Synthesis of highly functionalised tetrathiafulvalenes

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SYNTHESIS OF HIGHLY FUNCTIONALISED TETRATHIAFULVALENES

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at the University of Durham

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DECLARATION

The work described in this thesis was carried out by the author, in the Department of Chemistry, University of Durham and at the Kemisk Institut, Odense Universitet, Denmark, between October 1990 and September 1993. It has not been submitted previously for a degree at this, or any other, University.

STATEMENT OF COPYRIGHT

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ABSTRACT

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by

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A range of functionalised symmetrical and unsymmetrical tetrathiafulvalene (TTF) derivatives containing substituted 4,5-(propylene-1,3-dithio) units fused to the TTF framework has been prepared. In particular, TTF derivatives bearing hydroxy or ketone functionality have been obtained. Cyclic voltammetric studies establish that the new TTF derivatives are efficient π-electron donors; they undergo two reversible, single-electron redox waves.

A series of new bis- and tris-tetrathiafulvalene derivatives has been prepared. The TTF-thiolate anion has been used as a key intermediate and shown to be a particularly versatile reagent for this purpose. 4-(Benzoylthio) tetrathiafulvalene has been prepared and serves as a convenient shelf-stable precursor of the TTF-thiolate anion. A novel pentakis-tetrathiafulvalene macromolecule has been efficiently synthesised. The solution electrochemistry of the new multi-TTF derivatives has been studied by cyclic voltammetry, which reveals that the TTF moieties do not interact to any significant extent.

Methodology has been developed for the preparation of highly functionalised analogues of TTF containing the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene unit. These are versatile electron donor systems and have been used in the construction of novel redox assemblies.

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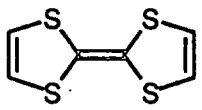
CHAPTER ONE

INTRODUCTION

1.1 GENERAL INTRODUCTION

This thesis is concerned with the synthesis of highly functionalised, redox-active organic compounds. Such compounds can act as potential building blocks for incorporation into a variety of novel organic materials, whose applications will appeal to a diverse range of chemists and material scientists. Particular interest should stem from scientists engaged in the design and synthesis of highly conducting organic materials (both crystalline and thin films) and from those whose research lies within the areas of polymer, macrocyclic and supramolecular chemistry.

All the key compounds described in this thesis have one structural feature in common - they can be regarded as derivatives of the same parent system, namely, tetrathiafulvalene (TTF) 1.



Tetrathiafulvalene (TTF) 1

It is the remarkable properties of this particular system which has lent tetrathiafulvalene and its derivatives to thorough investigation, not just from chemists, but from physicists and material scientists alike. This collaboration has been most productive and has led to important discoveries and advances both within the fields of synthetic and solid-state chemistry.

1.2 TETRATHIAFULVALENE AND ITS REDOX BEHAVIOUR

The parent molecule TTF 1 was first synthesised in 1970 by Wudl *et al.*[1] along with the chloride salts of the corresponding radical cation and dication species#. The crystal structure, obtained the following year[3], showed

#The first TTF derivative, dibenzo-TTF, had however, been reported 44 years earlier by Hurtley and Smiles[2].

the neutral TTF molecule to be nearly planar and highly symmetric. TTF consists of two fused 1,3-dithiole rings and has a highly conjugated π-system. Due to the presence of the sulphur atoms, the molecule is highly polarizable.

The efficiency of TTF as a π-electron donor can be attributed to the resonance stabilisation associated with the dithiolium cation formed upon oxidation. The ability of the sulphur atoms to accommodate much of the spin-density also accounts for the high thermodynamic stability of the radical species. The redox behaviour of TTF is illustrated in Figure 1.1. Oxidation of the neutral molecule to the radical cation results in a resonance-stabilised, 6π Hückel-type aromatic system. Further oxidation to the dication affords a system containing two linked 6π-electron moieties. This redox behaviour is in general reversible. Consequently, reduction of the dication will afford initially the radical cation, with further reduction yielding the neutral species.

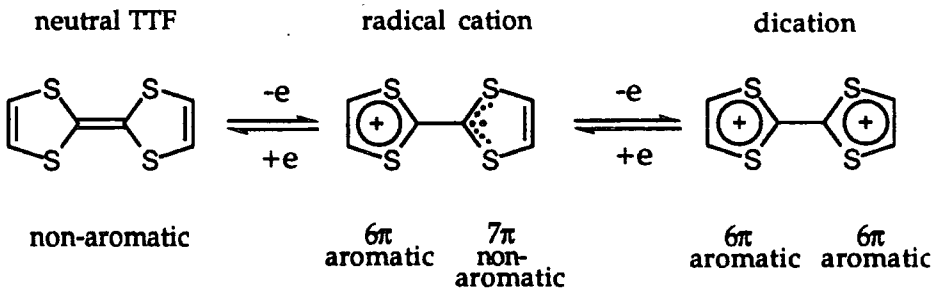


Figure 1.1. - The redox behaviour of TTF.

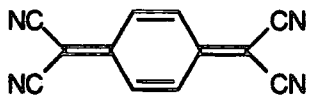
1.3 ORGANIC METALS

It is within the field of conducting organic materials that TTF and its derivatives have made their biggest contribution[4]. In fact, were it not for the unusual solid-state properties exhibited by such compounds, it is almost certain that our knowledge on the synthesis and construction of tetrathiafulvalenes would not have arrived at the level it has reached today.

This is an area of research still actively being pursued by both chemists and physicists alike. A brief account of the theory and concepts behind these 'organic metals' is given below[5].

1.3.1 Historical perspective

The first conducting molecular compound was reported in 1954 - an unstable perylene-bromine salt[6], discovered by Japanese workers (σ_{rt} = *ca.* 1 Scm^{-1}). Following the synthesis of the new powerful electron acceptor, 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) **2**[7], the early 1960's produced a number of semi-conducting charge-transfer salts[8] containing the TCNQ anion radical.



7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) **2**

1.3.2 The complex of TTF and TCNQ - the prototype organic metal

It was not until 1973 that the foundation stone for the science of organic conductors was laid, with the preparation of the first true 'organic metal'. This was the stable, crystalline 1:1 charge-transfer complex formed between the newly synthesised donor tetrathiafulvalene (TTF) **1** and the acceptor tetracyano-*p*-quinodimethane (TCNQ) **2**. This complex exhibited metallic behaviour - a room temperature conductivity of σ_{rt} = 500 Scm^{-1}, rising to a maximum of $\sigma_{max} = 10^4$ Scm^{-1} at 59K.

The metallic complex formed between TTF and TCNQ illustrated the general features common to all conducting charge-transfer salts. The X-ray structure of the complex[10], shows that in the crystal lattice, the nearly planar TTF and TCNQ molecules crystallise into two well defined segregated stacks - one composed of the donor (TTF) molecules, the other of acceptor (TCNQ) molecules. The planes within which the molecules lie are tilted with respect

to the stacking axis, the tilt of the donor molecules being in the opposite direction to that of the acceptor molecules. This gives rise to the so-called 'herringbone structure' (Figure 1.2.).

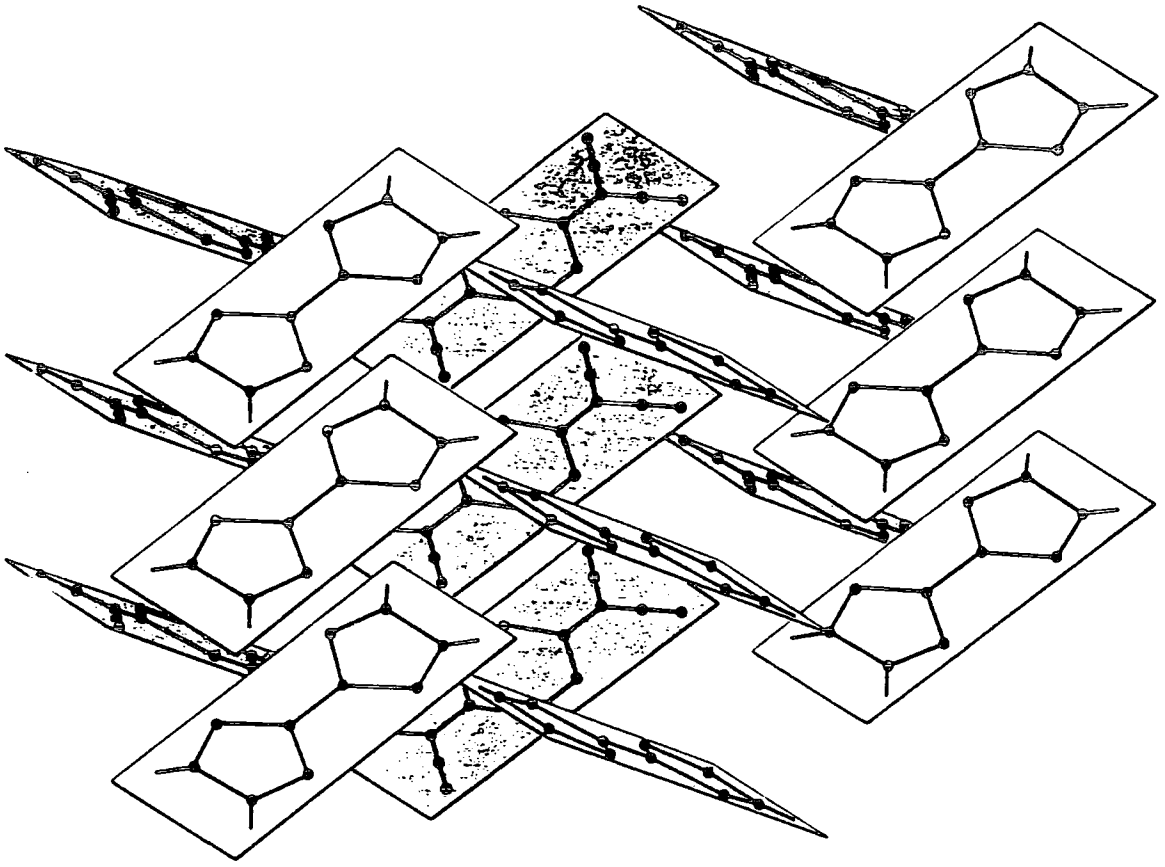


Figure 1.2. - 'Herringbone' stacking in crystals of TTF-TCNQ.

Within these segregated donor and acceptor columns, the molecules do not lie directly on top of one another. There is a lateral displacement so that the exocyclic carbon-carbon double bond of one molecule, lies directly over the ring of the molecule adjacent to it in the stack : the so called 'ring-over-bond' overlap (Figure 1.3.). This structure results in only weak inter-stack interactions, but gives rise to strong intra-stack interactions.

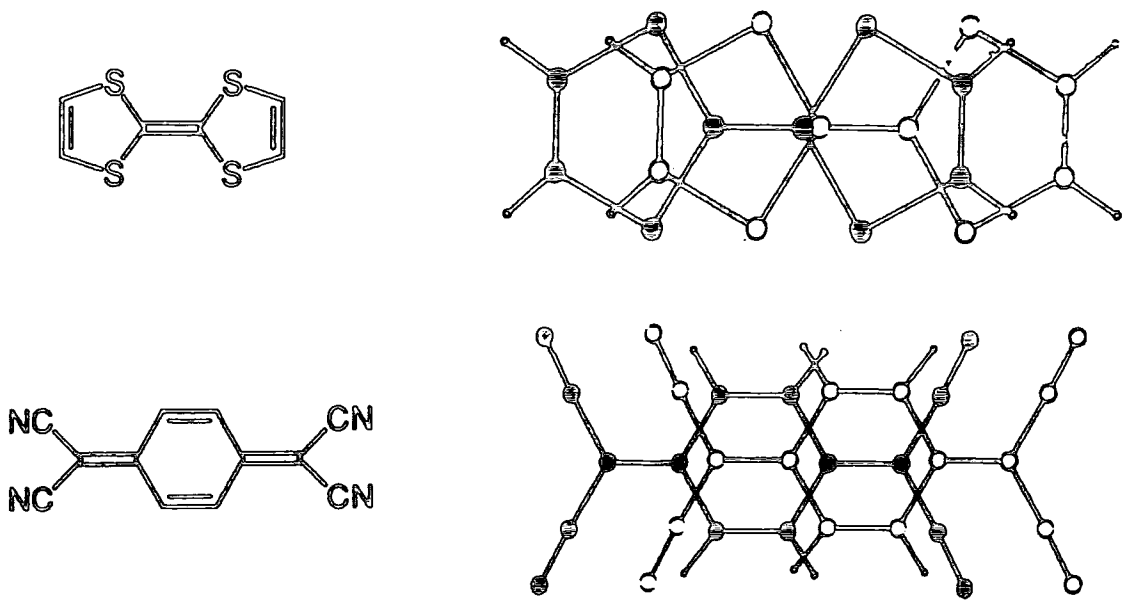


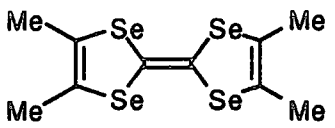
Figure 1.3. - 'Ring-over-bond' overlap in crystals of TTF-TCNQ.

Close face-to-face stacking within these columns leads to extensive π-electron overlap and delocalization, resulting in the formation of an energy band along the stacking axis. Consequently, the conductivity is highly anisotropic, being highest along the stacking axis and several orders of magnitude lower in the remaining two crystal axis directions. Many organic metals are, therefore, termed 'pseudo-one-dimensional' conductors.

For a metallic donor-acceptor complex of 1:1 stoichiometry there must be partial charge-transfer from donor to acceptor. The partial transfer of electrons is crucially important for the system to be an organic metal. This requires a delicate balance between the ionisation potential of the donor and the electron affinity of the acceptor. For the TTF-TCNQ complex, the degree of charge-transfer is 0.59 (as ascertained by infra-red spectroscopy[11] and diffuse X-ray scattering techniques[12]) *i.e.* 0.59 electrons are transferred, on average, from each TTF to each TCNQ molecule. So, with both bands partially filled, both stacks contribute to the conduction process.

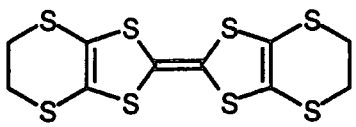
1.3.3 Sulphur-based systems and organic superconductivity

A most significant advance in the field of organic conductors has been the discovery of organic superconductivity (the conduction of electricity without resistance). In 1980, collaboration between Bechgaard and Jerome led to superconductivity being observed in the hexafluorophosphate radical ion salt of tetramethyltetraselenafulvalene with a superconducting transition temperature (T_c) of 1K under 12 kbar pressure[13]. Superconductivity has since been observed in many tetramethyltetraselenafulvalene (TMTSF) **3** salts, with $(TMTSF)_2ClO_4$ being a superconductor (T_c = 1.2K) at ambient pressure.



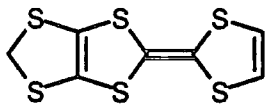
Tetramethyltetraselenafulvalene (TMTSF) **3**

Since the discovery in 1983 of superconductivity in salts of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) **4**[14], sulphur-based systems have attracted the most attention. Several superconducting salts of BEDT-TTF **4** are now known[15], and their structures are characterised by short two- and three-dimensional sulphur-sulphur interactions. Those with highest T_c values do not comprise stacks or sheets of the donors but, instead, interacting dimers which are positioned approximately orthogonal to each other, forming a conducting two-dimensional S---S network. Currently, the highest T_c organic superconductor at ambient pressure is $(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ with T_c = 11.6K[16].

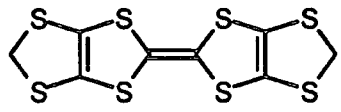


Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) **4**

Many other sulphur-carbon organic donors that are variants of TTF 1 or BEDT-TTF 4 have been reported recently[17]. Only one of these, methylenedithio-tetrathiafulvalene (MDT-TTF) 5 has provided new superconductors[18]. It is interesting to note that neither of the parent symmetrical donors, *i.e.* TTF 1 and bis(methylenedithio)tetrathiafulvalene (BMDT-TTF) 6, yield superconductors. The discovery of this type of superconductor based on an unsymmetrical donor has therefore shown the need for efficient synthetic routes to unsymmetrical systems.



MDT-TTF 5



BMDT-TTF 6

1.4 APPLICATIONS OF THE TETRATHIAFULVALENE UNIT IN MODERN MATERIALS SCIENCE

The 1,3-dithiole-2-ylidene heterocyclic ring system has found widespread use in modern materials science[19]. As such, its chemistry has been the subject of great interest and the fundamental properties of this ring system intensively investigated[20]. The main feature which makes the dithiole system so interesting is the different oxidation states that are possible for this ring system.

The basic TTF framework has been electronically and structurally modified in several ways to give new functionalised π-donor systems useful for specific applications. These modifications can be summarised as shown in Figure 1.4.

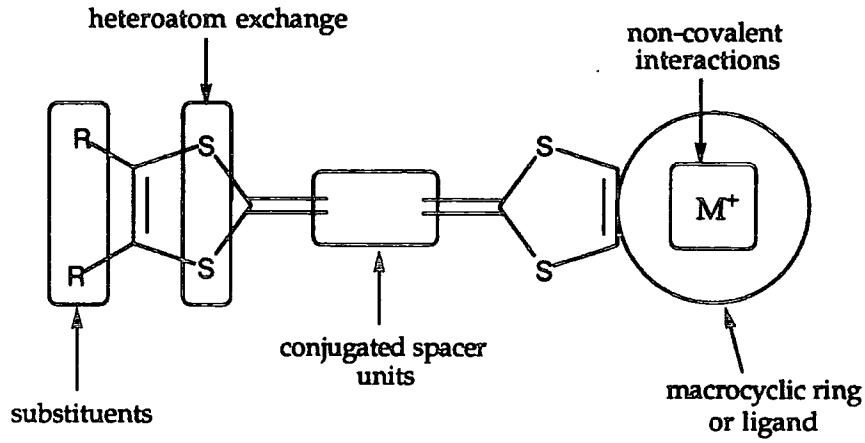
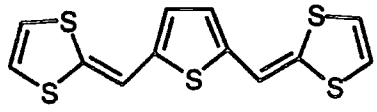


Figure 1.4. - Modifications of the basic TTF framework.

Although the mainstream focus has been on new TTF donors, new materials based on the versatile 1,3-dithiole-2-ylidene unit have been developed in the last decade. These other applications seem likely to develop further because of the intrinsic molecular properties of the fundamental dithiole building block. A few brief examples of some of the applications of the TTF framework in modern materials science follow:

i) **New donors.** Early efforts in the area of dithiole based donors were towards centrosymmetric, substituted TTF derivatives. This was later extended towards their selenium and tellurium analogues. Studies on these materials has contributed significantly to the present knowledge of low-dimensional conductors and much work has been done on the modification of the basic TTF unit. The introduction of conjugated or heterocyclic spacer groups between the dithiole units has recently been investigated. An example of such a system is the thiophene derivative **7**[21]. Another current development in this field is towards "multiple-TTFs", for example compound **8**[22].



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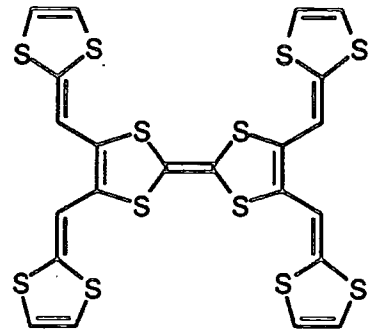

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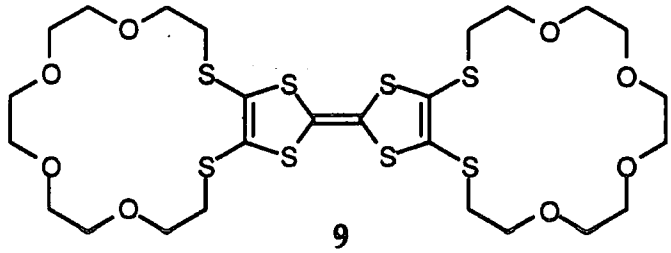
ii) **Sensors**. A "molecular sensor" based on a TTF derivative has been reported recently[23]. The model compound **9** is a hybrid between TTF and a crown ether. In the presence of sodium ions the first redox potential of **9** is shifted by 80mV to a more positive potential; the second potential remains unchanged. This indicates a non-covalent interaction between a sodium cation present in the crown ether cavity and the TTF radical cation. Although the stability constant was rather low, this might be enhanced by future synthesis of an all-oxygen crown TTF.



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iii) **Molecular Shuttles**. A spectacular use of a TTF derivative has recently been reported by Stoddart *et al.*[24] in a [2] rotaxane with "molecular shuttling" properties (Figure 1.5.). The presence of different donor residues in the chain not only makes self-assembly of the rotaxane possible, but also enables the controlled shuttling of the tetracationic macrocycle along the chain. This can be achieved by electrochemical control of the redox state of the donor residues along the chain. The chemically stable and fully reversible redox-active TTF unit, make it particularly attractive for such applications, as well as in systems such as TTF catenanes and rotaxanes.

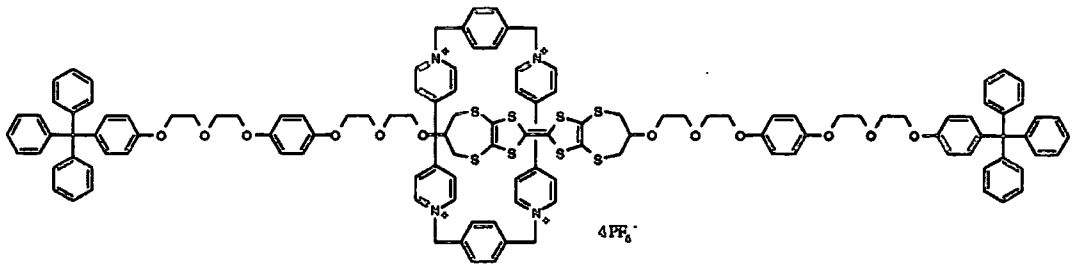
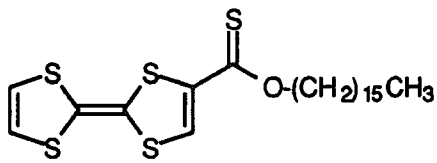


Figure 1.5. - The "molecular shuttle" concept applied to TTF systems.

iv) **Electroactive Langmuir-Blodgett Films.** TTF derivatives are at the forefront of attention in the application of the Langmuir-Blodgett (LB) technique to organic electron donor and electron acceptor molecules at the molecular level. The aim here is to produce highly conducting ultrathin films suitable for incorporation into molecular electronic devices. In the LB technique, amphiphilic molecules are spread onto a surface of ultrapure water to form a monolayer. This layer can be deposited onto a solid support with a well-defined multilayer structure. In our own group, we have recently reported[25] the synthesis of the long chain TTF system **10** and characterisation of its LB films. Although the conductivity values obtained were quite high (iodine doping resulted in conductivities up to $\sigma_{max} = 1.0 \pm 0.2$ Scm^{-1}), there are stability problems associated with this technique. However, the potential applications of cheap, conducting thin films are certainly important and research in this area is still being actively pursued.



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v) **C_{60} Complexes.** Izuoka *et al.* have recently reported[26] the preparation of a charge-transfer (CT) complex between BEDT-TTF **4** and the fullerene C_{60}. The $(BEDT\text{-}TTF)_2C_{60}$ CT complex appears as black needles and the X-ray crystallographic study reveals remarkably short S - C_{60}

intermolecular distances. The parent TTF does not give a similar CT complex and the complex formation is likely to be a result of the flexibility of the BEDT-TTF molecule. It will be interesting to learn more about the properties of this new type of complex.

1.5 SYNTHETIC ROUTES TO TTF DERIVATIVES

In this section, a brief account of the different synthetic routes for the construction of tetrathiafulvalenes will be given. A number of extensive review articles on this subject have appeared[27], reflecting the tremendous amount of work that has been put into this area within the last couple of decades.

The methods for the synthesis of tetrathiafulvalenes (as outlined in Figure 1.6.) can be classified according to the part of the TTF molecule that is constructed in the last step. There are three general categories, in which the last step involves:

Type A - the functionalisation of TTF or side chain modification of its analogues (Section 1.5.1);

Type B - formation of the dithiole rings (Section 1.5.2);

Type C - formation of the central double bond (Section 1.5.3).

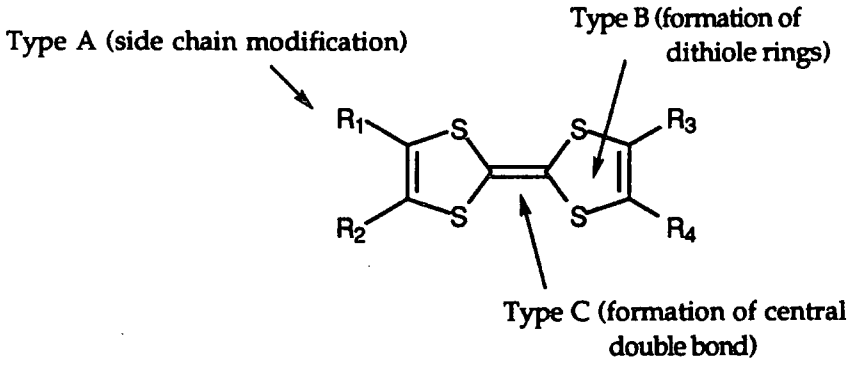


Figure 1.6. - Synthetic routes to TTF derivatives, ordered according to the part of the molecule that is constructed in the last step.

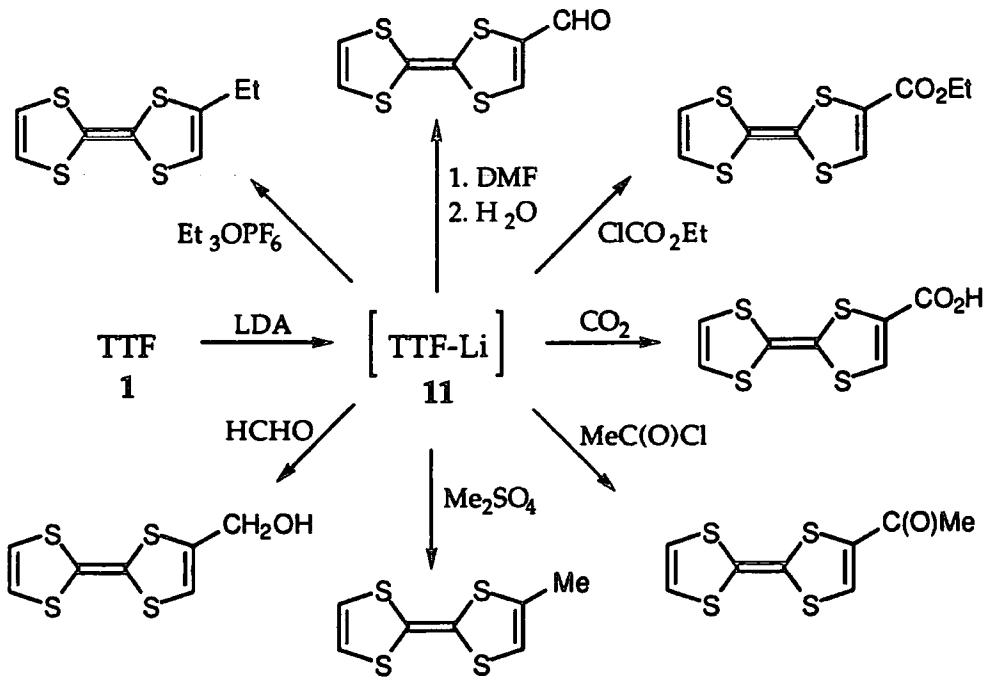
1.5.1 Type A - The functionalisation of TTF or side chain modification of its analogues

This approach to tetrathiafulvalene synthesis utilises starting materials in which the central TTF-unit is already in place. The simplest examples of this type of reaction are those that start from TTF itself.

1.5.1.1 The TTF anion and its chemistry

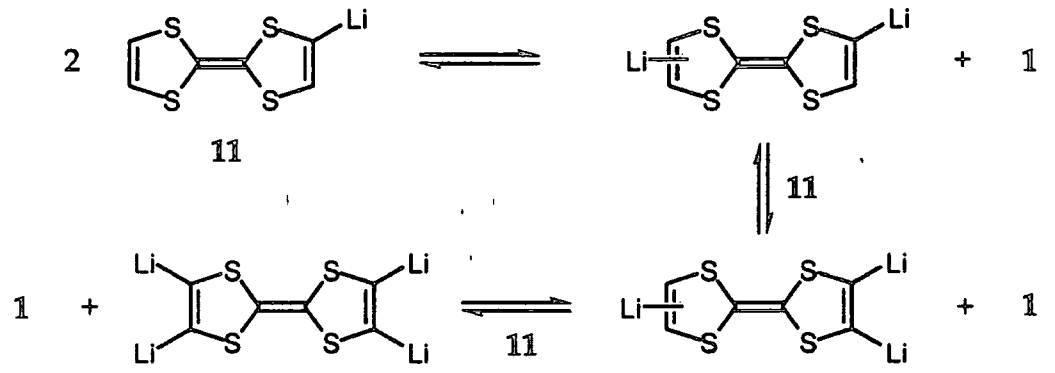
The first monofunctionalised TTF derivatives prepared directly from TTF 1 were reported by Green[28], via formation of tetrathiafulvalenyl-lithium 11. The TTF monoanion 11 was generated by the use of butyllithium, and trapped with CO_2 and Et_3OPF_6 to give modest yields of the acid and ethyl derivatives, respectively.

Green later showed[29] that formation of the TTF anion 11 could be accomplished via the action of either *n*-BuLi or lithium diisopropylamide (LDA) in ether at -78°C, and trapped with a wide range of electrophiles, to give mono-substituted derivatives in modest yields (Scheme 1.1.).



Scheme 1.1. - Substituted tetrathiafulvalenes via the TTF - anion.

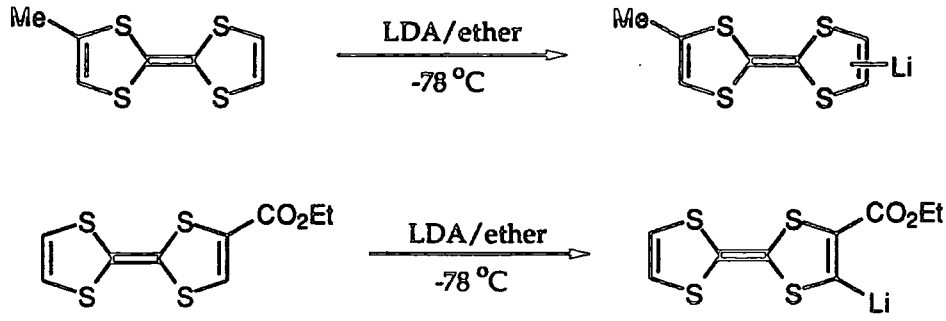
Strict temperature control is essential for the success of this reaction. At temperatures above -78°C, disproportionation of the TTF monoanion 11 occurs readily, to give multi-lithiated species (and therefore multi-substituted products) along with TTF 1 (Scheme 1.2.). However, if the temperature is carefully 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 procedure direct from commercially available TTF.



Scheme 1.2. - The disproportionation of the TTF anion.

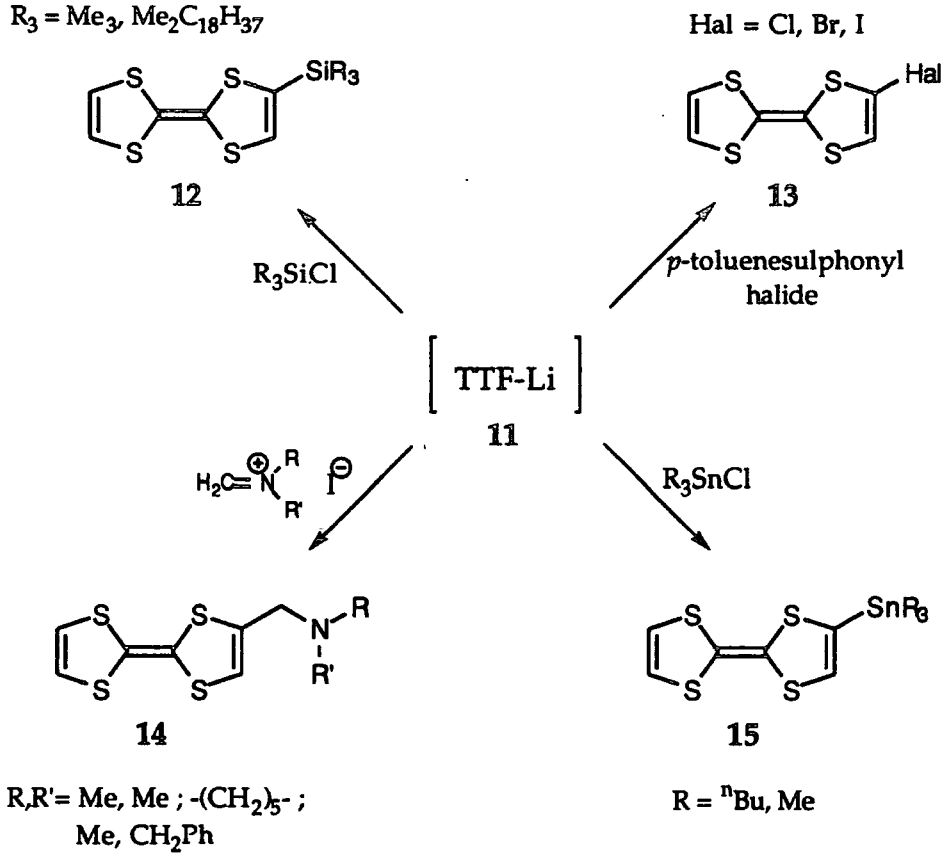
The presence of substituents on TTF exerts an important directional effect, allowing control over the position of metallation. The presence of an electron donating substituent on one of the rings (*e.g.* an alkyl group), decreases the acidity of the adjacent proton (by inductively destabilising the formation of the corresponding anion) and hence favours metallation (and therefore substitution) on the other ring. Conversely, the presence of an electron withdrawing substituent on one of the rings (*e.g.* an ester group), increases the acidity of the adjacent proton, hence favouring substitution on the same ring (Scheme 1.3.).

It has been shown that all four protons of TTF 1 can be readily removed by the reaction of four equivalents of LDA or phenyllithium at -78°C, and the resultant tetra-anion reacts with elemental sulphur, selenium or tellurium, followed by alkyl halides, to yield TTF derivatives substituted with four thioalkyl, selenoalkyl or telluroalkyl chains[30].



Scheme 1.3. - The directional effect of substituents towards further substitution on TTF.

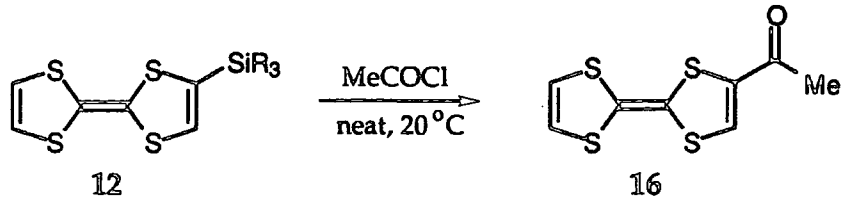
In recent years, a number of new, monofunctionalised TTF derivatives have been reported. These have all been formed from the TTF-monoanion, and are summarised in Scheme 1.4.



Scheme 1.4. - Recent mono-functionalised TTF derivatives from TTF-anion 11.

In our own laboratory the TTF-monoanion **11** has been reacted with silicon reagents to yield the first mono-silylated TTF derivatives **12**[31]. These

compounds serve as efficient, shelf-stable equivalents of the TTF-monoanion 11. For example, reaction of 12 with acetyl chloride, neat at 20°C affords acetyl-TTF 16 in good yield (Scheme 1.5.).



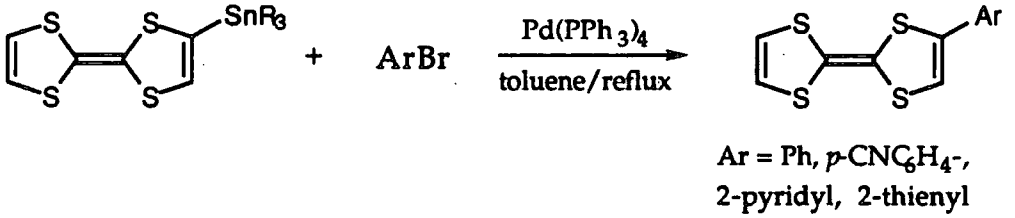
12 16

Scheme 1.5. - Mono-silylated derivatives serve as an equivalent of the TTF-monoanion.

A series of halogenated tetrathiafulvalenes has been prepared[32]. Reaction of tetrathiafulvalenyl-lithium 11 with the appropriate *p*-toluene-sulphonyl halide yields the corresponding mono-halo TTFs 13 in 34-48% yield.

The first synthesis of N,N-disubstituted aminomethyl tetrathiafulvalene derivatives has been reported by Garin *et al.*[33]. These were prepared by reaction of 11 with Eschenmoser's salts to afford the corresponding derivatives 14 in reasonable yield. This method increases the limited number of synthetic routes to nitrogen substituted tetrathiafulvalenes.

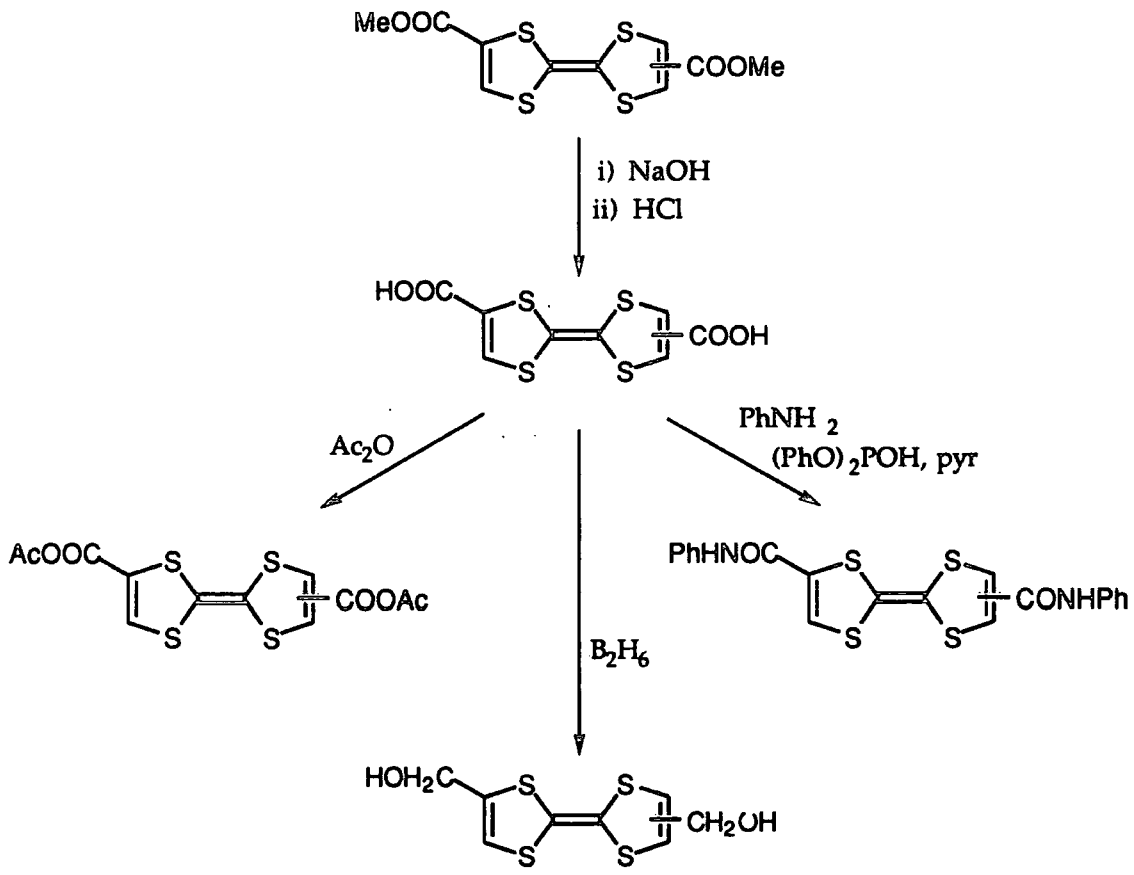
Finally, Japanese workers have recently reported the preparation of trialkylstannyl-tetrathiafulvalenes[34]. Reaction of 11 with trialkyltin chlorides affords the corresponding trialkylstannyl-TTFs 15 in 75-85% yield. Subsequent reaction with aryl halides in the presence of $Pd(PPh_3)_4$ in refluxing toluene, gives the corresponding aryl-tetrathiafulvalene in good yield (Scheme 1.6.).



Scheme 1.6. - Cross-coupling reactions of trialkylstannyl-TTFs.

1.5.1.2 Side chain modification of tetrathiafulvalenes

Other reactions leading to functionalised TTF derivatives are those which involve a modification of one or several functional groups on the starting tetrathiafulvalene. Many accessible functionalised TTF derivatives can be converted to other TTF derivatives using standard reactions[35]. Such an approach is possible in basic or weakly acidic media because the TTF unit is stable under these conditions. Transformations that can be accomplished include the hydrolysis of ester groups and the formation of anhydrides, amides and alcohols (Scheme 1.7.).



Scheme 1.7. - Standard reactions compatible with the central TTF unit.

1.5.1.3 The TTF-tetrathiolate intermediate

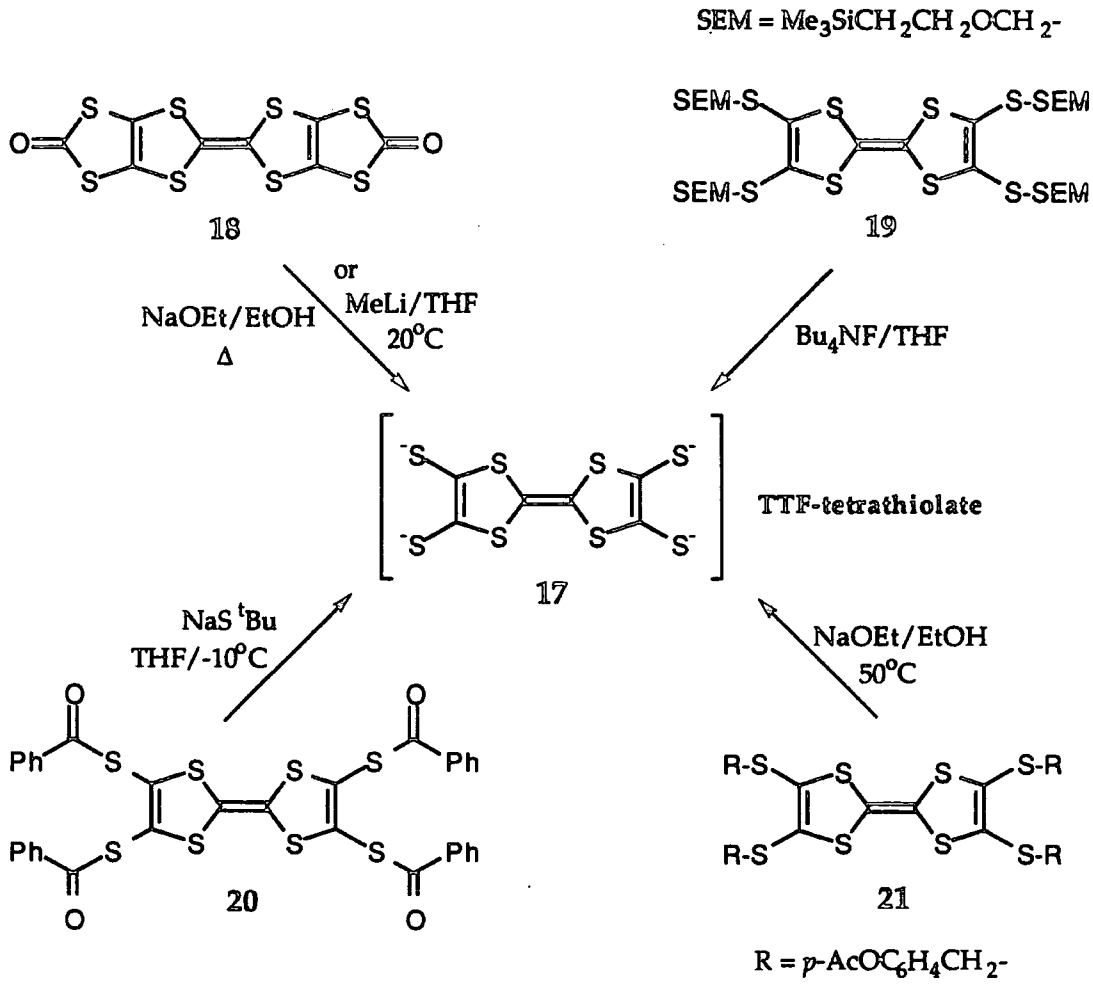
Since the discovery of superconductivity in salts of BEDT-TTF **4**, considerable efforts have been invested in synthesising TTF derivatives

substituted with sulphur atoms in all four positions. Some of these make use of the TTF-tetrathiolate intermediate **17**, several routes to which have been reported, and these are outlined in Scheme 1.8.

