Novel Functionalised Tetrathiafulvalene Derivatives.

A thesis submitted as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

By

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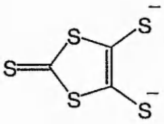
Declaration

I hereby certify that the work embodied in this thesis is the result of my own investigations except where reference has been made to published literature.

Abstract

This thesis describes the synthesis of a range of functionalised derivatives of bis (ethylenedithio) tetrathiafulvalene, known as BEDT- TTF or ET, and preliminary investigations of the radical cation salts for several of these materials. The syntheses involve reactions of the dithiolate **1** or the trithione **2**.



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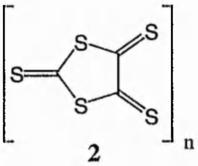

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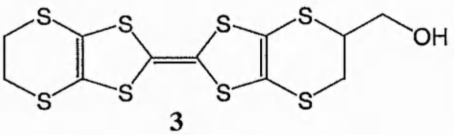
Chapter 2 is concerned with the synthesis of hydroxy- functionalised ET donors, namely racemic HMET, **3** and racemic HEET, **4**. The preparation of radical cation salts of HMET, with simple non- magnetic and magnetic anions, and measurement of their properties is discussed.



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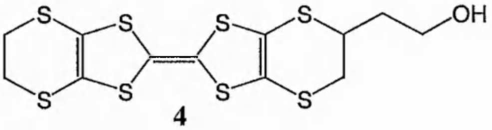

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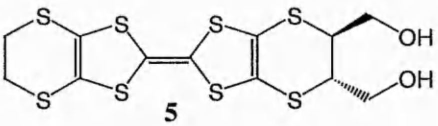
Chapter 3 describes the preparation of novel ET derivatives functionalised with more than one hydroxyl substituent in order to introduce extra hydrogen bonding potential. The investigation centred on the preparation of the *trans*- diol ET, **5** and the ET-tetrol, **6**. The first diastereoselective reaction of trithione **2** is reported.



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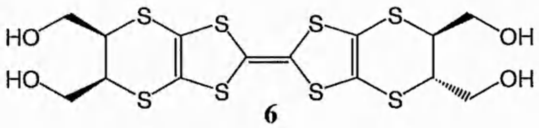

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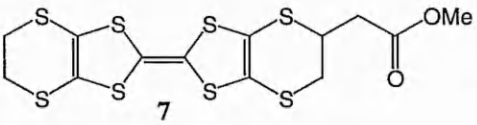
Chapter 4 reports on the preparation of ET derivatives appended with ester or amide functionality. Investigations into the synthesis of both racemic and enantiomeric forms of the ET- ethanoate **7** were carried out successfully. The preparation of amide **8** and a number of N- substituted amides are described. It is envisaged that the dual nature of the amide group in molecules such as **8** will provide strong hydrogen bonding interactions from both donor to donor and also from donor to anion. Initial investigations into the preparation of radical cation salts of ET- amides is discussed.



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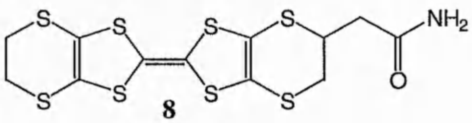

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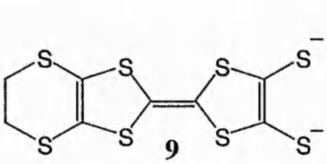
Chapter 5 reports on further synthetic approaches into novel organosulfur donors related to ET. Investigations were focused on obtaining ET or TTF- type donors endowed with multi- hydroxy functionality via the dithiolate **9**, or trithione **2**.



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Acknowledgements

I would like to thank my supervisor Professor John Wallis for all of his encouragement, guidance and support during the past three years and for always making the time to help me. I will always be thankful for your enthusiasm and having faith in the 'Chemistry Gods', unlike the latest England cricketing bunch of chancers!

Thank you to Professor Peter Day for providing the grant and opportunity for me to carry out the Ph.D., and to Dr. Scott Turner whose help in guiding me during my time at the Royal Institution has been invaluable.

Thank you to Jane for her love and support over the last five years and especially the past year during my writing up. What are we going to do with all that time on our hands?!

My thanks to all of the fellow students in the Lab who have made life enjoyable during the past three years, especially J.P. whose energy and storytelling kept the lab going and gave us all a chuckle. Thanks to all of the project students, particularly Bertrand, Kris and Gemma. To Dr. Pat Huddleston I offer thanks for always offering his sound advice and ideas. Thank you Mick for the many NMR's.

Finally, a big thank you to my family who have always supported me and spurred me on. For all the friends who helped me to leave the chemistry behind when it needed it, thank you.

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Abbreviations

BEDO- TTF - Bis(ethylenedioxo)- tetrathiafulvalene

BEDSe- TSeF - Bis(ethylenediseleno)- tetraselenafulvalene

BEDSe- TTF - Bis(ethylenediseleno)- tetrathiafulvalene

BEDT- TSeF - Bis(ethylenedithio)- tetraselenafulvalene

BEDT- TTF or ET - Bis(ethylenedithio)- tetrathiafulvalene

CDW - Charge Density Wave

CONECTUS - Consortium of European Companies Determined to use Superconductivity

CT - Charge Transfer

cv - Cyclic voltammetry

DCC - Dicyclohexlcarbodiimide

DCM - Dichloromethane

DDQ - Dicyanodihydroxyquinone

DFRL - Davy Faraday Research Laboratory

DIBAL - Diisobutylaluminiumhydride

DMAD - Dimethylacetylenedicarboxylate

DMF - Dimethylformamide

DMHD - Dimethyl- hex- 2- en- 4- yne- 1,6- dioate

DMSO - Dimethylsulfoxide

emu - Electromagnetic unit

EtOAc - Ethyl acetate

FG - Functional group

FISDW - Field Induced Spin Density Wave

FTIR - Fourier Transform Infrared

HEET - Hydroxyethyl bis(ethylenedithio)- tetrathiafulvalene

HMET - Hydroxymethyl bis(ethylenedithio)- tetrathiafulvalene

HPLC - High Performance Liquid Chromatography

HRMS - High Resolution Mass Spectrometry

ICT - Intermolecular Charge Transfer

IR - Infrared

LG - Leaving Group

LRMS - Low Resolution Mass Spectrometry

MeOH - Methanol

Meso - Mesomeric

MI - Metal- Insulator

MRI - Magnetic Resonance Imaging

NLO - Non- Linear Optic

NMR - Nuclear Magnetic Resonance

Oligo - Oligomeric

RMM - Relative Molecular Mass

SAM - Self- Assembled Monolayer

SDW - Spin Density Wave

SQUID - Superconducting Quantum Interference Device

TBA - Tetrabutylammonium

TBDPSCl - Tertiarybutyldiphenylsilylchloride

T_c - Critical Temperature

TCE - 1,1,2- Trichloroethane

TCNQ - Tetracyano- p- quinodimethane

THF - Tetrahydrofuran

TLC - Thin Layer Chromatography

TMS - Tetramethylsilane

TMTSF - Tetraselenafulvalene

TMTTF - Tetramethyl- tetrathiafulvalene

TTF - Tetrathiafulvalene

Vic - Vicinal

VT - Bis(vinylenedithio)- tetrathiafulvalene

YBCO - Yttrium Barium Copper Oxide

Chapter 1

Introduction

1. Introduction.

After one hundred years of organic chemistry being synthesis led, it has become increasingly common for projects to be driven by the expected properties of the compounds, in order that the properties can be exploited in devices. Molecules can be tailored by the organic chemist to provide certain responses to external influences such as electrical or magnetic fields or light. Thus, organic chemistry plays an increasingly dominant role in materials science. Applications include electrical conductors and superconductors, liquid crystals for data storage, non-linear optical materials and fuel cells. Our particular interest is in electroactive materials, especially in the development of new organic superconductors.

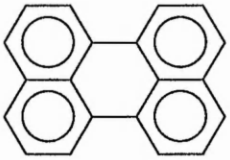
2. Organic superconductors.

Ahead of their time?

In 1911, the year that superconductivity was discovered, McCoy and Moore suggested that organic solids might exhibit metallic electrical conductivities even though they contain no metallic elements.[1] In 1964, Little of Stanford University went even further when he suggested the possibility of organic (carbon-based) superconductors, and proposed a model of a superconductor that could possibly superconduct at very high temperatures.[2] Little's suggestions led to a great deal of research effort into the preparation of organic superconductors.

The history of organic conductors and superconductors

The first indication that molecular materials could exhibit a high electrical conductivity was observed in 1954 when the bromide salt of perylene **1** was found to have a conductivity of 10^{-1} S cm^{-1} compared with *ca* 10^{-15} in perylene itself.[3]



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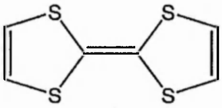
The field of crystalline organic metals (or synmetals) started in 1972 when Wudl *et al.* reported the high electrical conductivity of the chloride salt of TTF.[4] Most materials composed of organic molecules are normally not metals because their conduction and valence bands are filled. This property was first overcome in 1972 when Ferraris *et al.* reacted TTF (tetrathiafulvalene) **2** (an electron donor) with TCNQ (tetracyano-p-quinodimethane) **3** (an electron acceptor) to obtain a charge- transfer (CT) salt, TTF-TCNQ, thus resulting in the appearance of partially filled conduction and/or valence bands.[5] This has become known as the first true synmetal as it was metallic down to 54K.



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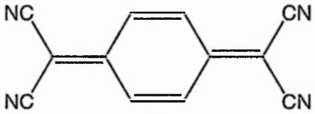

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The crystal structure of this salt (Fig.1) consists of segregated stacks of the donor and acceptor molecules.[6] Within the stacks, the molecules are arranged to show good intermolecular face-to-face overlap, and the arrangement of stacks is such that there are interstack interactions between sulfur and nitrile groups. Around 58 % of the molecules in the salt have lost or gained an electron. From the results obtained from TTF-TCNQ it was realised that CT salts formed by reacting an electron donor and an electron acceptor molecule could form metallic materials with reasonably high electrical conductivities.

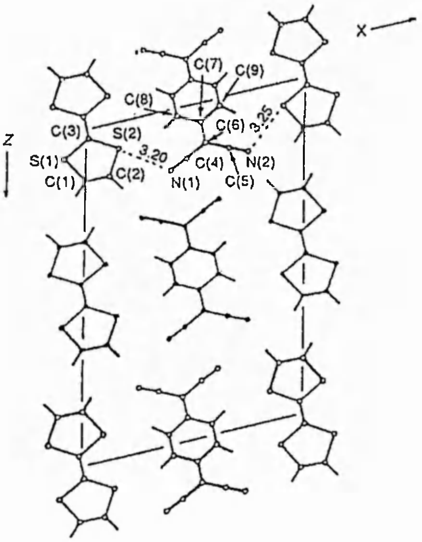
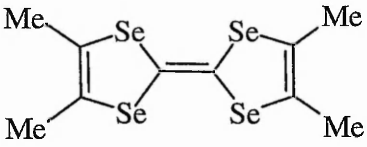


Figure 1. Crystal structure of TTF-TCNQ.

This discovery dramatically increased research interest in the search for new donor and acceptor species related to TTF and TCNQ. One of the earliest electron donors related to TTF, TMTSF (tetramethyltetraselenafulvalene) **4** was synthesised in 1974 by Bechgaard *et al.*[7]



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The first superconductor based on carbon (as predicted by Little some 16 years earlier) was successfully synthesized in 1980. Bechgaard *et al.* began to use monovalent anions such as PF_6^- and BF_4^- in place of TCNQ.[8] The salts were of the form $(TMTSF)_2X$, where X is a singly charged anion, and were prepared using the technique of electrocrystallisation. Only one stoichiometry for each salt was obtained. In the series of CT salts that were produced, those containing the monovalent anions PF_6^-, AsF_6^-, TaF_6^-, NbF_6^-, and ReO_4^- were found to be superconductors (T_c = 1-2 K), but had to be cooled to incredibly cold transition temperatures and subjected to high pressures (~ 5-12 kbar) to superconduct.

In 1981 Bechgaard synthesized $(TMTSF)_2ClO_4$, the first organic material that was superconducting at ambient pressure.[9] Although, it has a relatively low superconducting transition temperature (1.2 K), the interest in superconductivity and other rather unusual properties in organic materials exploded after this discovery.

The crystal structure of $(TMTSF)_2ClO_4$ indicates that the tetrahedral ClO_4^- anion resides in an asymmetric H-atom environment, with numerous short H···O contacts.[10] These $H_2C\text{-}H \cdots OClO_3^-$ interactions result in a "pinning" of the ClO_4^- anion, which may be associated with a "sluggish" anion ordering transition observed at 24 K (resulting from slow cooling of the sample), and which is a necessary prerequisite to the development of superconductivity in the ClO_4^- derivative.

Thus, in these systems it is strongly believed that crystallographic order is required to reduce electron scatter, which tends to destroy high superconductivity. By comparison, rapidly cooled samples of $(TMTSF)_2ClO_4$ may not become superconducting because, apparently, the ClO_4^- anions remain in a "frozen" disorder.

$(TMTSF)_2X$ compounds have been prepared with a wide range of inorganic ‘spectator’ anions and represent the first series of synmetals and superconductors to be investigated extensively and reviewed.[11] This was particularly important in that a range of salts was obtained possessing similar crystal structures but exhibiting a wide range of different properties at low temperatures or under pressure. This has enabled some understanding of the subtle interplay of structure and physical properties of these compounds.

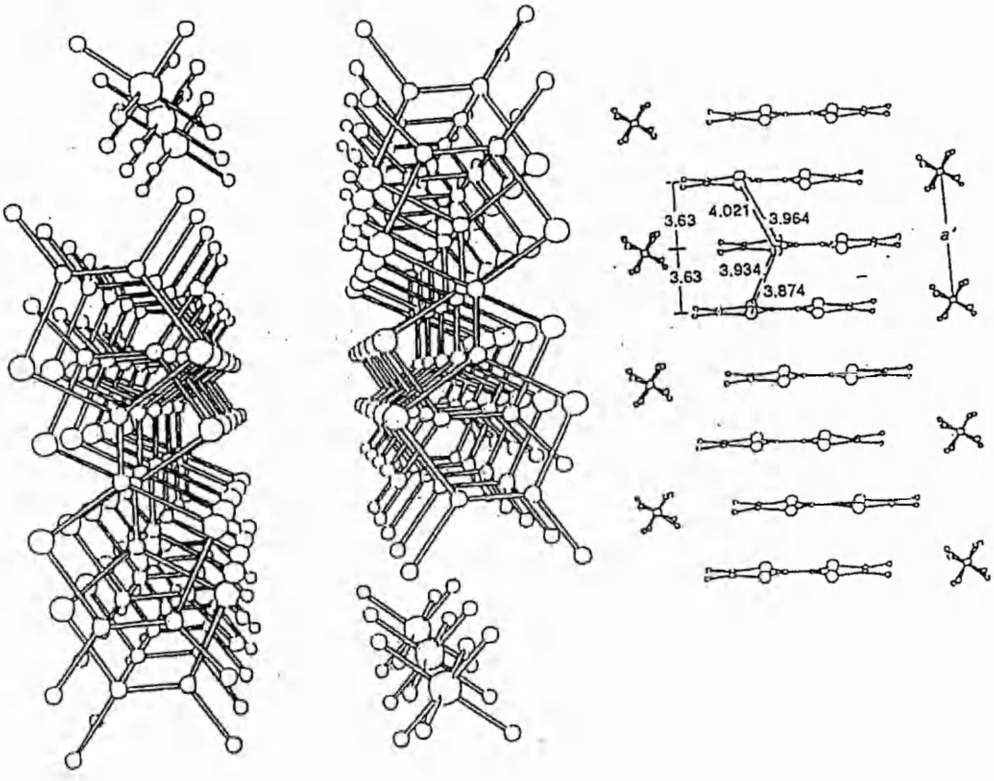


Figure 2. Structure of $(TMTSF)_2 ClO_4$.

Since 1981, over 400 organic conductors have been synthesized, over 50 of which are superconducting. During this time the superconducting transition temperature in these materials has risen from 1.2 K to 11.6 K. The most important family of superconductors have been those based on the organosulfur donor bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF).

3. History of superconductivity.

In 1911 the phenomena of superconductivity was first observed in mercury by Dutch physicist Heike Kamerlingh Onnes of Leiden University, during research on the properties of materials at very low temperatures.[12] When he cooled it to the temperature of liquid helium, 4 K, its resistance suddenly disappeared. Thus, it was necessary for Onnes to come within 4 K of the coldest temperature that is theoretically attainable to witness the phenomenon of superconductivity. Following this discovery, similar experiments were conducted and many other metals were found to superconduct. However, all of these metals, like mercury, would only superconduct when cooled down to very near absolute zero. Later, in 1913, he won a Nobel Prize in physics for his research in this area.

