthesised a powerful electron acceptor 7,7,8,8-tetracyano-p-quinodimethane (TCNQ,1)[3]. Many complexes of the TCNQ radical anion with various π-electron donors were found to be semiconductors (σ_{rt}= ca. 10^{-5} Scm^{-1}).

In 1973 a crystalline 1:1 charge-transfer (C-T) complex was formed with the newly synthesised donor tetrathiafulvalene (TTF,2)[4] and TCNQ, which was found to exhibit metallic behaviour (σ_{rt}= 500 Scm^{-1}, σ_{max}= 10^4 Scm^{-1} at 59K)[5]. This discovery led to the synthesis of a myriad of analogous π- donors and π- acceptors[6].



(1)



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Today, C-T complexes remain an important aspect of conducting organic materials. The phenomena of metallic conductivity and superconductivity have been well established in many crystalline systems, and recently, attention has turned to the novel optical and magnetic properties C-T materials can display. The relatively new science of conducting Langmuir-Blodgett (LB) films has produced some fascinating results, which will be discussed in detail presently.

1.2 THEORY OF CONDUCTING ORGANIC MATERIALS.

1.2.1 Background.

In order to understand why certain organic materials conduct, one must consult the basic concepts of band theory, as conduction properties depend upon the electronic structure of the energy levels of these materials. Conducting organic materials differ from their inorganic counterparts in that the electron transport is usually highly anisotropic in organic materials, which has led to many organic metals being termed one dimensional metals.

1.2.2 Band Theory.

When a large number of atoms or molecules are brought together to form a crystalline solid, Langmuir-Blodgett film, or polymer, and sufficient mixing of the constituent atomic or molecular orbitals occurs, an energy band will form. This supermolecular orbital provides a mechanism for conductive delocalisation of electrons, by producing a conduction band, whose width is dependant upon the mixing of the molecular orbitals of neighbouring molecules. The occupancy of these bands is very important. When the energy gap between the highest occupied (valence) band and the lowest unoccupied (conduction) band is large the material is an insulator. An intrinsic semiconductor is formed when the gap decreases, thus allowing thermal excitation of electrons from the valence band into the conduction band. As the gap between the bands becomes very small, and a large number of charge carriers move easily from the highest occupied state (Fermi level) into higher energy states within the band, the material adopts metallic behaviour. A schematic representation of this is shown in Fig.1.1.

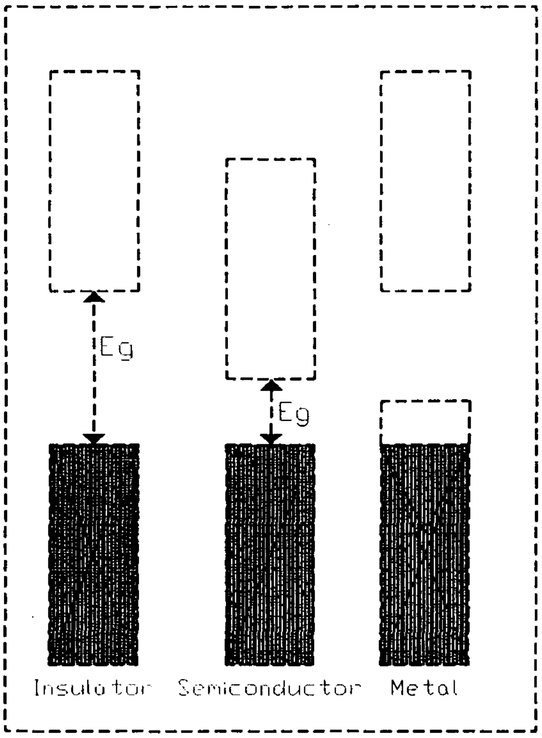


Fig. 1.1: *Band theory for insulators semiconductors and metals. The shaded areas represent electronic states occupied by electrons. Eg is the energy gap between occupied and empty states.*

The temperature dependency of conductivity in organic metals is controlled by the mutual interactions of electrons with lattice vibrations. As the temperature is lowered, there are fewer lattice vibrations which, in effect, increases the intermolecular orbital overlap, so the conductivity increases. However, the conductivity of a semiconductor decreases as the temperature is lowered as there is less energy to promote electrons from the Fermi level across the band gap (Fig. 1.2). Superconductivity is caused by highly coordinated motion of electron pairs (Cooper pairs) which contrasts with metallic behaviour, where individual electrons act as charge carriers.

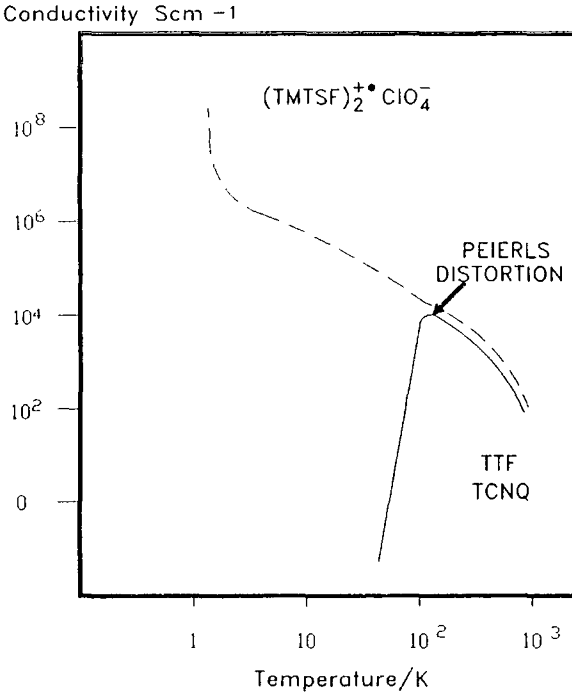


Fig. 1.2: *Schematic representation the temperature dependency of conductivity for a typical metal (TTF-TCNQ) and superconductor ($(TMTSF)_2^{+\cdot}$ ClO_4^-).*

The behaviour of metallic systems was first considered by Fröhlich[7a] and Peierls[7b] in the mid 1950's, who postulated that at low temperatures, a quasi one dimensional metal could not support long range order due to lattice distortions. Experimentation over the last 20 or so years has shown this to be correct, and has become known as the Peierls distortion. The Peierls distortion occurs due to the electronic stability obtained from the splitting of the conduction band, into a lower energy band which is fully occupied and an empty band of higher energy. This band splitting, and the subsequent band gap which forms due to structural changes connected with the Peierls distortion, may transform a metallic conductor to a semiconducting or insulating material.

1.2.3 The complex of TTF and TCNQ - The prototype organic metal.

The complex of TTF-TCNQ illustrates the salient structural features required for conducting organic materials. The X-ray crystal structure of the complex (Fig. 1.3) shows that the near planar TTF and TCNQ molecules crystallise in a 1:1 complex with well defined segregated stacks of radical ions[8], which are tilted with respect to the stacking axis (crystallographic axes b) to give rise to the so-called "herringbone" structure. It is clear from the structure that each molecule is equidistant from its neighbour and is skewed to such an extent that the exocyclic bond of one molecule lies directly over the ring of its neighbour. These combined effects lead to weak interstack delocalisations but gives rise to strong intrastack interactions, creating the highly anisotropic conductivity, which is 500 times that in the crystallographic a or c axes.

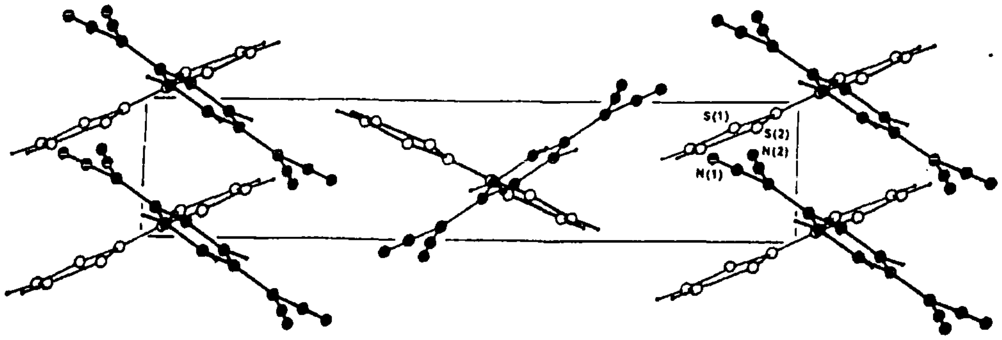


Fig. 1.3: *X-Ray structure of TTF-TCNQ.*

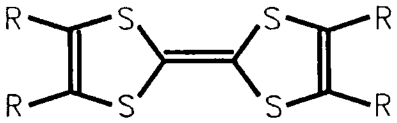
The TTF-TCNQ complex exhibits typical metallic behaviour, as when it is cooled the conductivity rises from 500 Scm^{-1} to ca. 1 x 10^4 Scm^{-1} at 59K. If the complex is cooled further three phase changes occur at 53, 47 and 38K, leading to an insulating state. X-Ray and neutron scattering spectroscopy have associated these transitions to Peierls distortions occurring both within, and across, the individual stacks leading to a fully 3-D system.

X-Ray scattering[9] and infrared spectroscopy[10] has found the degree of charge transfer to be 0.59 electrons per molecule from TTF to TCNQ. The associated partly filled conduction band allows high conductivity to occur. Other analogous salts of TTF, such as $TTF^{+\cdot}$-Br^-, have a degree of charge transfer of 1. This gives rise to a filled band and hence, a low conductivity value of σ_{rt}= 1 x 10^{-11} Scm^{-1} [11].

1.3 ORGANIC DONOR MOLECULES BASED ON TTF.

1.3.1 Modified TTF molecules.

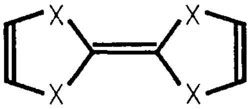
The basic structure of TTF (2) lends itself excellently to structural modification, and this has provided a fruitful framework for chemists to explore synthetic routes to new tetrathiafulvalenes[12]. The first modification to TTF was to increase the donor properties of the molecule by alkylation. The most notable example is tetramethyl-TTF (TMTTF, 3)[13], which was found to form a metallic complex with TCNQ (σ_{rt}= 200-500 Scm^{-1}). The metal-insulator transition occurred at a temperature which was above that for TTF-TCNQ. This can be explained in terms of reduction of interstack coupling which causes an increase in one-dimensionality. Introduction of electron withdrawing groups (4) tends to yield either insulating or semiconducting complexes[12a].



(3) R= CH_3
(4) R= CF_3

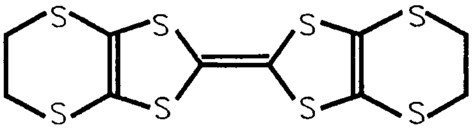
Another modification to TTF has been the insertion of the larger chalcogen atoms, selenium and tellurium, which offer more diffuse 'p' and 'd' orbitals. The associated increased intrastack π interactions, gives rise to greater conduction bandwidths. The enlargement in orbital size also causes an increase in 2-dimensional character due to an increase in interchain interactions, which has a cumulative effect of helping to thwart the Peierls distortion.

Tetraselenafulvalene (TSF, 5)[14,15] and tetratellurafulvalene (TTeF, 6)[16,17] both show an increased stability of the metallic state as compared to the TTF complex with TCNQ. Indeed, TTeF-TCNQ shows no Peierls distortion down to 2K[18]. The conductivity increases as the heteroatom varies from Se to Te (σ_{rt} = 800 Scm^{-1} and 2200 Scm^{-1} respectively), which is primarily caused by conductivity enhancement in the donor stack.



(5) X= Se
(6) X= Te

The multi-sulphur donor bis(ethylene-dithio)tetrathiafulvalene (BEDT-TTF, 7), forms certain salts that are superconducting. The first pressure induced superconducting salt was that of (BEDT-TTF)$_2$ ReO$_4$[19], which has led to a range of analogous complexes of the type (BEDT-TTF)$_2$ X. X-Ray analysis has shown that the salts are isostructural.



(7)

The donor was found to be non-planar, giving rise to the lack of columnar stacking and hence reducing close π-π^* interactions. The structure is dominated by close interstack S--S interactions giving rise to a 2-D 'corrugated sheet network', which brings about the conductivity in these systems. The anions are ordered at room temperature and reside in the cavities produced by the CH_2 hydrogen atoms.

1.4 CONDUCTING LANGMUIR-BLODGETT (LB) FILMS.

1.4.1 Introduction.

The solid state electronic properties of C-T salts, are dependent upon both inter- and intra-molecular interactions within the crystal. However, recent reports concerning conducting LB Films of C-T salts, offer the exciting possibility of producing organic structures with a greater level of control over the inter-molecular architecture as compared to the corresponding single crystal materials.

The LB technique allows the transfer of a monolayer of an amphiphilic material from a water surface to a solid substrate, in such a way that well organised, ultra thin films of controlled thickness and regular molecular arrangement are assembled[20]. The method of film deposition and intermolecular side chain interactions may result in close ordered face to face stacking of molecules.

From a practical viewpoint, LB films offer advantages over single crystalline materials in that the thin films are easier to fabricate into electronic devices as compared to the more frail single crystals. It is thought that newer technological applications can be achieved by the tailor made intermolecular interactions that can occur at a LB solid surface interface[21].

1.4.2 LB Technique.

An analytically pure amphiphilic compound is dissolved in a volatile solvent (eg chloroform, acetone). A small aliquot is spread on an ultra pure water surface of a LB trough (Fig. 1.4) and the solvent is allowed to evaporate. Pressure is applied to the air water interface *via* electronically controlled barriers, so that a condensed orientated monolayer is formed.

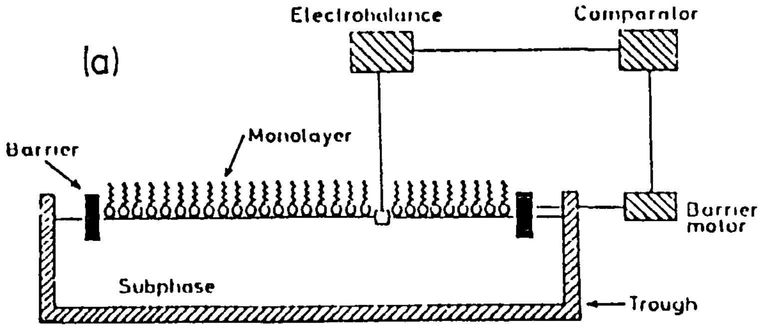


Fig.1.4: *Schematic diagram of a LB trough.*

This monolayer can be transferred onto a solid substrate (typically glass) as it is passed perpendicularly through the air water interface. Providing the molecule is hydrophobic, no pick up occurs during the first immersion, the first layer only being deposited when the solid substrate is withdrawn. Following the first immersion there are a number of possible deposition modes that can be observed. In Y-type deposition, which is the most common, a monolayer is transferred from the water surface on both the inward and outward movement of the solid substrate, which gives a head to tail type configuration (Fig. 1.5). In X-type deposition, the monolayer is transferred as the substrate is lowered into the subphase, whereas in Z-type, deposition only occurs as the substrate is being raised.

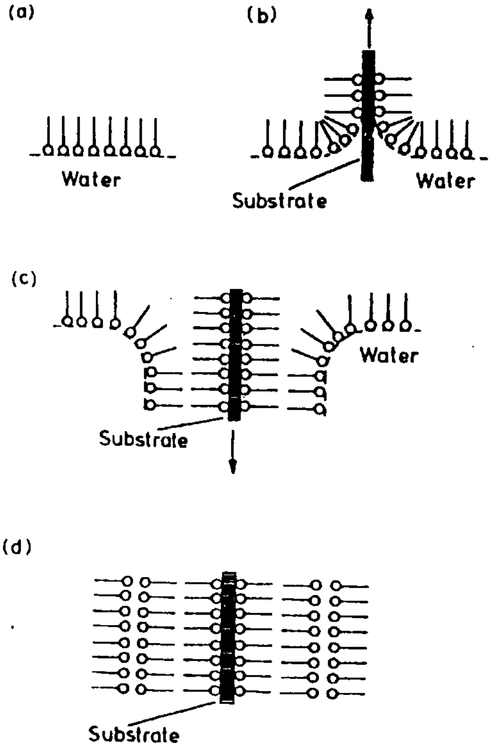


Fig. 1.5: *Y-type LB deposition.*

In essence, the LB films thus formed on the glass substrate are segregated stacks of donor and/or acceptor molecules, which generally possess a crystalline lamellar structure. Oxidative doping is brought about by exposure to chemical gaseous oxidants (such as iodine), which can permeate the film to yield a mixed-valence conducting system. Another possibility of producing a conducting LB film, is *via* electrochemical oxidation during, or after, film deposition using dopant anions (ClO_4, PF_6 etc.) which can be introduced into the structure[21a].

A major shortcoming of the LB technique is the poor long term chemical, thermal or mechanical stability of the films. Although film preparation takes place under ambient conditions in which most molecules are stable at the air-water interface, the floating film is in a metastable state which is far removed from thermodynamic equilibrium. As a result, structural defects in the assembled multilayer structure may occur due to spontaneous reorientation of the molecules, following transfer of material to a solid substrate.

1.4.3 Criteria for donor molecules for LB films.

The molecule must have a hydrophilic head group, which is connected to a hydrophobic portion, which usually consists of a long alkyl chain (>C16) or chains (Fig. 1.6).

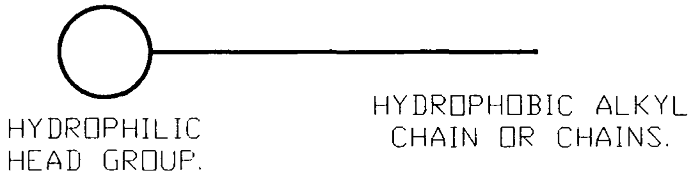


Fig.1.6: *Diagrammatic representation of amphiphilic molecules required for LB films.*

Work by Lerstrup *et al* has suggested that a hydrophilic functionality in the side chain must be located at, or very near to, the hydrophilic head group if high quality films are to be produced[22]. However, in recent years completely different types of compounds which do not possess the classic 'cylindrical' geometry, have found to produce good quality films. Notable examples include: porphyrins,[23] phthalocyanines,[24] oligothiophenes,[25] and buckminsterfullerene[26].

1.4.4 Characterisation of LB films.

There are a number of methods available to gain an insight into the physical nature of the molecules within the film, both prior to, and after, the doping process that brings about conductivity. A direct technique that can be used prior to the transferral of the monolayers to the solid substrate is the measurement of a surface pressure (π) *versus* area per molecule (A) isotherm (Fig. 1.7). The isotherm is recorded as the barriers of the LB trough are slowly closed and a condensed orientated monolayer is formed. The isotherm is indicative of the quality of the monolayer formed, as one can extrapolate to zero surface pressure and hence, estimate the area per molecule. This value can be compared to data derived from conventional space filling models and X-ray crystal structures, which can give an insight into the compounds purity and solubility in the subphase, together with how the side chains are orientated relative to the subphase plane.

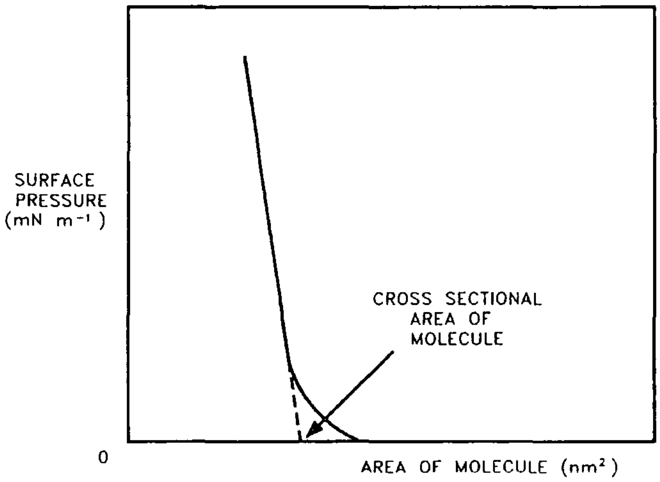


Fig. 1.7 *Typical isotherm for an amphiphilic mono-substituted compound.*

Conductivity measurements of the deposited monolayers are usually obtained using a two probe technique (Fig. 1.8). Measurements of the lateral direct current conductivity can be obtained both prior to, and after, doping with iodine vapour.

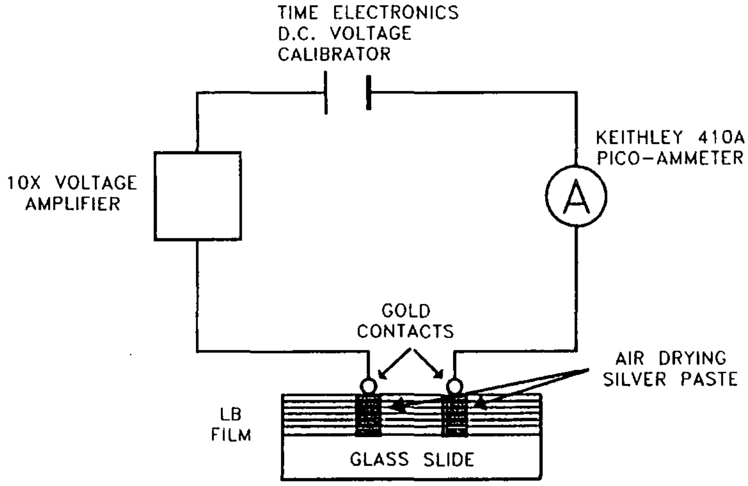


Fig. 1.8: *Experimental arrangement for lateral d.c. conductivity measurement.*

UV-visible spectroscopy is a most valuable spectral method for characterising LB films. UV data give critical information both prior to, and after doping, with respect to the amount of π-π^* intermolecular transitions and C-T absorptions that occur in the film. Optical density *versus* the number of deposited layers can reflect the reproducibility of monolayer deposition.

Transmission IR spectra, and in particular, the more sensitive FTIR technique is a very useful tool for extracting bonding information within the film. IR spectroscopy on the undoped films gives information concerning the bonding in the LB material. The spectra obtained after doping often show the presence of C-T bands and other new features due to mobile conduction electrons in the film.

1.5 LB FILMS OF C-T SALTS.

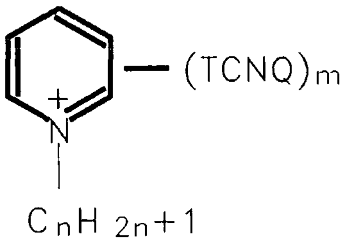
1.5.1 Introduction.

The following sections will review the important families of C-T materials that are known to form conducting LB films. Practical emphasis will be placed on the cation radical salts, as this is the most relevant to the authors research.

1.5.2 LB Films of anion radical salts.

The first conducting LB films of a C-T material were reported in 1985 by Barraud and co-workers, who found that LB films of a 1:1 charge transfer complex N-docosylpyridinium-TCNQ[27] (8), had low lateral conductivity in the undoped state.

However, upon doping with iodine vapour, much higher conductivity was attained ($\sigma_{\parallel}$= 10^{-1} Scm^{-1}). A more detailed investigation[28] revealed that before doping there existed sheets of $(TCNQ^{-})_2$ dimers with their molecular plane parallel to the plane of the substrate; reorientation of TCNQ occurred upon doping.



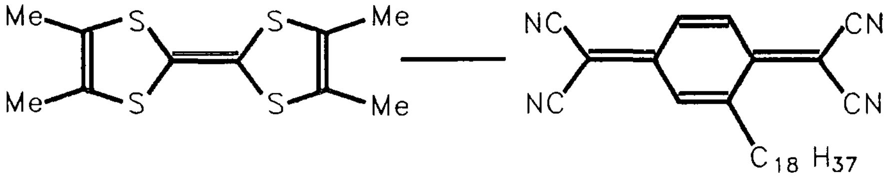
	n	m
(8)	22	1
(9)	22	2
(10)	18	1

Nakamura *et al*[29] confirmed that as deposited the films were not highly conducting and showed that orientation of the TCNQ molecules could be changed by varying the LB deposition conditions. LB films of the 1:2 complex (9), without any doping, showed high conductivity ($\sigma_{\parallel}$= 10^{-2} Scm^{-1})[30].

At Durham, studies of multilayers of the 1:1 salt (10) gave rise to a conductivity of $\sigma_{\parallel}$= 10^{-2} Scm^{-1} in the as-deposited state[31]. Infrared, UV and low-angle X-ray diffraction studies show that both components have their long axes inclined at an angle of about 30^0 to normal. This orientation is different from that obtained by Barraud[29] for complex (8). The nature of conduction in LB films of (10) is unclear and may involve OH^- ions, which were unintentionally introduced during deposition[31c].

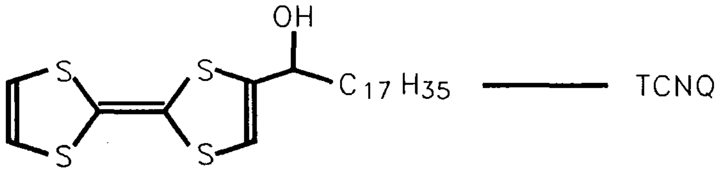
1.5.3 TTF-TCNQ C-T complexes.

In this class of LB materials, the hydrophobic chain may be attached to either the TTF, the TCNQ moiety, or to both. The first reported example was in 1986[32] by Nakamura *et al*, who prepared a 1:1 complex (11) which displayed a maximum conductivity of σ_{rt}= 10^{-2} Scm^{-1} without doping.



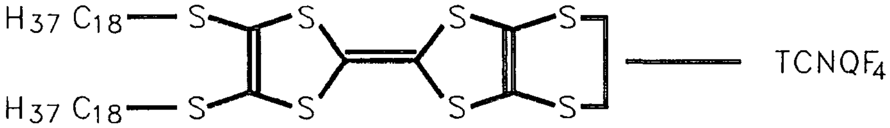
(11)

At Durham, Dhindsa *et al* have studied LB films of the 1:1 complex (12) which had low conductivity (σ_{rt}= 10^{-3} Scm^{-1}) which was further reduced (σ_{rt} = 10^{-6} Scm^{-1}) upon doping with iodine[33]. Attempts to form LB films of the donor moiety alone were unsuccessful. This is probably due to the OH group hindering the formation of a condensed monolayer.



(12)

Barraud and co-workers formed a LB film of complex (13), which was insulating as deposited due to complete charge transfer, but upon doping with iodine a mixed valence complex was formed and the conductivity rose to $\sigma_{rt}= 5x10^{-2}$ Scm^{-1} [34].



(13)

Spectroscopic studies have suggested that the $TCNQF_4$ molecules are fully ionised both prior to, and after, doping. The conduction properties displayed by the complex, are therefore due to the doping process converting the donor to a mixed valence species.

Alternate-layers of octadecyl-TCNQ and octadeconyl-TTF have been formed using a specially designed trough, which enforces segregated stacking of the donor/acceptor complex. A semi-conducting multilayer structure was formed, which can be represented as in (Fig. 1.9), which displayed a maximum conductivity of $\sigma_{rt}= 5x10^{-3}$ Scm^{-1} [35].

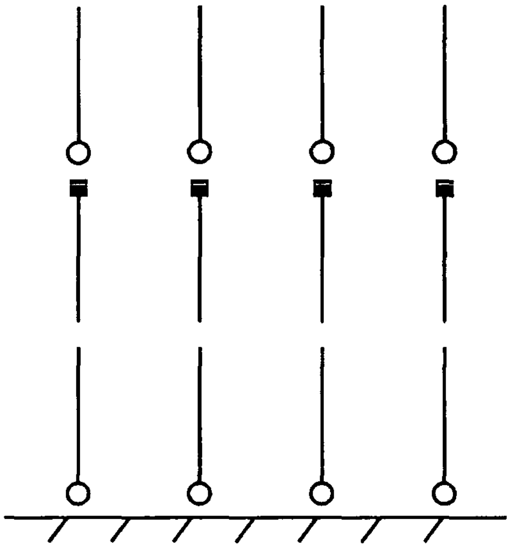
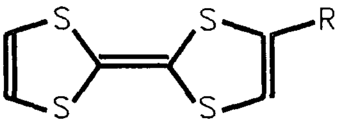


Fig. 1.9: *Schematic representation of the molecular arrangement showing alternate layer structure.*

1.5.4 Cation radical salts.

To date, cation radical salts have provided the best quality semiconducting films. The films are formed of the neutral donor, which is subsequently oxidised to yield a conducting salt with a partly filled band structure, of the type (Donor^{+}),(X^{-})n (where n<1). This has obvious advantages over the donor/acceptor complexes mentioned earlier, since only one bulky species must be ordered to form regular films.

At Durham, previous workers have attached one hydrophobic chain by several functional groups eg. (14)-(17)[36], which appear to play a profound role in ordering the LB film when deposited in a Y-type manner.



(14) R = $C(O)(CH_2)_{16}CH_3$
(15) = $C(O)(CH_2)_{14}CH_3$
(16) = $C(S)O(CH_2)_{15}CH_3$
(17) = $C(O)O(CH_2)_{15}CH_3$

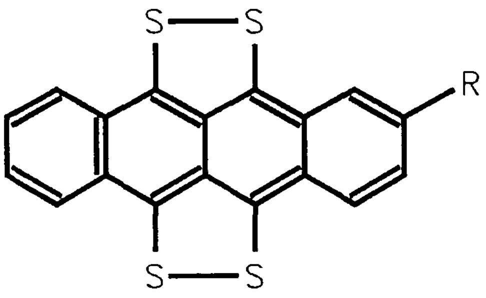
Cyclic voltammetry has shown that the attachment of the electron withdrawing functionality reduces the donor ability. This may be offset however, by making the TTF portion of the molecule more polar, which should aid film deposition.

LB films of hexadeconyl-TTF (15) gave an insulating film as deposited[37]. Upon doping with iodine vapour the films initially become more insulating; the conductivity increased to $\sigma_{rt} = 10^{-2}$ Scm^{-1} after several hours in air. The doping process was studied using UV, IR and X-ray photoelectron spectroscopy which showed that immediately following doping, an insulating state occurs due to full charge transfer. Partial release of iodine from the film, with time, forms a conducting stable mixed-valence state.

Absorption spectra of compound (15) after doping, show an intermolecular C-T band at 2100nm for the iodine doped films, which is characteristic of an organic conductor. The optical density of the doped film varies approximately linearly with the number of layers in the LB film, thus indicating the ordered nature of the film is not disrupted upon doping throughout the multilayers. Polarised i.r. and low angle X-Ray diffraction studies on these films have shown that the donor molecules are orientated near vertical to the substrate surface, with lateral electron mobility *via* well-ordered, partly oxidised TTF rings[37c].

The thioester (16) forms excellent quality LB films, which exhibit a lateral room temperature conductivity of σ_{rt}= 1.0 Scm^{-1} after doping; two orders of magnitude higher than the acyl (15) or ester (17) derivatives[38].

Good quality films of tetrathiatetracene (TTT) derivatives (18)[39] and (19)[40] have been reported. This donor (unsubstituted) is known to form highly conducting complexes[41]. LB film formation of (18) and (19) required mixing the donors with methylarachidate (3:1 ratio) to form Y-type films. Oxidation to form conducting films was brought about in three ways: (i) treatment with iodine vapour, (ii) treatment with aqueous KI_3 solution before or after film formation, (iii) anodic oxidation with aqueous $LiClO_4$ solution during, or after, film formation.



(18) R = CF_3
(19) R = $O(CH_2)_{17}CH_3$

The doping methods employed seemed to have profound effect on the conductivity and ordering within the film[40]. As deposited films were insulating (σ_{rt}= 1x10^{-7} Scm^{-1}), the conductivity rising to σ_{rt}= 1.3x10^{-4} and 10^{-2} Scm^{-1} after doping for (18) and (19), respectively. However, the doped TTT films were quite unstable to the loss of iodine, which in turn reduced the conductivity of the films. This is markedly different from that of the mixed valence TTF materials (14)-(17), which retain their high conductivity for several weeks in air.

1.5.5 Organometallic systems.

Conducting LB films of metal (dmit)$_2$ complexes with long chain ammonium or pyridinium cations (20)-(22), have been studied with the hope that increased dimensionality within the film structure would be observed. Japanese workers in 1988[42] found that LB films of the bromine doped complex (20), had a room temperature conductivity of 10^{-2} Scm^{-1}. Unfortunately, to prevent the films on the water surface from collapsing, up to 50% icosonoic acid had to be added and a horizontal lifting technique had to be employed. The analogous Au(dmit)$_2$ complex (21) gave a much higher conductivity (σ_{rt}= 25 Scm^{-1}), which was retained on cooling down to 200K[43].

$Me_2N^+(C_{10}H_{21})_2$ ----- $Ni(dmit)_2$
(20)

$MeN^+(C_{10}H_{21})_3$ ----- $Au(dmit)_2$
(21)

$(Py^+\text{-}C_{18}H_{37})_2$ ----- $Ni(dmit)_2$
(22)

Work at Durham has shown that the long chain pyridinium-Ni(dmit)$_2$ complex (22) forms stable films without any fatty acid being required to aid film stability[44]. Y-type LB deposition was employed, which gave films that reached a maximum conductivity of σ_{rt}= 8x10^{-1} Scm^{-1} after doping. IR and XPS studies have shown that during the doping process, oxidation occurs in the vicinity of the nickel atom to yield a mixed valence C-T system.

1.6 SYNTHETIC ROUTES TO FUNCTIONALISED TTF DERIVATIVES.

1.6.1 Introduction.

It is clear from the discussion of LB materials, that LB films of the cation radical salts produce the best results in terms of film quality, conductivity and stability. Work in our laboratory has suggested that the TTF derivatives should be monofunctionalised amphiphilic molecules, with the long alkyl chain attached to the TTF moiety *via* a functional group. There are two possible strategies for synthesising, monofunctional TTF derivatives suitable for LB film formation: (i) direct synthesis from TTF; (ii) building up the TTF unit so that it incorporates the functionality. However, both of these methodologies have their limitations.

1.6.2 Synthesis of mono-functionalised TTF's.

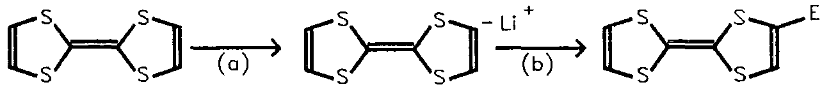
The low ionisation potential of TTF (2), makes it difficult to substitute the ring system directly by most known methods. Coupling techniques which couple substituted 1,3-dithiole-2-thione moieties using trialkyl phosphites, have had some success in producing symmetrically substituted TTF's. However, this method is limited by the incompatibility of many functional groups with the coupling reagent[45]. The formation of unsymmetrical derivatives using cross-coupling techniques is often unsatisfactory due to the formation of other coupled products, which can be difficult to separate from the desired material.

In an attempt to circumvent this, Cava *et al* reported in 1978[46] a series of unsymmetrical TTF derivatives synthesised by the reaction of dithiolium salts with dithiolium phosphoranes, and other unsymmetrical derivatives have been prepared by the Hurtly Smiles synthesis[47], but this is not a general method.

The first monofunctionalised TTF derivatives formed directly from TTF were reported by Green[48], by reaction of the TTF anion (23) formed using non oxidising nBuLi. The TTF anion (23) was trapped with solid CO_2 and $Et_3O^+PF_6^-$ to give moderate yields of the acid and ethyl derivatives, respectively.