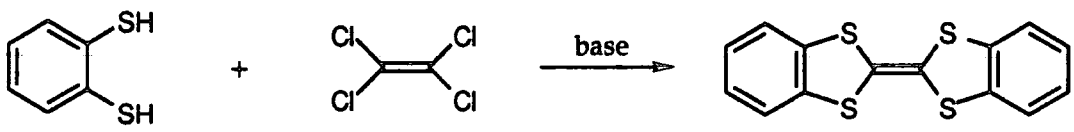
Compound **18**, reported by Schumaker *et al.* in 1977[36], is converted into TTF-tetrathiolate **17** by treatment with nucleophiles (*e.g.* NaOEt, MeLi). This is also the case for compounds **20** (developed by Hansen and co-workers[37] in 1991) and compound **21** (made by Kilburn *et al.* in 1992[38]). Deprotection of **19** (synthesised by Zambounis *et al.* in 1991[39]) is achieved using tetrabutylammonium fluoride. The TTF-tetrathiolate **17** can then be trapped with electrophiles such as 1,2-dibromoethane and iodomethane, to afford BEDT-TTF derivatives. One disadvantage of all these routes is that unsymmetrical products cannot be formed specifically.

1.5.2 Type B - Formation of the dithiole rings in the final step

Syntheses in which the dithiole rings are formed in the final step are relatively few. In 1926, Hurtley and Smiles reported that sodium *o*-benzenedithiolate reacts with tetrachloroethylene to give dibenzo-tetrathiafulvalene in 16% yield[2] (Scheme 1.9.). This represents the first published synthesis of any tetrathiafulvalene derivative.

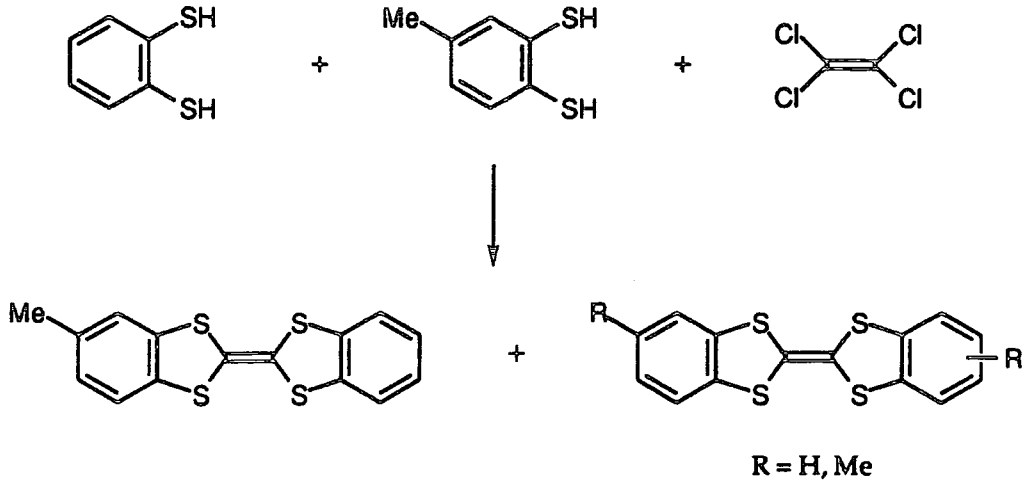


Scheme 1.8. - Alternative routes to the TTF-tetrathiolate intermediate.



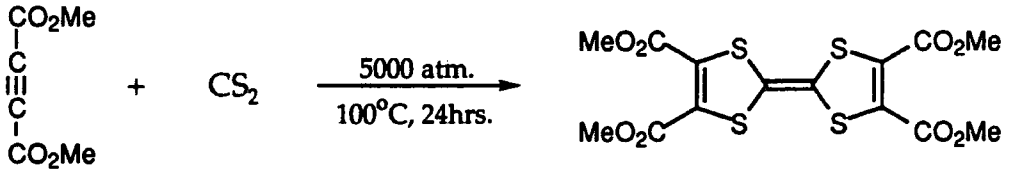
Scheme 1.9. - The original Hurtley-Smiles synthesis of dibenzo-TTF.

This method can be used to obtain the unsymmetrical dibenzo-TTFs starting from tetrachloroethylene and two variously substituted *o*-benzenedithiols (Scheme 1.10.). This synthesis is not selective and leads to a mixture of different benzo-tetrathiafulvalenes from which the desired derivatives can be separated[40].



Scheme 1.10. - This non-selective synthesis leads to a mixture of different benzo-TTFs.

Attempts at the synthesis of mixed tetrathiafulvalenes, especially monobenzo-TTFs have been generally unsuccessful[41]. Another example of this type of synthesis (formation of the dithiole rings in the final step), is the reaction of electrophilic or strained acetylene derivatives with carbon disulphide. This reaction is attractive because it allows one to obtain tetrathiafulvalenes substituted by electron-withdrawing groups. For example, dimethyl acetylenedicarboxylate reacts with CS_2 under 5000 atm. pressure at 100°C to give tetrakis(carbomethoxy)tetrathiafulvalene in 87% yield (Scheme 1.11.)[42].



Scheme 1.11. - Reaction of an electrophilic acetylene with CS_2 under high pressure.

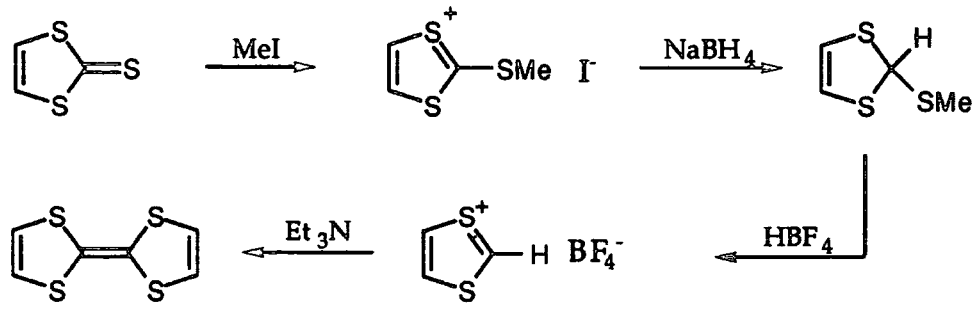
1.5.3 Type C - Formation of the central double bond in the final step

This approach to TTF synthesis is the most important and constitutes the largest number of methods. The π-bond is formed via an elimination

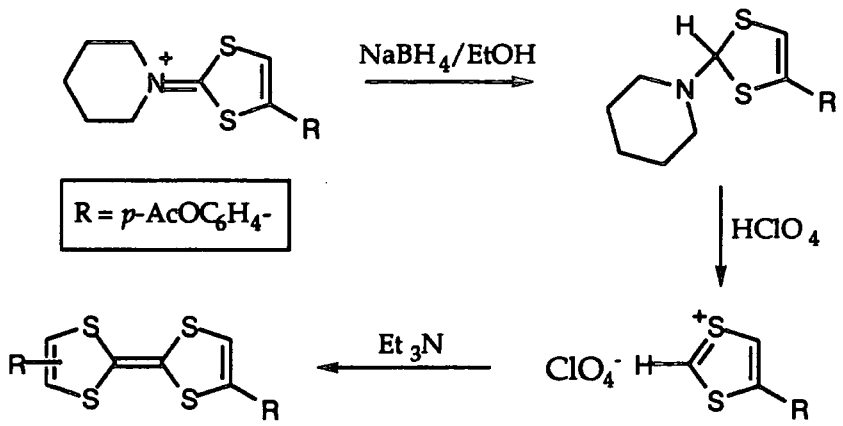
reaction, involving loss of either protons or heteroatoms. In addition, the σ- and π-bonds can be formed simultaneously by a coupling reaction of two carbenes.

1.5.3.1 i) Via elimination of a proton in the last step

This route involves the reaction of a carbene or of a phosphorus ylide with a 1,3-dithiolium salt possessing a hydrogen at carbon-2. The adduct is usually transformed into the heterofulvalene by an amine, which acts as a base. The dithiolium salt can be obtained via alkylation of 1,3-dithiole-2-thiones (Scheme 1.12.) or via 1,3-dithiole-2-iminium salts (Scheme 1.13.).

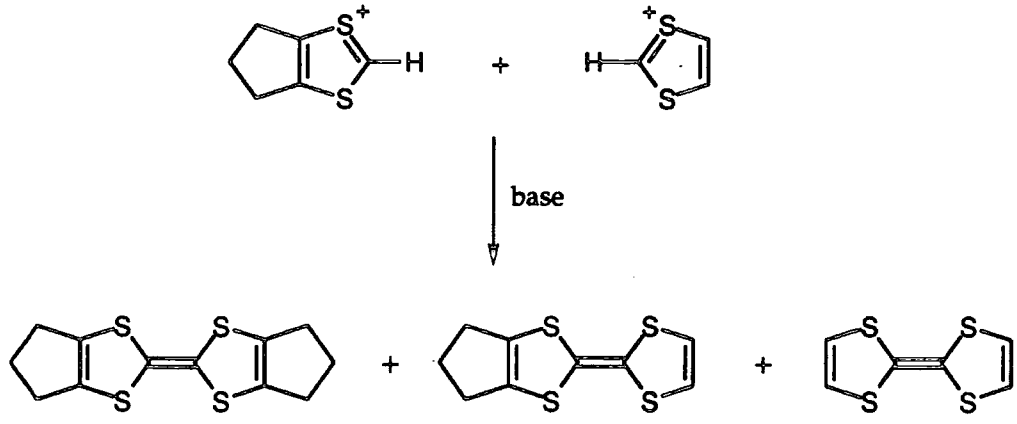


Scheme 1.12. - Synthesis of the dithiolium salt via alkylation of 1,3-dithiole-2-thiones[43].



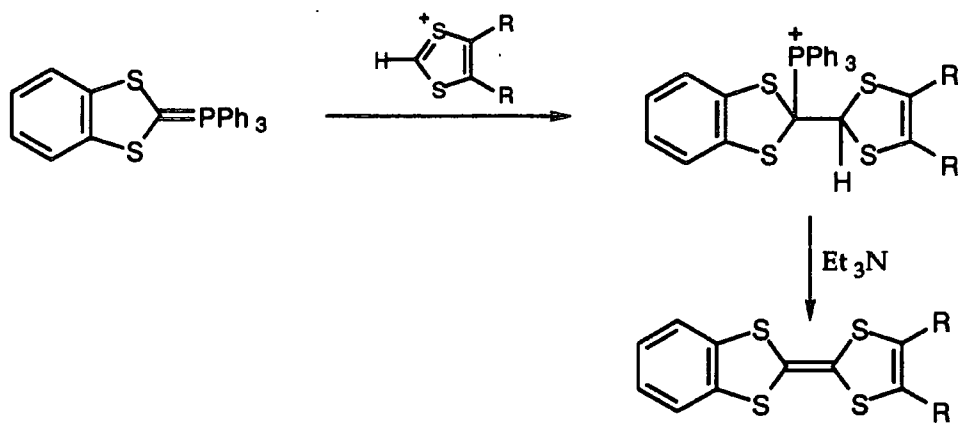
Scheme 1.13. - Synthesis via 1,3-dithiole-2-iminium salts[35].

Reaction of base with a mixture of two different symmetrical 1,3-dithiolium salts gives a mixture, often purifiable, of the three possible tetrathiafulvalenes[44] (Scheme 1.14.).



Scheme 1.14. - Product mixtures from two different, symmetrical 1,3-dithiolium salts.

2-Triphenylphosphino-1,3-dithioles react with 1,3-dithiolium salts to give products which, on treatment with base (*e.g.* Et_3N) at low temperature, give tetrathiafulvalenes[45] (Scheme 1.15.). This method permits the selective preparation, from variously substituted 1,3-dithioles, of unsymmetrical tetrathiafulvalenes in which the two heterocycles can be substituted with hydrogens, aryl, alkyl or cycloalkyl groups.

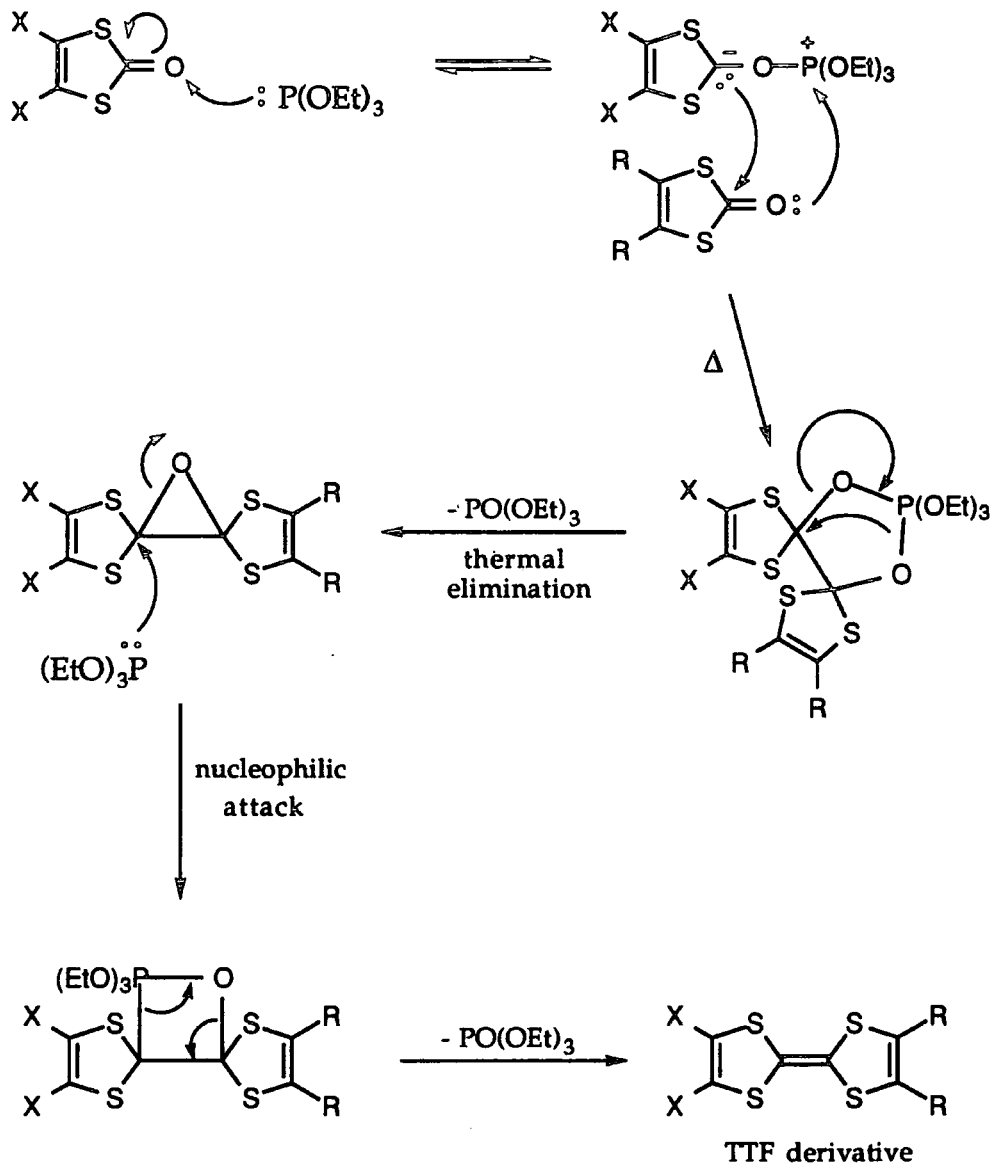


Scheme 1.15. - Synthesis involving the elimination of a proton and triphenylphosphine in the final step.

1.5.3.2 ii) Synthesis of tetrathiafulvalenes by elimination of two heterosubstituted entities in the final step

The trivalent derivatives of phosphorus react at *ca.* 80°C with 2-oxo-, 2-thioxo-, and 2-selenoxo-1,3-dithioles to give the corresponding fulvalenes

in various yields (Scheme 1.16.)[46]. This method is attractive because it allows access to a large variety of tetrathiafulvalenes bearing unsubstituted rings or rings substituted by either electron-donating groups (alkyls, cycloalkyls), electron-withdrawing groups (nitriles, esters or trifluoromethyl) or by aromatic rings.

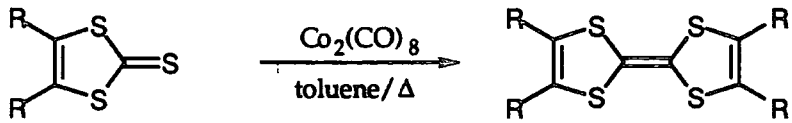


Scheme 1.16. - Mechanism of phosphite-induced coupling.

Triphenylphosphine and phosphites have been used as desulphurizing agents, although the latter have been shown to be the most efficient. Unsymmetrical 1,3-dithiole-2-thiones (or their oxo- or selenoxo-

analogues) react with phosphines or phosphites to give a mixture of the two possible isomers, whereas reaction with mixtures of 1,3-dithiole-2-thiones gives a mixture of all possible tetrathiafulvalenes.

Desulphurization can also be achieved by the use of certain transition metal complexes. Thus, treatment of 1,3-dithiole-2-thiones with dicobalt octacarbonyl in refluxing benzene or toluene solutions, affords tetrathiafulvalenes directly in modest yields[47]. This desulphurization reaction seems general, and has been applied to 1,3-dithiole-2-thiones with various substituent groups (Scheme 1.17.).

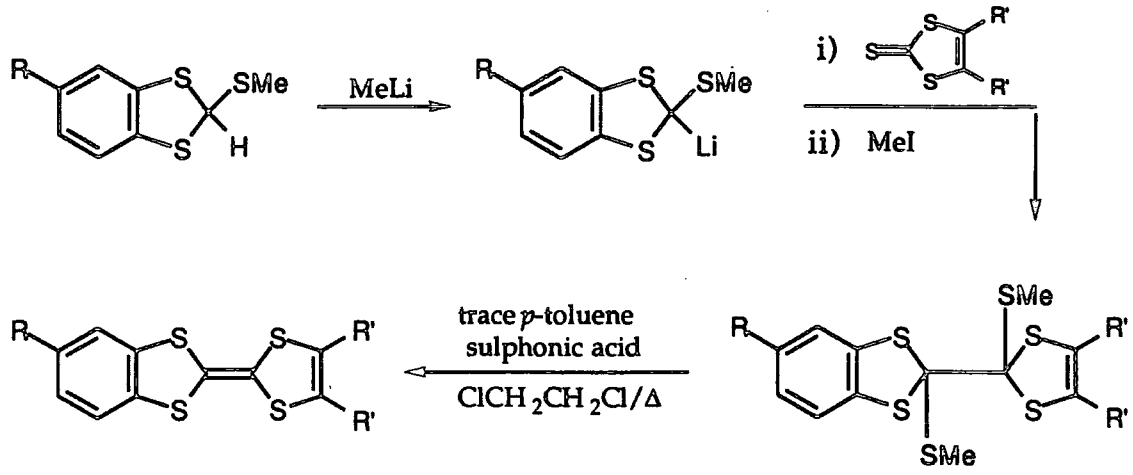


R = H, Me, Ph, $-CH_2CH_2CH_2-$, CO_2Me

Scheme 1.17. - Coupling via dicobalt octacarbonyl.

Tetrathiafulvalenes are also accessible by thermal decomposition of the corresponding hexathioorthooxalates[48]. The presence of a trace of *p*-toluenesulphonic acid lowers the decomposition temperature and increases the rate of reaction. This reaction can be applied not only to symmetrical hexathioorthooxalates, but also to those possessing two differently substituted heterocycles (Scheme 1.18.).

The reactions outlined above detail the major synthetic routes to tetrathiafulvalenes. Other, less common methods, which have found limited use include electrochemical reduction[49], photochemical coupling[50] and electrochemical oxidative dimerization[51].



Scheme 1.18. - TTF synthesis via thermal decomposition of hexathioorthooxalates.

1.6 EXTENDED TTF SYSTEMS

As an alternative to placing different substituents around the periphery of the TTF unit, it is also possible to synthesise new donors by changing the basic skeletal structure. Thus, recent work has concerned modification of the TTF framework by extending the π-electron conjugation between the two 1,3-dithiole rings. This has been achieved by the incorporation of cyclic or vinylogous 'spacer' groups.

Interest in these systems stems from the significantly different redox and conformational properties they should display compared to TTF **1**. Extending the conjugation between the 1,3-dithiole rings should modify the system in three ways:

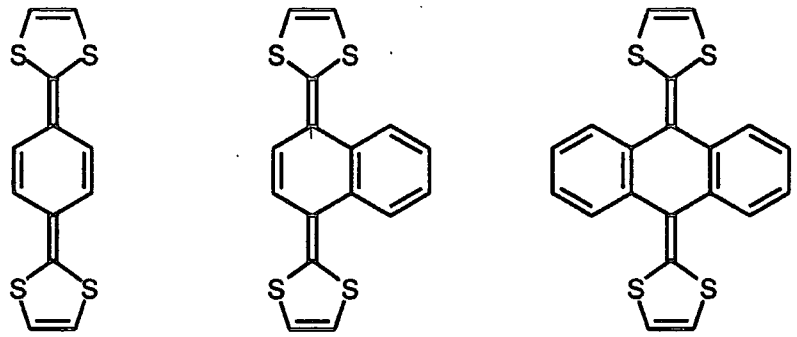
i) stabilisation of the radical cation state due to extended conjugation and greater delocalization;

ii) separation of the dithiole rings reduces on-site, intramolecular Coulombic repulsion and hence stabilises the dication state;

iii) due to rotation about the units linking the dithiole rings, these new derivatives may no longer be planar. This may induce

novel inter- and intra-molecular interactions, although major deviations from planarity may inhibit such effects.

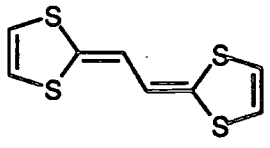
The initial research in this area concerned the insertion of aromatic spacer units, such that the neutral donors are in a quinonoid form (compounds 22-24)[52]. Oxidation to the radical cation and dication species affords aromatisation of the system. This stabilises the oxidised states, resulting in lower oxidation potentials of the neutral donors compared to TTF 1. In the case of donors 22 and 23, the oxidation potential is lowered to such an extent, that they undergo air-oxidation. In fact, many donors of this type only show one single, two-electron oxidation, directly yielding the dication species. Accordingly, the donors with quinonoid structures form dications more readily upon oxidation due to the decreased Coulombic repulsion.



22 23 24

Another group of extended donors are those in which the dithiole rings are separated by a polyene spacer unit. The simplest examples are those in which two or four sp^2 carbon atoms are inserted between the 1,3-dithiole rings. Both of these (compounds 25 and 26) have been reported by Yoshida's group[53]. This increased conjugation has two effects on the donor properties of the molecule. Firstly, the oxidation potentials are lowered compared to those of TTF, demonstrating that the vinylogues are more powerful π-electron donors. The second effect is to decrease the separation

of the two oxidation potentials. In the case of compound 26, this separation is eliminated and a single, two-electron oxidation is observed. This clearly indicates the decrease in Coulombic repulsion in the dication states of these systems, compared with the doubly-ionized state for TTF.



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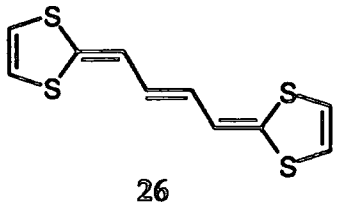

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1.7 CONCLUSION

The suitability of the redox-active TTF unit for use in modern materials science and supramolecular chemistry has been demonstrated, widespread applications having already been found. The use of the general TTF framework is likely to remain an important theme in the ongoing search for new electron donor systems and research into advanced materials in the future.

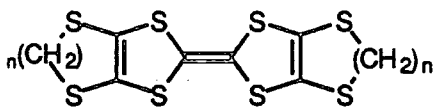
Modification of the TTF unit changes the redox characteristics of the system and hence its donor properties. There remains, however, the need for continued investigation into new synthetic methodology towards the assembly and functionalisation of the basic tetrathiafulvalene system.

CHAPTER TWO

FUNCTIONALISED TETRATHIAFULVALENE SYSTEMS DERIVED FROM 4,5-(PROPYLENE-1,3-DITHIO)-1,3-DITHIOLE UNITS

2.1 INTRODUCTION

The design and synthesis of new π-electron donor molecules which form stable radical cations is central to the development of new organic metals and organic superconductors. Particular attention has recently been directed to the tetrathiafulvalene system substituted with fused heterocycles. Prime examples are the donors BEDT-TTF 4 and BPDT-TTF 27, comprising the C_6S_8 core, and their unsymmetrical analogues[54]. The attachment of chalcogen atoms to the TTF frame can lead to an increase in intra-stack π-interactions and induce inter-stack interactions. This has the effect of increasing the dimensionality of these materials and thus helping to stabilise the metallic state by suppressing lattice distortions.

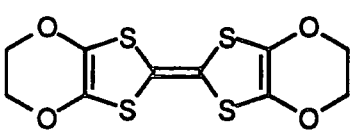


4 n=2 BEDT-TTF
27 n=3 BPDT-TTF

BEDT-TTF 4 has attracted considerable attention, due to the fact that it has formed so many superconducting salts. Various modifications have been made to the BEDT-TTF structure:

i) the attachment of oxygen atoms to the periphary of TTF to give bis(ethylenedioxo)TTF (BEDO-TTF) 28, reported in 1989 by Wudl *et al.*[55];

ii) the replacement of the ethylene bridges with vinylene units, in order to increase the planarity of the BEDT-TTF structure, giving donor 29, synthesised by Japanese workers in 1987[56];



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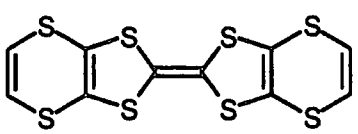

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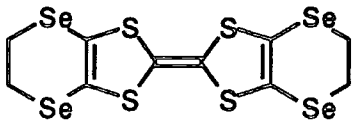
iii) replacing the outer sulphur atoms with larger selenium and tellurium atoms to afford compounds such as 30[57] and 31[58].



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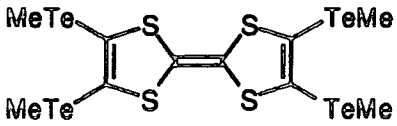

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These modifications were carried out to investigate the effect of the changes on the physical properties of cation radical salts and charge-transfer complexes of the new donors. This chemistry lies within TTF's traditional area of research - that of organic conductors or 'organic metals'.

2.2 NEW BUILDING BLOCKS IN ADVANCED MATERIALS SCIENCE

In the last few years, it has been recognised that the chemical stability and fully reversible redox-activity of the TTF unit, make it a particularly attractive building block in the development of new molecular materials with specific applications. A few examples of such applications in modern materials science have already been given in Section 1.4.

However, until recently, TTF derivatives endowed with functionalised substituents have been largely neglected. The attachment of suitable substituents to the TTF core, would provide compounds which can act as building blocks for incorporation into the following classes of materials:

i) salts and complexes with increased inter- and intra-stack interactions *e.g.* hydrogen bonding;

ii) macrocyclic and supramolecular TTF derivatives;

iii) electroactive Langmuir-Blodgett films;

iv) oligomeric and polymeric TTF derivatives.

In this context, a range of symmetrical and unsymmetrical tetrathiafulvalene derivatives containing functionalised propylenedithio units fused to the TTF framework has been prepared.

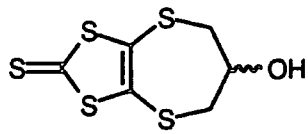
2.2.1 Synthesis of 4,5-[2-(hydroxy)propylene-1,3-dithio]-1,3-dithiole-2-thione 33

4,5-[2-(Hydroxy)propylene-1,3-dithio]-1,3-dithiole-2-thione 33 was identified as an attractive building block for functionalised TTF derivatives for the following reasons:

i) the compound should be readily available in large quantities from either the zincate salt 32[59] or from the caesium salt 36[60];

ii) the hydroxy group should serve as a reactive 'handle' enabling a variety of substituents to be attached to the system;

iii) the coupling of derivatives of 33 should proceed under standard conditions to yield TTF derivatives.



33

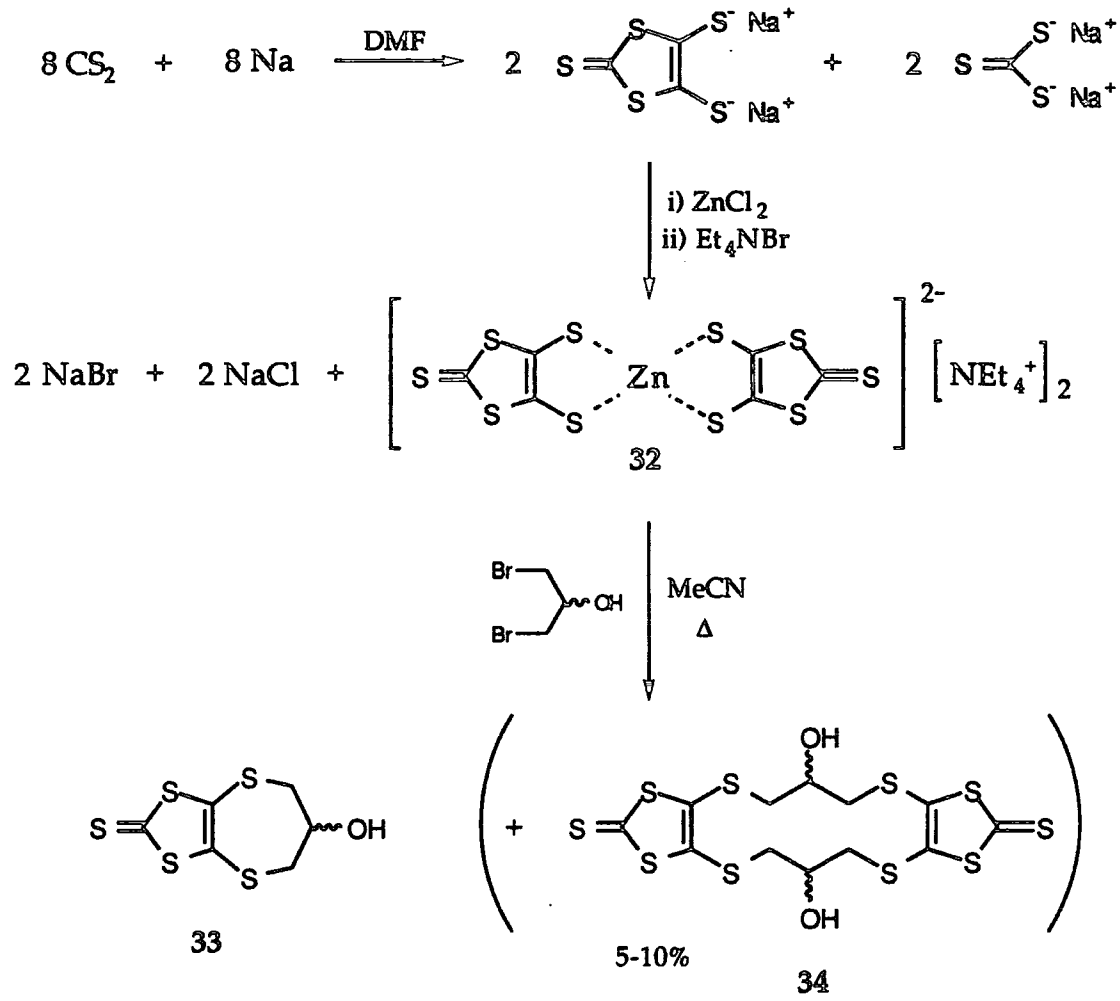
The preparation of compound 33 has been achieved by three different routes (Scheme 2.1.). The reaction of the zincate salt 32 (prepared by reaction of carbon disulphide with sodium in the presence of DMF[59]) with 1,3-dibromopropan-2-ol in refluxing acetonitrile affords compound 33 in 66% yield. A second highly insoluble product was obtained from this reaction. Mass spectrometry gave an EI molecular ion peak at 508 (M^+) tentatively identifying it as the macrocyclic compound 34. This was formed in 5-10% yield, its formation arising from the template effect of the zinc metal ion, to which two dithiolate units are co-ordinated.

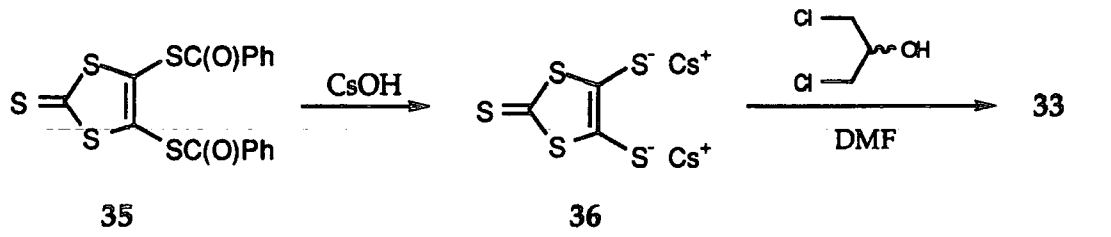
Alternatively, caesium salt 36 [prepared from di(benzoylthio) derivative 35[60]] reacted with 1,3-dichloropropan-2-ol to afford compound 33 in 60% yield. Since the templating effect of the zinc metal ion is now removed, the formation of macrocycle 34 is not observed.

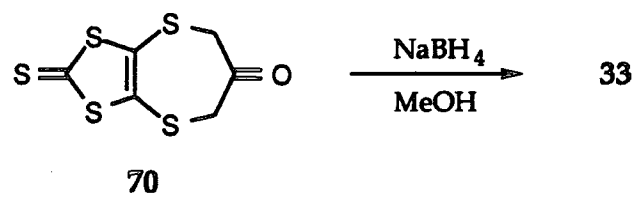
While this work was in progress, an alternative route to compound 33 (by reduction of compound 70) was reported by Russian workers[61]. We have also used this route and found it to be appropriate for the preparation of large-scale batches (*ca.* 10g) of alcohol 33.

2.2.2 X-Ray crystal structure of compound 33

The structure of compound 33 has been examined by single crystal X-ray analysis. Compound 33 was studied to establish the solid state conformation of the molecule and the preferred configuration of the hydroxy group. The molecular structure of compound 33 is shown in Figure 2.1. Atoms S(3), S(4) and S(7) are in the same plane as the 1,3-dithiole ring. Bond angles at S(3) and S(4) are 100.5° and 101.9°, respectively. The fragment O(2)-C(4)-C(5)-S(4) is exclusively in the *s-trans* configuration. The only intermolecular contact that is significantly shorter than the sum of the van der Waals radii is the S(1)---S(1) distance of 3.335Å. The shortest intermolecular sulphur-oxygen distances are S(7)---O(2) 3.364Å and S(2)---O(2) 3.405Å, which are indicative of very weak interactions between these atoms.







Scheme 2.1. - Synthetic routes to 4,5-[2-(hydroxy)propylene-1,3-dithio]-1,3-dithiole-2-thione.

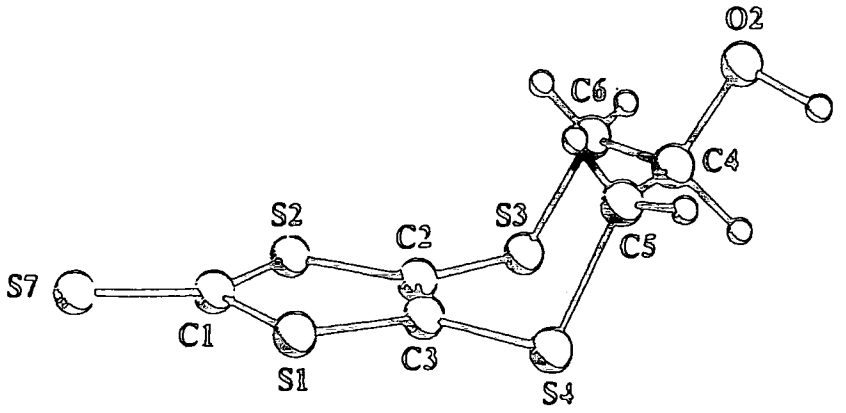
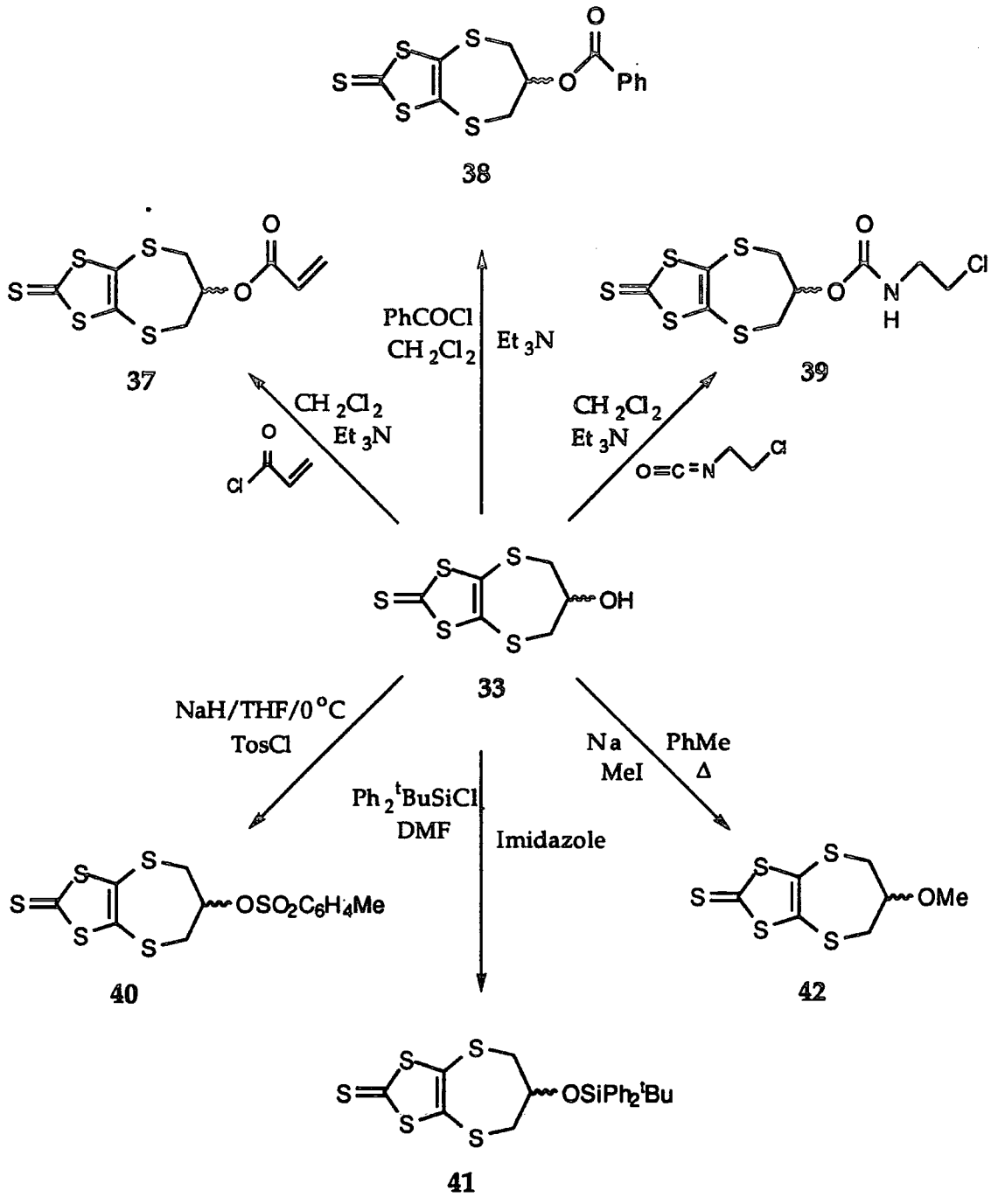


Figure 2.1. - X-Ray molecular structure of compound 33 and crystallographic numbering scheme.

2.2.3 Reactions of compound 33

To explore the versatility of alcohol **33** as a potential reactive 'handle' in further synthesis (in particular, once incorporated into a TTF framework), the hydroxy group has been reacted with a variety of electrophiles, affording the functionalised derivatives **37** - **42**, as shown in Scheme 2.2.

Reaction of alcohol **33** with acryloyl or benzoyl chloride at room temperature, in the presence of triethylamine, affords the acrylate and benzoyl ester derivatives **37** and **38**, respectively, in *ca.* 75% yield. 2-Chloroethylisocyanate reacted with alcohol **33**, under similar conditions, to give urethane derivative **39** in 56% yield. The tosylate derivative **40** was obtained in 74% yield by reaction of alcohol **33** with tosyl chloride at 0°C, in the presence of sodium hydride. Finally, silyl derivative **41** was formed in 98% yield by reaction of alcohol **33** with *tert*-butyl-diphenylchlorosilane in DMF in the presence of imidazole.

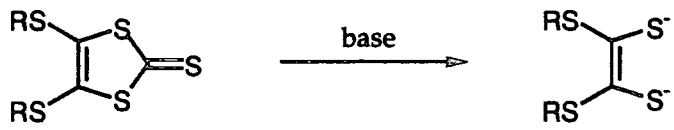


Scheme 2.2. - Reactions of 4,5-[2-(hydroxy)propylene-1,3-dithio]-1,3-dithiole-2-thione.

These transformations demonstrate the facile reactivity of the secondary alcohol group with acid and sulphonyl chlorides, isocyanates and chlorosilanes. However, despite this reactivity with these functional groups, exhaustive attempts to generate and subsequently trap the corresponding alkoxide, largely failed. Treatment of alcohol **33** with a variety of bases,

followed by the addition of alkyl halide gave none of the desired product. Similar results were observed on treatment of 33 with base in the presence of the alkyl halide, in an attempt to trap the alkoxide *in situ*. In each case, TLC showed small traces of the starting alcohol, the major product remaining on the base line.

This observation is best explained by ring opening of the 1,3-dithiole-2-thione unit, which is known to occur under basic conditions[36], generating the corresponding dithiolate species (Scheme 2.3.). In this case, the reagent base or small traces of initially formed alkoxide could be responsible for the ring opening reaction.



Scheme 2.3. - Ring opening of 1,3-dithioles under basic conditions.

The methyl ether derivative 42, however, could be obtained, though in only 5% yield, by reaction of alcohol 33 with sodium metal in toluene in the presence of iodomethane.

Attempts to displace the tosylate group of 40 with nucleophiles were unsuccessful. For example, both sodium bromide and sodium azide failed to react with tosylate 40. In both cases the starting material was recovered. Inspection of CPK molecular models of 40 suggests that the lack of reactivity towards substitution is because the tosylate group of 40 is sterically very hindered to displacement, due to the folded conformation of the seven-membered ring (*cf.* the X-ray crystal structures of compounds 33 and 82).