The next great milestone in understanding how matter behaves at extreme cold temperatures occurred in 1933. Walter Meissner and Robert Ochsenfeld discovered that a superconducting material will repel a magnetic field. A magnet moving by a conductor induces currents in the conductor. This is the principle upon which the electric generator operates. But, in a superconductor the induced currents exactly mirror the field that would have otherwise penetrated the superconducting material - causing the magnet to be repelled. This phenomenon is known as diamagnetism and is today often referred to as the "Meissner effect". The Meissner effect is so strong that a magnet can actually be levitated over a superconductive material.

In subsequent decades other superconducting metals, alloys and compounds were discovered. In 1941 niobium- nitride was found to superconduct at 16 K.[13] In 1953 vanadium- silicon displayed superconductive properties at 17.5 K.[13] In 1962 scientists at Westinghouse developed the first commercial superconducting wire, an alloy of niobium and titanium.[14] The first use of this wire in high-energy, particle-accelerator electromagnets, however, did not come until 1987 when it was employed at the Fermilab Tevatron, Illinois, USA, the world's highest- energy particle accelerator.

In 1986, a truly breakthrough discovery was made in the field of superconductivity. Alex Müller and Georg Bednorz, researchers at the IBM Research Laboratory in Rüschlikon, Switzerland, created a brittle ceramic compound, $LaBa_2Cu_3O_7$, that superconducted at the highest temperature then known: 30 K.[15] What made this discovery so remarkable was that ceramics are normally insulators and do not conduct electricity well at all, so researchers had not considered them as possible high-temperature superconductor candidates. This discovery of the first of the superconducting copper- oxides (cuprates) won the two men a Nobel Prize the following year. It was later found that tiny amounts of this material were actually superconducting at 58 K, due to a small amount of lead having been added as a calibration standard - making the discovery even more noteworthy.

Müller and Bednorz' discovery triggered a flurry of activity in the field of superconductivity. Researchers around the world began "cooking" up ceramics of every imaginable combination in a quest for higher and higher T_c's. In January of 1987 a research team at the University of Alabama- Huntsville substituted yttrium for lanthanum in the Müller and Bednorz substance and achieved an incredible T_c of 92 K.[16] For the first time a material (today referred to as YBCO) had been found that would superconduct at temperatures warmer than liquid nitrogen - a commonly available coolant.

Additional milestones have since been achieved using exotic - and often toxic - elements in the base perovskite ceramic. The current class (or "system") of ceramic superconductors with the highest transition temperatures are the mercuric- cuprates. The first synthesis of one of these compounds was achieved in 1993 by Prof. Dr. Ulker Onbasli at the University of Colorado and by the team of A. Schilling, M. Cantoni, J. D. Guo, and H. R. Ott of Zurich, Switzerland. The world record T_c of 138 K at ambient pressure is now held by a thallium-doped, mercuric- cuprate comprised of the elements mercury, thallium, barium, calcium, copper and oxygen, with structural formula $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8.33}$. Under extreme pressure its T_c can be coaxed up even higher – by approximately 25 to 30 degrees at 300,000 atmospheres.[17]

Materials based on organic molecules have also been found to superconduct, although at much lower temperatures than the perovskites. The first organic superconductor at ambient pressure to be reported was $(TMTSF)_2ClO_4$, in 1981 with a T_c of 1.2 K.[9] The highest T_c reported for an organic superconductor at ambient pressure is 11.6 K, in κ-$(ET)_2[Cu(CN)_2]Br$.[18] Research into buckminsterfullerenes (C_{60}) has found that fullerenes doped with alkali metals such as potassium and rubidium have superconducting properties. K_3C_{60} becomes superconducting at 18K[15] and Rb_3C_{60} at 30K.[19]

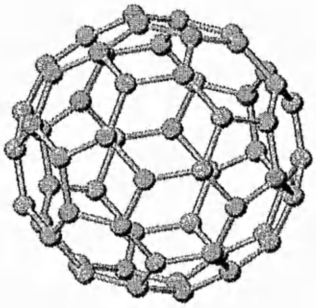


Figure 3. C_{60} 'Buckyball'.

The structure of a fullerene superconductor is a face centred cubic lattice, with fullerene molecules at the corners of the cube, and the alkali atoms in the centre of each face, and thus these materials have none of the anisotropy observed in other organic superconductors.

While no significant advancements in superconductor T_c's have been achieved in recent years, other discoveries of equal importance have been made. In 1997 researchers discovered that at a temperature very near absolute zero an alloy of gold and indium was both a superconductor and a natural magnet.[20] Since then, over a half-dozen such compounds have been found. Recent years have also seen the discovery of the first high-temperature superconductor that does NOT contain any copper (2000); crystals of WO_3 doped with sodium ($Na_{0.5}WO_3$) which enters a superconducting state at 91 K,[21] the first all-metal perovskite superconductor[22] (2001), $MgCNi_3$, with $T_c = 8$ K and the discovery that MgB_2 becomes superconducting at 39 K (2001).[23]

4. General properties of superconductors.

Zero Resistance:

The most well known property of superconductors is that they have zero resistance. If a current is created in a superconducting ring, the current will flow without diminishment for as long as the ring is kept in a superconducting state.

Perfect Diamagnet:

In a small magnetic field, a superconductor will exclude all magnetic fields from within the bulk of the superconductor. This property does not arise in a conductor. This property is called the Meissner effect, and is one of the defining criteria of superconductivity.

5. Specific properties of superconductors.

Critical Temperature (T_c):

This is the temperature at which a material enters the superconducting state on cooling in the absence of an applied magnetic field or a current within the superconductor. The lowest T_c for any known superconductor, is below 0.001 Kelvin (K) for rhodium,[24] and the highest known T_c for any superconductor at ambient pressure is 138K, for a mercury based copper oxide material.[17]

Type of Superconductor:

Superconductors are classified as one of two types. This classification is based on a superconductor's response to an applied magnetic field. A Type I superconductor has a magnetization which increases linearly as the strength of the applied magnetic field increases, until the field reaches a certain strength, at which point the superconductive state is destroyed and the magnetization of the material returns to its initial value. The magnetic field at which this occurs is known as the critical field, H_c. A Type II superconductor has a linear response of its magnetisation to an applied magnetic field up to a certain field strength, H_{c1}. As the strength of the applied field is increased further, the magnetization initially drops rapidly but quickly smoothes out into a flat slope that reaches zero at H_{c2}. The critical field, H_c, for a Type II superconductor is defined as the H_c of a Type I superconductor that has the same area under the magnetization curve and the same initial slope as the Type II superconductor, which H_c is being defined for.

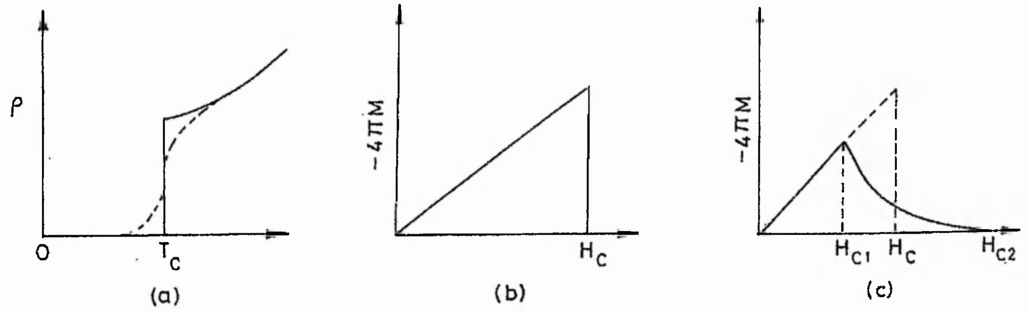


Figure 4. Properties of superconductors: (a) resistivity-temperature curve for a pure (solid) and an impure (broken) superconductor: (b) magnetisation as a function of external field for type I superconductor: (c) magnetisation curve for a type II superconductor.

Critical Current (I_c):

Although a superconductor has zero resistance, it is not possible to send an infinite current through a superconductor. This is because a moving current creates a magnetic field, which will magnetize the superconducting material. When the magnetic field associated with the current exceeds H_c, the superconducting state is destroyed and resistance is restored.

6. The theory of superconductivity.

The first widely- accepted theoretical understanding of superconductivity was advanced in 1957 by American physicists John Bardeen, Leon Cooper, and John Schrieffer.[25] Their *Theories of Superconductivity* became known as the BCS theory - and won them a Nobel prize in 1972. The mathematically- complex BCS theory explained superconductivity at temperatures close to absolute zero for elements and simple alloys. However, at higher temperatures and with different superconductor systems, the BCS theory has subsequently become inadequate to fully explain how superconductivity is occurring.

The BCS theory of superconductivity built on earlier work by Frölich and Cooper. Frölich's work showed that given the right conditions, electrons could experience an attractive interaction mediated by phonons (lattice vibrations in a solid). Cooper then showed that given this attractive interaction occurred, then if two electrons were to be scattered from near the Fermi surface to just above the Fermi surface, it would be energetically preferable for the two electrons to form a pair with both electrons above their former energy, than for the electrons to return to their former state. Such a pair of electrons is known as a Cooper pair.

The mechanism by which two negatively charged electrons are bound together is still controversial in "modern" superconducting systems such as the copper oxides or alkali metal fullerides, but well understood in conventional superconductors such as aluminium in terms of the mathematically complex BCS theory. The total momentum of a Cooper pair is constant, and the spins of the two electrons forming the Cooper pair are opposite to each other.

The BCS theory showed that it was possible for a number of Cooper pairs to form above the same Fermi surface. These Cooper pairs form a homogenous condensate, and for a pair to leave the condensate, it must split apart into separate electrons, which requires a certain amount of energy. The condensate has long range coherence, and it is this coherence that leads to superconductivity. If an electric field is applied across a superconductor, it is not possible for individual Cooper pairs to move in response to the field, but the condensate must move as a whole. Provided that the electric field does not provide enough energy to split the Cooper pairs, the condensate will move throughout the medium without resistance.

Another significant theoretical advancement came in 1962 when Brian D. Josephson, predicted that electrical current would flow between 2 superconducting materials - even when they are separated by a non-superconductor or insulator. His prediction was later confirmed and won him a share of the 1973 Nobel Prize in Physics. This tunneling phenomenon is today known as the "Josephson effect" and has been applied to electronic devices such as the SQUID, an instrument capabable of detecting even the weakest magnetic fields.

7. Theoretical research into organic superconductors.

The main area of theoretical interest is in trying to determine the exact nature of the mechanism by which superconductivity occurs in the organic superconductors. Determining the nature of this pairing would be a significant step in understanding organic superconductors. Recent experiments performed by researchers at Argonne National Laboratory have shown that the critical temperature of superconducting ET salts have a BCS like dependence on the mass of atoms in the molecules.[26] This suggests that phonon-electron interactions play a role in the superconductivity of organic superconductors.

While the BCS theory of superconductivity accounts for many of the properties of organic superconductors, there are also many properties that are not in agreement with the BCS theory. These organic materials have emerged as experimental test-beds for ideas about more exotic forms of superconductivity. In particular, researchers have recently discovered that superconductivity in organic molecules can be induced – rather than destroyed – by high magnetic fields.[27]

Since 1981, a number of other interesting electronic states have been observed in organic conductors including charge density waves (CDW), spin density waves (SDW), field induced spin density waves (FISDW), the quantum Hall effect, and angular magnetoresistance oscillations. In contrast to the cuprates, organic superconductors are very “clean” systems. Physicists have therefore been able to carry out many detailed measurements of their electronic properties that would have otherwise been impossible in other high temperature superconductors.

8. Applications of superconductors.

There are many potential applications of superconductors that would bring many benefits, such as superconducting power cables or using superconductors in computers to minimise power losses and reduce heating, but are unfeasible due to the low temperatures required for materials to superconduct. Also, there is the problem that many of the best superconductors are not readily mass produced or shaped easily. Despite these difficulties, a number of useful applications for superconducting devices have been found.

SQUID’s:

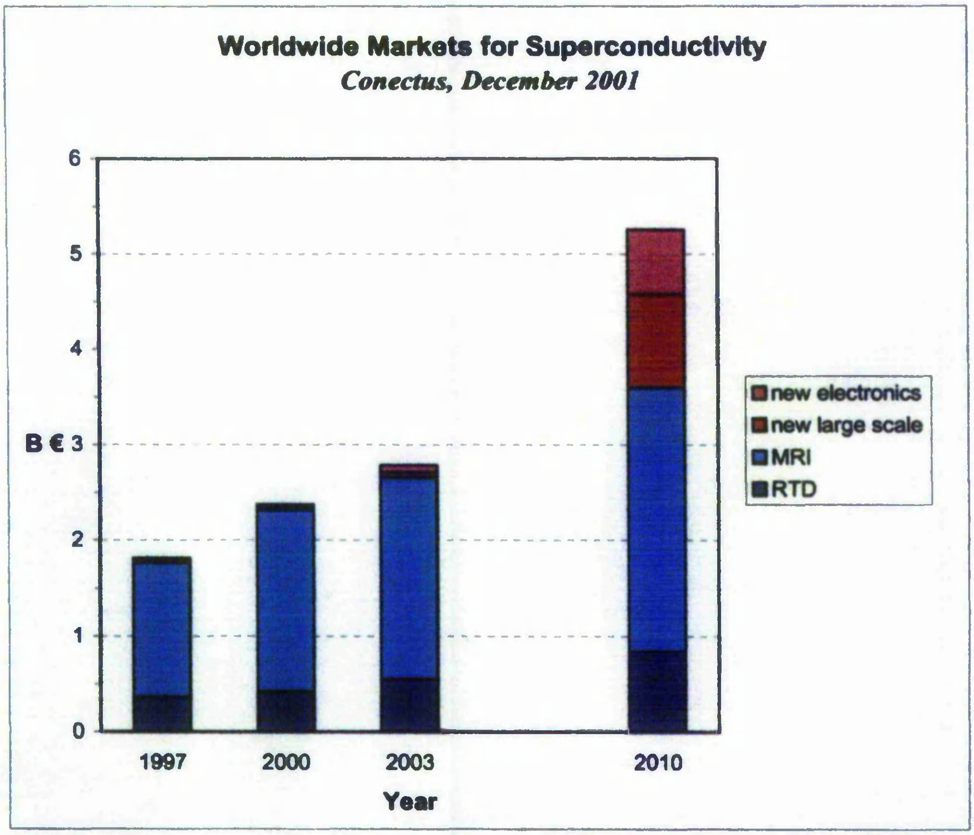
Superconducting **QU**antum **I**nterference **D**evices, SQUID’s, use the quantum mechanical properties of Cooper pairs to detect the presence of magnetic fields much smaller than that of the earth's magnetic field. SQUID’s are sensitive enough to detect the magnetic fields caused by electrical currents in the human brain, and are used in Magnetic Resonance Imaging (MRI) scanners.

Particle accelerators:

High power magnets made out of superconducting materials such as niobium, which have very high critical fields, are used in particle accelerators such as Fermilab and CERN. Because of the properties of superconductors, these magnets are able to create the large magnetic fields required to accelerate elementary particles to close to the speed of light, using much less power than would be needed using ordinary electromagnets. Without superconducting magnets, the cost of running such facilities would be many times larger than they are, making research into the fundamental components of nature much more difficult.

Market forecasts for products based on superconducting components:

A new superconductivity market survey, published in June 2002, carried out by CONECTUS (**Con**sortium of **E**uropean **C**ompanies Determined **T**o **U**se **S**uperconductivity) for 2000 – 2010, announced market forecasts for major products based on superconducting components. Well established businesses such as MRI scanners and particle accelerators listed above were addressed, as well as emerging new businesses such as electric power, industrial processing, transportation and information and communication. In summary, the survey states that the total market for superconducting products may reach €40 Billion by 2020. In the graph below these emerging new businesses are summarised under large scale and electronics applications. Science, research and technological development are summarised as RTD. Magnetic Resonance Imaging applications are summarised as MRI.



Market figures represent the annual sales of materials, components and (sub-) systems providing a specific technical function for which superconductivity is indispensable. All after sales services, warranties and related maintenance are included. Commercial orders and pre-commercial orders related to RTD activities, prototype testing and field tests, are included, whereas RTD contracts are excluded.

Worldwide Markets for Superconductivity & Market Shares for Low-Tc / High-Tc Superconductors (in M €)

Business Field	Year 1997	Year 2000	Year 2003	Year 2010
Research & Technological Development (RTD)	355	415	550	840
Magnetic Resonance Imaging (MRI)	1400	1900	2100	2750
TOTAL of RTD & MRI	**1755**	**2315**	**2650**	**3590**
New Large Scale Applications	35	25	55	980
New Electronics Applications	20	30	75	680
TOTAL of Emerging New Businesses	**55**	**55**	**130**	**1660**
TOTAL WORLDWIDE MARKET	**1810**	**2370**	**2780**	**5250**
Market Shares for Low-Tc Superconductors	1805	2355	2730	3650
Market Shares for High-Tc Superconductors	5	15	50	1600

Conectus, December 2001

Figure 5. Predicted worldwide markets for superconductivity.