1.6.3 The TTF anion and its chemistry.

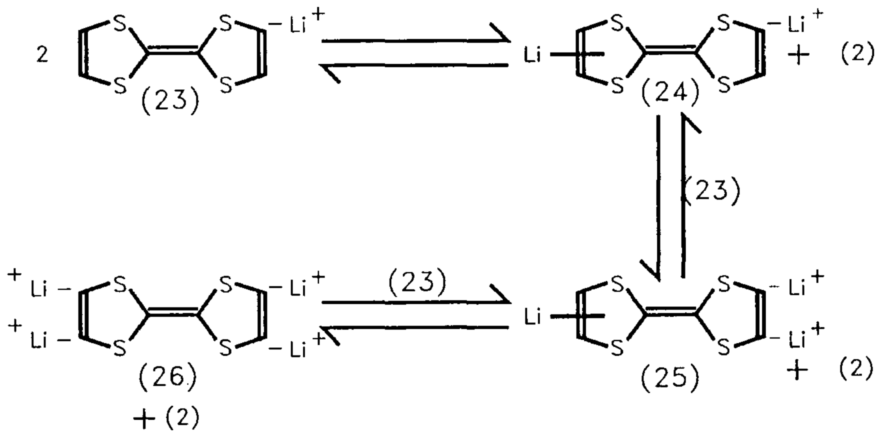
Green's later work showed that the TTF anion (23) could be formed *via* the action of LDA or nBuLi in ether at -78°C and could be trapped with a wide range of electrophiles (Scheme 1.1) to give mono-substituted, highly functionalised derivatives, in modest yields (30-67%)[49].



(2) (23)

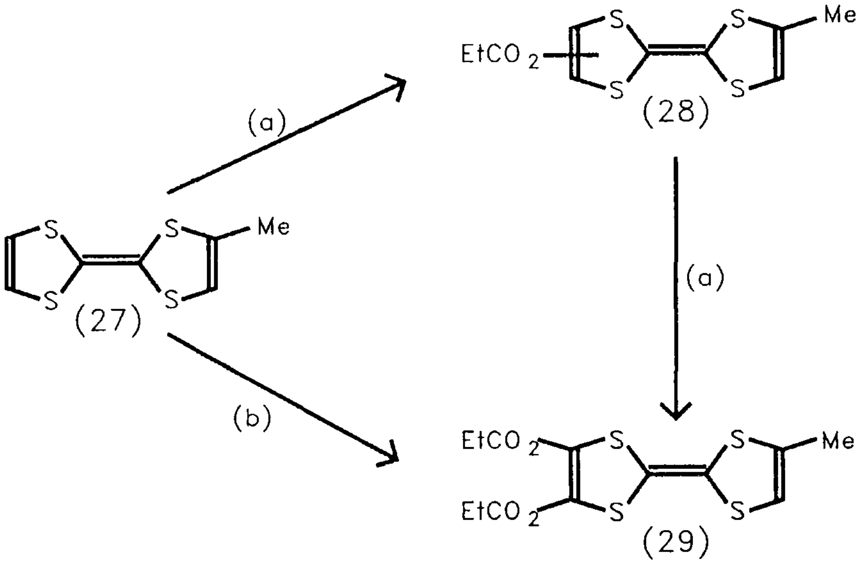
Scheme 1.1: Reagents: *(a) LDA (1.0 equiv.), -78°C; (b) Electrophile (E).*

A major problem with this methodology is the ready disproportionation of the TTF anion (23), at temperatures above -78°C, to give multilithiated species, and hence, multi-substituted products (Scheme 1.2). However, if the temperature is carefully maintained at -78°C, this technique allows a wide range of functional groups to be introduced, to give mono-functionalised derivatives, in a one-pot reaction direct from commercially available TTF.



Scheme 1.2: *The disproportionation of the TTF anion*

The multilithiated products were trapped as carboxylic acid derivatives, by the addition of solid CO_2, when the reaction was carried out at -20°C, or when (23) was formed at -78°C and then warmed to -20°C. The addition of two equivalents of LDA to TTF gave the 4,4'(5')-disubstituted product; none of the 4,5-disubstituted product was observed, possibly due to steric reasons. Dilithiation of 4-methyl-TTF (27) gave the 4',5'- diester (29) exclusively, upon the addition of ethyl chloroformate (Scheme 1.3).



Scheme 1.3: Reagents: *(a) LDA, $ClCO_2Et$ (1 equiv.); (b) LDA, $ClCO_2Et$ (2 equiv.).*

The above substitution patterns can be rationalised by the electron donating effect of the methyl group of (29) making the adjacent vinyl hydrogen less acidic and hence making the 4',5' product more favourable. In general, it was shown that electron donating substituents on TTF decreased the acidity of the adjacent proton and therefore directed the sustitution on the other ring. Conversely, electron withdrawing groups favoured substitution on the same ring.

Cyclic voltammetry studies on the substituted TTF's showed that substitution causes quite profound changes in the oxidation potentials as compared to (2). Electron withdrawing substituents seemed to destabilise the radical cation and dication states, giving rise to increased oxidation potentials and subsequently, rendering them poorer donors. Electron donating substituents give rise in general to better donors than the parent TTF (Table 1.1).

COMPOUND	$E_1^{1/2}$	$E_2^{1/2}$
(2)	0.34	0.71
(27)	0.33	0.70
(28)	0.45	0.81
(29)	0.54	0.87

Table 1.1: *Oxidation potentials of TTF derivatives. (Peak potentials volts vs SCE, CH_3CN, 0.1 M tetraethylammonium perchlorate, 0.2 V sweep rate, Pt electrode).*

It has been shown that all four protons of TTF (2) can be readily removed by the reaction of four equivalents of LDA[50] or phenyllithium[51] at -78°C. The resultant tetra-anion (26) can be reacted with elemental sulphur, selenium or tellurium, followed by alkyl halides, to yield TTF derivatives with thioalkyl, selenoalkyl or telluroalkyl chains in good yield (50-70%)[52].

1.7 CONCLUSIONS.

The study of crystalline C-T salts based on TTF, continues to provide new metallic and superconducting compounds. The development of high quality, highly conducting LB films is, and should continue, to go hand in hand with the development of new C-T materials. The development of new conducting heterocyclic systems often lend themselves well to functionalising with long alkyl chains and hence, offer the potential of forming LB films. A wide range of good quality LB films of TTF systems have been reported, particularly the radical cation salts with carbonyl and thiocarbonyl groups adjacent to the ring, but unfortunately the conductivity remains lower than the single crystal materials. However, as our knowledge increases concerning what factors govern the degree of conductivity in these systems, more highly conducting materials should be produced.

The methods of synthesising mono-substituted, highly functionalised long chain TTF materials necessary for film formation are few. The TTF anion route offers the best possibility for producing highly functionalised compounds in simple one-pot procedures. Unfortunately, this is often offset by the modest yields obtained and complex product mixtures, which exaggerates the already difficult purification inherent with long chain materials.

CHAPTER TWO.

HALOGENATION AND CHALCOGENATION OF TTF.

2.1 INTRODUCTION.

The TTF mono-anion route has been extended to lead to two classes of compounds, namely those with halogen and those with chalcogen substituents attached directly to the periphery of TTF. The materials produced were not in themselves suitable for LB film formation, but the information gleaned from their synthesis should open up routes to new LB materials, as well as TTF derivatives suitable for the formation of C-T salts.

2.2 HALOGENATION OF TTF.

2.2.1 Background.

There are few examples of halogens bound directly to the TTF framework. Such derivatives could be important in two main ways: (i) by thwarting the Peierls distortion, as the halogens may participate in intermolecular interactions and so stabilise the metallic state; (ii) new functionalised TTF's could be prepared from them due to the chemical reactivity of the halogen atoms.

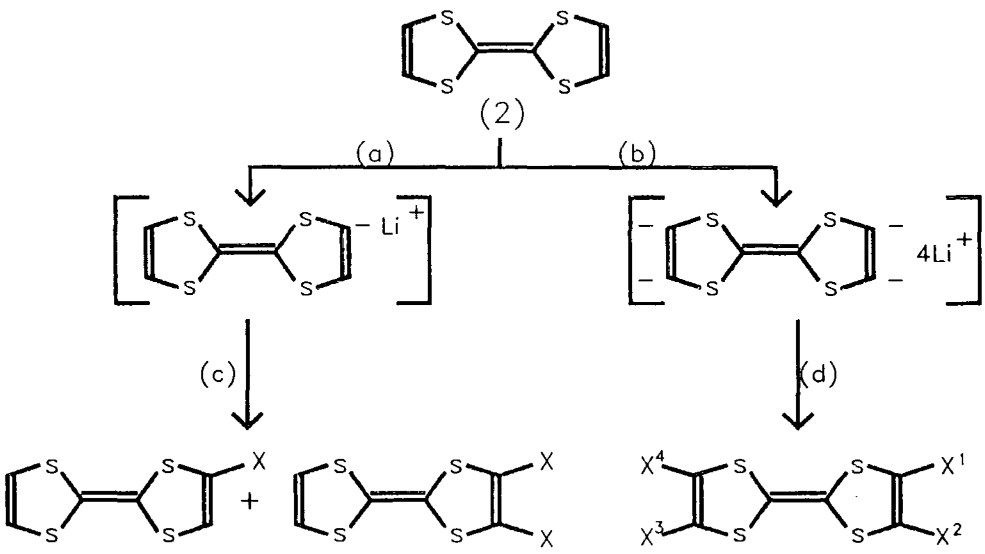
The first report of halo-TTF's was in 1976[53] by Engler, who discussed the cyclic voltammetry of isomeric mixtures of dibromo-TTF's. Cyclic voltammetry of monoiodo-TTF (34)[54] has also been reported, and spectroscopic data have been reported for the tetrabromo derivative[55]. However, no synthetic details were given for these compounds. More recently, Bechgaard[51] reported the synthesis of tetrachloro- and tetrabromo-TTF (14-15%) from tetralithio-TTF (26) and hexachloroethane and 1,2-

dibromotetrachloroethane, respectively. While our work was in progress, Becker and co-workers[56] reported the synthesis of mono-bromo (32) and 4,5-dibromo-TTF (33) including an X-ray crystal structure of the latter. However, this route using one equivalent of 1,2-dibromotetrachloroethane as the brominating agent and LDA or PhLi as the metallating agent, led to complicated mixtures including tri- and tetrabromo-TTF.

2.2.2 A new route to halogenated TTF's.

Work in our laboratory has provided the first simple route to monochloro- (30), monobromo- (32) and monoiodo-TTF (34)[57] in reasonable yield, direct from the TTF anion (23) using the appropriate p-toluenesulphonyl halides[58], which are known to be effective halogenating agents for organolithium compounds[59]. This use of p-toluenesulphonyl chloride has also provided an improved route for forming tetrachloro-TTF (35).

TTF (2) was lithiated following a similar procedure described by Green[49]. The addition of the appropriate p-toluenesulphonyl halide to the TTF anion gave the mono-halogenated TTF derivatives (30) (48%), (32) (38%), and (34) (34% yield), together with a small amount of di-halogenated species (31) and (33). Surprisingly, no diiodo-TTF was observed; possibly due to steric hindrance *via* the iodine atom preventing any second substitution. For all of these halogenation reactions, as much as 30% of the starting TTF was recovered, which could be used in subsequent reactions.



(30) X= Cl
(32) X= Br
(34) X= I

(31) X= Cl
(33) X= Br

(35) X= Cl

Scheme 2.1: Reagents: *(a) LDA (1.1 equiv.); (b) LDA (4.4 equiv.); (c) TsX' (1.1 equiv.); (d) TsCl (4.4 equiv.).*
[Ts= p-toluenesulphonyl. X'= Cl, Br (36), I (37)]

The disubstituted TTF derivatives were clearly identified as the 4,5-disubstituted isomers (31) and (33) from their proton NMR spectra. Compound (30) displayed two singlets at δ 6.33 (2H, protons X^3 and X^4) and 6.15 (1H, proton X^2), while for the dichloro- derivative (31), only one singlet was observed at δ 6.29, ie. the resonance of substituent X^2 in structure (30) was absent, whereas the chemical shift of protons X^3 and X^4 was essentially unchanged by the introduction of the second chlorine atom. The NMR data were similar for the mono- and dibromo- derivatives (32) and (33) but the separation of the singlets for (32) was less when compared to (30). Interestingly, for the monoiodo derivative (34) the resonance from proton X^2 is now observed at a lower field than the resonance from protons X^3 and X^4.

The 4,5- disubstitution was further proved by Becker's group by obtaining an X-ray crystal structure for 4,5- dibromo-TTF which had identical spectral properties and melting point, to the product we obtained using our route[56]. The formation of the di- halo species by our route was not unexpected bearing in mind the ready disproportionation of the TTF mono-anion to multi-lithiated species. Also, the first halogenation causes the adjacent proton to become more acidic due to the electron - withdrawing effect of halogen atom, which thus accelerates this disproportionation and directs the second lithiation and hence the second substitution, to the adjacent site of the ring. Thus, the formation of products (31) and (33) is consistent with Green's[49] observation that the presence of an electron withdrawing group on TTF leads to a second substitution at the adjacent carbon.

The efficacy of this route to halogenate TTF was further demonstrated by the formation of (35) which we obtained in 30% yield, double that produced by Bechgaard's route[51]. Tetralithiation of TTF[50] followed by the addition of p-toluenesulphonyl chloride, gave (35) together with recovered TTF (25%). However, when the synthesis of tetraiodo-TTF was attempted using the same methodology, t.l.c. and mass spectral evidence suggested that the major product was monoiodo-TTF (34).

Solution electrochemistry studies using cyclic voltammetry are consistent with previously reported CV data[51,54]. The results show that the addition of a halogen atom to the periphery of TTF causes the ionisation potential to be considerably increased. The addition of a second halogen atom causes further destabilisation of the radical cation and dication states resulting in an increased oxidation potential (Table 2.1).

Compound	X^1	X^2	X^3	X^4	$E_1^{1/2}$	$E_2^{1/2}$
(2)	H	H	H	H	0.34	0.78
(30)	Cl	H	H	H	0.56	0.78
(31)	Cl	Cl	H	H	0.70	0.97
(32)	Br	H	H	H	0.55	0.76
(33)	Br	Br	H	H	0.65	0.95
(34)	I	H	H	H	0.55	0.80
(35)	Cl	Cl	Cl	Cl	0.8	0.95

Table 2.1: *Half wave potentials for halogenated TTF derivatives. ($1x10^{-5}$M solution in CH_2Cl_2, under argon, Pt electrode, relative to Ag/AgCl with tetrabutylammonium perchlorate (0.01M) Scan rate 100mv s^{-1}).*

Attempts to displace the halogen of (30) and (32) with sodium methoxide in order to form the much sought after alkoxy TTF's was unsuccessful, giving rise to recovered starting material.

2.2.3 TCNQ Complexes of (30) and (32).

To date, there are no published details concerning the TCNQ salts of halogenated TTF's. We have obtained charge transfer complexes, in powder form, of TCNQ with both (30) and (32). The stoichiometry based on CHN analysis found the complexes to be of the type $(30)_2$ $(TCNQ)_1$, [complex (38)], and $(32)_2$ $(TCNQ)_1$, [complex (39)]. Compressed pellet conductivity measurements gave a very high conductivity of 1.0 Scm^{-1} for both (38) and (39). Unfortunately, X-ray quality crystals could not be obtained for these complexes.

2.3 CHALCOGENATION OF TTF.

2.3.1 Background.

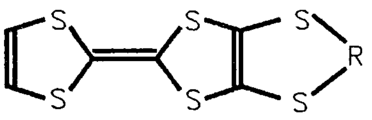
At the outset of our work there were no examples in the literature which described the introduction of one or two sulphur, or selenium atoms, to the periphery of TTF, directly from lithiated species. The only reports in the literature involved the synthesis of tetra-substituted species by tetra-lithiation of TTF, followed by the addition of excess elemental chalcogen and electrophile, to give fully substituted TTF's[52]. Engler *et al*[60] reported that dithiapendione (108) under basic conditions, offers a route to TTF tetrathiolate salts, which can be trapped with electrophiles to yield tetrathioalkyl-TTF's.

Alternative strategies involving the phosphite coupling of 4,5-dithio-1,3-dithiole-2-thione moieties, synthesised from lithiated vinylene trithiocarbonate[34a] or by alkylation of the zincate salt[61] (46) have been reported. However, synthesis of the required thioalky-TTF using self- and cross-coupling methodologies often led to difficult chromatographic purification. Recent work by Kilburn *et al*[62], has used bis acetoxybenzyl protected 4,5-dithio-1,3-dithiole-2-thione precursors, which offers a versatile route to symmetrical and unsymmetrical tetrathioalkyl-TTF's.

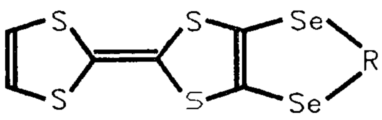
In view of the limited accessibility of mono- and bithioalkyl TTF's, we set out to attach one and two chalcogen atoms directly to the TTF frame using the TTF anion (23). This route allows the increased nucleophilicity of the TTF-X$^-$ anion (X= S or Se), relative to (23), to improve the low yields of reactions with electrophiles, which has hampered TTF anion chemistry. Also, the TTF-X$^-$ route has allowed the synthesis of compounds with highly-functionalised side chains (Chapter 4), that could not be synthesised by the cross-coupling route due to functional group incompatibility with the coupling reagents (*viz.* trialkyl phosphites or octacarbonyldicobalt.)

2.3.2 New synthesis of unsymmetrical tetrathiafulvalenes.

Only a few reports exist concerning unsymmetrical TTF's, where two chalcogen atoms are bound to one of the dithiole rings and are linked *via* methylene (40),(43), ethylene (41),(44) and propylene units (42),(45)[63,64].



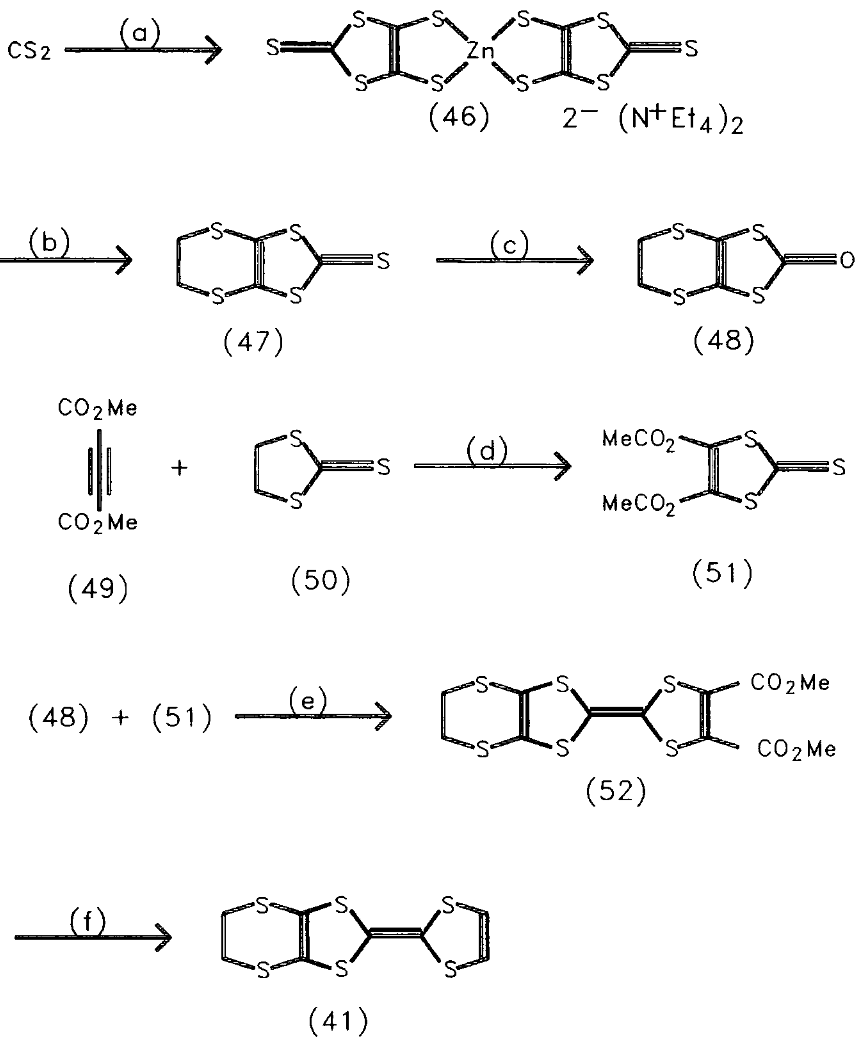
(40) R = $-CH_2-$
(41) R = $-(CH_2)_2-$
(42) R = $-(CH_2)_3-$



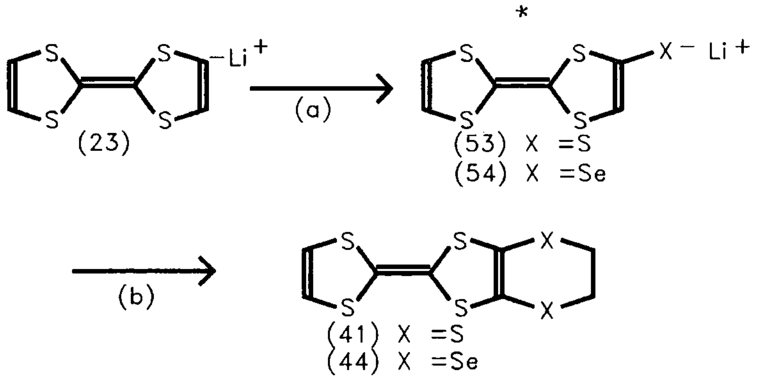
(43) R = $-CH_2-$
(44) R = $-(CH_2)_2-$
(45) R = $-(CH_2)_3-$

Salts of these donors with various anions show high conductivity, and in particular, the salt of methylenedithiotetrathiafulvalene (40) $(MDT\text{-}TTF)_2$ AuI, was found to exhibit superconducting behaviour (Tc= 3.5 K at ambient pressure)[65]. However, the synthesis of (40)-(45) in the literature by Papavassiliou *et al*, involves a multi-step route as exemplified by the synthesis of ethylenedithio-TTF (EDT-TTF) (41)[63] (Scheme 2.2).

When we repeated this synthesis, we found the methyl ester groups in (52) were resilient to decarboxylation using lithium bromide and hence low yields (5-8%) were obtained for the final step. Thus, we developed the route of chalcogen insertion to circumvent this multi-step synthesis. Compounds (41) and (44) are now available in a one-pot procedure[66], initially from the TTF mono-anion (23), in moderate yields (15-28%) (Scheme 2.3).



Scheme 2.2: Reagents: *(a) Na, DMF, $ZnCl_2$; (b) $Br(CH_2)_2Br$ (2 equiv.) reflux in CH_3CN; (c) $Hg(OAc)_2$, acetic acid/ CH_2Cl_2; (d) reflux in toluene; (e) reflux in triethylphosphite; (f) LiBr, HMPA.*



* species initially formed prior to any disproportionation.

Scheme 2.3: Reagents: *(a) S_8 or Se_8 (1.5 equiv.); (b) $Br(CH_2)_2Br$ (0.5 equiv.).*

The optimum reaction conditions were achieved by maintaining the reaction mixture at -78°C for at least 7 h., following the addition of the elemental sulphur or selenium, thus allowing the chalcogen to be fully soluble before addition of the alkylating reagent. The unsymmetrical derivatives were readily purified from TTF using silica gel column chromatography, and the recovered TTF (60%) could be used in subsequent reactions.

In an attempt to further increase the yield of the (41) or (44), an extra equivalent of LDA was added 2 hours after the addition of 2 equivalents of elemental chalcogen. However, this methodology did not increase the yield of (41) or (44) significantly.

2.3.3 X-Ray crystal structure of ethylenediseleno-TTF (EDS-TTF) (44).

X-Ray quality crystals of (44) were obtained from dichloromethane/hexane (1:1 v/v). The X-ray crystal structure (Fig. 2.1a) shows the interchanging conformational isomers that this structure exhibits in the X-ray diffractometer time scale. The X-ray crystal structure (Fig. 2.1b) shows what we believe to be a novel type of packing for a neutral TTF system. Pairs of molecules, related by an inversion centre, can be regarded as dimers with typical ring-over-bond overlap (Figs. 2.1a and 2.1b). Within each dimer, there exists a short (3.35 Å) interplanar separation between the tetrathioethene fragments (Fig 2.1b). Dimers of (44), with molecular planes orthogonal to each other, are arranged in a chess board fashion.

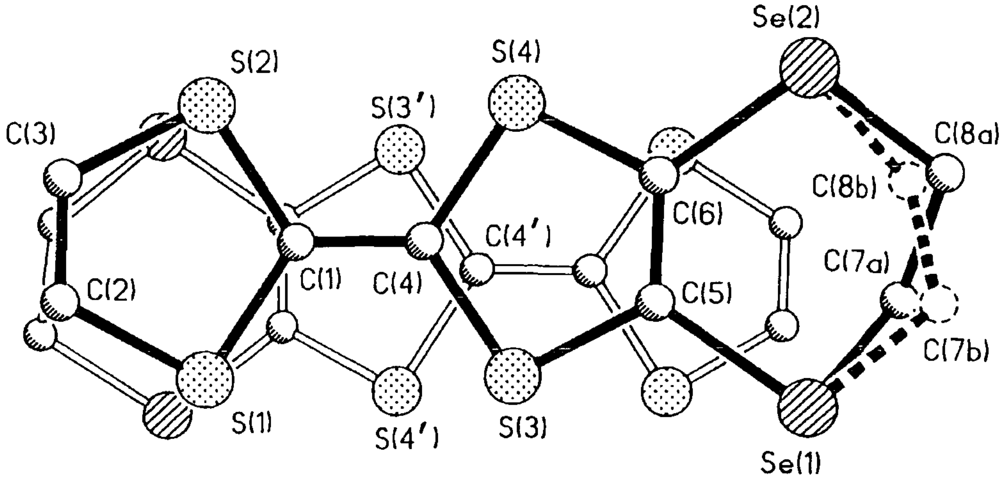


Fig. 2.1a: *X-Ray crystal structure showing the ring over bond dimerisation of (44).*

The type of packing that (44) displays, is similar to that of the κ-phases of (BEDT-TTF)$_2$X salts. However, in the κ-phases, the molecules are aligned with the long axis perpendicular to a layer (and parallel to each other), whilst the X-ray structure of (44) shows they lie within the layer and perpendicular to each other. Papavassiliou *et al*[67], reported the X-ray crystal structure of the complex (EDT-TTF)$_2$IBr$_2$. The structure showed that the complex had a similar structure to the β-form of the (BEDT-TTF)$_2$X superconducting salts, with close S-S contacts generating a "corrugated-sheet" network. This augers well for crystallisation of conducting salts of EDS-TTF (44).

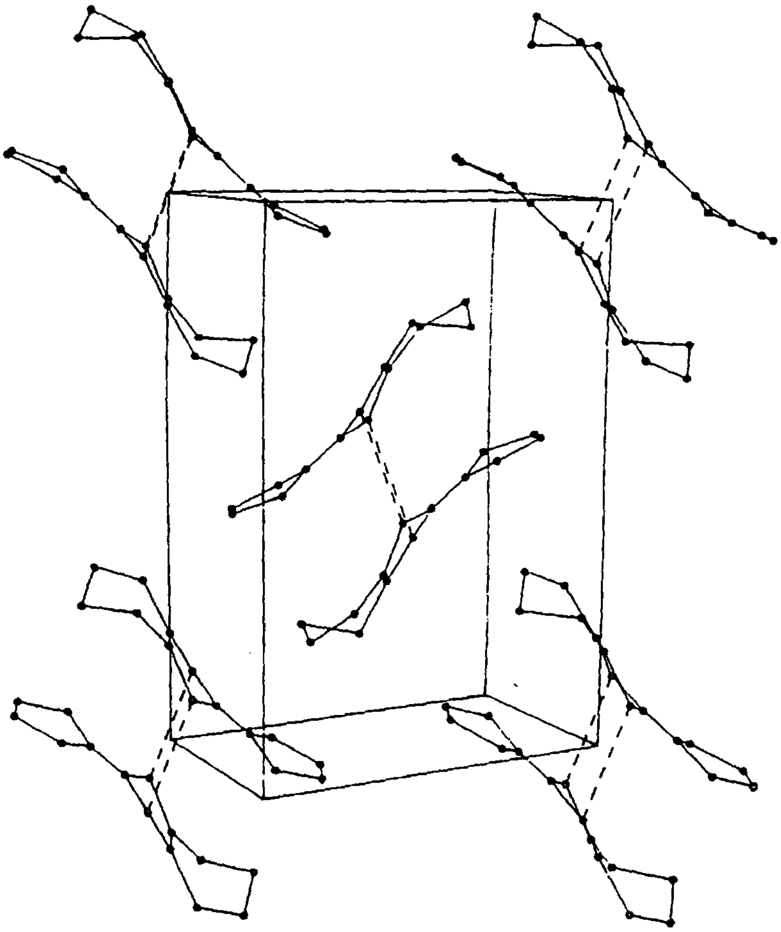


Fig. 2.1b: *X-Ray crystal structure of (44) showing arrangement of dimers.*

2.3.4 Attempts to perform anion chemistry on (41).

Endeavours to produce suitable LB materials derived from EDT-TTF (41), led us to attempt to lithiate (41). It was hoped that the acidic vinyl protons would allow us to form an anion which we could react with electrophiles in a similar fashion to lithiated TTF.

Initial efforts to form the mono-anion of (41) in THF, ether or toluene using LDA as base, were severely hindered by the insolubility of (41) in any of the aforementioned solvents at -78°C. Attempts were made to trap any anions which might be formed with acetyl chloride. Unfortunately, t.l.c. and mass spectroscopic evidence showed that none of the desired product was formed.

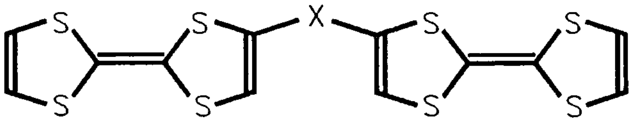
We also attempted to form the di-anion (41) by using 2 equivalents of LDA in the hope that this species would be more soluble. Again, very low solubility was observed both at -78°C and at room temperature (THF and ether). When one equivalent of acetyl chloride was added none of the desired product was observed in the mass spectrum. The pKa values of the vinyl protons, as compared to the CH_2 protons adjacent to the sulphur, were calculated using the computer program Cameo[68]. The calculated values showed that the latter protons (pKa = 35) were more acidic than the vinyl protons (pKa = 48), which may be a contributing factor to the lack of formation of the vinyl anion.

2.4 SYNTHESIS OF NEW BIS-TTF'S BRIDGED BY CHALCOGENS.

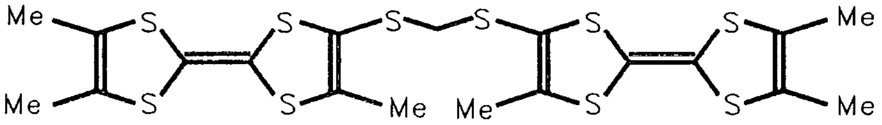
2.4.1 Background.

Recently, in the attempt to form C-T salts which exhibit metallic and superconducting behaviour, synthetic methods have been established to prepare covalently linked dimers (and higher multiples) of TTF[69-76]. The interest lies in the fact that these systems could display novel multi-stage redox behaviour with high oxidation states being accessible at relatively low potentials (eg. the tetracation for a dimeric TTF)[71]. In addition, these systems offer the potential for controlling the stoichiometry, band filling and superstructure in derived charge-transfer complexes and ion radical salts, as the juxtaposition of adjacent TTF molecules can be modified by the nature of the linking group.

To these ends, the TTF moieties have been linked by aromatic rings[70,71,75](55), alkyl and thioalkyl chains[71b,72,73,76](56),(58) and tellurium[69] (57). The use of sulphur and selenium atoms as linking groups was particularly attractive to us, as it is well known that these atoms readily participate in intra- and inter-stack interactions in other donor systems, thereby increasing the dimensionality and suppressing the Peierls distortion[77].



(55) X= -C_6H_4-
(56) -$S(CH_2)_3S$-
(57) -Te-
(59) -S-
(60) -Se-



(58)

2.4.2 Synthesis of Bis(tetrathiafulvalenyl)sulphide (59) and selenide (60).

The TTF anion methodology was applied to the synthesis of (59) and (60) using a one-pot procedure, with the corresponding di(phenylsulphonyl)sulphide (61)[78] and diselenide (62)[79] providing the bridging chalcogen atom. The monolithiated TTF (23) species was reacted with 0.4 equivalents of the di(phenylsulphonyl) reagents (61) and (62), to form the bis TTF's (59) and (60) (14% and 9% respectively)[80].

$PhSO_2$-X-SO_2Ph
(61) X = S
(62) X = Se-Se
(63) X = S-S

In endeavours to synthesise the analogous disulphide $(TTF)_2S_2$, reagent (63) was synthesised and reacted with (23) to give (59) (8%) exclusively. Attempts to oxidise the bridging sulphur of (59), using 1 equivalent of 3-chloroperbenzoic acid, led to oxidation of the TTF moieties.

2.4.3 Solution electrochemistry of (59) and (60).

The solution electrochemistry of (59) and (60) has been studied by cyclic voltammetry. The cyclic voltammograms, which are identical for both compounds (Fig. 2.2), reveal three distinct oxidation waves. The first two oxidations ($E_1^{1/2}$= 0.49 V and $E_2^{1/2}$= 0.61 V) are both one-electron processes and repeated cycling between 0.0 V and 0.70 V established that these two oxidations are reversible. However, cycling between 0.60 V and 1.10 V showed the third oxidation to be irreversible.

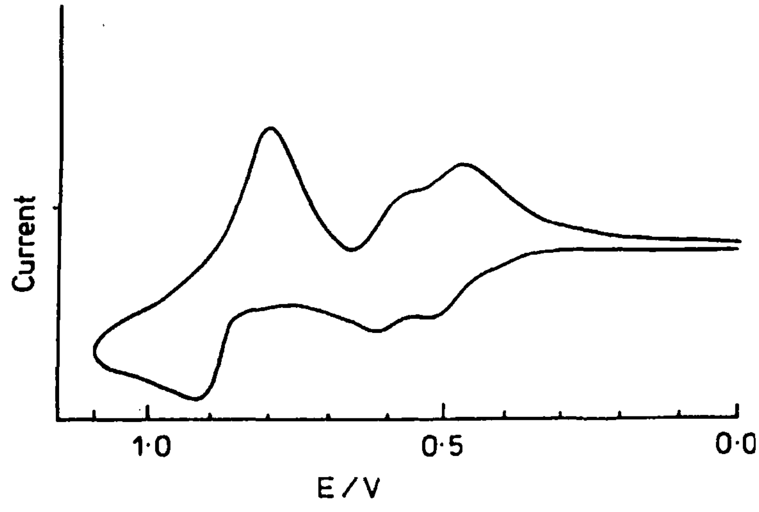


Fig. 2.2: *Cyclic voltammogram of compound (59). [Compound (59) (ca. 1 x 10^{-5} mol dm^{-3}), $Et_4N^+PF_6^-$ (ca. 0.01 M) in dry dichloromethane, under nitrogen, 20 °C, versus Ag/AgCl, Pt electrode, scan rate 100 mV s^{-1}].*

The aforementioned data are consistent with the sequential formation of mono- and di-cationic species TTF-S-$TTF^{+\bullet}$ and $TTF^{+\bullet}$-S-$TTF^{+\bullet}$, respectively. The third irreversible oxidation corresponds to the formation of the tri- and tetra-cationic species at $E_3^{1/2}$= 0.86 V. The oxidations $E_1^{1/2}$ and $E_2^{1/2}$ are separated by 0.12 V which is probably due to intra- or inter-molecular Coulombic effects. This value is different from that reported for the tellurium analogue (57)[69] (ΔE= 0.34 V *versus* Ag/AgCl, glassy carbon electrode, in MeCN-THF). However, the value observed for (59) is similar to that reported for (58) (ΔE= 0.135 V), in which the TTF's are electronically isolated by methylene linkages[71]. It was thought that the bridging chalcogen atoms in (59) and (60) could electronically couple the two TTF moieties to some extent. However, extended Hückel calculations by other workers have recently suggested that through-bond interactions between TTF units within the dimers, will be very weak irrespective of the linking group[74]. The very similar electrochemical results for (59) and (60) support this.