2.2.4 TTF synthesis using silyl-protected 1,3-dithiole half-unit 41

The attempted self-coupling of both acrylate and urethane derivatives 37 and 39, respectively, using neat triethylphosphite to give directly the corresponding symmetrical bis-functionalised TTF derivatives was

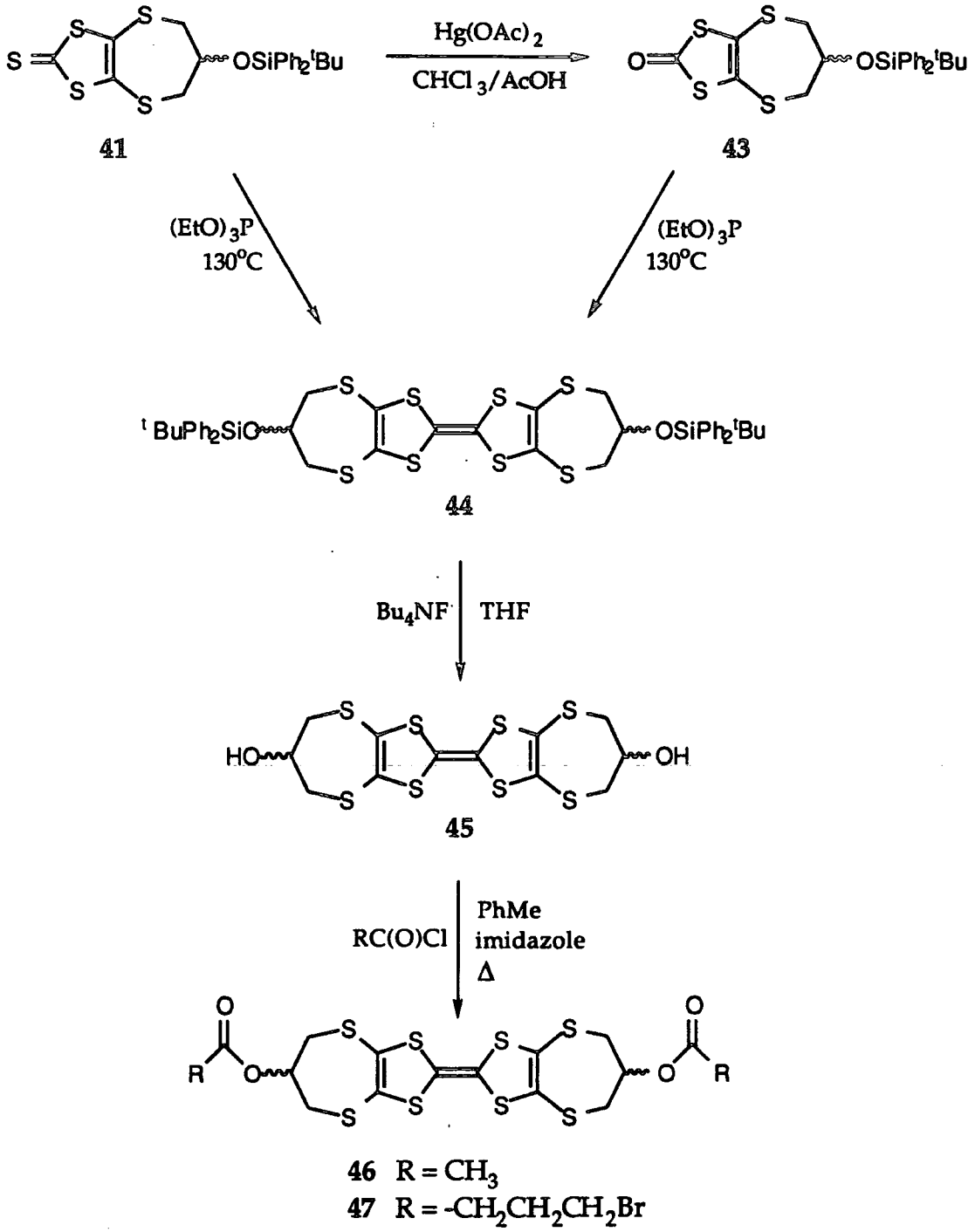
unsuccessful; no TTF derivative was detected. Likewise, although alcohol 33 self-coupled to give bis[2-(hydroxy)propylene-1,3-dithio]TTF 45, the yield was very low (< 5%). This illustrates the incompatibility of the acrylate, urethane and hydroxy functional groups with the triethylphosphite coupling reagent and conditions. TTF derivative 45 can be more efficiently synthesised via a two-step procedure by self-coupling the silyl derivative 41, to yield 44, followed by removal of the *tert*-butyl-diphenylsilyl (*tert*-BDPSi) protecting group with fluoride ion (Scheme 2.4.).

In our experience, coupling of 1,3-dithiole-2-thiones normally proceeds in low yield compared to the corresponding 1,3-dithiole-2-ones. Conversion of the trithiocarbonate functionality of 41 to the corresponding dithiocarbonate 43 was achieved in quantitative yield using mercuric acetate in chloroform/acetic acid. It is noteworthy that the *tert*-BDPSi protecting group withstands both these acidic and phosphite coupling conditions, which probably would have caused cleavage of silyl ethers with less bulky alkyl substituents. The self-coupling of ketone 43, under the same conditions, afforded 44 in 50% yield, compared to a 33% yield for the corresponding thione 41.

Diol 45 is only sparingly soluble in most common organic solvents. Nonetheless, both hydroxy groups of 45 could be functionalised to yield compounds 46 and 47 in *ca.* 70% yield, by reaction with acetyl and 4-bromobutyryl chloride, respectively, in refluxing toluene containing imidazole.

Due to the fact that the C-2 carbon atom in the propylene-dithio bridge of compounds 41 and 43 is prochiral, compound 44 is formed as a mixture of diastereomers. Consequently, the derived products 45-47 are also obtained as a diastereomeric mixture. Additionally, two conformational isomers of compounds 44-47 can exist. The presence of isomers is confirmed by the ^{1}H NMR data. The hydroxy protons of diol 45 appear as two separate doublets in the 250 MHz ^{1}H NMR spectrum, most likely arising from the

two conformational isomers present. Furthermore, the 500 MHz ^{1}H NMR spectrum of compound 44 shows two sets of complex multiplet systems, at very similar chemical shift values, from the methine protons. It was not considered necessary at this stage of our studies on these compounds to attempt to separate the diastereomers, which appear as one product on TLC.



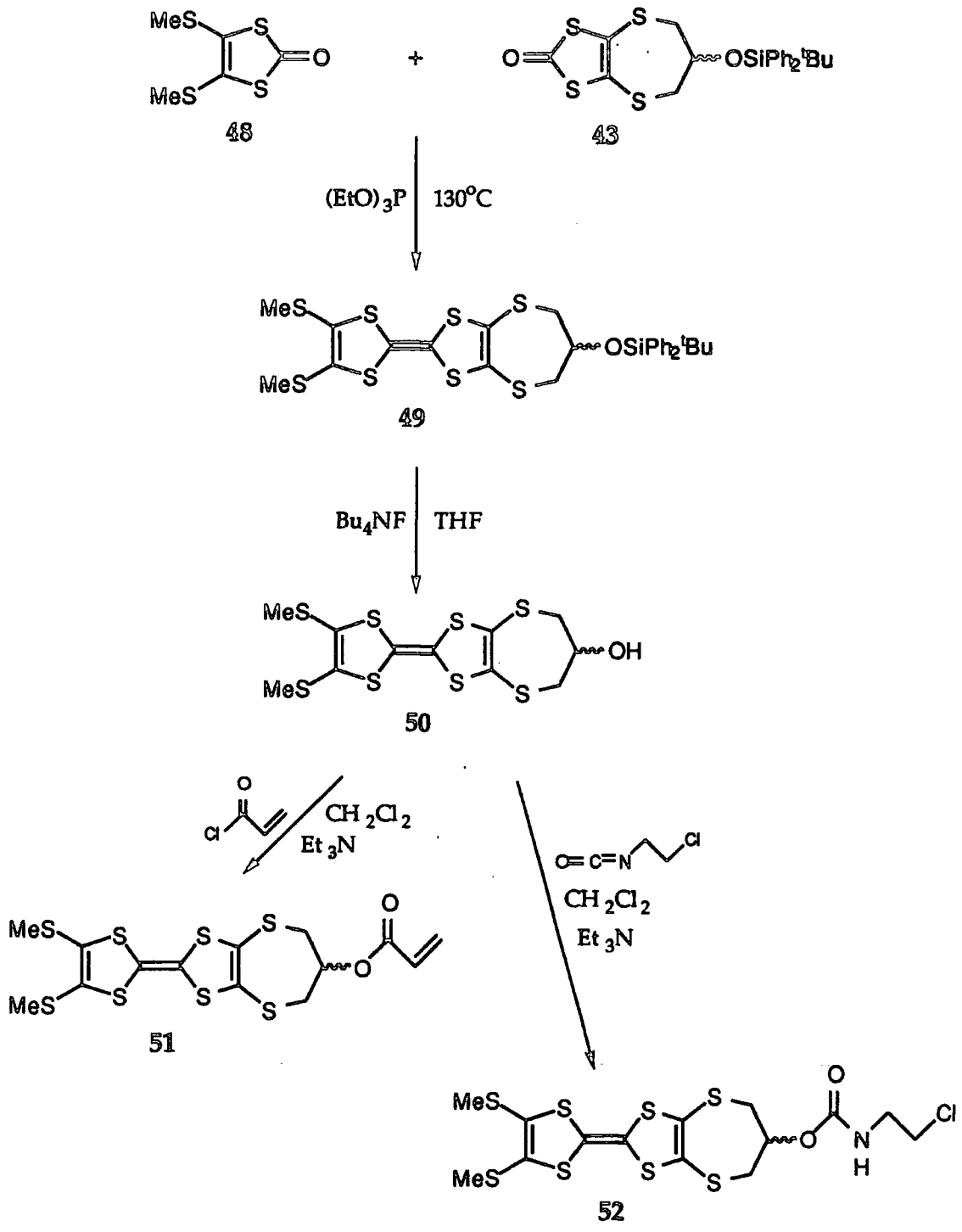
Scheme 2.4. - Synthesis of symmetrically functionalised TTF derivatives.

Cross-coupling of ketone 43 with 4,5-dimethylthio-1,3-dithiole-2-one 48 in the presence of triethylphosphite yielded the unsymmetrical TTF system 49 in *ca.* 30% yield (Scheme 2.5.). This compound could not be completely separated from self-coupled products, even after extensive chromatography. Deprotection of derivative 49 afforded the TTF-alcohol 50 in *ca.* 67% yield, which could be obtained analytically pure.

Functionalisation of the alcohol group of TTF derivative 50 can be achieved under the same conditions used to prepare the corresponding 1,3-dithiole half-units. Hence the TTF acrylate 51 and urethane 52 were obtained by reaction of alcohol 50 with acryloyl chloride (31% yield) and 2-chloroethylisocyanate (80% yield), respectively, in the presence of triethylamine.

2.2.5 TTF systems containing the 4,5-[2-(hydroxymethyl)propylene-1,3-dithiol unit

The lack of reactivity of the tosylate group of compound 40 towards nucleophilic substitution severely limits the use of this compound as a potential starting material for further functionalisation and subsequent incorporation into more complex TTF systems. As explained earlier, this lack of reactivity is probably due to the folded conformation of the seven-membered ring making the tosylate group sterically very hindered to displacement. It was considered that the introduction of a methylene spacer unit between the hydroxy group and the seven-membered ring could overcome this problem, by removal of the reactive site from the steric hindrance of the ring. The formation of a primary rather than a secondary functional group should also increase the general reactivity of such derivatives.



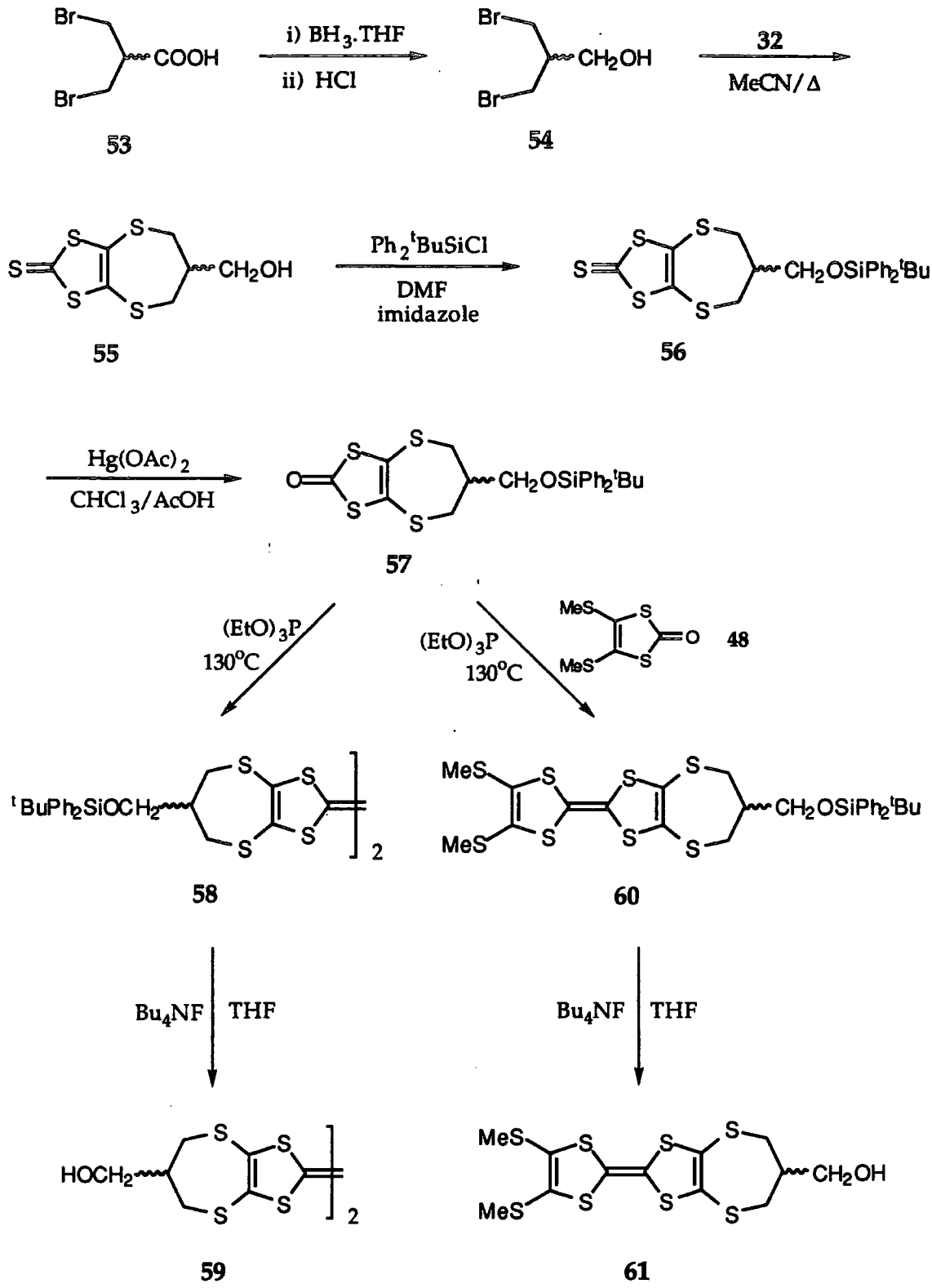
Scheme 2.5. - Synthesis of unsymmetrically functionalised TTF derivatives.

The synthesis of symmetrical and unsymmetrical TTF derivatives containing the 4,5-[2-(hydroxymethyl)propylene-1,3-dithio] unit is outlined in Scheme 2.6. The starting 3-bromo-2-(bromomethyl)propan-1-ol 54 was prepared by borane reduction of commercially available 3-bromo-2-

(bromomethyl)propanoic acid 53 in *ca.* 96% yield[62]. The sequence of reactions leading to the symmetrical dihydroxy- and unsymmetrical monohydroxy-TTF derivatives 59 and 61, respectively, is analogues to those for the 4,5-[2-(hydroxy)propylene-1,3-dithio] systems (Schemes 2.4. and 2.5.). Reaction of 3-bromo-2-(bromomethyl)propan-1-ol 54 with zincate salt 32 in refluxing acetonitrile afforded 4,5-[2-(hydroxymethyl)propylene-1,3-dithio]-1,3-dithiole-2-thione 55 in 79% yield. Protection of the hydroxy group as its *tert*-butyl-diphenylsilyl ether was achieved in 83% yield using *tert*-butyl-diphenyl-chlorosilane in DMF in the presence of imidazole to give thione 56. Oxidation of the trithiocarbonate functionality of 56 to the corresponding dithiocarbonate 57 using mercuric acetate in chloroform/acetic acid proceeded in 97% yield.

Self-coupling of 57 in the presence of triethylphosphite at 130°C gave the disilyl derivative 58 in 55% yield, which, on removal of the *tert*-BDPSi protecting groups with fluoride ion afforded, in 57% yield, the symmetrical dihydroxy-TTF derivative 59. As with disilyl derivative 44, compound 58 is formed as a mixture of diastereomers resulting from the prochiral carbon atom at C-2 in the propylene-dithio bridge. Additionally, two conformational isomers can exist. The derived product 59 consequently also exists as a mixture of both diastereomeric and conformational isomers.

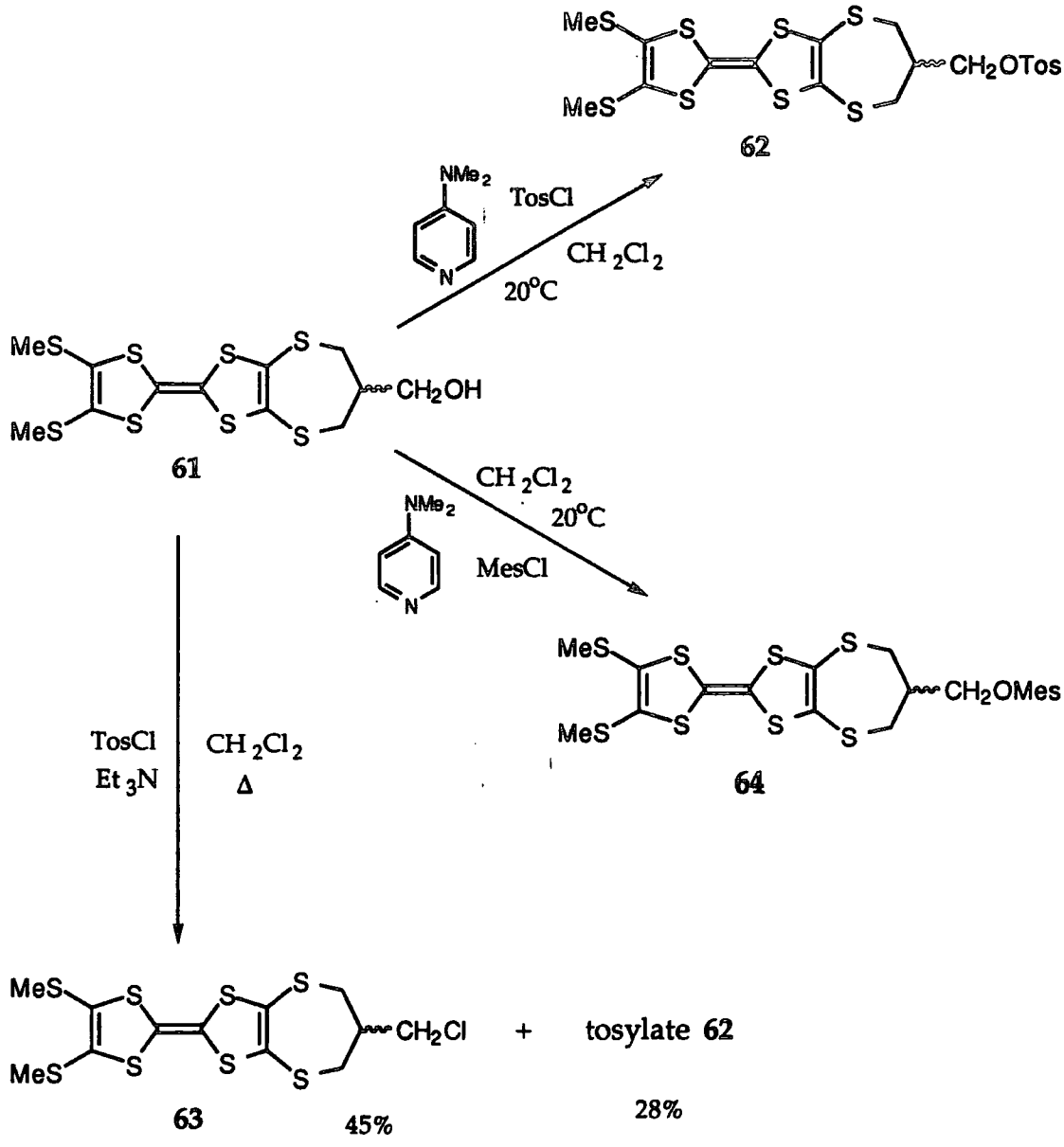
Cross-coupling of 57 with 4,5-dimethylthio-1,3-dithiole-2-one 48 under the same conditions, gave compound **60** which, on deprotection, afforded the unsymmetrical hydroxy-TTF derivative **61** in 34% overall yield for the two steps.



Scheme 2.6. - Synthesis of symmetrical and unsymmetrical TTF derivatives containing the 4,5-[2-(hydroxymethyl)propylene-1,3-dithio] unit.

2.2.6 Reactions of compound 61 and its derivatives

To investigate the effect of the incorporation of the methylene spacer unit on the reactivity of derivatives towards nucleophilic substitution, the corresponding *p*-toluene- and methyl-sulphonate esters of compound **61** were prepared (Scheme 2.7.).



Scheme 2.7. - Reactions of compound 61.

Reaction of alcohol **61** with *p*-toluenesulphonyl chloride at 20°C in the presence of 4-dimethylaminopyridine (DMAP), afforded the required

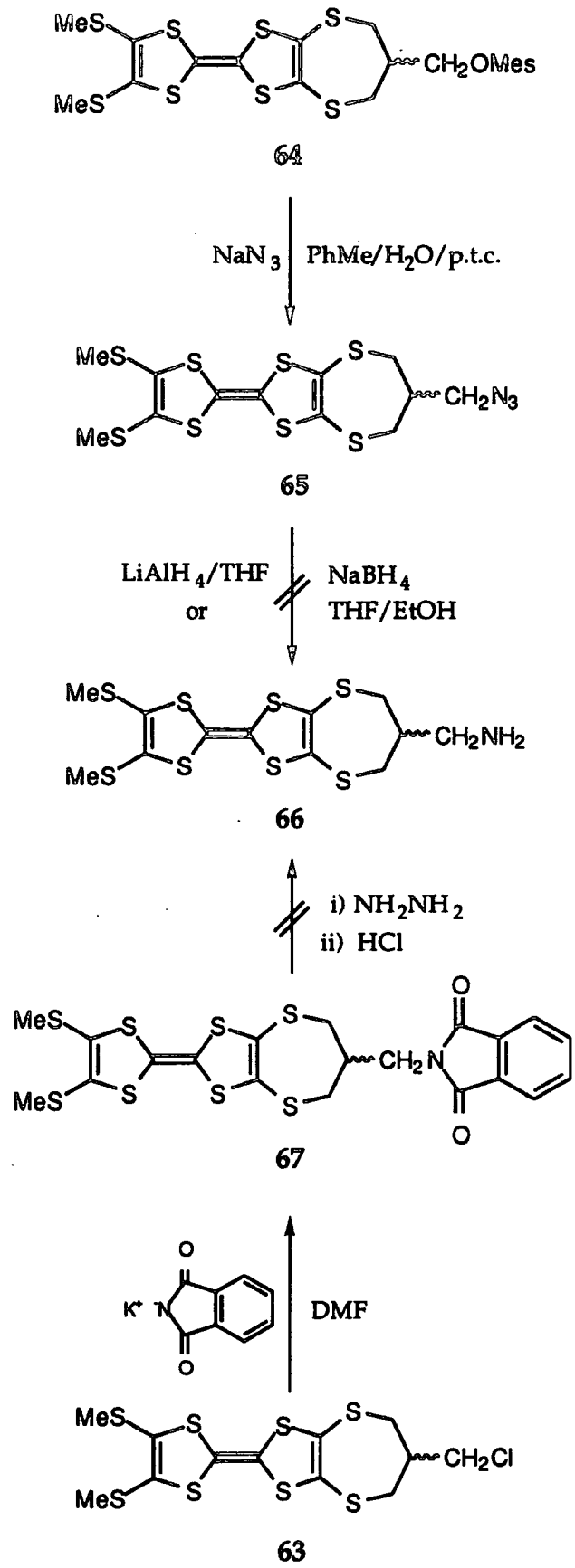
tosylate **62** in 55% yield. In an attempt to increase the yield of this reaction, triethylamine was used as base and the reaction refluxed in dichloromethane for 48 hours. Investigation of the reaction mixture after this time showed that the desired tosylate was present, but in only 28% yield, the major reaction product being the corresponding chloride derivative **63**, formed in 45% yield. The observation of this product can be explained by nucleophilic substitution by chloride ion on the initially formed *p*-toluenesulphonate ester. The mesylate derivative **64** was prepared, in 76% yield, by reaction of alcohol **61** with methanesulphonyl chloride, at 20°C, in the presence of DMAP.

The formation of chloride **63** from tosylate **62** shows the reactivity of the -CH_2OTos group in compound **62** towards nucleophilic substitution. Thus, the introduction of the methylene spacer group has overcome the lack of reactivity towards displacement observed earlier for compound **40**.

2.2.7 Attempts to synthesise a TTF primary amine

There are very few synthetic routes to nitrogen substituted tetrathiafulvalenes[33]. It was therefore considered an attractive target to convert the hydroxy group of alcohol **61** to a primary amine functionality. This amine should lend itself to incorporation into TTF systems containing, in particular, the amide link. Three different methodologies were tried in an attempt to synthesise such an amine system.

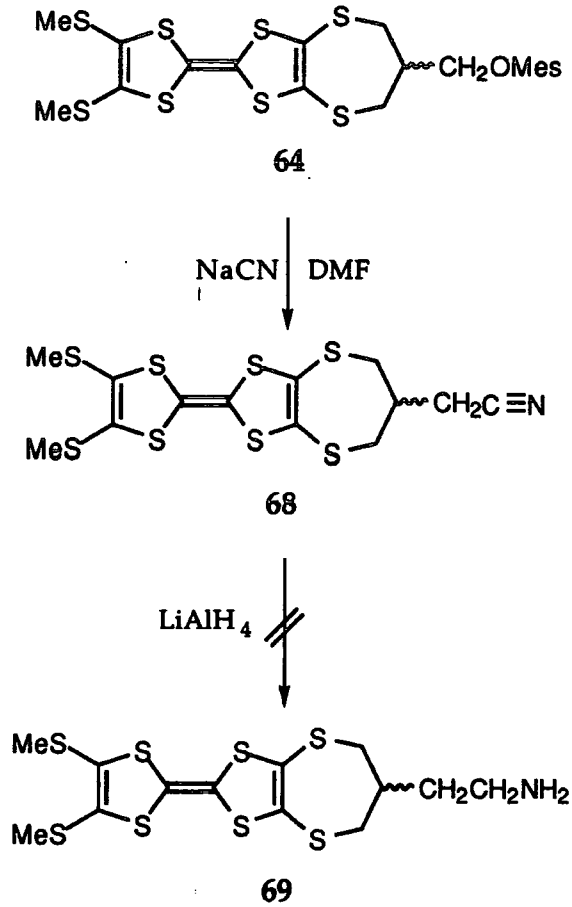
Reaction of mesylate **64** with sodium azide in toluene/water in the presence of a phase transfer catalyst afforded the azide derivative **65** (Scheme 2.8.). However, treatment with either lithium aluminium hydride or sodium borohydride failed to reduce the azide to the amine group **66**; no TTF derivative could be isolated from the reaction mixture.



Scheme 2.8. - Attempts to synthesise an amine substituted tetrathiafulvalene.

In an attempt to perform a Gabriel synthesis, the phthalimide derivative **67** was prepared, in 40% yield, by reaction of chloride **63** with potassium phthalimide. However, treatment with hydrazine followed by acidification failed to yield the desired amine **66**. As before, no TTF derivative could be isolated.

Finally, although reaction of mesylate **64** with sodium cyanide afforded the nitrile derivative **68** in 66% yield (Scheme 2.9.), attempts to reduce the cyano functionality to the corresponding amine **69** with lithium aluminium hydride, were unsuccessful. Therefore, although different approaches have been tried, it has not been possible to prepare a TTF primary amine by functionalisation of the hydroxy group of alcohol **61**.

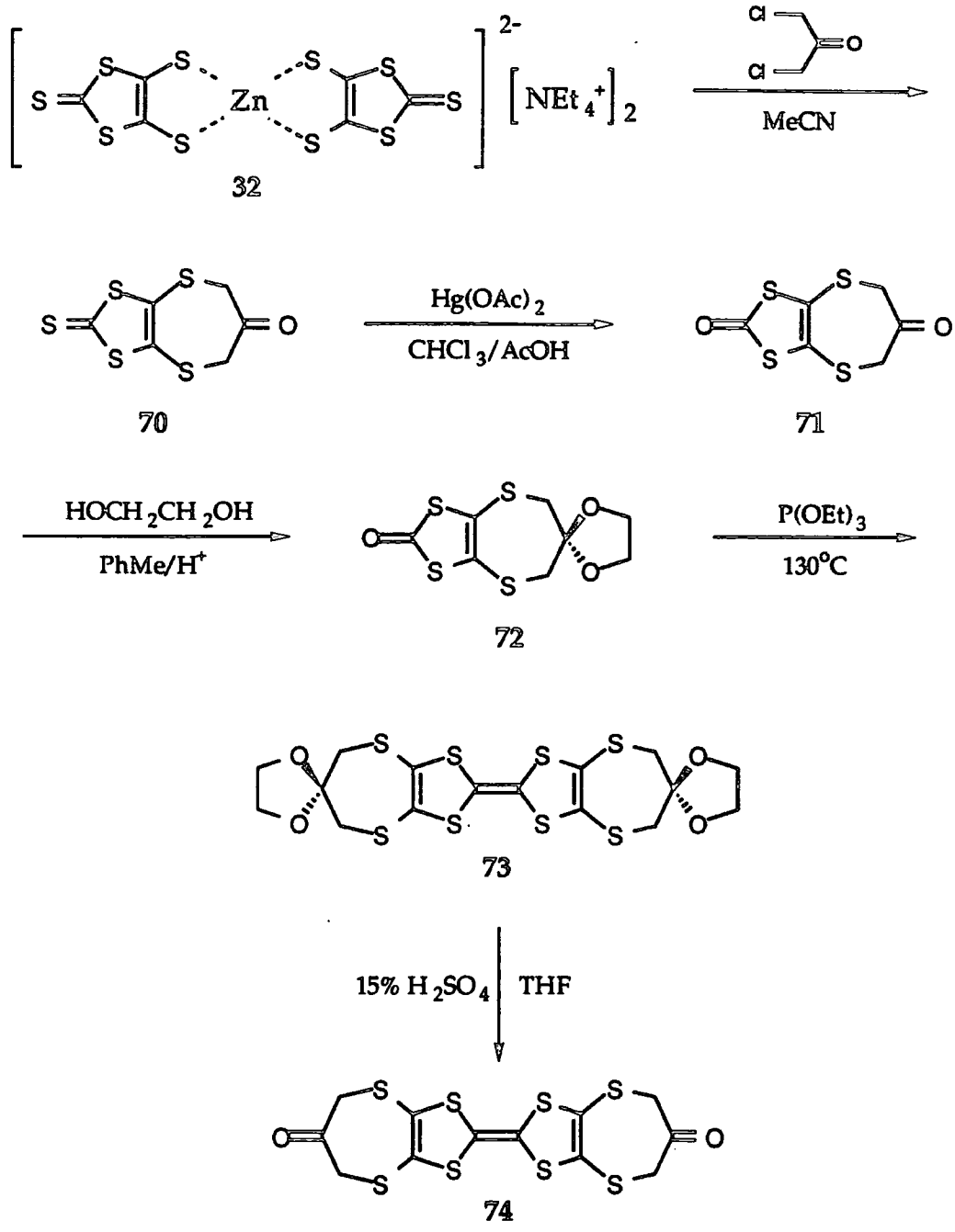


Scheme 2.9. - Attempted amine synthesis via hydride reduction of a nitrile functionality.

2.2.8 TTF synthesis using ketal-protected 1,3-dithiole half-unit 72

The reactions of 1,3-dithiole derivative 70 have also been explored with the aim of obtaining propylenedithio-TTF derivatives with exocyclic ketone functionality. The zincate salt 32 reacted with 1,3-dichloropropan-2-one to yield keto-thione derivative 70 in 76% yield (Scheme 2.10.). Conversion into the diketone 71 was achieved in quantitative yield by mercuric acetate oxidation. Attempts to self-couple either thione 70 or ketone 71, using triethylphosphite, gave complex product mixtures from which no TTF derivative could be isolated. This result again illustrates the incompatibility of certain functional groups (in this case, the ketone group) towards the phosphite coupling reagent and conditions.

However, the exocyclic ketone group of compound 71 could be selectively protected, in 84% yield, as the ketal 72 by reaction with ethylene glycol in refluxing toluene in the presence of an acid catalyst. Self-coupling of 72 under the same conditions, proceeded smoothly to afford the symmetrical TTF derivative 73 in 66% yield. Removal of the ketal protecting group of 73 required remarkably harsh conditions. Compound 73 was recovered unchanged from refluxing in a 10% solution of hydrochloric acid in THF. However, upon refluxing in a 15% solution of sulphuric acid in THF, the symmetrical diketone-TTF derivative 74 was obtained in 87% yield (an overall yield of 37% from zincate salt 32). It is noteworthy that the C_6S_8 core of the TTF unit is able to withstand these strongly acidic conditions. This is a result of the attachment of sulphur atoms to the periphery of TTF increasing its resistance to chemical oxidation under such conditions.

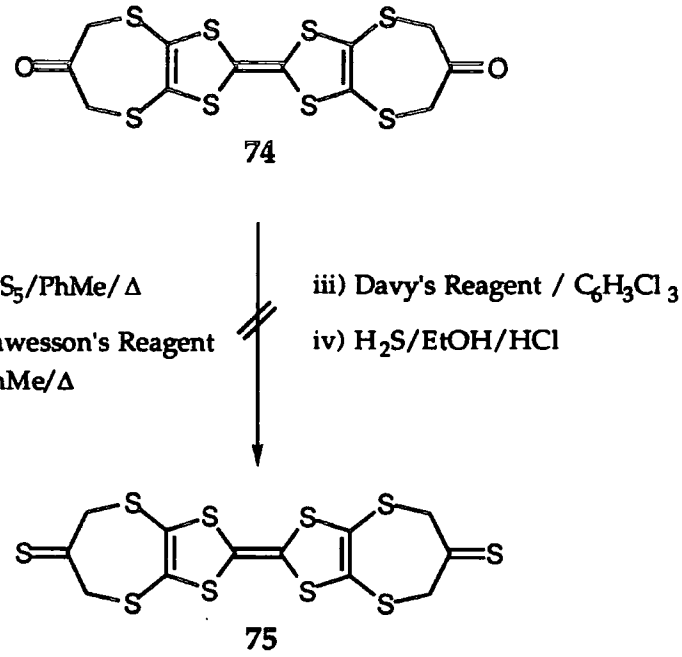


32 70 71 72 73 74

Scheme 2.10. - Synthesis of a symmetrical TTF derivative containing exocyclic ketone functionality.

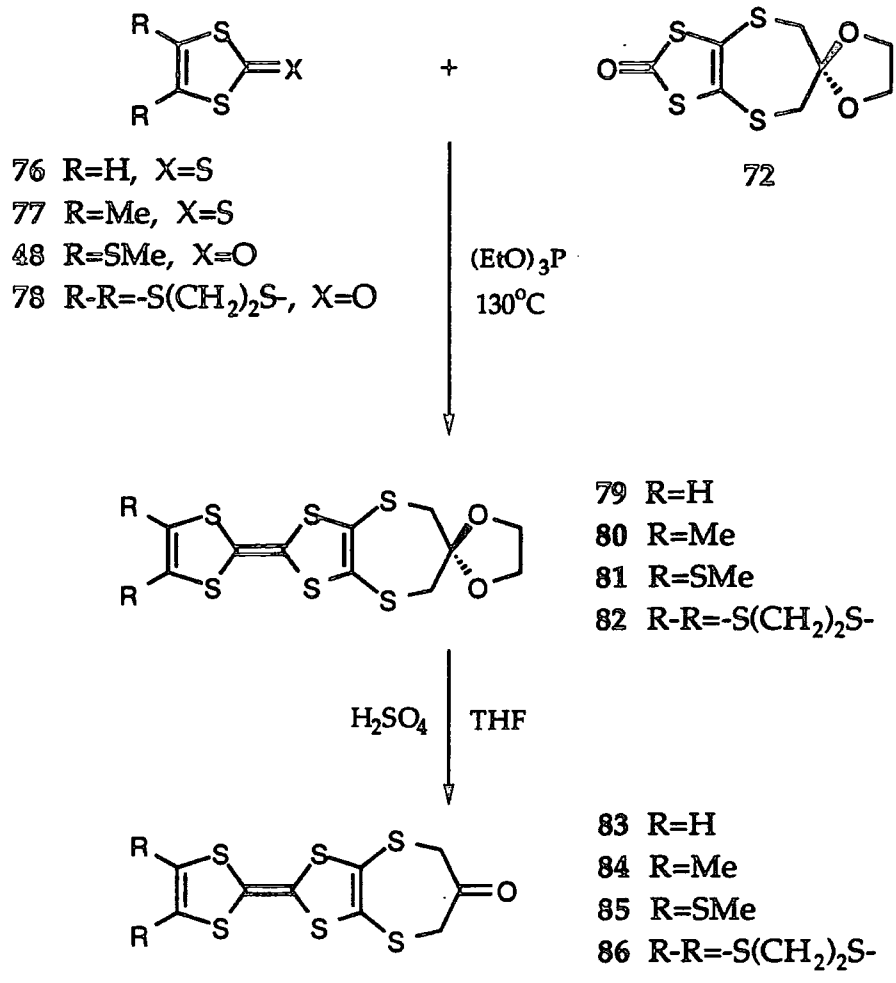
Attempts were made to convert the carbonyl groups of compound 74 to their corresponding thiocarbonyl system. However, although a variety of methods were tried (phosphorus pentasulphide, Lawesson's Reagent, Davy's Reagent and hydrogen sulphide), in each case, the unreacted starting material was recovered, with none of the desired symmetrical dithione 75

being formed (Scheme 2.11.). It is suggested that the lack of reactivity may result from the insolubility of diketone derivative **74**, which was found to be readily soluble only in DMSO and hot 1,1,2-trichloroethane.



Scheme 2.11. - Attempted thionation of symmetrical diketone-TTF derivative **74**.

The ketal-protected half-unit **72** has been cross-coupled with 1,3-dithiole-2-thione (or 2-one) derivatives **48** and **76-78** to give the unsymmetrical TTF derivatives **79-82** in 18-37% yields (Scheme 2.12.). For these reactions, the yield of the desired cross-coupled product was optimised by using the thione derivatives **76** and **77** of the unsubstituted and 4,5-dimethyl substituted half-units, respectively (3 mol equivalents), and the ketone derivatives **48** and **78** of the 4,5-alkylthio substituted half-units (1 mol equivalent). Deprotection was achieved using the same acidic conditions as for the symmetrical diketone analogue **74**, to afford the unsymmetrical ketone-substituted TTF donors **83-86** in high yield.



Scheme 2.12. - *Synthesis of unsymmetrical TTF derivatives containing exocyclic ketone functionality.*

2.2.9 X-Ray crystal structure of compound 82

The structure of compound 82 has been examined by single crystal X-ray analysis. This was determined for the following reasons: (i) relatively few structural studies have been reported on neutral, *unsymmetrical* TTF derivatives, although their potential in the construction of organic conductors is well recognised[63]; (ii) compound 82 provides a unique opportunity to study the effect of *spiro* substitution on the crystal packing of the molecules, and (iii) it was considered that possibly the oxygen atoms of the ketal group might engage in close intermolecular O---S contacts. Such interactions have been observed recently in the structure of

bis(ethylenedioxo)TTF, (BEDO-TTF) 28[55] and it would, therefore, be of interest to find other TTF systems possessing similar O---S contacts.

The molecular structure of compound 82, and the atom numbering scheme are shown in Figure 2.2. The TTF framework of compound 82 adopts a non-planar, boat-like conformation, which is typical of many neutral (symmetrical) TTF derivatives, *e.g.* BEDT-TTF 4[64]: the central tetrathioethane fragment of compound 82 is essentially planar with both 1,3-dithiole rings folded in the same direction, by 15° along the S(1)---S(2) axis, and by 20° along the S(5)---S(6) axis. The conformation of the seven-membered ring is essentially identical to that of compound 33, and the six-membered ring of compound 82 is a similar shape to that of BEDT-TTF 4[64], with bond angles C(9)-S(7)-C(11) and C(8)-S(8)-C(10) of 102.3° and 97.5°, respectively. The bond angles at the *spiro* centre C(4) are in the range 107-115°, the angle C(5)-C(4)-C(6), within the seven-membered ring, showing the largest deviation from tetrahedral geometry.

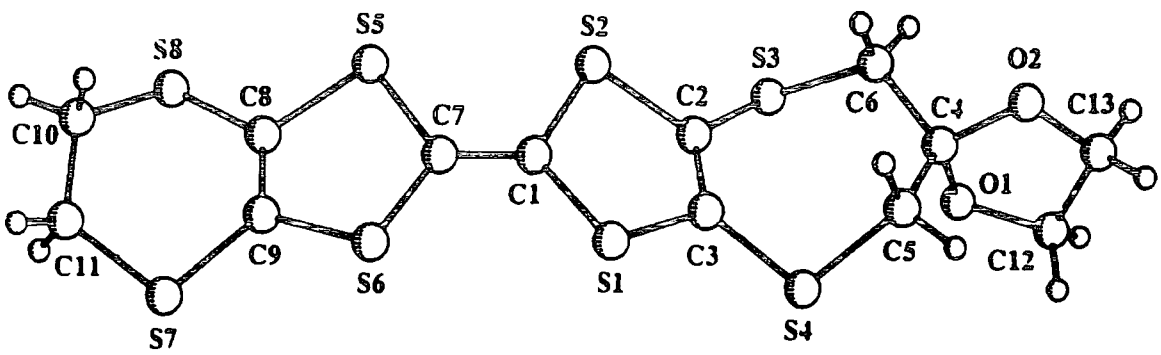


Figure 2.2. - X-Ray molecular structure of compound 82 and crystallographic numbering scheme.

The packing of the molecules of compound 82 within the crystal is shown in Figure 2.3. Centrosymmetrically related pairs of molecules are arranged in columns along the *c* axis of the crystal, with the axes of the TTF framework at 45° and 135°, respectively, in adjacent columns. This results in

the arrangement of molecules along the *b* direction forming a 'herring-bone'-like packing. The closest intermolecular contacts involving sulphur and oxygen are as follows: S(1)---S(1) 3.498Å, S(2)---S(4) 3.475Å, S(3)---O(1) 3.390Å and O(1)---O(1) 3.31Å, none of which is significantly shorter than the sum of the van der Waals radii for the two atoms (1.80Å for sulphur and 1.40Å for oxygen).