9. Overview of organic conductors and superconductors.

Organic conductors and superconductors are generally based on the radical cation salts of planar molecules. The organic salts are layered materials, consisting, more or less, of rows and stacks of the organic donor (or acceptor) molecules separated by planar arrays of anions. Perpendicular to the layers, the conductivity is generally very small compared to conductivities within the plane of the organic layers. Because of this arrangement, and the nature of the orbitals involved in the movement of electrons, these salts show a large anisotropy in properties such as electrical conductivity and magnetic susceptibility. The organic superconductors, because of this anisotropy, display behaviour associated with reduced dimensionality.

They are also conductors, but generally when cooled under ambient pressure enter an insulating state. Applying pressure to the salt reduces the temperature at which the metal-insulator transition occurs, and when sufficient pressure is applied, the insulating phase is completely suppressed and a superconducting phase is observed. Organic superconductors phase diagrams are very rich and show a large number of different behaviours. At low temperature and pressure, an anti-ferromagnetic insulating state is observed. At slightly higher pressures a superconducting state is found, and at extremely high pressures, an ordinary conducting state is seen. The phase diagram of an organic superconductor is very similar to that of the cuprate superconductors, which also show behaviour associated with reduced dimensionality. The organic superconductors found so far have low critical temperatures and are Type II superconductors.

While there are relatively strong coulombic forces binding together the anionic and cationic constituents, the valence bands, which comprise the highest occupied energy levels analogous to the valence energy levels of a molecule, are derived from the intermolecular π-π overlaps of the orbitals of adjacent organic donor molecules, in particular, the orbitals of the heteroatoms. Intermolecular π-π overlaps in two (or higher) dimensions leads to two-dimensional (or higher) band electronic structures, thus precluding the metal-insulator or metal-semiconductor transitions ubiquitous in systems of lower electronic dimensionality.

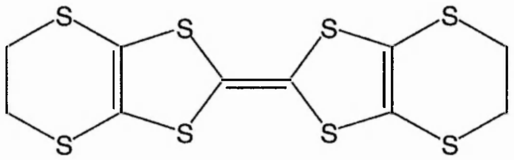
If the organic moieties were neutral molecules with even numbers of electrons, the valence bands would be completely filled, and the compound would have an insulating electronic state. Charge-transfer of an odd number of electrons per formula unit (usually one electron) partially depletes a valence band (or partially fills an unoccupied valence band), thus creating a conduction band and therefore a metallic electronic state.

For weak interactions, intermolecular orbital bonding and antibonding combinations are not widely spread in energy, so that conduction and valence bands are narrow, in contrast to the wide bands of conventional metals and insulators. The inorganic anion, in addition to serving as a charge balance, acts as a spacer between organic layers and stacks, that is crucial, in terms of its size and coordination, in modifying the strengths of the interactions between the organic moieties and in giving the anisotropic dispersions in the energy bands.

Considerable empirical evidence exists that many of the organic charge-transfer (CT) salts can be adequately interpreted in terms of a conduction band. As presently understood, charge-carriers other than conduction band electrons are not required for the organic CT salts.

10. Organic superconductors based on BEDT-TTF (ET).

The family of salts based on the molecule bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF), (further abbreiviated to ET **5**) has provided all of the superconductors with $T_c > 10$ K. ET has proved to be one of the most useful organic electron donors in the preparation of synmetals and superconductors. In the past 25 years since the synthesis of ET in 1978 by Mizuno *et al.*,[28] a great deal of research effort has been directed towards the synthesis of ET salts with a transition to a superconducting state high enough to hint at practical applications.



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The structure of ET is symmetrical and essentially planar due to the π electron system, but at least one of each pair of the outer ethylene carbon atoms is out of the plane.[29] This can lead to disorder in the crystal structure of some ET salts.

ET salts are formed by electrocrystallisation, as for TMTSF, and the typical, but not exclusive, formula is $(ET)_2X$, thus 50 % of the ET's are present as a radical cation. Very little work has been carried out on the chemical oxidation of ET. The ET salts form layer structures, with the donor molecules oriented "on end" in the planes which are stacked on top of each other. The anions lie in layers acting as fillers between the planes. There are a number of different ways in which the ET molecules can be arranged within the plane, denoted α, β … etc (Fig 6). The ET metallic salts in a number of important cases are quasi two-dimensional materials in the sense that the conductivity is essentially isotropic in a plane coincident with the two dimensional

S···S network of the sulfur atoms of the donor molecules. Conductivity within the planes is much greater than that between planes. Disorder in the structures of the ET metallic salts is usually accompanied by a suppression of any superconducting transition temperature.

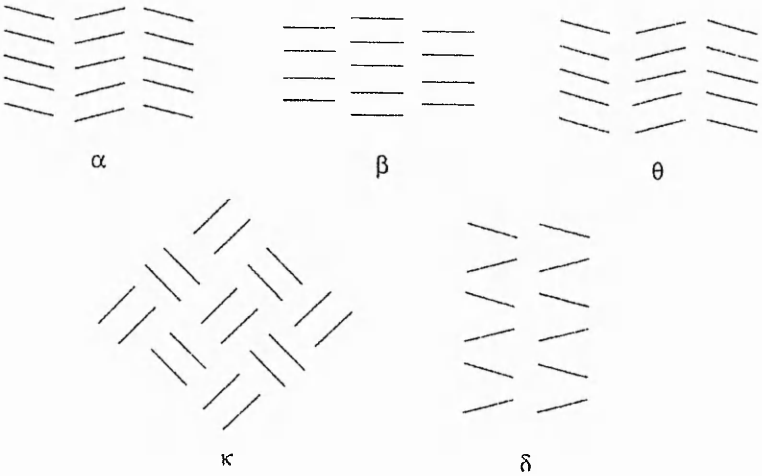


Figure 6. Packing phases of ET salts.

The electrical properties of the ET salts are determined by the packing of the radical cations in the crystal structure, it is mostly the sulfur···sulfur contacts that determine the intermolecular electronic interactions. For a superconducting state to arise, effective overlap of the sulfur atom orbitals has to occur between neighbouring radical cations, the intermolecular sufur···sulfur contacts being closer (~3.3Å) than the sum of their van der Waals radii (3.6Å). This leads to the formation of a supermolecular conduction band and the extended sulfur network allows the conduction electrons to form Cooper pairs and travel through the crystal lattice.

The packing of the radical cations is determined in part by the anion present in the material. The size and coordination of the anion can govern the strength of the interactions between the organic moieties, and can give rise to a number of different phases, which ultimately determine the electrical properties observed in the material. Investigations into structure – property relationships have been carried out, and the results of these have led to the chemist having some 'guidelines' in designing new ET salts.

Many of the ET salts that have been synthesised however, are not superconducting, but are metallic at room temperature with conductivities for a typical organic metal < 10^3 Scm^{-1}. Conductors such as copper or gold have conductivities ≈ 10^6 Scm^{-1} at ambient temperature. Upon cooling, many of the ET salts undergo a metal – semiconductor transition and become semiconducting in their electrical behaviour. A lattice distortion (Peierls distortion), typical of low-dimensional electronic materials, results in the partially filled conduction band splitting into filled and empty bands, leaving a band gap and converting the material from a metal to a semiconductor. On further cooling some ET salts do become superconducting, at a critical temperature, $T_{c.}$ The transition to a superconducting state is not always sharp but can be over a few Kelvin.

The superconducting salts of ET

The superconducting salts of ET usually have the formula $(ET)_2X$, where X is a singly charged anion, like the Bechgaard salts. In contrast to TMTSF, the ET- donor molecule yields salts of different stoichiometries and salts of the same anion can have a variety of different structures, sometimes even forming simultaneously in the same preparation, each with different conducting properties.

The majority of the ET based organic superconductors can be classified as belonging to one of the two structural groups denoted as the β- phase superconductors, which have linear triatomic anions (I_3^-, AuI_2^-, and IBr_2^-),[30a,b,c] and the κ- phase or κ- like superconductors, which include the Hg halide salts such as $(ET)_4Hg_{(2.89)}Br_8$,[31] and salts containing halogen or metal atoms such as κ- $(ET)_2I_3$,[32] κ- $(ET)_2Cu(NCS)_2$,[33] κ- $(ET)_2[Cu(CN)_2]Br$[18] and κ- $(ET)_2[Cu(CN)_2]Cl$.[34] Until the discovery in 1990 of superconductivity below 11.6 K in κ- $(ET)_2[Cu(CN)_2]Br$ and below 12.8 K with a minimal applied pressure of ~ 0.3 kbar in κ- $(ET)_2[Cu(CN)_2]Cl$, the κ- $(ET)_2Cu(NCS)_2$ salt, with T_c below 10 K, represented the maximum temperature for organic superconductivity.

ET salts with polyhedral anions

The only superconducting ET salt reported with a polyhedral anion is $(ET)_2ReO_4$, although to become superconducting the salt requires applied pressure.[35] The octahedral anions PF_6^-, AsF_6^-, and SbF_6^- form ET salts of stoichiometry $(ET)_2X$ which are all one-dimensional (1D) metals, with metal-insulator (MI) transitions very near room temperature.[36, 37]

The tetrahedral anion ClO_4^- gives three salts with ET, two of which have 2:1 stoichiometry for the cation: anion ratio, but they incorporate neutral solvent molecules in their structures. Both of these salts are semiconductors at room temperature. The salt $(ET)_2ClO_4(TCE)_{0.5}$, where TCE denotes 1,1,2-trichloroethane, is important as the first example of a two-dimensional (2D) organic metal.[38] The conductivity is highest along the inter-stacking direction, but is nearly isotropic in the plane defined by the stacking and interstacking directions. This plane shows an extended approximately 2D network of S···S interactions. At room temperature the conductivity $\sigma \approx 26$ Scm^{-1}. The second 2:1 salt of ET, $(ET)_2ClO_4(C_4H_8O_2)$, where $C_4H_8O_2$ is 1, 4- dioxane, is a 2D semiconductor at and below room temperature with $\sigma \approx$ 1 Scm^{-1}.[39] It is interesting that the change in solvent molecule and its stoichiometry strongly affects the conductive properties. The third salt in the series is γ-$(ET)_3(ClO_4)_2$, which is metallic from room temperature down to 170 K, with a room temperature conductivity $\sigma \approx 50$ Scm^{-1}.[40] The salt also has a 2D network of S···S interactions.

ET salts with linear anions and the effect of crystallographic disorder:

About twenty of the many reported salts of ET with the linear anions possess metallic conductive properties near room temperature, and a dozen of these are metallic down to the lowest attainable temperature. β- $(ET)_2I_3$, prepared by Shchegolev *et al.*, was the first ambient pressure superconductor based on ET, undergoing a superconducting transition at 1.5 K.[30a] This was the incentive to a search for additional superconducting salts of ET derived from other linear anions.

Williams *et al.* carried out an extensive study into the properties of ET salts with a series of linear triatomic anions and were able to conclude that if there is disorder in the crystal structure then it is either not superconducting, or is superconducting at a lower than expected transition temperature. When looking at ordered structures, by contrast, a good match between increasing T_c and an increase in the size of the anion was found (Fig7).[19] So it looked as though incorporating larger anions might be one way to improve the transition temperature of ET- based superconductors.

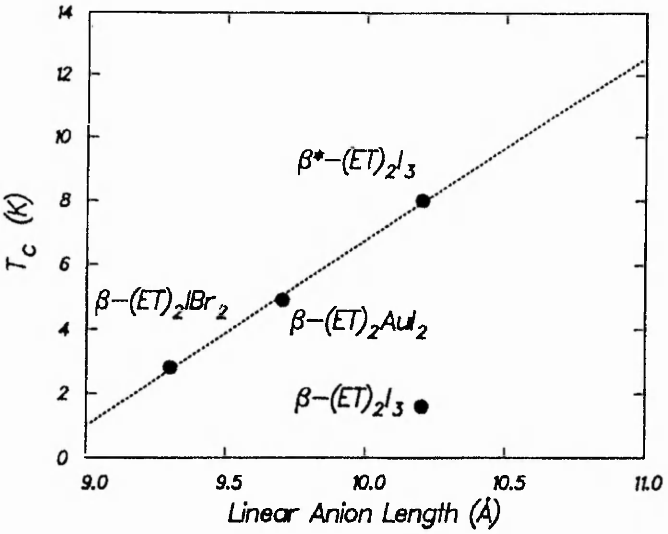


Figure 7. Correlation between increasing T_c and an increase in the size of the anion.

Examples of similar metallic salts prepared by Williams *et al.* include β- $(ET)_2\,AuI_2$[30b] and β- $(ET)_2\,IBr_2$[30c] which undergo superconducting transitions at ambient pressure near 5 K and 3 K respectively. These two compounds along with β- $(ET)_2I_3$ form a series of superconducting salts based on a common crystal structure. The electrical conductivities of the three salts at room temperature are ~ 10 – 50 $(\Omega cm)^{-1}$ in the plane of the stacking and interstacking directions of the ET donor molecule, and as such can be classified as quasi 2D metals. However it was found that salts with other shorter anions such as dichloroiodide (ICl_2^-) turned out to be insulating.[41]

The salt β- $(ET)_2\,I_2Br$ is isostructural with β- $(ET)_2\,IBr_2$ and is also 2D metallic to the lowest temperatures, but exhibits no superconductivity at ambient pressure down to 0.5 K or under applied pressures up to 5 kbar near 1 K.[42] The anion of the non-superconducting salt β-$(ET)_2\,I_2Br$ is longer than IBr_2^-, which suggests that it should be superconducting (Fig 7). The lack of superconductivity has been attributed to crystallographic disorder of the I-I-Br$^-$ anion.[43] In the β- phase superconductors (linear triatomic anions), the anions are symmetrical and perfectly ordered in all cases.

β- $(ET)_2I_3$, however, represents another case of the suppression of superconductivity caused by crystallographic disorder, but in this case the disorder arises from the arrangement of the terminal ethylene groups of the ET- donor molecules instead of the anions. At ambient pressure, the terminal ethylene group at one end of each ET-donor molecule is disordered. As the temperature is lowered, the crystal exhibits some partial, long range, but incomplete ordering.[44] This structural modulation persists to low temperatures where the salt becomes superconducting near 1.5 K. Under pressure however, β- $(ET)_2I_3$ becomes perfectly ordered, and T_c increases from 1.4 K to 8 K.[45]

Often accompanying the formation of the β- phase salts is the non-superconducting α-modification. Examples of these are: α- $(ET)_2I_3$,[46] α- $(ET)_2IBr_2$[30c] and α- $(ET)_2I_2Br$.[47] These α- phase salts have structures involving a herringbone rearrangement of the ET donor molecule stacks, in contrast to the uniform arrangement of adjacent stacks in the β- phase structures (see Fig 6). The α- phase salts are 2D systems with conductivities at room temperature that are comparable to those of other ET salts.

The ET/I system yields at least nine additional phases, most of which are metallic, and three of which are superconducting in the region of 4 K. The stoichiometry of these salts range from 1:1 donor: anion, δ- $(ET)I_3$,[48] to salts such as ζ- $(ET)_2(I_2)(I_8)_{0.5}$.[49] If ET contained a group capable of a specific interaction with the anion, then the production of many phases may be avoided.

Along with β- phase ET salts, κ- phase ET salts are metallic and in some cases superconducting. The structure of κ- $(ET)_2I_3$ consists of a twisted arrangement of $(ET)_2^+$ dimers. κ- $(ET)_2I_3$ is classified as a 2D metal with $\sigma = 50\ Scm^{-1}$ at ambient temperature in the plane of the organic donor molecules.[32] κ-$(ET)_2Cu(NCS)_2$, a 2D metal, has the κ- phase packing motif and a polymeric network of anions (see Fig 8.), and it possesses a superconducting transition temperature of ~ 10 K at ambient pressure.[33] The salt is metallic at room temperature with $\sigma \sim 40\ Scm^{-1}$ in the plane of the organic donor molecules.

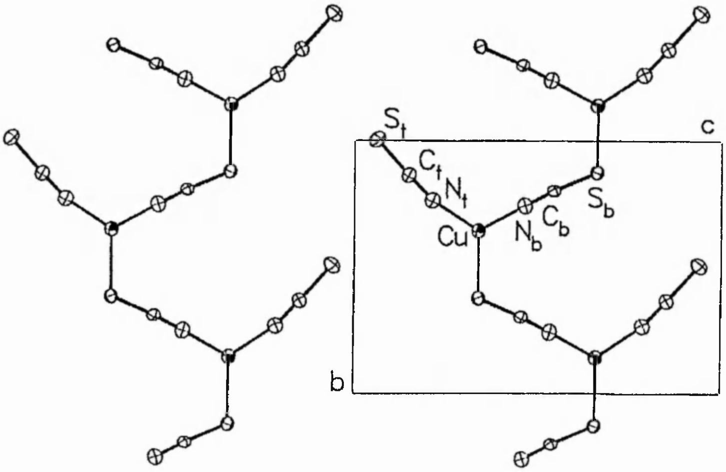


Figure 8. $Cu(NCS)_2$ polymeric network.

κ- $(ET)_2[Cu(CN)_2]Br$ with T_c near 11.6 K represents the highest T_c organic superconductor at ambient pressure based on ET.[18] Its structure is based on the κ-phase packing motif and a polymeric network of anions (Fig 9). The room temperature conductivity in the plane of the organic donor molecules is ~ 48 Scm^{-1}. On cooling from ambient temperature the salt changes from weakly metallic through to semicondutive behaviour below 220 K. This could be due to crystallographic imperfections due to anion disorder or impurities or defects in the crystal. On further cooling the superconducting transition is obtained at 11.6 K.