2.4.4 X-Ray crystal structure of (59).

The X-ray crystal structure of (59) (Fig. 2.3a), shows that there are two independent molecules per unit cell. The molecule is bent about the bridging sulphur with a C(6)-S(5)-C(7) angle of 100.6°.

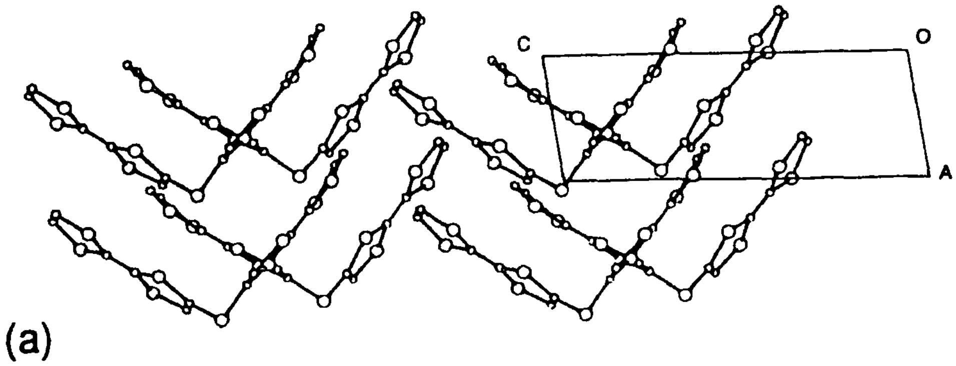


Fig. 2.3a: *Single crystal X-ray structure of compound (59): view along the b axis.*

A view along the b axis (Fig. 2.3a) shows that each TTF unit is slightly distorted into the chair conformation (like TTF itself)[81] and the molecules of the dimer pack are reminiscent of a flock of flying seagulls. A two-dimensional network of close sulphur-sulphur contacts (Fig. 2.3b) occurs as the stacks are 'tied' together with contacts considerably shorted than the Van der Waals distance. A much weaker 3-dimensional interaction is observed due to a non-bonded interaction g. This tight packing of a neutral TTF donor is observed in only a few other examples, notably bis(ethylenedithio)-TTF (7)[19] and (57) for which the closest intermolecular S--S distances are 3.482 and 3.53 Å, respectively.

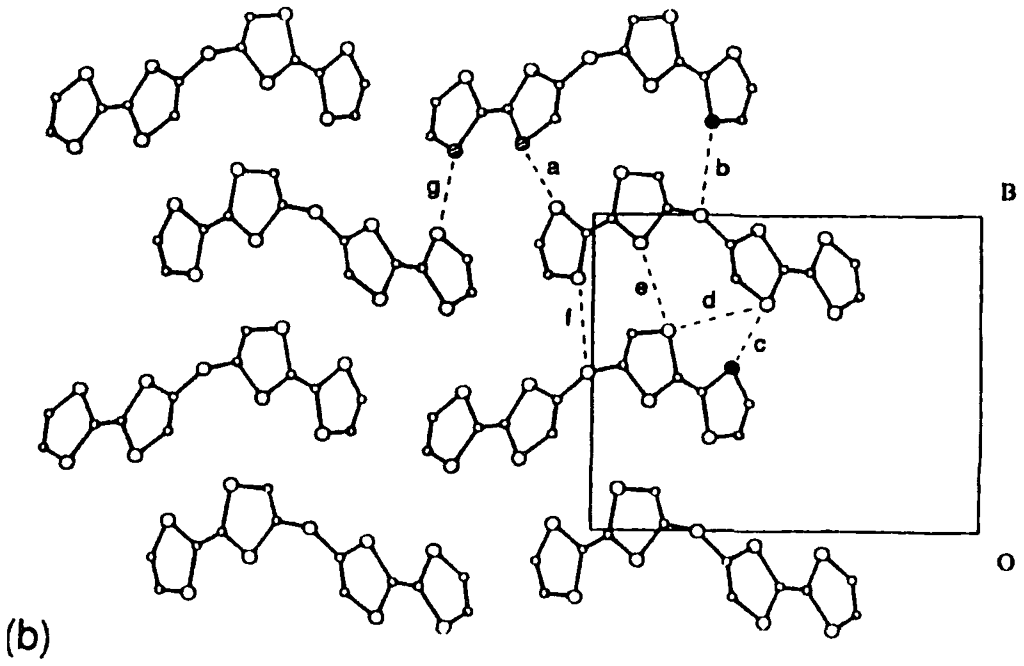


Fig. 2.3b: *Single crystal X-ray structure of (59): view along the a axis showing the network of intermolecular S--S contacts, many of which are shorter than the sum of the Van der Waals radii (3.8 Å). Distance a= 3.449, b= 3.658, c= 3.497, d= 3.815, e= 3.517, f= 3.662, g = 3.918 Å.*

2.4.5 TCNQ complexes.

In view of the close sulphur-sulphur contacts in (59), novel redox behaviour, and the possibility of producing a complex of the type $(TTF\text{-}X\text{-}TTF)_1$ $(acceptor)_1$, analogous to the superconducting architectures of stoichiometry $(BEDT\text{-}TTF)_2$ X^-, attempts were made to produce TCNQ complexes with (59) and (60). Unfortunately, no complexes were formed.

2.5 CONCLUSIONS.

The new improved route to mono- and multi-halogenated TTF's, provides a simple and comparatively high yielding method of producing these donor molecules. Compounds (30) and (32) have been complexed with TCNQ to provide highly conducting C-T complexes. Attempts to form alkoxy-TTF's by displacing the halogen of (30) or (32) with sodium methoxide were unsuccessful.

The chalcogen insertion route has provided a one-pot procedure for the synthesis of (41) and (44). X-Ray crystal structures of (44) presents, we believe, a novel type of packing for a TTF system.

The use of the electrophilic thionating and selenating reagents (61) and (62) has provided the first examples of bis-TTF's bridged by sulphur or selenium atoms. The multistage redox behaviour and the extensive sulphur-sulphur network that exists in the solid state structure of (59), are particularly interesting features of these new donors.

CHAPTER THREE.

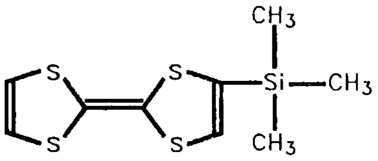
SYNTHESIS OF TTF DERIVATIVES WITH C=X (X=O,S) FUNCTIONALITIES DIRECTLY ATTACHED TO THE TTF RING.

3.1 INTRODUCTION.

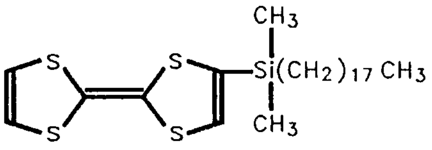
The TTF mono-anion methodology has been extended to produce a range of highly functionalised, mono-substituted TTF's. The rationale behind this work was to produce new compounds with either carbonyl or thiocarbonyl groups adjacent to the TTF ring, as the long chain ketones (14) and (15) and thioester (16) derivatives are known to form highly conducting LB films[37,38].

3.2 A NEW METHOD OF PRODUCING MONOFUNCTIONALISED TTF'S.

The TTF anion route is a useful method of producing highly functionalised TTF derivatives, but it suffers from the fact that the anion (23) readily disproportionates to multilithiated species[49] and consequently, moderate yields of products characterise this route. It is well known in the literature[82-84], that vinylsilanes react readily with electrophiles in a similar manner to carbanions. It was, therefore, thought that trialkylsilyl-TTF derivatives may serve as shelf-stable equivalents for the TTF mono-anion (23), which may overcome the obstacles inherent with the anion methodology. It was found that the TTF anion (23) could be trapped with chlorotrimethylsilane and chloro-octadecyldimethylsilane, to give the silylated TTF's (64) (26%) and (65) (27%), respectively[36].



(64)

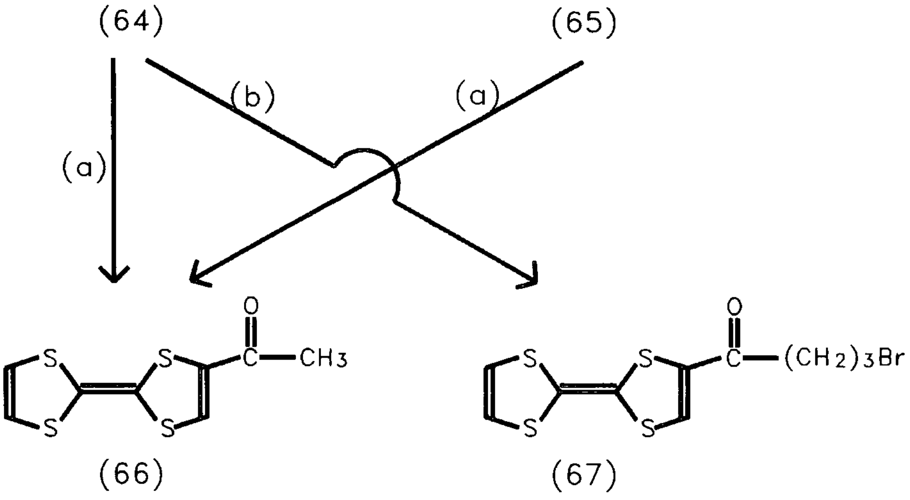


(65)

Compounds (64) and (65) are air-stable, and there was no evidence for any multi-substituted species from mass spectroscopic data, proton NMR spectra and CHN analysis data. The long chain derivative (65), could be purified very simply by crystallisation from the crude reaction mixture by the addition of methanol, whereas (64) required preparative t.l.c. to afford the pure silyl derivative.

Compounds (64) and (65) were, indeed, found to be shelf-stable equivalents for the TTF anion, by their reaction with acid chlorides at room temperature, to give derivatives (66) and (67) (55 - 60%) (Scheme 3.1). Thus, the silylated TTF's gave an alternative route to the ketones (66) and (67), which circumvents the problem of complicated chromatographic separation of mixtures of multisubstituted species, which is observed with the synthesis of these compounds from (23)[36]. A contributing factor to the increased yields of (66) and (67) from the silyl derivatives, as opposed to the TTF anion (23)[36] (ca. 25%), may be the increased solubility of the electrophile at room temperature, as compared to -78°C. Unfortunately, the reactivity of the anion was not enhanced by the silylation, since like the anion itself, no reaction of (64) was observed with methyl iodide, even under reflux.

The solution electrochemistry of (64) and (65) studied by CV, revealed that the addition of a trialkylsilyl functionality to TTF, increases the oxidation potential of the donor ($E_1^{1/2}$= 0.40 and $E_2^{1/2}$=0.88 V, Ag/AgCl,Pt), relative to TTF (2). The long chain silyl derivative (65) was found not to form LB films: no reproducible isotherm was observed, which may be due to the methyl groups, adjacent to the TTF, preventing ordered monolayer formation at the air/water interface.



Scheme 3.1: Reagents: *(a)* $CH_3C(O)Cl$, 20°C; *(b)* $Br(CH_2)_3C(O)Cl$, 20°C.

After the completion of this work, a Japanese group[85] reported that trialkylstannylated TTF's also serve as shelf-stable equivalents for the TTF anion (23), by their palladium catalysed reactions with aryl halides.

3.3 SYNTHESIS OF MONOFUNCTIONALISED TTF'S WITH A CARBONYL GROUP ADJACENT TO THE TTF RING.

3.3.1 Background.

Our group has established that the presence of a carbonyl functionality adjacent to the TTF ring has a profound effect on the conductivity of doped LB films of cation radical salts[37]. Previous workers at Durham, obtained a single crystal X-ray crystal structure of 4-(6-Bromohexanoyl)TTF (68) (Fig. 3.1), which revealed the TTF units form dimerised pairs, within which there is ring-over-bond overlap. The carbonyl group of (68) lies in the same plane as the TTF ring; this configuration maximises the interaction of the carbonyl and the TTF π-system. This is consistent with the marked increase in ionisation potential that occurs when an acyl substituent is attached to the TTF ring.

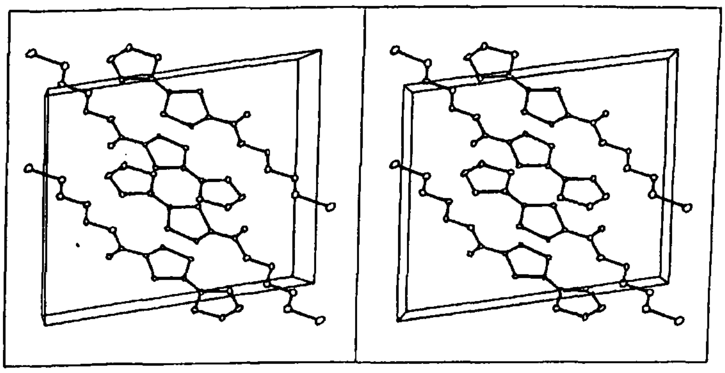


Fig. 3.1: *Single crystal X-ray structure of (68): stereo view along the b axis.*

Thus, the high conductivity and excellent film quality displayed by amphiphiles bearing carbonyl groups adjacent to the ring may be due to: (i) the TTF ketones have higher oxidation potentials (as assigned by CV) than the parent TTF[36], which lessens the tendency for total charge transfer occurring upon doping with iodine; (ii) the electron withdrawing C=O group, in conjugation with the TTF ring, may result in the TTF end of the amphiphile becoming more polar, thus aiding film deposition and, hence, conductivity (Fig 3.2).

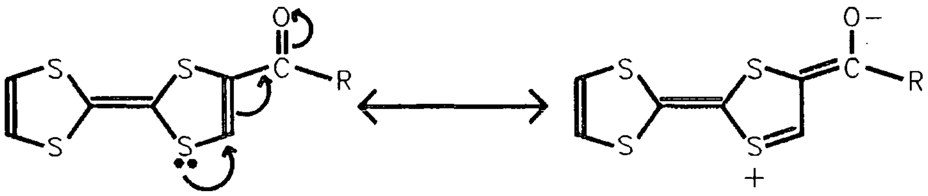
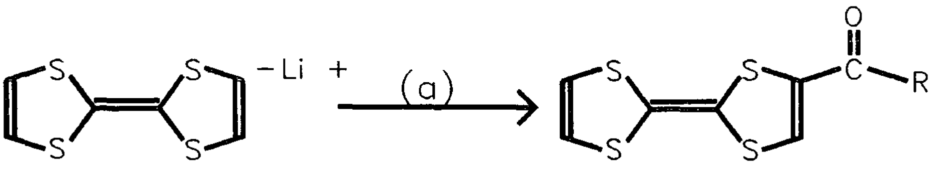


Fig. 3.2: *Proposed resonance of TTF ketones.*

3.3.2. Reaction of (23) with acid chlorides.

The TTF anion (23) can be trapped with acid chlorides to yield TTF ketones (68) and (69) in moderate yields (20-30%) (Scheme 3.2). The cyclic voltammograms of the these compounds showed reduced donor ability ($E_1^{1/2}$= 0.52 and $E_2^{1/2}$ 0.90 V *versus* Ag/AgCl in dichloromethane), due to the electron withdrawing effects of the ketone functionality[36].



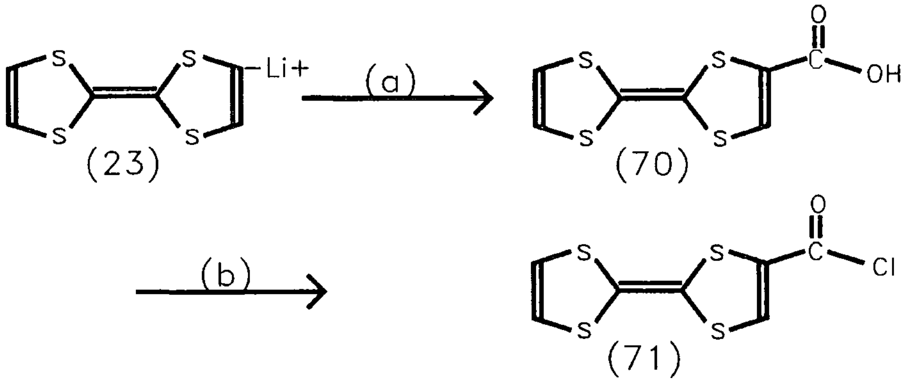
(23)

(68) R=$(CH_2)_5Br$
(69) R= $(CH_2)_{12}CH_3$

Scheme 3.2: Reagents: *(a) RC(O)Cl (1.1 equiv.).*

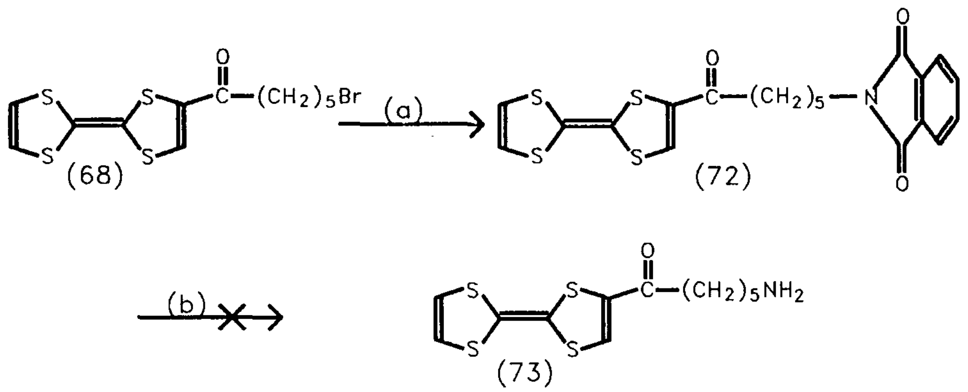
The carbonyl group of (68) and (69) was found to be remarkably unreactive, by the lack of reaction with tosyl-hydrazide[86] and ethylene glycol[87]. Attempts to convert the carbonyl group to -CH_2- *via* the Wolf-Kishner[88] or Clemmensen reduction[89] were also unsuccessful. The lack of reactivity can be attributed to the aforementioned resonance affect (Fig. 3.1), or possibly due to steric interference from the alkyl chain or the neighbouring 'd' orbitals of the sulphur atoms.

Several attempts were made to synthesise a bis-TTF derivative linked through a carbonyl group. Firstly, the TTF anion (23) was reacted with 1/6 equivalent of triphosgene, but none of the desired bis-TTF was observed. An alternative strategy was employed by reacting the TTF acid chloride (71)[36], formed from the TTF acid (70) (Scheme 3.3), with the TTF anion (23), but again none of the desired product was observed.



Scheme 3.3: Reagents: *(a)* CO_2; *(b) oxalyl chloride, benzene/acetonitrile (5:1 v/v).*

TTF derivatives with a functional group, eg. an amide, at some position along the chain, as well as adjacent to the TTF ring, are prime targets. The functionality in the chain may cause increased ordering in the LB films, due to inter-chain hydrogen bonding. To these ends the halogen in (68) was converted to the phthalimide derivative (72) in 80% yield (Scheme 3.4). Unfortunately, the subsequent hydrolysis with hydrazine *via* Gabriels route[90], failed to give the desired amine (73), possibly due to interference by the carbonyl group. This approach was therefore abandoned.

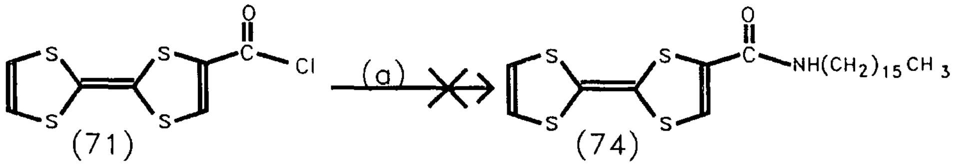


Scheme 3.4: Reagents: *(a) Potassium phthalimide, under reflux DMF for 2 h.;*
(b) NH_2NH_2*, under reflux in ethanol for 1 h.*

3.3.3 Synthesis of TTF amides.

There is only one report concerning the synthesis of a TTF derivative bearing an amide functionality adjacent to the ring[91], which was synthesised by the reduction of the TTF isocyanate, giving the -NH portion and not the carbonyl group adjacent to the ring. For our requirements, it was beneficial for the carbonyl and not the NH portion to be adjacent to the TTF ring. TTF amides would be particularly attractive in view of the fact that there may be some hydrogen bonding effects, which may cause increased coherence of the monolayer at the air/water interface and hence increase the quality of the transferred monolayer.

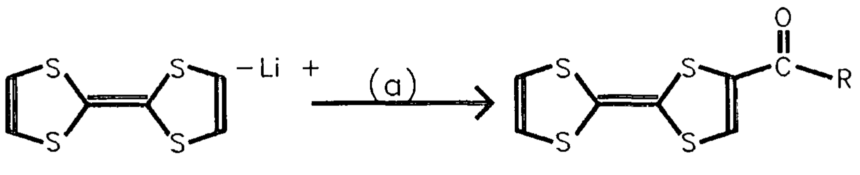
To these ends, a route was developed (Scheme 3.5) in which the TTF acid chloride (71), was reacted with hexadecylamine in an attempt to produce the long chain derivative (74). Unfortunately, the nucleophilic attack of the long chain amine on the acid chloride was unsuccessful giving rise to unreacted starting materials.



Scheme 3.5: Reagents: *(a) hexadecylamine, pyridine (1.1 equiv.), stirred for 6 h. at at room temperature.*

3.3.4. Reaction of the TTF anion with isocyanates.

It is well established in the literature that organic isocyanates react with organolithium reagents to give amides[92]. The synthesis of TTF amides was achieved by reacting the TTF anion (23) with alkyl and phenyl isocyanates (Scheme 3.6), to give (75)-(77) in respectable yields (30%-50%).



(23)

(75) R = $N(CH_2)_2$
(76) R = NHPh
(77) R = $NH(CH_2)_{17}CH_3$

Scheme 3.6: Reagents: *(a) R'-N=C=O (1.1 equiv.), (R'= $Cl(CH_2)_2$, Ph, $CH_3(CH_2)_{17}$).*

The reaction of the TTF anion (23) with 2-chloroethyl isocyanate gave no 4-(2-chloroethylamido)tetrathiafulvalene, instead the aziridine derivative (75) was formed exclusively (38% yield). Presumably, the deprotonated secondary amide, subsequently underwent nucleophilic displacement of the chlorine atom giving rise to the three membered ring. The cyclic voltammetry of (75)-(77) showed that the electron withdrawing amide functionality reduces the donor ability of the derivative, as would be expected.

COMPOUND	$E_1^{\frac{1}{2}}$	$E_2^{\frac{1}{2}}$
(75)	0.50	1.00
(76)	0.45	1.00
(77)	0.45	1.00

Table 3.1: *Cyclic voltammetry data for compounds (75) to (77). (1 x 10^{-5} M solution in CH_2Cl_2, under nitrogen. Pt electrode, relative to Ag/AgCl with tetrabutylammonium perchlorate (0.01M). Scan rate 100 mVs^{-1}).*

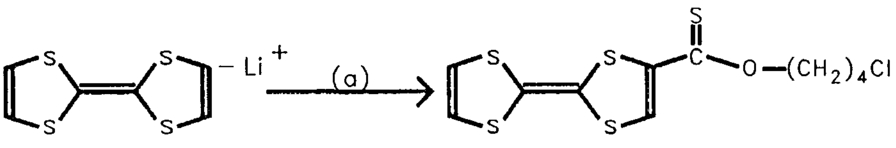
3.4. SYNTHESIS OF MONOFUNCTIONALISED TTF's WITH A THIOCARBONYL GROUP ADJACENT TO THE MOIETY.

3.4.1.Background.

Like the TTF derivatives with carbonyl functionalities adjacent to the TTF moiety, long chain thiocarbonyl compounds are clearly prime targets for producing new materials for LB films, as previous work in our laboratory had shown that the thioester (16) was highly conducting[38].

3.4.2 Synthesis and X-ray crystal structure of (79).

In an attempt to discover the role that the C=S group might play in the high conductivity of iodine doped LB films of (16), the shorter chain thioester (79) was synthesised from the TTF anion (23) and the chlorothioformate (78) (Scheme 3.7). It was hoped that X-ray quality crystals could be obtained; the halogen atom in the side chain was included in the expectation that this would facilitate crystallisation.



(23) (79)

Scheme 3.7: Reagents: *(a)* $ClC(S)O(CH_2)_4Cl$ *(78).*

The TTF anion (23) reacted cleanly with the chlorothioformate (78) (which was synthesised from thiophosgene and 4-chlorobutan-1-ol), to give (79) in 58% yield. X-Ray quality purple needles were obtained from a 1:1 mixture of hexane:dichloromethane. Fig. 3.3 shows the crystal structure of (79).

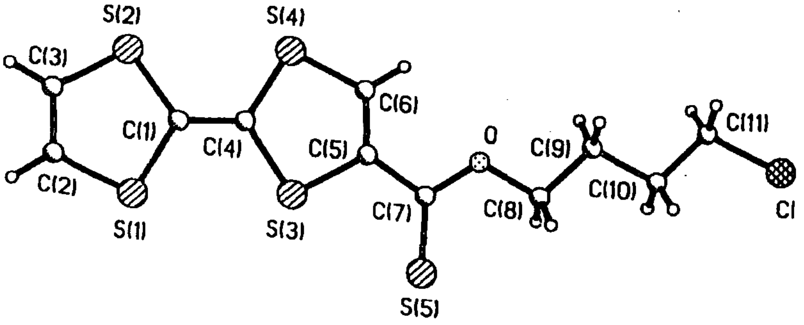


Fig. 3.3a: *Single crystal X-ray structure of compound (79) showing the numbering scheme.*

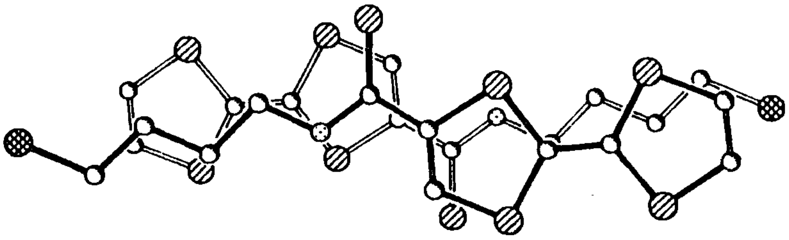


Fig. 3.3b : *View of the dimerised pair, normal to the least squares molecular plane of the four sulphur atoms of molecule (79).*

The thiocarbonyl group is in the plane of the TTF ring system thus maximising the interaction of the C=S group and the TTF π-system (Fig. 3.3a). This feature is similar to that displayed by the crystal structure of 6-bromohexanoylTTF (68)[36]. There is evidence for the formation of the canonical form of (79), similar to that in Fig. 3.1. The interatomic bond distances S(4)-C(6) (1.714 Å) and C(5)-C(7) (1.448 Å) are shorter than the corresponding bonds C(3)-S(2) (1.723 Å) and C(9)-C(10) (1.528 Å). Similarly, the thiocarbonyl bond length between C(7)-S(5) is 1.633 Å, which is an intermediate bond distance for a typical C=S bond (1.55 Å) and C-S bond (1.82 Å). The double bond C(6)-C(5) (1.334 Å) is longer than the corresponding bond between C(3)-C(2) (1.323 Å). Fig. 3.3(b) shows that the molecules dimerise ring-over-chain, which is markedly different from the ring-over-bond overlap of 6-bromohexanoylTTF[36] and of many TTF systems[93]. The separation between the mean molecular planes of neighbouring molecules is ca. 3.7Å.

3.4.3 Attempted synthesis of TTF dithiocarbonates and thioketones.

In attempts to extend the range of materials with thiocarbonyl functionality adjacent to the TTF ring, reaction schemes were proposed to introduce the dithiocarbonate functionalities to the periphery of TTF. For example the TTF anion (23) was reacted with CS_2, in the hope of forming the dithio-acid derivative. However, mass spectral evidence suggested that no dithio acid derivative was produced. When the reaction was repeated in the presence of methyl iodide, mass spectral evidence suggested that no methyl-dithioester was observed.

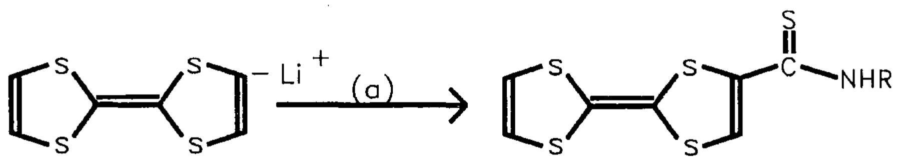
An alternative strategy to synthesise a dithioester, analogous to that of the thioester (79) was tried. Hexadecylthiol was used instead of hexadecanol to synthesise the dithioacid chloride from thiophosgene. Unfortunately, upon reaction with the TTF anion (23), this route failed to give any of the desired product.

Ketone (69) was reacted with P_2S_5 and Lawesson's reagent in refluxing toluene, however, mass spectral and infrared evidence showed that the starting material was recovered even under prolonged reflux times of several days.

In an attempt to synthesise a bis-TTF derivative linked through a thiocarbonyl group, the TTF anion (23) was reacted with 0.4 equivalents of thiophosgene or 1,1'-thiocarbonyldiimidazole, but none of the desired material was produced.

3.4.4 Synthesis of TTF thioamides.

Isothiocyanates react in a similar fashion to organic isocyanates with organolithium reagents to give the corresponding thioamides[92]. In an effort to produce the thioamide analogues of the TTF amides (75)-(77), the TTF anion (23) was reacted with methyl- and octadecylisothiocyanate to give the thioamides (80) and (81) in acceptable yield (50 and 42%, respectively) (Scheme 3.8).



(23)

(80) R = CH_3
(81) R = $(CH_2)_{17}CH_3$

Scheme 3.8: Reagents: *(a) R-N=C=S (1.1 equiv.).*

The solution electrochemistry of (80) and (81) was studied by cyclic voltammetry, which showed that the addition of the thioamide functionality to the periphery of TTF, like the amide functionality, reduces the donor ability of the TTF.

COMPOUND	$E_1^{\frac{1}{2}}$	$E_2^{\frac{1}{2}}$
(80)	0.43	0.98
(81)	0.43	1.00

Table 3.2: *Cyclic Voltammetry data for TTF thioamides (80) and (81). (1x10^{-5}M Solution in CH_2Cl_2, under nitrogen, Pt electrode relative to Ag/AgCl with tetrabutylammonium perchlorate (0.01M). Scan rate $100mVs^{-1}$).*

3.4.5 X-Ray crystal stucture of (80).

X-Ray quality crystals of (80) were obtained from toluene. Preliminary X-ray data reveal that the structure of (80) is markedly different from thioester (79). The TTF ring system is distorted into a bow-like shape and the thiocarbonyl group is not in the same plane as the adjacent 1,3-dithiole ring (Fig. 3.4).

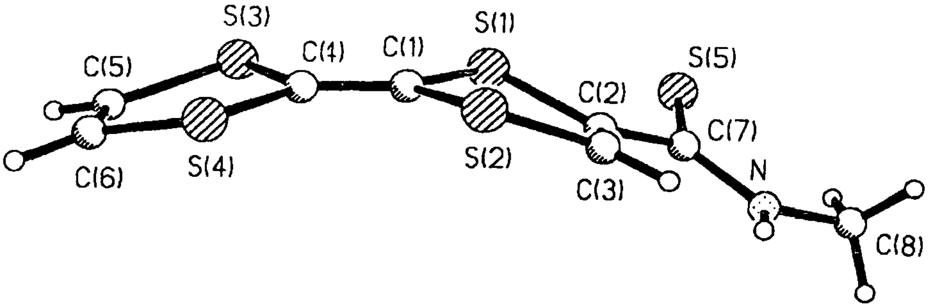


Fig. 3.4: *X-Ray crystal structure of (80).*

3.4.6 Preliminary studies of LB Films of (81).

A fresh solution of the thioamide (81) in chloroform (200μL of 2x10^{-3} M), was spread onto the surface of ultrapure water. The solvent was allowed to evaporate, and the film was compressed by barriers at a rate of 5 cm^2 min^{-1}, while the surface pressure (π) *versus* trough area (A) was monitored. The π *versus* A isotherm is shown in Fig. 3.5.

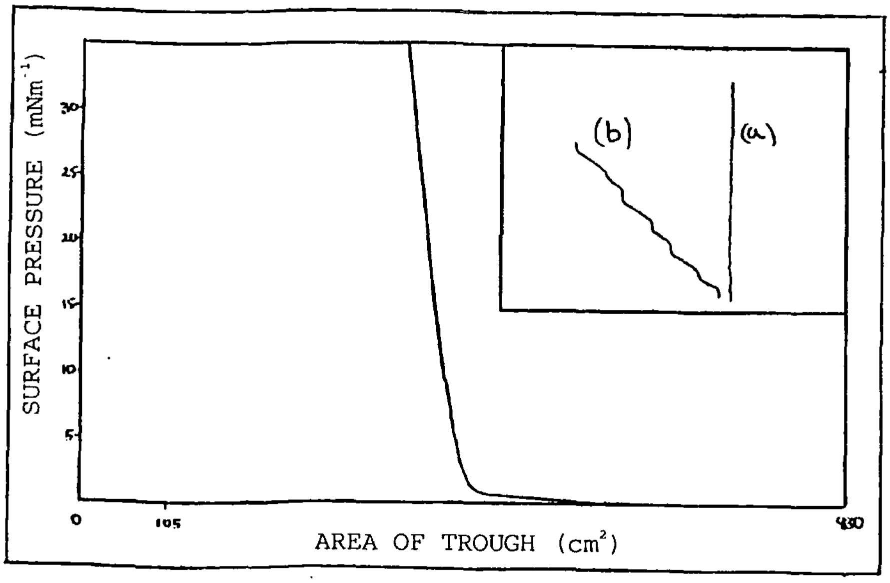


Fig 3.5: *Surface pressure vs area of trough isotherm for thioamide (81), measured at 20 +/- 2°C. Inset shows dipping record of (81) onto a glass substrate [(a)= surface pressure, (b)= area per molecule].*

The monolayers of (81) on the water surface were found to be very stable, as changes in the isotherm on repeated compression were negligible. The area per molecule in the condensed phase, assuming monolayer coverage of the subphase, was 0.20 nm^2 (at 20 mN m^{-1}). This value is in good agreement with the value for ester (17) (0.23 nm^2) and thioester (16) (0.18 nm^2), which are thought to have their alkyl chains near normal to the plane of the subphase[38].

Y-Type deposition of the thioamide was achieved onto a scrupulously clean glass slide, using a constant dipping pressure of 20 mNm^{-1} and a dipping speed of 2mm min^{-1} on both the inward and outward movements of the substrate. Films of 20 layers have been achieved without any major loss of quality. Visual inspection of the multilayers showed excellent film uniformity with very few optically diffusing effects. A typical dipping record is shown in Fig. 3.5 (inset).