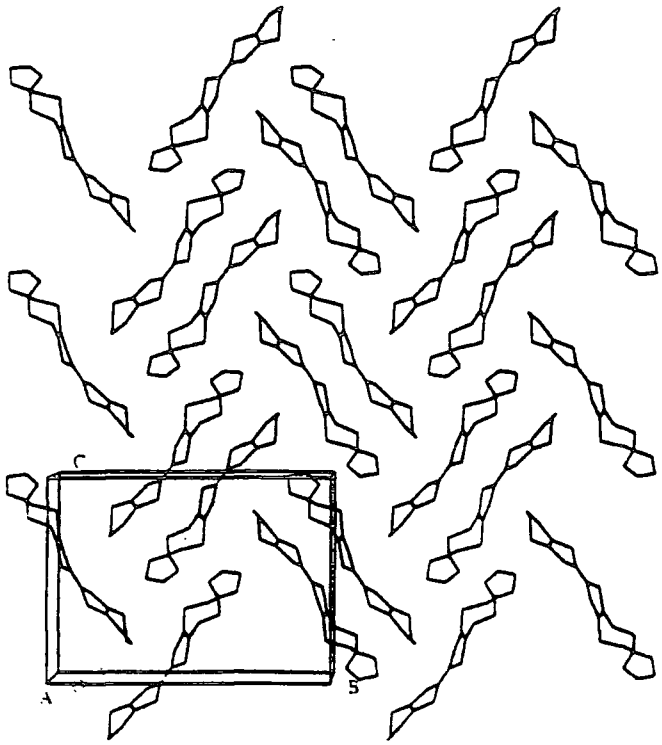
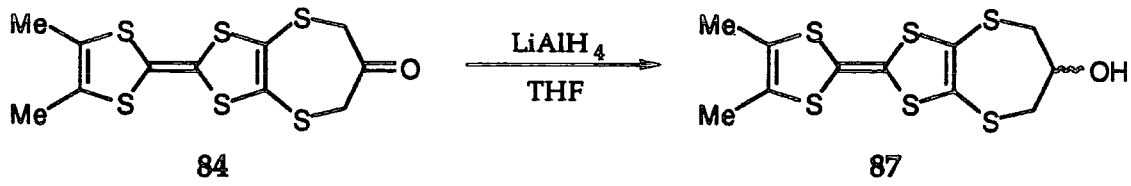


Figure 2.3. - X-Ray crystal structure of compound 82 projected along the a axis.

2.2.10 Further synthesis of unsymmetrical TTF derivatives

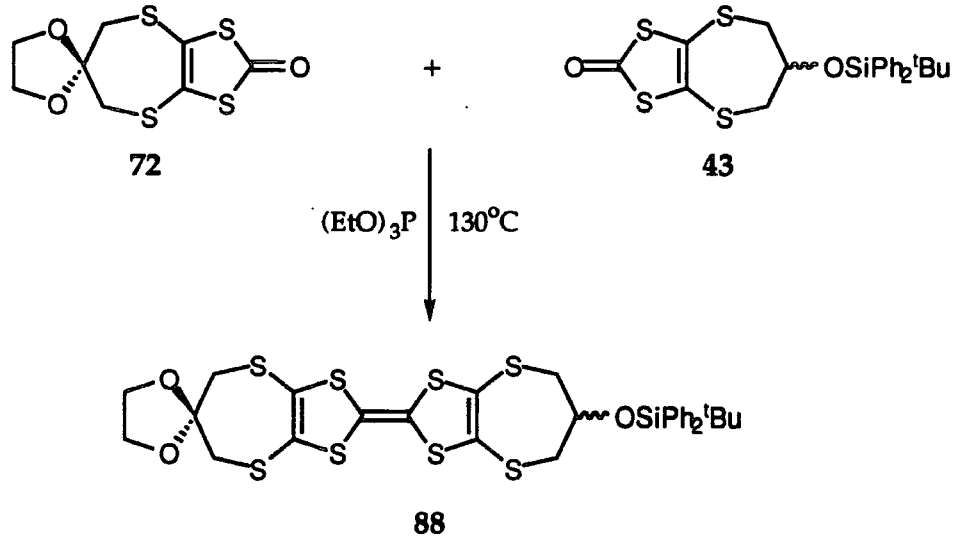
The ketone group of compound **84** was cleanly reduced, in 90% yield, with lithium aluminium hydride to yield the unsymmetrical TTF alcohol **87** (Scheme 2.13.). This route, via the ketal protected ketone functionality, therefore provides an alternative route to mono-alcohol substituted TTF systems. This pathway therefore complements the previously described route (Scheme 2.5.), in which a silyl ether derivative was employed as a protecting group.



84 87

Scheme 2.13. - Synthesis of a mono-alcohol TTF system via hydride reduction of a ketone group.

Cross-coupling of the silyl-protected half-unit **43** with the ketal-protected half-unit **72** proceeded, in 37% yield, to afford the TTF derivative **88** (Scheme 2.14.). This unsymmetrical TTF is a particularly attractive system, since it should be possible to selectively remove the two different hydroxy protecting groups, thereby providing an efficient method for unsymmetrical functionalisation of TTF-diol **45**.



72 43 88

Scheme 2.14. - Synthesis of a 'TTF-diol' with two different hydroxy protecting groups.

2.2.11 Electrochemical redox properties of the new TTF derivatives

The solution redox chemistry of the new TTF derivatives **45**, **50-52**, **59**, **61**, **74** and **83-86** has been studied by cyclic voltammetry. Each donor shows two, single-electron, reversible redox waves at the expected potentials for TTF derivatives with a C_6S_6 or C_6S_8 core[65] (Table 2.1.). These data are a

reliable confirmation that the TTF system has remained intact during all the synthetic transformations accomplished at the periphery of the molecule. The oxidation potential of a TTF derivative is known to be raised by the attachment of alkylthio substituents due to destabilisation of the radical-cation and dication species by the electron-withdrawing effect of the sulphur atoms. Conversely, the attachment of alkyl groups lowers the oxidation potential of a TTF derivative through inductive stabilisation of the radical-cation and dication species by the electron-donating effect of the substituents. Thus, within the series of donors with exocyclic ketone functionality, compound **84**, which carries two methyl substituents, is the most easily oxidised. The oxidation potentials are not affected by the presence of the substituents on the propylenedithio bridge(s), which are electronically isolated from the TTF core in all the new derivatives.

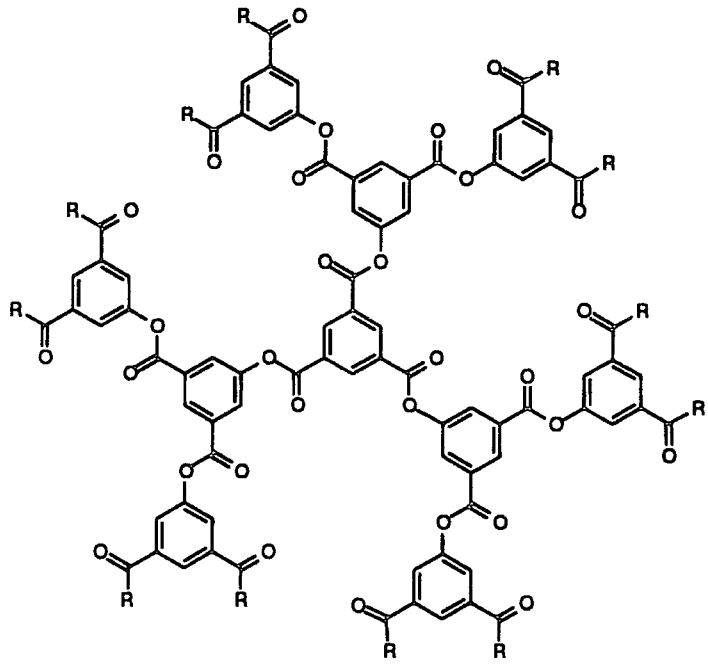
Donor	Solvent	$E_1^{1/2}$/V	$E_2^{1/2}$/V
45	CH_2Cl_2	0.66	1.03
50	CH_2Cl_2	0.56	0.92
51	CH_2Cl_2	0.57	0.93
52	CH_2Cl_2	0.56	0.92
59	CH_2Cl_2	0.51	0.92
61	CH_2Cl_2	0.55	0.92
74	$CHCl_2CH_2Cl$	0.68	1.04
83	$CHCl_2CH_2Cl$	0.60	0.91
84	$CHCl_2CH_2Cl$	0.51	0.96
85	$CHCl_2CH_2Cl$	0.64	0.98
86	$CHCl_2CH_2Cl$	0.64	1.02

Table 2.1. *- Cyclic voltammetric data for TTF derivatives. Data were obtained at 20°C versus Ag/AgCl, under argon using a platinum button electrode and a platinum wire counter electrode, ca. 5 x 10^{-4} M compound, 0.1 M tetrabutylammonium hexafluorophosphate, scan rate 100 $mVsec^{-1}$, using a BAS 100 Electrochemical Analyser.*

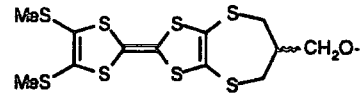
2.3 CONCLUSION

A range of functionalised symmetrical and unsymmetrical tetrathiafulvalene derivatives containing substituted propylenedithio units fused to the TTF framework has been prepared. As well as potential components of charge-transfer and radical-cation salts within the field of 'organic-metals', compounds **45, 50, 59, 61** and **87** bearing hydroxy functionality, can act as building blocks for incorporation into new classes of redox-active materials. Until recently, the construction of such materials has been largely neglected, due to the lack of suitably functionalised TTF derivatives. Work in our own laboratory and by T. Jørgensen at the University of Odense, Denmark, has already led to a number of exciting results.

Derivatives of diol **45** have been incorporated into macrocyclic and supramolecular systems[66]. Alcohol **61** has been used as the starting monomer unit in the construction of redox-active dendritic macromolecules[67]. By a convergent synthetic strategy, the symmetrical dendrimer **89** containing 12 TTF units at the periphery of the macromolecule, has been assembled. This is the first example of a dendritic macromolecule containing TTF units and is an important advance in the supramolecular aspects of TTF chemistry. Dendrimer **89** exhibits the characteristic redox behaviour typical of the TTF system.

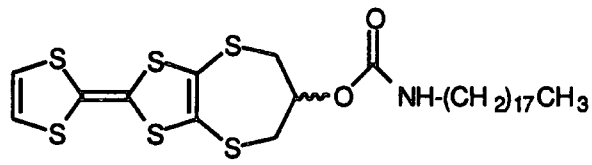


R =



89

The unsubstituted analogue of TTF-alcohol **50** has been synthesised by G. Cooke at Durham and used in the preparation of the amphiphilic derivative **90**[68], which is being evaluated in the formation of conducting Langmuir-Blodgett films. Finally, the synthesis of TTF-acrylate **51** has provided a material that could potentially act as a monomer unit in the preparation of redox-active polymeric materials.



90

In summary, the successful synthesis of suitably functionalised tetrathiafulvalene derivatives described in this chapter, should find widespread use in the construction of new, redox-active molecular

materials. The first few examples, paving the way for future derivatives, have already become apparent during the course of this work.

CHAPTER THREE

MULTIPLE TETRATHIAFULVALENES AND THE TTF-THIOLATE ANION

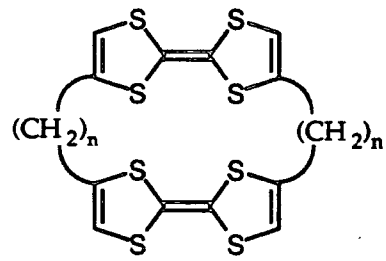
3.1 INTRODUCTION

The tetrathiafulvalene ring system has been extensively modified in recent years in the search for new donor molecules suitable for the formation of low dimensional organic metals[27]. Following the suggestion of Wudl *et al.* that molecules containing two, or more, linked donor units might yield complexes of higher than one-dimensionality[69], there has been consistent interest in the synthesis of covalently-linked dimers, and higher multiples, of TTF. As well as challenging synthetic targets, both the structural and electronic properties of such systems are of interest.

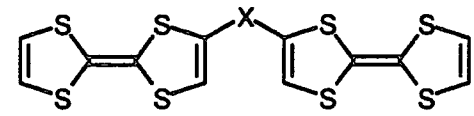
These systems have the special feature that by varying the linking group it is possible to control the relative juxtaposition of neighbouring TTF units in the crystal structure[70], and this may be a means of regulating the band filling in derived salts[71]. Also, these systems could display novel multi-stage redox behaviour with high oxidation states being accessible at relatively low potentials. The solution electrochemical properties of some covalently tethered TTFs are considerably more complex than monomeric TTFs, probably due to a combination of both inter- and intra-molecular interactions[71,72]. These materials are also of bourgeoning interest in the wider context of supramolecular chemistry, where the construction of multi-stage redox assemblies is a topical theme, *e.g.* molecular wires and switches, of relevance to the development of molecular electronic devices[73].

Within this context, TTF moieties have been joined by a variety of linking groups. The [2.2]- and [3.3]tetrathiafulvalenophanes **91** and **92**, respectively, have been reported by Ippen *et al.* [74]. Although the products are formed as a mixture of isomers, a crystal structure of **91** has been obtained, confirming the molecule has the step-like *anti*-conformation. No redox behaviour was reported for these "TTF-phanes". The synthesis of the chalcogen bridged bis-TTFs, TTF-X-TTF (X=S, Se, Te), **93-95** has been achieved[70a,f]. The X-ray crystal structure of sulphide **93** reveals a remarkable

network of very close, intermolecular S---S interactions in the solid state. The solution electrochemistry of the series of donors has been studied by cyclic voltammetry. In each case, three distinct oxidation waves are observed. The first two oxidations are electrochemically reversible and are both one-electron processes consistent with the sequential formation of mono- and di-cationic species TTF-X-TTF$^{+\cdot}$ and TTF$^{+\cdot}$-X-TTF$^{+\cdot}$, respectively. Further oxidation to the tri- and tetra-cationic species, $(TTF)_2X^{3+\cdot}$ and $(TTF)_2X^{4+}$, is observed as a single, irreversible, two-electron wave. The separation between the potentials of $E_1^{1/2}$ and $E_2^{1/2}$ is probably due to intra- (or inter-) molecular Coulombic effects.

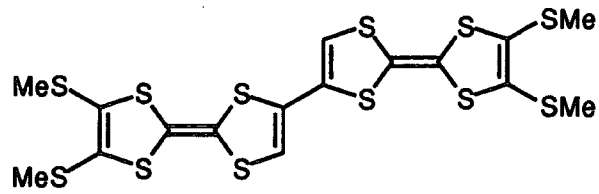


91 n=2
92 n=3

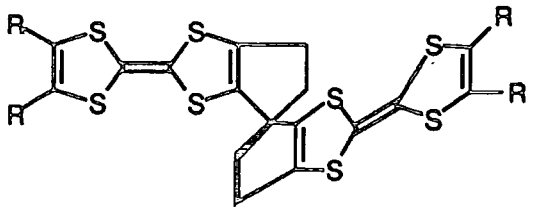


93 X=S
94 X=Se
95 X=Te

Tatemitsu *et al.* have reported[75] the synthesis of **96** and the spiro "TTF-dimers" **97** and **98**, all three donors showing reversible redox potential waves. Compound **96** exhibits three redox waves, the first and second involving one-electron transfer with the third indicating a two-electron reaction. Therefore, as with the chalcogen bridged bis-TTFs **93-95**, more complex redox behaviour is observed for electronically coupled bis-TTFs than when the TTF units are electronically isolated.

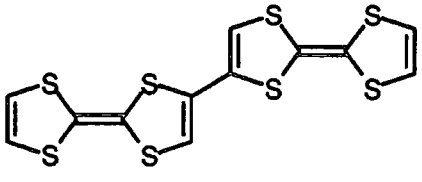


96



97 R = H
98 R-R = -SCH_2CH_2S-

Japanese workers have recently reported[34] the synthesis of the bis-TTFs **99-101**. However, although the TTF moieties are electronically linked, all three compounds exhibit only two redox waves, corresponding to two two-electron transfers. Therefore, the compounds **99-101** are oxidised by two two-electron steps.



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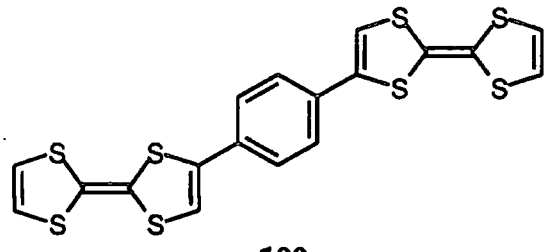

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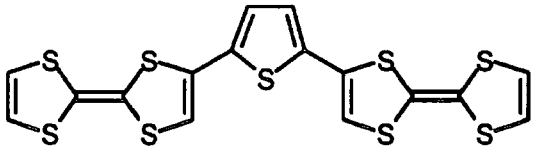
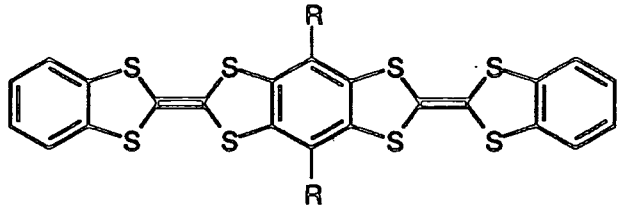
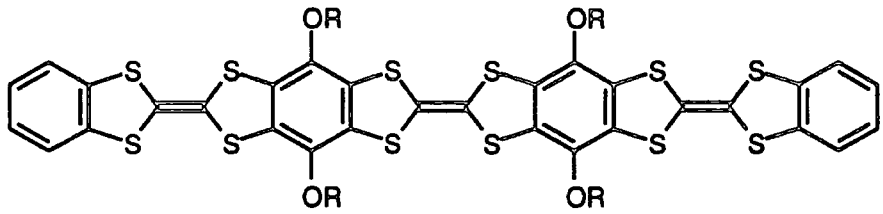


101

Müllen *et al.* have reported[76] the preparation of the conjugated bis- and tris-TTF systems **102** and **103**, respectively. The TTF 'dimer' **102** can be charged reversibly up to the tetra-cation in four separate potential steps, whereas the 'trimer' **103** can be oxidised to a hexa-cation.

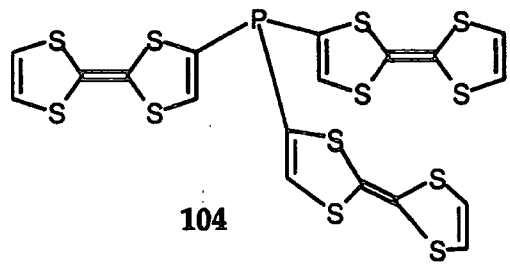


102 R = 3,5-Di-*tert*-butylbenzyloxy



103 R = *n*-hexyl

$P(TTF)_3$ **104**, a unique electron-rich phosphine has been efficiently synthesised by Fourmigué *et al.* [70c,d]. In cyclic voltammetry experiments, two reversible oxidation waves are observed, at very similar values to those for TTF, under the same experimental conditions. This demonstrates that the three TTFs do not interact strongly with each other across the phosphorus atom.

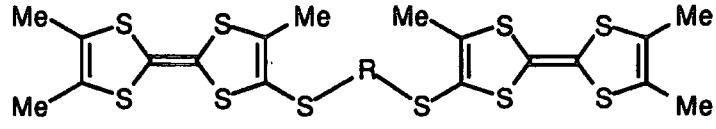


104

A series of alkylthio bridged bis-TTFs **105-111** have been prepared by M. Jørgensen *et al.*[72], in order to investigate the mutual effect on the redox potentials of the close proximity of two TTF moieties. The electrochemistry of the bis-TTF series shows some interesting effects. In most cases (**107-111**) both TTF moieties are oxidized at the same potential and only two two-electron oxidation waves are seen. However, a broadening of the first

oxidation wave is observed for compounds **107** and **109** in which the spacer groups are propylene or α,α'-*o*-xylene. In compounds **105** and **106**, where the two TTF-thio moieties are separated by a methylene or an ethylene group, respectively, three oxidation steps are seen. Also, the first oxidation potentials of compounds **105** and **106** are lower than those of **107-111** *i.e.*, the proximity of the second TTF somehow makes the removal of the first electron easier.

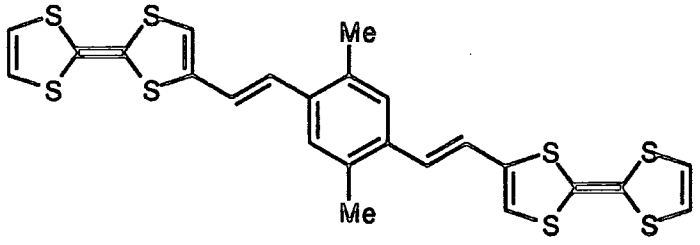
The explanation given for these findings is that for compounds **105** and **106** the two TTF moieties form a "sandwich complex" with some degree of sharing of the π-electrons, which may lower the first oxidation potential by stabilising the mono radical cation. Removal of the second electron from the molecule causes the dimer to 'unfold' because of the Coulombic repulsion between the two TTF units. The TTFs now behave like individual molecules and the third and the fourth electrons are removed at the same potential. When the spacer becomes longer, the distance between the TTFs will increase together with the number of degrees of freedom for the molecule and hence the "sandwich effect" becomes less pronounced. The implication from these results is that the interaction does not occur through bonds to any significant extent.



R	R
105 $-CH_2-$	**109** α,α'- *o* -xylene
106 $-(CH_2)_2-$	**110** α,α'- *m* -xylene
107 $-(CH_2)_3-$	**111** α,α'- *p* -xylene
108 $-(CH_2)_{10}-$	

Finally, Mizutani *et al.* have synthesised the novel donor **112**, which contains two conjugated TTF moieties linked with divinyl xylene[77]. The cyclic voltammogram exhibits two sharp oxidation peaks and one broad

oxidation peak, all of which are irreversible. This indicates that the donor cannot be described in terms of two independent TTF units and there is π-conjugation extending between the TTF moieties.



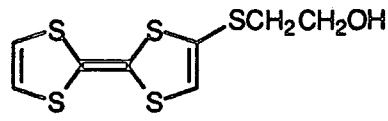
112

3.2 THE TTF-THIOLATE ANION

It has been shown that all four protons of TTF 1 are removed by reaction with four equivalents of LDA at -78°C, and the resultant tetra-anion can be treated with elemental sulphur, selenium or tellurium, followed by alkyl halides, to yield TTF derivatives substituted with four thioalkyl, selenoalkyl or telluroalkyl chains[30]. This work established that the TTF-chalcogenate anions are considerably more reactive towards electrophiles than are lithiated TTF species; for example, metallated TTF will not react with alkyl halides, whereas TTF-chalcogenate anions are readily alkylated. However, prior to the present work, the synthesis of mono-alkylthio TTF derivatives via insertion of elemental sulphur into the carbon-lithium bond of mono-lithiated TTF, was virtually unexplored.

Previous workers in our group had successfully synthesised the first mono(alkylchalcogeno)-TTF derivatives in the preparation of amphiphilic materials[31]. However, the yields of these reactions were very poor (10-15%) which, at the time, was ascribed to an inefficient chalcogen insertion step. More recently though, 4-[2-(hydroxy)ethylthio]tetrathiafulvalene **113** has been efficiently synthesised in 65% yield via the same sulphur insertion methodology[78]. It is now considered that the low yields in the preparation

of amphiphilic derivatives are probably due to the poor solubility of the alkyl halide at low temperatures, possibly combined with steric factors associated with the conformational flexibility of the long-chain alkylating agent.



113

3.3 MULTIPLE TETRATHIAFULVALENE SYSTEMS

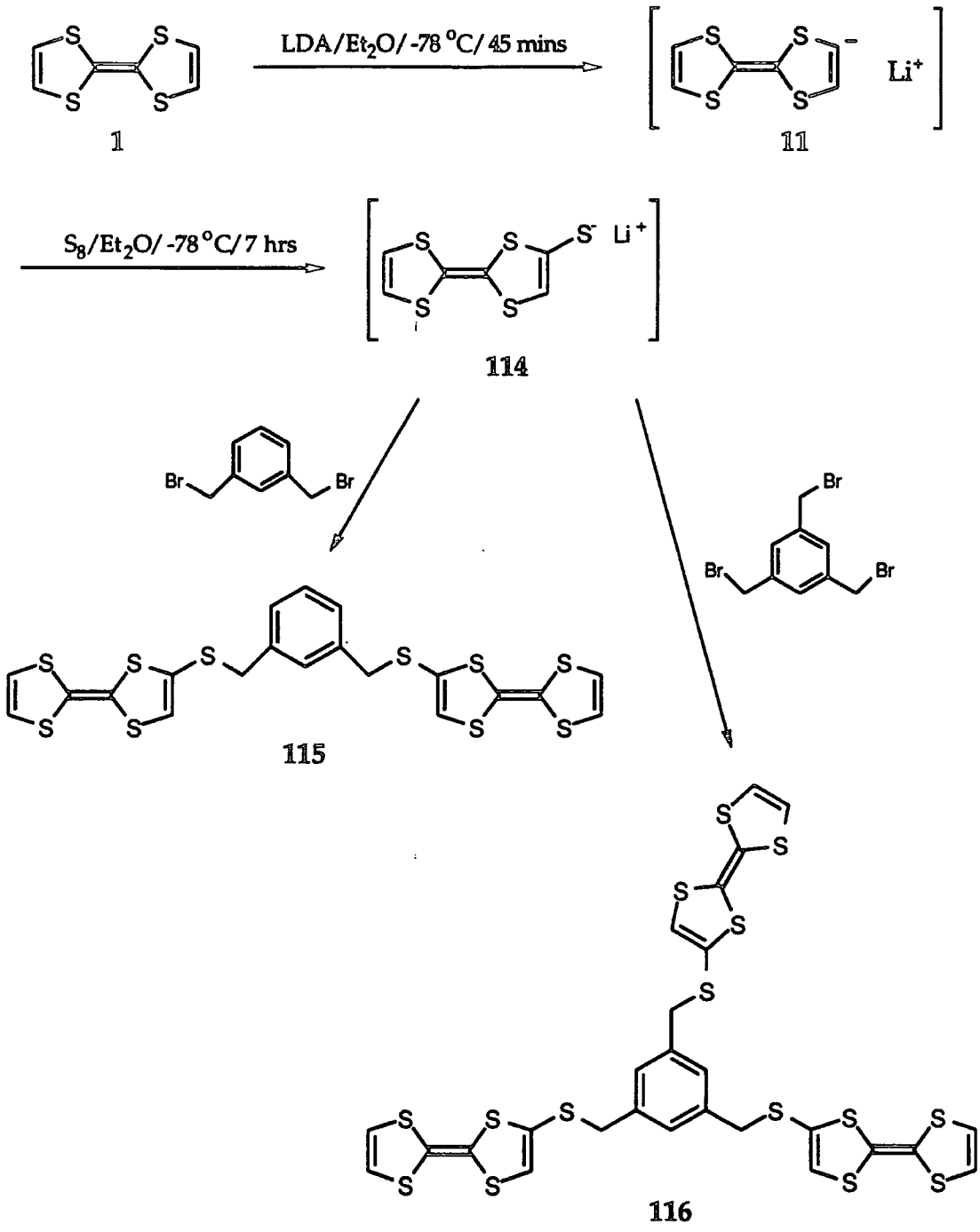
The high reactivity of the TTF-thiolate anion **114** has been developed for covalently linking TTF units via a range of spacer groups. This approach to multi-TTF systems is quite distinct from previously reported routes and has provided a number of symmetrical dimeric and trimeric tetrathiafulvalenes.

3.3.1 Bis- and tris-TTFs derived from reactions of the TTF-thiolate anion

Mono-lithiated TTF **11** was generated using standard conditions[29] and treated with one equivalent of elemental sulphur at -78°C, affording the intermediate TTF-thiolate anion **114** which can be treated *in situ* with a range of electrophiles. Trapping with 1,3-bis(bromomethyl)benzene and 1,3,5-tris(bromomethyl)benzene yields the aryl-bridged bis- and tris-TTF derivatives **115** and **116**, respectively, in 10-17% yields (Scheme 3.1.).

In an attempt to form bis-TTF **117**, in which two tetrathiafulvalene units are linked by an ethylenedithio bridge, 1,2-dibromoethane (0.5 equivalents) was added to the TTF-thiolate anion **114**. Investigation of the reaction mixture showed that none of the desired bis-TTF **117** had been formed. However, the known donor 4,5-(ethylenedithio)tetrathiafulvalene (EDT-TTF) **118** was isolated in 10-20% yield (Scheme 3.2.). This is a new, one-

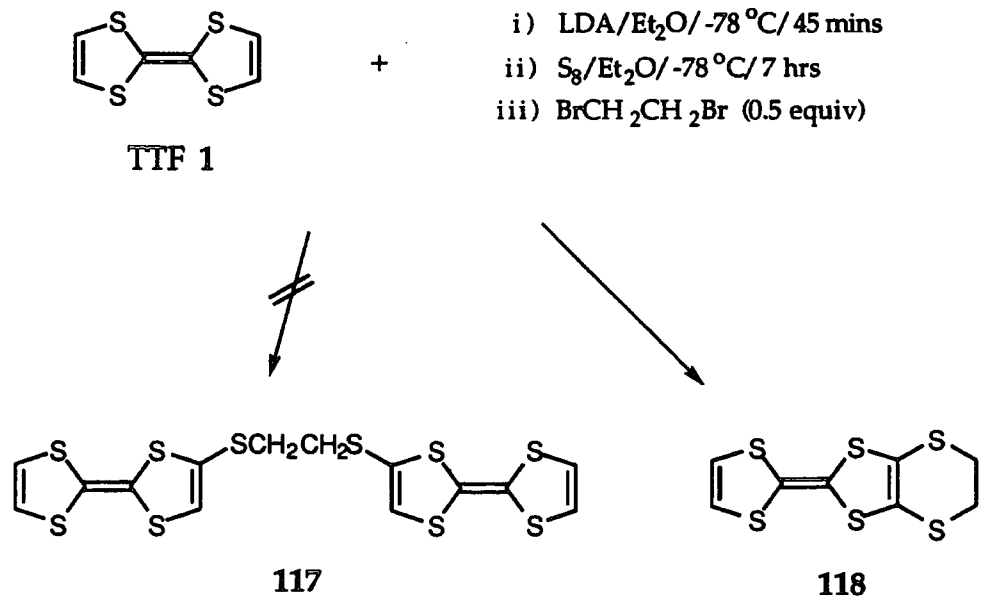
pot route to the unsymmetrical donor 118, that although the yield is very low, is considerably shorter than the previous method which involved phosphite-mediated cross-coupling of two 1,3-dithiole half units[79].



Scheme 3.1. - Synthesis of aryl-bridged multi-TTFs.

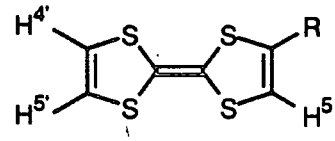
The sequence of events leading to the formation of the disubstituted product **118** is unclear. Disproportionation of lithiated TTF **11** and chalcogenated TTF anion **114** may occur to yield transient dianion species. An alternative, and perhaps more likely mechanism, does not involve dianion species, but, instead, alkylation of species **114** occurs prior to the second deprotonation and chalcogenation of the TTF system. The directing influence of an alkylthio substituent on further substitution onto the TTF ring has not been investigated previously.

In early work, Green established that attachment of an electron-withdrawing substituent (*e.g.* an ester group) to TTF activated the adjacent position to metallation, affording 4,5-disubstituted products, while an electron-donating substituent (*e.g.* a methyl group) directed a second substitution into the 4′ or 5′ positions (*i.e.* on the other dithiole ring, Scheme 1.3.)[29]. The formation of the 4,5-disubstituted compound **118** is, therefore, consistent with other work on the di-substitution of TTF, given the electron-withdrawing nature of the alkylthio substituent.



Scheme 3.2. - One-pot route to the unsymmetrical donor EDT-TTF.

The computer program CAMEO has been used to examine the effect that a range of substituents on the TTF frame has on the pK_a values of the remaining TTF protons. It has been shown previously that there is agreement to within 1-2 pK_a units between calculated and experimental values for protons on unsaturated sites adjacent to sulphur[80]. The calculated data for TTF derivatives are collated in Table 3.1. It can be seen that attachment of an electron-withdrawing ester or acyl substituent increases the acidity of the adjacent proton by 3 pK_a units; a bromine atom or a methylthio group has less effect, but, nonetheless, the data for these compounds are consistent with deprotonation being favoured at the adjacent site, giving rise to the observed 4,5-disubstituted product. A methyl substituent on TTF does not change any of the pK_a values of the remaining ring protons.

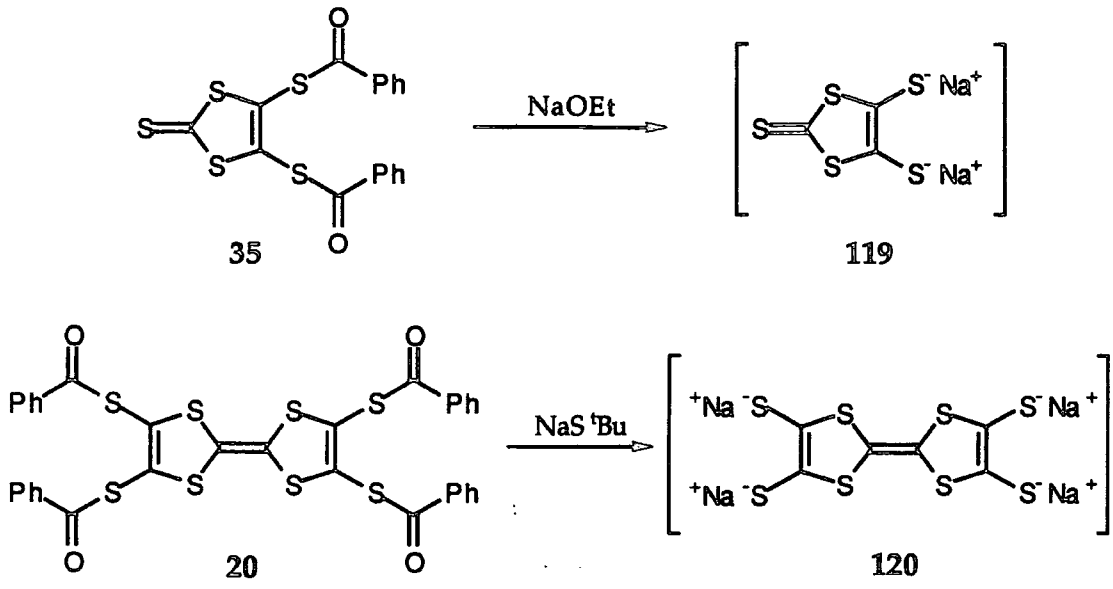


R	5-H	4'-H	5'-H
H	48	48	48
Me	48	48	48
C(O)OMe	45	48	48
C(O)Me	45	48	48
Br	47	48	48
SMe	47	48	48

Table 3.1. *- pK_a Values of hydrogen atoms in TTF derivatives, calculated using the computer program CAMEO.*

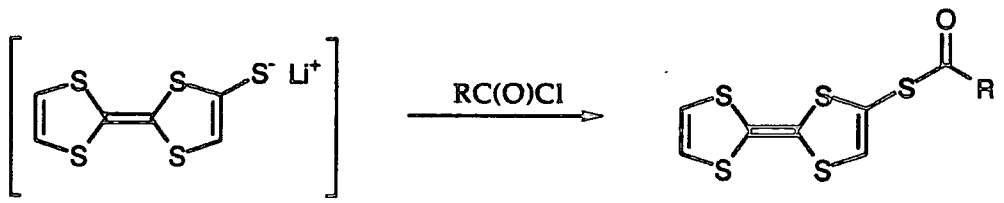
The observation of disubstituted products makes the generation of the TTF-thiolate anion from TTF **1**, inappropriate for the formation of certain mono-alkylthio substituted derivatives. In order to perform such

reactions it was necessary to prepare a convenient shelf-stable equivalent of the TTF- monothiolate. Shelf-stable precursors of 4,5-dithiolato-1,3-dithiole-2-thione 119[81] and TTF-tetrathiolate 120[37] were already known, being readily generated from the corresponding benzoylthioesters 35 and 20, respectively, under basic conditions (Scheme 3.3.).



Scheme 3.3. - The use of benzoylthioesters as precursors to thiolate anions.

The TTF-thiolate anion 114 was generated (by base treatment of TTF 1, followed by elemental sulphur) and acetyl chloride added to afford thioester 121 in 79% yield (Scheme 3.4.). The corresponding reaction with benzoyl chloride gave thioester 122 in 70-78% yield. These yields are much higher than the analogous reactions for the TTF-anion (typically 20-40%) indicating the enhanced reactivity of the TTF-thiolate anion towards electrophiles.

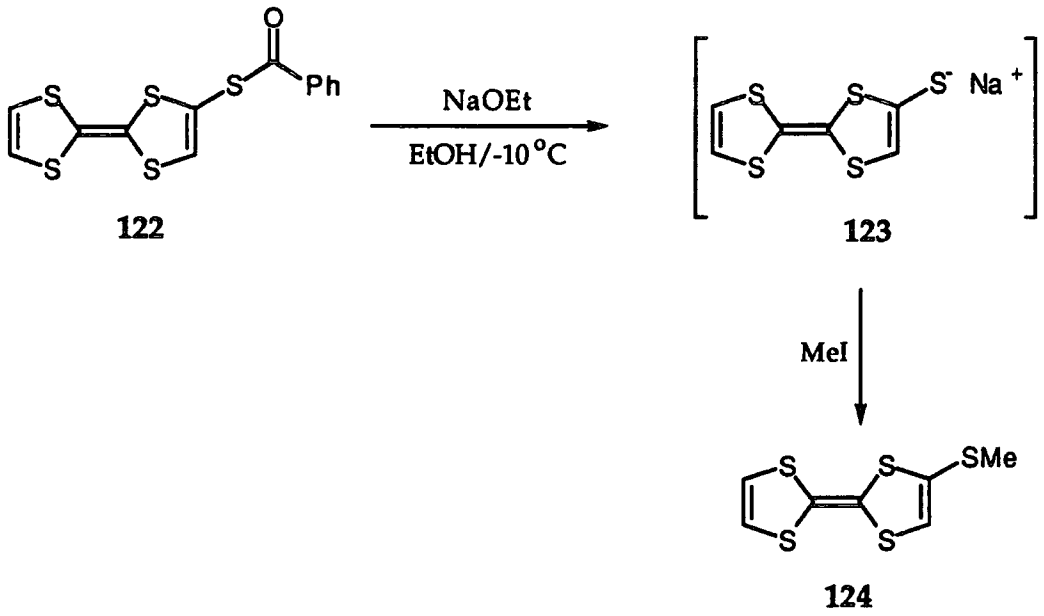


114

121 R = Me
122 R = Ph

Scheme 3.4. - The preparation of thioesters from the TTF-thiolate anion.

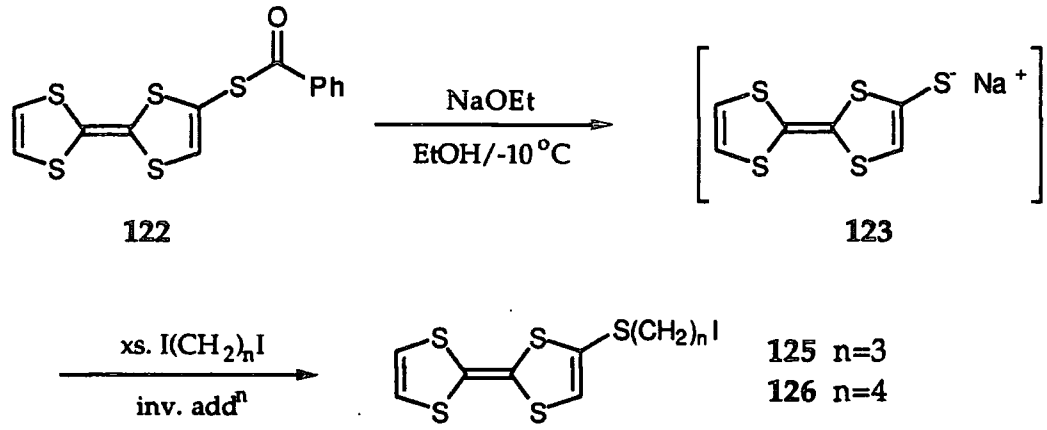
The TTF-thiolate anion can be efficiently regenerated (as the sodium salt) by treatment of benzoyl ester **122** with sodium ethoxide, in ethanol, at -10°C; this was established by trapping anion **123**, generated in this way, with iodomethane, which gave 4-(methylthio)TTF **124** in 96% yield (Scheme 3.5.). The same reaction at 20°C gave compound **124** in only 41% yield. The lower yield obtained at 20°C is probably due to decomposition of the intermediate TTF-thiolate species **123**, which is suppressed at low temperature. Benzoylthio ester **122** serves, therefore, as a convenient shelf-stable equivalent of the TTF-thiolate anion. This methodology has the added advantage of avoiding the use of ether at -78°C, conditions which can give rise to poor solubility and low reactivity of certain reagents.



122 **123** **124**

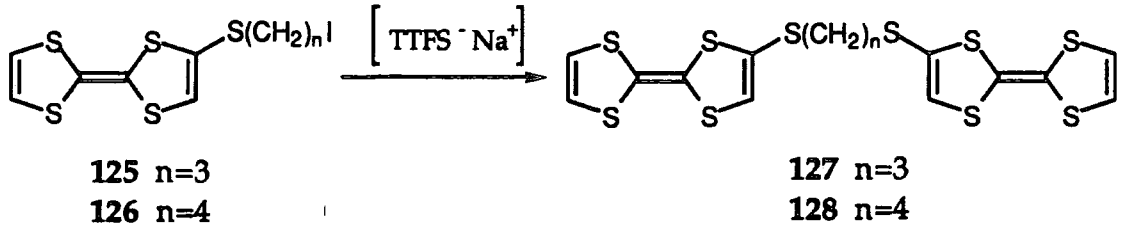
Scheme 3.5. - Benzoylthio-TTF as a shelf stable precursor to the TTF-thiolate anion.

The slow addition of thiolate anion 123, generated from reagent 122, to an excess of 1,3-diiodopropane and 1,4-diiodobutane yielded iodides 125 and 126, respectively, in 43-50% yields (Scheme 3.6.). The analogous reaction with 1,2-diiodoethane to afford 4-[2-(iodo)ethylthio]tetrathiafulvalene failed to give any of the desired product. Iodides 125 and 126 represent compounds in which a redox-active TTF unit and a leaving group (halogen) are incorporated into the same molecule. There are very few examples of such systems and, as such, these materials should find use in the future construction of larger redox-active assemblies.



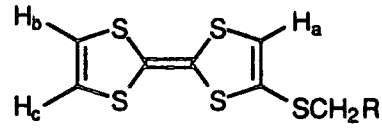
Scheme 3.6. - Synthesis of TTF iodides from the benzoylthio ester.

Reaction of iodides **125** and **126** with a second equivalent of thiolate anion **123** (also generated from thioester **122**) proceeded less efficiently to provide the bis-TTF systems **127** and **128**, respectively, in 11-26% yield (Scheme 3.7.). This two-step route was more efficient than one-pot syntheses of **127** and **128** (from two equivalents of thiolate **123** and one equivalent of diiodoalkane) which proceeded in only *ca.* 5% yield.



Scheme 3.7. - Synthesis of alkylthio-bridged bis-TTFs.

It is interesting to note the effect of the alkylthio substituent on the chemical shift of the adjacent TTF proton in the ^1H NMR spectra. The observed chemical shifts for some of the alkylthio substituted TTFs are collated in Table 3.2. In each case, the chemical shifts of the protons on the unsubstituted dithiole ring (δ $H_{b,c}$) are unaffected by the nature of the substituent. However, whereas for compounds 115, 116 and 124 the single proton singlet is at a lower chemical shift than the two proton singlet, for compounds 125-128 the single proton resonates at a higher frequency. Therefore, despite the presence of the (normally) electron-withdrawing sulphur atom, the relative positions of the proton chemical shifts is dependant on the nature of the alkyl group.



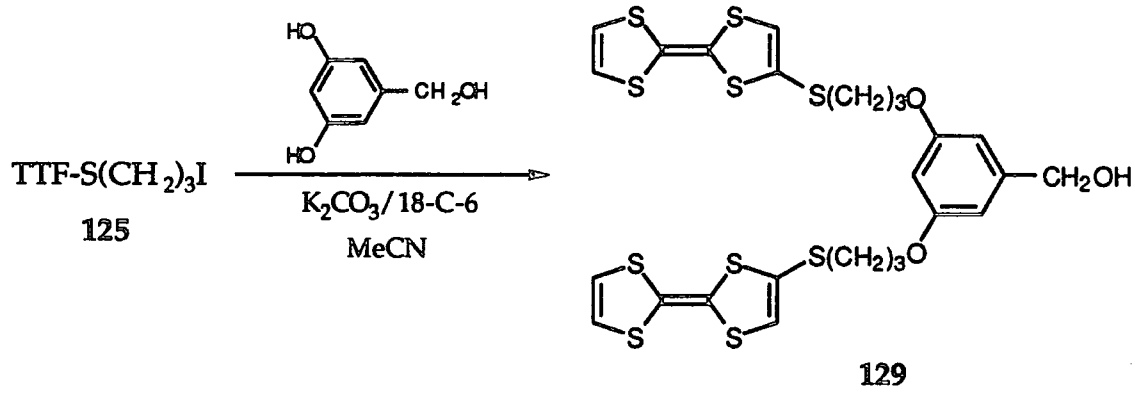
Cmpd.	R	δ H_a (s)	δ $H_{b,c}$ (s)
115	3-(TTFSCH$_2$)C$_6$H$_4$	6.11	6.30
116	3,5-(TTFSCH$_2$)$_2$C$_6$H$_3$	6.13	6.32
124	H	6.28	6.32
125	CH$_2$CH$_2$I	6.38	6.32
126	CH$_2$CH$_2$CH$_2$I	6.37	6.32
127	CH$_2$CH$_2$STTF	6.39	6.32
128	CH$_2$CH$_2$CH$_2$STTF	6.36	6.32

Table 3.2. - Observed chemical shifts of TTF protons in various alkylthio substituted derivatives ($CDCl_3$ solvent).