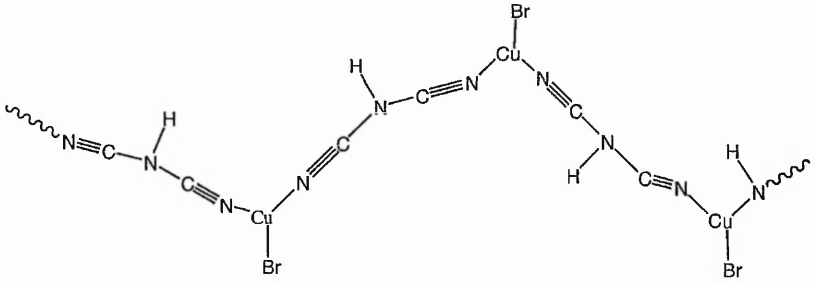


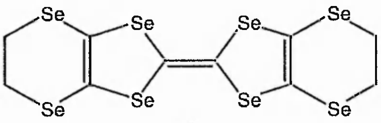
Figure 9. $[Cu(CN)_2]Br$ polymeric network.

11. Modifications to the TTF and ET frameworks.

The initial development of ET superconductors was based on the role of the counteranion, and its effect on the structure and solid state properties of the compounds in general and on T_c in particular, and therefore counteranions of all shapes and sizes have been investigated. The effect of the anion has been extensively reviewed.[19]

The introduction of heteroatoms other than sulfur into the ET framework

An alternative approach has been to modify the ET molecule to change the intermolecular interactions. Several electron donor molecules that incorporate the features of the ET molecule (e.g. a large number of sulfur or heteroatoms along the periphery of highly conjugated molecules) have been reported. Modifications have included the replacement of some or all of the S atoms with Se to yield compounds such as bis(ethylenediseleno)tetraselenafulvalene (BEDSe-TSeF)[50] **6** , bis(ethylenediseleno)tetrathiafulvalene (BEDSe-TTF) [51] **7** and bis(ethylenedithio)-tetraselenafulvalene (BEDT-TSeF)[52] **8**. It was envisaged that the incorporation of the larger selenium atoms for sulfur into the framework of ET would provide greater intermolecular orbital overlap, producing wider conduction bands, in turn stabilising the cation radicals and increasing T_c. However, these modifications have failed to deliver an increase in T_c, for radical cation salts based on ET.



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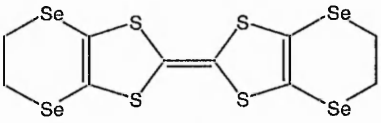

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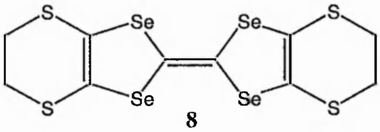

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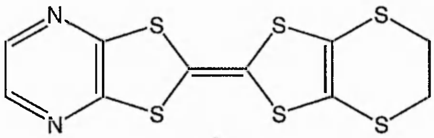
The introduction of N and O atoms into the outermost heterocyclic ring affords compounds such as the pyrazine derivative of ET **9**[53] and bis(ethylenedioxo)tetrathiafulvalene (BEDO-TTF) **10**[54], but these alterations to the ET framework have not led to an increase in T_c observed for the radical cation salts based on these novel donors.



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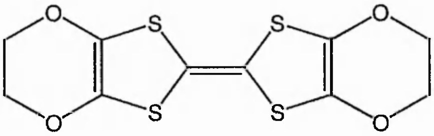

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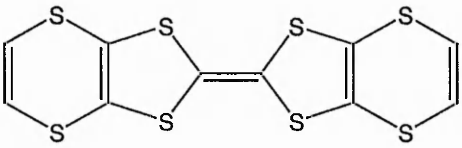
For ET-based superconductors it was proposed that the π-electronic system of the conducting component should be extended to its periphery to increase T_c. Replacement of the outer ethylene groups of ET with vinylene groups results in the formation of bis(vinylenedithio)tetrathiafulvalene **11**, abbreviated to VT.[52]



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An investigation into the conducting behaviour and structural analysis of $(VT)_2PF_6$ has revealed that this salt undergoes an MI (metal-insulator) transition near 180 K due to its 1D character.[55] This is due to the non- planarity of the donor molecule; the end vinylene groups are far out of the molecular plane (boat conformation) in both neutral and charged molecules. It should be noted at this point that ET has been converted to a far greater number of radical cation salts than these hetero- derivatives.

With such modifications of the ET skeleton not advancing T_c, the development of new methodology for the efficient synthesis of desired TTF- type donors has been the major focus of attention for synthetic chemists.[56] Thus, in the quest for higher T_c's, major attempts to modify the TTF skeleton in recent years can be broadly divided into two classes:

(i) The introduction of extended π-electron conjugation.

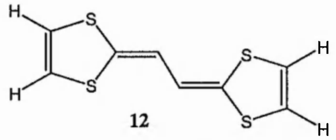
(ii) TTF donors functionalised with substituents capable of intermolecular hydrogen bonding.

The introduction of extended π-electron conjugation

Molecules with extended π-electron conjugation should be capable of stronger intermolecular interactions with each other in their radical cation salts by virtue of having a greater number of π-bonds and chalcogen atoms. This in turn should lead to a greater observed dimensionality. It is also possible that new packing motifs may be observed.

Extension of π-electron conjugation has followed three main areas of investigation:

(i) Replacement of the central C=C bond of the TTF core with the –C=CH-CH=C- grouping leads to salts which exhibit non-planarity in the crystal structure, due to the flexibility given to the donor molecules by the incorporation of the spacer group. This leads to an increase in dimensionality of the materials, and affords compounds of type **12**,[57] **13**[58] and **14**.[59] Although cyclic voltammetry measurements indicate that **12** is a stronger electron donor than ET, and as such is an ideal candidate for electrocrystallisation studies, obtaining crystalline salts has been very much harder than for TTF or ET.



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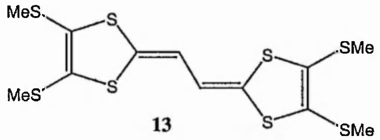

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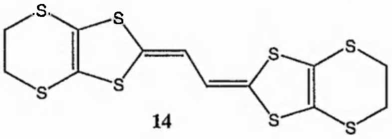

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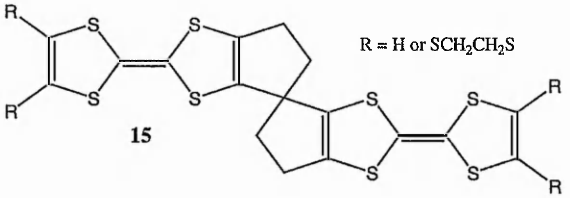
The use of spiroconjugation has been claimed as a way of increasing dimensionality in organic molecular materials. Thus TTF spirodimers such as **15** have been synthesized in which two TTF units are annealated on spirocyclic systems and hence are rigidly fixed in orthogonal directions.[60] However, redox potentials indicate that their donor abilities are somewhat reduced when compared with those of corresponding TTF monomers. Charge transfer complexes of **15** have been formed with DDQ.



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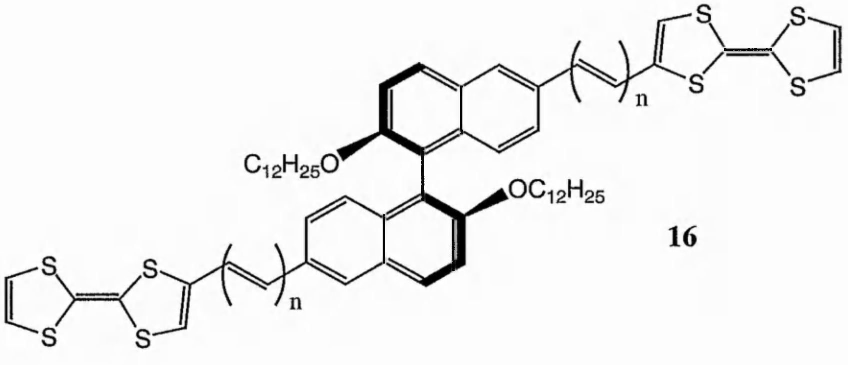
R = H or SCH_2CH_2S

Martín and Segura have recently reported the first optically active TTF dimers **16**, prepared from Wittig or Wittig-Horner reactions from the bis(triphenylphosphonium) salt of a binaphthyl system and the respective formyl-TTF unit.[61] Charge- transfer complexes have been formed, although X-ray data has not been obtained to confirm the salts have increased dimensionality.



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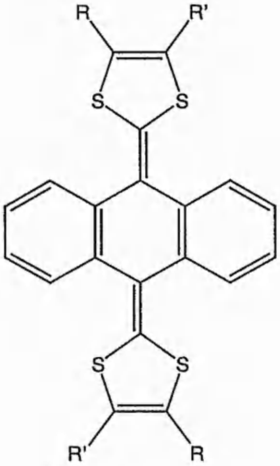
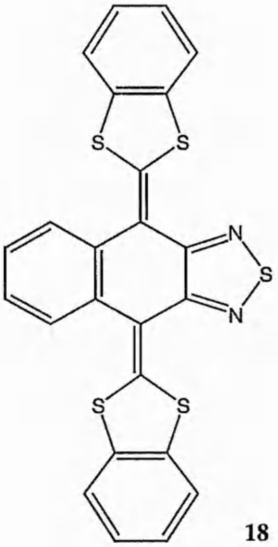
Insertion of a cyclic spacer group between the central C=C bond of the TTF core has afforded compounds of type **17**,[62] **18**[63] and **19**.[64]



17a R = R' = Me
17b R = SMe, R' = Me



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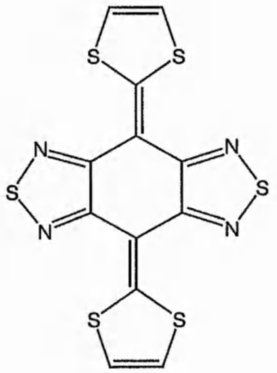

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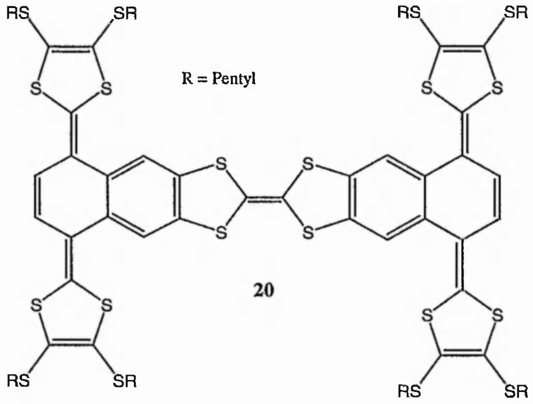
17a exhibits a highly distorted geometry with the central quinoid ring bent into a boat conformation. This distortion allows relief of steric contact between the *peri*-hydrogens and the sulfur atoms. Upon oxidation the anthracenyl system adopts an almost planar conformation, but with the two dithiolium cation rings nearly orthogonal, therby preventing conjugation between the two heterocyclic rings. **17a**$^{2+}$ $(TCNQ)_4^{2-}$ has a room temperature conductivity of 60 Scm^{-1},[65] and retains this high conductivity on cooling to 90 K, when a structural transition occurs and the metallic state is lost. **17b** does not form a conducting salt with TCNQ.

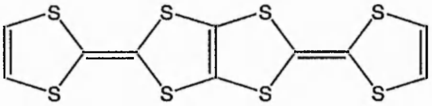
Replacement of one or more of the benzene rings of **17** with thiadazole rings leads to **18** and **19** respectively. Investigations by Yamashita *et al.* observed that this raises the oxidation potentials and results in a planar structure for **19**.[64] This structure is attributed to the N···S interactions between the thiadazole and the dithiole rings. Salts of **18** with PF_6^- and ClO_4^- have 1:1 stoichiometries and are semiconductors with room temperature conductivities of 8.3 and 2.1 x 10^{-2} S cm^{-1} respectively.

The highly extended, cross-conjugated and sulfur rich π-electron donor **20** was prepared by Gorgues *et al.*, introducing the H-shape as a new approach in the TTF array.[66] The formation of novel packing motifs leading to increased dimensionality is possible in the salts of **20**.



20

(ii) Increasing dimensionality by the formation of bis-TTF derivatives and TTF oligomers has been the focus of much research and has recently been reviewed by Becher.[67] These kinds of TTF derivatives display multi-stage redox behaviour that may provide the possibility of controlling the stoichiometry, band filling and molecular assembly in desired conductive complexes.



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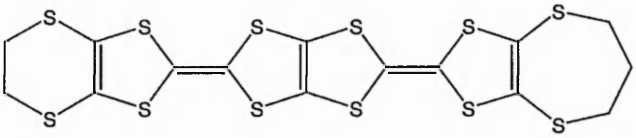
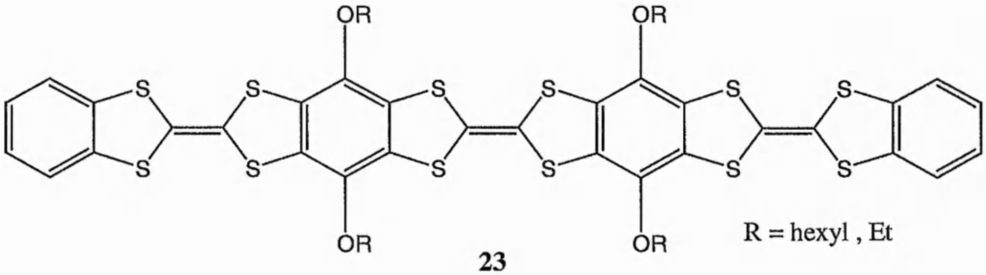


22

The structure and properties of radical cation salts of **21**[68] and **22**[69] with linear, tetrahedral and octahedral anions have been reported. Several of these are metallic down to liquid helium temperatures.

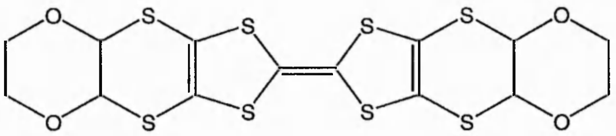
The synthesis of fully π-conjugated 'tris' TTF's such as **23** were reported by Adam and Müllen.[70] The TTF subunits are linked by fusion to a common benzene ring. The possibility of introducing functional groups on the dimers or oligo- TTF's allows more soluble materials to be obtained and also makes poly condensation reactions possible. This would enable the materials to be used as conducting rods.[71]



23

R = hexyl , Et

(iii) An alternative molecular design strategy that holds considerable promise for conducting materials with increased dimensionality is to append substituents and/ or additional heterocyclic rings to the TTF system, in anticipation of these addenda dominating intermolecular interactions, and leading to new molecular packing patterns conducive to formation of 2-D electronic structures. A number of variations have been synthesized, examples of this strategy are shown by compounds **24**,[72] **25** [73] and **26**.[74]



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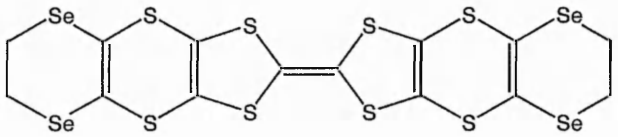

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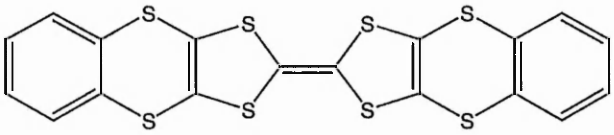


26

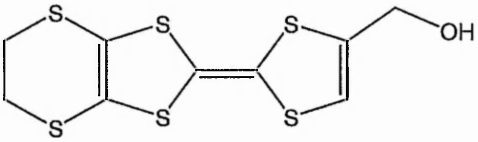
TTF donors functionalised with substituents capable of intermolecular hydrogen bonding

Disorder in the structures of the ET salts leads to incomplete intermolecular π-π overlaps of the orbitals of adjacent organic donor molecules, thereby lowering conductivity by creating localised electrons and introducing Peierls distortions. The lack of strong directed attractions between the donor molecules and the anions can also lead to anion disorder, as witnessed in β- $(ET)_2\ I_2Br$.[43] As earlier examples have shown, disorder is usually accompanied by a suppression of the superconducting transition temperature.