The lateral d.c. conductivity of the as-deposited film was measured using a two probe technique. The as-deposited films displayed a conductivity of $\sigma_{rt}= 10^{-5}$ Scm^{-1}. The resistance scales with the distance apart of the probes. The 20 layers of (81) were exposed to iodine vapour for about 5 minutes in a sealed container. A drop in the conductivity of the film was observed immediately upon doping which is consistent with the complete oxidation of (81). Over a period of time the room temperature conductivity rose to a value of 9×10^{-3} Scm^{-1} after 1.25 hours. This behaviour is consistent with the formation of the mixed valence species $TTF^{+\bullet}(I_3^-)_X$ (where x<1) from the unstable fully oxidised $TTF^{+\bullet}(I_3^-)$. This observation is similar to that observed for (15)[37] and (16)[38].

3.5 SYNTHESIS OF 4,5-DISUBSTITUTED TTF DIESTERS.

3.5.1 Background.

TTF amphiphiles bearing two alkyl chains connected to the ring are rare. The most notable example in the literature concerns LB films of the $TCNQF_4$ complex of (ethylenedithio)-di(octadecylthio)TTF (13)[34]. We identified analogues bearing two chains connected to the ring system by polar functional groups, such as esters, as prime targets for cation radical salt LB films. Such derivatives would give rise to tubular shaped amphiphiles, of high polarity at the TTF end, which may aid film deposition and conductivity.

3.5.2 Synthesis of TTF diesters.

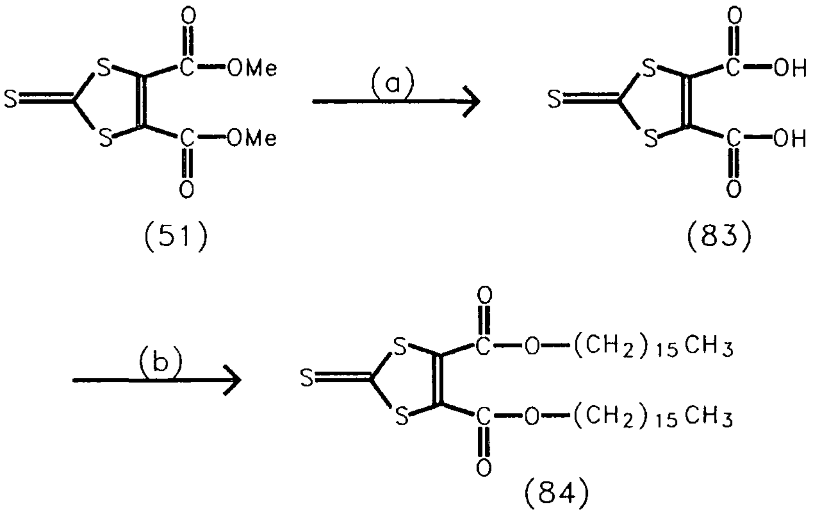
Green showed that addition of two equivalents of LDA and ethylchloroformate to TTF (2) at -78°C gave the 4,4'(5') isomer only[49]. The 4,5-diester could only be synthesised by the sequential addition of 1 equivalent of LDA and ethylchloroformate to 4-(ethoxycarbonyl)-TTF. We thought that the addition of 1 equivalent of LDA and hexadecylchloroformate to the long chain ester (17), would not substitute the adjacent position due to steric hinderence of the long chain. Acid catalysed trans-esterification of a short chain 4,5-diester derivative would be impractical due to the incompatibility of TTF system with acid.

The best methodology seemed, therefore, to be to synthesise the long chain diester derivative of vinylene trithiocarbonate (84), which could then be cross coupled with unsubstituted vinylene trithiocarbonate (82) to give the desired 4,5-disubstituted-TTF. It is known that certain ester derivatives can withstand trialkylphosphite mediated coupling reactions[63].

Initial attempts of this approach involved the reaction of the dianion of vinylene trithiocarbonate[34] with excess hexadecylchloroformate. Unfortunately, this route led to a complex mixture of products, none of which was the required diester.

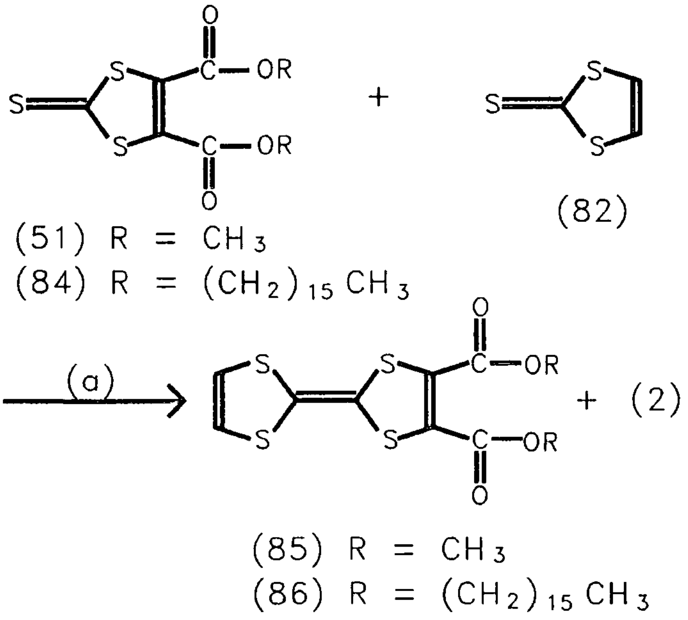
As an alternative strategy, dimethyl 1,3-dithiole-2-thione-4,5-dicarboxylate (51), was hydrolysed quantitatively to the diacid (83) *via* aqueous HCl[94]. The diacid (83) was then esterified with H_2SO_4 and a large excess of hexadecanol to give (84) in

82% yield (Scheme 3.9).



Scheme 3.9: Reagents: *(a) Aqueous HCl, acetic acid, reflux 2h.;*
(b) hexadecanol (10 equiv.), H_2SO_4*, reflux in toluene 3 h.*

Initial attempts to cross couple equimolar amounts of (51) or (84) and vinylene trithiocarbonate (82) using trimethyl- or triethylphosphite provided the TTF diesters (85) and (86) in 21% and 7% yield, respectively. Together with the desired material, TTF (2) (15%) was also formed. T.l.c. evidence suggested that in both cases, none of the self-coupled tetraester was formed. The yields of (85) and (86) were increased slightly to 25% and 10%, respectively, by use of 2 mole equivalents of (51) or (84) (Scheme 3.10). A major shortcoming of this methodology is the complex chromatographic separation of (86) from (84), primarily caused by the trialkyl phosphite eluting with a similar R_f to these compounds.



Scheme 3.10: Reagents:*(a) P(OR'')$_3$ (R''= CH$_3$ or CH$_2$CH$_3$), reflux 3h; or (a) Co$_2$CO$_8$ stirred in toluene 50^{0}C, 2 h.*

Alternative strategies to couple thione and ketone moieties using dicobaltoctacarbonyl have been reported[95,96], giving highly functionalised self and cross-coupled TTF's in modest yields (10-25 %). In an attempt to improve yields of (85) and (86) and to facilitate ready chromatographic separation, the long chain ester (84) and methyl ester (51) were reacted with one equivalent of vinylene trithiocarbonate (82), using dicobaltoctacarbonyl as the coupling agent. The desired esters (85) and (86) were obtained in 10% and 9% yield, respectively. The low yield of (86) was offset by its comparatively easier isolation by chromatography and, therefore, this is the method of choice for the preparation of (86).

Solution electrochemistry studied by CV showed that, as expected, (85) and (86) are significantly poorer donors than TTF (2). The addition of the second ester group to the ring system further destabilised the radical cation and dicationic states as compared to (17) ($E_1^{\frac{1}{2}}$= 0.47 V, $E_2^{\frac{1}{2}}$= 0.83 V *versus* Ag/AgCl, Pt, CH_3CN).

COMPOUND	$E_1^{\frac{1}{2}}$	$E_2^{\frac{1}{2}}$
(85)	0.62	1.08
(86)	0.63	1.10

Table 3.3: *Cyclic voltammetry data for (85) and (86).*
($1x10^{-4}$ M solution in CH_2Cl_2 under nitrogen, Pt electrode relative to Ag/AgCl with tetrabutylammonium perchlorate (0.01M).
Scan rate $100mVs^{-1}$).

3.6 CONCLUSIONS.

The use of the silylated TTF's to produce functionalised derivatives should find widespread use, particularly for those reactions where the low temperatures which the TTF anion route demands, causes problems due to the low solubility of the electrophile.

The use of isocyanates and isothiocyanates for producing TTF amides and thioamides directly from the anion, provides a relatively high yielding route to the desired compounds. The preliminary studies of LB films of (81) shows that this compound forms high quality LB films. Preliminary conductivity studies indicate that iodine doped LB films of multilayers of (81) are semiconducting.

The synthesis of the diester (84) provides routes to the target TTF diester (86). This methodology offers routes to other amphiphilic TTF derivatives since (84) should couple with a wide range of thiones and ketones, to give a range of amphiphilic TTF derivatives.

CHAPTER FOUR.

AMPHIPHILIC ALKYLTHIO-TTF DERIVATIVES AND RELATED SYSTEMS: SYNTHESIS AND CHARACTERISATION OF LB FILMS.

4.1 INTRODUCTION.

TTF amphiphiles with sulphur linking the TTF ring to the long alkyl chain are rare[22,34]. Such materials were of interest to us because: (i) the thioalkyl group should make the material a comparatively better donor than (15) or (16); (ii) the sulphur atom of the side-chain may be involved in interstack interactions thus increasing the conductivity of the doped LB film.

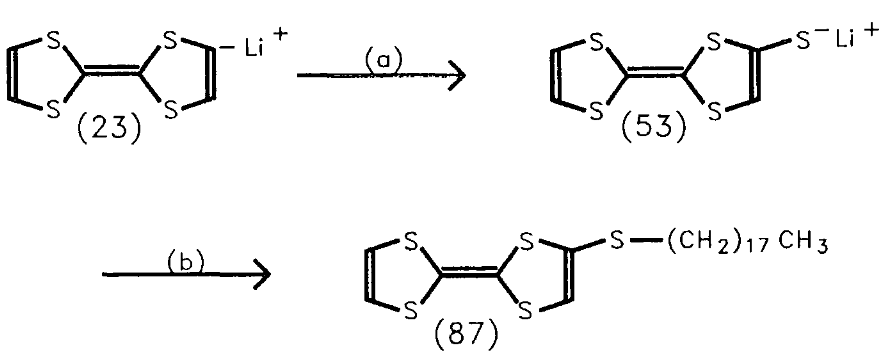
4.2 SYNTHESIS OF NEW MATERIALS FROM THE TTF MONOTHIOLATE ANION (53).

4.2.1 Background.

The TTF thiolate (53) route has been extended to produce long chain derivatives suitable for LB films. The increased nucleophilicity of (53) relative to lithiated TTF (23), allows direct reaction with alkyl halides to provide S-alkylated TTF derivatives.

4.2.2 Synthesis of octadecylthio-TTF (87) and the subsequent LB films.

The TTF anion (23) was formed as described in Chapter 2 and reacted with 1.1 equivalents of elemental sulphur to form the thiolate anion (53). After 7 hours at -78°C, when all the sulphur had dissolved, one equivalent of 1-iodooctadecane was added, and the mixture was allowed to warm to room temperature overnight to give (87) in 12% yield[36] (Scheme 4.1).



Scheme 4.1: Reagents: *(a) S_8 (1.1 equiv.), -78°C, 7h.; (b) $CH_3(CH_2)_{17}I$ (1 equiv.).*

Solution electrochemistry studied by CV, showed that the thioalkyl chain increased the oxidation potentials for this compound, as compared to TTF (2), giving values of $E_1^{1/2}$ 0.50 V and $E_2^{1/2}$ 0.88 V (Ag/AgCl, Pt, $Bu_4N^+ClO_4^-$, CH_3CN).

4.2.3 LB Film formation.

A fresh 2×10^{-3}M solution of (87) in chloroform was spread onto a pure water surface at 20°C[97]. The solvent was allowed to evaporate and the film was compressed at a rate of 2×10^{-3} nm^2 molecule^{-1}s^{-1}, whilst monitoring the surface pressure *versus* area per molecule isotherm (Fig. 4.1). The area per molecule in the condensed phase, assuming monolayer coverage, was found to be 0.16nm^2 which is significantly lower than that expected from the cross-sectional area of the molecule (estimated using conventional space filling models and X-ray crystal structure data) which gives a value of ca. 30 Å^2 for similar TTF derivatives. This difference may be due to small amounts of impurities in the compound (although correct C and H analyses were obtained), or slight solubility of the compound in the subphase. The isotherm suggests that the molecules are arranged with the side chains near normal to the subphase plane (Fig. 4.1), and it is probable that the relatively hydrophilic TTF ring is in contact with the water surface by analogy with compounds (15) and (16)[37,38].

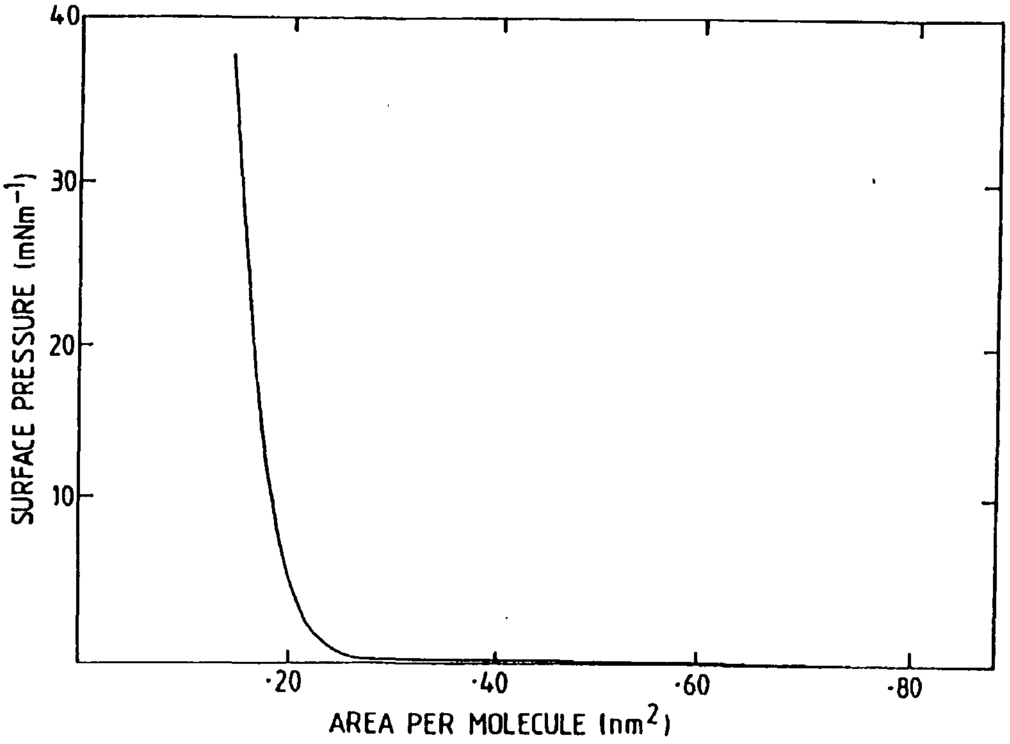


Fig. 4.1: *Surface pressure versus area per molecule isotherm for (87). (Temperature 20°C, compression rate 5.0 cm^2 min^{-1}).*

Monolayers of (87) were transferred to a glass slides in a Y-type fashion, with a dipping pressure of 30 mNm^{-1} and at a maximum dipping speed of 1 cm min^{-1}. Film quality was increased when 15% stearic acid was added to the solution of (87).

Conductivity studies of LB films of (87) initially gave a conductivity value of 10^{-5} Scm^{-1}, which increased to a value of $8x10^{-2}$ Scm^{-1}, 18 hours after exposing the film to iodine vapour for 2 minutes.

4.2.4 Ultraviolet spectroscopy of LB films of (87).

The solution spectra of compound (87) in acetonitrile showed absorptions at 235, 320 and 375nm, which are consistent with the neutral form of the compound. Fig. 4.2 shows the UV-vis-near IR spectra for LB films of (87). Curve (a) was obtained for 36 layers deposited onto glass, which showed absorptions at 218, 285 and 316nm which can assigned to π-π* transitions of the TTF unit[98].

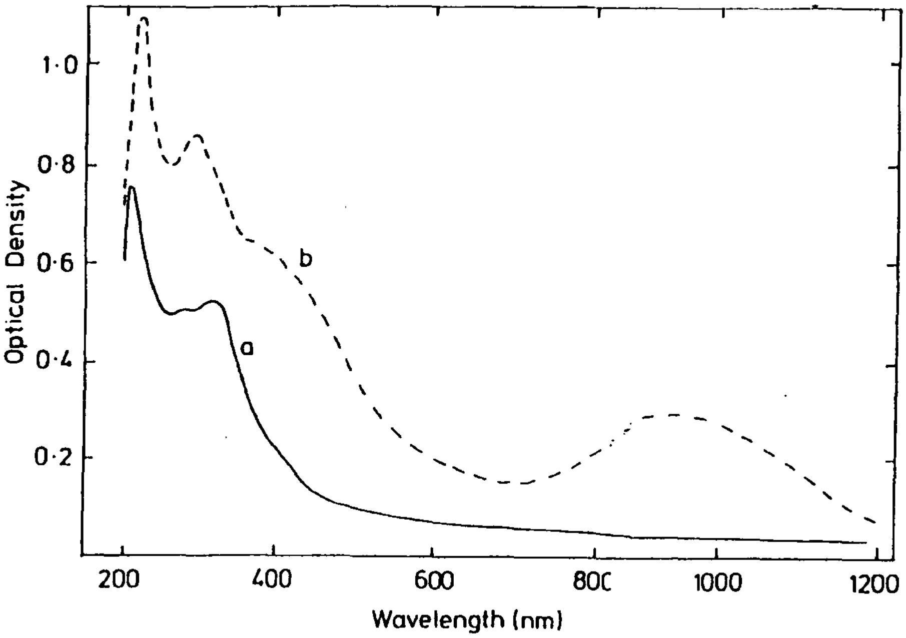


Fig. 4.2: *UV-visible -near IR absorption spectra of LB films of compound (87) (36 layers): (a), as deposited; (b) 1 hour after iodine doping.*

Curve (b) was measured for the same thickness of sample one hour after doping with iodine, and shows that oxidation has a marked effect on the absorption spectrum of the LB film. Absorption bands at 225, 290, 375 (shoulder) and 985 nm are now observed, and there is a marked increase in intensity of the absorption bands relative to the undoped sample. The new bands at 375 and 985 nm can be assigned to π-π^* intramolecular electronic transitions of the TTF radical cations and charge-transfer absorptions, respectively, which are produced upon doping[98]. The optical density of the 285/290 nm absorption band of the undoped and doped films varies approximately linearly with the number of layers in the LB assembly (data for 20,30 and 40 layers), which is indicative of reproducible monolayer deposition.

4.2.5 Infrared Spectroscopy of LB films of compound (87).

The transmission IR spectra for LB films of compound (87), deposited on a calcium fluoride substrate, were obtained before and after doping. Fig. 4.3 shows the spectra for 36 layers: (a) as deposited; (b) 5 minutes after iodine doping; and (c) 26 hours after doping. The majority of the features observed in curve (a) are due to absorptions of the thioalkyl chain. The strong bands at 2918 and 2852 cm^{-1} are assigned to asymmetric and symmetric CH_2 stretching vibrations. The absorption at 2958 cm^{-1} is associated with terminal CH_3 stretching vibrations, and the band at 1472 cm^{-1} is the CH_2 scissoring vibration. The band at 2350 cm^{-1} is due to atmospheric carbon dioxide absorption.

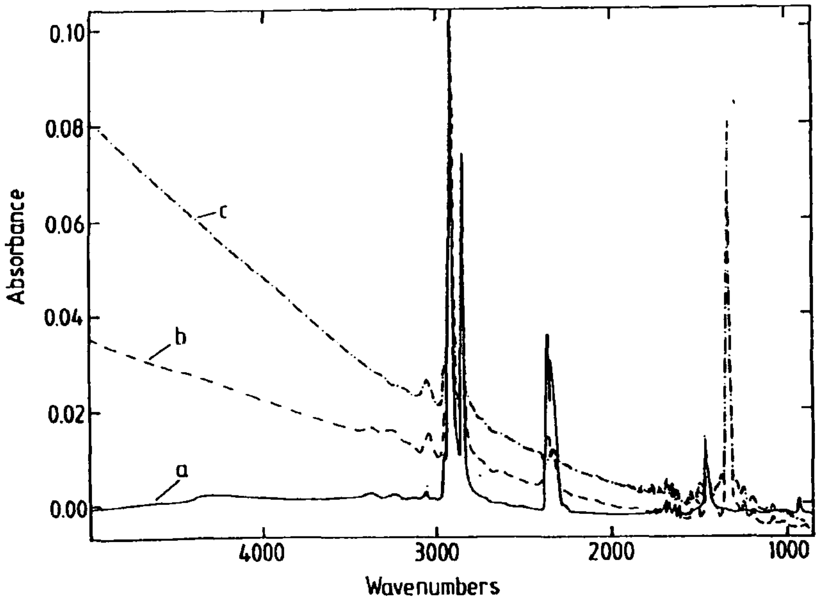


Fig 4.3: *IR transmission spectra for LB films of compound (87) (36 layers):(a) as deposited; (b) 5 minutes after iodine doping; (c) 26 hours after iodine doping.*

The IR spectra obtained after doping with iodine vapour show two important new features: a charge-transfer band extends from around 1800 cm^{-1} to beyond 5000 cm^{-1} and an intense absorption has appeared at 1333 cm^{-1}. This last peak can be explained by the coupling of conduction electrons to the vibrational modes of compound (87) which allows the previously inactive IR bands to become active[99]. Similar data have been obtained previously for LB films of related charge-transfer materials[31,34,37].

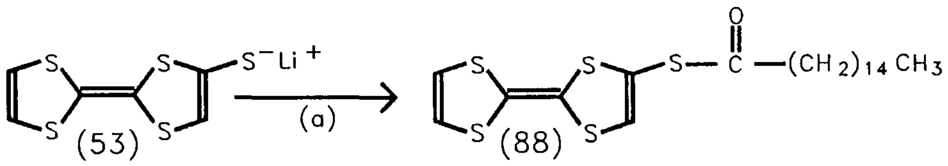
4.3 SYNTHESIS OF HEXADECANOYLTHIO-TTF (88) AND THE SUBSEQUENT LB FILMS.

4.3.1 Background.

Hexadecanoylthio-TTF (88) was synthesised in an attempt to produce an LB material where the carbonyl group is isolated by a sulphur atom, so that no resonance between the C=O group and the TTF ring can occur: a factor which is thought to have a profound effect on film deposition and conductivity.

4.3.2 Synthesis of hexadecanoylthio-TTF (88).

Hexadecanoylthio-TTF (88) was sythesised analogously to (87), but on this occasion the long chain iodide was replaced with hexadecanoyl chloride to yield the desired thioester (88) in 36% yield[66] (Scheme 4.2).



Scheme 4.2: Reagents: *(a)* $CH_3(CH_2)_{14}C(O)Cl$ *(1.1 equiv.).*

CV studies showed that, as anticipated, the donor ability was reduced with respect to TTF. However, the carbonyl group of (88) did not exert any observable effect in destabilsing the radical cation and dication states ($E_1^{1/2}$= 0.46 V, $E_2^{1/2}$= 0.93 V), as compared to analogous data for (15)[37] ($E_1^{1/2}$= 0.52 V and $E_2^{1/2}$= 0.90 V) measured under identical conditions (Ag/AgCl, Pt, $Bu_4N^+PF_6^-$, CH_2Cl_2).

4.3.3 LB Films of (88).

A freshly prepared solution of (88) in chloroform ($2x10^{-3}M$) was spread onto a pure water surface at 20°C. The solvent was evaporated and the film was compressed at a rate of 5 cm^2 min^{-1}, whilst the surface pressure *versus* area per molecule isotherm was monitored (Fig. 4.4).

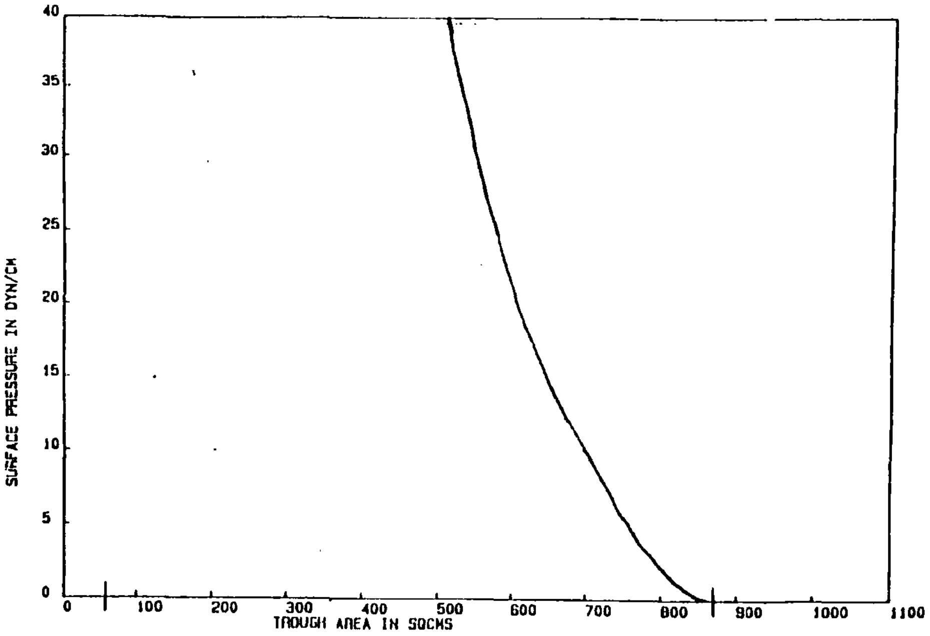


Fig. 4.4: *Surface pressure versus area per molecule isotherm for (88). (Temperature 20 +/- 2 °C, compression rate 5.0 cm^2 min^{-1}).*

The monolayers of (88) were readily transferred to a glass slide; giving 17 layers of material deposited in a Y-type fashion. The films were dipped using a dipping pressure of 20 mN m^{-1} and a dipping speed of 1 cm min^{-1}. The addition of 20% stearic acid aided film formation. The as-deposited films had a conductivity of 10^{-6} Scm^{-1}. Upon doping with iodine vapour, the conductivity rose slightly to a value of $\sigma_{rt}= 10^{-5}$ Scm^{-1}, 30 minutes after doping. This value is much less than that reported for (15) which had a maximum conductivity of $\sigma_{rt}= 10^{-2}$ Scm^{-1}.

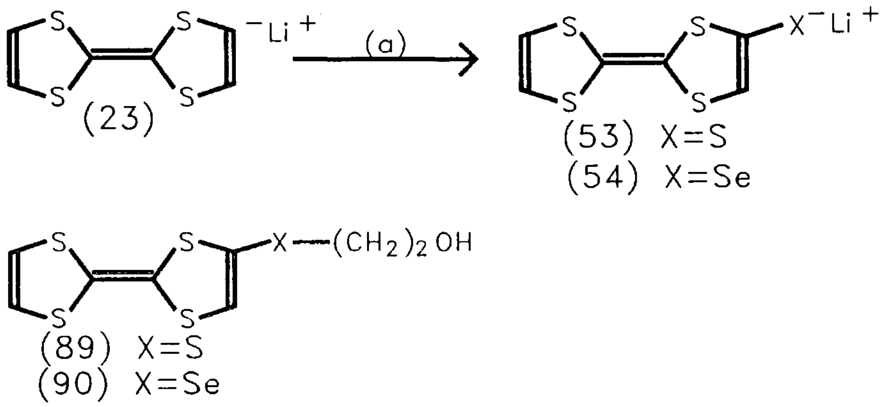
4.4 SYNTHESIS OF RELATED MATERIALS WITH A RANGE OF FUNCTIONALITIES IN THE SIDE CHAIN.

4.4.1 Introduction.

We next turned our attention to the synthesis of TTF-based materials suitable for forming LB films with some form of functionality at a position along the side chain. It was hoped that this functionality could enforce film coherence, perhaps by hydrogen bonding, which could in turn favour close stacking of the TTF units. Lerstrup *et al*[22] reported the synthesis of materials bearing terminal carboxylic acid groups, in an attempt to make the TTF end of the amphiphile the hydrophobic portion. Unfortunately, these materials were found to form poor quality films of low conductivity, probably due to the acid and TTF parts of the amphiphile competing to become the hydrophilic end of the molecule, thereby disrupting the film structure. In view of this some new materials were synthesised with the side chain functionality in the proximity of the TTF head group.

4.4.2 Synthesis of precursors to new LB materials.

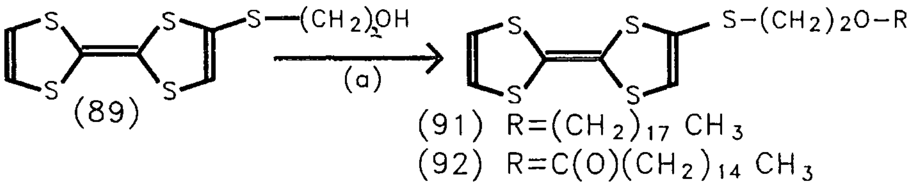
Recent work in our laboratory, has established that the TTF thiolate (53) can be trapped with 2-bromoethanol (68%) to give compound (89)[100]. This methodology was extended to give the selenium analogue (90) in 54% yield[66] (Scheme 4.3).



Scheme 4.3: Reagents: *(a)* X_8 *(X=S or Se, 1.1 equiv.), -78°C, 7h.; (b)* $Br(CH_2)_2OH$.

4.4.3 Synthesis of new LB materials.

The TTF alcohol (89) was reacted with 1-iodooctadecane utilising Williamson's synthesis, to give the long chain TTF ether (91) in 78% yield, while the reaction of (89) with hexadecanoyl chloride under basic conditions, gave ester (92) in 79% yield (Scheme 4.4)[66]. Attempts to produce the urethane analogue using octadecylisocyanate did give the correct product by mass spectroscopy, but unfortunately the amphiphile could not be obtained analytically pure. The cyclic voltammograms of (91) and (92) are identical, and gave oxidation potentials of $E_1^{\frac{1}{2}}$= 0.45 V, $E_2^{\frac{1}{2}}$= 0.92 V.



Scheme 4.4: Reagents: *(a)* $CH_3(CH_2)_{17}I$, *Na, (reflux in toluene, 48h.) (91).*
(a) $CH_3(CH_2)_{14}C(O)Cl$, *pyridine, (stirred in* CH_2Cl_2, *2h.) (92).*

4.4.4 Preliminary studies of LB films of (91) and (92).

LB films were deposited under conditions described above for compound (87). The isotherms of these materials are shown in Fig. 4.5a (91) and Fig. 4.5b (92).

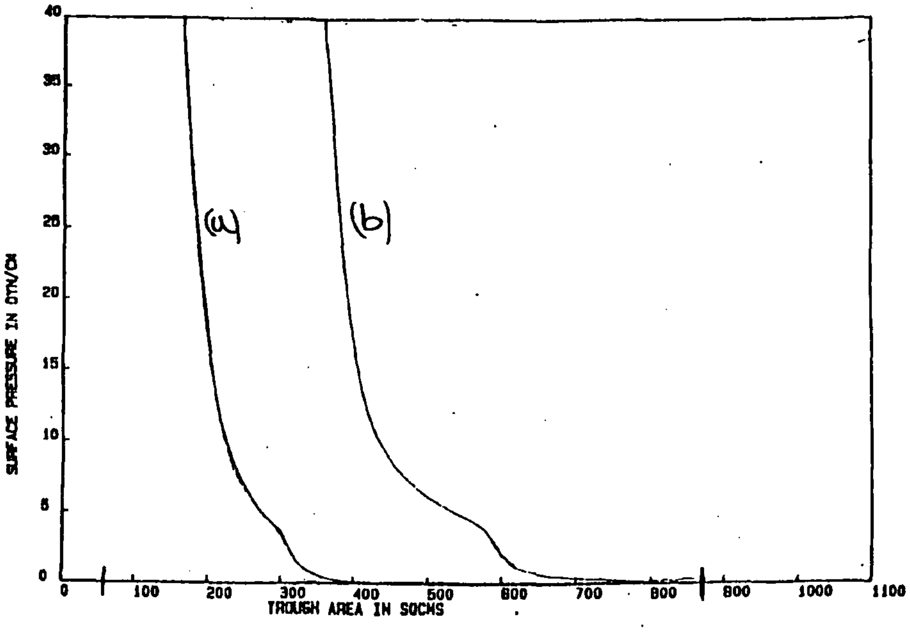


Fig. 4.5a: *Isotherms for compound (91): (a) 100 microlitres; and (b) 200 microlitres of (91) (1mg/ml in chloroform).*

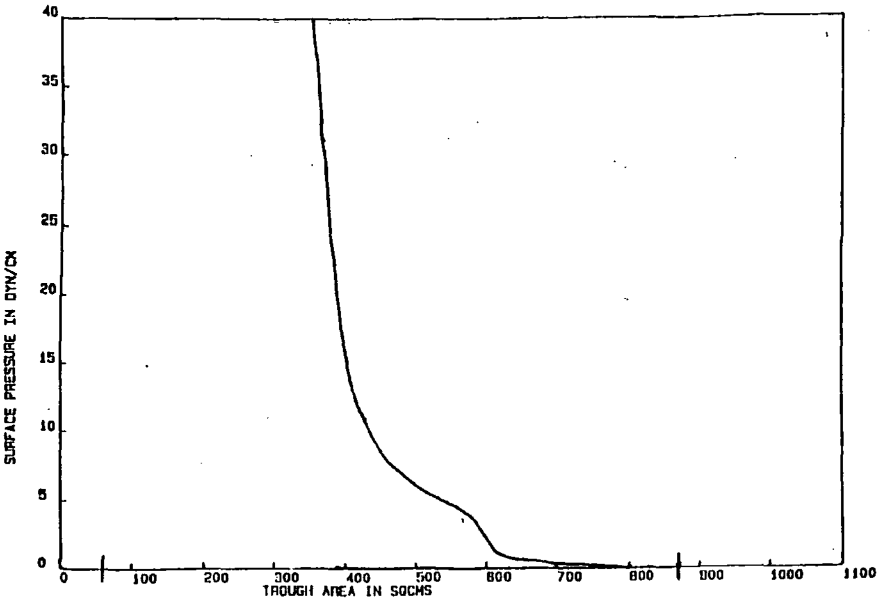


Fig. 4.5b: *Isotherms for compound (92): (a) 200 microlitres of (92) (1mg/ml in chloroform).*

The isotherms show that the area per molecule for both (91) and (92) (0.21 nm^2 at 30 mN m^{-1}) are less than predicted values from X-ray crystal structures and space filling models. The as-deposited films were found to be insulating (σ_{rt}= $10^{-7}Scm^{-1}$). Upon doping the conductivity of both (91) and (92) increased slightly and reached a maximum of σ_{rt}= $10^{-5}Scm^{-1}$, 30 minutes after doping. This conductivity is much less than that observed (87), which displayed a maximum conductivity of σ_{rt}= 8 x 10^{-2} Scm^{-1}.

The ultraviolet spectra of 22 layers of (91) was recorded: (a) prior to; (b) 2 mins after; (c) and 30 minutes after doping with iodine (Fig. 4.6). For the undoped sample, absorptions were present at 285 and 316 nm [curve (a)] which can be assigned to intramolecular π-π* transitions of the TTF unit[98]. Upon doping new bands at 290, 375 (shoulder) and 980nm are now observed [curves (b) and (c))]. The latter two bands can be assigned to π-π* intermolecular electron transitions of TTF radical cations and charge transfer absorptions, respectively.