3.3.2 Other approaches to multi-TTF systems

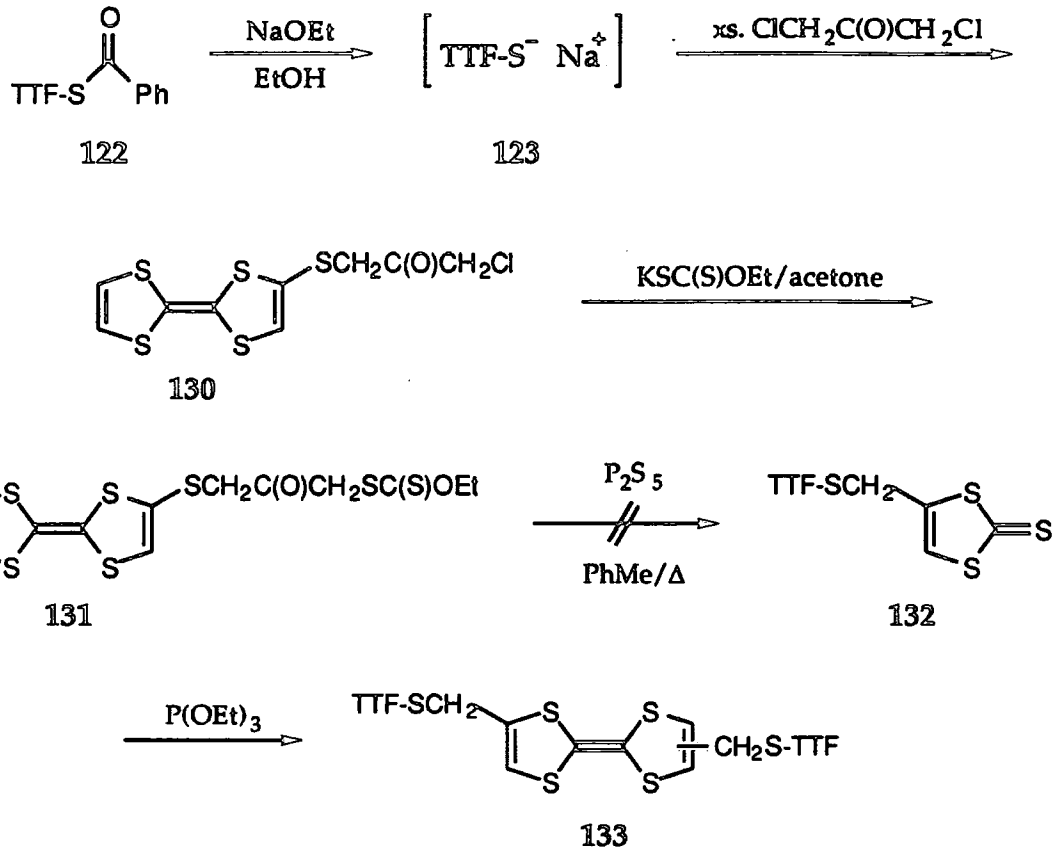
To investigate further the reactivity of TTF derivative 125, this compound was reacted with 3,5-dihydroxybenzyl alcohol in the presence of potassium carbonate and 18-crown-6 (acetonitrile solvent) to afford the bis-

TTF 129 in 20% yield (Scheme 3.8.). Despite the rather low yield of this reaction, compound 129 is potentially a building block in the construction of higher redox assemblies (*e.g.* dendritic systems) by using the hydroxy group as a 'reactive handle' for further functionalisation. The possibility of the removal of the acidic methylene protons adjacent to the sulphur atom on the thioalkyl chain of 125, could account for the disappointing yield of this reaction.



Scheme 3.8. - Synthesis of a bis-TTF suitable for further functionalisation.

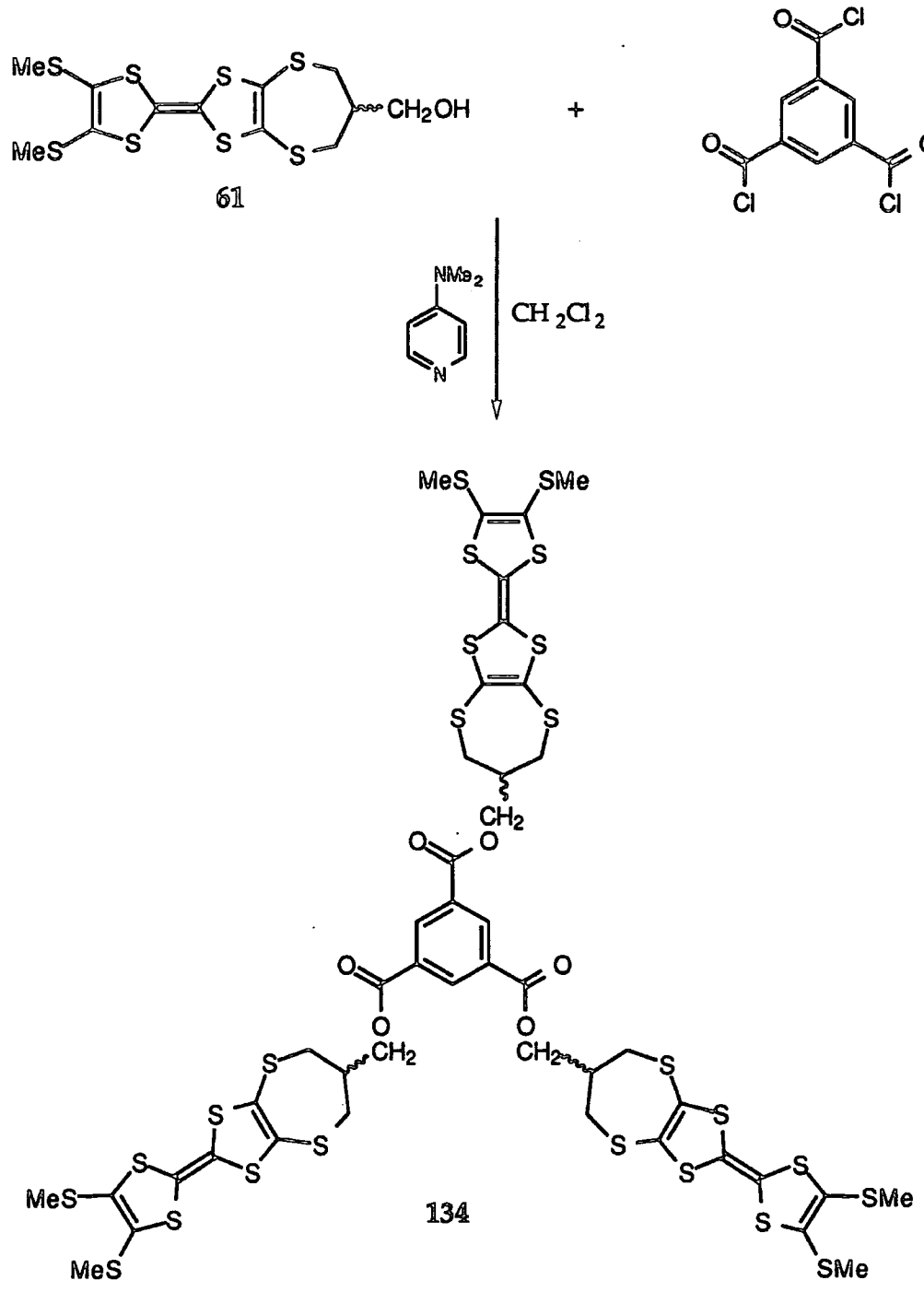
Another approach towards a multi-TTF system is outlined in Scheme 3.9. The synthesis of a molecule such as compound **132** should, via a phosphite mediated coupling, allow the construction of the tris-TTF **133**. The sodium thiolate salt **123** (generated from thioester **122**) on addition to an excess of 1,3-dichloroacetone afforded **130** in 44% yield. However, although **130** on reaction with the potassium salt of O-ethylxanthic acid afforded **131** (71% yield), treatment with phosphorus pentasulphide in refluxing toluene failed to give the desired dithiole-thione **132**. No TTF derivative could be isolated from the reaction mixture and the conditions were considered too harsh for **131** to withstand the thionation and cyclisation step.



122 123 130 131 132 133

Scheme 3.9. - Synthesis of a 'tris-TTF' via coupling of a dithiole-thione.

Finally, the tris-TTF **134** was formed, in 59% yield, by 3-fold esterification of 1,3,5-benzenetricarbonyl trichloride with TTF alcohol **61** in the presence of 4-dimethylaminopyridine (Scheme 3.10.).



Scheme 3.10. - A tris-TTF via 3-fold esterification.

3.3.3 Electrochemical studies of the multi-TTFs

The electrochemical redox properties of all the new TTF derivatives have been investigated by cyclic voltammetry; these data, along with those of the reference compound TTF 1, are collated in Table 3.3. The monomeric TTF derivatives 121, 122 and 124-126 display two, reversible, single-electron

oxidation waves, typical of the TTF system. Predictably, the values of E_1 and E_2 are raised slightly by the alkylthio substituent. The symmetrical dimers 115 and 127-129 and the symmetrical trimers 116 and 134 each show two reversible redox waves at very similar potentials to the monomers, due to simultaneous oxidation of the two or three TTF units at the same potentials. Thus, the dimers sequentially form dications and tetracations, and the trimers form trications and hexacations, with no intermediate oxidation states being detected.

Donor	$E_1^{1/2}$/V	$E_2^{1/2}$/V
TTF 1	0.34	0.71
115	0.45	0.79
116	0.47	0.81
121	0.45	0.84
122	0.45	0.81
124	0.42	0.80
125	0.46	0.86
126	0.44	0.81
127	0.44	0.78
128	0.44	0.81
129	0.41	0.76
134	0.52	0.83

***Table 3.3.** - Cyclic voltammetric data for TTF derivatives. Data were obtained at 20°C versus Ag/AgCl, in dry dichloromethane under argon using a platinum button electrode and a platinum wire counter electrode, ca. 5 x 10^{-4} M compound, 0.1 M tetrabutylammonium hexafluorophosphate, scan rate 100 $mVsec^{-1}$, using a BAS 100 Electrochemical Analyser.*

There is no apparent broadening of either of the two oxidation waves, suggesting that there are no inter- or intra-molecular Coulombic repulsion effects between charged TTF moieties and that the individual TTF units are

electronically isolated by the spacer groups and do not interact to any significant extent. Previous workers on bis-TTF systems have observed intramolecular effects in cyclic voltammetric studies, but only when shorter spacer groups[72], or single atoms[70a,c,d,f], are bridging the TTF units.

3.4 TETRATHIAFULVALENE MACROMOLECULES

A particularly attractive target to us in the development of supramolecular assemblies based on TTF units, was a system in which tetrathiafulvalene units are linked through a central TTF core (Figure 3.1.). The solid-state structure of such a system could display novel macromolecular architecture. In particular, the effect of a particular TTF unit on the stacking of its neighbours in the system, and the possibility of the packing of the molecules in both the neutral donors and their charge-transfer salts to form "pillars" of stacking units, would be of special interest.

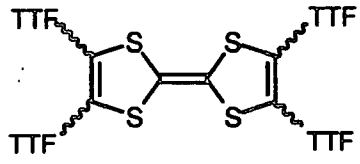
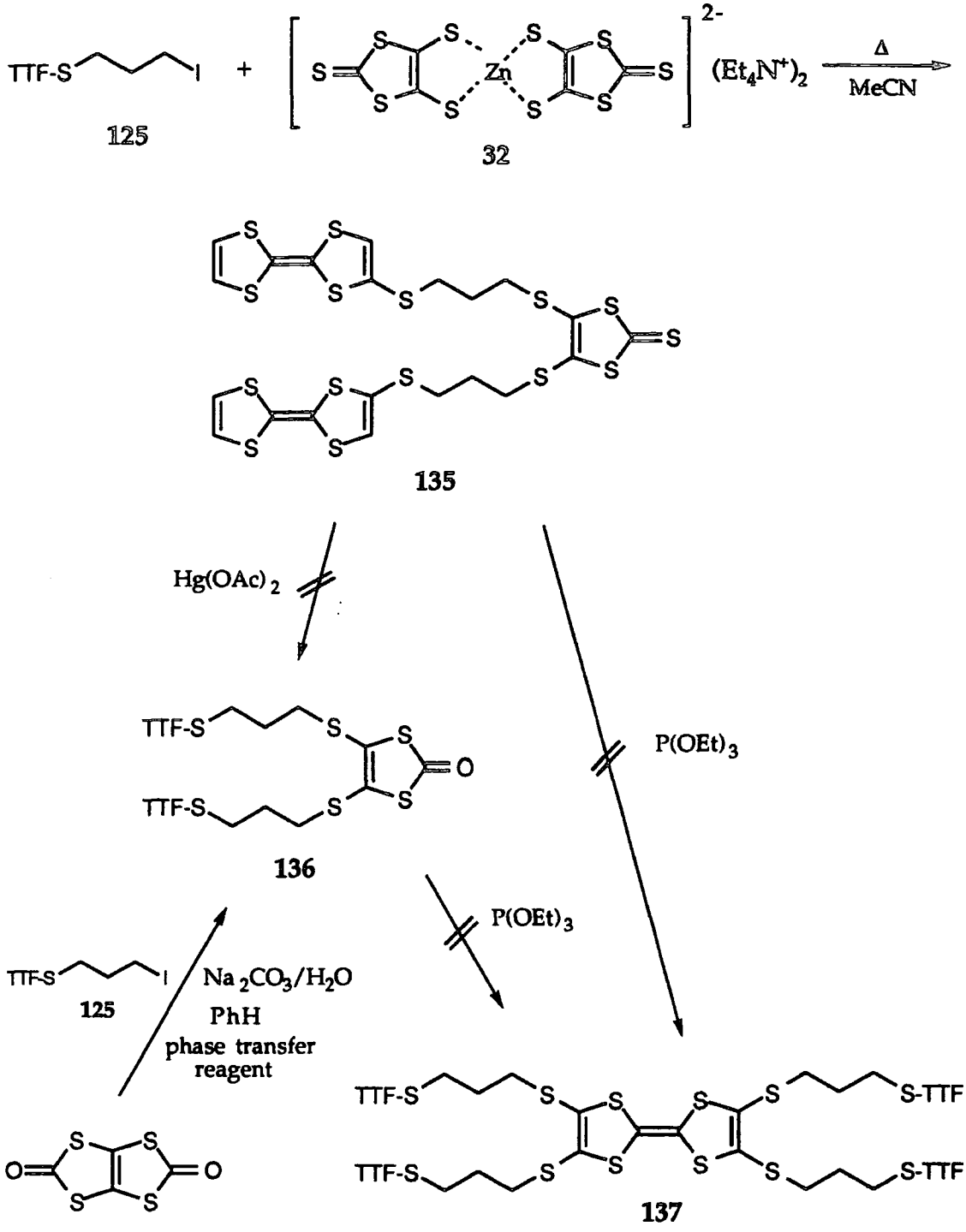


Figure 3.1. - A supramolecular assembly based on TTF units.

3.4.1 The assembly of TTF macromolecules

The first approach towards such a system utilised TTF iodide **125**. Reaction of zincate salt **32** with iodide **125** in refluxing acetonitrile afforded the bis-TTF **135** in 20% yield (Scheme 3.11.). This system links two TTF units to a 1,3-dithiole-2-thione moiety. Unfortunately, attempts to self-couple **135** using triethylphosphite under standard conditions failed to give the desired penta-TTF **137**. An unidentified phosphorus-containing product was obtained which could not be characterised. The attempted conversion of the trithiocarbonate functionality of **135** to the corresponding dithiocarbonate

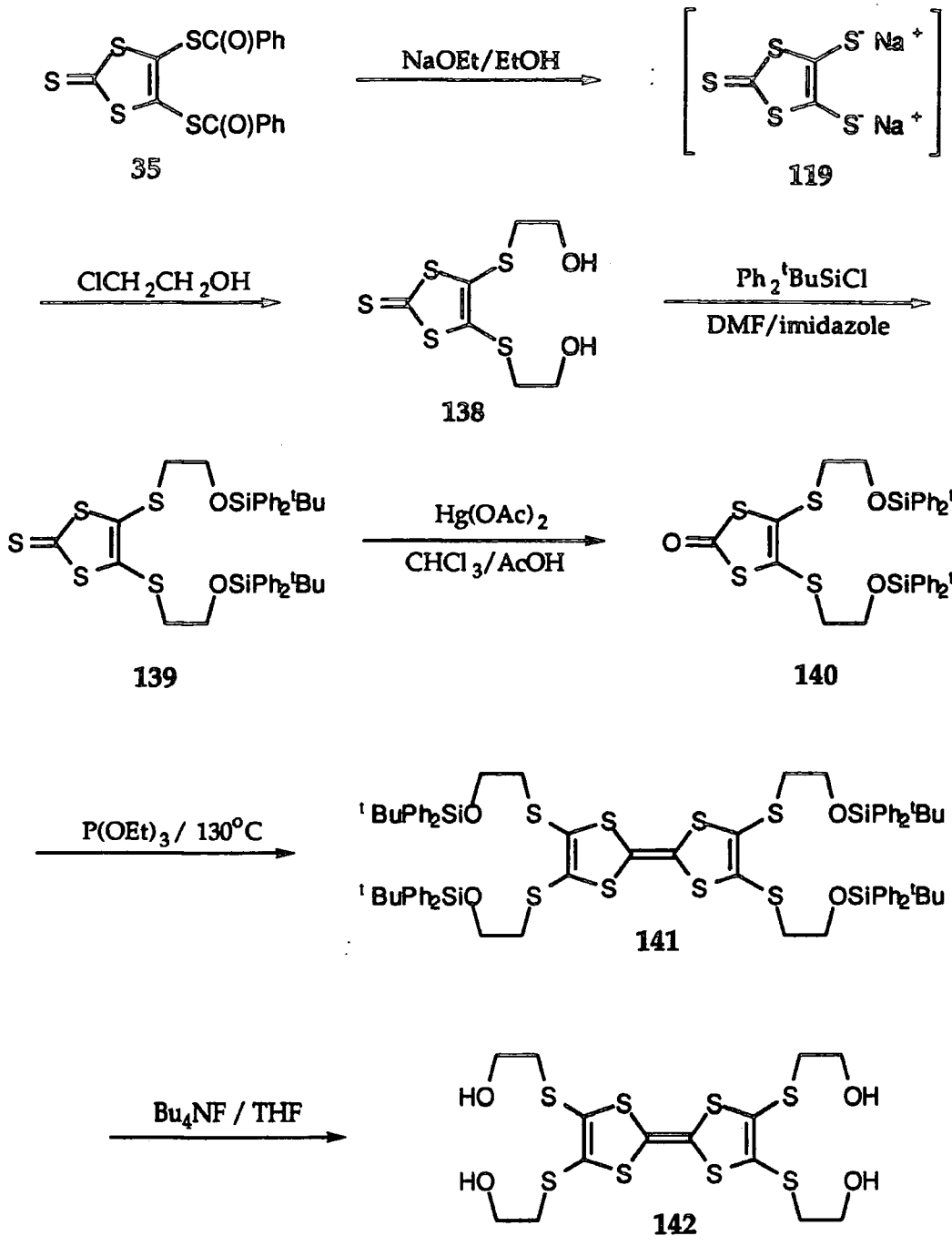
136 was unsuccessful. On the addition of mercuric acetate to a solution of thione 135, an immediate colour change from orange to deep green was observed. It is suggested that oxidation of the TTF units has occurred (no product was seen to move by TLC) as a result of the oxidative conditions of the mercuric acetate.



Scheme 3.11. - Syntheses of bis-TTF 1,3-dithioles.

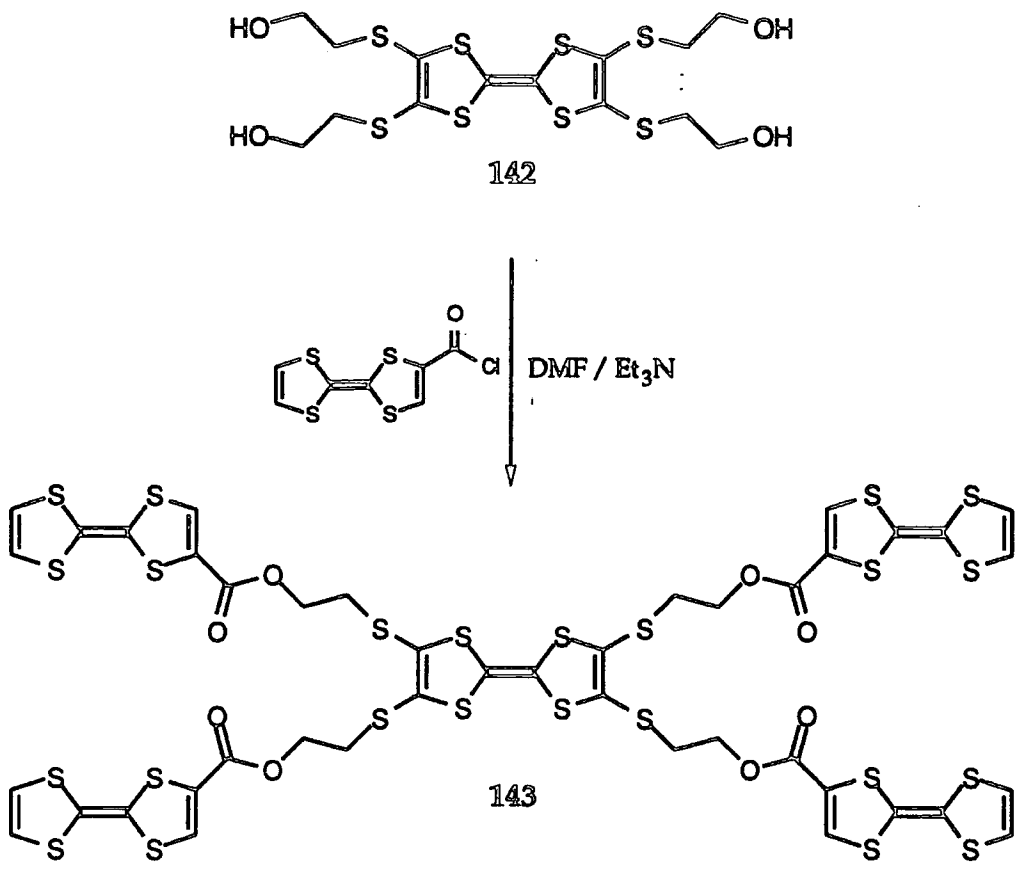
The bis-TTF ketone 136 could be synthesised, in 50% yield, by the addition of an aqueous solution of sodium carbonate to the TTF iodide 125 and 1,3,4,6-tetrathiapentalene-2,5-dione in the presence of a phase-transfer reagent. However, the attempted self-coupling of ketone 136 to give penta-TTF 137 also failed. As before, treatment with triethylphosphite gave a product which could not be identified. This approach to the synthesis of a penta-TTF macromolecule, via coupling of two 1,3-dithiole half-units, was now abandoned.

The second approach to the synthesis of a supramolecular assembly based on TTF units proved to be more successful and involves tetrafunctionalisation of a central TTF core unit. The key starting material in the synthesis is 4,5-di(benzoylthio)-1,3-dithiole-2-thione 35[81] which was readily deprotected and reacted with 2-chloroethanol via the transient sodium salt 119 to afford 4,5-bis[2-(hydroxy)ethylthio]-1,3-dithiole-2-thione 138 in high yield[82] (Scheme 3.12.). The attempted direct coupling of 138 to 142 using triethylphosphite failed, indicating the incompatibility of the hydroxy groups with the coupling reagent and conditions. Consequently, a suitable protection of the hydroxy groups as the *tert*-butyl-diphenylsilyl ether was carried out using *tert*-butyl-diphenylchlorosilane in DMF in the presence of imidazole. The silylation reaction afforded 139 in quantitative yield at 20°C. Conversion of the trithiocarbonate functionality of 139 to the corresponding dithiocarbonate 140 was achieved, in quantitative yield, using mercuric acetate in chloroform/acetic acid. The protected compound 140 self-coupled smoothly under standard conditions, in 62% yield, to give the TTF derivative 141. Deprotection of 141 was achieved, in 75% yield, using tetrabutylammonium fluoride in THF, affording the desired 4,4',5,5'-tetrakis[2-(hydroxy)ethylthio]tetrathiafulvalene 142. [This compound has previously been prepared by Russian workers[92], although via a different route.] Tetrahydroxy-TTF derivative 142 was designed to serve as a core unit in the multiple-TTF system 143.



Scheme 3.12. - Synthesis of a tetrafunctionalised TTF core unit.

Assembly of the penta-TTF macromolecule **143** by four-fold esterification of compound **142** with TTF-carbonyl chloride[83] was achieved, in 57% yield, using DMF as solvent and triethylamine as base (Scheme 3.13.). Elemental analysis, Plasma Desorption Mass Spectrometry (PDMS), ^{1}H NMR and IR spectroscopic data for compound **143** were all entirely consistent with its assigned structure.



Scheme 3.13. - Assembly of a penta-TTF macromolecule.

3.4.2 Solution redox behaviour

The redox behaviour of compounds **142** and **143** has been investigated by cyclic voltammetry and the data are collated in Table 3.4. Compound **142** exhibits two quasi-reversible redox couples typical of the TTF system, occuring at a higher potential than the parent TTF **1** in accord with the presence of four thioalkyl substituents attached to the TTF frame. The penta-TTF **143** shows three quasi-reversible redox couples (Figure 3.2.). The first couple corresponds to the first oxidation of the four peripheral TTF-units to form a tetracation by simultaneous loss of four electrons. The first oxidation of the central TTF-core with loss of one electron gives rise to the second couple. The second oxidations of the central TTF and the four peripheral TTFs appear to coincide to give the third redox couple, generating a species bearing ten positive charges.

Donor	E_1^{ox}/V	E_2^{ox}/V	E_3^{ox}/V	E_1^{red}/V	E_2^{red}/V	E_3^{red}/V
TTF 1[a]	0.36	0.75	-	0.30	0.69	-
142[a]	0.57	0.80	-	0.51	0.72	-
143[b]	0.63	0.75	0.95	0.56	0.72	0.90

Table 3.4. - Cyclic voltammetric data.
Data were obtained at 20°C versus standard calomel, using platinum working and counter electrodes, ca. 1 x 10^{-5} M compound, 0.1 M tetrabutylammonium hexafluorophosphate, scan rate 100 mVsec^{-1}. [a]recorded in MeCN; [b]recorded in THF.

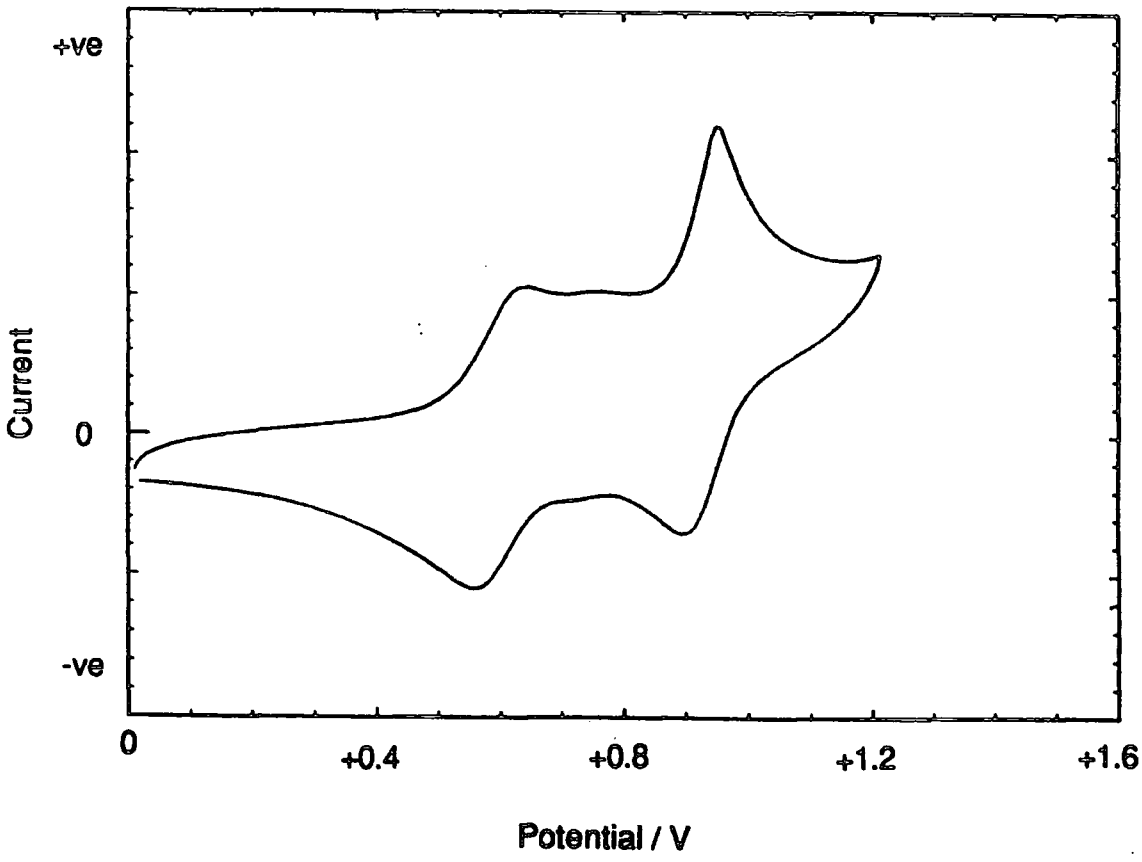


Figure 3.2. - Cyclic Voltammogram of compound 143.

3.4.3 Attempted crystal growth and charge-transfer salt formation

The solid state structures of both the neutral donor and charge-transfer salts of compounds 142 and 143 have the potential to display novel macromolecular architecture. TTF-tetraol 142 could display an extensive network of intra- and/or inter-molecular hydrogen bonding. The powder and single crystal conductivities of charge-transfer salts would also be of interest.

Unfortunately, it was not possible to obtain X-ray quality crystals of either of the neutral donors 142 and 143. Attempts to complex the donors with the electron acceptors 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), tetracyanoethylene (TCNE) or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) also proved unsuccessful. Although a colour change was observed on mixing donor 143 with DDQ, no charge-transfer salt could be isolated.

3.5 CONCLUSION

New methodology has been developed for the construction of redox-active multi-TTF systems. The TTF-thiolate anion 114 has been shown to be a particularly versatile reagent for this purpose: it should enjoy future use in the preparation of new systems of this type. The efficient synthesis of the novel pentakis-tetrathiafulvalene 143 is a significant step forward in the development of supramolecular assemblies based on TTF units. Multistage redox systems and dendritic macromolecules incorporating TTF derivatives may be prepared using building blocks reported in this chapter.

CHAPTER FOUR

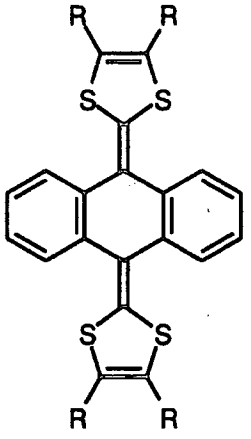
HIGHLY FUNCTIONALISED ANTHRACENEDIYLIDENE

π-ELECTRON DONORS

4.1 INTRODUCTION

Redox-active building blocks with reactive functional groups are of importance in supramolecular chemistry[73]. In this context, the synthesis of functionalised tetrathiafulvalene systems is not straightforward and very few methods are available for constructing the TTF ring from highly substituted components. There is, therefore, a need to explore new π-electron donor systems that can be readily functionalised.

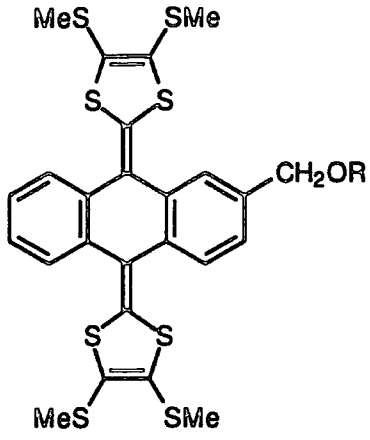
From this viewpoint, 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydro-anthracene **24**, which is an analogue of TTF with extended conjugation between the two 1,3-dithiole rings, has attracted recent attention. The parent system **24** and the tetramethyl derivative **144** have been studied as new π-donor components for the formation of organic metals[52,84]. A notable consequence of the extended conjugation is the reduction of on-site, intramolecular Coulombic repulsion (due to a greater separation of charges) and hence increased stability of dication states, relative to the parent donor TTF **1**. Many of these molecules undergo single- or multi-stage redox reactions at relatively low oxidation potentials (Section 1.6).



24 R = H
144 R = Me

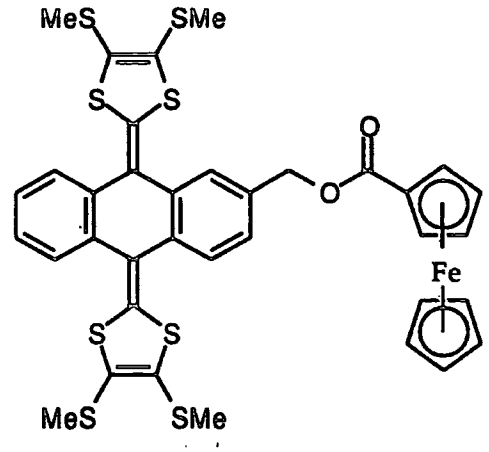
The first functionalised derivatives of system **24** were recently synthesised in our group[85]. Compound **145** is the key intermediate with the hydroxymethyl substituent providing a versatile 'handle' for further elaboration. The suitability of compound **145** as a building unit for highly

functionalised π-donor systems was demonstrated by efficient reactions to afford the acrylate and urethane derivatives 146 and 147, respectively.



145 R = H
146 R = C(O)CH=CH_2
147 R = C(O)NHCH_2CH_2Cl

The alcohol 145 also reacted with ferrocenecarbonyl chloride to furnish the multi-stage redox assembly 148.



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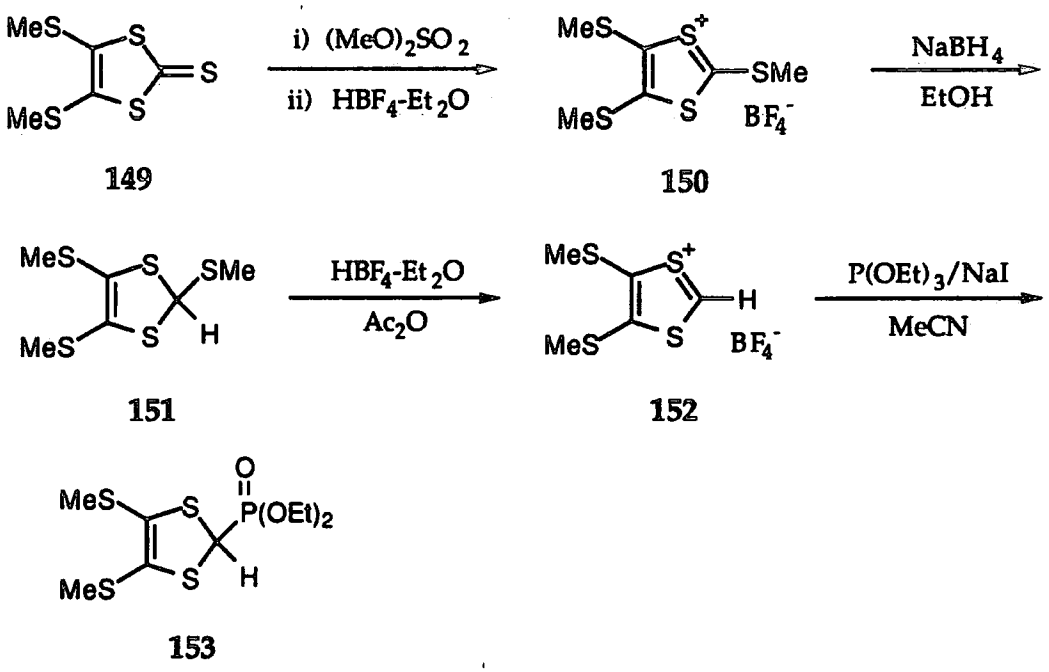
4.2 FUNCTIONALISED ANTHRACENEDIYLIDENE DONORS

The present work set out to extend this methodology for the preparation of highly functionalised analogues of TTF, as versatile electron donor systems. In particular, the synthesis of bis-substituted derivatives and multi-stage redox assemblies was to be pursued.

4.2.1 Systems containing functionality on the anthracene unit

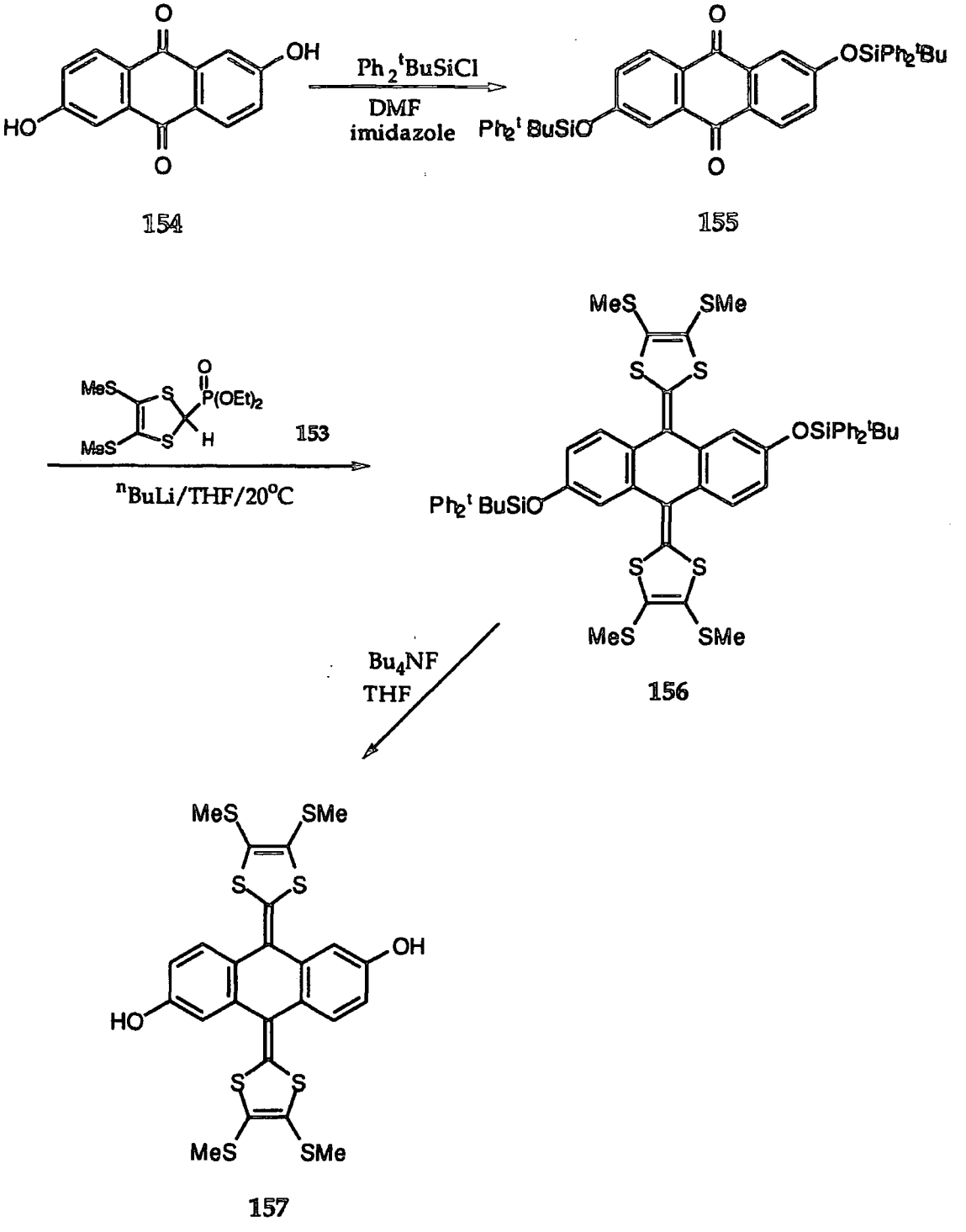
Compound 157 was targeted, since the hydroxy substituents can provide a suitable 'handle' for further reactions. Methylthio substituted 1,3-dithiole rings were chosen for three reasons: (i) the Horner-Wittig reagent 153 is readily available from cheap starting materials, (ii) the methylthio substituents have the benefit of raising the oxidation potential (compounds 24 and 144 are both very easily oxidised[52]) and thereby increasing the stability of the anthracenediylidene system in air, and (iii) the solubility of such systems is improved by the presence of the methylthio groups.

Reagent 153 was prepared, in four steps[86], as outlined in Scheme 4.1. Thione 149 (prepared by alkylation of zincate salt 32 with iodomethane) was methylated using neat dimethylsulphate to yield the dithiolium cation, which was isolated, after anion exchange, as the tetrafluoroborate salt 150. Reduction of cation salt 150, in ethanol, with sodium borohydride gave thioether derivative 151, which, on treatment with tetrafluoroboric acid, gave dithiolium cation salt 152. Salt 152 reacted with triethylphosphite in the presence of sodium iodide to afford phosphonate ester 153.



Scheme 4.1. - Preparation of the 4,5-dimethylthio substituted Horner-Wittig reagent.