A way of ordering the constituent molecules is to introduce intermolecular hydrogen bonding. These weak interactions (~1-2 kcal mol^{-1} for C-H···O) are credited in controlling the structure of many solid state assemblies.[75] It is envisaged that the incorporation of substituents (hydroxy, amido etc) onto the TTF framework which form stronger hydrogen bonds with the anion will exert an orienting effect on the crystal structure, removing anion disorder and leading to increasing dimensionality and T_c. Furthermore, a substituent may "freeze" the conformation of the outer ring, whose disorder has sometimes been observed in ET salts.[44]

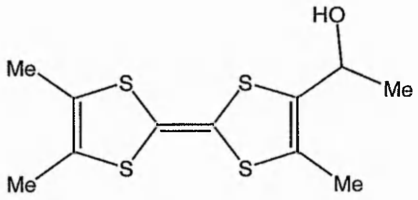
TTF molecules with appended hydroxyl functionalities

4-(Hydroxymethyl)ethylenedithio-TTF **27** was synthesised by Gorgues *et al.*[76] Salts of **27** were obtained with ReO_4^- and ClO_4^-, both of 2:1 donor: anion stoichiometry. Both salts are semiconductors (σ_{rt} = 0.27 and 3.0 S cm^{-1}, respectively), and exhibit weak O-H···O (donor···anion) hydrogen bonding interactions. A κ- phase donor packing arrangement is observed in $(\mathbf{27})_2ClO_4$, which is observed in the ET salts with the highest T_c values.



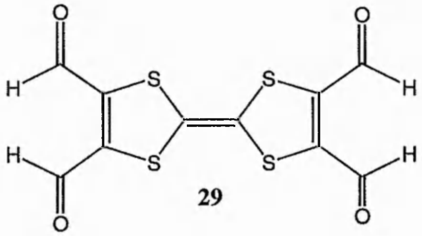
27

Racemic **28** is obtained via lithiation of trimethyl-TTF, followed by reaction with acetyl chloride in ether, and reduction with $NaBH_4$ in refluxing ethanol.[77] A 1:1 insulating mixed stack structure is formed between **28** and TCNQ. A weak intrastack hydrogen bond (O-H···NC) is observed that serves to link dimers of π-donor and π-acceptor along the stacks.



28

When tetraformyl-TTF **29** is submitted to a four-fold nucleophilic attack, compounds such as tetrakis- (hydroxymethyl)-TTF **30** are formed.[78]



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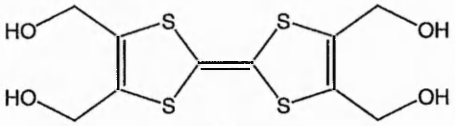
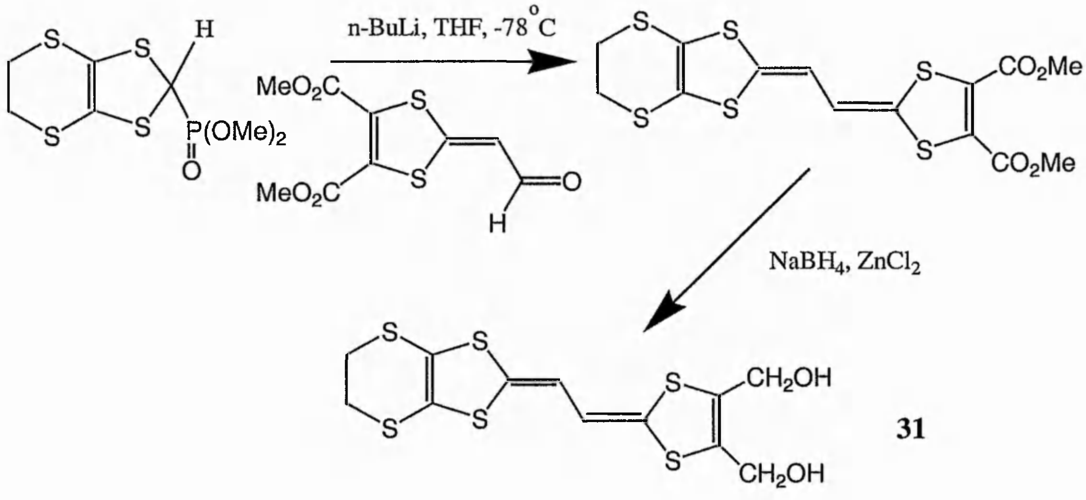


30

TTF derivatives endowed with extended π-electron conjugation and hydroxy groups have been synthesised. Gorgues *et al.* have reported the synthesis of **31** via a phosphonate coupling with an aldehyde to furnish the desired compound **31** in high yield.[79] Reduction of the ester moieties was achieved efficiently with $NaBH_4$-$ZnCl_2$.



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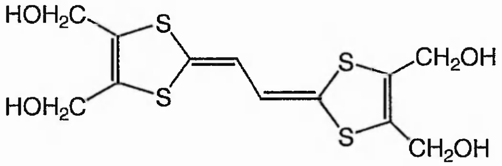
Further investigation by Gorgues *et al.* has led to the formation of the extended TTF-tetrol **32.**[80]



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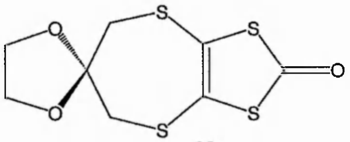
Investigations into the formation of new TTF derivatives using the ketal protected 1,3-dithiole-2-one **33**, led Bryce *et al.* to synthesise the TTF derivative **34.**[81]



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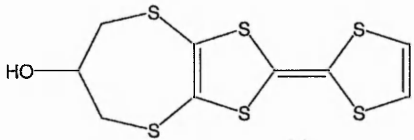
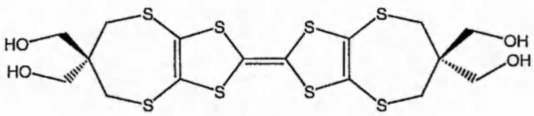


34

The group of Wallis *et al.* have synthesised a number of TTF derivatives endowed with hydrogen bonding functionalities. TTF derivatives with fused 1,4-dithiepine rings bearing hydroxymethyl side chains such as **35** and **36**[82] and with fused 1,4-dithiocene rings bearing hydroxyl functionalities such as **37** and **38**[83] have been obtained; the latter three having chiral structures.



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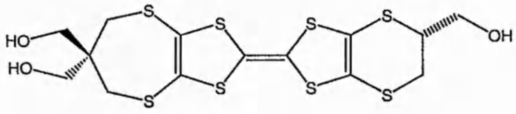

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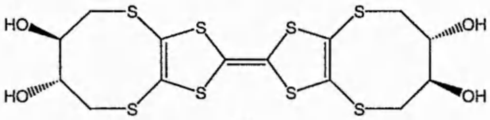

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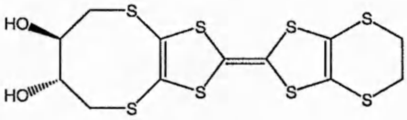
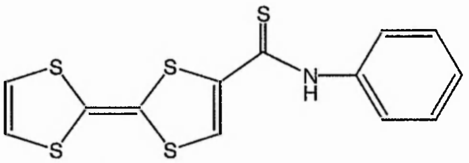


38

TTF molecules with appended thioamide and amido functionalities

The first TTF molecules bearing thioamide functionality were prepared by Bryce *et al.* via reaction of tetrathiafulvalenyllithium with isothiocyanates.[84] Phenyl- and methylisothiocyanate were employed to furnish **39** and **40** respectively. In the crystal structures of neutral molecules the packing is of a herringbone type and an extended hydrogen bonded chain network is observed, formed by the thioamide moieties.



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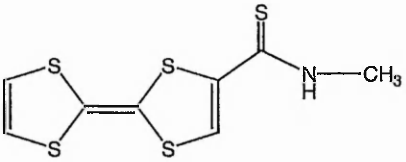
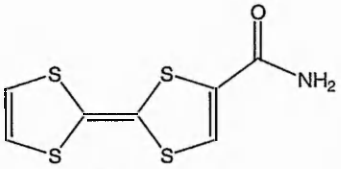


40

The dual hydrogen bond donor (N-H group) and hydrogen bond acceptor (oxygen atom of the carbonyl group) character of primary and secondary amides have been shown to drive the formation of well defined supramolecular arrays,[85] *via* N-H···O hydrogen bonds.[86] Hence, the amide functionalisation of the TTF core has given rise to a number of salts whose crystal structure is dependent upon a range of competing interactions; hydrogen bonding, van der Waals and SOMO···SOMO overlap interactions.

Several TTF's substituted with amido groups have been prepared. The simplest primary amide of TTF **41** was reported by Powell *et al.*[87] Hydrolysis of the cyano derivative TTF-CN furnished **41**. However, attempts to form CT salts were unsuccessful. In a similar fashion, the hydrolysis of tetracyano-TTF by Yoshida *et* al. afforded the tetrakisamido- TTF **42** as a purple crystalline solid.[88]



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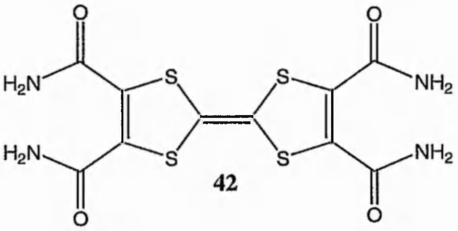
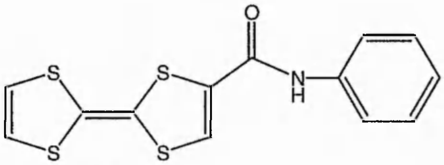


42

Using similar methodology, secondary amides such as **43** were prepared by Bryce *et al.* by reaction of tetrathiafulvalenyllithium with phenylisocyanate.[89] The tertiary amide **44** was prepared from reaction of the acid chloride TTF-COCl with dimethylamine.[90]



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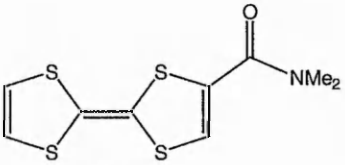
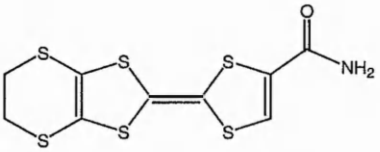


44

Fourmigué, Batail *et al.* have prepared a series of EDT-TTF functionalised amides **45-48**, where the amide functionality is directly attached to the TTF core.[91] Cyclic voltammetry measurements indicate that compared with EDT-TTF, the first oxidation potential is anodically shifted by 60-80 mV, indicating the electron withdrawing affect of the amido group. The oxidation potentials however are still lower than ET, thus radical cation salts are expected to form by electrocrystallisation.



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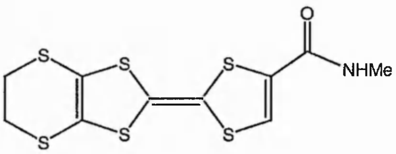

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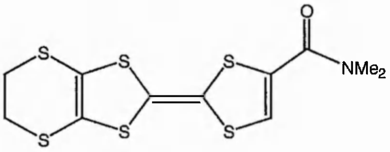

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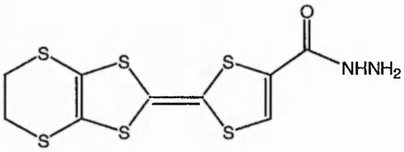
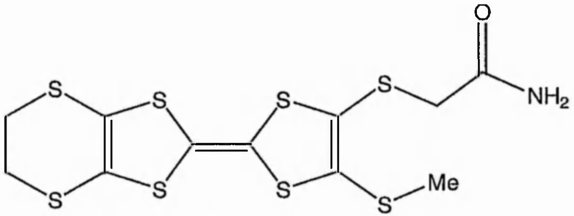


48

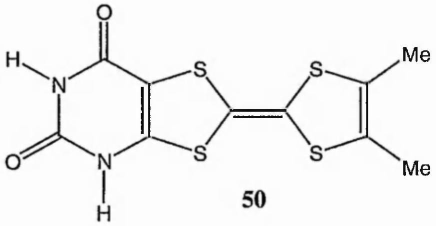
The solid state structure of the neutral molecule **46** indicates N-H···O hydrogen bonds and C-H···O hydrogen bonds arising from the H atom located *ortho* to the amidic group and the O atom of the carbonyl ordering the crystal structure. The tertiary amide **47** lacks any of the strong NH or OH hydrogen bond donors found in **45** and **46**.

TTF derivatives with spacers between the TTF core and the amido functionality have been used in the preparation of Langmuir-Blodgett films.[92] TTF derivatives with short spacers have also been prepared to investigate hydrogen bonding interactions. Adding a spacer group also aids solubility of these materials, but hampers crystallisation due to the degrees of freedom introduced by the spacer. Sugawara *et al.* have prepared a TTF derivative **49** carrying a carbamoylmethyl group ($CH_2CO_2NH_2$).[93]



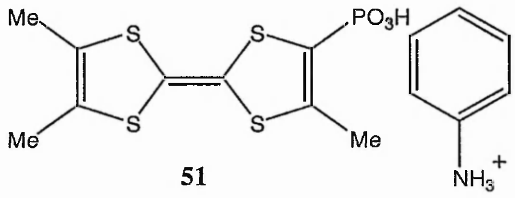
49

The molecules of **49** in the neutral crystal form stacks parallel stacks due to N-H···O interactions between adjacent molecules. The structure is in contrast to the crystal structure of neutral ET, which adopts the herringbone packing arrangement.



50

The TTF derivative **50** containing a uracil moiety, synthesised by Neilands *et al.*, gives rise to dimers of **50** in the solid state due to intermolecular hydrogen bonds between uracil moieties (two strong N-H···O hydrogen bonds, N···O separation 2.85Å).[94] Strong hydrogen bonding interactions are observed in the anilinium phosphonate salt **51**.[95] The radical cation salt obtained on oxidation of **51** is a neutral zwitterion $[Me_3TTF\text{-}P(O)(OH)O^-]^{+\cdot}$.



51

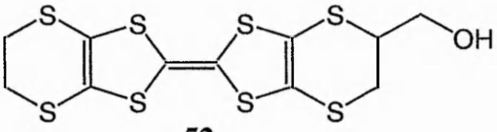
Recently, the synthesis and characterisation of TTF salts based on the $TTF(CO_2H)_2(CO_2^-)_2$ dianion was reported.[96] The salt exhibits 2:1 donor: anion stoichiometry ($(TTF^+)_2$ (dianion)). This is a wholly novel approach to the synthesis of radical cation salts where TTF-derived anions are incorporated into the donor slabs, thus the anion layers do not exist. The packing of the salt observes a β- type structure. A strong hydrogen bond network with various C-H···O interactions help to regulate the crystal packing (Fig 10).

Figure 10. β-type crystal packing structure of TTF_2 (TTF $(CO_2H)_2(CO_2^-)_2$ (left) indicating six nearest neighbours, hydrogen bonding network (right). Picture from ref 96.

ET molecules with appended functionalities capable of intra- and intermolecular hydrogen bonding interactions

Most synthetic efforts to attach substituents capable of hydrogen bonding have been carried out on the TTF framework and very little progress has been reported to functionalise ET. This is somewhat surprising, considering that ET has provided all of the organic superconductors with $T_c > 10$ K. The following compounds are the only ET derivatives that have been reported that carry appended hydrogen bonding substituents:

Hydroxymethyl-ET (HMET) **52** has been prepared in both enantiomeric[97] and racemic[98] forms by Wallis *et* al. Zhang *et al.* have also recently published their own synthetic route to racemic HMET **52.**[99]



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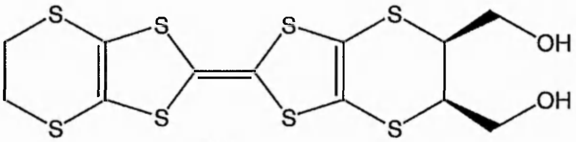
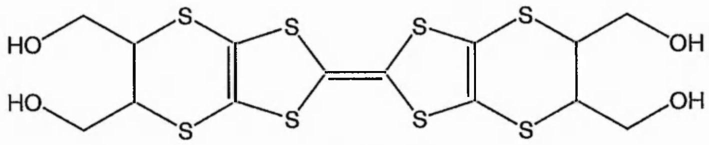
Further investigations by Zhang *et al.* has led to compound **53** being prepared, where the hydroxymethyl groups are in a *cis* conformation.[99]



53

Two groups have reported the synthesis of **54** as a mixture of diastereoisomers.[100, 101] The two strategies for the formation of **54** are identical, differing in the choice of protecting groups for the hydroxy functionalities. To date, no radical cation salts of **54** have been published. No ET derivatives appended with amido functionalities have been reported.



54

This thesis is concerned with the synthesis of novel ET derivatives functionalised with one or more hydrogen bonding substituents as hydroxyls or amides for ordering the crystal structures of the radical cation salts, by donor – anion interactions. Furthermore, the synthetic routes developed will open up ways of attaching ET to new molecular systems, and this will lead to new applications for ET derivatives.

12. New applications for TTF-based molecules.

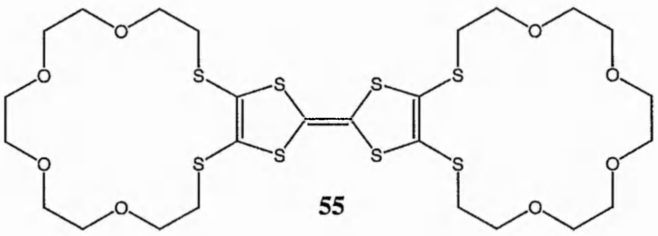
Coronado *et al.*[102] have synthesised a new hybrid conducting- magnetic material based on ET, formed by infinite sheets of a magnetic coordination polymer (a bimetallic oxalato complex) interleaved with layers of the organic conducting cation, $(ET)_3^+$. The molecule-based compound displays both ferromagnetism and metallic conductivity and is the first reported example involving molecular materials. In conventional metallic ferromagnets, the mobile electrons play a crucial role in both the magnetic interactions and in the electrical conductivity. But in the new system of Coronado *et al.*, the conducting electrons in the organic layer do not appear to interact with the magnetic moments of the ferromagnetic layer. This unique feature, which is only possible because of the molecular nature of the system, may yield unforseen physical behaviour. If routes to functionalised ET's can be found, then the ET molecule could be bound into the magnetic system.