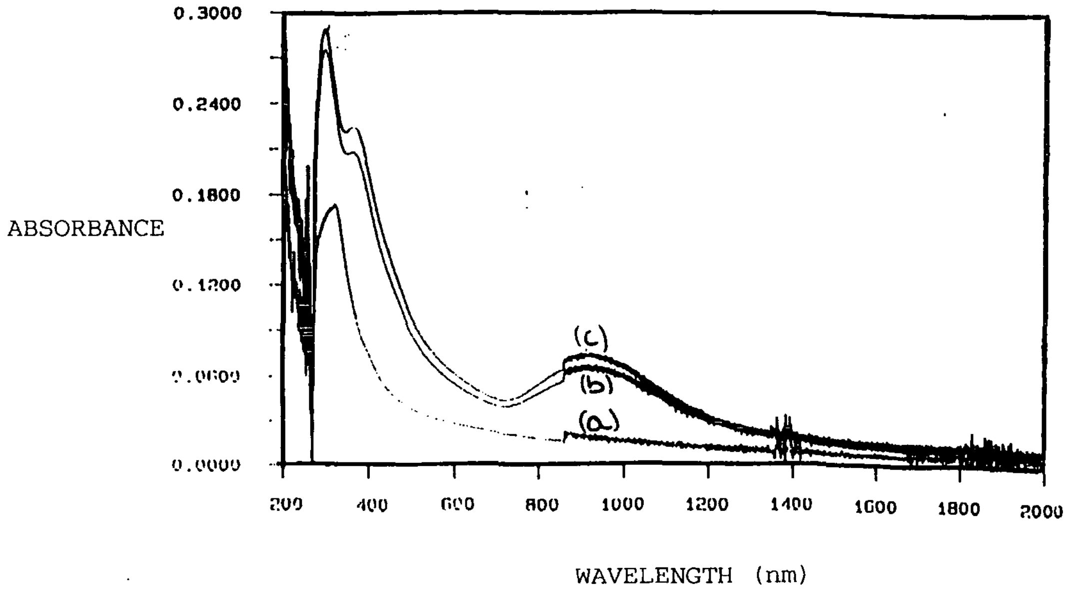


Fig. 4.6: *UV spectra for 22 layers of (91): (a) prior to doping; (b) 2 minutes after doping; (c) and 30 minutes after doping.*

The infrared spectra of (91) (22 layers on CaF_2) were recorded: (a) as deposited; (b) one minute after doping with iodine (Fig. 4.7). Most of the features in the undoped spectrum (a), are due to absorptions of the thioalkyl chain (eg. 1109 cm^{-1} C-O stretch). The infrared spectrum of the doped sample (b), showed the presence of a new band at 1340 cm^{-1}, which can be attributed to the coupling of conduction electrons to the vibrational modes of the compound, allowing previously inactive bands to become active[99].

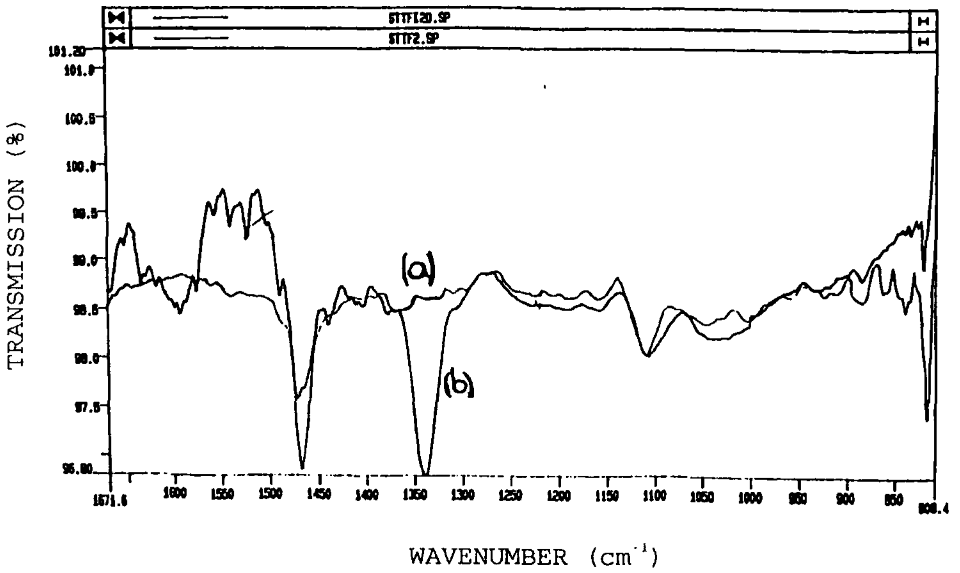
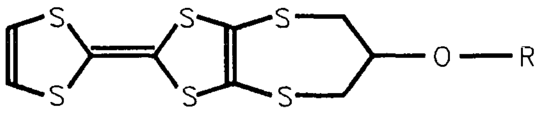


Fig. 4.7: *IR spectra for 22 layers of (91): (a) as-deposited; (b) one minute after doping.*

4.5 SYNTHESIS OF POTENTIAL C-T AND LB MATERIALS BASED ON THE 4,5-DITHIO-TTF FRAMEWORK.

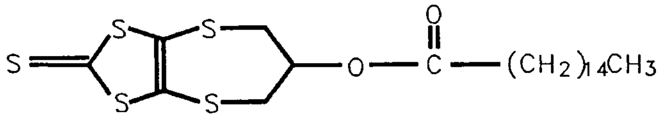
4.5.1 Introduction.

In order to produce new materials suitable for C-T salts and LB films, molecule (93) was targeted for synthesis. Such a molecule could be important in two main ways: (i) there is the potential of enhanced conductivity in LB films which contain this unit, due to the increased number of sulphur atoms in the head group of the amphiphile; (ii) hydrogen bonding in salts and complexes of (93) may give increased inter- and intrastack interactions. Amphiphilic derivatives derived from alcohol (93) bearing a urethane (94) or ester (95) connecting groups, were prime targets as these functionalities would make the TTF end of the amphiphile more polar, aiding hydrophilicity and film formation.



(93) R= H
(94) R= $C(O)(CH_2)_{14}CH_3$
(95) R= $C(O)NH(CH_2)_{17}CH_3$

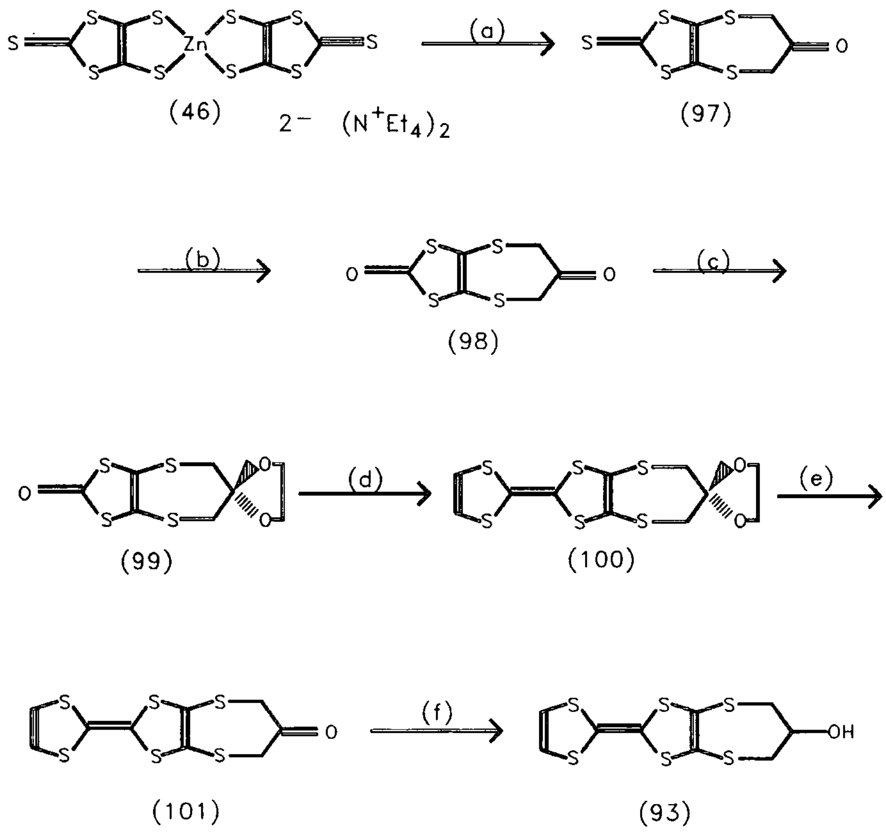
From a synthetic point of view, two strategies can be adopted in order to synthesise (94) and (95). Firstly, the TTF alcohol (93) can be synthesised; the reactivity of the hydroxyl group then allowing attachment of the long alkyl chain. Alternatively, the thione (96) could be synthesised, which could allow a cross coupling reaction with vinylene trithiocarbonate (82) to produce the required TTF with an ester link (94).



(96)

4.5.2 Synthesis of alcohol (93).

Previous workers at Durham, synthesised the unsymmetrical ketone (101) in a five step route from the zincate salt (46)[101] (Scheme 4.5). Clearly, the reduction of the ketone group of (101) could offer a route to alcohol (93). Following this route, the cross coupling to form (100) and its subsequent deprotection to form (101), progressed to give modest yields of 12% and 60%, respectively. However, the reduction to give (93) from (101) worked efficiently (80% yield).

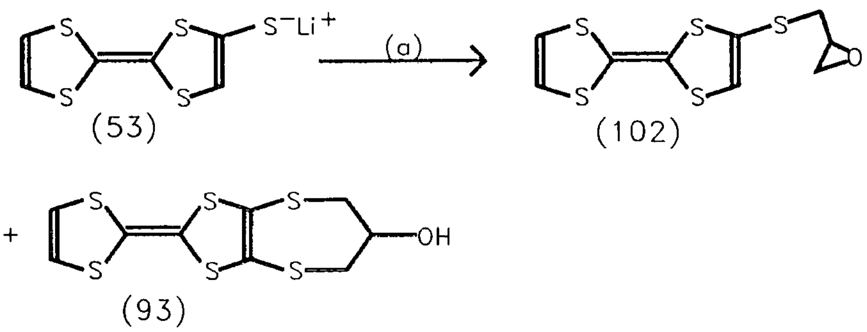


Scheme 4.5: Reagents: *(a) 1,3-dichloroacetone (2.2 equivs., acetonitrile, 50°C 4h.),*
(b) $Hg(OAc)_2$ (stirred in $CH_3COOH/CHCl_3$ 1:3, 3h.),
(c) ethylene glycol (H_2SO_4, reflux in toluene),
(d) (82), triethylphosphite (reflux, 2h.),
(e) conc. H_2SO_4 (refluxed in THF, 16h.),
(f) $LiAlH_4$ (reflux in THF, 2h.).

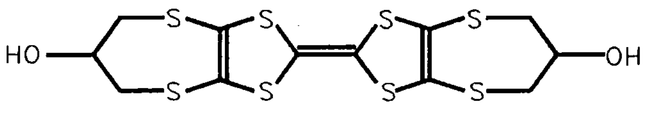
4.5.3 Synthesis of (93) direct from the TTF anion.

It has been established that the 4,5-TTF-dithiolate anion can be generated (Chapter 2) and reacted with bifunctionalised electrophiles to give unsymmetrical donor species[66]. Extending this methodology, the TTF monothiolate (53) was reacted with 1.1 equivalents of 1,3-dibromopropan-2-ol, to give (93) in 8% yield[66], along with the epoxide (102) as the major product in 30% yield (Scheme 4.6).

When 0.5 equivalents of 1,3-dibromopropan-2-ol was used, the epoxide (102) was formed exclusively (38% yield). Alternatively, when 2 equivalents of LDA and sulphur were reacted with TTF at -78°C, followed by the addition of one equivalent of 1,3-dibromopropan-2-ol, compound (93) was formed (14% yield) together with the highly insoluble compound (103) (7% yield).



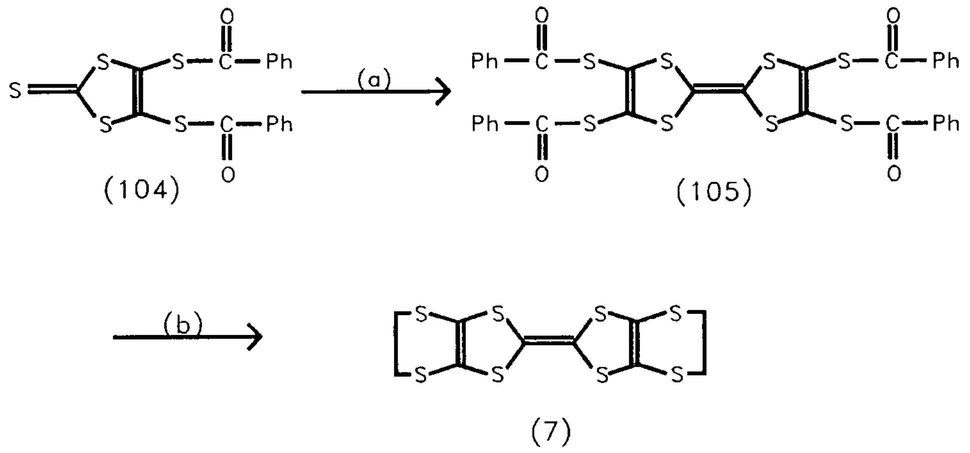
Scheme 4.6: Reagents: *(a)* $BrCH_2CHOHCH_2Br$ *(1.1 equiv.)*.



(103)

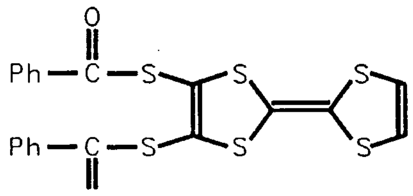
4.5.4 Attempted synthesis of (93) from dithiolates derived from the zincate salt (46).

The zincate salt (46) offers an efficient and economical route to thiones functionalised with sulphurs at the 4,5- position. Recently Hansen *et al* reported the synthesis of (105)[95], which can be deprotected under basic conditions and trapped with bifunctionalised electrophiles to give symmetrical donor species (Scheme 4.7).



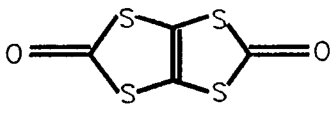
Scheme 4.7: Reagents: *(a) Co_2CO_8, (reflux in toluene, 2h.);*
(b) Sodium tert-butyl thiolate , $Br(CH_2)_2Br$.

It was thought that this methodology could offer a route to (93), if the unsymmetrical species (106) could be synthesised. Unfortunately, attempts to cross-couple vinylene trithiocarbonate (82) and the dithioester (104) using octacarbonyldicobalt, gave none of the desired unsymmetrical species (106), only the symmetrical (self-coupled) TTF (2) and (105) were formed in 10% and 7% yields, respectively.

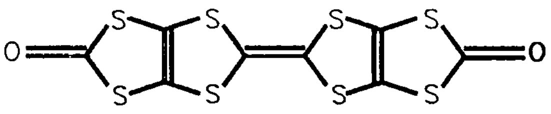


(106)

In 1977 Schumaker *et al*[61] reported the trialkylphosphite mediated self coupling of thiapendione (107) to give (108), which under basic conditions, gave the TTF tetrathiolate anion. We recognised that if thiapendione (107) could be cross-coupled with vinylene trithiocarbonate (82), the product could under basic conditions yield the desired dithioanion, which could be trapped with 1,3-dibromopropan-2-ol to afford alcohol (93). Unfortunately, the attempted cross-coupling of (107) with (82) using triethylphosphite, gave TTF (2) and (108) exlcusively.



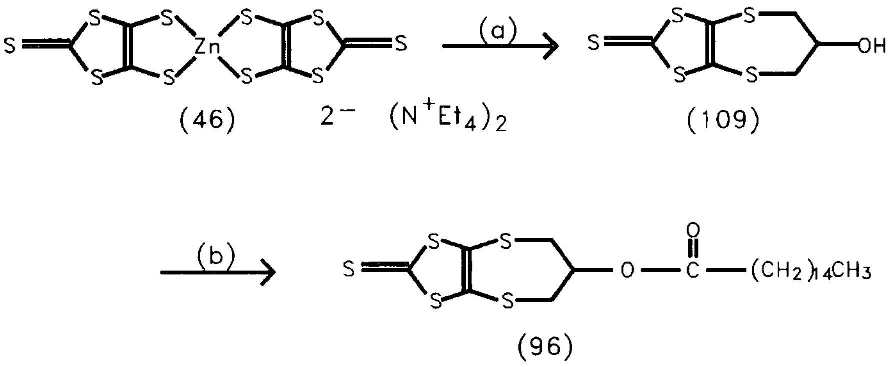
(107)



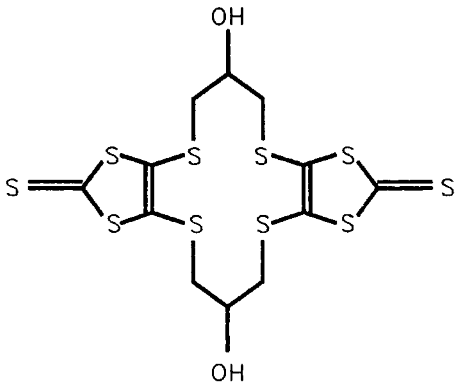
(108)

As an alternative strategy, the zincate salt (46) was reacted with 1,3-dibromopropan-2-ol, to yield alcohol (109) (66% yield), together with a highly insoluble material, which has been tentatively assigned to be macrocycle (110) (4%)[101]. By carefully varying the reaction conditions, the ratio of (109) to (110) has been optimised: a high dilution and a mild reaction temperature of 50°C, favours the formation of the former.

The alcohol (109) was functionalised with hexadecanoyl chloride to give the long chain ester species (96) in 50% yield (Scheme 4.8). Unfortunately, endeavours to cross couple (96) with (82) using triethylphosphite gave TTF (2) and unreacted starting materials only.



Scheme 4.8: Reagents: *(a)* $BrCH_2CH(OH)CH_2Br$ *(2.2 equivs., stirred in acetonitrile 50°C, 6h.),*
(b) $CH_3(CH_2)_{14}C(O)Cl$*, pyridine (stirred in dichloromethane, 20°C 16h.)*

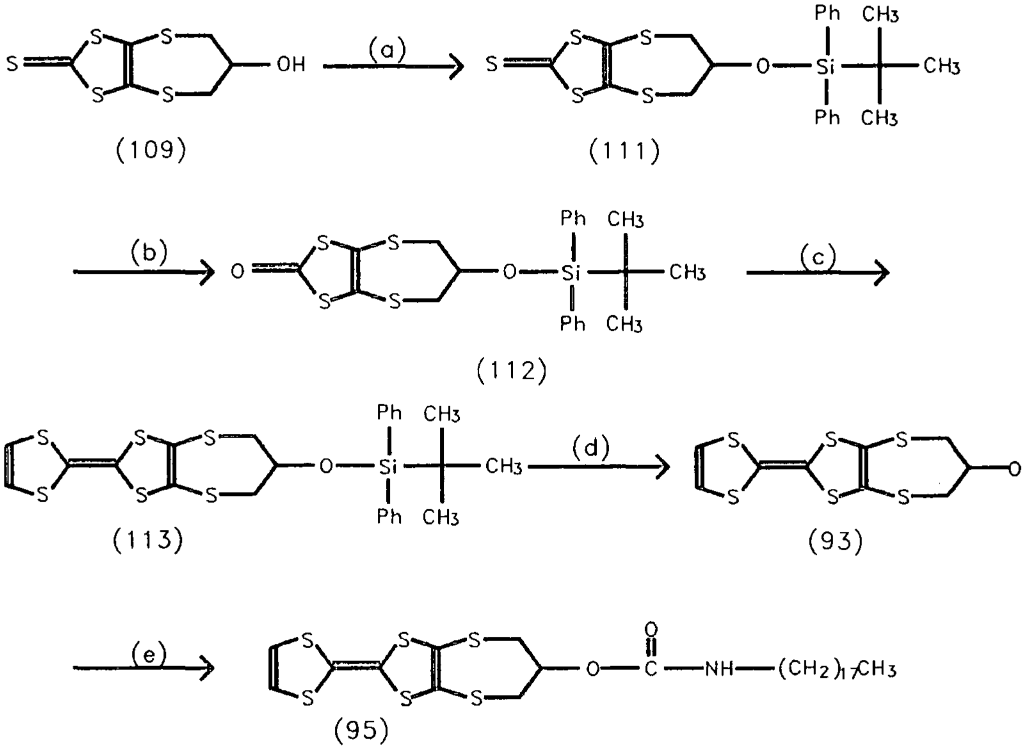


(110)

4.5.5 Synthesis of (93) *via* a *tert*-butyldiphenylsilyl ether protected derivative.

Previous attempts in this group to couple alcohol (109) with (82) using triethylphosphite to give the TTF alcohol (93) were unsuccessful. This may be due to the incompatibility of the hydroxyl group of (109) with the coupling reagent. The *tert*-butyldiphenylsilyl (TBDPS) protected alcohols are known to be stable to a wide range of reaction conditions including: acids, hydrogenolysis and phosphites[102]. The TBDPS protecting group can readily be cleaved using fluoride anions, to regenerate the parent alcohol, typically in high yield (80-95%).

Alcohol (109) was protected with *tert*-butyldiphenylsilyl chloride to give (111) in 70% yield[101]. The thione (111) was then quantitatively converted to the ketone (112) using mercuric acetate. Derivative (112) was cross-coupled with (82) to afford the protected TTF derivative (113) (32% yield). Alcohol (93) was formed from (113) in 89% yield by the action of two equivalents of tetrabutylammonium fluoride (Scheme 4.9).



Scheme 4.9: Reagents: *(a)* $(CH_3)_3CSi(Ph)_2Cl$ *(1.1 equiv.), imidazole (2.2 equiv.);*
(b) $Hg(OAc)_2$, $CH_3COOH/CHCl_3$ *(1:3);*
(c) (82), triethylphosphite, reflux 2 h.;
(d) $Bu_4N^+F^-$, *THF,* $0^\circ C$ *(2 equiv.),*
(e) octadecylisocyanate, triethylamine, stirred in dichloromethane at 20 °C for 4 days.

The attachment of a long chain to (93), was best realised by reacting (93) with octadecylisocyanate, under basic conditions, to give a urethane connecting group. This was achieved concurrently with other work in our group which established that acid chlorides react with (93) to give esters in moderate yields[101]. Thus, when (93) was reacted with the long chain isocyanate, under basic conditions, the amphiphilic urethane derivative (95) was formed in low yield (7%).

The CV data for (93) and (95) revealed two oxidations at $E_1^{1/2}$ = 0.50 V and $E_2^{1/2}$ = 0.89 V. As anticipated, the addition of the second sulphur to the periphery of TTF increased the oxidation potentials of the donor, as compared to the alcohol (88) ($E_1^{1/2}$ = 0.43 V and $E_2^{1/2}$ = 0.85 V). Attempts to form a complex of (93) with TCNQ (1) were unsuccessful.

4.6 CONCLUSIONS.

TTF amphiphiles with chalcogens linking the long chain to the TTF unit form reasonable quality LB films. Unfortunately, the conductivity of these materials is considerably less than LB films of (14), (15) and (16). This observation indicates that the conjugated carbonyl and thiocarbonyl groups adjacent to the TTF ring, may also play an important role in conductivity as well as film quality.

The LB materials (91) and (92) with a functionality in the side chain also form reasonable quality LB films. Unfortunately, the conductivity is drastically reduced as compared to compounds with carbonyl and thiocarbonyl groups adjacent to the ring. This may be due to complete charge-transfer occurring upon doping, preventing the formation of a highly conducting mixed valence state.

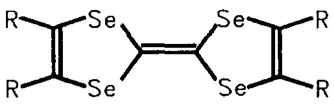
The reactivity of the hydroxyl group of (93) offers the possibility of producing highly functionalised TTF derivatives suitable for: charge-transfer complexes, LB films and polymeric materials. The TTF anion route has established a one-pot synthesis of the alcohol (93) in modest yield. An improved route from the zincate salt (46) to yield alcohol (109) has also been established, which allows (93) to be produced on a larger scale.

CHAPTER 5.

SYNTHESIS OF MONOFUNCTIONALISED TETRASELENAFULVALENES.

5.1. INTRODUCTION.

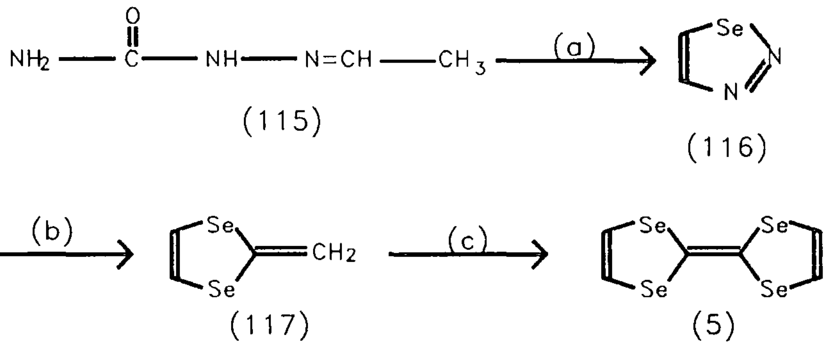
The discovery of metallic and superconducting salts of tetraselenafulvalene[103] (TSF, 5) and tetramethyl-TSF (TMTSF, 114)[104], has led to the synthesis of a range of TSF analogues in attempts to extend the intriguing conductivity properties of these materials. At the outset of this present work, there were no examples of monofunctionalised amphiphilic TSF's suitable for LB film formation; those with carbonyl or thiocarbonyl groups adjacent to the TSF moiety are clearly prime targets, in view of the high conductivity and excellent film quality of the analogous TTF materials[37,38]. A route has now been developed to produce monofunctionalised amphiphilic TSF's with carbonyl groups linking the long alkyl chain to the TSF ring[105].



(5) R = H
(114) R = CH_3

5.2 SYNTHESIS OF TETRASELENAFULVALENE (5).

Tetraselenafulvalene was first synthesised in 1974, but has not enjoyed the same profusion of derivatives of its sulphur brethren, principally due to its limited accessibility. There exist four routes to TSF; the first two by Engler[106a] and Cava[106b] involve the use of the pernicious reagent CSe_2, which is notoriously difficult to obtain. Another synthesis by Bechgaard[106c] involves a complex multi-step route. In 1987 Cava[106d] reported a short, economic synthesis of TSF starting from the readily available acetaldehyde semicarbizone (115)[107] (Scheme 5.1).



Scheme 5.1: Reagents: *(a) SeO_2, HOAc, dichloromethane; (b) tert-BuOK/ tert-BuOH, DMF; (c) Iodine, morpholine, DMF.*

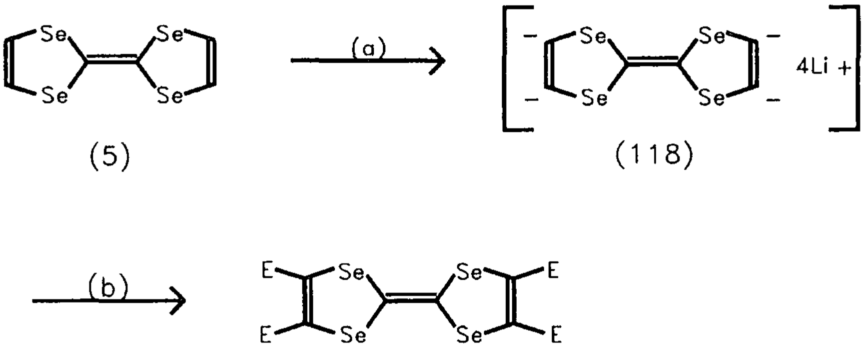
In our laboratory, the conversion of (115) to 1,2,3-selenadiazole (116) occurred in moderate yield (27%, cf. 30-40% quoted by Cava[107b]), even when a large excess of the phase transfer reagent cetyltrimethyl ammonium bromide was utilised. An improved purification method for (116) was developed using flash silica column chromatography, eluting with dichloromethane, which overcomes the hazardous distillation technique used previously[107b].

The basic decomposition of (116) with potassium *t*-butoxide progressed cleanly to give (117) in 79% yield. Compound (117) was used directly, without purification, in the next step of the synthesis to give TSF (30% yield).

5.3 SYNTHESIS OF FUNCTIONALISED TSF's.

5.3.1 Synthesis of tetrasubstituted TSF's.

There exist two main routes to produce functionalised TSF's. The most widely used of these involves the coupling of substituted 1,3-diselenoles[108] to give the fully substituted TSF's. However, in practice this proves to be an inefficient method when applied to unsymmetrical derivatives due to the problematic separation of cross-coupled and self-coupled products. However, TSF can be tetralithiated with LDA to yield intermediate (118) (analogously to TTF[50,51]), which can be trapped by the addition of excess electrophile to give the tetrasubstituted products (119)-(122) in moderate yields[109,110] (Scheme 5.2).



(5)
(118)

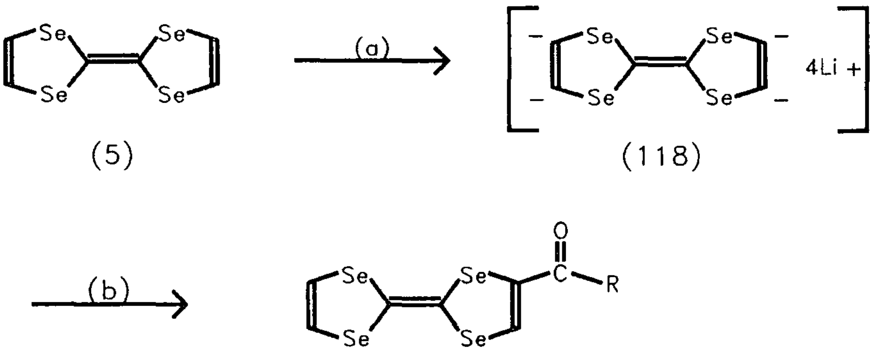
(119) E = S-Ph.
(120) = Se-Ph.
(121) = $C(O)OCH_3$.
(122) = C(O)OH.

Scheme 5.2: Reagents: *(a) LDA (4 equiv.), -100°C, THF;*
(b) electrophile (E), (excess).

5.3.2 Synthesis of monofunctionalised TSF's.

In 1977, Green claimed that TSF could be mono-substituted under similar conditions of TTF (2), using nBuLi as base[48], but no yields or experimental details were given and this claim has not been substantiated. Recently, Cava *et al* have shown that under the aforementioned conditions, TSF is destroyed, yielding ring opened products and not monosubstituted derivatives[110].

In our laboratory, we have extended the work of Cava[110] and critically modified the route of Green[48], to produce mono-functionalised TSF's in modest yield. Our procedure involves the reaction of 4 equivalents of LDA with (5), to generate (118), followed by the addition of 0.8 equivalents of an acid chloride (Scheme 5.3). Under these conditions, mono-acyl TSF derivatives (123)-(127) were the only isolated products alongside regenerated TSF (5) (60%).



(123) R= CH_3.
(124) = $(CH_2)_3CH_3$.
(125) = $(CH_2)_{12}CH_3$.
(126) = $(CH_2)_{14}CH_3$.
(127) = $(CH_2)_{16}CH_3$.

Scheme 5.3: Reagents: *(a) LDA (4 equiv.), -100°C; RC(O)Cl (0.8 equiv.).*

In an attempt to produce a TSF derivative which has terminal functionality in the side chain, the TSF tetra-anion (118) was reacted with 4-bromobutyryl chloride. However, the debrominated product (124) was formed, presumably by lithium-halogen exchange.

The long chain derivatives (125) and (126), are the first examples of amphiphilic TSF's; compound (127) unfortunately could not be obtained analytically pure. Endeavours to insert sulphur into one of the C-Li bonds of (118), followed by the trapping of the resultant thiolate anion with 2-bromoethanol was unsuccessful. Likewise, the reaction of (118) with 0.8 equivalents of the chlorothioformate (78) was also unsuccessful.

The redox potentials of (123)-(126) are identical by cyclic voltammetric studies; two, reversible, single-electron oxidations are observed at $E_1^{\frac{1}{2}}$= 0.62 and $E_2^{\frac{1}{2}}$= 1.00 V (relative to Ag/AgCl, Pt electrode in CH_2Cl_2). The data are consistent with the fact that the acyl-TSF derivatives (123)-(126) are harder to oxidise than acyl-TTF derivatives[36,37](Fig. 5.1), in accordance with known data for the parent, unsubstituted systems[111].

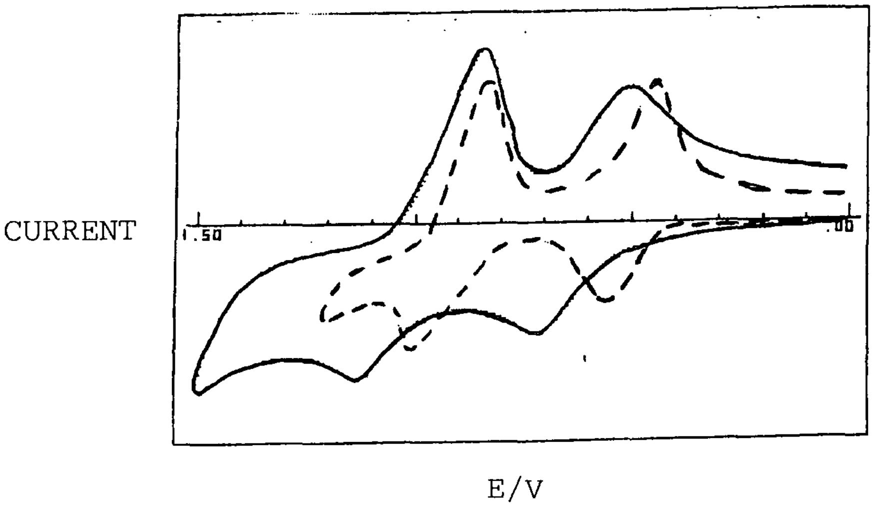


Fig. 5.1: *Comparison of cyclic voltammetric data for 4-acetyltetraselenafulvalene (123) (-) and 4-acetyltetrathiafulvalene (67) (- -), under identical conditions (Ag/AgCl, Pt, CH_2Cl_2).*

5.3.3 X-Ray crystal structure of (123).

In view of the known formation of ring-opened products from the lithiation of TSF[110], X-ray quality crystals of 4-acetylTSF (123) was grown from a 50:50 mixture of CS_2/hexane. The crystal structure unequivocally shows that the TSF ring stays intact under our conditions, and no 1,4- diselenin derivatives were observed, which could conceivably be formed from TSF by a ring opening, ring closure sequence as with tetratellurafulvalene[112].

Figure 5.2 shows that there are two independent molecules A and B in the unit cell of compound (123). The carbonyl group of (123), like the carbonyl group in 6-bromohexanoyl-TTF[36] (68), is in the plane of the TSF ring, thus maximising its conjugation to the TSF π system. A notable feature of the crystal structure of (123) is the significant deviation of planarity of the TSF system, which is not observed in the crystal structure of the other neutral TSF derivatives, namely, tetramethyl-TSF[113] and dibenzo-TSF[114].

5.4 ATTEMPTED FORMATION OF LB FILMS OF (125) AND (126).

The attempted formation of LB films of amphiphiles (125) and (126) were unsuccessful; no reproducible isotherm was obtained.