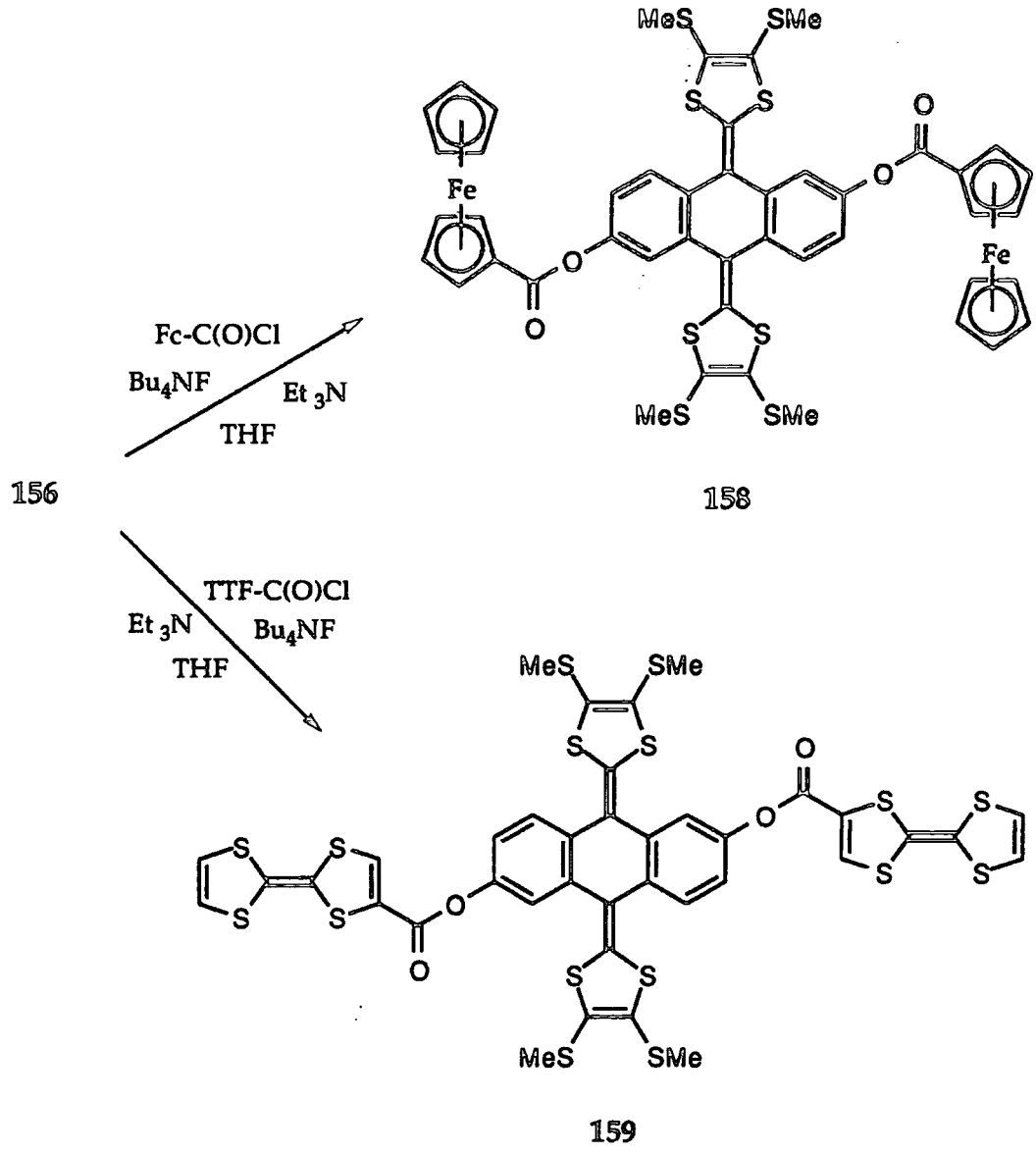
2,6-Dihydroxyanthraquinone 154 reacted with *tert*-butyl-diphenyl-chlorosilane in the presence of imidazole to afford, in 61% yield, the disilyl ether derivative 155 (Scheme 4.2.).



Scheme 4.2. - Synthesis of an extended-TTF with functionality on the anthracene unit.

Two-fold reaction of the quinone 155 with the phosphorus-stabilised carbanion generated from reagent 153, using butyllithium at 20°C, gave the anthracenediylidene derivative 156 in 59% yield. Deprotection to give the diol 157 (*ca.* 70% yield) was achieved using tetrabutylammonium fluoride in THF. The product was found to be only sparingly soluble in common organic solvents. It was not possible to obtain the compound analytically pure and its insolubility precluded its use in further reactions.

However, the insolubility of this 'extended-TTF diol' did not prevent the synthesis of derivatives of this system. Due to the nature of the silyl protecting group, the solubility of compound 156 in common organic solvents is very good. Functionalisation could be achieved from silyl derivative 156, in a one-pot procedure, by treatment with fluoride ion in the presence of an acid chloride and triethylamine as base. This method deprotects the silyl ether and traps *in situ* without the need to isolate the insoluble diol 157. Accordingly, reaction with ferrocene and TTF carbonyl chlorides furnished the multi-stage redox assemblies 158 (55% yield) and 159 (30% yield), respectively, both of which could be obtained analytically pure (Scheme 4.3.). These reactions demonstrate the suitability of compound 157 as a building unit for highly functionalised π-donor systems, albeit from silyl protected derivative 156.



Scheme 4.3. - Synthesis of multi-stage redox assemblies.

4.2.2 Solution electrochemistry

The solution electrochemistry of compounds **158** and **159** has been studied by cyclic voltammetry, and the data are collated in Table 4.1. The cyclic voltammogram of compound **158** is shown in Figure 4.1. Oxidation of the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene moiety occurs as a single, two-electron, quasi-reversible wave (E_1^{ox} = 0.61V, E_1^{red} = 0.32V) to yield the dication species. Simultaneous oxidation of the two ferrocene units gives the ferrocene/ferrocinium redox couple, observed as a cleanly

reversible wave at $E^{1/2}$ = 0.75V, to afford a system bearing four positive charges.

Donor	E_1^{ox}/V	E_2^{ox}/V	E_1^{red}/V	E_2^{red}/V	E_3^{red}/V
158	0.61	0.78	0.32	0.73	-
159	0.50	0.94	0.36	0.42	0.82

Table 4.1. - Cyclic voltammetric data.
Data were obtained at 20°C versus Ag/AgCl, in dry dichloromethane under argon using a platinum button electrode and a platinum wire counter electrode, ca. 5 x 10^{-4} M compound, 0.1 M tetrabutylammonium hexafluorophosphate, scan rate 100 $mVsec^{-1}$, using a BAS 100 Electrochemical Analyser.

The cyclic voltammogram of compound 159 is shown in Figure 4.2. The two-electron oxidation of the anthracenediylidene and the first oxidation of the two TTF units (neutral TTF -> $TTF^{\cdot+}$) are not resolved and occur as a single, broad peak at E_1^{ox} = 0.50V. The second oxidation of the TTF units ($TTF^{\cdot+}$ -> TTF^{2+}) occurs as a quasi-reversible couple (E_2^{ox} = 0.94V, E_3^{red} = 0.82V) to generate a system bearing six positive charges. The reduction of the TTF radical cations to neutral TTF and the two-electron reduction of the anthracenediylidene moiety are just resolved, occuring at E_2^{red} = 0.42V and E_1^{red} = 0.36V, respectively.

For both compounds there are no apparent inter- or intra-molecular interactions between the different redox moieties in the system which are electronically isolated from each other by the spacer groups. The irreversibility of the anthracenediylidene oxidation process arises jointly from a change in conformation and aromatic stabilisation[87]. At the dication redox stage there is a gain in aromaticity of the newly-formed anthracene system, together with the additional stabilisation within the 6π, 1,3-dithiolium rings. The marked conformational change that must occur on reduction (planar anthracene -> buckled anthraquinodimethane) is the other factor accounting for the observed redox behaviour in this system.

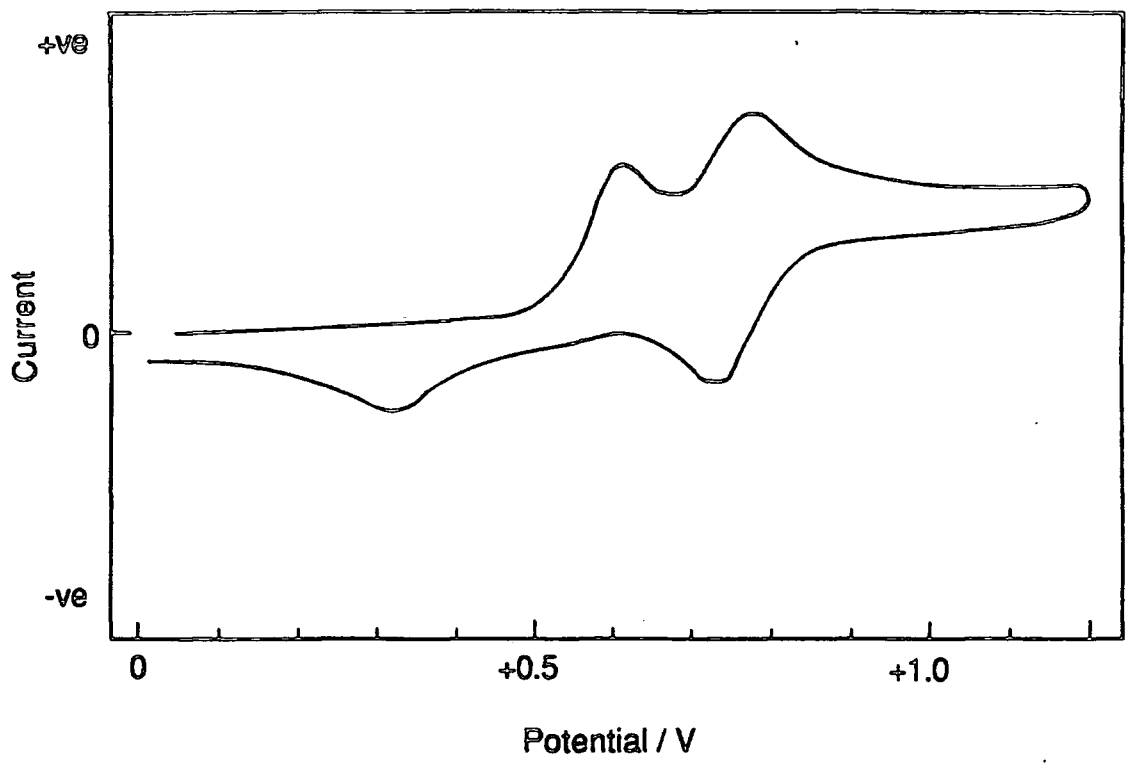


Figure 4.1. - Cyclic voltammogram of compound 158.

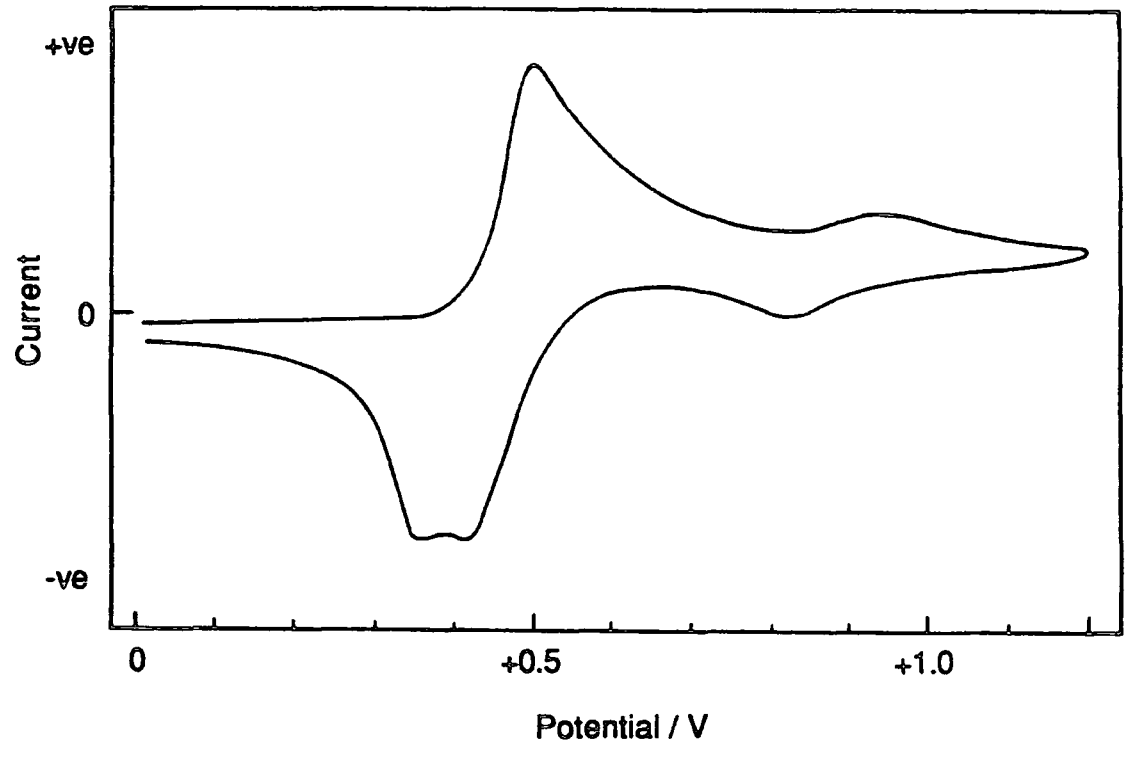
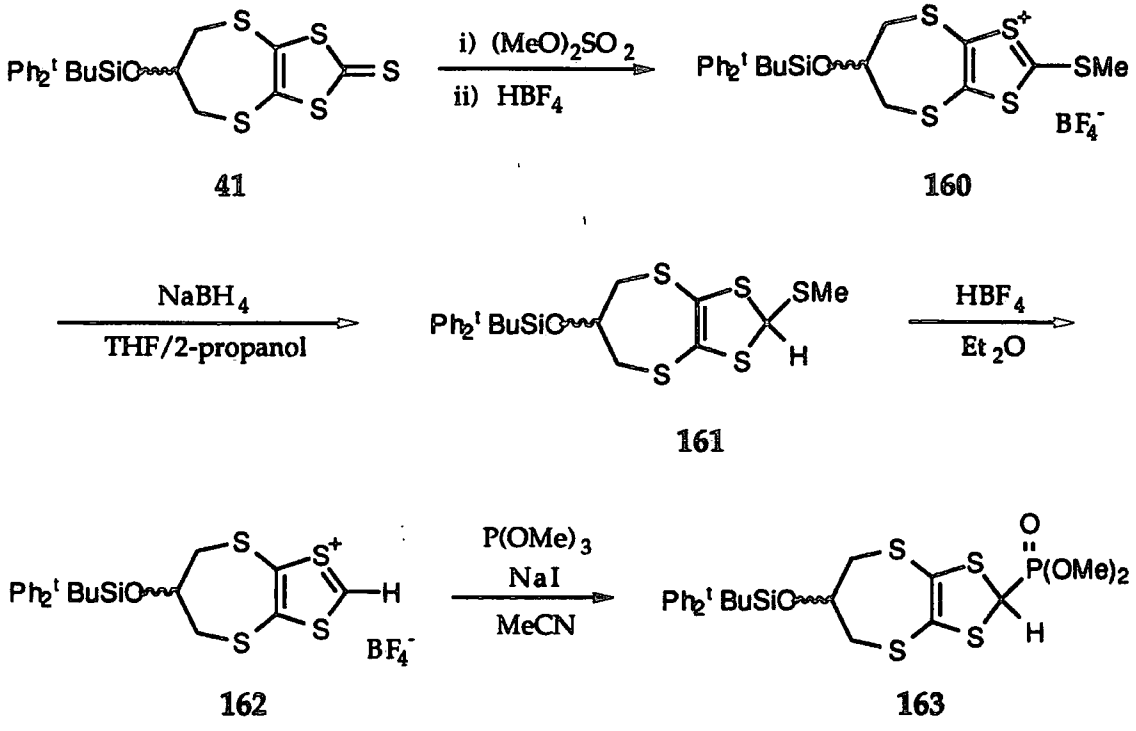


Figure 4.2. - Cyclic voltammogram of compound 159.

4.2.3 Systems containing functionality on the 1,3-dithiole units

A related system to be investigated as a functionalised analogue of TTF, was the extended donor **165**, in which 2-(hydroxy)propylene-1,3-dithio units are fused to the dithiole rings. This compound is the anthracenediylidene analogue to the previously prepared TTF-diol **45**. The key intermediate is the silyl protected Horner-Wittig reagent **163** whose synthesis (Scheme 4.4.) utilises the thione **41** reported earlier.



Scheme 4.4. - Synthesis of silyl protected Horner-Wittig reagent.

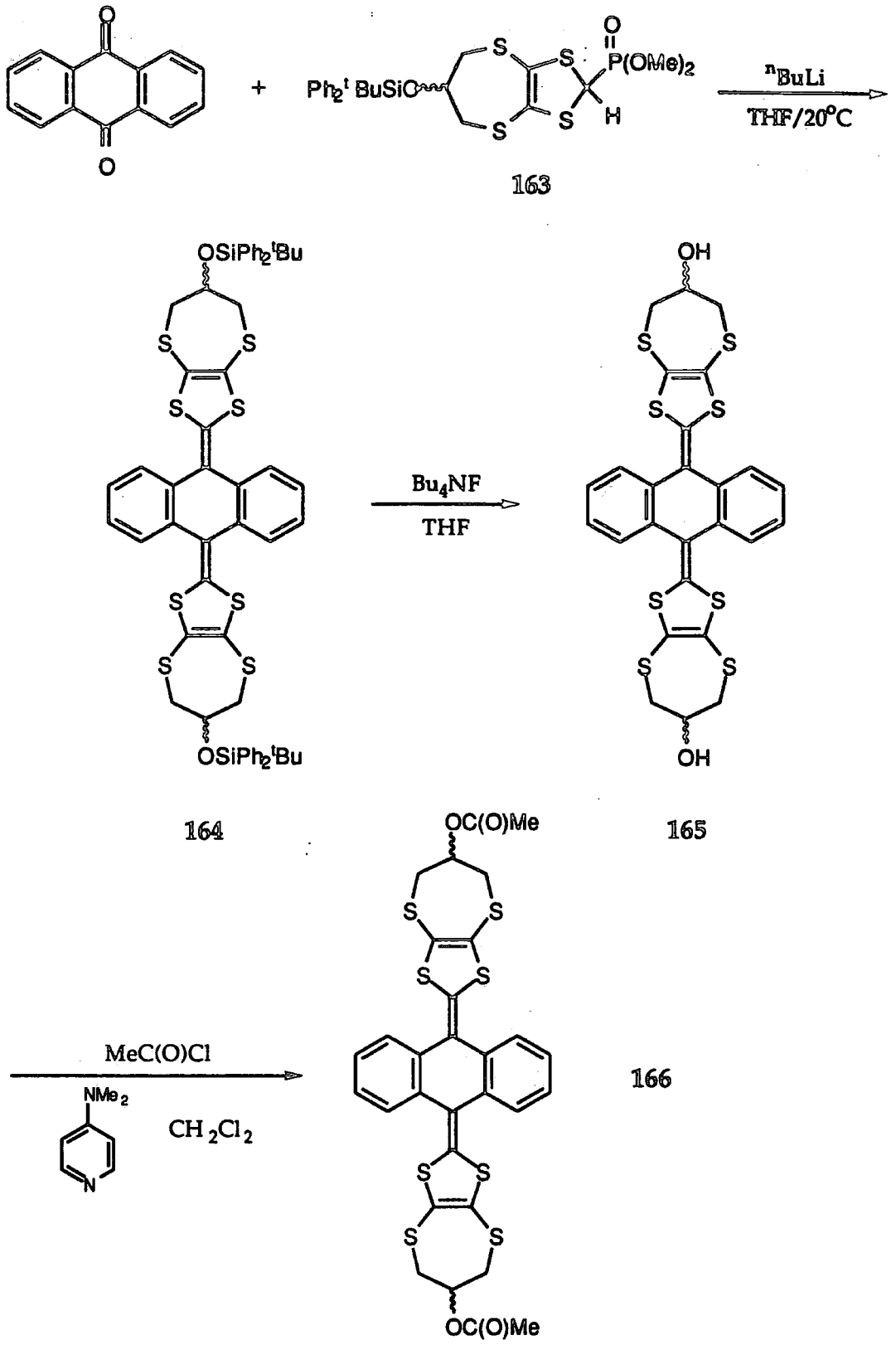
Methylation of thione **41** in neat dimethylsulphate, followed by anion exchange with tetrafluoroboric acid afforded, in 81% yield, the tetrafluoroborate salt **160** of the dithiolium cation. Reduction to the thioether derivative **161** was achieved, in 95% yield, by the use of sodium borohydride in THF/2-propanol. Initial attempts to reduce **160** in ethanol afforded the product in which the cation salt had been attacked by the solvent. Treatment of **161** with tetrafluoroboric acid gave, in 72% yield, the dithiolium cation salt **162** which, on reaction with trimethylphosphite in

the presence of sodium iodide afforded, in 82% yield, the desired phosphonate ester 163.

As a result of the prochiral carbon atom at C-2 in the propylene-1,3-dithio bridge, compounds 161 and 163 are formed as a mixture of isomers. This is confirmed by the ^{1}H NMR data which show two sets of signals for each of the expected proton resonances, one from each of the isomers obtained.

Two-fold reaction of anthraquinone with the phosphorus-stabilised carbanion generated from the Horner-Wittig reagent 163, using butyllithium at 20°C, afforded the extended-TTF derivative 164 in 47% yield (Scheme 4.5.). Deprotection to diol 165 was achieved, in 71% yield, by the use of tetrabutylammonium fluoride in THF. The suitability of diol 165 as a building unit for highly functionalised systems was demonstrated by the efficient reaction with acetyl chloride in the presence of 4-dimethylaminopyridine to afford the diester derivative 166 in 79% yield.

As with the analogous non-extended TTF systems, compound 164 is formed as a mixture of both diastereomeric and conformational isomers. Consequently, the derived products 165 and 166 are also obtained as isomeric mixtures. The presence of isomers is confirmed by the ^{1}H NMR data. This is best illustrated in the 250 MHz ^{1}H NMR spectrum of diol 165. The hydroxy protons clearly appear as two separate doublets at δ = 5.63 and 5.44 ppm. (Figure 4.3.). The doublet arises from coupling to the single proton in the adjacent methine group. The inequivalence of the peak intensities of the two doublets suggests that each corresponds to one of the two conformational isomers present, rather than arising from the diastereomers. No attempt was made to separate the diastereomers, which appear as one product on TLC.



Scheme 4.5. - Synthesis of extended-TTF derivatives with functionalised 1,3-dithiole units.

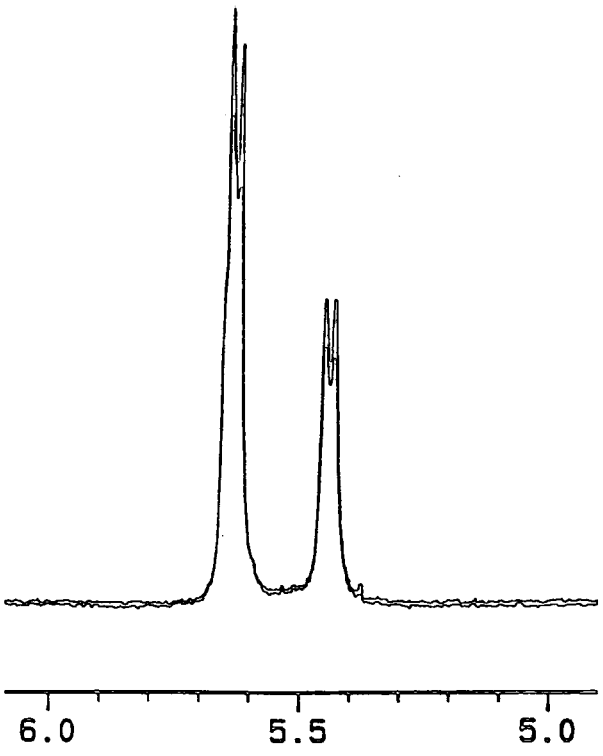


Figure 4.3. - Part ^1H NMR spectrum of diol 165 showing the two separate doublets of the hydroxy protons.

4.3 CONCLUSION

Methodology has been developed for the preparation of highly functionalised analogues of TTF containing the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene unit. These are versatile electron donor systems and can be used in the preparation of novel redox assemblies such as **158** and **159**.

It should be possible to combine the silyl protected anthraquinone and Horner-Wittig reagents **155** and **163**, respectively, to produce an extended-TTF containing functionality, both on the anthracene unit and attached to the dithiole rings. Such a donor could find widespread use in the future construction of macrocyclic and supramolecular systems.

CHAPTER FIVE

EXPERIMENTAL

5.1 GENERAL METHODS

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

Infra-red spectra were recorded on Perkin-Elmer 377, 547, 577 and 1720 FT-IR spectrophotometers; samples were either embedded in KBr discs, nujol mulls or analysed neat between KBr plates, as indicated.

Proton NMR spectra were recorded on Bruker AC 250 and Varian Gemini 200 instruments. ^{13}C NMR spectra were recorded on a Varian Unity 500 spectrometer. Chemical shifts are quoted in ppm, relative to tetramethylsilane (TMS) as internal reference (0 ppm).

Mass spectra were obtained on VG 7070E and Varian MAT 311A instruments, with ionisation modes as indicated; ammonia was used as the impingent gas for chemical ionisation mode. Plasma Desorption Mass Spectrometry was carried out on a BioIon 10 K time of flight instrument (Biosystems, Uppsala, Sweden) over 5×10^5 fissions (^{252}Cf).

Elemental analyses were performed on a Carlo-Erba Strumentazione or at the Microanalytical Lab., University of Copenhagen.

Column chromatography was carried out using Merck silica gel (70-230 mesh) or Merck alumina (activity II to III, 70-230 mesh), the latter neutralised by pre-soaking in ethyl acetate overnight. All solvents were distilled prior to use in chromatography.

Nitrogen was dried by passing through a column of phosphorus pentoxide. Solvents were dried over and distilled from the following reagents, under a dry nitrogen atmosphere: diethyl ether and THF (sodium metal); benzene and toluene (lithium aluminium hydride); chlorocarbons (phosphorus pentoxide); acetonitrile (calcium hydride); acetone (potassium carbonate); methanol (magnesium methoxide) and ethanol (magnesium ethoxide). All other reagents were reagent grade and used as supplied, unless otherwise stated.

Tetraethylammonium bis-(1,3-dithiole-2-thione-4,5-dithio) zincate 32 was prepared following the literature procedure[59] by reaction of carbon disulphide with sodium in the presence of DMF (*ca.* 80% yield).

4,5-Dimethylthio-1,3-dithiole-2-one 48 was prepared by mercuric acetate oxidation of 4,5-dimethylthio-1,3-dithiole-2-thione[88] (*ca.* 100% yield).

3-Bromo-2-(bromomethyl)propan-1-ol 54 was prepared following the literature procedure[62] by borane reduction of 3-bromo-2-(bromomethyl)-propanoic acid (*ca.* 95% yield).

4,5-Dimethyl-1,3-dithiole-2-thione 77 was prepared following the literature procedure[89] from 3-chloro-2-butanone, O-ethylxanthic acid potassium salt and phosphorus pentasulphide (*ca.* 85% yield).

4,5-Ethylenedithio-1,3-dithiole-2-one 78 was prepared following the literature procedure[54a] from zincate salt 32 and 1,2-dibromoethane, followed by mercuric acetate oxidation (*ca.* 90% yield).

4,5-[2-(Hydroxy)propylene-1,3-dithio]-1,3-dithiole-2-thione 33.

Method (a): from caesium salt 36. Caesium salt 36[60] (9.20 g, 0.02 mol) was dissolved in dry dimethylformamide (100 mL); 1,3-dichloropropan-2-ol (5.00 g, excess) was added and the mixture stirred under nitrogen at 20°C for 16 h. Precipitated caesium chloride was removed by filtration and the filtrate was evaporated to dryness *in vacuo*. The brown product was washed sequentially with water and ether, then recrystallised from ethanol, using decolourising charcoal, to afford compound 33 (3.00 g, 59%) as a yellow solid, m.p. 188-189°C. (Found: C, 28.4; H, 2.4; S, 63.2; $C_6H_6OS_5$ requires C, 28.4; H,

2.4; S, 63.0%); m/z (EI) 254 (M^+); δ_H[$(CD_3)_2SO$] 5.62 (1H, broad s), 4.04 (1H, m), 3.05 (2H, m) and 2.64 (2H, m); ν_{max}(KBr)/cm^{-1} 3436 (OH) and 1056 (C=S).

Method (b): from zincate salt 32. To a solution of zincate salt 32 (8.20 g, 11.4 mmol) in dry acetonitrile (150 mL), 1,3-dibromopropan-2-ol (5.00 g, 22.9 mmol) was added and the mixture was refluxed with stirring under nitrogen for 4 h. A highly insoluble yellow precipitate was removed by filtration and tentatively identified as *macrocycle* 34 (0.58 g, 10%), m.p. >350°C; m/z (EI) 508 (M^+). Evaporation of the filtrate *in vacuo*, followed by purification of the residue on silica gel, eluent dichloromethane afforded compound 33 (3.83 g, 66%) identical with the sample described above.

Compounds 37-39. General Procedure. To a solution of alcohol 33 (500 mg, 1.97 mmol) in dry dichloromethane (80 mL) was added either acryloyl chloride (0.19 mL, 2.34 mmol), benzoyl chloride (0.28 mL, 2.40 mmol) or 2-chloroethylisocyanate (0.20 mL, 2.35 mmol) followed by dry triethylamine (0.55 mL, 3.95 mmol). The mixture was stirred under nitrogen at 20°C for 16 h. Water (50 mL) was added and the mixture extracted into dichloromethane (2 x 50 mL). The combined organic extracts were water washed, dried ($MgSO_4$) and solvent removed *in vacuo*. Chromatography of the residue on silica gel, eluent cyclohexane/dichloromethane (2:1 v/v) afforded compounds 37-39. There was obtained:

4,5-[2-(Acrylate)propylene-1,3-dithio]-1,3-dithiole-2-thione 37.

A yellow solid (450 mg, 74%), m.p. 122-123°C (from dichloromethane/ hexane). (Found: C, 34.9; H, 2.6. $C_9H_8O_2S_5$ requires C, 35.0; H, 2.6%); m/z (DCI) 309 (M^++1); δ_H($CDCl_3$) 6.46, 6.12 and 5.92 (3H, ABX, J_{AX} = 17.2, J_{BX} = 10.3 and J_{AB} = *ca.* 1.0 Hz), 5.37 (1H, m), 3.09 (2H, m) and 2.80 (2H, m); ν_{max} (nujol)/cm^{-1} 1715, 1410, 1295, 1200, 1070, 980, 970 and 810.

4,5-[2-(Benzoate)propylene-1,3-dithio]-1,3-dithiole-2-thione 38.

A yellow solid (520 mg, 74%), m.p. 155-157°C (from dichloromethane/ hexane). (Found: C, 43.4; H, 2.7. $C_{13}H_{10}O_2S_5$ requires C, 43.5; H, 2.8%); m/z (DCI) 359 (M^++1); δ_H($CDCl_3$) 8.04 (2H, m), 7.61 (1H, m), 7.49 (2H, m), 5.58 (1H, m), 3.19 (2H, m) and 2.94 (2H, m); ν_{max}(nujol)/cm^{-1} 1720, 1600, 1340, 1270, 1235, 1100, 1065 and 710.

4,5-[2-(2-Chloroethylcarbamate)propylene-1,3-dithio]-1,3-dithiole-2-thione 39.

A yellow solid (395 mg, 56%), m.p. 222°C (sublimes) (from dichloromethane/hexane). (Found: C, 29.7; H, 2.7; N, 3.8. $C_9H_{10}ClNO_2S_5$ requires C, 30.0; H, 2.8; N, 3.9%). m/z (DCI) 360 (M^++1); δ_H($CDCl_3$) 5.30-5.20 (2H, m), 3.63 (2H, m), 3.55 (2H, t, J = 5.5 Hz), 3.08 (2H, m) and 2.79 (2H, m); ν_{max}(nujol)/cm^{-1} 3320, 1690, 1545, 1265, 1240, 1150, 1060 and 1020.

4,5-[2-(*p*-Toluenesulphonate)propylene-1,3-dithio]-1,3-dithiole-2-thione 40.

To a suspension of sodium hydride (60% dispersion in mineral oil, 90 mg, 2.25 mmol) in dry THF (100 mL) cooled to 0°C under nitrogen, was added alcohol **33** (500 mg, 1.97 mmol) and the mixture was stirred at 0°C for 1.5 h. Tosyl chloride (450 mg, 2.36 mmol) was added and the mixture allowed to warm to 20°C overnight. Work-up and purification as described for compound **37**, afforded compound **40** (595 mg, 74%) as an orange solid, m.p. 107-109°C. (Found: C, 38.2; H, 3.0. $C_{13}H_{12}O_3S_6$ requires C, 38.2; H, 3.0%); m/z (DCI) 409 (M^++1); δ_H($CDCl_3$) 7.82 (2H, d, J = 8.3 Hz), 7.39 (2H, d, J = 8.0 Hz), 4.96 (1H, m), 3.02 (2H, m), 2.73 (2H, m), and 2.48 (3H, s); ν_{max}(nujol)/ cm^{-1} 1600, 1360, 1335, 1190, 1175, 1065, 900 and 870.

4,5-[2-(*tert*-Butyl-diphenylsilyloxy)propylene-1,3-dithio]-1,3-dithiole-2-thione 41.

Alcohol 33 (2.3 g, 9.0 mmol) was dissolved in dry DMF (200 mL); imidazole (7.0 g, 0.10 mol) and *tert*-butyl-diphenylchlorosilane (3.0 g, 0.01 mol) were added and the mixture stirred at 20°C for 16 h. Dichloromethane (250 mL) was then added and the organic layer separated and washed sequentially with ice-cold hydrochloric acid (3 M, 3 x 50 mL) and water (50 mL). The organic layer was separated, dried ($MgSO_4$) and solvent removed *in vacuo*. Chromatography of the residue on silica gel, eluent dichloromethane/cyclohexane (1:1 v/v) afforded compound 41 (4.4 g, 98%) as a yellow solid, m.p. 109-111°C. (Found: C, 53.9; H, 5.0. $C_{22}H_{24}OS_5Si$ requires C, 53.7; H, 4.9%); m/z (EI) 492 (M^+); $\delta_H(CDCl_3)$ 7.62-7.48 (10H, m), 4.28 (1H, m), 2.94 (2H, m), 2.77 (2H, m) and 1.04 (9H, s); ν_{max}(KBr)/cm^{-1} 1060 (C=S).

4,5-[2-(Methoxy)propylene-1,3-dithio]-1,3-dithiole-2-thione 42.

To a solution of alcohol 33 (500 mg, 1.97 mmol) and iodomethane (0.12 mL, 1.97 mmol) in dry toluene (50 ml), was added sodium shavings (200 mg, excess) and the mixture was heated at reflux for 24 h. Filtration removed excess sodium, and aqueous work-up of the filtrate, followed by chromatography on silica gel, eluent toluene afforded compound 42 (27 mg, 5%) as a yellow solid, m.p. 76-79°C. (Found: C, 31.1; H, 2.9. $C_7H_8OS_5$ requires C, 31.3; H, 3.0%); m/z (DCI) 269 (M^++1); $\delta_H(CDCl_3)$ 3.79 (1H, m), 3.45 (3H, s), 3.06 (2H, m) and 2.61 (2H, m); ν_{max}(nujol)/cm^{-1} 1060 (C=S).

4,5-[2-(*tert*-Butyl-diphenylsilyloxy)propylene-1,3-dithio]-1,3-dithiole-2-one 43.

To a solution of thione 41 (4.5 g, 9.0 mmol) in chloroform/glacial acetic acid (100 mL, 3:1 v/v), mercuric acetate (7.0 g, excess) was added and the mixture was stirred at 20°C for 16 h after which time a white precipitate

had formed. The precipitate was removed by filtration, and the filtrate washed sequentially with saturated sodium hydrogencarbonate (3 x 100 mL) and water (100 mL), dried ($MgSO_4$) and solvent removed *in vacuo* to yield a colourless oil which crystallised upon storage *in vacuo*. There was obtained compound 43 (4.3 g, 100%), m.p. 119-120°C. (Found: C, 55.2; H, 4.9. $C_{22}H_{24}O_2S_4Si$ requires C, 55.5; H, 5.0%); m/z (DCI) 477 (M^++1); $\delta_H(CDCl_3)$ 7.63 (4H, m), 7.46 (6H, m), 4.20 (1H, m), 2.82 (2H, m), 2.61 (2H, m) and 1.04 (9H, s); ν_{max}(nujol)/cm^{-1} 3040, 1670, 1610, 1430, 1110, 1055, 840 and 740.

Bis[2-(*tert*-butyl-diphenylsilyloxy)propylene-1,3-dithio]tetrathiafulvalene 44.

Thione 41 (4.0 g, 8.5 mmol) or ketone 43 (4.0 g, 8.1 mmol) were suspended in triethylphosphite (10 mL) under nitrogen and the mixture was slowly heated to 130°C and then held at that temperature for 45 min. The mixture was cooled to 20°C and chromatographed on silica gel, eluent cyclohexane/toluene (4:1 v/v) to afford compound 44 (1.3 g, 33%, from thione 41; 1.8 g, 50%, from ketone 43) as an orange solid, m.p. 201-202°C (from dichloromethane/methanol). (Found: C, 57.4; H, 5.3. $C_{44}H_{48}O_2S_8Si_2$ requires C, 57.4; H, 5.2%); m/z (EI) 920 (M^+); $\delta_H(CDCl_3)$ 7.61 (8H, m), 7.40 (12H, m), 4.16 (2H, m), 2.70 (4H, m), 2.48 (4H, m) and 1.06 (18H, s).

Bis[2-(hydroxy)propylene-1,3-dithio]tetrathiafulvalene 45.

To a solution of compound 44 (200 mg, 0.22 mmol) in THF (50 mL) under nitrogen, tetrabutylammonium fluoride (270 mg, 0.44 mmol) was added and the mixture stirred at 20°C for 2 h. Solvent was removed *in vacuo* and the resulting orange solid was washed with methanol and ether to afford compound 45 (80 mg, 80%), m.p. >230°C (decomp.). (Found: C, 32.4; H, 3.0. $C_{12}H_{12}O_2S_8$ requires C, 32.4; H, 2.7%); m/z (DCI) 445 (M^++1); δ_H [$(CD_3)_2SO$] 5.61 (d, J = 5.0 Hz) and 5.52 (d, J = 5.0 Hz) [together 2H], 3.93 (2H, m), 2.93 (4H, m) and 2.49 (4H, m); ν_{max}(nujol)/cm^{-1} 3300 (OH).

Compounds 46 *and* 47. General Procedure. To a stirred suspension of diol 45 in dry toluene (50 mL) under nitrogen, was added acetyl chloride or 4-bromobutyryl chloride (an excess) followed by imidazole (1.00 g), and the mixture refluxed for 16 h. After hot filtration of the precipitate, the toluene was removed *in vacuo* and the residue purified by chromatography on silica gel, eluent dichloromethane. There was obtained:

Bis[2-(acetate)propylene-1,3-dithio]tetrathiafulvalene 46.

From diol 45 (220 mg) and acetyl chloride (5 mL) as an orange solid (180 mg, 69%), m.p. >230°C. (Found: C, 36.3; H, 3.0. $C_{16}H_{16}O_4S_8$ requires C, 36.4; H, 3.0); m/z (EI) 528 (M^+); $\delta_H(CDCl_3)$ 5.30 (2H, m), 2.92 (4H, m), 2.60 (4H, m) and 2.08 (6H, s).

Bis[2-(4-bromobutanoate)propylene-1,3-dithio]tetrathiafulvalene 47.

From diol 45 (140 mg) and 4-bromobutyryl chloride (3 mL), as an orange solid (100 mg, 43%), m.p. 224-225°C (from toluene). (Found: C, 32.4; H, 3.1%. $C_{20}H_{22}Br_2O_4S_8$ requires C, 32.4; H, 3.0%); m/z (EI) 742 (M^+); δ_H ($CDCl_3$) 5.30 (2H, m), 3.61 (4H, t, J = 6.5 Hz), 2.92 (4H, m), 2.55 (4H, m), 2.51 (4H, m) and 2.10 (4H, m); ν_{max}(nujol)/cm^{-1} 1733 (C=O).

4,5-Dimethylthio-4',5'-[2-(*tert*-butyl-diphenylsilyloxy)propylene-1,3-dithio] tetrathiafulvalene 49.

Ketone 43 (3.45 g, 7.25 mmol) and ketone 48 (1.52 g, 7.24 mmol) were suspended in triethylphosphite (8 mL) and the mixture warmed to 130°C with stirring under nitrogen, whereupon dissolution of the ketones was complete. After 2 h at 130°C the deep red reaction mixture was cooled to 20°C and chromatographed on silica gel, eluent cyclohexane/toluene (3:1 v/v) to afford the product as an orange solid. Compound 49, which could not be completely separated from self-coupled products (TLC and mass spectroscopic evidence) even after repeated chromatography, was obtained

(*ca.* 1.43 g, 30%). m/z (DCI) 655 (M^++1); $\delta_H(CDCl_3)$ 7.62 (4H, m), 7.41 (6H, m), 4.12 (1H, m), 2.72 (2H, m), 2.49 (2H, m), 2.38 (6H, s) and 1.06 (9H, s).

4,5-Dimethylthio-4',5'-[2-(hydroxy)propylene-1,3-dithio] tetrathiafulvalene 50.

To a solution of compound 49 (1.43 g, 2.18 mmol) in THF (80 mL), tetrabutylammonium fluoride trihydrate (1.38 g, 4.37 mmol) was added and the reaction mixture was stirred under nitrogen at 20°C for 16 h. Water (50 mL) was then added and the mixture extracted with dichloromethane (2 x 80 mL). The combined extracts were washed with water, dried ($MgSO_4$) and solvent removed *in vacuo*. Chromatography of the residue on silica gel, eluent dichloromethane afforded compound 50 (610 mg, 67%) as an orange solid, m.p. 143-144°C (from dichloromethane/hexane). (Found: C, 31.6; H, 2.8. $C_{11}H_{12}OS_8$ requires C, 31.7; H, 2.9%); m/z (DCI) 417 (M^++1); $\delta_H(CDCl_3)$ 4.39 (1H, m), 3.47 (1H, broad), 2.82 (4H, m) and 2.41 (6H, s); ν_{max}(nujol)/cm^{-1} 3440, 1290, 1170, 1030, 970, 900, 855 and 765.

Compounds 51 *and* 52. General Procedure. To a solution of compound 50 (200 mg, 0.48 mmol) in dry dichloromethane (80 mL) was added either acryloyl chloride (0.05 mL, 0.61 mmol) or 2-chloroethylisocyanate (0.05 mL, 0.59 mmol) followed by dry triethylamine (0.13 mL, 0.93 mmol) and the mixture stirred at 20°C for 16 h. Water (50 mL) was then added and the mixture extracted with dichloromethane (2 x 50 mL). The combined extracts were washed with water, dried ($MgSO_4$) and solvent removed *in vacuo*. Chromatography of the residue on silica gel, eluent dichloromethane afforded the product. There was obtained:

4,5-Dimethylthio-4′,5′-[2-(acrylate)propylene-1,3-dithio] tetrathiafulvalene 51.

A yellow solid (70 mg, 31%), m.p. 156-157°C (from dichloromethane/ hexane). (Found: C, 35.5; H, 3.0. $C_{14}H_{14}O_2S_8$ requires C, 35.7; H, 3.0%); m/z (DCI) 471 (M^++1); $\delta_H(CDCl_3)$ 6.45, 6.11 and 5.90 (3H, ABX, J_{AX} = 17.0, J_{BX} = 10.7 and J_{AB} = *ca.* 1.0 Hz), 5.30 (1H, m), 2.95 (2H, m), 2.67 (2H, m) and 2.41 (6H, s); ν_{max}(nujol)/cm^{-1} 1720, 1620, 1425, 1410, 1330, 1270, 1195 and 1045.

4,5-Dimethylthio-4′,5′-[2-(2-chloroethylcarbamate)propylene-1,3-dithio] tetrathiafulvalene 52.

A yellow solid (200 mg, 80%), m.p. 219-221°C (from dichloromethane/ hexane). (Found: C, 32.0; H, 3.0; N, 2.7. $C_{14}H_{16}ClNO_2S_8$ requires C, 32.3; H, 3.1; N, 2.7%); m/z (DCI) 522 (M^++1); $\delta_H(CDCl_3)$ 5.16 (2H, m), 3.62 (2H, m), 3.54 (2H, t, J = 5.5 Hz), 2.95 (2H, m), 2.64 (2H, m) and 2.41 (6H, s); ν_{max} (nujol)/cm^{-1} 3300, 1695, 1550, 1270, 1240, 1150, 1020 and 770.

4,5-[2-(Hydroxymethyl)propylene-1,3-dithio]-1,3-dithiole-2-thione 55.

To a solution of zincate salt 32 (6.97 g, 9.73 mmol) in dry acetonitrile (100 mL), 3-bromo-2-(bromomethyl)-propan-1-ol (4.51 g, 19.44 mmol) was added and the reaction refluxed with stirring under nitrogen for 4-5 h. Chromatography of the crude reaction mixture on silica gel, eluent dichloromethane/acetone (5:1 v/v) afforded compound 55 (4.10 g, 79%) as an orange solid, m.p. 128-130°C. (Found: C, 31.6; H, 3.0; $C_7H_8OS_5$ requires C, 31.3; H, 3.0%); m/z (DCI) 269 (M^++1); $\delta_H[(CD_3)_2CO]$ 4.07 (1H, t, J = 5.2 Hz), 3.71 (2H, m), 3.16 (2H, m), 2.81 (2H, m) and 2.47 (1H, m); ν_{max}(nujol)/cm^{-1} 3300, 1265, 1230, 1060, 1025, 1005, 895 and 815.