T_c for TTF-based superconductors has held at 11.6 K for over a decade. Since then, many studies have been aimed at investigating the redox properties of TTF-derivatives at the macromolecular[103] and supermolecular[104] level. Both have been reviewed recently. TTF- dendrimers have been synthesised, giving rise to new and exciting redox behaviour for multi-TTF systems. Incorporation of TTF into dendrimers offers well-controlled redox behaviour with the increased solubility that these macromolecules possess. TTF-derivatives have also been incorporated into polymers. The incorporation of TTF-derivatives into these larger molecular systems allows the possibility of novel materials being obtained which are stable and can be processed easily.

Also during this time a number of unconventional applications of TTF-based molecules have been studied with a view to incorporating these molecules into devices such as chemical sensors, molecular shuttles and new molecular switches. New applications for TTF-based molecules have recently been extensively reviewed.[105, 106] It is the purpose of this section to highlight some of the advances made over the past decade.

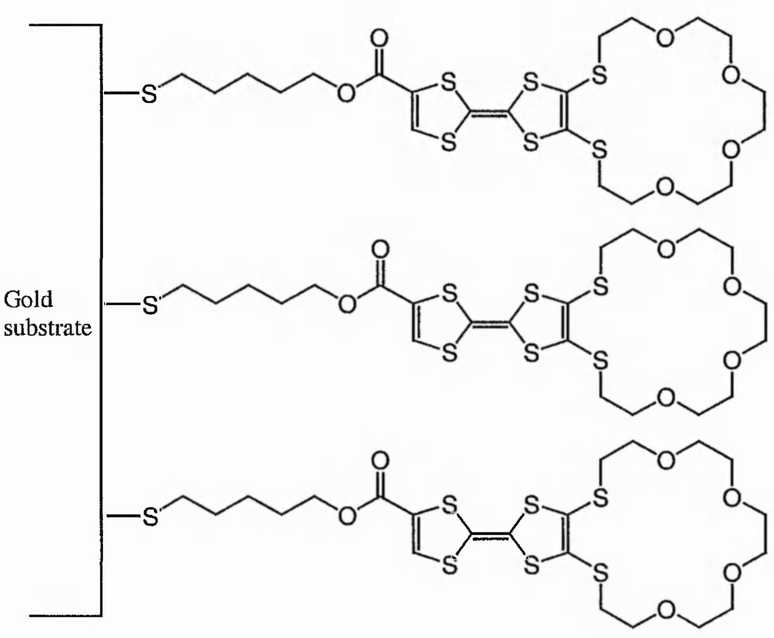
Cation sensors:

TTF based molecules appended with crown ethers[107] such as **55** are able to selectively ‘trap’ cations, in this case, sodium.[108] The presence of the cation within the crown ether is observed by the inductive effect this has on the first oxidation potential of TTF. A positive shift is noted in cyclic voltammetry experiments. Changes in the ^{1}H NMR spectrum of the crown ether moiety also give an indication to complexation.



55

Self assembled monolayers (SAM's) of TTF derivatives appended with crown ethers have been synthesised and offer a realistic chance of exploiting the redox properties of TTF for commercial purposes.[106] The TTF derivatives carrying thiol functionalites such as **56** have been assembled on gold or platinum solid supports and show stable and reproducible redox behaviour.[109]



56

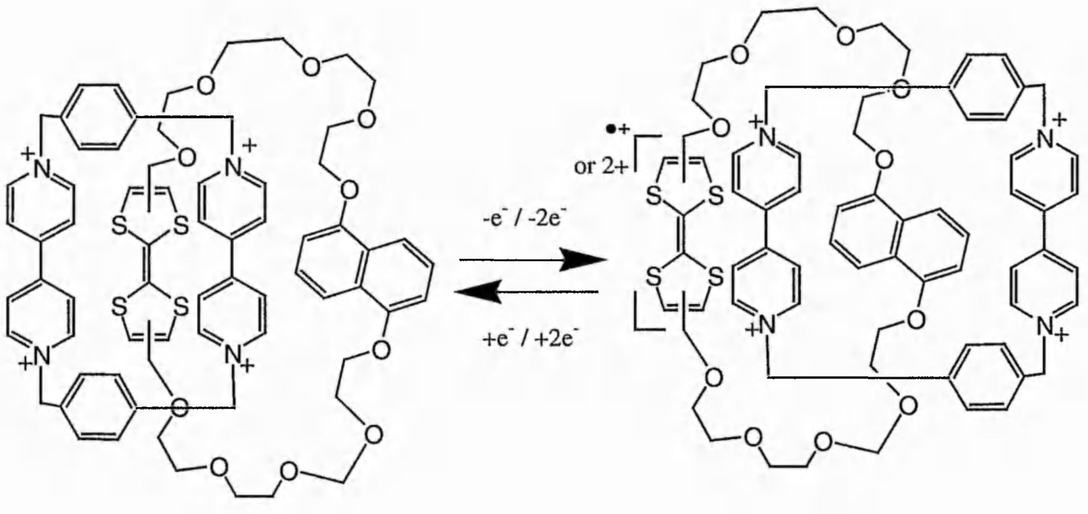
56

56

Figure 11. Self assembled monolayer of **56** on gold substrate.

Molecular switches:

TTF is an ideal building block for molecular switches due to the reversible oxidation to its radical cation that can be controlled both chemically and electrochemically. The chemically and electrochemically controlled [2]catenane **57^{4+}** contains two electron rich sites in the ring, the TTF molecule on one side and the 1,5-dioxynaphthalene ring system in the other.[110] These are connected by polyether linkages. The neutral TTF molecule sits inside the electron- deficient cavity, the colour of the complex being green. On oxidation, the ring rotates to leave the TTF radical cation (or dication) outside and the naphthalene unit within the cavity. The colour of the solution on oxidation turns maroon. The stabilisation of either state is due to charge transfer interactions between the electron deficient bis (pyridinium) ring and the planar electron rich system.



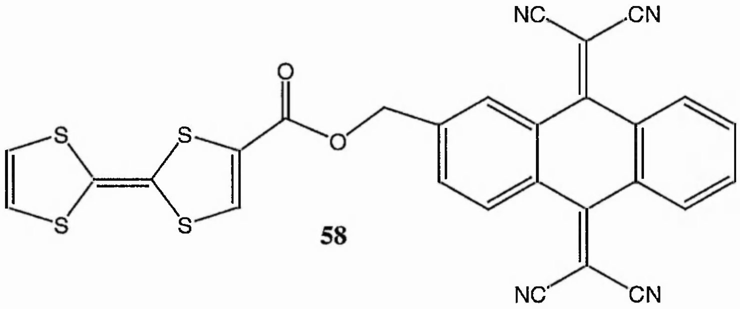
57^{4+} **$57^{5\bullet+}$/ 57^{6+}**

Figure 12. Reversible redox process – 'molecular switch'.

TTF derivatives as intramolecular charge transfer (ICT) and non- linear optical (NLO) devices:

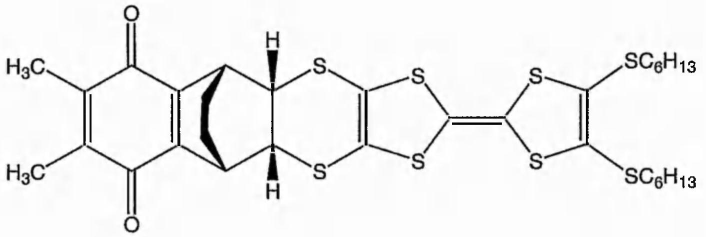
In 1974 Aviram and Ratner proposed rectification of electrical current through a single D-σ-A molecule, in which a strong donor moiety is covalently attached to a strong acceptor moiety through a covalent saturated bridge.[111] Intramolecular charge transfer (ICT) processes in donor-acceptor molecules are key to studies on chromophores in dyes, nonlinear optics and synthetic light harvesting systems.

The study of ICT processes in TTF derivatives offers considerable scope for potential and has commenced. One of the key challenges to the synthetic chemist in the formation of intramolecular ICT molecules is to avoid the formation of a stable intermolecular CT complex of donor and acceptor prior to the introduction of the covalent linking group. **58** represents the first readily available, analytically pure, TTF-spacer-TCNQ derivative.[112]



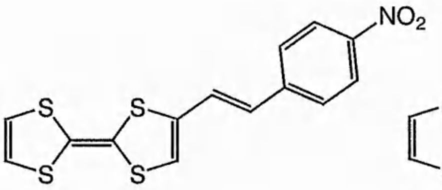
58

Single component molecules have also been synthesised such as **59**.[113] The molecule is oriented in such a way as to have the acceptor p-benzoquinone portion above the central portion of the TTF donor moiety. This gives rise to short intramolecular distances between the planes of donor and acceptor molecules and results in a weak charge transfer occurring.

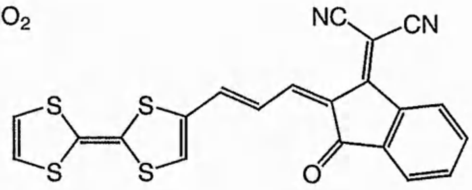


59

An increase in the NLO properties of TTF derivatives has been observed by using stronger electron acceptors attached to the TTF core by conjugated pathways. Advances in this field have been made with the introduction of compounds **60**[114] and **61**.[115]



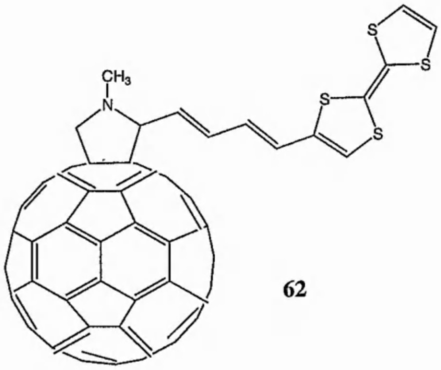
60



61

Photovoltaic applications of TTF- containing fullerenes

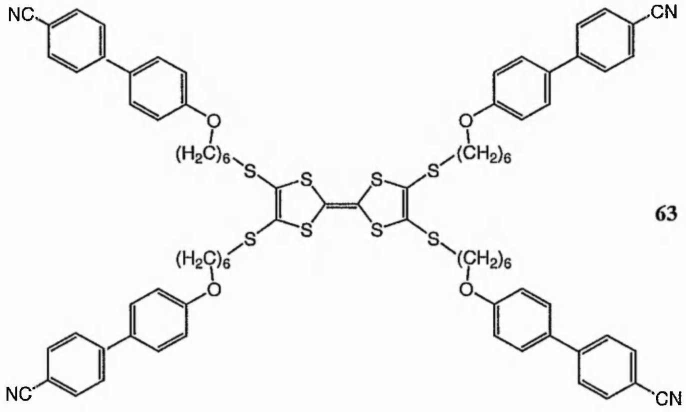
Apart from investigations into the conductivity of fullerene CT salts, C_{60} has been the focus of attention for many other studies including potential photovoltaic applications of TTF-C_{60} derivatives.[105] The use of these compounds such as **62** as artificial photosynthetic systems to transform sunlight into chemical energy is one of the more realistic applications of fullerenes.



62

Liquid crystalline derivatives of TTF

The incorporation of TTF molecules into liquid crystalline materials provides a way of ordering the TTF moieties with respect to one another and also introduces the possibility of novel materials for liquid crystal display technologies. On doping compound **63** with iodine, a nematic phase is observed below 84°C.[116] The result is an indication that highly ordered multiproperty materials could be obtained using TTF-derivatives.



63

13. Future technological applications of electric organic materials.

The most intense effort in organic superconductor research is now occurring in Japan. Analysts there believe that small organic molecules are most likely to be used as individual components or devices. The presence of a single extra electron on a small organic molecule can cause the molecule to charge up to about 1V. Such molecules could therefore be used as single electron switches at room temperature, particularly because thermal fluctuations under these conditions are equivalent to just 0.025 V. The use of individual molecules as functional electronic devices was first proposed by Aviram and Ratner in 1974,[111] and since then molecular electronics has attracted much interest, particularly because it could lead to conceptually new miniaturization strategies in the electronics and computer industries. On a practical level, one important difference between organic superconductors and all others is the low density of the organic materials, about 2 gcm^{-3}. This makes them only 20-30 % as dense as superconducting metals such as niobium.

In general, current molecular electronics is an approach which uses assemblies of individual molecules to mimic larger conventional structures such as switches or semiconductors, with the goal of full control over the composition, size, and function of the molecules, and thus of their behaviour. This means that molecular electronic devices are tunable and can more readily be tailored to respond to the changing demands of technology. During the past several decades, some of the basic building blocks needed for molecular electronics have been created, including so-called "single-molecule magnets". By combining an organic conductor and a magnetic complex, Coronado *et al.* have now introduced the possibility of materials with multiple functions.[102]

The self-arranging properties of small organic molecules will also allow three-dimensional arrays of such devices to be built up. Unlike silicon chips – which are essentially flat and therefore cause the flow of information to be trapped in bottlenecks – a three-dimensional array of organic devices would allow information to flow along multiple directions and in complex patterns. Needless to say, such device arrays will not come onto the market for at least 10 years. Key challenges include refining the techniques used to make electrical contact with individual molecules, and replicating simple devices such as diodes in single polar molecules.

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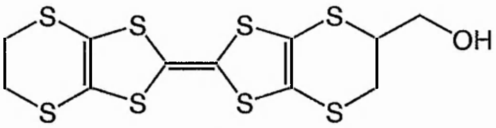
Chapter 2

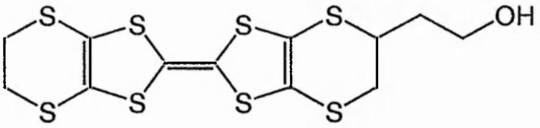
Synthesis of hydroxy- functionalised ET donors

Preparation and properties of radical cation salts of HMET

1. Introduction.

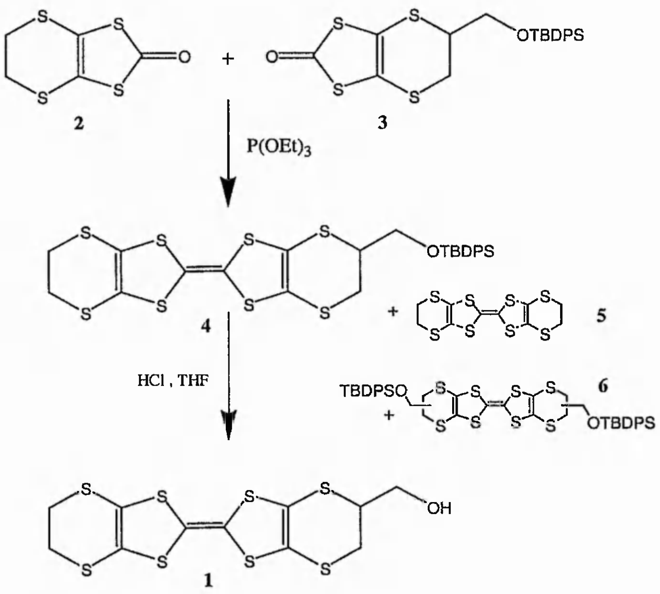
The synthesis of racemic hydroxymethyl ET (HMET) **1** has previously been carried out in the Wallis group and the synthetic strategy published, [1] but extensive investigations into the radical cation salts of this compound have not been made. Zhang *et al.* [2] have also recently published their own synthetic route to racemic HMET **1** and have reported the preparation and characterisation of two radical cation salts. A single crystal of (HMET)I_x formed by electrocrystallisation was found to have a room temperature conductivity of 0.08 S cm^{-1}. Transport measurements showed the salt to be a semiconductor. [3] A second salt was prepared, [2] the semiconductor (**1**)$_2$ClO$_4$, with a room temperature conductivity of 0.68 S cm^{-1}.