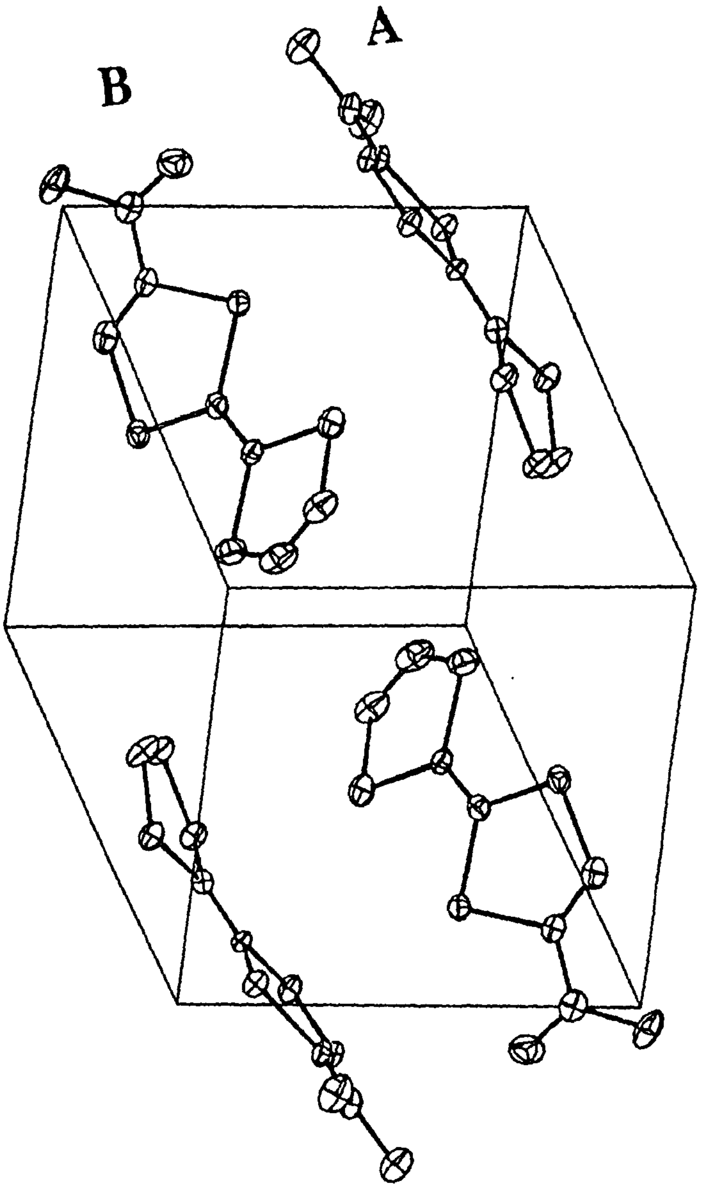


Fig. 5.2: *Single crystal structure of (123), showing the two independent molecules A and B in the unit cell.*

5.5 CONCLUSIONS.

By extension of previously reported routes to functionalised TSF's, we have established a route to monofunctionalised TSF's bearing ketone groups adjacent to the heterocycle. The yields of the acyl-TSF's (123)-(126) are comparable to their TTF analogues synthesised from the TTF anion (23) (ca. 20-25%). The X-ray crystal structure of 4-acetyltetraselenafulvalene (123) proves that under these reaction conditions, the TSF ring stays intact.

Attempts to synthesise TSF's bearing alklythio and thiocarbonyl groups, in a similar fashion to that which works efficiently with TTF, were unsuccessful. This indicates that the synthesis of monofunctionalised TSF's is much harder than the monofunctionalisation of TTF.

Unfortunately, the exciting possibility of forming the first LB films of the TSF containing amphiphiles (125) and (126) was not realised. The lack of a reproducible isotherm suggests that either (125) and (126) are more water soluble than their sulphur brethren, or alternatively, the TSF head group is unstable when a condensed orientated monolayer is formed.

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CHAPTER SIX.

EXPERIMENTAL.

CYCLIC VOLTAMMETRY DATA FOR TTF DERIVATIVES.

COMPOUND	$E_1^{1/2}$	$E_2^{1/2}$	$E_3^{1/2}$
(2)	0.34	0.78	
(30)	0.56	0.78	
(31)	0.70	0.97	
(32)	0.55	0.76	
(33)	0.65	0.95	
(34)	0.55	0.80	
(35)	0.80	0.95	
(59)	0.49	0.61	0.85
(60)	0.49	0.61	0.85
(64)	0.40	0.88	
(65)	0.40	0.88	
(75)	0.50	1.00	
(76)	0.45	1.00	
(77)	0.45	1.00	
(79)	0.49	0.86	
(80)	0.43	0.98	
(81)	0.43	1.00	
(85)	0.62	1.08	
(86)	0.63	1.10	
(87)	0.50	0.88	
(88)	0.46	0.90	
(91)	0.45	0.92	
(92)	0.45	0.92	
(93)	0.50	0.89	
(95)	0.50	0.90	
(123)	0.62	1.00	
(124)	0.63	1.00	
(125)	0.62	0.98	
(126)	0.62	1.00	

Cyclic voltammograms for TTF derivatives. [1 x 10^{-5} *Mol* dm^{-3} *solution in dichloromethane,* $Et_4N^+PF_6^-$ *(ca. 0.01 M), under nitrogen, versus Ag/AgCl, Pt electrode, scan rate 100 mV* s^{-1}*, 20 °C.*

6.1 GENERAL METHODS.

Melting points were recorded on a Kofler hot-stage microscope apparatus and are uncorrected. Elemental analyses were performed using a Carlo-Erba Strumentazione. Infrared spectra were recorded on a Perkin-Elmer 577 Spectrophotometer as Nujol mulls (neat, if liquids). Solution state ultra-violet spectra were recorded on a Kontron Uvikon 930 instrument. UV-visible-near-IR spectra were obtained on a Cary 2300 spectrophotometer.

Proton NMR spectra were recorded on a Bruker AC 250 instrument, operating at 250.134 MHz. The chemical shifts, in ppm, are relative to tetramethylsilane as internal standard. Mass spectra were obtained on a VG 7070E instrument, operating at 70eV, with ionisation mode as indicated. High resolution masses were measured in the EI mode.

TLC data were obtained using Merck pre-coated silica or alumina (0.2 mm.) on aluminium sheets. For column chromatography, Merck silica gel (70-230 mesh) or Merck alumina (activity II, 70-230 mesh) were used as indicated. Neutral alumina refers to alumina pre-soaked in ethyl acetate for 24h. All solvents were distilled prior to use in chromatography.

Solvents were dried over the following agents under a nitrogen atmosphere: diethyl ether and THF (sodium metal); benzene and toluene (sodium metal); chlorocarbons (P_2O_5); acetonitrile (CaH_2). All other reagents were reagent grade, and were used as supplied.

GENERAL PROCEDURE FOR FORMING LB FILMS.

A fresh solution of the analytically pure* amphiphilic TTF derivative in hplc grade chloroform (1mg/ml), was spread onto a ultrapure water surface of an LB trough. The solvent was allowed to evaporate, and the film was compressed by electronically controlled barriers (typically at a rate of 5 cm^2 min^{-1}). The surface pressure *versus* trough area isotherm was monitored during the formation of the condensed orientated monolayer.

Deposition onto a clean glass slide was achieved by selecting a dipping pressure which corresponded to the formation of a condensed orientated monolayer at the air/water interface (typically 20-30 mN m^{-1}). The electronically controlled dipping head maintained a constant dipping speed (typically 2-5 mm min^{-1}) of the glass substrate as it passed through the air/water interface of the trough. The progress of the deposition was monitored by inspection of the area per molecule and surface pressure graphs, throughout the deposition of the 10-20 layers.

The lateral d.c. conductivity of the deposited LB films were measured using a two probe technique, following doping by exposing the films to iodine vapour for 2 minutes. Electrical contacts to the film were made by air drying silver paste. The doped films were placed in a high pressure vessel, which was then evacuated using a high vacuum pump for 5 minutes. A range of voltages were applied laterally to the monolayers, and the subsequent current was recorded. The voltage and current readings were used to calculate the resistance, and hence the lateral conductivity could be obtained.

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* In order to obtain the analytically pure amphiphilic derivatives, repeated chromatography using the conditions described later in this chapter were required.

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 the donor (ca.$1x10^{-5}$ M) with oven dried tetrabutylammonium perchlorate (0.01M) as the supporting electrolyte in dry acetonitrile or dichloromethane. All solutions were purged with nitrogen and retained under the inert atmosphere while the CV data were recorded.

Compressed pellet conductivity measurements on powdered samples were obtained using the two probe technique; the samples were manually compressed between two steel probes and the sample resistance monitored with a Fluka 8000A Digital multimeter. Conductivity measurements on LB films were performed using a two probe technique, contacts on the film were made with air-drying silver paste. A Keithley 414A Current source and a Time electronics 2003S Voltage Source were used to monitor the resistance.

6.2 EXPERIMENTAL TO CHAPTER TWO.

6.2.1 Materials.

Tetrathiafulvalenyllithium (23) was prepared by a revised route to the literature[49]. TTF (2) (0.25 g, 1.23 mmol) in dry ether (30 ml) was cooled to -78°C. To this, freshly prepared LDA [from n-BuLi 1.6 M (1.6 ml, 1.35 mmol) and diisopropylamine (0.2 ml, 1.35 mmol)] in dry ether (10 ml) was added dropwise over 1 min. The reaction was maintained for 1h. at -78°C, by which time a thick yellow precipitate of (23) had formed.

p-Toluenesulphonyl bromide (36) was prepared according to the literature from p-toluenesulphonyl hydrazide and bromine in chloroform (90 %). Mpt. 94-96°C (lit.[58] 96°C).

p-Toluenesulphonyl iodide (37) was prepared according to the literature from p-toluenesulphonyl hydrazide, 10 % solution of iodine in methanol, stirred in chloroform (76 % yield). Mpt. 84-85°C (lit.[58] 84-85°C).

Zincate salt (46) was prepared according to the literature from CS_2, sodium shavings and $ZnCl_2$ in DMF (85%). Mpt. 199-206°C (lit.[61] 200-206°C).

2,5,7,9-Tetrathiabicyclo[4.3.0]non-1(6)-en-8-thione (47) was prepared according to the literature procedure from (46) and 1,2-dibromoethane in refluxing acetonitrile (60% yield). Mpt. 118-120°C (lit.[61] 119-120°C).

2,5,7,9-Tetrathiabicyclo[4.3.0]non-1(6)-en-8-one (48) was prepared according to the literature procedure from (47) and mercuric acetate in chloroform and acetic acid

(3:1) (100% yield). Mpt. 127°C (lit.[61] 127-128°C).

Dimethyl 1,3-dithiole-2-thione-4,5-dicarboxylate (51) was prepared according to the literature procedure from dimethyl acetylenedicarboxylate and ethylene trithiocarbonate in refluxing toluene (60% yield). Mpt. 84-85°C (lit.[94] 86-87°C).

Bis(methylcarboxy)ethylenedithiotetrathiafulvalene (53) was prepared according to the literature procedure from (48) and (52) in refluxing triethylphosphite (32% yield). Mpt. 119°C (lit.[63] 119°C).

Ethylenedithiotetrathiafulvalene (41) was prepared according to the literature procedure from (52) and LiBr in refluxing HMPA (5% yield). Mpt. 199-201°C (lit.[63] 200°C).

Bis(phenylsulphonyl)sulphide (61) was prepared according to the literature procedure from benzenesulphinic acid (sodium salt), sulphur dichloride in dry benzene (74% yield). Mpt. 128-129°C (lit.[78] 128-130°C).

Bis(phenylsulphonyl)diselenide (62) was prepared analogously to (61) from benzenesulphinic acid (sodium salt) and selenium monochloride in dry benzene (72% yield). Mpt. 64-65°C (lit.[79] 64-66°C).

Bis(phenylsulphonyl)disulphide (63) was prepared analogously to (61) from benzenesulphinic acid (sodium salt) and sulphur monochloride in dry benzene (73% yield). Mpt. 66-68°C (lit.[79] 68°C).

6.2.2 4-Chlorotetrathiafulvalene (30).

p-Toluenesulphonyl chloride (0.26 g, 1.35 mmol) was added to an ethereal slurry of (23) [from 0.25g of (2)] at -78°C. The mixture was maintained at -78°C for 5h. and then allowed to warm to room temperature overnight. The crude mixture was poured onto distilled water (100 ml), the ether layer was separated, dried ($MgSO_4$) and evaporated *in vacuo* to give the crude product which was purified using preparative t.l.c. plates (silica coated), eluted with cyclohexane (R_f= 0.65), to give (30) (0.139 g,48%) as an orange solid. Mpt. 57-58°C; Analysis found: C, 30.00; H, 1.24; Required for $C_6H_3ClS_4$: C, 30.18; H, 1.26%; m/e EI: 238 (M^+); ν_{max} (Nujol): 1253, 1090, 945, 812, 797, 775, 740, 720, 635, 630 cm^{-1}; δ_H ($CDCl_3$): 6.33 (2H,s), 6.15 (1H,s) ppm.

6.2.3 4,5-Dichlorotetrathiafulvalene (31).

Compound (31) was isolated as a faster moving band (R_f 0.75), (0.013 g, 4%) as a red solid. Mpt. 103-106°C; HRMS: m/e $C_6H_2Cl_2S_4$ calc: 271.8395; found : 271.8395; ν_{max} (Nujol): 1305, 1255, 1150, 1090, 1025, 933, 925, 797, 785, 772, 735, 718, 632, cm^{-1}, δ_H ($CDCl_3$): 6.29 (2H,s) ppm.

6.2.4 4-Bromotetrathiafulvalene (32).

Compound (32) was formed using an identical procedure and scale to (30), using p-toluenesulphonyl bromide (0.317 g, 1.35 mmol), to give (32) (0.132 g, 38%) as an orange solid (R_f 0.65). Mpt. 40-45°C (dec). Analysis found: C, 25.51; H, 1.02;

Required for $C_6H_3BrS_4$: C, 25.44; H, 1.06%; m/e EI: 283 (M^+); ν_{max} (Nujol): 1257, 1088, 898, 795, 772, 757, 735, 645, 635 cm^{-1}; δ_H ($CDCl_3$): 6.26 (2H,s), 6.20 (1H,s) ppm.

6.2.5 4,5-Dibromotetrathiafulvalene (33).

Compound (33) was isolated as a faster moving band (R_f= 0.75), (0.022 g, 5%) as a red solid. Mpt. 129-130°C; Analysis found: C, 19.83; H. 0.60%; Required for $C_6H_2Br_2S_4$: C, 19.89; H, 0.55 %; m/e EI: 362 (M^+); δ_H ($CDCl_3$): 6.26 (2H,s) ppm.

6.2.6. 4-Iodotetrathiafulvalene (34).

Compound (34) was formed using an identical procedure and scale to (30) using p-toluenesulphonyl iodide (0.282 g, 1.35 mmol), to give (34) (0.137 g, 34%) as an orange solid, which darkens on standing. Mpt. 110-112°C (dec). Analysis found: C, 21.72; H, 0.87; Required for $C_6H_3IS_4$: C, 21.81; H, 0.91%; m/e EI: 330 (M^+); ν_{max} (Nujol): 1300, 1260, 1150, 800, 770, 720 cm^{-1}; δ_H ($CDCl_3$): 6.35 (1H,s), 6.26 (2H,s) ppm.

6.2.7 Tetrachlorotetrathiafulvalene (36).

TTF (2) (0.25 g, 1.23 mmol) was dissolved in dry ether (50 ml) and cooled to -78°C under a nitrogen atmosphere. Freshly-prepared LDA (4.4 equiv.) [from diisopropylamine (0.8 ml, 5.4 mmol) and n-BuLi 1.6M (3.6 ml, 5.4 mmol)] in dry ether (10 ml) was added dropwise to form the green tetralithiated intermediate.

After 1.5 h., p-toluenesulphonyl chloride (1.0 g, 5.4 mmol) was added and the reaction was allowed to warm to 20°C. The mixture was poured onto water (100 ml), dried ($MgSO_4$) and evaporated *in vacuo* to yield a crude product which was purified on a silica column eluted with cyclohexane (R_f= 0.85), to give (36) (0.125 g, 30%) as a red solid. Mpt. 221-223°C (lit.[51] 221-223°C).

6.2.8 4-Chlorotetrathiafulvalene - 7,7,8,8-tetracyano-p-quinodimethane complex (2:1 stoichiometry) (38).

A boiling solution of compound (30) (0.05 g) in dichloromethane (5 ml) was added to a boiling solution of TCNQ (1) (0.1 g) in dry dichloromethane (5 ml) and the resultant green solution refluxed for 0.5h under nitrogen. After slow cooling to 20°C., the solid was collected by filtration, washed with ice-cold dichloromethane (2 x 5 ml) and dried *in vacuo* to afford complex (37) as a black solid (0.07 g). Mpt. >250°C; Analysis found : C, 42.0; H, 1.5; N, 7.8%; Required for $C_{24}H_{10}Cl_2N_4S_8$ (ie. a 2:1 complex): C, 42.4; H, 1.5; N, 8.2%.

6.2.9 4-Bromotetrathiafulvalene-7,7,8,8-tetracyano-p-quinodimethane complex (2:1 stoichiometry) (39).

Complex (38) was prepared analogously to complex (37). Compound (31) (0.05 g) and TCNQ (1) (0.100 g) in dry dichloromethane (10 ml), yielded complex (38) as a black powder (0.075 g). Mpt. >250°C; Analysis found: C 36.08; H, 1.22; N, 6.98; Required for $C_{24}H_{10}Br_2N_4S_8$ (ie. 2:1 complex): C, 37.40; H, 1.29; N, 7.27%.

6.2.10 Ethylenedithiotetrathiafulvalene (41).

To an ethereal slurry of (23) [from 0.25 g of (2)], elemental sulphur was added (0.06 g, 1.84 mmol). The reaction was maintained at -78°C for 7h., then 1,2-dibromoethane (0.1 ml, 1.23 mmol) in dry ether (2 ml), was added dropwise over 2 minutes. The resulting orange solution was allowed to warm to room temperature overnight. The crude mixture was poured onto distilled water (100 ml), the aqueous layer was separated and further extracted with toluene (2 x 50 ml). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated *in vacuo* to give the crude product. Column chromatography (silica) of the residue, eluting with cyclohexane/toluene (3:1 v/v), gave (41) (0.095 g, 26%) as an orange solid. Mpt. 199°C (lit.[63] 200°C). Analysis found: C, 32.44; H, 2.09; $C_8H_6S_6$ requires: C, 32.65; H, 2.04%.

6.2.11 Ethylenediselenotetrathiafulvalene (44).

Compound (44) was synthesised using an identical procedure and scale to (41) using elemental selenium (0.145 g, 1.84 mmol), to give (44) (0.83 g, 18%) as an orange/brown solid. Mpt. 194-197°C (dichloromethane/hexane 1:1v/v) (lit.[64] 195°C). Analysis found: C, 33.25; H, 2.66; $C_8H_6S_4Se_2$ requires: C, 33.33; H, 2.77%.

6.2.12 Bis(tetrathiafulvalenyl)sulphide (59).

To an ethereal slurry of (23) [from 0.25 g of (2)] at -78°C, di(phenylsulphonyl)sulphide (0.154 g, 0.49 mmol) was added. The reaction mixture was maintained at -78°C for 5 h. and then allowed to warm to room temperature overnight. The crude mixture was poured onto distilled water (100 ml), the aqueous layer was separated and further extracted with dichloromethane (2 x 100 ml). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated *in vacuo* to give the crude product. Column chromatography (silica) of the residue, eluting with cyclohexane/toluene (3:1 v/v), gave (59) (0.040 g, 14%) as an orange/brown solid. Mpt. 144-147°C (CS_2/hexane). Analysis found: C, 32.79; H, 1.30; Required for $C_{12}H_6S_9$: C, 32.88; H, 1.37%; m/e DCI: 439 (M^++1); ν_{max} (Nujol): 2710, 1310, 1250, 1160, 1085, 920, 850, 790, 770, 730, 720, 655, 635, 520 cm^{-1}; δ_H ($CDCl_3$): 6.52 (1H,s), 6.32 (2H,s) ppm.

6.2.13 Bis(tetrathiafulvalenyl)selenide (60).

Compound (60) was prepared using an identical procedure to (59) using di(phenylsulphonyl)diselenide (0.22 g, 0.49 mmol), to give (60) (0.028 g, 9%) as a brown solid. Mpt. 161-164°C. Analysis found: C, 29.74; H, 1.23; Required for $C_{12}H_6S_8Se$: C, 29.69; H, 1.24%; m/e DCI: 486 (M^+1); ν_{max} (Nujol): 2710, 1310, 1250, 1160, 1085, 920, 850, 790, 770, 730, 720, 655, 635, 520 cm^{-1}; δ_H ($CDCl_3$): 6.53 (1H,s), 6.32 (2H,s) ppm.

6.3 EXPERIMENTAL TO CHAPTER THREE.

6.3.1 Materials.

4-Carboxytetrathiafulvalene (70) was prepared according to the literature from the TTF anion (23) and dry ice in anhydrous ether (45% yield).

Mpt. 180-181°C [lit.[91] 182-184 (dec)°C].

4-Chlorocarbonyltetrathiafulvalene (71) was prepared according to the literature from 4-carboxytetrathiafulvalene (70) and oxalyl chloride in dry benzene and acetonitrile (5:1) (65% yield). Mpt. 130°C (dec) (lit.[91] 130-135°C).

1,3-Dithiole-2-thione-4,5-dicarboxylic acid (83) was prepared according to the literature from dimethyl 1,3-dithiole-2-thione-4,5 dicarboxylate and aqueous HCl (96% yield). Mpt. 165-166°C (lit.[94] 164-167°C).

6.3.2 4-(Trimethylsilyl)tetrathiafulvalene (64).

To an ethereal slurry of (23) at -78°C [from 0.25 g of (2)], chlorotrimethylsilane (0.34 ml, 1.35 mmol) was added dropwise over 2 minutes. The reaction mixture was maintained at this temperature for 5 h. and was allowed to warm to ambient temperature overnight. The crude mixture was poured onto distilled water (100 ml) and the aqueous layer was separated and extracted with dichloromethane (2 x 50 ml). The combined organic extracts were dried ($MgSO_4$), filtered, evaporated *in vacuo* to give crude product which was purified using silica gel preparative tlc eluting with cyclohexane, to give (64) (0.88 g, 26%) as an amber oil. Analysis found: C, 38.87; H, 4.36; $C_9H_{12}S_4Si$ requires: C, 39.13; H, 4.31%; m/e

EI: 276 (M^+); δ_H($CDCl_3$): 6.33 (3H,s), 0.21 (9H,s) ppm.

6.3.3 4-Dimethyloctadecylsilyltetrathiafulvalene (65).

Compound (68) was prepared analogously to (64) using chlorodimethyloctadecylsilane (0.42 g, 1.35 mmol), to give (65) (0.17 g, 27%) as a yellow solid. Mpt. 39-41°C. Analysis found: C, 60.64; H, 9.16; $C_{26}H_{46}S_4Si$ requires: C, 60.70; H, 8.94%; m/e EI: 514 (M^+); ν_{max} (Nujol): 2920, 2840, 1255, 930, 840, 810, 790, 770, 750, 730, 720, 640 cm^{-1}.

6.3.4. 4-(4-Bromobutyryl)tetrathiafulvalene (66).

Compound (64) (0.1 g, 0.37 mmol) was placed in a dry nitrogen flushed flask. To this was added 4-bromobutyrylchloride (10 ml) (freshly distilled) and the resulting solution became bright red on stirring for 24h. at 20°C. Distilled water (100 ml) and dichloromethane (50 ml) were added and the aqueous layer was separated and further extracted with dichloromethane (50 ml). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated *in vacuo* to give the crude product. Column chromatography of the residue, eluting with toluene, gave (66) (0.068 g, 52%) as a red solid. Mpt. 121-123°C. Analysis found: C, 33.85; H, 2.39; $C_{10}H_9BrOS_4$ requires: C, 33.99; H, 2.55%; m/e EI: 353 (M^+); δ_H ($CDCl_3$): 7.32 (1H,s), 6.33 (2H,s), 3.48 (2H,t), 2.90 (2H,t), 2.22 (2H,p) ppm.

6.3.5 4-Acetyltetrathiafulvalene (67).

Compound (67) was prepared analogously to (66) using acetyl chloride (10 ml.) and (64) (0.1 g, 0.37 mmol) or (65) (0.1 g, 0.19 mmol) [yield 60% from (64), 55% from (65)] as a red solid. Mpt. 149-152°C (lit.[49] 152-153 °C). Analysis found: C, 39.07; H, 2.60; $C_8H_6OS_4$ requires: C, 39.02; H, 2.44%; m/e EI: 246(M^+); ν_{max} (Nujol): 2710, 1640, 1300, 1260, 1150, 1060, 1010, 930, 850, 840, 790, 770, 720, 600 cm^{-1}; δ_H ($CDCl_3$): 7.32 (1H,s), 6.33 (2H,s), 2.40 (3H,s) ppm.

6.3.6 4-(6-Bromohexanoyl)tetrathiafulvalene (68).

To an ethereal slurry of (23) [from 0.25 g of (2)] at -78°C, 6-bromohexanoyl chloride (0.21 ml, 1.35 mmol) was added. The mixture was maintained at -78°C for 5h and then allowed to warm to room temperature overnight. The crude mixture was then poured into distilled water (100 ml), the aqueous layer was separated and further extracted with dichloromethane (50 ml). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated *in vacuo* to yield the crude product. Column chromatography (silica) of the residue, eluting with cyclohexane/toluene (3:1 v/v), gave (68) (0.143 g, 30%) as a red solid. Mpt. 113-114°C. Analysis found C, 37.60; H, 3.62; $C_{12}H_{13}BrOS_4$ requires: C, 37.89; H, 3.42%; m/e EI: 380 (M^+); ν_{max} (Nujol): 3060, 2720, 1645, 1400, 1300, 1250, 1225, 1190, 1170, 1110, 1090, 1030, 970, 870, 840, 790, 780, 720, 655, 640 $cm.^{-1}$; δ_H($CDCl_3$): 7.32 (1H,s), 6.32 (2H,s), 3.41 (2H,t), 2.69 (2H,t), 1.90 (2H,m), 1.75 (2H,m), 1.47 (2H,m) ppm.

6.3.7 4-Tetradecanoyltetrathiafulvalene (69).

Compound (69) was prepared analogously to (68) using tetradecanoyl chloride (0.25 ml, 1.35 mmol), to give (69) (0.13 g, 25%) as a red solid. Mpt. 80-81°C. Analysis found: C, 57.83; H, 7.27; $C_{20}H_{30}S_4O$ requires: C, 57.97; H, 7.25%; m/e EI: 414 (M^+); ν_{max} (Nujol): 3050, 1650, 1300, 1260, 1160, 800, 720, 630 cm.$^{-1}$

6.3.8 4-(6-Phthalimidohexanoyl)tetrathiafulvalene (72).

Potassium phthalimide (1 g, 5.4 mmol) was slowly added to a stirred solution of (68) (0.28 g, 0.73 mmol) in DMF (30 ml). The solution was heated to 90°C until all of potassium phthalimide had dissolved (ca. 1 h). The solution was allowed to cool to room temperature, whence chloroform (50 ml) was added and the mixture was poured onto distilled water (100 ml). The aqueous layer was separated and extracted with chloroform (2 x 50 ml). The combined organic extracts were washed with 0.2 M NaOH (2 x 20 ml), then with water (20 ml). The solution was dried ($MgSO_4$), filtered and evaporated *in vacuo* to yield the crude product. Column chromatography (silica) of the residue, eluting with cyclohexane/toluene (3:1 v/v), gave (72) (0.26 g, 80%) as a red solid. Mpt. 149-154°C; Analysis found: C, 53.47; H, 3.78; N, 3.13; $C_{20}H_{17}NO_3S_4$ requires: C, 53.69; H, 3.80; N, 3.13%; m/e EI: 447 (M^+); ν_{max} (Nujol): 3050, 1730, 1705, 1650, 1400, 1340, 1300, 1170, 1050, 940, 875, 840, 790, 770, 660, 530 cm^{-1}.

6.3.9 4-(N,N-ethylamido)tetrathiafulvalene (75).

To on ethereal slurry of (23) [from 0.25 g of (2)] at -78°C, 2-chloroethylisocyanate (0.12 ml, 1.35 mmol) in dry ether (5 ml), was added dropwise over 5 minutes. The reaction mixture was maintained at -78°C for 5h. and then allowed to warm to room temperature overnight. The mixture was poured onto distilled water (100 ml), the aqueous layer was separated and further extracted with dichloromethane (50 ml). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated *in vacuo* to yield the crude product. Column chromatography (neutral alumina) of the residue, eluting with cyclohexane/toluene (3:1 v/v), gave (75) (0.14 g, 42%) as a yellow solid. Mpt. 121-123°C. Analysis found: C, 39.41; H, 2.62, N, 4.97; $C_9H_7NOS_4$ requires: C, 39.56; H, 2.56; N, 5.13%; m/e DCI: 274 (M^++1); ν_{max} (Nujol): 3010, 1690, 1340, 1320, 1290, 1270, 1250, 1220, 1140, 1125, 1020, 1000, 970, 940, 920, 910, 895, 870, 845, 790, 770, 750, 690, 660, 600, 525 cm^{-1}. δ_H [$(CD_3)_2CO$]: 7.26 (1H,s); 6.66 (2H,s), 4.40 (2H,t) 3.93 (2H,t) ppm.

6.3.10. 4-(N-Benzamido)tetrathiafulvalene (76).

Compound (76) was prepared analogously to (75) using phenylisocyanate (0.13 ml, 1.23 mmol) in dry ether (5 ml), to give (76) (0.2 g, 50%) as a red solid. Mpt. 147-150°C. Analysis found: C, 48.25; H, 2.83; N, 4.22; $C_{13}H_9S_4NO$ requires: C, 48.29; H, 2.79; N, 4.33%; m/e DCI: 324 (M^++1); ν_{max} (Nujol): 3330, 3010, 1720, 1640, 1605, 1530, 1500, 1450, 1325, 1310, 1270, 1220, 1180, 1160, 1075, 1030, 910, 880, 840, 810, 800, 770, 760, 750, 740, 690, 640 cm^{-1}; δ_H [$(CD_3)_2CO$]: 7.73

(2H,m), 7.56 (1H,s), 7.38 (2H,m), 7.16 (1H,s), 6.71 (2H,s) ppm.

6.3.11. 4-(N-Octadecylamido)tetrathiafulvalene (77).

Compound (77) was prepared analogously to (75) using octadecylisocyanate (0.41 g, 1.35 mmol), to give (77) (0.185 g, 30%) as an orange solid. Mpt. 96-99°C. Analysis found: C, 60.36; H, 8.41; N, 2,97; $C_{25}H_{41}NOS_4$ requires: C, 60.12; H, 8.22; N, 2.81%; m/e DCI: 500 (M^{+}+1); ν_{max} (Nujol): 3320, 1620, 1530, 1315, 1300, 1280, 1265, 1230, 1150, 840, 810, 800, 770, 720, 630 cm.$^{-1}$

6.3.12. 4-(Chlorobutyl)chlorothioformate (78).

A solution of pyridine (3.7 ml, 46 mmol) in dry ether (5 ml), was added dropwise to a stirred solution of thiophosgene (3.52 ml, 46 mmol) and 4-chloro-1-butanol (4.6 g, 46 mmol) in dry ether (75 ml) under nitrogen at 0°C. The solution was maintained at this temperature for 2h., by which time a heavy white precipitate had formed. The precipitate was removed by filtration and the filtrate was concentrated *in vacuo* to give a brown oil. ν_{max} (neat): 2950, 2880, 1750, 1460, 1450, 1390, 1270, 1170, 1110, 1020, 990, 900, 750, 730, 680, 650 cm^{-1}.

6.3.13. O-[(4-Chlorobutyl)thiocarboxy]tetrathiafulvalene (79).

To an ethereal slurry of (23) at -78°C., (78) in dry ether (5 ml) was added dropwise over 2 minutes. The mixture was maintained at -78°C. for 5h. and then was allowed to warm to room temperature overnight. The mixture was poured onto distilled water (100 ml), the aqueous layer was separated and further extracted with dichloromethane (2 x 50 ml). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated *in vacuo* to give a crude product. Column chromatography (silica) of the residue, eluting with toluene, gave (79) (0.25 g, 58%) as a purple solid. Mpt. 95-97°C Analysis found: C, 37.19; H, 3.15; $C_{11}H_{11}ClOS_5$ requires: C, 37.08: H, 3.09%; m/e EI: 256 (M^+); ν_{max} (Nujol): 1530, 1510, 1290, 1230, 1190, 1095, 1040, 1010, 890, 830, 810, 800, 780, 745, 730, 650, 630 cm^{-1}; δ_H ($CDCl_3$): 7.32 (1H,s), 6.29 (2H,s), 4.43 (2H,t), 3.53 (2H,t), 1.86 (2H,m), 0.86 (2H,m) ppm.

6.3.14. 4-(N-Methylthioamido)tetrathiafulvalene (80).

To an ethereal slurry of (23) [from 0.25 g of (2)] at -78°C., methylisothiocyanate (0.09 ml, 1.35 mmol) in dry ether (2 ml) was added dropwise over 2 mins. The mixture was maintained at -78°C for 5 h. and then allowed to warm to room temperature overnight. The mixture was poured onto distilled water, the aqueous layer was separated and further extracted with dichloromethane (3 x 50 ml). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated *in vacuo* to give the crude product. Column chromatography (neutral alumina) of the residue, eluting with toluene, gave (80) (0.2 g, 50%) as a purple solid. Mpt. 188-190°C. Analysis found: C, 35.16; H, 2.68; N, 4.91, $C_8H_7NS_5$ requires: C, 34.66; H, 2.53; N, 5.05%; m/e DCI: 278 (M^++1); ν_{max} (Nujol): 3300, 3050, 1530, 1500, 1350, 1230, 1205, 1135, 1085, 1040, 895, 855, 800, 790, 780, 730, 720, 650 cm^{-1}; δ_H [$(CD_3)_2CO$]: 7.23 (1H,s), 6.63 (2H,s), 3.13 (3H,d) ppm.

6.3.15. 4-(N-Octadecylthioamido)tetrathiafulvalene (81).

Compound (81) was prepared analogously to (80) using octadecylisothiocyanate (0.43 g, 1.35 mmol), added portionwise over 5 mins, to give (80) (0.26 g, 42%) as a purple solid. Mpt. 107-111°C. Analysis found: C, 58.15; H, 8.12; N, 2.57; $C_{25}H_{41}NS_5$ requires: C, 58.25; H, 7.96; N, 2.72%; m/e EI: 515 (M^+); ν_{max} (Nujol): 3300, 3030, 1530, 1500, 1320, 1300, 1280, 1270, 1255, 1230, 1210, 1200, 1180, 820, 800, 720, 660, 630 $cm.^{-1}$

6.3.16. Dihexadecyl 1,3-dithiole-2-thione-4,5-dicarboxylate (84).

A solution of (83) (0.5 g, 2.25 mmol), hexadecanol (5.45 g, 22.5 mmol) and H_2SO_4 (1 ml) in toluene (50 ml) were refluxed for 6h. This solution was then poured onto distilled water, the aqueous layer was separated and further extracted with toluene (50 ml). The toluene extracts were combined and washed with 5% sodium bicarbonate solution (2 x 25 ml) and water (50 ml). The organic phase was dried ($MgSO_4$), filtered and evaporated *in vacuo* to give the crude product. Column chromatography (neutral alumina) of the residue, eluting with toluene, gave (84) (1.25

g, 82%) as a yellow solid. Mpt. 31-33°C. Analysis found: C, 66.33; H, 9.74; $C_{34}H_{66}O_4S_3$ requires: C, 66.27; H, 9.85%; m/e DCI: 671 (M^++1); ν_{max} (Nujol): 3030, 1740, 1550, 1245, 1190, 1080, 1010, 960, 890, 880, 820, 720, 590, 560, 510 cm^{-1}.