4,5-[2-(*tert*-Butyl-diphenylsilyloxymethyl)propylene-1,3-dithio]-1,3-dithiole-2-thione 56.

To a solution of alcohol 55 (700 mg, 2.61 mmol) in DMF (80 mL), *tert*-butyl-diphenylchlorosilane (1.44 g, 5.24 mmol) and imidazole (1.78 g, 26.2 mmol) was added and the reaction stirred under nitrogen at 20°C for 16 h. The DMF was removed *in vacuo* and the residue dissolved in dichloromethane, washed with water, dried ($MgSO_4$) and solvent removed *in vacuo*. Chromatography of the residue on silica gel, eluent dichloromethane/cyclohexane (1:1 v/v) afforded compound 56 (1.10 g, 83%) as a viscous orange oil. m/z (DCI) 507 (M^++1); δ_H($CDCl_3$) 7.63 (4H, m), 7.38 (6H, m), 3.73 (2H, d, J = 6.1 Hz), 2.96 (2H, m), 2.66 (2H, m), 2.52 (1H, m) and 1.06 (9H, s); ν_{max}(nujol)/cm^{-1} 3070, 1430, 1110, 1090, 1065, 830, 820 and 700.

4,5-[2-(*tert*-Butyl-diphenylsilyloxymethyl)propylene-1,3-dithio]-1,3-dithiole-2-one 57.

To a solution of thione 56 (1.10 g, 2.17 mmol) in chloroform/glacial acetic acid (100 mL, 3:1 v/v), mercuric acetate (an excess) was added and the reaction stirred under nitrogen at 20°C for 16 h. Water was added and the reaction mixture stirred for an additional 0.5 h whence the resulting white precipitate was removed by filtration. The organic phase was washed with a solution of sodium hydrogencarbonate, dried ($MgSO_4$) and solvent removed *in vacuo* to afford compound 57 (1.03 g, 97%) as a viscous colourless oil. m/z (DCI) 508 (M^++18); δ_H($CDCl_3$) 7.64 (4H, m), 7.39 (6H, m), 3.73 (2H, d, J = 5.9 Hz), 2.93 (2H, m), 2.62 (2H, m), 2.46 (1H, m) and 1.06 (9H, s); ν_{max}(nujol)/cm^{-1} 3070, 1670, 1620, 1430, 1100, 820, 735 and 700.

Bis[2-(*tert*-butyl-diphenylsilyloxymethyl)propylene-1,3-dithio] tetrathiafulvalene 58.

A solution of ketone 57 (1.28 g, 2.61 mmol) in neat triethylphosphite (5 mL) was heated to 130°C and held at this temperature with stirring under

nitrogen for 2 h. Chromatography of the crude reaction mixture on silica gel, eluent dichloromethane/cyclohexane (1:1 v/v) afforded compound **58** (680 mg, 55%) as an orange solid, m.p. 72-74°C. (Found: C, 58.1; H, 5.6. $C_{46}H_{52}O_2Si_2S_8$ requires C, 58.2; H, 5.5%); m/z (DCI) 949 ($M^+ + 1$); $\delta_H(CDCl_3)$ 7.63 (8H, m), 7.42 (12H, m), 3.69 (4H, m), 2.86 (4H, m), 2.62-2.45 (6H, m) and 1.04 (18H, s); ν_{max}(KBr)/cm^{-1} 3068, 2928, 2855, 1427, 1111, 824, 702 and 504.

Bis[2-(hydroxymethyl)propylene-1,3-dithio]tetrathiafulvalene 59.

To a solution of compound **58** (600 mg, 0.63 mmol) in THF (50 mL), tetrabutylammonium fluoride (1 M in THF, 2.53 mL, 2.53 mmol) was added and the reaction stirred under nitrogen at 20°C for 16 h. The solvent was removed *in vacuo* and methanol added to precipitate an orange solid. Stirring in methanol was continued for 1 h after which the product was filtered off and washed with ether and methanol to afford compound **59** (170 mg, 57%) as an orange solid, m.p. >230°C (decomp.). (Found: C, 35.3; H, 3.4. $C_{14}H_{16}O_2S_8$ requires C, 35.6; H, 3.4%); m/z (EI) 472 (M^+); $\delta_H[(CD_3)_2SO]$ 4.83 (2H, m), 3.53 (d, J = 6.2 Hz) and 3.46 (d, J = 6.3 Hz) [together 4H], 2.93 (4H, m), 2.55 (4H, m) and 2.22 (2H, m); ν_{max}(KBr)/cm^{-1} 3400, 2917, 1399, 1384, 1062, 1031, 894 and 771.

4,5-Dimethylthio-4',5'-[2-(*tert*-butyl-diphenylsilyloxymethyl)propylene-1,3-dithio]tetrathiafulvalene 60 and 4,5-Dimethylthio-4',5'-[2-(hydroxymethyl) propylene-1,3-dithio]tetrathiafulvalene 61.

A suspension of ketone **48** (430 mg, 2.05 mmol) and ketone **57** (1.00 g, 2.04 mmol) in neat triethylphosphite (5 mL) was warmed to 130°C upon which dissolution was complete. The reaction was maintained with stirring under nitrogen at this temperature for 2 h after which time the solution had turned deep red. Chromatography of the crude reaction mixture on silica gel, eluent cyclohexane/dichloromethane (3:1 v/v) afforded a mixture of the

cross-coupled product 60 along with self-coupled products, which could not be separated by chromatography.

The mixture of products was dissolved in THF (50 mL) and tetrabutylammonium fluoride (1 M in THF, 4.10 mL, 4.10 mmol) was added and the reaction stirred under nitrogen at 20°C for 16 h. Chromatography of the crude reaction mixture on silica gel, eluent dichloromethane/acetone (5:1 v/v) followed by recrystallisation from dichloromethane/hexane afforded compound 61 (300 mg, 34% overall yield) as an orange solid, m.p. 128-130°C. (Found: C, 33.0; H, 3.2. $C_{12}H_{14}OS_8$ requires C, 33.5; H, 3.3%); m/z (DCI) 431 (M^++1); $\delta_H(CDCl_3)$ 3.78 (2H, d, J = 6.0 Hz), 2.89 (2H, m), 2.58 (2H, m), 2.45 (1H, m) and 2.41 (6H, s); ν_{max}(nujol)/cm^{-1} 3300, 1310, 1280, 1060, 1030, 960, 890 and 770.

4,5-Dimethylthio-4',5'-[2-(methyl-*p*-toluenesulphonate)propylene-1,3-dithio] tetrathiafulvalene 62.

To a solution of alcohol 61 (400 mg, 0.93 mmol) in dry dichloromethane (60 mL), tosyl chloride (240 mg, 1.26 mmol) followed by 4-dimethylaminopyridine (140 mg, 1.15 mmol) was added and the reaction stirred under nitrogen at 20°C for 16 h. Chromatography of the crude reaction mixture on silica gel, eluent dichloromethane followed by recrystallisation from dichloromethane/hexane afforded compound 62 (300 mg, 55%) as a yellow solid, m.p. 135-136°C. (Found: C, 39.0; H, 3.5. $C_{19}H_{20}O_3S_9$ requires C, 39.0; H, 3.5%); m/z (DCI) 585 (M^++1); $\delta_H(CDCl_3)$ 7.77 (2H, d, J = 8.2 Hz), 7.36 (2H, d, J = 8.1 Hz), 4.23 (2H, d, J = 3.5 Hz), 2.78 (2H, m), 2.67-2.54 (3H, m), 2.45 (3H, s) and 2.39 (6H, s); ν_{max}(KBr)/cm^{-1} 2918, 1597, 1360, 1174, 970, 821, 665 and 553.

4,5-Dimethylthio-4',5'-[2-(chloromethyl)propylene-1,3-dithio] tetrathiafulvalene 63.

To a solution of alcohol **61** (600 mg, 1.40 mmol) in dry dichloromethane (60 mL), tosyl chloride (400 mg, 2.09 mmol) and dry triethylamine (1.95 mL, 14.0 mmol) was added and the reaction refluxed under nitrogen with stirring for 48 h. Chromatography of the crude reaction mixture on silica gel, eluent dichloromethane/hexane (1:1 v/v) afforded initially chloride **63** (280 mg, 45%). Continued elution with dichloromethane gave tosylate **62** (230 mg, 28%). Compound **63**:- an orange solid, m.p. 147-149°C. (Found: C, 32.1; H, 2.9. $C_{12}H_{13}ClS_8$ requires C, 32.1; H, 2.9%); m/z (DCI) 449 (M^++1); $\delta_H(CDCl_3)$ 3.78 (2H, d, J = 5.6 Hz), 2.93 (2H, m), 2.77-2.62 (3H, m) and 2.42 (6H, s); $\nu_{max}(KBr)/cm^{-1}$ 2915, 1426, 1411, 1267, 898, 882, 768 and 753.

4,5-Dimethylthio-4',5'-[2-(methyl-methanesulphonate)propylene-1,3-dithio] tetrathiafulvalene 64.

To a solution of alcohol **61** (500 mg, 1.16 mmol) in dry dichloromethane (60 mL), methanesulphonylchloride (0.10 mL, 1.29 mmol) followed by 4-dimethylaminopyridine (175 mg, 1.43 mmol) was added and the reaction stirred under nitrogen at 20°C for 16 h. Chromatography of the crude reaction mixture on silica gel, eluent dichloromethane afforded compound **64** (450 mg, 76%) as an orange oil. The product was characterised by ^1H NMR and then immediately used in further reactions. $\delta_H(CDCl_3)$ 4.46 (2H, broad s), 3.05 (3H, s), 2.88 (2H, m), 2.79-2.67 (3H, m) and 2.40 (6H, s).

4,5-Dimethylthio-4',5'-[2-(N-methyl-phthalimide)propylene-1,3-dithio] tetrathiafulvalene 67.

To a solution of chloride **63** (200 mg, 0.45 mmol) in dry DMF (50 mL), potassium phthalimide (110 mg, 0.59 mmol) was added and the reaction refluxed with stirring under nitrogen for 3 h. Water was added and the

product extracted into dichloromethane, washed with water, dried ($MgSO_4$) and solvent removed *in vacuo*. Chromatography of the residue on silica gel, eluent dichloromethane afforded compound **67** (100 mg, 40%) as an orange solid, m.p. 180-182°C. (Found: C, 42.8; H, 3.0; N, 2.4. $C_{20}H_{17}NO_2S_8$ requires C, 42.9; H, 3.1; N, 2.5%); m/z (DCI) 560 (M^++1); $\delta_H(CDCl_3)$ 7.84 (2H, m), 7.75 (2H, m), 3.86 (2H, broad s), 2.87 (2H, m), 2.73-2.52 (3H, m) and 2.41 (6H, s); ν_{max} (KBr)/cm^{-1} 2917, 1710, 1431, 1397, 1367, 1046, 899 and 718.

4,5-Dimethylthio-4',5'-[2-(cyanomethyl)propylene-1,3-dithio] tetrathiafulvalene 68.

To a solution of mesylate **64** (720 mg, 1.42 mmol) in dry DMF (40 mL), sodium cyanide (90 mg, 1.84 mmol) was added and the reaction heated to 90°C and maintained at this temperature with stirring under nitrogen for 2 h. The solvent was removed *in vacuo* and dichloromethane added. The product was washed with water, dried ($MgSO_4$) and solvent removed *in vacuo*. Chromatography of the residue on silica gel, eluent dichloromethane followed by recrystallisation from dichloromethane/ hexane afforded compound **68** (410 mg, 66%) as an orange solid, m.p. 166-168°C. (Found: C, 35.2; H, 2.9; N, 3.0. $C_{13}H_{13}NS_8$ requires C, 35.5; H, 3.0; N, 3.2%); m/z (DCI) 440 (M^++1); $\delta_H(CDCl_3)$ 2.95-2.68 (7H, m) and 2.41 (6H, s); ν_{max}(KBr)/cm^{-1} 2918, 2247, 1422, 1283, 1174, 976, 881 and 769.

4,5-[2-(Oxo)propylene-1,3-dithio]-1,3-dithiole-2-thione 70.

To a solution of the zinc complex **32** (1.17 g, 1.64 mmol) in dry acetonitrile (100 mL), 1,3-dichloroacetone (0.50 g, 3.94 mmol) was added and the reaction refluxed with stirring under nitrogen for 2-3 h, after which time the solution had changed from a deep red to an orange colour. Acetonitrile was removed *in vacuo* and the residue dissolved in dichloromethane and washed with water, dried ($MgSO_4$) and solvent removed *in vacuo*. Chromatography of the residue on silica gel, eluent dichloromethane

afforded compound 70 (630 mg, 76%) as an orange solid, m.p. 153-156°C. (Found: C, 28.8; H, 1.5. $C_6H_4OS_5$ requires C, 28.5; H, 1.6%); m/z (EI) 252 (M^+); $\delta_H(CDCl_3)$ 3.50 (4H, s); $\delta_C(CDCl_3)$ 42.71 (CH_2), 138.96 (C=C), 200.24 (C=O) and 208.72 (C=S); ν_{max}(nujol)/cm^{-1} 1705, 1670, 1405, 1250, 1180, 1150, 1050 and 1020.

4,5-[2-(Oxo)propylene-1,3-dithio]-1,3-dithiole-2-one 71.

To a solution of compound 70 (100 mg, 0.40 mmol) in chloroform/ glacial acetic acid (30 mL, 3:1 v/v), mercuric acetate (an excess) was added. The reaction was stirred under nitrogen at 20°C for 2 h, after which time a white precipitate had formed. The precipitate was removed by filtration and the filtrate washed sequentially with water and a solution of sodium hydrogencarbonate, dried ($MgSO_4$) and solvent removed *in vacuo*. Chromatography of the residue on silica gel, eluent dichloromethane afforded compound 71 (95 mg, 100%) as a white solid, m.p. 184-187°C (decomp.). (Found: C, 30.8; H, 1.9. $C_6H_4O_2S_4$ requires C, 30.5; H, 1.7%); m/z (EI) 236 (M^+); $\delta_H(CDCl_3)$ 3.46 (4H, s); $\delta_C(CDCl_3)$ 42.80 (CH_2), 130.60 (C=C), 187.39 (C=O) and 200.85 (C=O); ν_{max}(nujol)/cm^{-1} 1700, 1670, 1610, 1250, 1200, 1160, 895 and 750.

4,5-[2-(Ethyleneketal)propylene-1,3-dithio]-1,3-dithiole-2-one 72.

To a solution of compound 71 (130 mg, 0.55 mmol) in dry toluene (50 mL), ethylene glycol (0.04 mL, 0.66 mmol) and conc. sulphuric acid (3 drops) were added. A Dean-Stark apparatus was assembled and the reaction refluxed with stirring under nitrogen for 2-3 h. The organic phase was washed with a solution of sodium hydrogencarbonate, dried ($MgSO_4$) and solvent removed *in vacuo* to afford compound 72 (130 mg, 84%) as a white solid, m.p. 143-145°C. (Found: C, 34.4; H, 2.8. $C_8H_8O_3S_4$ requires C, 34.3; H, 2.9%); m/z (CI) 280 (M^+); $\delta_H(CDCl_3)$ 4.03 (4H, s) and 2.75 (4H, s); ν_{max}(nujol)/ cm^{-1} 1670, 1615, 1250, 1110, 1080, 1025, 980 and 900.

Bis[2-(ethyleneketal)propylene-1,3-dithio]tetrathiafulvalene 73.

Compound 72 (0.75 g, 2.68 mmol) was placed in triethylphosphite (8 mL) and the mixture heated to 130°C, upon which dissolution occurred. The reaction mixture was maintained at this temperature with stirring under nitrogen for 2 h. The solution was allowed to cool to 20°C and methanol added. The precipitated solid was filtered off and purified by chromatography on silica gel, eluent dichloromethane to afford compound 73 (465 mg, 66%) as a yellow solid, m.p. > 230°C. (Found: C, 36.0; H, 2.9. $C_{16}H_{16}O_4S_8$ requires C, 36.3; H, 3.1%); m/z (DCl) 529 (M^++1); $\delta_H(CDCl_3)$ 3.93 (8H, s) and 2.53 (8H, s); ν_{max}(nujol)/cm^{-1} 1250, 1110, 1020, 980, 945, 895, 720 and 670.

Bis[2-(oxo)propylene-1,3-dithio]tetrathiafulvalene 74.

A solution of compound 73 (100 mg, 0.19 mmol) in THF (75 mL) was acidified with conc. sulphuric acid (10 mL) and the reaction mixture refluxed with stirring under nitrogen for 16 h. The solution was cooled to 20°C and the precipitated solid filtered off and washed with methanol to afford compound 74 (75 mg, 87%) as an orange solid, m.p. >340°C. (Found: C, 32.5; H, 1.7. $C_{12}H_8O_2S_8$ requires C, 32.7; H, 1.8%); m/z (DCl) 441 (M^++1); δ_H [$(CD_3)_2SO$] 3.46 (8H, s); ν_{max}(nujol)/cm^{-1} 1705, 1250, 1190, 1160, 1060, 900, 770 and 720.

Compounds **79-82**. General Procedure. A mixture of compound **72** (1 mol equiv) and either thione **76** or **77** (3 mol equiv) or ketone **48** or **78** (1 mol equiv) were suspended in triethylphosphite (*ca.* 5 mL) and heated to 130°C with stirring under nitrogen and maintained at this temperature for 2 h. The solution was cooled to 20°C and dichloromethane added. The solution was washed with water, dried ($MgSO_4$) and solvent removed *in vacuo*. Chromatography of the residue on silica gel, eluting initially with hexane/

dichloromethane (3:1 v/v) gradually changing to hexane/dichloromethane (1:1 v/v) afforded the required products. There was obtained:

4,5-[2-(Ethyleneketal)propylene-1,3-dithio]tetrathiafulvalene 79.

[From compound 72 (250 mg, 0.89 mmol) and compound 76 (360 mg, 2.69 mmol)] an orange solid (120 mg, 37%), m.p. 200-203°C. (Found: C, 35.8; H, 2.8. $C_{11}H_{10}O_2S_6$ requires C, 36.0; H, 2.7%); m/z (DCI) 367 (M^++1); δ_H [$(CD_3)_2CO$] 6.66 (2H, s), 4.05 (4H, s) and 2.87 (4H, s); ν_{max}(nujol)/cm^{-1} 3070, 1410, 1250, 1100, 1020, 985, 900 and 795.

4,5-Dimethyl-4',5'-[2-(ethyleneketal)propylene-1,3-dithio] tetrathiafulvalene 80.

[From compound 72 (160 mg, 0.57 mmol) and compound 77 (280 mg, 1.73 mmol)] an orange solid (45 mg, 20%), m.p. 218-220°C. (Found: C, 39.4; H, 3.6. $C_{13}H_{14}O_2S_6$ requires C, 39.6; H, 3.6%); m/z (DCI) 395 (M^++1); δ_H ($CDCl_3$) 4.05 (4H, s), 2.70 (4H, s) and 1.93 (6H, s); ν_{max}(nujol)/cm^{-1} 1250, 1100, 1020, 970, 950, 900, 775 and 720.

4,5-Dimethylthio-4',5'-[2-(ethyleneketal)propylene-1,3-dithio] tetrathiafulvalene 81.

[From compound 72 (300 mg, 1.07 mmol) and compound 48 (225 mg, 1.07 mmol)] an orange solid (90 mg, 18%), m.p. 152-154°C. (Found: C, 34.0; H, 3.2. $C_{13}H_{14}O_2S_8$ requires C, 34.0; H, 3.1%); m/z (DCI) 459 (M^++1); δ_H ($CDCl_3$) 4.06 (4H, s), 2.72 (4H, s) and 2.41 (6H, s); ν_{max}(nujol)/cm^{-1} 1250, 1110, 1090, 1020, 980, 940, 910 and 770.

4,5-Ethylenedithio-4',5'-[2-(ethyleneketal)propylene-1,3-dithio] tetrathiafulvalene 82.

[From compound 72 (400 mg, 1.43 mmol) and compound 78 (300 mg, 1.44 mmol)] an orange solid (165 mg, 25%), m.p. 226-228°C. (Found: C, 34.0;

H, 2.5. $C_{13}H_{12}O_2S_8$ requires C, 34.2; H, 2.6%); m/z (DCl) 457 (M^++1); δ_H ($CDCl_3$) 4.07 (4H, s), 3.29 (4H, s) and 2.72 (4H, s); ν_{max}(nujol)/cm^{-1} 1245, 1100, 1080, 1015, 975, 940, 890 and 765.

Compounds 83-86. General Procedure. A solution of ketal 79-82 in THF was acidified with conc. sulphuric acid and the mixture refluxed with stirring under nitrogen for 16 h. Water was added and the product extracted into dichloromethane. The organic layer was separated, washed with a solution of sodium hydrogencarbonate, dried ($MgSO_4$) and the solvent removed *in vacuo*. The products were purified by chromatography on silica gel with dichloromethane/hexane mixtures as the eluting solvent. There was obtained:

4,5-[2-(Oxo)propylene-1,3-dithio]tetrathiafulvalene 83.

[From compound **79** (70 mg, 0.19 mmol) in THF (50 mL) and conc. sulphuric acid (5 mL)] as an orange solid (58 mg, 94%) which exhibits two distinct crystalline forms: needles, m.p. 186-187°C (decomp.) and cubes, m.p. 179-182°C (decomp.). (Found: C, 33.7; H, 1.7. $C_9H_6OS_6$ requires C, 33.5; H, 1.9%); m/z (DCl) 323 (M^++1); δ_H($CDCl_3$) 6.35 (2H, s) and 3.34 (4H, s); ν_{max} (nujol)/cm^{-1} 3060, 1700, 1415, 1400, 1180, 795, 770 and 660.

4,5-Dimethyl-4',5'-[2-(oxo)propylene-1,3-dithio]tetrathiafulvalene 84.

[From compound **80** (40 mg, 0.10 mmol) in THF (25 mL) and conc. sulphuric acid (3 mL)] as a red solid (33 mg, 93%), m.p. 220-222°C. (Found: C, 37.8; H, 3.0. $C_{11}H_{10}OS_6$ requires C, 37.7; H, 2.9%); m/z (DCl) 351 (M^++1); δ_H ($CDCl_3$) 3.33 (4H, s) and 1.96 (6H, s); ν_{max}(nujol)/cm^{-1} 1700, 1250, 1180, 1150, 1090, 900, 775 and 720.

4,5-Dimethylthio-4′,5′-[2-(oxo)propylene-1,3-dithio]tetrathiafulvalene 85.

[From compound 81 (60 mg, 0.13 mmol) in THF (30 mL) and conc. sulphuric acid (4 mL)] as an orange solid (50 mg, 92%), m.p. 175-178°C. (Found: C, 31.9; H, 2.5. $C_{11}H_{10}OS_8$ requires C, 31.9; H, 2.4%); m/z (DCI) 415 (M^++1); $\delta_H(CDCl_3)$ 3.35 (4H, s) and 2.43 (6H, s); ν_{max}(nujol)/cm^{-1} 1700, 1245, 1185, 1060, 960, 895, 885 and 760.

4,5-Ethylenedithio-4′,5′-[2-(oxo)propylene-1,3-dithio]tetrathiafulvalene 86.

[From compound 82 (140 mg, 0.31 mmol) in THF (100 mL) and conc. sulphuric acid (10 mL)] as a yellow solid (120 mg, 95%), m.p. 218-220°C. (Found: C, 31.8; H, 1.8. $C_{11}H_8OS_8$ requires C, 32.0; H, 2.0%); m/z (DCI) 413 (M^++1); $\delta_H(CDCl_3)$ 3.34 (4H, s) and 3.30 (4H, s); ν_{max}(nujol)/cm^{-1} 1710, 1405, 1300, 1250, 1180, 1105, 1060 and 770.

4,5-Dimethyl-4′,5′-[2-(hydroxy)propylene-1,3-dithio]tetrathiafulvalene 87.

To a solution of compound 84 (60 mg, 0.17 mmol) in dry THF (60 mL), lithium aluminium hydride (an excess) was added and the mixture stirred at 20°C for 1 h. Water was slowly added and the product extracted into dichloromethane, washed with water, dried ($MgSO_4$) and solvent removed *in vacuo*. Chromatography of the residue on silica gel, eluent dichloromethane afforded compound 87 (55 mg, 90%) as a dark orange solid, m.p. 207-210°C. m/z (DCI) 353 (M^++1); $\delta_H(CDCl_3)$ 4.39 (1H, m), 3.48 (1H, broad), 2.81 (4H, m) and 1.94 (6H, s); ν_{max}(nujol)/cm^{-1} 3400, 2920, 1410, 1380, 1285, 1260, 1175 and 1060.

4,5-[2-(Ethyleneketal)propylene-1,3-dithio]-4′,5′-[2-(*tert*-butyl-diphenyl-silyloxy)propylene-1,3-dithio]tetrathiafulvalene 88.

Compound 43 (1.0 g, 2 mmol) and compound 72 (0.6 g, 2 mmol) were suspended together in triethylphosphite (10 mL) following the procedure reported for compound 49 and heated to 130°C with stirring under nitrogen

for 2 h. Chromatography on silica gel, eluent dichloromethane/hexane (1:1 v/v) cleanly separated compound **88** from the self-coupled products **44** and **73**. Compound **88** was isolated (270 mg, 37%) as an orange solid, m.p. >230°C. (Found: C, 49.5; H, 4.4. $C_{30}H_{32}O_3S_8Si$ requires C, 49.7; H, 4.4%); m/z (EI) 724 (M^+); $\delta_H(CDCl_3)$ 7.62 (4H, m), 7.41 (6H, m), 4.09 (1H, m), 4.05 (4H, s), 2.70 (6H, m), 2.52 (2H, m) and 1.05 (9H, s).

5.3 EXPERIMENTAL TO CHAPTER THREE

1,3,5-Tris(bromomethyl)benzene was prepared following the literature procedure[90] by reductive bromination of trimethyl 1,3,5-benzene-tricarboxylate (*ca.* 60% yield).

3,5-Dihydroxy-benzyl alcohol was prepared following the literature procedure[91]. M.p. 187-189°C (lit. 189°C[91]).

4,5-Bis[2-(hydroxy)ethylthio]-1,3-dithiole-2-thione 138 was prepared following the literature procedure[82] from 4,5-di(benzoylthio)-1,3-dithiole-2-thione **35** and 2-chloroethanol (*ca.* 80% yield).

Tetrathiafulvalene carbonyl chloride was prepared following the literature procedure[83] from TTF-carboxylic acid and oxalyl chloride (*ca.* 60% yield).

General Procedure. **Generation and Trapping of TTF-thiolate Anion 114.** *Preparation of Compounds* **115** *and* **116.** Into a stirred solution of TTF **1** (500 mg, 2.5 mmol) in dry ether (50 mL) at -78°C under nitrogen, was syringed a freshly-prepared solution of LDA [obtained from di-isopropylamine (0.40 mL, 2.9 mmol) and *n*-butyllithium (1.6 M, 1.80 mL, 2.9 mmol) in dry ether (7 mL) at -78°C] over a period of 10 min. A yellow precipitate of monolithiated-TTF began to form after *ca.* 10 min, and stirring was continued for a further

45 min at -78°C. Elemental sulphur (100 mg, 3.1 mmol) was then added in one portion against a positive pressure of nitrogen and stirring was continued at -78°C for 7 h, after which time either 1,3-bis(bromomethyl) benzene (320 mg, 1.2 mmol) or 1,3,5-tris(bromomethyl)benzene (175 mg, 0.5 mmol) was added. The mixture was stirred at -78°C for 2 h and then slowly warmed to 20°C over 12 h. Water (60 mL) was added and the mixture extracted into dichloromethane (4 x 50 mL), the combined extracts were washed with water (50 mL), dried ($MgSO_4$) and the solvent removed *in vacuo*. Chromatography of the residue on silica gel, eluting first with hexane/dichloromethane (4:1 v/v) gave unreacted TTF 1 (*ca.* 100 mg, 20%) then with dichloromethane to afford the products. There was obtained:

α,α'-Bis(tetrathiafulvalenylthio)-*m*-xylene 115.

A yellow solid (70 mg, 10%), m.p. 73-75°C (from ether/methanol). (Found: C, 41.4; H, 2.3. $C_{20}H_{14}S_{10}$ requires C, 41.8; H, 2.5%); m/z (DCI) 575 (M^++1); $\delta_H(CDCl_3)$ 7.28-7.13 (4H, m), 6.30 (4H, s), 6.11 (2H, s) and 3.89 (4H, s); ν_{max}(KBr)/cm^{-1} 3060, 1085, 930, 790, 770, 730, 700 and 630.

α,α',α''-Tris(tetrathiafulvalenylthio)-mesitylene 116.

An orange solid (70 mg, 17%), m.p. 49-52°C (from ether/methanol). (Found: C, 39.1; H, 2.1. $C_{27}H_{18}S_{15}$ requires C, 39.4; H, 2.2%); $\delta_H(CDCl_3)$ 7.06 (3H, s), 6.32 (6H, s), 6.13 (3H, s) and 3.86 (6H, s); ν_{max}(KBr)/cm^{-1} 3060, 1600, 930, 790, 770, 730, 705 and 640.

4,5-(Ethylenedithio)tetrathiafulvalene 118.

To an ethereal slurry of anion **11** [obtained from TTF **1** (250 mg, 1.23 mmol) as described above] at -78°C, was added elemental sulphur (60 mg, 1.84 mmol) and the reaction mixture was maintained at -78°C for 7 h. 1,2-dibromoethane (0.1 mL, 1.23 mmol) dissolved in dry ether (2 mL) was added dropwise over 2 min. The resulting orange solution was allowed to warm to

20°C over 16 h. Standard aqueous workup, with extraction into toluene, followed by chromatography on silica gel, eluent cyclohexane/toluene (3:1 v/v) gave an analytically pure product (35-75 mg, 10-20%), m.p. 199°C (lit.[79] 200°C).

Compounds 121 *and* 122. General Procedure. Reaction conditions and molar ratios were identical with those described above for the preparation of compounds 115 and 116 using either acetyl chloride (0.21 mL, 2.94 mmol) or benzoyl chloride (0.34 mL, 2.92 mmol). There was obtained:

4-(Acetylthio)tetrathiafulvalene 121.

An orange solid (540 mg, 79%), m.p. 109-110°C (from dichloromethane/hexane). (Found: C, 34.2; H, 2.1. $C_8H_6OS_5$ requires C, 34.5; H, 2.2%); m/z (DCI) 279 (M^++1); $\delta_H(CDCl_3)$ 6.50 (1H, s), 6.32 (2H, s) and 2.39 (3H, s); ν_{max}(nujol)/cm^{-1} 3060, 1700, 1110, 940, 795, 780, 660 and 610.

4-(Benzoylthio)tetrathiafulvalene 122.

An orange solid (650 mg, 78%), m.p. 126-127°C (from dichloromethane/cyclohexane). (Found: C, 45.6; H, 2.2. $C_{13}H_8OS_5$ requires C, 45.8; H, 2.4%); m/z (DCI) 341 (M^++1); $\delta_H(CDCl_3)$ 7.93 (2H, m), 7.63 (1H, m), 7.48 (2H, m), 6.60 (1H, s) and 6.32 (2H, s); ν_{max}(nujol)/cm^{-1} 3060, 1680, 1210, 1180, 895, 800, 680 and 640.

Compounds **124-126**. General Procedure. A suspension of thioester **122** (200 mg, 0.59 mmol) in dry ethanol (100 mL) was cooled to -10°C under nitrogen and sodium ethoxide (4.6 mL of an 0.14 M solution in dry ethanol, 0.64 mmol) was added and the mixture stirred at -10°C for 0.5 h. This solution was then added dropwise to an excess of the electrophile (either iodomethane, 1,3-diiodopropane or 1,4-diiodobutane) over a period of 0.5 h. The reaction mixture was stirred at -10°C for 2 h and then allowed to warm

to 20°C. Ethanol was removed *in vacuo* and the residue dissolved in dichloromethane, washed with water, dried ($MgSO_4$) and solvent removed *in vacuo*. Chromatography of the residue on silica gel, eluent cyclohexane/ toluene (3:1 v/v) afforded the products. There was obtained:

4-(Methylthio)tetrathiafulvalene **124**.

An orange oil (142 mg, 96%). m/z (DCI) 251 (M^++1); $\delta_H(CDCl_3)$ 6.32 (2H, s), 6.28 (1H, s) and 2.39 (3H, s); ν_{max}(neat)/cm^{-1} 3060, 2920, 1520, 1430, 1310, 930, 790 and 770.

4-[3-(Iodo)propylthio]tetrathiafulvalene **125**.

A yellow oil (120 mg, 50%). m/z (DCI) 405 (M^++1); $\delta_H(CDCl_3)$ 6.38 (1H, s), 6.32 (2H, s), 3.28 (2H, t, J = 6.8 Hz), 2.85 (2H, t, J = 6.9 Hz), 2.11 (2H, pentet, J = 6.8 Hz); ν_{max}(neat)/cm^{-1} 3060, 1530, 1420, 1210, 930, 800, 775 and 640.

4-[4-(Iodo)butylthio]tetrathiafulvalene **126**.

A yellow oil (106 mg, 43%). m/z (DCI) 419 (M^++1); $\delta_H(CDCl_3)$ 6.37 (1H, s), 6.32 (2H, s), 3.19 (2H, t, J = 6.8 Hz), 2.76 (2H, t, J = 7.1 Hz), 1.93 (2H, m) and 1.74 (2H, m); ν_{max}(neat)/cm^{-1} 3060, 1525, 1265, 1200, 930, 795, 775 and 640.

Compounds **127** *and* **128**. General Procedure. To a solution of the sodium thiolate salt **123**, generated from thioester **122** (100 mg, 0.29 mmol) as described above for compounds **124-126**, was added either TTF derivative **125** (120 mg, 0.30 mmol) or **126** (125 mg, 0.30 mmol). The mixture was stirred under nitrogen at -10°C for 2 h, then allowed to warm to 20°C over 16 h. Aqueous work-up as described for compounds **124-126**, followed by chromatography on silica gel, eluent cyclohexane/toluene (3:1 v/v) afforded the products. There was obtained:

1,3-Bis(tetrathiafulvalenylthio)propane 127.

An orange oil (40 mg, 26%). m/z (DCI) 513 (M^++1); $\delta_H(CDCl_3)$ 6.39 (2H, s), 6.32 (4H, s), 2.83 (4H, t, J = 7.0 Hz) and 1.95 (2H, pentet, J = 7.0 Hz).

1,4-Bis(tetrathiafulvalenylthio)butane 128.

An orange solid (17 mg, 11%), m.p. 124-126°C. (Found: C, 36.3; H, 2.5. $C_{16}H_{14}S_{10}$ requires C, 36.5; H, 2.7%); m/z (DCI) 527 (M^++1); $\delta_H(CDCl_3)$ 6.36 (2H, s), 6.32 (4H, s), 2.75 (4H, m) and 1.74 (4H, m).

3,5-Bis[3-(tetrathiafulvalenylthio)propoxy]-benzyl alcohol 129.

To a solution of compound 125 (350 mg, 0.87 mmol) in dry acetonitrile (80 mL), 3,5-dihydroxy-benzyl alcohol (60 mg, 0.43 mmol), dried potassium carbonate (150 mg, 1.09 mmol) and 18-crown-6 (25 mg, 0.09 mmol) was added and the reaction refluxed with stirring under nitrogen for 16 h. Chromatography of the crude reaction mixture on silica gel, eluent cyclohexane/toluene/acetone (2:1:1 v/v/v) afforded compound 129 (60 mg, 20%) as a yellow oil. m/z (DCI) 693 (M^++1); $\delta_H[(CD_3)_2CO]$ 6.73 (2H, s), 6.63 (4H, s), 6.55 (2H, m), 6.39 (1H, m), 4.56 (2H, d, J = 5.3 Hz), 4.23 (1H, t, J = 5.8 Hz), 4.10 (4H, t, J = 6.0 Hz), 3.01 (4H, t, J = 7.1 Hz) and 2.10 (4H, pentet, J = 6.6 Hz); ν_{max}(neat)/cm^{-1} 3440 (OH).

4-(3-Chloro-2-oxo-propylthio)tetrathiafulvalene 130.

A solution of the sodium thiolate salt **123**, generated from thioester **122** (380 mg, 1.12 mmol) as described above for compounds **124-126**, was added dropwise to a solution of 1,3-dichloroacetone (1.42g, 11.2 mmol) in dry ethanol (10 mL) with stirring under nitrogen. The reaction was stirred at 20°C for 16 h, after which chromatography of the crude reaction mixture on silica gel, eluent toluene/cyclohexane (1:1 v/v) followed by recrystallisation from dichloromethane/hexane afforded compound **130** (160 mg, 44%) as an orange solid, m.p. 82-85°C. (Found: C, 32.5; H, 2.1. $C_9H_7ClOS_5$ requires C,

33.1; H, 2.2%); m/z (DCI) 327 (M^++1); $\delta_H(CDCl_3)$ 6.50 (1H, s), 6.31 (2H, s), 4.24 (2H, s) and 3.75 (2H, s); ν_{max}(nujol)/cm^{-1} 3060, 1725, 1210, 1150, 930, 800, 775 and 655.

4-[3-(Ethoxythiocarbonylthio)-2-oxo-propylthio]tetrathiafulvalene 131.

To a solution of compound 130 (200 mg, 0.61 mmol) in dry acetone (50 mL), O-ethylxanthic acid potassium salt (120 mg, 0.75 mmol) was added and the reaction stirred under nitrogen at 20°C for 16 h. Aqueous workup of the reaction mixture (extraction into dichloromethane) followed by chromatography on neutral alumina, eluent dichloromethane/cyclohexane (1:1 v/v) afforded compound 131 (180 mg, 71%) as an orange/brown oil. m/z (DCI) 413 (M^++1); $\delta_H(CDCl_3)$ 6.49 (1H, s), 6.31 (2H, s), 4.61 (2H, q, J = 7.1 Hz), 4.11 (2H, s), 3.76 (2H, s) and 1.41 (3H, t, J = 7.1 Hz).

Tris{4,5-dimethylthio-4',5'-[2-(methylene)propylene-1,3-dithio] tetrathiafulvalene}-1,3,5-benzenetricarboxylate 134.

To a solution of alcohol 61 (200 mg, 0.47 mmol) in dry dichloromethane (50 mL), 1,3,5-benzenetricarbonyl trichloride (37 mg, 0.14 mmol) followed by 4-dimethylaminopyridine (70 mg, 0.57 mmol) was added and the reaction stirred under nitrogen at 20°C for 16 h. Chromatography of the crude reaction mixture on silica gel, eluent dichloromethane followed by recrystallisation from dichloromethane/hexane afforded compound 134 (120 mg, 59%) as an orange solid, m.p. 133-135°C. (Found: C, 37.7; H, 3.0. $C_{45}H_{42}O_6S_{24}$ requires C, 37.3; H, 2.9%); m/z (PDMS) 1448.4 (M^+). Calc. for $C_{45}H_{42}O_6S_{24}$ 1448.3; $\delta_H(CDCl_3)$ 8.73 (3H, s), 4.57 (6H, broad s), 2.96 (6H, m), 2.78-2.66 (9H, m) and 2.40 (18H, s); ν_{max}(KBr)/cm^{-1} 2915, 1728, 1416, 1235, 998, 893, 771 and 737.

4,5-Bis[3-(tetrathiafulvalenylthio)propylthio]-1,3-dithiole-2-thione 135.

To a solution of iodide **125** (230 mg, 0.57 mmol) in dry acetonitrile (100 mL), zincate salt **32** (100 mg, 0.14 mmol) was added and the reaction refluxed with stirring under nitrogen for 16 h after which time the solution had changed colour from deep red to orange. Chromatography of the crude reaction mixture on silica gel, eluent cyclohexane/toluene (2:1 v/v) afforded compound **135** (42 mg, 20%) as an orange oil. $\delta_H(CDCl)_3$ 6.40 (2H, s), 6.32 (4H, s), 2.98 (4H, t, J = 7.0 Hz), 2.87 (4H, t, J = 6.9 Hz) and 1.99 (4H, pentet, J = 6.9 Hz); ν_{max}(neat)/cm^{-1} 3060, 2920, 1250, 1060, 795, 770, 730 and 640.

4,5-Bis[3-(tetrathiafulvalenylthio)propylthio]-1,3-dithiole-2-one 136.

A solution of 1,3,4,6-tetrathiapentalene-2,5-dione (30 mg, 0.14 mmol), iodide **125** (120 mg, 0.30 mmol) and tricaprylmethyl-ammonium chloride (140 mg, 0.28 mmol) in benzene (60 mL) was degassed by bubbling nitrogen through the solution for 10 min. A solution of sodium carbonate (62 mg, 0.58 mmol) in distilled water (10 mL) was slowly added with stirring at 40°C. Vigorous stirring was maintained under nitrogen at 40-45°C for 2 h and then at 20°C for 16 h. The organic layer was separated, washed with water, dried ($MgSO_4$) and solvent removed *in vacuo*. Chromatography of the residue on silica gel, eluent dichloromethane/cyclohexane (1:1 v/v) afforded compound **136** (51 mg, 50%) as a yellow oil. $\delta_H(CDCl_3)$ 6.39 (2H, s), 6.32 (4H, s), 2.96 (4H, t, J = 7.0 Hz), 2.88 (4H, t, J = 7.0 Hz) and 1.98 (4H, pentet, J = 7.1 Hz); ν_{max}(neat)/cm^{-1} 3060, 2905, 1665, 1610, 880, 790, 770 and 640.

4,5-Bis[2-(*tert*-butyl-diphenylsilyloxy)ethylthio]-1,3-dithiole-2-thione 139.

To a solution of 4,5-bis[2-(hydroxy)ethylthio]-1,3-dithiole-2-thione **138** (3.00 g, 10.5 mmol) in DMF (200 mL) was added sequentially *tert*-butyl-diphenylchlorosilane (6.92 g, 25.2 mmol) followed by imidazole (14.27 g, 0.21 mol) and the mixture stirred under nitrogen at 20°C for 16 h. The solvent was removed *in vacuo* and the residue dissolved in dichloromethane. The

product was washed with water (3 x 100 mL), dried (Na_2SO_4) and the solvent evaporated. Chromatography of the residue on silica gel, eluent dichloromethane afforded compound **139** (7.96g, 100%) as a viscous yellow oil. m/z (EI) 762 (M^+); $\delta_H(CDCl_3)$ 7.64 (8H, m), 7.38 (12H, m), 3.80 (4H, t, J = 6.7 Hz), 2.93 (4H, t, J = 6.7 Hz) and 1.05 (18H, s); ν_{max}(neat)/cm^{-1} 3070, 2931, 2858, 1471, 1428, 1112, 1068 and 702.

4,5-Bis[2-(*tert*-butyl-diphenylsilyloxy)ethylthio]-1,3-dithiole-2-one 140.

To a solution of thione **139** (7.96 g, 10.4 mmol) in chloroform/glacial acetic acid (300 mL, 3:1 v/v), mercuric acetate (an excess) was added and the mixture stirred under nitrogen at 20°C for 16 h. Water (100 mL) was added and stirring continued for 0.5 h. The heavy white precipitate was removed by filtration and the organic phase of the filtrate washed with sodium hydrogencarbonate solution (1 M, 3 x 100 mL), dried (Na_2SO_4) and the solvent removed *in vacuo* to afford compound **140** (7.82 g, 100%) as a viscous colourless oil. m/z (EI) 746 (M^+); $\delta_H(CDCl_3)$ 7.64 (8H, m), 7.38 (12H, m), 3.80 (4H, t, J = 6.8 Hz), 2.92 (4H, t, J = 6.8 Hz) and 1.05 (18H, s); ν_{max}(neat)/ cm^{-1} 3071, 2931, 2857, 1672, 1472, 1428, 1110 and 702.

4,4',5,5'-Tetrakis[2-(*tert*-butyl-diphenylsilyloxy)ethylthio] tetrathiafulvalene 141.