HMET


HEET

During the course of these current studies, racemic HMET **1** was synthesised several times in seven steps, and was purified by chromatography and stored carefully under nitrogen. Electrocrystallisations under constant current conditions conducted at The Royal Institution of Great Britain, London, have led to ten new radical cation salts, four of which have been characterised by chemical analysis, Raman and infrared spectroscopy[1]. The chemical analysis data for the four salts indicate a 2:1 stoichiometry of HMET to anion. Conductivity and magnetic data for the salts has also been obtained. The project has been extended to provide a simple synthesis of hydroxyethyl- ET, HEET. [4]

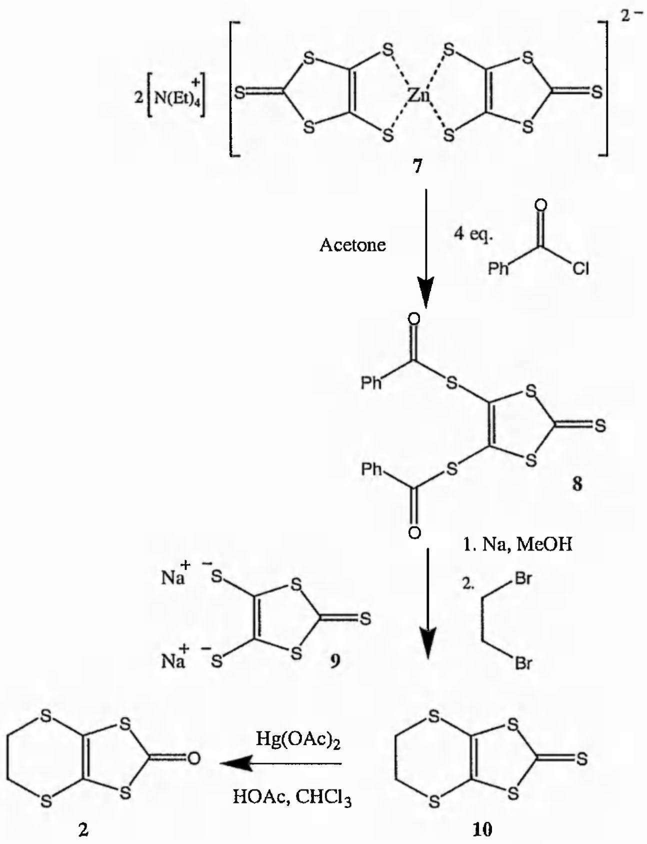
2. Synthesis of racemic HMET, 1.



Scheme 1. Coupling and deprotection methodology for **1**.

The synthetic route towards racemic HMET **1** involves the formation of the central C=C bond near the end of the synthesis (scheme 1). Treatment of a mixture of oxo compounds **2** and **3** with triethyl phosphite furnishes **4** in 39% yield after chromatographic separation from ET **5** and a mixture of isomeric disubstituted ET's **6**. The ^{1}H NMR of **4** shows a singlet at δ: 3.29 corresponding to 5'- & 6'- H_2, and the CH_2CHCCH_2 system at the other end of the molecule is described by the multiplet at δ: 3.74 which integrates for three hydrogens and is assigned as CH_2OH & 5- *H*, and the two double doublets at δ: 3.30 and 3.22 which correspond to the two protons on 6-*C*. These couple to each other with a *J* value of 13.5 Hz, and to 5- *H* with couplings of 5.0 and 3.4 Hz respectively. The ^{13}C NMR indicated three different sp^2 environments, shifts being observed at δ: 114.6, δ: 113.6 and δ: 113.2, where four might be expected. Thus, two shifts are probably the same, though these are the weakest peaks in the spectrum.

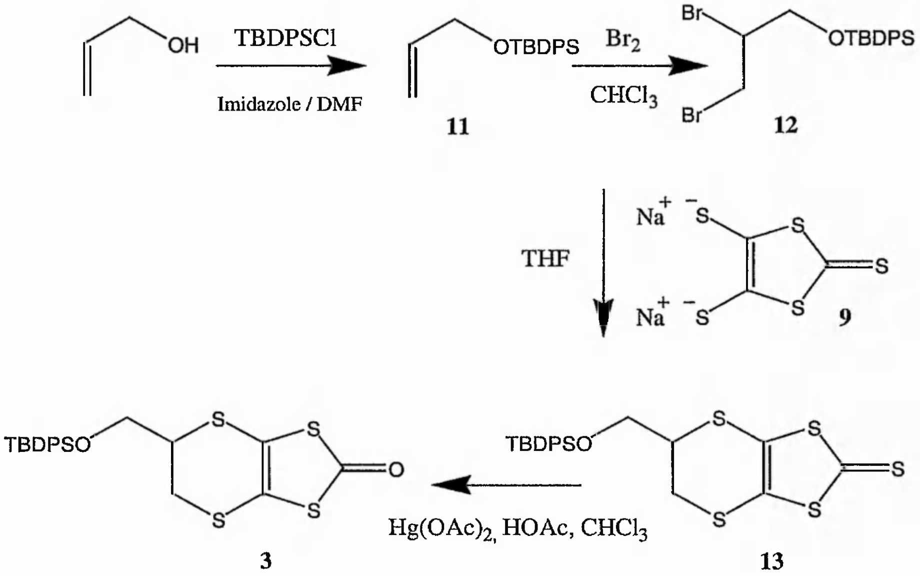
Deprotection of **4** with a 20% HCl solution in THF under N_2 affords racemic HMET **1** as an orange solid in 75 % yield. The structure of **1** was supported by the broad singlet observed in the ^{1}H NMR spectrum at δ: 1.58, indicating a hydroxy proton, a singlet at δ: 3.32 was assigned as 5'-, 6'- H_2. A characteristic broad OH absorption was present in the infrared spectrum. The protected material **4** is a stable compound and can be stored indefinitely. Due to its stability a 'stockpile' can be built up and an adequate quantity deprotected at a time to furnish **1** when required for a series of electrocrystallisation experiments. If exposed to atmospheric conditions **1** decomposes readily, therefore it is stored under nitrogen and ideally used within a couple of days of preparation. In this it is different from ET **5**, which is much less sensitive. This synthesis depended on access to the oxo compounds **2** and **3**, whose syntheses are described below.



Scheme 2. Synthesis of compound **2**.

The synthesis of compound **2** (scheme 2) is well known and has been documented previously in the literature. [5] Following the revised preparation for the formation of zinc complex **7** described by Bryce *et al.*[6], reaction of sodium with carbon disulfide in DMF for 8h., followed by the addition of zinc chloride and tetraethylammonium bromide and overnight stirring furnished the zinc complex **7** as a red solid in 76 % yield. Treatment of zinc complex **7** in acetone with 4eq. of benzoyl chloride yielded the dibenzoylated compound **8** after recrystallisation as a bright yellow solid in 88 % yield.

The disodium salt of dithiolate **9** was obtained *in situ* by stirring of **8** in sodium (1.2eq.) in methanol for 1h. under nitrogen. Reaction with 1eq. of 1,2-dibromoethane at room temperature under nitrogen for 12h. precipitated the bicyclic thione **10** which was obtained as a bright yellow solid after recrystallisation in 84 % yield. Treatment of **10** with mercuric acetate in chloroform and acetic acid led to the replacement of the exocyclic sulfur atom for oxygen to furnish oxo compound **2** as a light brown solid in 95 % yield.



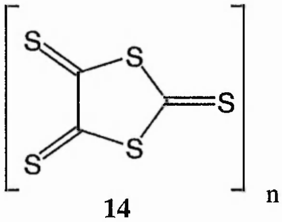
Scheme 3. Synthesis of compound **3**.

The synthesis of the protected oxo compound **3** (scheme 3) started from allyl alcohol. Treatment of the inexpensive starting material with *t*-butyldiphenylsilyl chloride to protect the hydroxyl group yielded **11** as a colourless oil in 96 % yield. In the ^{13}C NMR the expected sp^2 resonances (1- *C* & 2- *C*) were found at δ: 133.6 and δ: 113.8. Subsequent treatment of **11** with one equivalent of bromine furnished the dibromo compound **12** as a pale orange oil in 95 % yield. The ^{13}C NMR of **12** indicated the change in shift of 1- *C* & 2- *C* which were now found at δ: 32.6 and δ: 51.5 respectively.

The disodium salt of dithiolate **9** was obtained by the addition of dibenzoyl compound **8** to a solution of sodium in methanol and stirring for 1h. [7] Precipitation of **9** as a red solid in 95 % yield was achieved by the addition of a large volume of ether to the reaction mixture. The product was collected by filtration under a nitrogen atmosphere and dried under vacuum. After drying, the dithiolate salt **9** was used immediately. Reaction with dibromide **12** in THF at room temperature under nitrogen for 12h. provided the bicyclic thione **13** as a bright yellow solid in 54% yield after chromatography. The structure of **13** was supported by the ^{13}C NMR, the thione carbon was observed at δ: 207.1 and the sp^2 *C* atoms at δ: 123.7 and δ: 121.9, with sp^3 *C* atoms at 64.6, 45.1, 31.1, 26.7 and 19.1. The infrared spectrum of **13** shows an absorption at 1062 cm^{-1} corresponding to a C=S stretch.

Replacement of the exocyclic sulfur atom by treatment of **13** with mercuric acetate in chloroform and acetic acid led to oxo compound **3** as a pale yellow oil in 93 % yield. Evidence for the structure of **3** was given by the ^{13}C NMR, which showed the expected carbonyl resonance at δ: 188.7. The sp^2 *C* atoms were observed at δ: 114.4

and δ: 112.7, showing upfield shifts ~ 10 ppm from **13**, typical of these oxo systems. The carbonyl stretch was observed in the infrared spectrum at 1678 cm^{-1}.



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Zhang *et al.* [2] have recently published their own synthetic route to racemic HMET **1**, which involves cycloaddition of allyl alcohol with trithione **14**, followed by the same protection stategy as described here. The two synthetic routes are comparable. Their route consists of six steps from zinc complex, has an overall yield of *ca.* 8 %, and involves three chromatographic separations, while the synthesis described here from the same starting material, **1** requires one extra step, has slightly better overall yield *ca.* 11 %, and involves the same number of chromatographic separations.

3. Preparation and properties of radical cation salts of racemic HMET 1.

The results of cyclic voltammetric measurements on racemic **1** show the first two oxidation potentials at 0.48 and 0.74 V relative to Ag/AgCl. These are similar to those of ET (0.48 and 0.89 V relative to Ag/AgCl) and indicate that racemic **1** is a candidate for electrocrystallisation studies. Radical cation salts of HMET **1** are formed by the oxidation of HMET (by electrochemical means) in the presence of a particular anion.

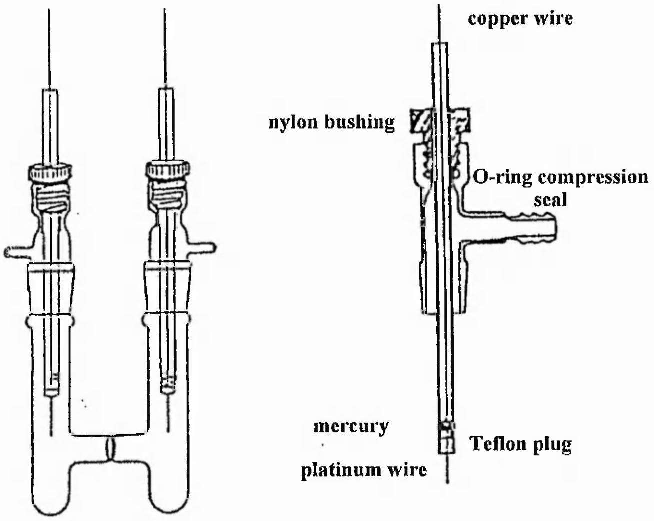


Figure 1. H-cell apparatus.

The apparatus shown above is used in the formation of the salts and is commonly known as an H-cell. The formation of the radical cation salts was carried out at the Davy Faraday Research Laboratory (DFRL) at the Royal Institution of Great Britain, London.

Key factors to the growth of large single crystals include purifying and drying the solvents. In the main, HPLC grade DCM was used as solvent. Initial experiments used undistilled DCM in order to obtain information for which salts would give crystalline products. If the product (if any) obtained looked crystalline the experiment was repeated with dry DCM. DCM was dried over P_2O_5 and distilled immediately prior to use onto molecular sieves. The platinum electrodes were prepared for electrocrystallisation by standing in dilute nitric acid overnight and washing with water and methanol before being dried in a hot oven. The electrocrystallisation experiment is summarised below:

10mg of HMET **1** is added to the anode compartment of the cell. A solution of the counter-ion (100mg in 50ml DCM) is added to the cathode compartment of the cell. This then flows through the frit, covering the donor material, until equilibrium is established and liquid levels in both sides are equal. N_2 is then bubbled through the solution in the anode compartment to remove O_2. The anode and cathode of the H-cell assembly are connected to an external current supply. The current is set to 1.0μA. Products are collected usually after 2-3 weeks or when the colour from the solution due to the donor is lost.

Radical cation salts of HMET with simple non-magnetic counter-ions

In the preparation of radical cation salts, the first counter-ions to be investigated were the tetrabutylammonium (TBA) salts of PF_6^-, BF_4^-, ClO_4^- and Cl^-. These were chosen as a starting point in order that the results obtained could be compared against the radical cation salts of ET with these counter-ions. Experiments gave black micro-crystalline products. These were analysed for donor : anion stoichiometry using elemental analysis. Results indicated that the salts were of 2:1 donor : anion stoichiometry, similar results were observed for the radical cation salts of ET with these counter-ions.[8]

The salts were also analysed by Raman spectroscopy which gives an indication of charge on the donor molecule, from the position of the central C=C stretching vibration (1400-1550cm^{-1}).[9] The central C=C stretching vibrations for all four salts were observed in the range 1464-1467cm^{-1}, typical of radical cation salts of ET with stoichiometry 2:1. The Raman spectrum from a 1:1 radical cation salt would show an absorption in the region 1410-1420 cm^{-1}, though the absorption from a 3:2 salt would be in the same region as that from a 2:1 salt. Analysis of the salts by infrared spectroscopy showed the expected stretching vibrations of the counter-ions; for example, the infrared spectrum of $HMET_2.PF_6$ indicated absorptions at 556.3 cm^{-1} and 843.4 cm^{-1}. These compared favourably with the literature values for the infrared active modes υ_3 and υ_4 for PF_6^-, which are observed at 840 cm^{-1} and 555 cm^{-1} respectively.[10] Crystals harvested from the experiments were unsuitable for X-ray crystallography due to their small size and also the stacking of the crystals upon one another during their growth. Thus, it is not known to date, which packing mode is adopted in each of these cases. The increasing progress in solving structures from very small crystals or even powders may help solve this problem in the future.

Conductivity measurements

Transport properties for each of the radical cation salts were carried out using the four probe conductivity method on compressed pellets using gold wires attached by platinum or silver paste. The pellets were formed in much the same manner as a KBr disc used in infrared spectroscopy. The die was made at the Royal Institution, pressure being applied to compress the crystals into a pellet by placing the die in a vice and tightening by hand. Typical cross sectional areas of the pellets obtained were ~ 0.002 cm^{-1}. Conductivity measurements were carried using an Oxford Instruments Mag lab 2000 with EP probe, capable of measurements in the range 1.8- 400K. The four probe d.c. conductivity experiment is explained below:

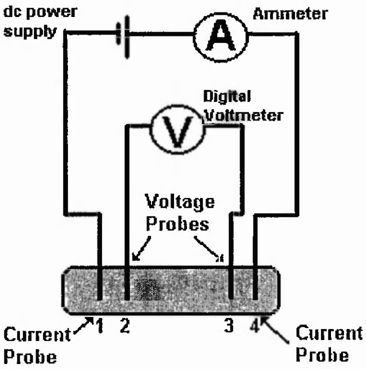


Figure 2. Schematic diagram of d.c. four point probe apparatus.

The four probe d.c. conductivity experiment is one of the most common methods of determining the T_c of a superconductor. Wires are attached to a material at four points with a conductive adhesive such as gold paste. As shown in figure 2, through two of these points (1 and 4) a voltage is applied and, if the material is conductive, a current will flow. Then, if any resistance exists in the material, a voltage will appear across the other two points (2 and 3) in accordance with Ohm's law ($V = I \cdot R$). When the material enters a superconductive state, its resistance drops to zero and no voltage appears across the second set of points. By using the four-point method, instead of just two points, resistance in the adhesive and wires can be ignored; as any current measured between the second set of points can therefore only reflect what voltage exists across the body of the material.

The conductivity σ, Scm^{-1}, or the resistivity P, is calculated as:

$$\sigma = 1/P = (I/V)\,(d/A)$$

Equation 1.

where A is the cross-sectional area of the pellet and d is the distance between the two central electrodes. In a single crystal sample, with probes attached along different axial directions, the conductive anisotropy can be determined.

Electrical conductivity or resistivity is an intrinsic property of the crystal. However, it may differ from crystal to crystal for different specimens of the same material because of differences in impurity levels, crystal imperfections and mechanical defects. Chemical impurities are presumed to be very low in concentration, but microcracks occur frequently and may be promoted by thermal stresses induced by the mechanical confinements of the resistance measuring probes. The experiments to measure conductivity carried out within this investigation used compressed pellets rather than a single crystal, but similar problems can be expected to those mentioned above. Electrical contacts between grain boundaries will vary from pellet to pellet, but repeated experiments on 3- 4 different pellets ensure reproducibility of results.

Table below lists the parameters for the four pellets involved in the calculation of conductivity using equation 1. Also listed is the activation energy of each radical cation salt. The activation energy is half the energy required for an electron to be promoted from the valence electron band of the ET molecule to the supramolecular conduction band throughout the crystal lattice. The activation energy is obtained by a plot of Ln resistance vs temperature and is the gradient of the line.