6.3.17 4,5-Bis(methoxycarbonyl)tetrathiafulvalene (85).

Method 1.

Compound (51) (1 g, 4 mmol) and vinylene trithiocarbonate (82) (0.27 g, 2 mmol) were refluxed in neat triethyl- or trimethylphosphite (5 ml) for two hours. The resultant deep red solution was cooled and immediately chromatographed using neutral alumina column chromatography, eluting with toluene/hexane (1:1 v/v), to give (85) (0.16 g, 25%) as a purple solid. Mpt. 124-127°C. Analysis found: C, 37.39; H, 2.47; $C_{10}H_8O_4S_4$ requires: C, 37.50; H, 2.50%; m/e DCI: 321 (M^++1); ν_{max} (Nujol): 3060, 1705, 1570, 1540, 1290, 1250, 1190, 1090, 1040, 925, 800, 770, 735, 750, 710, 675, 650 cm^{-1}, δ_H ($CDCl_3$): 6.35 (2H,s), 3.85 (6H,s) ppm.

Method 2.

To a solution of (51) (0.5 g, 2 mmol) and (82) (0.27 g, 2 mmol) in dry benzene (100 ml) at 40°C under nitrogen, octacarbonyldicobalt (0.27 g, 1 mmol) was added. The resulting black solution was heated to 50°C for 2h, then cooled and filtered to give a purple filtrate. The filtrate was poured into distilled water (50 ml) and the aqueous layer was separated and further extracted with dichloromethane

(2 x 50 ml). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated *in vacuo* to give the crude product. Column chromatography (neutral alumina) of the residue, eluting with toluene/cyclohexane (1:1 v/v), gave (85) (0.07 g, 10%) as a purple solid. Mpt. 125-127°C. Analysis found: C, 37.37; H, 2.57; $C_{10}H_8O_4S_4$ requires: C, 37.50; H, 2.50%.

6.3.18. 4,5-Bis(hexadecyloxycarbonyl)tetrathiafulvalene (86).

Method 1.

Compound (86) was prepared analogously to (85) (Method 1), using (84) (0.5 g, 0.75 mmol) and (82) (0.2 g, 1.5 mmol), to give (86) (0.06 g, 10%) as a red oil. Analysis found: C, 64.59; H, 9.07; $C_{40}H_{68}O_4S_4$ requires: C, 64.86; H, 9.19%; m/e DCI: 741 (M^{+}+1); ν_{max} (Nujol): 3060, 1705, 1570, 1450, 1290, 1250, 1190, 1090, 1040, 925, 800, 770, 750, 735, 710, 675, 650 cm^{-1}.

Method 2.

Alternatively, compound (86) was prepared analogously to (85) (Method 2), using (84) (0.5 g, 0.75 mmol), octacarbonyldicobalt (0.1 g, 0.375 mmol) and (82) (0.1 g, 0.75 mmol), to give (86) (0.05 g, 9%) as a red oil.

6.4 EXPERIMENTAL TO CHAPTER FOUR.

6.4.1 Materials.

4-(2-Hydroxyethylthio)tetrathiafulvalene (89) was prepared according to the literature from the TTF anion (23), elemental sulphur and 2-bromoethanol (60% yield). Mpt. 100°C (lit.[100] 101-102 °C).

4,5-(Propan-2-one)dithio-1,3-dithiole-2-thione (97) was prepared according to the literature from the zincate salt (46) and 1,3-dichloroacetone in refluxing acetonitrile (69% yield). Mpt 153-154°C. (lit.[101] 153-156°C).

4,5-(Propan-2-one)dithio-1,3-dithiole-2-one (98) was prepared according to the literature from (97) and mercuric acetate in chloroform/glacial acetic acid (3:1 v/v) (100% yield). Mpt. 184°C [lit.[101] 184-187 (decomp.)].

4,5-(Propan-2-acetal)dithio-1,3-dithiole-2-one (99) was prepared according to the literature from (98), ethylene glycol and conc. H_2SO_4 in refluxing toluene (79% yield). Mpt. 145-146°C (lit.[101] 143-145°C).

4,5-(Propan-2-acetal)dithiotetrathiafulvalene (100) was prepared according to the literature from (99) and vinylene trithiocarbonate (82) in refluxing triethylphosphite (17% yield). Mpt. 199°C (lit.[101] 200-203°C) .

4,5-(Propan-2-one)dithiotetrathiafulvalene (101) was prepared according to the literature from (100) and conc. H_2SO_4 in refluxing THF for 16h. (68% yield). Mpt. 189°C. (lit.[101] 186-187°C).

4,5-Bis(benzoylthio)1,3-dithiole-2-thione (106) was prepared according to the literature from the zincate salt (46) and benzoyl chloride in acetone (70% yield).

Mpt. 86°C. (lit.[63] 86°C.).

6.4.2. 4-Octadecylthiotetrathiafulvalene (87).

To an ethereal slurry of (23) [from 0.25 g of (2)] at -78°C, elemental sulphur (0.04 g, 1.25 mmol) was added. This temperature was maintained for 7h., whence 1-iodooctadecane (0.46 g, 1.35 mmol) was added and the mixture was then allowed to warm to room temperature overnight. The mixture was poured into distilled water (100 ml), the aqueous layer was separated and further extracted with toluene (100 ml). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated *in vacuo* to give the crude product. Column chromatography (silica) of the residue, eluting with cyclohexane, gave (87) (0.068 g, 11%) as a yellow solid. Mpt. 55-56°C. Analysis found: C, 59.19; H, 8.27; S, 32.94; $C_{24}H_{40}S_5$ requires: C, 59.02; H, 8.19; S, 32.79%; m/e EI: 488 (M^+).

6.4.3 4-Hexadecanoylthiotetrathiafulvalene (88).

Compound (88) was prepared analogously to (87) using elemental sulphur (40 mg) and hexadecanoyl chloride (0.5 ml, 1.34 mmol), to give (88) (36%, 0.2 g) as a yellow solid. Mpt. 79-83°C. Analysis found: C, 59.31, H, 7.68; $C_{22}H_{34}OS_5$, requires: C, 59.19; H, 7.62%; m/e DCI: 447 (M^++1); ν_{max} (Nujol): 3060, 1700, 1350, 1140, 1110, 940, 810, 795, 780, 770, 660, 640, 600 cm^{-1}.

6.4.4 4-(2-Hydroxyethylseleno)tetrathiafulvalene (90).

Compound (90) was prepared analogously to (87) using elemental selenium (0.1 g, 1.27 mmol) and 2-bromoethanol (1 ml, 4.5 mmol), to give (90) (53%, 0.214 g) as a yellow oil. Analysis found: C, 30.06; H, 2.40; $C_8H_8OS_4Se$ requires: C, 29.36; H, 2.45%, m/e DCI: 328 (M^++1); ν_{max} (Nujol): 3300, 3060, 1740, 1650, 1600, 1350, 1270, 1250, 1200, 1175, 1090, 1050, 980, 920, 900, 885, 790, 770, 760, 730, 700, 650 cm^{-1}; δ_H ($CDCl_3$): 6.44 (1H,s); 6.32 (2H,s), 3.87 (2H,t), 3.00 (2H,t), 2.18 (1H,s) ppm.

6.4.5 4-Octadecylethoxythiotetrathiafulvalene (91).

Compound (89) (0.1 g, 0.35 mmol), 1-iodooctadecane (0.14 g, 0.36 mmol) and sodium shavings (0.5 g) were refluxed in anhydrous toluene (100 ml) under nitrogen for 36h. The solution was cooled and filtered, poured into distilled water (100 ml). The toluene layer was separated, dried ($MgSO_4$) evaporated *in vacuo* to give the crude product, which was purified using column chromatography (silica), eluting with toluene/cyclohexane (1:3 v/v), to give (91) (79%, 0.147 g) as a pale yellow oil. Analysis found: C, 58.70; H, 8.06; $C_{26}H_{44}OS_5$ requires: C, 58.64; H, 8.27%; m/e DCI: 533 (M^++1); ν_{max} (Nujol): 3060, 2920, 1520, 1430, 1310, 1250, 1180, 1110, 1090, 970, 930, 790, 770, 730 cm^{-1}.

6.4.6 4-Hexadecanoylethoxythiotetrathiafulvalene (92).

Compound (89) (0.1 g, 0.35 mmol), hexadecanoyl chloride (0.11 ml, 0.36 mmol) and pyridine (0.3 ml, 0.35 mmol) were stirred in anhydrous dichloromethane (100 ml) under nitrogen for 24h. The mixture was then poured into distilled water (100 ml) and the dichloromethane layer was separated, dried ($MgSO_4$) and evaporated *in vacuo* to give the crude product. Column chromatography (neutral alumina) of the residue, eluting with toluene/cyclohexane (1:3 v/v), gave (92) (0.164 g, 88%) as a brown wax. Analysis found: C, 55.43; H, 7.29; $C_{24}H_{38}O_2S_5$ requires: C, 55.59; H, 7.34%; m/e DCI: 519 (M^++1); ν_{max} (Nujol): 1740, 1300, 1270, 1220, 1170, 1115, 965, 930, 830, 795, 770, 720, 690, 640 cm^{-1}.

6.4.7. 4,5-(Propan-2-ol)dithiotetrathiafulvalene (93).

Method (1):

To a solution of (101) (0.5 g, 1.55 mmol) in dry THF (40 ml), $LiAlH_4$ (1 g) was added and the reaction was stirred under reflux for 1h. under nitrogen. The mixture was then filtered and toluene (100 ml) and then water (50 ml) were added to the filtrate. The aqueous layer was separated and further extracted with dichloromethane (3 x 20 ml). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated *in vacuo* to give the crude product. Column chromatography (silica) of the residue, eluting with dichloromethane/hexane (1:1 v/v), gave (93) (80%, 0.4 g) as an orange solid. Mpt 190-192°C. Analysis found: C, 33.29; H, 2.50; $C_9H_8OS_6$ requires: C, 33.33; H, 2.47%; m/e DCI: 325 (M^++1); ν_{max} (Nujol):

3420, 1290, 1265, 1240, 1172, 1090, 1050, 895, 850, 795, 775, 720, 660 cm^{-1}; $\delta_H(CDCl_3)$: 6.32 (2H,s), 4.39 (1H,m), 3.47 (1H, broad OH), 2.82 (4H,m) ppm.

Method (2):

To an ethereal slurry of (23) [from 0.25 g of (2)] at -78°C, elemental sulphur (0.06 g, 1.84 mmol) was added. This temperature was maintained for 7h, then, 1,3-dibromopropan-2-ol (0.27 g, 1.23 mmol) was added and the reaction was allowed to warm to room temperature overnight. The mixture was then poured onto distilled water (100 ml) and the aqueous layer was separated and further extracted with dichloromethane (3 x 50 ml) and then toluene (100 ml). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated *in vacuo* to give the crude product. Column chromatography (silica) of the residue, eluting with hexane/dichloromethane (1:1 v/v), gave (93) (0.033 g, 8%) as a yellow solid. Mpt 190-191°C. Analysis found: C, 33.40; H, 2.51; $C_9H_8OS_6$ requires: C, 33.33; H, 2.47%.

6.4.8 4,5-(Propan-2-hexadecylcarboxy)dithio-1,3-dithiole-2-thione (96).

To a stirred solution of the alcohol (109) (0.5 g, 1.97 mmol) and hexadecanoyl chloride (0.6 ml, 1.97 mmol) in dry dichloromethane (100 ml), freshly distilled triethylamine (0.55 ml, 3.95 mmol) was added. The reaction was stirred for 24h. under a nitrogen atmosphere at 20°C. The mixture was poured into distilled water (100 ml), the dichloromethane layer was separated, dried ($MgSO_4$), filtered and evaporated *in vacuo* to give the crude product. Column chromatography (silica) of the residue, eluting with toluene, gave (96) (0.4 g, 41%) as a yellow powder. Mpt. 95-97°C. Analysis found C, 53.85; H, 7.09; $C_{22}H_{36}O_2S$ requires: C, 53.66; H, 7.32%; m/e DCI: 493 (M^++1); ν_{max} (Nujol): 1742, 1268, 1242, 1220, 1200, 1163, 1110, 1070, 960, 900, 860, 825, 720 cm^{-1}.

6.4.9 4-(Propan-2-epoxy)thiotetrathiafulvalene (102).

Compound (102) was prepared analogously to (93) using 1,3-dibromopropan-2-ol (0.14 g, 0.62 mmol) and elemental sulphur (0.04 g), to give (102) (0.135 g, 38%) as a yellow oil. Analysis found: C, 36.79; H, 2.64; $C_9H_8OS_5$, requires: C, 36.99; H, 2.73%; m/e DCI: 293 (M^++1); δ_H ($CDCl_3$): 6.49 (1H,s), 6.33 (2H,s), 3.19 (1H,m), 2.85 (2H, d), 0.92 (2H,d) ppm.

6.4.10 4,5,4',5'-Bis(propan-2-ol)tetrathiotetrathiafulvalene. (103).

To a solution of TTF (2) (0.25 g, 1.23 mmol) in dry ether (50 ml) at -78°C, LDA was added [DIA (0.4 ml, 2.46 mmol), n-BuLi 1.6M (1.8 ml, 2.46 mmol)] in ether (10 ml). After 1h. a thick yellow precipitate had formed, to which was added elemental sulphur (0.08 g). The reaction was maintained for 7h. at -78°C., then, 1,3-dibromopropan-2-ol (0.27 g, 0.123 mmol) was added and the reaction was allowed to warm to room temperature overnight. The ethereal solution was absorbed onto silica, and chromatographed on a short column eluting with dichloromethane, to give (103) (0.046 g, 7%) as an insoluble yellow solid. Mpt. >230°C. Analysis found: C, 32.55; H, 2.18; $C_{12}H_{12}O_2S_8$ requires: C, 32.40; H, 2.70%; m/e EI: 444 (M^+); ν_{max} (Nujol): 3300 cm^{-1}.

6.4.11 4,5-(Propan-2-ol)dithio-1,3-dithiole-2-thione (109).

To a solution of the zincate salt (46) (2 g, 2.78 mmol) in dry acetonitrile (500 ml), 1,3-dibromopropan-2-ol (1.2 g, 5.59 mmol) was added and the resulting solution was stirred at 50°C for 6h. under nitrogen. The acetonitrile was removed *in vacuo* and the product was absorbed onto silica gel. Column chromatography (silica) of the residue, eluting with dichloromethane, gave (109) (0.93 g, 66%) as a yellow powder. Mpt. 188°C. Analysis found: C, 28.30; H, 2.36; $C_6H_6OS_5$ requires: C, 28.35; H, 2.36%; m/e DCI: 254 (M^+); ν_{max} (Nujol): 3436, 1056 cm^{-1}; δ_H [$(CD_3)_2SO$]: 5.62 (1H, broad OH), 4.04 (1H,m), 3.05 (2H,m), 2.64 (2H,m) ppm.

6.4.12 4,5,4,5'-Bis(propan-2-ol)tetrathio-1,3-dithiole-2-thione (110).

Compound (110) was obtained as a slower moving band (R_F=0.2) (0.06 g, ca. 4%). m/e EI: 508 (M^+); ν_{max} (Nujol): 3430 cm^{-1}.

6.4.13 4,5-(Propan-2-*t*-butyldiphenylsilyl)dithio-1,3-dithiole-2-thione (111).

Alcohol (109) (2.3 g, 0.9 mol) was dissolved in dry DMF (200 ml); imidazole (7.0 g, 0.10 mol) and *tert*-butyldiphenylsilyl chloride (3.0 g, 0.01 mol) were added and the mixture stirred at 20°C for 16h. Dichloromethane (250 ml) was then added and the resulting solution was poured onto distilled water (100 ml). The organic layer was separated and washed sequentially with ice-cold hydrochloric acid (3M, 5 x 50 ml) and water (50 ml). The organic layer was separated, dried ($MgSO_4$), filtered and solvent evaporated *in vacuo* to give the crude product. The residue was chromatographed on a short silica gel column, eluting with cyclohexane/dichloromethane (1:1 v/v), to give (111) (4.4 g, 98%) as a yellow solid. Mpt. 109-111°C. Analysis found: C, 53.78; H, 4.95%; $C_{22}H_{24}OS_5Si$ requires: C, 53.65; H, 4.87%; m/e EI: 492 (M^+); δ_H ($CDCl_3$): 7.62 - 7.48 (10H,m) 4.28 (1H,m), 2.94 (2H,m), 2.77 (2H,m) and 1.04 (9H,s) ppm.

6.4.14 4,5-(Propan-2-*t*-butyldiphenylsilyl)dithio-1,3-dithiole-2-one (112).

Thione (112) (4.5 g, 0.9 mmol) was dissolved in a mixture of chloroform (75 ml) and acetic acid (25 ml). Mercuric acetate (7.0 g, 21 mmol) was added and the mixture stirred at 20°C for 16h, by which time a thick white precipitate had formed. The precipitate was removed by filtration and washed with dichloromethane (2 x 50 ml). The filtrate and washings were combined and washed with saturated sodium hydrogencarbonate (3 x 100 ml) and then water (100 ml). The dichloromethane extracts were dried ($MgSO_4$), filtered and evaporated *in vacuo* to give (112) (4.3 g, 100%) as a white solid. Mpt. 119-120°C. Analysis found C, 55.32; H, 4.97; $C_{22}H_{24}O_2S_4Si$ requires: C, 55.50; H, 5.00%; m/e DCI: 477 (M^{+}+1); ν_{max} (Nujol): 1668 (C=O)cm.$^{-1}$ δ_H ($CDCl_3$): 7.63 (4H,m), 7.46 (6H,m), 4.20 (1H,m), 2.82 (2H,M), and 2.61 (2H,m) ppm.

6.4.15 4,5-(Propan-2-*t*-butyldiphenylsilyl)dithiotetrathiafulvalene (113).

A suspension of the protected alcohol (112) (1 g, 2 mmol) and vinylene trithiocarbonate (82) (0.3 g, 2 mmol) in neat freshly distilled triethylphosphite (5 ml) were refluxed for 2h. The resulting red solution was cooled and directly chromatographed (silica), eluting with cyclohexane/toluene (3:1 v/v), to give a crude product which was further purified using preparative t.l.c., eluting with cyclohexane, to give (113) (0.365 g, 32%) as an orange powder. Mpt. 95-96°C. Analysis found: C, 53.26; H, 4.60; $C_{25}H_{26}OS_6Si$ requires: 53.38; H, 4.63%; m/e DCI: 563 (M^{+}+1): ν_{max} (Nujol): 1230, 1105, 1060, 1000, 900, 837, 820, 795, 770, 740, 700, 610, 510, 490 cm^{-1}; δ_H ($CDCl_3$): 7.62 (4H,m) 7.41 (6H,m), 6.33 (2H,s), 4.12 (1H,m), 2.72 (2H,m), 2.49 (2H,m), 1.06 (9H,s) ppm.

6.4.16 4,5-(Propan-2-ol)dithiotetrathiafulvalene (93).

Method 3.

To a solution of the silyl protected TTF derivative (113) (0.71 g, 2.18 mmol) in THF (80 ml), tetrabutylammonium fluoride (trihydrate) (1.38 g, 4.37 mmol) was added and the reaction was stirred at 20°C under nitrogen for 12h. The mixture was poured into distilled water (100 ml) and extracted with dichloromethane (3 x 100 ml). The combined organic extracts were dried ($MgSO_4$), filtered, and evaporated *in vacuo* to give the crude product. Column chromatography (silica) of the residue, eluting with dichloromethane/hexane (3:1, v/v), gave (93) (0.46 g, 70%) as an orange solid. Mpt 190-191°C. Analysis found C, 33.42; H, 2.53; $C_9H_8OS_6$ requires: C, 33.33; H, 2.47%.

6.4.17 4,5-(Propan-2-octadecylcarbamate)dithiotetrathiafulvalene (94).

To stirring solution of alcohol (93) (0.1 g, 0.31 mmol) and octadecylisocyanate (0.09 g, 0.31 mmol) in dry dichloromethane (50 ml), triethylamine (0.14 ml, 1 mmol) was added dropwise over 1 min. The reaction was stirred at room temperature for 3 days, whence, distilled water (100 ml) was added. The dichloromethane extract was separated, dried ($MgSO_4$), filtered and evaporated *in vacuo* to give the crude product. Column chromatography (neutral alumina) of the residue, eluting with hexane\toluene (3:1 v/v), gave (94) (0.02 g, 10%) as a yellow powder. Mpt 129-132°C. Analysis found: C, 54.07; H, 7.21; N, 2.35; $C_{28}H_{45}NO_2S_6$ requires: C, 54.28; H, 7.27; N, 2.26%; m/e DCI: 620 (M^++1).

6.5 EXPERIMENTAL TO CHAPTER FIVE.

6.5.1 Materials

Acetaldehyde semicarbazone (115) was prepared according to the literature from semicarbizide hydrochloride and acetaldehyde in water (40% yield). Mpt. 111°C. (lit.[107] 111-113°C.)

1,2,3-Selenadiazole (116) was prepared according to the literature from (115), SeO_2 and HOAc in dichloromethane (27% yield). Bpt. 55°C (16 mm) [lit.[107] 56-58°C (20 mm)].

Methylene-1,3-diselenole (117) was prepared according to the literature from 1,2,3-selenadiazole and t-BuOK/t-BuOH in DMF (79% yield). Mpt. 57-58°C. (lit.[106d] 58-60°C.).

Tetraselenafulvalene (5) was prepared according to the literature from (117) and iodine/morpholine in DMF (30% yield). Mpt. 132 (lit.[106d] 132-133°C).

6.5.2 Tetraselenafulvalenyltetralithium (118).

To a stirred solution of LDA [from n-BuLi 1.6M (1.6 ml, 2.56 mmol) and N,N-diisopropylamine (0.37 ml, 2.56 mmol)] in dry THF (20 ml) at -100°C, tetraselenanfulvalene (5) (0.25 g, 0.64 mmol) was added portionwise over 1 min. The reaction was maintained at -100°C for 0.5h, by which time an orange/brown precipitate of (118) had formed[110].

6.5.3 4-Acetyltetraselenafulvalene (123).

To a stirred solution of (118) at -100°C, freshly distilled acetyl chloride (0.036 ml, 0.51 mmol) in THF (5 ml) was added dropwise over 1 min., to give a scarlet solution. The mixture was poured onto distilled water (100 ml) and the aqueous layer was separated and further extracted with dichloromethane (2 x 50 ml). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated *in vacuo* to give the crude product. Column chromatography (silica) of the residue, eluting with cyclohexane/toluene (3:1v/v), gave (123) (0.056 g, 20 %) as a scarlet solid. Mpt. 147-149°C (CS_2/hexane). Analysis found: C, 22.08; H, 1.38; $C_8H_6OSe_4$ requires: C, 22.12; H, 1.38%; m/e EI: 434 (M^++1); υ_{max} (Nujol): 1650, 1308, 1255, 1170, 1155, 718 cm^{-1}; δ_H ($CDCl_3$): 8.42 (1H,s), 7.34 (2H,s), 2.46 (3H,s) ppm.

6.4.4 4-Butanoyltetraselanfulvalene (124).

Compound (124) was formed using an identical procedure and scale to (123), using 4-bromobutyryl chloride (0.059 ml, 0.51 mmol), to give (124) (0.053 g, 18 %) as a red solid. Mpt. 115-118° C. Analysis found C, 25.82; H, 2.16; $C_{10}H_{10}OSe_4$ requires: C, 25.97; H, 2.16%; m/e EI: 462 (M^+); υ_{max} (Nujol): 1650, 1310, 1255, 1170, 890, 720, 630, 555 cm^{-1}; δ_H ($CDCl_3$): 8.41 (1H,s), 7.34 (2H,s), 2.15 (2H,t), 1.16 (3H,t), 1.02 (2H,t) ppm.

6.5.5 4-Tetradecanoyltetraselenafulvalene (125).

Compound (125) was formed using an identical procedure and scale to (123), using tetradecanoyl chloride (0.13 ml, 0.51 mmol), to give (125) (0.064 g, 17%) as a red semi solid. Analysis found: C, 39.78; H, 4.97; $C_{20}H_{30}OSe_4$ requires: C, 39.86; H, 4.98%; m/e DCI: 603 (M^++1); ν_{max} (Nujol): 1630, 1310, 1150, 1040, 720, 620 cm^{-1}.

6.5.6 4-Hexadecanoyltetraselenafulvalene (126).

Compound (126) was formed using an identical procedure and scale to (123), using hexadecanoyl chloride (0.14 ml, 0.51 mmol), to give (126) (0.057 g, 14%) as a red solid. Mpt. 83-85°C (dichloromethane/methanol 1:1 v/v). Analysis found: C, 41.82, H, 5.30; $C_{22}H_{34}OSe_4$ requires: C, 41.90; H, 5.40%; ν_{max} (Nujol): 1650, 1310, 1255, 1170, 1150, 890, 720, 630 cm^{-1}.

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APPENDIX I

X-RAY CRYSTAL DATA.

I.1 Crystal data for ethylenediseleno-tetrathiafulvalene (44).

Chemical formula: $C_8H_6S_4Se_2$; M_r= 388.3; crystal system = monoclinic; space group $P2_1/n$; a= 6.536(2), b= 16.020(4), c= 11.366(3) Å; β= 92.95(2)°; U= 1188.5(5) $Å^3$; Z= 4; D_c= 2.17 gcm^{-1}; F(000)= 744; λ(Mo-Kα)= 0.71069 Å (graphite monochromator); μ= 68.81 cm^{-1}; 2114 independent reflections, of which 1521 with (F>2σ(F)), were used; R= 0.029, R_w= 0.033.

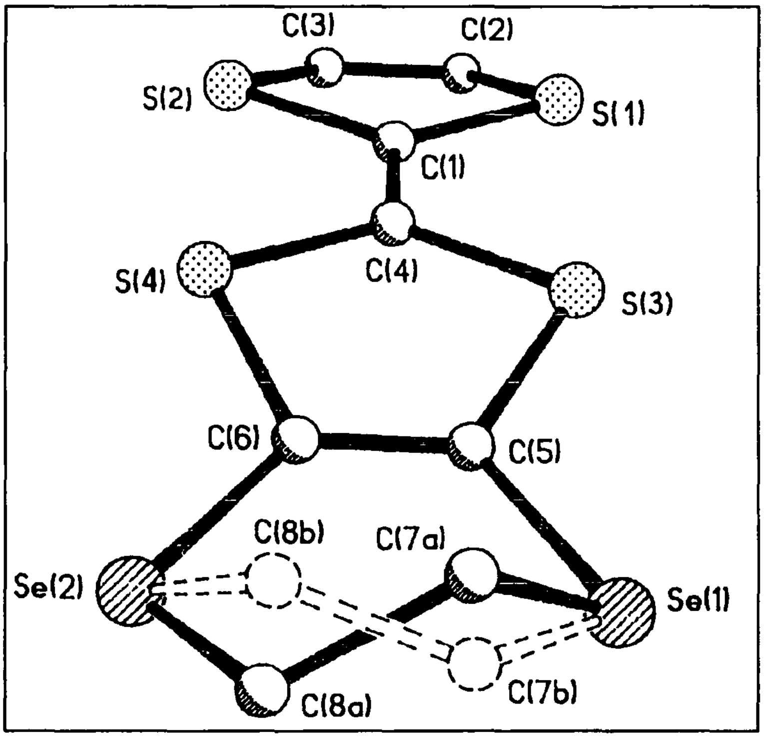

Fig. A.1: *Atom numbering scheme for compound (44).*

Data were collected using a Siemens R3M/V diffractometer. The structure was solved by direct methods (SHELXTL PLUS) and developed and refined using least squares procedures. Non-hydrogens atoms were refined anisotropically. The disordered atoms C(7) and C(8) and all hydrogens were refined isotropically. Bond lengths and angles are given in table A.1.

Se(1)-C(5)	1.905(5)	C(5)-Se(1)-C(7a)	91.6(4)
Se(1)-C(7b)	1.950(1)	C(6)-Se(2)-C(8a)	104.6(4)
Se(2)-C(8a)	1.870(1)	C(1)-S(1)-C(2)	93.8(3)
S(1)-C(1)	1.751(5)	C(4)-S(3)-C(5)	93.1(2)
S(2)-C(1)	1.756(5)	S(1)-C(1)-S(2)	114.1(3)
S(3)-C(4)	1.756(5)	S(2)-C(1)-C(4)	122.8(4)
S(4)-C(4)	1.751(5)	S(2)-C(3)-C(2)	118.4(5)
C(1)-C(4)	1.362(7)	S(3)-C(4)-C(1)	123.1(4)
C(5)-C(6)	1.329(7)	Se(1)-C(5)-S(3)	117.2(3)
C(7b)-C(8b)	1.440(2)	S(3)-C(5)-C(6)	118.0(4)
Se(1)-C(7a)	2.000(1)	Se(2)-C(6)-C(5)	126.5(4)
Se(2)-C(6)	1.888(5)	Se(1)-C(7a)-C(8a)	107.8(7)
Se(2)-C(8b)	2.040(1)	Se(2)-C(8a)-C(7a)	115.3(8)
S(1)-C(2)	1.743(7)	C(5)-Se(1)-C(7b)	102.4(4)
S(2)-C(3)	1.750(6)	C(6)-Se(2)-C(8b)	92.6(3)
S(3)-C(5)	1.751(5)	C(1)-S(2)-C(3)	93.2(3)
S(4)-C(6)	1.764(5)	C(4)-S(4)-C(6)	93.1(2)
C(2)-C(3)	1.297(9)	S(1)-C(1)-C(4)	123.1(4)
C(7a)-C(8a)	1.590(2)	S(1)-C(2)-C(3)	117.8(5)
		S(3)-C(4)-S(4)	114.3(3)
		S(4)-C(4)-C(1)	122.6(4)
		Se(1)-C(5)-C(6)	124.2(4)
		Se(2)-C(6)-S(4)	116.4(3)
		S(4)-C(6)-C(5)	116.7(4)
		Se(1)-C(7b)-C(8b)	120.5(9)
		Se(2)-C(8b)-C(7b)	114.1(8)

Table A.1: *Bond lengths (Å) and angles (°) for compound (44). See Fig. A.1 for numbering scheme.*

I.2 Crystal data for Bis(tetrathiafulvalenyl)sulphide (59).

Chemical formula: $C_{12}H_6S_9$; M_r 438.77; crystal system = triclinic; space group P_1; a = 5.107(1) Å; b = 11.978(2) Å; c = 14.056(2) Å; α = 89.22(3)°, β = 100.45(7)°, γ = 94.36(1)°; U = 843.17 Å^3; Z = 2 ; F (000) = 444; Mo-Kα radiation (λ = 0.71069 Å); 3145 independent reflection, of which 2747,with ($F>2\sigma F_o$), were used; R =0.043.

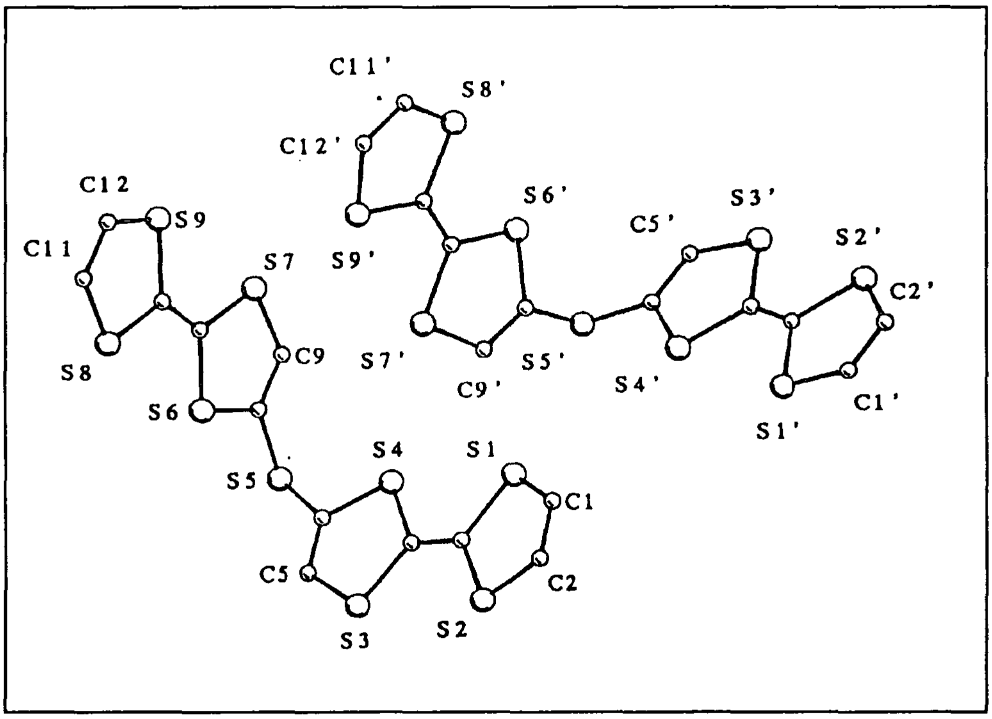

Fig. A.2.: *Atom numbering scheme for compound (59).*

Data were collected on a Enraf-Nonius FAST area detector diffractometer. The structure was solved by direct methods (SHELXS 86) and developed and refined using least-squares procedures. Non-hydrogen atoms were refined anisotropically, hydrogens isotropically. Bond lengths and angles are given in Table A.2.