A stirred solution of compound **140** (7.82 g, 10.5 mmol) in neat, freshly distilled triethylphosphite (20 mL) under nitrogen, was heated to 130°C and maintained at this temperature for 2 h after which time the reaction mixture was deep red in colour. Chromatography of the crude reaction mixture on silica gel, eluent dichloromethane/cyclohexane (1:1 v/v) afforded compound **141** (4.75 g, 62%) as a viscous orange oil. m/z (PDMS) 1461.0 (M^+). calc. for $C_{78}H_{92}O_4S_8Si_4$ 1462.5; $\delta_H(CDCl_3)$ 7.64 (16H, m), 7.34 (24H, m), 3.80 (8H, t, J = 6.7 Hz), 2.91 (8H, t, J = 6.8 Hz) and 1.04 (36H, s); ν_{max}(neat)/cm^{-1} 3071, 2917, 2849, 1472, 1428, 1110, 824 and 702.

4,4',5,5'-Tetrakis[2-(hydroxy)ethylthio]tetrathiafulvalene 142.

To a solution of compound 141 (3.16 g, 2.16 mmol) in THF (150 mL), tetrabutylammonium fluoride hydrate (3.62 g, 13.0 mmol) was added and the mixture stirred under nitrogen at 20°C for 16 h. Removal of the solvent *in vacuo* afforded a viscous orange oil. Addition of hexane (20 mL) followed by ether (100 mL) precipitated a waxy solid. Filtration, followed by recrystallisation from methanol afforded compound 142 (820 mg, 75%) as an orange solid, m.p. 140-141°C (Lit.[92] 137-138°C). (Found: C, 32.9; H, 3.9. $C_{14}H_{20}O_4S_8$ requires C, 33.0; H, 4.0%); m/z (EI) 508 (M^+); $\delta_H[(CD_3)_2SO]$ 5.06 (4H, s), 3.56 (8H, t, J = 6.7 Hz) and 2.93 (8H, t, J = 6.7 Hz); ν_{max}(KBr)/cm^{-1} 3367, 2919, 1398, 1296, 1065, 1010, 892 and 770.

4,4',5,5'-Tetrakis[2-(tetrathiafulvalenecarboxylate)ethylthio] tetrathiafulvalene 143.

To a stirred solution of compound 142 (150 mg, 0.30 mmol) in dry DMF (10 mL) under argon at 20°C was added TTF-carbonyl chloride[83] (400 mg, 1.50 mmol) in one portion, followed by triethylamine (2 drops, excess). The reaction was stirred for 3 h, after which the solvent was removed *in vacuo* and the residue dissolved in dichloromethane (20 mL). The product was washed with water (3 x 20 mL), dried ($MgSO_4$) and the solvent evaporated. Chromatography of the residue on silica gel, eluent dichloromethane afforded compound 143 (240 mg, 57%) as a red-orange solid, m.p. 191-195°C. (Found: C, 35.3; H, 2.0. $C_{42}H_{28}O_8S_{24}$ requires C, 35.3; H, 2.0%); m/z (PDMS) 1429.7 (M^+). Calc. for $C_{42}H_{28}O_8S_{24}$ 1430.2; $\delta_H(CDCl_3)$ 7.35 (4H, s), 6.31 (8H, broad), 4.43 (8H, t, J = 6.6 Hz) and 3.13 (8H, t, J = 6.6 Hz); ν_{max} (KBr)/cm^{-1} 3069, 1703, 1538, 1273, 1196, 1075, 728 and 647.

2-Diethoxyphosphoryl-4,5-dimethylthio-1,3-dithiole 153 was prepared, in four steps, following the literature procedure[86] starting from 4,5-dimethylthio-1,3-dithiole-2-thione 149 (*ca.* 75% yield).

Ferrocene carbonyl chloride was prepared following the literature procedure[93] from ferrocene carboxylic acid and phosphorus pentachloride (*ca.* 50% yield).

2,6-Di(*tert*-butyl-diphenylsilyloxy)anthraquinone 155.

To a solution of 2,6-dihydroxyanthraquinone (5.00 g, 20.8 mmol) in DMF (250 mL), *tert*-butyl-diphenylchlorosilane (13.75 g, 50.0 mmol) followed by imidazole (14.17 g, 208 mmol) was added and the reaction stirred under nitrogen at 20°C for 16 h. DMF was removed *in vacuo* and the residue dissolved in dichloromethane, washed with water, dried ($MgSO_4$) and solvent removed *in vacuo*. Chromatography of the residue on silica gel, eluent hexane/dichloromethane (2:1 v/v) afforded compound **155** (9.05 g, 61%) as a yellow solid, m.p. 226-228°C. (Found: C, 77.0; H, 6.2. $C_{46}H_{44}O_4Si_2$ requires C, 77.0; H, 6.2%); m/z (DCI) 717 (M^++1); $\delta_H(CDCl_3)$ 7.95, 7.63 and 6.94 (2 x AMX each 3H, J_{AX} = 8.4, J_{MX} = 2.7 and J_{AM} < 1 Hz), 7.70 (8H, m), 7.40 (12H, m) and 1.13 (18H, s); ν_{max}(KBr)/cm^{-1} 3070, 2931, 2857, 1672, 1587, 1313, 904 and 701.

2,6-Di(*tert*-butyl-diphenylsilyloxy)-9,10-bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 156.

To a solution of Horner-Wittig reagent **153** (4.65 g, 14.0 mmol) and compound **155** (4.01 g, 5.60 mmol) in dry THF (150 mL) at 20°C, *n*-butyl-lithium (1.6 M, 9.63 mL, 15.4 mmol) was added dropwise with stirring under nitrogen over 10 min. Stirring was continued for 16 h after which time

chromatography of the crude reaction mixture on silica gel, eluent hexane/ dichloromethane (2:1 v/v) afforded compound 156 (3.52 g, 59%) as a yellow solid, m.p. 242-244°C. (Found: C, 62.9; H, 5.4. $C_{56}H_{56}O_2S_8Si_2$ requires C, 62.6; H, 5.3%); m/z (DCI) 1073 (M^++1); $\delta_H(CDCl_3)$ 7.74 (8H, m), 7.39 (12H, m), 7.19, 6.93 and 6.66 (2 x AMX each 3H, J_{AX} = 8.6, J_{MX} = 2.6 and J_{AM} < 1 Hz), 2.34 (6H, s), 2.27 (6H, s) and 1.11 (18H, s); ν_{max}(KBr)/cm^{-1} 3070, 2928, 2856, 1465, 1312, 1226, 1110 and 705.

2,6-Dihydroxy-9,10-bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 157.

To a solution of compound 156 (520 mg, 0.49 mmol) in THF (60 mL), tetrabutylammonium fluoride (1 M in THF, 1.94 mL, 1.94 mmol) was added dropwise over 10 min and stirring continued under nitrogen at 20°C for 16 h. Removal of the solvent *in vacuo* followed by chromatography of the sparingly soluble residue on silica gel, eluent acetone afforded compound 157 (*ca.* 205 mg, 70%) as an orange solid. The compound could not be obtained analytically pure and its insolubility precluded its use in further reactions. m/z (DCI) 597 (M^++1); δ_H [$(CD_3)_2CO$] 8.99 (2H, s), 7.40, 7.05 and 6.86 (2 x AMX each 3H, J_{AX} = 8.5, J_{MX} = 2.3 and J_{AM} < 1 Hz) and 2.41 (12H, s); ν_{max} (KBr)/cm^{-1} 3369, 2919, 1564, 1539, 1456, 1289, 1221 and 1099.

2,6-Bis(ferrocenecarboxylate)-9,10-bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 158.

To a solution of compound **156** (250 mg, 0.23 mmol) in dry THF (60 mL) at 20°C, ferrocene carbonyl chloride[93] (140 mg, 0.56 mmol) followed by dry triethylamine (0.08 mL, 0.58 mmol) were added. Tetrabutylammonium fluoride (1 M in THF, 0.93 mL, 0.93 mmol) was added dropwise over 10 min and stirring continued under nitrogen at 20°C for 16 h. Chromatography of the crude reaction mixture on silica gel, eluent dichloromethane followed by recrystallisation from dichloromethane/hexane afforded compound **158**

(130 mg, 55%) as a yellow solid, m.p. > 200°C (decomp.). (Found: C, 53.9; H, 3.5. $C_{46}H_{36}Fe_2O_4S_8$ requires C, 54.1; H, 3.6%); m/z (DCI) 1021 (M^++1); $\delta_H(CDCl_3)$ 7.60, 7.40 and 7.16 (2 x AMX each 3H, J_{AX} = 8.3, J_{MX} = 1.7 and J_{AM} < 1 Hz), 5.00 (4H, broad s), 4.53 (4H, broad s), 4.34 (10H, s), 2.41 (6H, s) and 2.38 (6H, s); ν_{max}(KBr)/cm^{-1} 2920, 1735, 1450, 1262, 1193, 1152, 1110 and 1088.

2,6-Bis(tetrathiafulvalenecarboxylate)-9,10-bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 159.

To a solution of compound 156 (340 mg, 0.32 mmol) in dry THF (60 mL) at 20°C, TTF carbonyl chloride[83] (200 mg, 0.75 mmol) followed by dry triethylamine (0.11 mL, 0.79 mmol) was added. Tetrabutylammonium fluoride (1.1 M in THF, 1.15 mL, 1.26 mmol) was added dropwise over 10 min and stirring continued under nitrogen at 20°C for 16 h. Chromatography of the crude reaction mixture on silica gel, eluent dichloromethane afforded compound 159 (100 mg, 30%) as an orange solid, m.p. 178-180°C. (Found: C, 43.5; H, 2.4. $C_{38}H_{24}O_4S_{16}$ requires C, 43.2; H, 2.3%); m/z (PDMS) 1057.6 (M^+). Calc. for $C_{38}H_{24}O_4S_{16}$ 1057.6; $\delta_H[(CD_3)_2SO]$ 8.15 (2H, s), 7.57 (2H, m), 7.38 (2H, m), 7.28 (2H, m), 6.79 (4H, s) and 2.40 (12H, s); ν_{max} (KBr)/cm^{-1} 3066, 2916, 1720, 1534, 1461, 1256, 1223 and 1186.

2-Methylthio-4,5-[2-(*tert*-butyl-diphenylsilyloxy)propylene-1,3-dithio]-1,3-dithiolium tetrafluoroborate 160.

A suspension of thione 41 (6.00 g, 12.2 mmol) in neat dimethylsulphate (10 mL) was heated to 100°C with stirring under nitrogen and maintained at this temperature for 40 min after which dissolution was complete. The reaction was allowed to cool to 20°C and then placed in an ice bath. Tetrafluoroboric acid (in ether, an excess) was added followed by dry ether (250 mL). The precipitated salt was stirred for 30 min, then filtered off, washed with dry ether to afford compound 160 (5.87 g, 81%) as a yellow solid, pure enough for further reaction. Further purification can be achieved

by dissolution in acetonitrile and reprecipitation by addition of ether. M.p. 149-152°C. (Found: C, 46.0; H, 4.2. $C_{23}H_{27}BF_4OS_5Si$ requires C, 46.4; H, 4.6%); $\delta_H(CD_3CN)$ 7.71 (4H, m), 7.49 (6H, m), 4.42 (1H, broad s), 3.07 (2H, m), 3.06 (3H, s), 2.81 (2H, m) and 1.09 (9H, s); $\nu_{max}(KBr)/cm^{-1}$ 3070, 2931, 2857, 1428, 1084, 837, 705 and 509.

2-Methylthio-4,5-[2-(*tert*-butyl-diphenylsilyloxy)propylene-1,3-dithio]-1,3-dithiole **161.**

To a suspension of salt **160** (5.00 g, 8.42 mmol) in THF/2-propanol (250 mL, 4:1 v/v), powdered sodium borohydride (an excess) was slowly added portionwise and the reaction stirred at 20°C for 2-3 h. The solvent was removed *in vacuo* and the residue dissolved in dichloromethane (200 mL), washed with water (3 x 100 mL), dried (Na_2SO_4) and solvent evaporated. Chromatography of the residue on silica gel, eluent dichloromethane/ cyclohexane (2:1 v/v) afforded compound **161** (4.06 g, 95%) as a viscous colourless oil. m/z (EI) 508 (M^+); $\delta_H(CDCl_3)$ 7.63 (4H, m), 7.40 (6H, m), 5.80 (s) and 5.51 (s) [together 1H], 4.26 (m) and 4.05 (m) [together 1H], 2.74-2.57 (m) and 2.43-2.33 (m) [together 4H], 2.29 (s) and 2.14 (s) [together 3H] and 1.09 (s) and 1.05 (s) [together 9H]; $\nu_{max}(neat)/cm^{-1}$ 3069, 2932, 2859, 1429, 1083, 839, 741 and 708.

4,5-[2-(*tert*-Butyl-diphenylsilyloxy)-propylene-1,3-dithio]-1,3-dithiolium tetrafluoroborate 162.

To a solution of compound **161** (3.91 g, 7.70 mmol) in dry ether (10 mL) cooled to -40°C, tetrafluoroboric acid (in ether, an excess) followed by dry ether (200 mL) was added. Within a few minutes a white precipitate had formed. The suspension was stirred under nitrogen at 20°C for 16 h, after which the solid was filtered off and washed with dry ether to afford compound **162** (3.02 g, 72%) as a white solid. Darkening of the product occurs on standing and the salt was used within a few hours with no further

purification. $\delta_H(CD_3CN)$ 10.78 (1H, s), 7.72 (4H, m), 7.49 (6H, m), 4.50 (1H, m), 3.15 (2H, m), 2.92 (2H, m) and 1.10 (9H, s); $\nu_{max}(KBr)/cm^{-1}$ 3048, 2931, 2857, 1428, 1084, 839, 704 and 509.

2-Dimethoxyphosphoryl-4,5-[2-(*tert*-butyl-diphenylsilyloxy)propylene-1,3-dithio]-1,3-dithiole 163.

To a solution of salt 162 (2.83 g, 5.16 mmol) in dry acetonitrile (200 mL), trimethylphosphite (0.61 mL, 5.17 mmol) followed by sodium iodide (0.93 g, 6.20 mmol) was added and the reaction stirred under nitrogen at 20°C for 16 h. Chromatography of the crude reaction mixture on neutral alumina, eluent ethyl acetate/cyclohexane (1:1 v/v) afforded compound 163 (2.43 g, 82%) as a viscous colourless oil. $\delta_H(CDCl_3)$ 7.62 (4H, m), 7.41 (6H, m), 4.93 (d, J = 6.1 Hz) and 4.51 (d, J = 5.5 Hz) [together 1H], 4.19 (m) and 4.05 (m) [together 1H], 3.88 (d, J = 10.6 Hz) and 3.80 (d, J = 10.5 Hz) [together 6H], 2.71-2.62 (2H, m), 2.56-2.33 (2H, m) and 1.07 (s) and 1.05 (s) [together 9H]; ν_{max} (KBr)/cm^{-1} 3071, 2956, 2857, 1258, 1112, 1056, 838 and 704.

9,10-Bis{4,5-[2-(*tert*-butyl-diphenylsilyloxy)propylene-1,3-dithio]-1,3-dithiol-2-ylidene}-9,10-dihydroanthracene 164.

To a solution of anthraquinone (390 mg, 1.87 mmol) in dry THF (150 mL), the phosphonate ester 163 (2.38 g, 4.17 mmol) was added and the mixture stirred under nitrogen at 20°C. *n*-butyllithium (1.6 M, 3.13 mL, 5.01 mmol) was added dropwise over 10 min and the reaction maintained with stirring at 20°C for 16 h. Chromatography of the crude reaction mixture on silica gel, eluent cyclohexane/dichloromethane (2:1 v/v) followed by removal of the solvent *in vacuo* gave a yellow oil. Crystallisation was achieved by the addition of methanol to afford compound **164** (960 mg, 47%) as a yellow solid, m.p. 246-250°C. (Found: C, 63.8; H, 5.4. $C_{58}H_{56}O_2S_8Si_2$ requires C, 63.5; H, 5.2%); m/z (EI) 1096 (M^+); $\delta_H(CDCl_3)$ 7.63-7.24 (28H, m),

4.09 (2H, m), 2.73 (4H, m), 2.51 (4H, m) and 1.06 (18H, s); ν_{max}(KBr)/cm^{-1} 3070, 2921, 2852, 1626, 1428, 1112, 1068 and 703.

9,10-Bis{4,5-[2-(hydroxy)propylene-1,3-dithio]-1,3-dithiol-2-ylidene}-9,10-dihydroanthracene 165.

To a solution of compound 164 (500 mg, 0.46 mmol) in THF (50 mL), tetrabutylammonium fluoride hydrate (380 mg, 1.36 mmol) was added and the reaction stirred under nitrogen at 20°C for 16 h. Chromatography of the crude reaction mixture on silica gel, eluent dichloromethane/acetone (4:1 v/v) afforded compound 165 (200 mg, 71%) as a yellow solid, m.p. 234-237°C. (Found: C, 49.9; H, 3.1. $C_{26}H_{20}O_2S_8$ requires C, 50.3; H, 3.2%); m/z (EI) 620 (M^+); δ_H[$(CD_3)_2SO$] 7.58-7.36 (8H, m), 5.63 (d, J = 4.9 Hz) and 5.44 (d, J = 4.7 Hz) [together 2H], 4.07 (m) and 3.89 (m) [together 2H], 2.95 (4H, m) and 2.61-2.40 (4H, m); ν_{max}(KBr)/cm^{-1} 3436, 3061, 1631, 1537, 1504, 1446, 1055 and 756.

9,10-Bis{4,5-[2-(acetate)propylene-1,3-dithio]-1,3-dithiol-2-ylidene}-9,10-dihydroanthracene 166.

To a solution of diol 165 (100 mg, 0.16 mmol) in dry dichloromethane (60 mL), freshly distilled acetyl chloride (0.05 mL, 0.70 mmol) followed by 4-dimethylaminopyridine (80 mg, 0.66 mmol) was added and the reaction stirred under nitrogen at 20°C for 16 h. Chromatography of the crude reaction mixture on silica gel, eluent dichloromethane, followed by removal of solvent *in vacuo* and the addition of methanol, crystallised compound **166** (90 mg, 79%) as a yellow solid, m.p. 196-200°C. (Found: C, 50.8; H, 3.2. $C_{30}H_{24}O_4S_8$ requires C, 51.1; H, 3.4%); m/z (EI) 704 (M^+); δ_H ($CDCl_3$) 7.55-7.27 (8H, m), 5.29-5.13 (2H, m), 2.94 (4H, m), 2.76-2.57 (4H, m) and 2.07 (6H, s); ν_{max}(KBr)/cm^{-1} 1743, 1537, 1446, 1370, 1225, 1022, 756 and 644.

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APPENDIX ONE

X-RAY CRYSTALLOGRAPHIC DATA

A.1.1 Crystallographic data for 4,5-[2-(hydroxy)propylene-1,3-dithio]-1,3-dithiole-2-thione 33

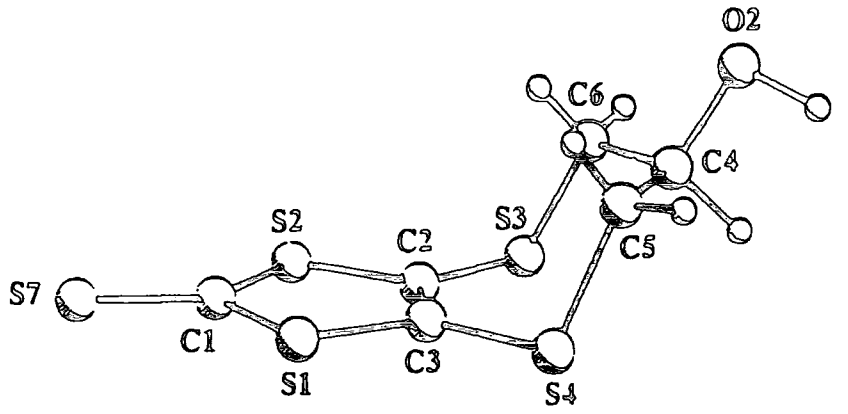

Figure A.1.1. - X-Ray molecular structure of compound 33 and crystallographic numbering scheme.

Crystal Data	
Empirical Formula	$S_5C_6OH_6$
Formula Weight	254.41
Crystal Colour, Habit	yellow, prism
Crystal Dimensions (mm)	1.000 x 0.600 x 0.150
Crystal System	triclinic
Lattice Parameters	a = 9.390(6) Å
	b = 11.295(6) Å
	c = 4.553(4) Å
	α = 94.96(7)°
	β = 91.05(6)°
	γ = 78.29(6)°
Space Group	$P\bar{1}$ (#2)
Z value	2
D_{calc}	1.793 gcm^{-3}
F_{000}	260
μ(MoKα)	11.29 cm^{-1}
Intensity Measurements	
Radiation	MoKα (λ = 0.71069 Å)
Temperature	-100°C
$2\theta_{max}$	50.0°

No. of Reflections Measured	Total: 1763 Unique: 1651

Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares
Residuals: R; R_w	0.049; 0.060
Goodness of Fit Indicator	2.88

Bond Lengths (Å)

S(1)-C(1)	1.726(5)	S(4)-C(5)	1.832(5)
S(1)-C(3)	1.741(5)	S(7)-C(1)	1.659(5)
S(2)-C(1)	1.731(5)	O(2)-C(4)	1.422(6)
S(2)-C(2)	1.748(5)	C(2)-C(3)	1.356(7)
S(3)-C(2)	1.751(5)	C(4)-C(5)	1.526(7)
S(3)-C(6)	1.825(5)	C(4)-C(6)	1.525(7)
S(4)-C(3)	1.760(5)		

Bond Angles (°)

C(1)-S(1)-C(3)	97.6(2)	S(3)-C(2)-C(3)	126.0(4)
C(1)-S(2)-C(2)	97.9(2)	S(1)-C(3)-S(4)	117.7(3)
C(2)-S(3)-C(6)	100.5(2)	S(1)-C(3)-C(2)	116.6(3)
C(3)-S(4)-C(5)	101.9(2)	S(4)-C(3)-C(2)	125.7(4)
S(1)-C(1)-S(2)	112.7(3)	O(2)-C(4)-(C5)	110.5(4)
S(1)-C(1)-S(7)	122.6(3)	O(2)-C(4)-C(6)	105.3(4)
S(2)-C(1)-S(7)	124.6(3)	C(5)-C(4)-C(6)	114.7(4)
S(2)-C(2)-S(3)	118.8(3)	S(4)-C(5)-C(4)	116.2(3)
S(2)-C(2)-C(3)	115.2(4)	S(3)-C(6)-C(4)	115.6(3)

Intermolecular Distances (Å)

S(1)-S(1)	3.335(3)	S(4)-S(4)	3.500(4)
S(1)-S(7)	3.496(3)	S(7)-O(2)	3.364(5)
S(1)-S(7)	3.591(4)	O(2)-C(6)	3.464(8)
S(2)-O(2)	3.405(5)	O(2)-C(6)	3.475(7)

A.1.2 Crystallographic data for 4,5-ethylenedithio-4',5'-[2-(ethyleneketal)-propylene-1,3-dithio]tetrathiafulvalene 82

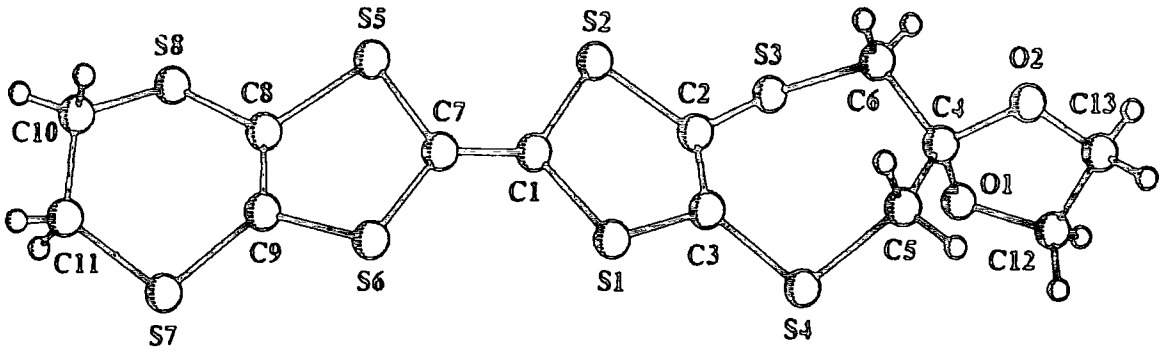

Figure A.1.2. - X-Ray molecular structure of compound 82 and crystallographic numbering scheme.

Crystal Data	
Empirical Formula	$C_{13}H_{12}O_2S_8$
Formula Weight	456.72
Crystal Colour, Habit	amber, plate
Crystal Dimensions (mm)	0.200 x 0.100 x 0.600
Crystal System	monoclinic
Lattice Parameters	a = 6.59(1) Å
	b = 19.865(8) Å
	c = 13.947(8) Å
	β = 91.68(9)°
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.662 gcm^{-3}
F_{000}	936
μ(MoKα)	9.44 cm^{-1}
Intensity Measurements	
Radiation	MoKα (λ = 0.71069 Å)
Temperature	24°C
$2\theta_{max}$	50.0°
No. of Reflections Measured	Total: 3632
	Unique: 3328

Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares
Residuals: R; R_w	0.058; 0.063
Goodness of Fit Indicator	2.61

Bond Lengths (Å)

S(1)-C(1)	1.75(1)	S(8)-C(8)	1.73(1)
S(1)-C(3)	1.77(1)	S(8)-C(10)	1.77(2)
S(2)-C(1)	1.77(1)	O(1)-C(4)	1.42(1)
S(2)-C(2)	1.77(1)	O(1)-C(12)	1.43(2)
S(3)-C(2)	1.76(1)	O(2)-C(4)	1.41(2)
S(3)-C(6)	1.79(2)	O(2)-C(13)	1.41(2)
S(4)-C(3)	1.73(1)	C(1)-C(7)	1.33(2)
S(4)-C(5)	1.81(1)	C(2)-C(3)	1.33(2)
S(5)-C(7)	1.76(1)	C(4)-C(5)	1.53(2)
S(5)-C(8)	1.78(1)	C(4)-C(6)	1.53(2)
S(6)-C(7)	1.76(1)	C(8)-C(9)	1.32(2)
S(6)-C(9)	1.77(1)	C(10)-C(11)	1.44(2)
S(7)-C(9)	1.75(1)	C(12)-C(13)	1.48(2)
S(7)-C(11)	1.78(2)		

Bond Angles (°)

C(1)-S(1)-C(3)	94.8(6)	O(1)-C(4)-C(5)	111(1)
C(1)-S(2)-C(2)	93.6(5)	O(1)-C(4)-C(6)	108(1)
C(2)-S(3)-C(6)	104.7(6)	O(2)-C(4)-C(5)	107(1)
C(3)-S(4)-C(5)	102.7(6)	O(2)-C(4)-C(6)	108(1)
C(7)-S(5)-C(8)	94.0(6)	C(5)-C(4)-C(6)	115(1)
C(7)-S(6)-C(9)	94.4(6)	S(4)-C(5)-C(4)	118(1)
C(9)-S(7)-C(11)	102.3(7)	S(3)-C(6)-C(4)	118(1)
C(8)-S(8)-C(10)	97.5(7)	S(5)-C(7)-S(6)	112.8(7)
C(4)-O(1)-C(12)	105(1)	S(5)-C(7)-C(1)	122.2(9)
C(4)-O(2)-C(13)	108(1)	S(6)-C(7)-C(1)	125(1)
S(1)-C(1)-S(2)	113.2(7)	S(5)-C(8)-S(8)	115.8(8)
S(1)-C(1)-C(7)	124.8(9)	S(5)-C(8)-C(9)	117(1)
S(2)-C(1)-C(7)	121.8(9)	S(8)-C(8)-C(9)	127(1)

S(2)-C(2)-S(3)	116.0(7)	S(6)-C(9)-S(7)	115.8(7)
S(2)-C(2)-C(3)	117.2(8)	S(6)-C(9)-C(8)	117(1)
S(3)-C(2)-C(3)	126.8(9)	S(7)-C(9)-C(8)	127(1)
S(1)-C(3)-S(4)	117.4(7)	S(8)-C(10)-C(11)	117(1)
S(1)-C(3)-C(2)	116.8(9)	S(7)-C(11)-C(10)	122(1)
S(4)-C(3)-C(2)	125.8(9)	O(1)-C(12)-C(13)	105(1)
O(1)-C(4)-O(2)	108(1)	O(2)-C(13)-C(12)	106(1)

Intermolecular Distances (Å)

S(1)-S(1)	3.498(7)	O(1)-C(12)	3.33(2)
S(2)-S(4)	3.475(7)	O(2)-C(10)	3.35(2)
S(3)-O(1)	3.390(9)	O(2)-C(11)	3.57(3)
O(1)-O(1)	3.31(2)		

APPENDIX TWO

RESEARCH COLLOQUIA, SEMINARS, LECTURES AND CONFERENCES

A.2.1 List of Research Colloquia, Seminars and Lectures

There follows a list of research colloquia, seminars and lectures that have been addressed by external speakers and arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student.

* Denotes presentations attended by the author.

Academic Year 1990-1991

11.10.90 Dr. W. A. MacDonald (I.C.I. Wilton)
Materials for the Space Age.

24.10.90* Dr. M. Bochmann (University of East Anglia)
Synthesis, Reactions and Catalytic Activity of Cationic Titanium Alkyls.

26.10.90* Prof. R. Soulen (South Western University, Texas)
Preparation and Reactions of Bicycloalkenes.

31.10.90* Dr. R. Jackson (University of Newcastle upon Tyne)
New Synthetic Methods: α-Amino Acids and Small Rings.

01.11.90* Dr. N. Logan (University of Nottingham)
Rocket Propellants.

06.11.90* Dr. P. Kocovsky (University of Uppsala)
Stereo-Controlled Reactions Mediated by Transition and Non-Transition Metals.

07.11.90 Dr. D. Gerrard (British Petroleum)
Raman Spectroscopy for Industrial Analysis.

08.11.90 Dr. S. K. Scott (University of Leeds)
Clocks, Oscillations and Chaos.

14.11.90* Prof. T. Bell (S.U.N.Y., Stoney Brook, New York)
Functional Molecular Architecture and Molecular Recognition.

21.11.90 Prof. J. Pritchard (Queen Mary and Westfield College, London)
Copper Surfaces and Catalysts.

28.11.90 Dr. B. J. Whitaker (University of Leeds)
Two-Dimensional Velocity Imaging of State-Selected Reaction Products.

29.11.90* Prof. D. Crout (University of Warwick)
Enzymes in Organic Synthesis.

05.12.90* Dr. P. G. Pringle (University of Bristol)
Metal Complexes with Functionalised Phosphines.

13.12.90 Prof. A. H. Cowley (University of Texas)
New Organometallic Routes to Electronic Materials.

15.01.91 Dr. B. J. Alder (Lawrence Livermore Labs., California)
Hydrogen in all its Glory.

17.01.91 Dr. P. Sarre (University of Nottingham)
Comet Chemistry.

24.01.91 Dr. P. J. Sadler (Birkbeck College, London)
Design of Inorganic Drugs: Precious Metals, Hypertension and HIV.

30.01.91* Prof. E. Sinn (University of Hull)
Coupling of Little Electrons in Big Molecules. Implications for the Active Sites of Metalloproteins and other Macromolecules.

31.01.91 Dr. D. Lacey (University of Hull)
Liquid Crystals.

06.02.91* Dr. R. Bushby (University of Leeds)
Biradicals and Organic Magnets.

14.02.91 Dr. M. C. Petty (University of Durham)
Molecular Electronics.

20.02.91* Prof. B. L. Shaw (University of Leeds)

Syntheses with Coordinated, Unsaturated Phosphine Ligands.

28.02.91* Dr. J. Brown (University of Oxford)

Can Chemistry Provide Catalysts Superior to Enzymes?

06.03.91 Dr. C. M. Dobson (University of Oxford)

NMR Studies of Dynamics in Molecular Crystals.

07.03.91* Dr. J. Markam (I.C.I. Pharmaceuticals)

DNA Fingerprinting.

24.04.91 Prof. R. R. Schrock (Massachusetts Institute of Technology)

Metal-Ligand Multiple Bonds and Metathesis Initiators.

25.04.91 Prof. T. Hudlicky (Virginia Polytechnic Institute)

Biocatalysis and Symmetry Based Approaches to the Efficient Synthesis of Complex Natural Products.

20.06.91 Prof. M. S. Brookhart (University of North Carolina)

Olefin Polymerisations, Oligomerisations and Dimerisations Using Electrophilic Late Transition Metal Catalysts.

29.07.91 Dr. M. A. Brimble (Massey University, New Zealand)

Synthetic Studies Towards the Antibiotic Griseusin-A.

Academic Year 1991-1992

17.10.91* Dr. J. A. Salthouse (University of Manchester)

Son et Lumiere: A Demonstration Lecture.

31.10.91* Dr. R. Keeley (Metropolitan Police, Forensic Science Dept.)

Modern Forensic Science.

06.11.91 Prof. B. F. G. Johnson (University of Edinburgh)

Cluster-Surface Analogies.

07.11.91* Dr. A. R. Butler (University of St. Andrews)

Traditional Chinese Herbal Drugs: a Different Way of Treating Disease.

13.11.91* Prof. D. Gani (University of St. Andrews)

The Chemistry of PLP-Dependent Enzymes.

20.11.91* Dr. R. More O'Ferrall (University College, Dublin)

Some Acid-Catalysed Rearrangements in Organic Chemistry.

28.11.91 Prof. I. M. Ward (University of Leeds, I.R.C.)

The SCI Lecture. Science and Technology of Orientated Polymers.

04.12.91* Prof. R. Grigg (University of Leeds)

Palladium-Catalysed Cyclisation and Ion-Capture Processes.

05.12.91* Prof. A. L. Smith (formerly of Unilever)

Soap, Detergents and Black-Puddings.

11.12.91* Dr. W. D. Cooper (Shell Research)

Colloid Science: Theory and Practice.

22.01.92 Dr. K. D. M. Harris (University of St. Andrews)

Understanding the Properties of Solid Inclusion Compounds.

29.01.92* Dr. A. Holmes (University of Cambridge)

Cycloaddition Reactions in the Service of the Synthesis of Piperidine and Indolizidine Natural Products.

30.01.92* Dr. M. Anderson (Shell Research, Sittingbourne)

Recent Advances in the Safe and Selective Chemical Control of Insect Pests.

12.02.92* Prof. D. E. Fenton (University of Sheffield)

Polynuclear Complexes of Molecular Clefts as Models for Copper Bio-sites.

13.02.92* Dr. J. Saunders (Glaxo Group Research Ltd.)

Molecular Modelling in Drug Discovery.

19.02.92* Prof. E. J. Thomas (University of Manchester)

Applications of Organostannanes to Organic Synthesis.

20.02.92 Prof. E. Vogel (University of Cologne)

The Musgrave Lecture. Porphyrins: Molecules of Interdisciplinary Interest.

25.02.92 Prof. J. F. Nixon (University of Sussex)

The Tilden Lecture. Phospha-Alkynes: New Building Blocks in Inorganic and Organometallic Chemistry.

26.02.92 Prof. M. L. Hitchman (University of Strathclyde)

Chemical Vapour Deposition.

05.03.92 Dr. N. C. Billingham (University of Sussex)

Degradable Plastics - Myth or Magic?

11.03.92 Dr. S. E. Thomas (Imperial College)

Recent Advances in Organoiron Chemistry.

12.03.92* Dr. R. A. Hann (I.C.I. Imagedata)

Electronic Photography - An Image of the Future.

18.03.92* Dr. H. Maskill (University of Newcastle upon Tyne)

Concerted or Stepwise Fragmentation in a Deamination-Type Reaction.

07.04.92 Prof. D. M. Knight (University of Durham, Dept. of Philosophy)

Interpreting Experiments: the Beginning of Electrochemistry.

13.05.92* Dr. J.-C. Gehret (Ciba Geigy, Basel)

Some Aspects of Industrial Agrochemical Research.

Academic Year 1992-1993

15.10.92 Dr. M. Glazer and Dr. S. Tarling (University of Oxford & Birkbeck College)

The Chemist's Role as an Expert Witness in Patent Litigation.

20.10.92 Dr. H. E. Bryndza (Dupont Central Research)
Synthesis, Reactions and Thermochemistry of Metal (Alkyl) Cyanide Complexes and Their Impact on Olefin Hydrocyanation Catalysis.

22.10.92 Prof. A. Davies (University College, London)
The Ingold-Albert Lecture. The Behaviour of Hydrogen as a Pseudometal.

28.10.92 Dr. J. K. Cockcroft (University of Durham)
Recent Developments in Powder Diffraction.

29.10.92 Dr. J. Emsley (Imperial College, London)
The Shocking History of Phosphorus.

04.11.92 Dr. T. P. Kee (University of Leeds)
Synthesis and Coordination Chemistry of Silylated Phosphites.

05.11.92* Dr. C. J. Ludman (University of Durham)
Explosions: A Demonstration Lecture.

11.11.92* Prof. D. Robins (University of Glasgow)
Pyrrolizidine Alkaloids: Biological Activity, Biosynthesis and Benefits.

12.11.92 Prof. M. R. Truter (University College, London)
Luck and Logic in Host-Guest Chemistry.

18.11.92 Dr. R. Nix (Queen Mary College, London)
Characterisation of Heterogeneous Catalysts.

25.11.92* Prof. Y. Vallée (University of Caen)
Reactive Thiocarbonyl Compounds.

25.11.92 Prof. L. D. Quin (University of Massachusetts, Amherst)
Fragmentation of Phosphorus Heterocycles as a Route to Phosphoryl Species with Uncommon Bonding.

26.11.92* Dr. D. Humber (Glaxo, Greenford)
AIDS - The Development of a Novel Series of HIV Inhibitors.

02.12.92* Prof. A. F. Hegarty (University College, Dublin)

Highly Reactive Enols Stabilised by Steric Protection.

02.12.92 Dr. R. A. Aitken (University of St. Andrews)

The Versatile Cycloaddition Chemistry of $Bu_3P.CS_2$.

03.12.92 Prof. P. Edwards (University of Birmingham)

The SCI Lecture. What is a Metal?

09.12.92 Dr. A. N. Burgess (I.C.I. Runcorn)

The Structure of Perfluorinated Ionomer Membranes.

20.01.93* Dr. D. C. Clary (University of Cambridge)

Energy Flow in Chemical Reactions.

21.01.93 Prof. L. Hall (University of Cambridge)

NMR - Window to the Human Body.

27.01.93 Dr. W. Kerr (University of Strathclyde)

Development of the Pauson-Khand Annulation Reaction: Organocobalt Mediated Synthesis of Natural and Unnatural Products.

28.01.93* Prof. J. Mann (University of Reading)

Murder, Magic and Medicine.

03.02.93* Prof. S. M. Roberts (University of Exeter)

Enzymes in Organic Synthesis.

10.02.93* Dr. D. Gillies (University of Surrey)

NMR and Molecular Motion in Solution.

11.02.93 Prof. S. Knox (University of Bristol)

The Tilden Lecture. Organic Chemistry at Polynuclear Metal Centres.

17.02.93 Dr. R. W. Kemmitt (University of Leicester)

Oxatrimethylenemethane Metal Complexes.

18.02.93 Dr. I. Fraser (I.C.I. Wilton)

Reactive Processing of Composite Materials.

22.02.93 Prof. D. M. Grant (University of Utah)
Single Crystals, Molecular Structure and Chemical-Shift Anisotropy.

24.02.93* Prof. C. J. M. Stirling (University of Sheffield)
Chemistry on the Flat-Reactivity of Ordered Systems.

10.03.93 Dr. P. K. Baker (University College of North Wales, Bangor)
Chemistry of Highly Versatile 7-Coordinate Complexes.

11.03.93 Dr. R. A. Y. Jones (University of East Anglia)
The Chemistry of Wine Making.

17.03.93* Dr. R. J. K. Taylor (University of East Anglia)
Adventures in Natural Product Synthesis.

24.03.93* Prof. I. O. Sutherland (University of Liverpool)
Chromogenic Reagents for Cations.

13.05.93 Prof. J. A. Pople (Carnegie-Mellon University, Pittsburgh)
The Boys-Rahman Lecture. Applications of Molecular Orbital Theory.

21.05.93 Prof. L. Weber (University of Bielefeld)
Metallophospha-Alkenes as Synthons in Organometallic Chemistry.

01.06.93 Prof. J. P. Konopelski (University of California, Santa Cruz)
Synthetic Adventures with Enantiomerically Pure Acetals.

02.06.93 Prof. F. Ciardelli (University of Pisa)
Chiral Discrimination in the Stereospecific Polymerisation of Alpha Olefins.

07.06.93 Prof. R. S. Stein (University of Massachusetts)
Scattering Studies of Crystalline and Liquid Crystalline Polymers.

16.06.93 Prof. A. K. Covington (University of Newcastle upon Tyne)
Use of Ion Selective Electrodes as Detectors in Ion Chromatography.

17.06.93 Prof. O. F. Nielsen (University of Copenhagen)
Low-Frequency IR and Raman Studies of Hydrogen Bonded Liquids.

A.2.2 List of Conferences Attended

There follows a list of conferences attended by the author during the period when the research for the thesis was carried out.

April 1991 — The Royal Society of Chemistry.
150th Anniversary Annual Chemical Congress.
Imperial College, London.

September 1991 — The Royal Society of Chemistry.
Autumn Meeting.
University of York.

June 1992 — Science & Engineering Research Council.
Graduate School (C.R.A.C.).
University of Stirling.

September 1992 — The Royal Society of Chemistry, Perkin Division and The Israel Chemical Society.
International Symposium on Structure and Reactivity in Organic and Bioorganic Chemistry.
University of Durham.

January 1993 — Zeneca Medicinal Chemistry Workshop.
Macclesfield.

June 1993 — Annual Meeting of the Danish Chemical Society.
University of Odense, Denmark.
A poster was presented entitled: "Functionalised Tetrathiafulvalene (TTF) Systems Derived From 4,5-(Propylenedithio)-1,3-dithiole Units".

APPENDIX THREE

PUBLICATIONS

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

1. "Synthesis of New Multi-Sulphur π-Electron Donors Containing Ketone Functionality."
   M. R. Bryce and G. J. Marshallsay, *Tetrahedron Lett.*, 1991, 32, 6033.

2. "Bis- and Tris(tetrathiafulvalenes) (TTFs) Derived from Reactions of the TTF-thiolate Anion."
   M. R. Bryce, G. J. Marshallsay and A. J. Moore, *J. Org. Chem.*, 1992, 57, 4859.

3. "Functionalised Tetrathiafulvalene (TTF) Systems Derived from 4,5-(Propylenedithio)-1,3-dithiole Units."
   G. J. Marshallsay, M. R. Bryce, G. Cooke, T. Jørgensen, J. Becher, C. D. Reynolds and S. Wood, *Tetrahedron*, 1993, 49, 6849.

4. "Synthesis and Properties of New Functionalised Tetrathiafulvalene (TTF) π-Electron Donors."
   M. R. Bryce, A. J. Moore, M. A. Coffin, G. J. Marshallsay, G. Cooke, P. J. Skabara, A. S. Batsanov, J. A. K. Howard and W. Clegg, *Phosphorus, Sulfur, and Silicon*, 1993, 74, 279.

5. "Chalcogenation of Tetrathiafulvalene (TTF): Synthesis of Alkylthio-TTF and Alkylseleno-TTF Derivatives and X-Ray Crystal Structure of Ethylenediseleno-TTF (EDS-TTF)."
   A. J. Moore, M. R. Bryce, G. Cooke, G. J. Marshallsay, P. J. Skabara, A. S. Batsanov, J. A. K. Howard and S. T. A. K. Daley, *J. Chem. Soc., Perkin Trans. 1*, 1993, 1403.

6. "Synthesis of 4,5-Bis- and 4,4',5,5'-Tetrakis-(2-hydroxyethylthio) tetrathiafulvalene: The Assembly of Tris- and Pentakis-(tetrathiafulvalene) Macromolecules."
   G. J. Marshallsay, T. K. Hansen, A. J. Moore, M. R. Bryce and J. Becher, *Synthesis*, accepted for publication, February 1994.