C(1)-S(1)	1.722(13)	C(3)-S(1)-C(1)	94.6(6)
C(2)-C(1)	1.314(17)	S(2)-C(2)-C(1)	116.2(10)
C(3)-S(2)	1.763(11)	S(2)-C(2)-S(1)	112.9(5)
S(3)-C(4)	1.776(10)	C(4)-C(3)-S(2)	123.3(7)
C(5)-S(3)	1.729(12)	S(4)-C(4)-C(3)	123.2(7)
S(4)-C(6)	1.742(10)	C(5)-S(3)-C(4)	94.6(5)
C(7)-S(5)	1.758(11)	S(4)-C(6)-C(5)	117.2(8)
C(9)-C(7)	1.337(14)	S(5)-C(6)-S(4)	118.2(6)
S(7)-C(8)	1.765(13)	C(7)-S(5)-C(6)	100.6(5)
C(9)-S(7)	1.724(12)	C(9)-C(7)-S(5)	123.3(9)
S(9)-C(10)	1.774(12)	C(8)-S(6)-C(7)	95.4(6)
C(12)-C(11)	1.311(22)	C(10)-C(8)-S(6)	122.9(9)
C(1')-S(1')	1.731(14)	C(9)-S(7)-C(8)	95.1(6)
C(2')-C(1')	1.307(22)	S(8)-C(10)-C(8)	122.9(9)
C(3')-S(2')	1.787(12)	S(9)-C(10)-S(8)	112.1(7)
S(3')-C(4')	1.792(12)	C(12)-C(11)-S(8)	118.4(12)
C(5')-S(3')	1.707(11)	C(12)-S(9)-C(10)	96.1(7)
S(4')-C(6')	1.762(11)	C(2')-C(1')-S(1')	118.1(10)
C(7')-S(5')	1.750(12)	C(3')-S(2')-C(2')	94.1(7)
C(9')-C(7')	1.316(14)	C(4')-C(3')-S(1')	123.4(9)
S(7')-C(8')	1.775(10)	S(3')-C(4')-C(3')	124.9(9)
C(9')-S(7')	1.740(13)	S(4')-C(4')-S(3')	111.6(6)
S(9')-C(10')	1.757(12)	C(6')-C(5')-S(3')	120.6(8)
C(12')-C(11')	1.306(20)	S(5')-C(6')-C(5')	125.2(8)
C(3)-S(1)	1.761(10)	C(6')-S(4')-C(4')	96.3(5)
S(2)-C(2)	1.741(14)	S(6')-C(7')-S(5')	118.5(6)
C(4)-C(3)	1.308(12)	C(9')-C(7')-S(6')	116.4(9)
S(4)-C(4)	1.744(11)	S(7')-C(8')-S(6')	114.2(6)
C(6)-C(5)	1.312(13)	C(10')-C(8')-S(7')	122.3(8)
S(5)-C(6)	1.771(10)	S(7')-C(9')-C(7')	119.2(8)
S(6)-C(7)	1.746(12)	S(9')-C(10')-C(8')	123.8(8)
C(8)-S(6)	1.763(12)	C(11')-S(8')-C(10')	94.8(6)
C(10)-C(8)	1.299(16)	S(9')-C(12')-C(11')	118.4(12)
S(8)-C(10)	1.773(13)	C(2)-C(1)-S(1)	119.7(10)
C(11)-S(8)	1.748(16)	C(3)-S(2)-C(2)	95.5(6)
S(9)-C(12)	1.712(16)	C(4)-C(3)-S(1)	123.8(8)
C(3')-S(1')	1.752(12)	S(3)-C(4)-C(3)	123.2(8)
S(2')-C(2')	1.730(15)	S(4)-C(4)-S(3)	113.6(6)
C(4')-C(3')	1.277(14)	C(6)-C(5)-S(3)	118.9(8)
S(4')-C(4')	1.780(11)	S(5)-C(6)-C(5)	124.4(7)
C(6')-C(5')	1.322(13)	C(6)-S(4)-C(4)	95.6(5)
S(5')-C(6')	1.756(10)	S(6)-C(7)-S(5)	119.9(6)
S(6')-C(7')	1.755(11)	C(9)-C(7)-S(6)	116.7(9)
C(8')-S(6')	1.736(12)	S(7)-C(8)-S(6)	113.8(7)

C(10’)-C(8’)	1.320(14)	C(10)-C(8)-S(7)	123.2(9)
S(8’)-C(10’)	1.763(10)	S(7)-C(9)-C(7)	118.9(9)
C(11’)-S(8’)	1.727(16)	S(9)-C(10)-C(8)	124.9(9)
S(9’)-C(12’)	1.725(15)	C(11)-S(8)-C(10)	94.7(7)
		S(9)-C(12)-C(11)	117.9(11)
		C(3’)-S(1’)-C(1’)	95.2(7)
		S(2’)-C(2’)-C(1’)	118.8(10)
		S(2’)-C(3’)-S(1’)	113.2(6)
		C(4’)-C(3’)-S(2’)	123.3(9)
		S(4’)-C(4’)-C(3’)	125.5(9)
		C(5’)-S(3’)-C(4’)	95.7(5)
		S(4’)-C(6’)-C(5’)	115.6(5)
		S(5’)-C(6’)-S(4’)	119.1(6)
		C(7’)-S(5’)-C(6’)	100.4(5)
		C(9’)-C(7’)-S(5’)	124.8(8)
		C(8’)-S(6’)-C(7’)	95.8(5)
		C(10’)-C(8’)-8(6’)	123.5(7)
		C(9’)-S(7’)-C(8’)	94.2(5)
		S(8’)-C(10’)-C(8’)	123.1(8)
		S(9’)-C(10’)-S(8’)	113.1(6)
		C(12’)-C(11’)-S(8’)	118.0(11)
		C(12’)-S(9’)-C(10’)	94.7(7)

Table A.2: *Bond lengths (Å) and angles (°) for compound (59). See Figure A.2 for numbering scheme.*

I.3 Crystal Data for O-[(4-Chlorobutyl)thiocarboxy]tetrathaifulvalene (79).

Chemical formula: $C_{11}H_{11}S_5OCl$; M_r 354.9; crystal system = prismatic; space group p1; a = 7.530(6) Å; b = 10.033(6) Å; c = 11..526(10) Å; α = 65.51 (8)°; β = 71.25 (6)°, γ = 81.47(6)°; U= 750.2(9) $Å^3$; Z = 2; F(000) = 364; Mo-Kα radiation (graphite monochromator) (λ = 0.71073 Å); μ (Mo-Kα) = 0.934mm^{-1}, D_c=1.571 mg/m^3; 2027 independent reflections of which 1659, (with F>4.0σ(F)), were used; 163 parameters refined; R = 3.50%, R_w = 4.93%.

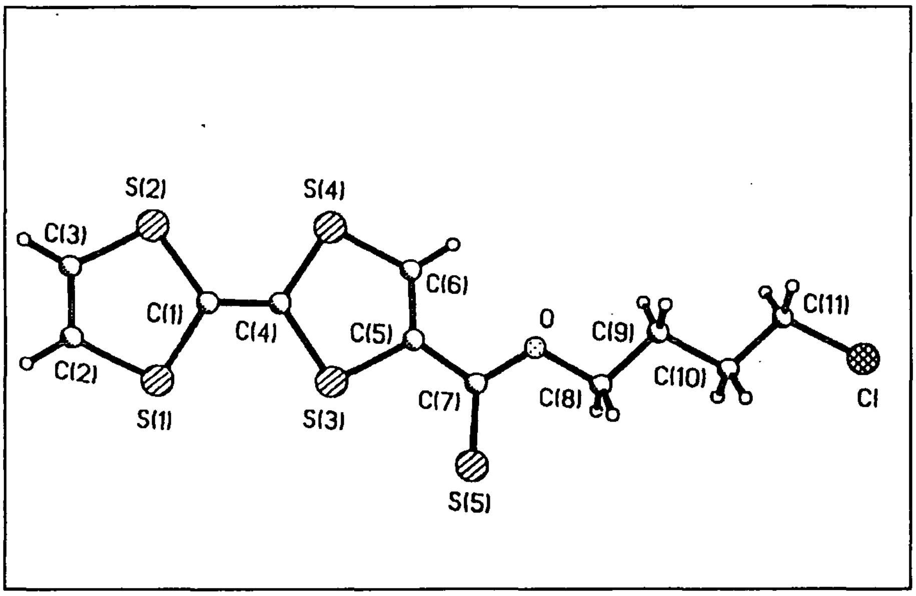

Fig. A.3:*Atom numbering scheme for compound (79).*

Data were collected on a Siemens R3M/V diffractometer. The structure was solved by direct methods (SHELXTL Plus (VMS)). Non Hydrogen atoms were refined using full-matrix least squares, all hydrogens placed in calculated positions [C-H= 0.96 Å, HCH = 109.5° (CH_2)]. Bond lengths and angles are given in Table A.3.

S(1)-C(1)	1.753(5)	C(1)-S(1)-C(2)	94.8(2)
S(2)-C(1)	1.751(4)	C(4)-S(3)-C(5)	94.3(2)
S(3)-C(4)	1.765(4)	C(7)-O-C(8)	117.5(3)
S(4)-C(4)	1.757(5)	S(1)-C(1)-C(4)	122.0(3)
S(5)-C(7)	1.633(5)	S(1)-C(2)-C(3)	117.8(4)
O-C(7)	1.334(5)	S(3)-C(4)-S(4)	114.7(2)
C(1)-C(4)	1.345(5)	S(4)-C(4)-C(1)	123.4(3)
C(5)-C(6)	1.334(6)	S(3)-C(5)-C(7)	116.5(3)
C(8)-C(9)	1.509(6)	S(4)-C(6)-C(5)	119.2(3)
C(10)-C(11)	1.503(6)	S(5)-C(7)-C(5)	121.9(3)
S(1)-C(2)	1.728(4)	O-C(8)-C(9)	107.9(3)
S(2)-C(3)	1.723(5)	C(9)-C(10)-C(11)	111.4(3)
S(3)-C(5)	1.757(4)	C(1)-S(2)-C(3)	94.8(2)
S(4)-C(6)	1.714(4)	C(4)-S(4)-C(6)	94.8(2)
Cl-C(11)	1.790(4)	S(1)-C(1)-S(2)	114.3(2)
O-C(8)	1.447(4)	S(2)-C(1)-C(4)	123.7(3)
C(2)-C(3)	1.323(8)	S(2)-C(3)-C(2)	118.2(3)
C(5)-C(7)	1.448(5)	S(3)-C(4)-C(1)	121.8(3)
C(9)-C(10)	1.528(4)	S(3)-C(5)-C(6)	116.8(2)
		C(6)-C(5)-C(7)	126.7(3)
		S(5)-C(7)-O	125.5(2)
		O-C(7)-C(5)	112.5(3)
		C(8)-C(9)-C(10)	109.7(3)
		Cl-C(11)-C(10)	111.2(3)

Table A.3: *Bond lengths (Å) and angles (°) for compound (79). See Figure A.3 for numbering scheme.*

I.4 Crystal Data for 4-(N-Methylthioamido)tetrathiafulvalene (80).

Chemical Formula: $C_8H_7NS_5$; M_r= 277.4; Crystal system = monoclinic; space group $P2_1/c$; a = 11.720(3) Å; b = 8.474(2) Å; c= 11.231(2) Å; β = 92.88(2)°; U= 1114.0(4) $Å^3$; Z = 4; F(000) = 568; Mo-Kα radiation (graphite monochromator), λ = 0.71073 Å; μ(Mo-Kα) = 0.997 mm^{-1}; D_c = 1.654 mgm^{-3}; 2084 independent reflections, of which 1264, with F> 4.0σ(F0), were used; R_w = 0.0328.

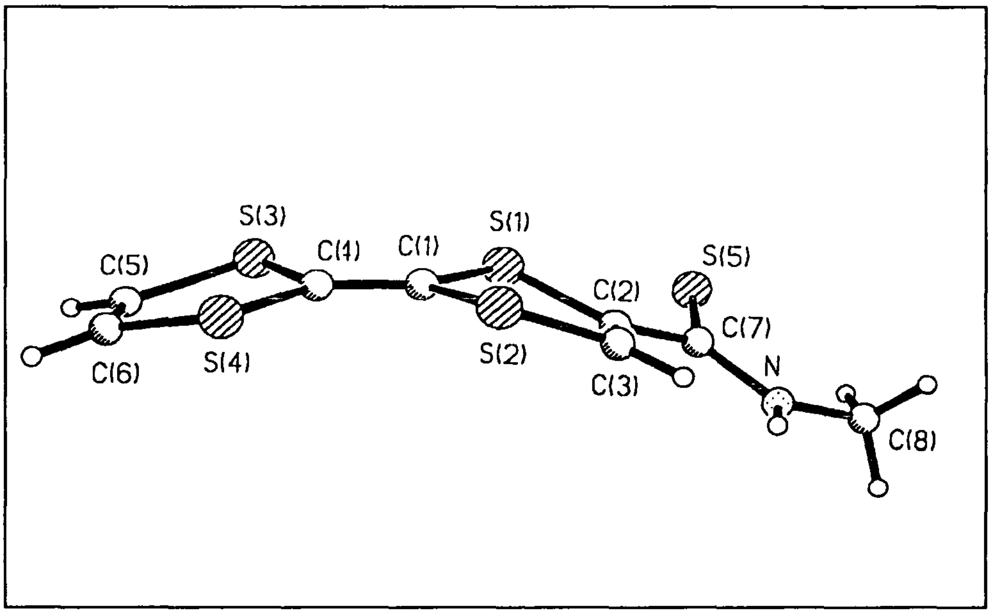

Fig. A.4: *Atom numbering scheme for (80).*

Data were collected on a Siemens R3m/V diffractometer. The structure was solved by direct methods (SHELX 84) and developed and refined using standard Fourier and least-squares procedures. Non-hydrogen atoms were refined anisotropically, hydrogens isotropically. Bond lengths and angles are given in Table A.4.

S(1)-C(1)	1.757(4)	C(1)-S(1)-C(2)	93.4(2)
S(2)-C(1)	1.753(4)	C(4)-S(3)-C(5)	94.7(2)
S(3)-C(4)	1.758(4)	C(7)-N-C(8)	123.9(4)
S(4)-C(4)	1.753(4)	S(1)-C(1)-C(4)	123.5(3)
S(5)-C(7)	1.667(4)	S(1)-C(2)-C(3)	115.9(3)
N-C(8)	1.439(6)	C(3)-C(2)-C(7)	127.0(3)
C(2)-C(3)	1.344(5)	S(3)-C(4)-S(4)	113.8(2)
C(5)-C(6)	1.312(7)	S(4)-C(4)-C(1)	123.8(3)
S(1)-C(2)	1.762(4)	S(4)-C(6)-C(5)	119.0(4)
S(2)-C(3)	1.719(4)	S(5)-C(7)-C(2)	120.2(3)
S(3)-C(5)	1.737(5)	C(1)-S(2)-C(3)	93.9(2)
S(4)-C(6)	1.736(5)	C(4)-S(4)-C(6)	94.0(2)
N-C(7)	1.327(5)	S(1)-C(1)-S(2)	113.8(2)
C(1)-C(4)	1.337(6)	S(2)-C(1)-C(4)	122.6(3)
C(2)-C(7)	1.454(5)	S(1)-C(2)-C(7)	116.8(3)
		S(2)-C(3)-C(2)	118.7(3)
		S(3)-C(4)-C(1)	122.4(3)
		S(3)-C(5)-C(6)	117.0(4)
		S(5)-C(7)-N	122.4(3)
		N-C(7)-C(2)	117.4(3)

Table A.4: *Bond lengths (Å) and angles(°) for compound (80). See Figure A.4 for numbering scheme.*

I.5. Crystal data for 4-Acetyltetraselenafulvalene (123).

Chemical formula: $C_8H_6O_1Se_4$; M_r 433.98; crystal system = triclinic; space group P1; a = 8.890(1) Å, b = 10.666(2) Å, c = 11.688(3) Å; α = 95.43(1)°; β = 95.43(1)°; γ = 96.31(1)°; U = 1090.37 Å^3; Z = 4; F(000) 792; Mo-Kα radiation (λ=0.71069Å); 3514 independent reflections, of which 2496 with F(o)>3σ(Fo), were used; R_w = 0.037.

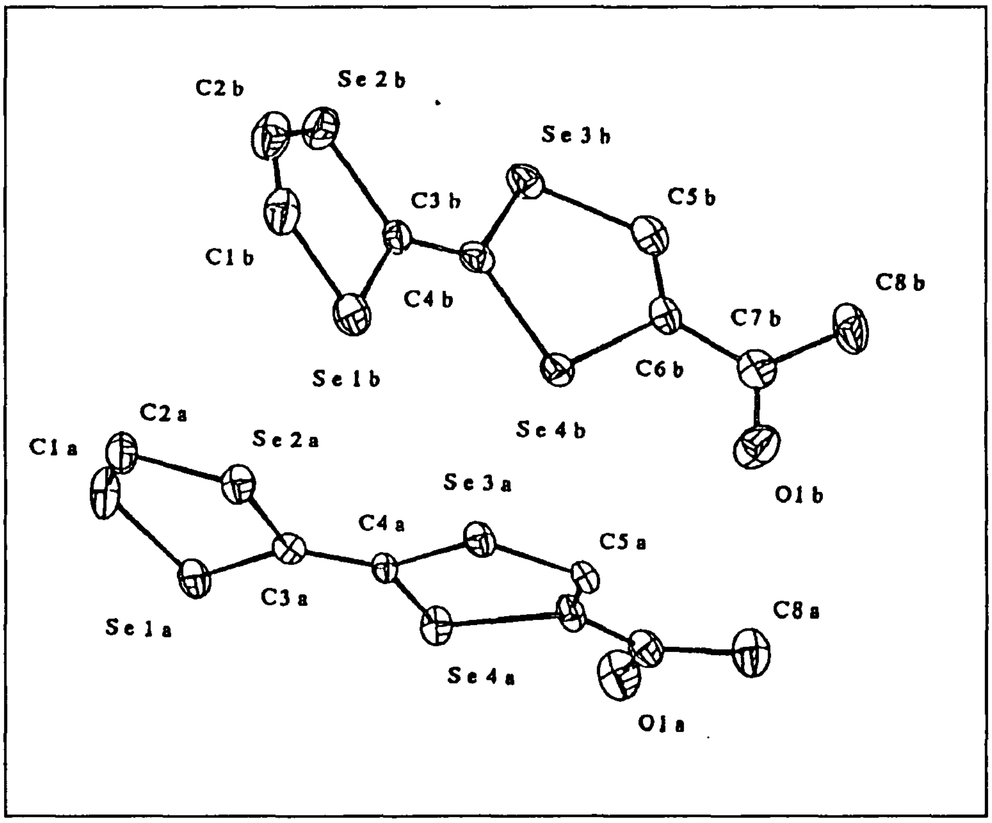

Fig. A.5: *Atom numbering scheme for compound (123).*

Data were collected on a Enraf-Nonius FAST area detector diffractometer. The structure was solved by direct methods (SHELXS 86) and developed and refined using least squares procedures. Non-hydrogens were refined anisotropically, hydrogens isotropically. Bond lengths and angle are given in table A.5.

C(1a)-Se(1a)	1.876(12)	C(3a)-Se(1a)-C(1a)	91.6(5)
C(2a)-C(1a)	1.344(15)	Se(2a)-C(2a)-C(1a)	118.2(8)
C(3a)-Se(2a)	1.893(10)	Se(2a)-C(3a)-Se(1a)	114.2(5)
Se(3a)-C(4a)	1.913(9)	C(4a)-C(3a)-Se(2a)	124.6(6)
C(5a)-Se(3a)	1.852(12)	Se(4a)-C(4a)-C(3a)	124.6(6)
Se(4a)-C(6a)	1.900(10)	C(5a)-Se(3a)-C(4a)	92.3(5)
O(1a)-C(7a)	1.235(12)	Se(4a)-C(6a)-C(5a)	117.9(8)
C(1b)-Se(1b)	1.927(11)	C(7a)-C(6a)-Se(4a)	115.7(7)
C(2b)-C(1b)	1.301(14)	O(1a)-C(7a)-C(6a)	117.2(9)
C(3b)-Se(2b)	1.893(9)	C(8a)-C(7a)-O(1a)	122.3(10)
Se(3b)-C(4b)	1.926(9)	C(2b)-C(1b)-Se(1b)	117.2(9)
C(5b)-Se(3b)	1.860(11)	C(3b)-Se(2b)-C(2b)	91.3(5)
Se(4b)-C(6b)	1.903(11)	C(4b)-C(3b)-Se(1b)	122.0(6)
O(1b)-C(7b)	1.213(11)	Se(3b)-C(4b)-C(3b)	122.3(6)
C(3a)-Se(1a)	1.907(9)	Se(4b)-C(4b)-Se(3b)	112.7(5)
Se(2a)-C(2a)	1.887(11)	C(6b)-C(5b)-Se(3b)	121.6(8)
C(4a)-C(3a)	1.362(12)	C(6b)-Se(4b)-C(4b)	92.2(4)
Se(4a)-C(4a)	1.888(9)	C(8b)-C(7b)-C(6b)	120.8(8)
C(6a)-C(5a)	1.338(13)	C(2a)-C(1a)-Se(1a)	120.5(8)
C(7a)-C(6a)	1.477(14)	C(3a)-Se(2a)-C(2a)	92.5(5)
C(8a)-C(7a)	1.501(15)	C(4a)-C(3a)-Se(1a)	121.2(7)
C(3b)-Se(1b)	1.912(10)	Se(3a)-C(4a)-C(3a)	120.5(6)
Se(2b)-C(2b)	1.898(13)	Se(4a)-C(4a)-Se(3a)	114.9(5)
C(4b)-C(3b)	1.314(13)	C(6a)-C(5a)-Se(3a)	121.8(8)
Se(4b)-C(4b)	1.917(9)	C(7a)-C(6a)-C(5a)	126.3(9)
C(6b)-C(5b)	1.347(11)	C(6a)-Se(4a)-C(4a)	92.9(4)
C(7b)-C(6b)	1.458(12)	C(8a)-C(7a)-C(6a)	120.5(9)
C(8b)-C(7b)	1.507(16)	C(3b)-Se(1b)-C(1b)	91.9(5)
		Se(2b)-C(2b)-C(1b)	121.7(9)
		Se(2b)-C(3b)-Se(1b)	113.4(5)
		C(4b)-C(3b)-Se(2b)	124.6(6)
		Se(4b)-C(4b)-C(3b)	125.0(6)
		C(5b)-Se(3b)-C(4b)	91.5(5)
		Se(4b)-C(6b)-C(5b)	117.4(8)
		C(7b)-C(6b)-Se(4b)	116.3(6)
		O(1b)-C(7b)-C(6b)	119.0(9)
		C(8b)-C(7b)-O(1b)	120.2(9)
		C(7b)-C(6b)-C(5b)	126.9(2)

Table A.5: *Bond lengths (Å) and angles (°) for compound (123). See Figure A.5 for numbering scheme.*

APPENDIX II

PUBLICATIONS.

Parts of the work contained in this thesis have been reported in the following publications:

1. *"Synthesis of Amphiphilic, Mono-functionalised Tetrathiafulvalenes; X-Ray Crystal Structure of 4(6-Bromohexanoyl)-tetrathiafulvalene."* M.R. Bryce, G. Cooke, A.S. Dhindsa, D. Lorcy, A.J. Moore, M.C. Petty, M.B. Hursthouse and A.I. Karaulov, *J. Chem. Soc. Chem. Commun.*, 816 (1990).

2. *"Halogenation of Tetrathiafulvalene."* M.R. Bryce, G. Cooke, *Synthesis,* 4, 263 (1991).

3. *"Semiconducting Langmuir-Blodgett films of New Long-Chain Tetrathiafulvalene Derivatives."* A.S. Dhindsa, G. Cooke, K. Lerstrup, K. Bechgaard, M.R. Bryce, M.C. Petty, *Chem. Mater.*, 342, (1992).

4. *"Bis(tetrathiafulvalenyl)sulphide [$(TTF)_2S$]: Synthesis and X-Ray Crystal Structure".* M.R. Bryce, G. Cooke, A.S. Dhindsa, D.J. Ando, M.B. Hursthouse, *Tetrahedron. Lett.*, 33, 1783 (1992).

5. *"Monofunctionalisation of Tetraselenafulvalene: X-Ray Crystal Structure of 4-Acetyltetraselenafulvalene".* G. Cooke, M.R. Bryce, M.C. Petty, D.J. Ando, M.B. Hursthouse. *Synthesis,* (in press 1992).

6. *"Chalcogenation of Tetrathiafulvalene (TTF) and Synthesis of Alkylthio-TTF Derivatives: X-Ray Crystal Structure of Ethylenediseleno-TTF (EDS-TTF)".* M.R. Bryce, A.J. Moore, G. Cooke, G.J. Marshallsay, P. Skabara, A. Batsonov, J.A.K. Howard. S.T.A.K. Daley. Manuscript in preparation.

7. *"Functionalised Tetrathiafulvalene (TTF) systems derived from 4,5-(Propylenedithio)-1,3-dithiole Units: X-Ray Crystal Structure of a 4,5-(ethylenedithio)-4',5'-(Propylenedithio)-TTF Derivative Containing a Spiro Ketal Group".* G.J. Marshallsay, M.R. Bryce, G. Cooke, T. Jørgensen, J. Becher, C. Reynolds, S. Wood. Manuscript in preparation.

APPENDIX III.

LECTURES, COLLOQUIA AND CONFERENCES.

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

1. All research colloquia, research seminars and lectures arrangement by the Department of Chemistry and the Chemical Society during the period of residence as a postgraduate student. (* - indicates those Colloquia attended by the author).

2. All research conferences attended, and papers presented by the author, during the period when the research for the thesis was carried out.

III.1 Lectures and Colloquia organised by The Department of Chemistry.

(A) 1st August 1989 to 31st July 1990.

BADYAL, Dr. J.P.S. (Durham University) 1st November,1989
Breakthroughs in Heterogeneous Catalysis

* BECHER, Dr. J. (Odense University) 13th November,1989
Synthesis of New Macrocyclic Systems using
Heterocyclic Building Blocks

* BERCAW, Prof. J.E. (California Institute of Technology) 10th November,1989
Synthetic and Mechanistic Approaches to Ziegler-Natta
Polymerization of Olefins

* BLEASDALE, Dr.C. (Newcastle University) 23rd February,1990
The mode of Action of some Anti-tumour Agents

BOWMAN, Prof. J.M. (Emory University) 23rd March,1990
Fitting Experiment with theory in Ar-OH

* BUTLER, Dr. A. (St. Andrews University) The Discovery of Penicillin: Facts and Fancies	7th December,1989
CHEETHAM, Dr. A.K. (Oxford University) Chemistry of Zeolite Cages	8th March,1990
CLARK, Prof. D.T. (ICI Wilton) Spatially Resolved Chemistry (using Natures's Paradigm in the Advanced Materials Arena)	22nd February,1990
COLE-HAMILTON, Prof. D.J. (St. Andrews University) New Polymers from Homogeneous Catalysis	29th November,1989
* CROMBIE, Prof. L. (Nottingham University) The Chemistry of Cannabis and Khat	15th February,1990
DYER, Dr. U. (Glaxo) Synthesis and Conformation of C-Glycosides	31st January,1990
FLORIANI, Prof C. (University of Lausanne, Switzerland) Molecular Aggregates - A Bridge between Homogeneous and Heterogeneous Systems	25th October,1989
GERMAN, Prof. L.S. (USSR Academy of Sciences - Moscow) New Synthesis in Fluoroaliphatic Chemistry: Recent Advances in the Chemistry of Fluorinated Oxiranes	9th July,1990
* GRAHAM, Dr. D. (B.P. Research Centre) How Proteins Absorb to Interfaces	4th December,1989
GREENWOOD, Prof. N.N. (University of Leeds) Novel Cluster Geometries in Metalloborane Chemistry	9th November,1989
HOLLOWAY, Prof. J.H. (University of Leicester) Noble Gas Chemistry	1st February,1990
* HUGHES, Dr. M.N. (King's College, London) A Bug's Eye View of the Periodic Table	30th November,1989
* HUISGEN, Prof. R. (Universität München) Recent Mechanistic Studies of [2+2] Additions	15th December,1989
KLINOWSKI, Dr. J. (Cambridge University) Solid State NMR Studies of Zeolite Catalysis	13th December,1989

LANCASTER, Rev. R. (Kimbolton Fireworks) Fireworks - Principles and Practice	8th February,1990
LANUZZI, Prof. L. (University of Bologna) Application of Dynamic NMR to the Study of Conformational Enantiomerism	12th February,1990
PALMER, Dr. F. (Nottingham University) Thunder and Lightning	17th October,1989
* PARKER, Dr. D. (Durham University) Macrocycles, Drugs and Rock 'n' Roll	16th November,1989
PERUTZ, Dr. R.N. (York University) Plotting the Course of C-H Activations with Organometallics	24th January,1990
PLATONOV, Prof. V.E. (USSR Academy of Sciences - Novosibirsk) Polyfluoroindanes: Synthesis and Transformation	9th July,1990
* POWELL, Dr. R.L. (ICI) The Development of CFC Replacements	6th December,1989
POWIS, Dr. I. (Nottingham University) Spinning off in a huff: Photodissociation of Methyl Iodide	21st March,1990
ROZHKOV, Prof. I.N. (USSR Academy of Sciences Moscow) Reactivity of Perfluoroalkyl Bromides	9th July,1990
* STODDART, Dr. J.F. (Sheffield University) Molecular Lego	1st March,1990
* SUTTON, Prof. D. (Simon Fraser University, Vancouver B.C.) Synthesis and Applications of Dinitrogen and Diazo Compounds of Rhenium and Iridium.	14th February,1990
THOMAS, Dr. R.K. (Oxford University) Neutron Reflectometry from Surfaces	28th February,1990
THOMPSON, Dr. D.P. (Newcastle University) The role of Nitrogen in Extending Silicate Crystal Chemistry	7th February,1990

B 1st AUGUST 1990 TO 31st JULY 1991

ALDER, Dr. B.J. (Lawrence Livermore Labs., California) Hydrogen in all its Glory	15th January,1991
* BELL†, Prof. T. (SUNY, Stoney Brook, U.S.A.) Functinal Molecular Architecture and Molecular Recognition	14th November,1990
* BOCHMAN†, Dr. M. (University of East Anglia) Synthesis, Reactions and Catalytic Activity of Cationic Titanium Alkyls	24th October,1990
BRIMBLE, Dr. M.A. (Massey University, New Zealand) Synthetic Studies Towards the Antibiotic Griseusin-A	29th July,1991
BROOKHART, Prof. M.S (University of N. Carolina) Olefin Polymerizations, Oligomerizations and Dimerizations Using Electrophilic Late Transition Metal Catalysts	20th June,1991
BROWN, Dr. J. (Oxford University) Can Chemistry Provide Catalysts Superior to Enzymes?	28th February,1991
* BUSHBY†, Dr. R. (Leeds University) Biradicals and Organic Magnets	6th February,1991
* COWLEY, Prof. A.H. (University of Texas) New Organometallic Routes to Electronic Materials	13th December,1990
CROUT, Prof. D. (Warwick University) Enzymes in Organic Synthesis	29th November,1990
* DOBSON†, Dr. C.M. (Oxford University) NMR Studies of Dynamics in Molecular Crystals	6th March,1991
* GERRARD†, Dr. D. (British Petroleum) Raman Spectroscopy for Industrial Analysis	7th November,1990
HUDLICKY, Prof. T. (Virginia Polytechnic Institute) Biocatalysis and Symmetry Based Approaches to the Efficient Synthesis of Complex Natural Products	25th April,1991
* JACKSON†, Dr. R. (Newcastle University) New Synthetic Methods: α-Amino Acids and Small Rings	31st October,1990

KOCOVSKY[†], Dr. P. (Uppsala University) 6th November,1990
Stereo-Controlled Reactions Mediated by Transition
and Non-Transition Metals

* LACEY, Dr. D. (Hull University) 31st January,1991
Liquid Crystals

LOGAN, Dr. N. (Nottingham University) 1st November,1990
Rocket Propellants

MACDONALD, Dr. W.A. (ICI Wilton) 11th October,1990
Materials for the Space Age

* MARKHAM, Dr. J. (ICI Pharmaceuticals) 7th March,1991
DNA Fingerprinting

* PETTY, Dr. M.C. (Durham University) 14th February,1991
Molecular Electronics

* PRINGLE[†], Dr. P.G. (Bristol University) 5th December,1990
Metal Complexes with Functionalised Phosphines

PRITCHARD, Prof. J. (Queen Mary & Westfield College - London University) 21st November,1990
Copper Surfaces and Catalysts

* SADLER, Dr. P.J. (Birbeck College London) 24th January,1991
Design of Inorganic Drugs: Precious Metals, Hypertension + HIV

SARRE, Dr. P. (Nottingham University) 17th January,1991
Comet Chemistry

SCHROCK, Prof. R.R. (Massachusetts Institute of Technology) 24th April,1991
Metal-ligand Multiple Bonds and Metathesis Initiators

SCOTT, Dr. S.K. (Leeds University) 8th November,1990
Clocks, Oscillations and Chaos

* SHAW[†], Prof. B.L. (Leeds University) 20th February,1991
Synthesis with Coordinated, Unsaturated Phosphine Ligands

* SINN[†], Prof. E. (Hull University) 30th January,1991
Coupling of Little Electrons in Big Molecules.
Implications for the Active Sites of (Metalloproteins and
other) Macromolecules

SOULEN[†], Prof. R. (South Western University, Texas) Preparation and Reactions of Bicycloalkenes	26th October,1990
* WHITAKER[†], Dr. B.J. (Leeds University) Two-Dimensional Velocity Imaging of State-Selected Reaction Products	28th November,1990

C 1st AUGUST 1991 TO 31st JULY 1992

* BUTLER, Dr. A.R. (St. Andrews University) Traditional Chinese herbal drugs: A different way of treating disease	7th November,1991
COOPER[†], Dr. W.D. (Shell Research) Colloid science, theory and practice	11th December,1991
* FENTON[†], Prof. D.E. (Sheffield University) Polynuclear complexes of molecular clefts as models for copper biosites	12th February,1992
* GANI[†], Prof. D. (St. Andrews University) The chemistry of PLP dependant enzymes	13th November,1991
* GEHRET, Dr. J.C. (Ciba Geigy) Some aspects of industrial agrochemical research	13th May,1992
* GRIGG[†], Prof. R. (Leeds University) Palladium catalysed cyclisation and ion capture processes	4th December,1991
* HARRIS[†], Dr. K.D.M. (St. Andrews University) Understanding the properties of solid inclusion compounds	22th January,1992
HITCHMAN[†], Prof. M.L. (Strathclyde University) Chemical vapour deposition	26th February,1992
* HOLMES[†], Dr. A. (Cambridge University) Cycloaddition reactions in the service of the synthesis of piperidine and indolizidine natural products.	29th January,1992
JOHNSON, Prof. B.F.G. (Edinburgh University) Cluster-surface analogies.	6th November,1991

* KEELEY, Dr. R. (Metropolitan Police Forensic Science) Modern forensic science.	31th October,1991
KNIGHT[†], Prof. D.M. (Philosphy Dept., University of Durham) Interpreting experiments: The beginning of electrochemistry	7th April,1992
MASKILL[†], Dr. H. (Newcastle University) Concerted or stepwise fragmentation in a deamination-type reaction	18th March,1992
* MORE O'FERRALL[†], Dr. R. (University College, Dublin) Some acid-catalysed rearrangements in organic chemistry	20th November,1991
* NIXON, Prof. J.F. (University of Sussex) The Tilden Lecture: Phosphaalkynes, new building blocks in inorganic and organometallic chemistry	25th February,1991
SALTHOUSE, Dr. J.A. (University of Manchester) Son et Lumiere - a demonstration lecture	17th October,1991
SMITH, Prof. A.L. (ex Unilever) Soap, detergents and black puddings	5th December,1991
* THOMAS[†], Prof. E.J. (Manchester University) Applications of organostannanes to organic synthesis	19th February,1992
* THOMAS[†], Dr. S.E. (Imperial College) Recent advances in organoiron chemistry	11th March,1992
WARD, Prof. I.M.(IRC in Polymer Science, University of Leeds) The SCI lecture: The science and technology of oriented polymers	28th November,1991

* Attended by the Author

[†] Invited specifically for the postgraduate training programme.

III.2 Research Conferences Attended by the Author During the Period Between October 1989 - September 1992.

1. An Introduction to Molecular Electronics, Durham, 25th - 28th September, 1989.

2. R.S.C. International Symposium on New Organic Materials, Durham, 10th - 12th September, 1990.

3. R.S.C. Graduate Symposium, Newcastle, April, 1991.

4. R.S.C. 150th Anniversary, Annual Chemical Congress, Imperial College, 8 - 11th April, 1991.

5. R.S.C. Autumn Meeting, York, 24th - 26th September, 1991. A poster was presented entitled "New Organic Conductors Formed by Stable Organosulphur Radical Cations".

6. R.S.C. 25th Annual Meeting on "Modern Aspects of Stereochemistry", Sheffield, 18th December, 1991.