Table 1: Data used to obtain values of conductivity for radical cation salts at 300K.

Anion	Distance between electrodes (cm)	cross-sectional area (cm^2)	Activation energy E_a (eV)	conductivity at 300K Scm^{-1}
PF_6^-	0.026	0.002	0.06	0.57
BF_4^-	0.030	0.00056	0.04 - 0.07	2.95
ClO_4^-	0.010	0.0025	0.04	0.15
Cl^-	0.038	0.0033	0.042 (low temp) 0.054 (high temp)	0.57

The low values for the activation energy of the four HMET salts indicate an almost metallic-like state at room temperature. The salts however can be classified as semiconductors with good room temperature conductivity. A plot of resistance vs temperature shows typical semiconducting behaviour, i.e., increasing resistance with decreasing temperature. Shown below is the resistance vs temperature plot for a compressed pellet of $(HMET)_2PF_6$. This relationship is typical of all four compounds.

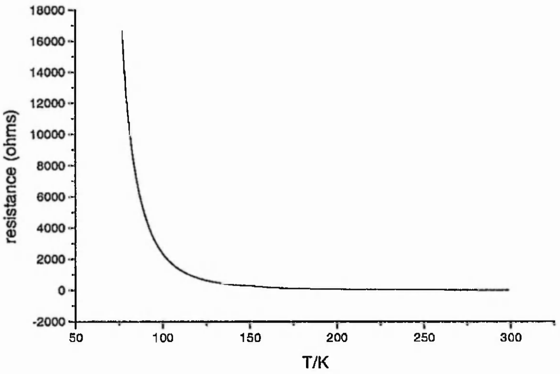


Figure 3. Resistance vs Temperature plot of $(HMET)_2PF_6$.

Radical cation salts of HMET with magnetic counter-ions

Studies aimed at producing radical cation salts with magnetic anions were carried out, since this opens up the possibility of magnetic interactions between cations and anions. With HMET as donor, initial counter-ions investigated were $[Fe^{III}(SCN)_6]^{3-}$, $[Ni(S_2C_2O_2)_2]^{2-}$, $[Cr(C_2O_4)_3]^{3-}$, and $[Cr(SCN)_4(isoquinoline)_2]^-$. These anions were chosen due to previous interesting results obtained with ET/ TTF/ BETS/ TMTSF. The Royal Institution had experience of growing radical cation salts with these particular magnetic complex ions.[11-14] The salts were grown in the same way as the non-magnetic salts, i.e. by electrocrystallisation. Variations in the solvents used and the addition of 18-crown-6 to some experiments to aid solubility of the inorganic salt are summarised in the table below.

Table 2: Solvents used in the preparation of radical cation salts with magnetic anions.

Salt	Solvent	18-C-6
$(NH_4)_3[Cr(C_2O_4)_3]^{3-}$	Benzonitrile	-
$[Cr(SCN)_4(isoquinoline)_2]^-$	Dichloromethane	Yes (200mg)
$[Fe^{III}(SCN)_6]^{3-}$	Dichloromethane	-
$[Ni(S_2C_2O_2)_2]^{2-}$	Benzonitrile	-

After 2-3 weeks the crystals were harvested. All salts obtained were dark brown/black and micro-crystalline in form. Under the microscope however, it was observed that many crystals had grown on top of one another as witnessed for the HMET salts of non-magnetic anions. They were therefore deemed inappropriate for x-ray crystal structure determination. Yields were often variable between two or more cells with the same content, although experimental conditions were identical. Attempted electrocrystallisations of HMET **1** with $[Ni(S_2C_2O_2)_2]^{2-}$ failed to give any products from two H-cells and further work with this counter-ion was abandoned.

A black/brown powder often accompanied the crystals that had formed on the anode. The products from the experiments were carefully removed from the H-cells and placed in petri dishes where they were washed with acetone in order to remove any impurities. The acetone could sometimes become quite coloured with what looked to be neutral organic donor molecule. After successive washings until no more colour was removed the crystals were first left to dry in the air and then in a warm oven before any characterisation or physical measurements were carried out.

Due to a lack of material produced from the experiments, no CHN analysis to indicate the composition of the salts was possible. Raman spectroscopy however, gave an indication as to the stoichiometry. The results of the Raman spectroscopy indicate that HMET. $[Cr(C_2O_4)_3]^{3-}$ could be a 1:1 salt, the values calculated for HMET. $[Cr(SCN)_4(isoquinoline)_2]^-$ indicate a 1:1 salt and HMET. $[Fe^{III}(SCN)_6]^{3-}$ could have 3:1, donor : anion stoichiometry.

Table 3: Raman spectroscopy data for HMET salts with $[Fe^{III}(SCN)_6]^{3-}$, $[Cr(C_2O_4)_3]^{3-}$, and $[Cr(SCN)_4(isoquinoline)_2]^-$ as anions.

Salt	υ_3 / cm^{-1}	υ_4 / cm^{-1}	Conclusions Donor: anion
HMET. $[Cr(C_2O_4)_3]^{3-}$	1463.2 (+0.88, +0.51)	1427.2 (+1.3, +0.9)	1: 1
HMET. $[Cr(SCN)_4(isoquinoline)_2]^-$		1420.0 (+1.38, +0.99)	1: 1
HMET. $[Fe^{III}(SCN)_6]^{3-}$	1461.4 (+0.90, +0.52)	1420.0 (+1.38, +0.99)	3: 1

Conductivity Measurements

Table 4 overleaf summarises the results obtained for the three radical cation salts using the four probe conductivity method. As with the HMET salts of non-magnetic anions, the salts were characterised as semiconductors with good room temperature conductivity for this class of materials. A plot of resistance vs temperature shows typical semiconducting behaviour for all three salts.

Table 4: Data used to obtain values of conductivity for radical cation salts at 300K.

Anion	**Distance between electrodes (cm)**	**cross-sectional area (cm^2)**	**Activation energy E_a (eV)**	**conductivity at 300K $(Scm)^{-1}$**
$[Cr(C_2O_4)_3]^{3-}$	0.036	0.000216	0.06 – 0.047	0.27
$[Cr(SCN)_4(isoquinoline)_2]^-$	0.036	0.0018	0.13	0.09
$[Fe^{III}(SCN)_6]^{3-}$	0.020	0.00074	0.11	0.41

Magnetic measurements

Magnetic interactions are typically characterised by their responses to variations in temperature and applied magnetic field. These responses are used to determine the specific type and strength of a magnetic interaction. The strength of an interaction between the sample and an applied magnetic field is defined by the magnetic susceptibility, χ. The definition of magnetic susceptibility is given in equation 2, where M is the magnetisation and H is the applied magnetic field.

$$\chi = M / H$$

Equation 2.

Molar magnetic susceptibility, χ_m, is the measure of the ability of a mole of material to become magnetised by an external magnetic field. χ_m can be determined experimentally by SQUID magnetometry using the equation shown below:

$$\chi_m = (\text{emu} / \text{field}) \times (\text{RMM} / \text{mass sample}) - \text{diamagnetic contribution}$$

Equation 3.

where emu (Electro Magnetic Unit) is the response of the SQUID.

With HMET as donor, the salts with counter-ions $[Cr(C_2O_4)_3]^{3-}$, and $[Cr(SCN)_4(isoquinoline)_2]^-$ were investigated.[11-14] The metal centres in these counter-ions are characterised by having unpaired electrons present. Whether or not these electrons have any interaction with the unpaired electron of the radical cation was the focus of the investigation by SQUID magnetometry. The magnetisation experiments were made with a Quantum Design MPSM7 SQUID magnetometer using randomly oriented polycrystalline material encased in a gel capsule.

Two classes of magnetic behaviour are possible in these systems. If, in the presence of the magnetic field, no interaction occurs between the unpaired electrons of the metal ion and the unpaired electron of the HMET molecule, then the electrons may be oriented at random and the substance can be classed as *paramagnetic*. However, because there are two chemical species possessing unpaired spins of unequal magnitude, if interaction occurs to align the spins in antiparallel fashion, a net magnetic moment will result and the substance can be classed as *ferrimagnetic*.[11, 15]

Analysis of magnetic data

Analysis of data obtained from the SQUID magnetometry measurements can lead to an understanding of the strength and type of magnetic interaction within a sample. Typically, the first analysis carried out is to examine the field- cooled temperature dependence as a function of susceptibility. In general, it is difficult to determine the type of magnetic interactions occurring in a sample from the plot of susceptibility as a function of temperature (Fig.4). A χ_m vs T plot is useful however for *antiferromagnetic* materials, which exhibit a maximum at low temperature at the Néel point.

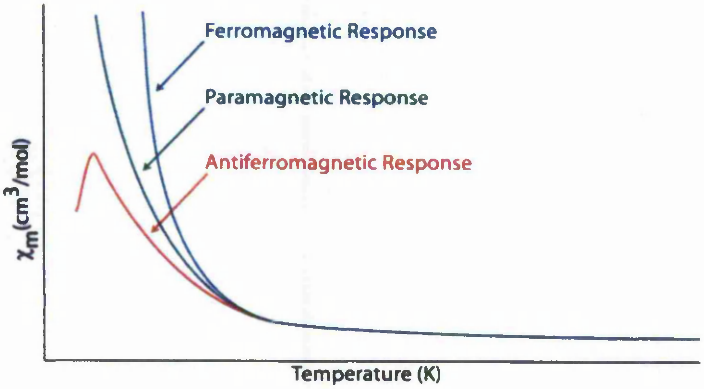


Figure 4. A typical χ_m vs T plot for *paramagnetic*, *ferromagnetic* and *antiferromagnetic* materials.

Analysis of the χ_mT product as a function of temperature is more useful, and provides information about the interactions occurring in magnetic materials. A typical χT vs T plot for an ideal *paramagnet*, *ferromagnet*, *antiferromagnet* and *ferrimagnet* are shown in figure 5.

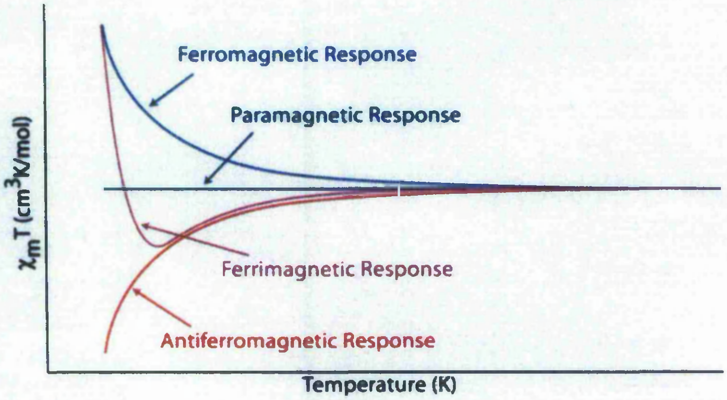


Figure 5. A typical χ_mT vs T plot for an ideal *paramagnet*, *ferromagnet*, *antiferromagnet* and *ferrimagnet*.

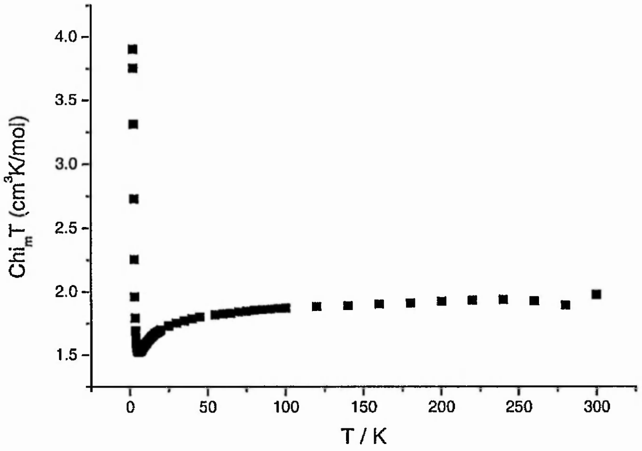


Figure 6. $\chi_m T$ vs T plot of HMET [$Cr(SCN)_4$(isoquinoline)$_2$].

Figure 6 above shows a plot of $\chi_m T$ vs T for HMET [$Cr(SCN)_4$(isoquinoline)$_2$]. From 300K to 150K $\chi_m T$ vs T is a horizontal straight line indicating *paramagnetism.* Below 150K $\chi_m T$ decreases gradually to 5.8K to a $\chi_m T$ value of 1.5 emu Kmol^{-1}. This indicates longer range *antiferromagnetic* ordering, but then due to uncompensated spins below 5.8K the $\chi_m T$ value increases dramatically indicating the long range order is *ferromagnetic.* Due to the presence of two chemically different species in the salt, *i.e.* S = 3/2 for Cr and S = 1/2 for donor, the overall behaviour is classed as *ferrimagnetic.* In addition, the small value of $\chi_m T$ observed is due to a canting effect,[16] *i.e.*, the Cr and donor spins are not aligned parallel to one another.

An ideal *paramagnet* has a linear relationship between inverse susceptibility and temperature that intersects at zero as defined by the Curie Law (equation 4), where C is the Curie constant and T, the temperature.

$$\chi_m = C / T$$

Equation 4.

Deviation from this linear relationship and the Curie law is observed for materials that exhibit cooperative magnetic effects. A modification of the Curie Law, known as the Curie- Weiss law (equation 5) describes this deviation, where θ is the Weiss constant.

$$\chi_m = C / T - \theta$$

Equation 5.

Positive Weiss constants indicate *ferromagnetic* interactions, while negative Weiss constants indicate *antiferromagnetic* interactions.

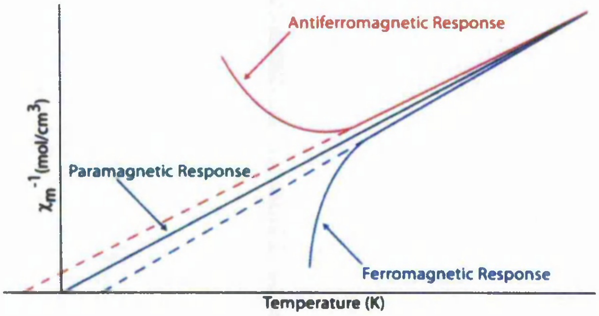


Figure 7. A plot of inverse susceptibility as a function of temperature is shown for a *paramagnet*, *ferrromagnet* and an *antiferromagnet*. The dotted lines indicate deviation of the high temperature data from the *paramagnetic* case.

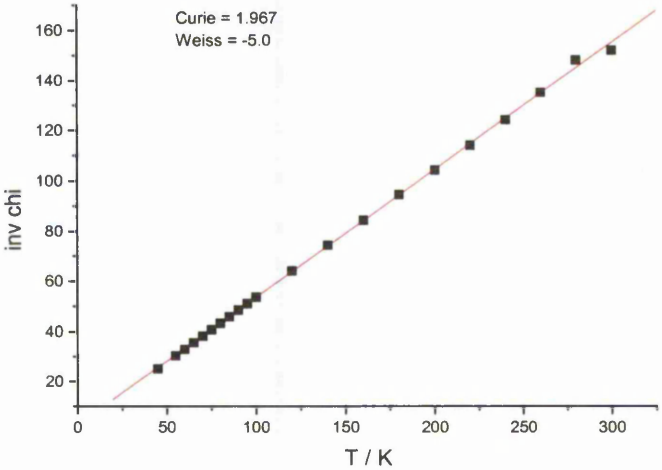


Figure 8. $1/\chi_m$ vs T plot of HMET [Cr(SCN)$_4$(isoquinoline)$_2$].

Figure 8 above is a plot of the inverse susceptibility as a function of temperature for HMET [$Cr(SCN)_4(isoquinoline)_2$]. C can be defined by equation 6, where N = Avogadros number, β = Bohr magneton, g = g value, S = spin and k = Boltzmanns constant.

$$C = \frac{N.\,\beta^2.\,g^2.S(S+1)}{3k}$$

Equation 6.

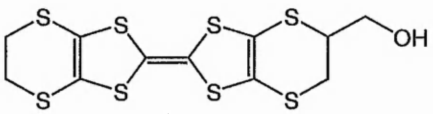
Taking the Curie- Weiss law in the form y = mx + c, then the gradient of the line is equivalent to 1/ C. From the high temperature gradient of the 1/ χ_m versus T plot, where all spins are acting independently, the Curie constant, C, has a value of 1.967. This is when there are no spin-spin interactions to lower or raise this figure. Using equation 6, and substituting for S = ½ and g = 2.0023 (g value for a free electron), then we obtain a value for C which is equal to 0.375. This would be the maximum possible contribution for one donor molecule towards the magnetism. Knowing that the value obtained for C = 1.967, and assuming the stoichiometry of the salt is 1: 1, then the contribution towards the magnetism from the chromium site is 1.967 – 0.375 = 1.591. Using equation 6 and substituting for C = 1.591 and S = 3/2, we obtain a g value of 1.84 for Cr. Ideally the g value for chromium is 2.1 but this is within experimental error and indicates that the assumption is correct and we have a 1:1 salt.

The Curie- Weiss plot above gives a negative value for the Weiss constant (x axis intercept) at -5.0, indicating significant short-range *antiferromagnetic* interactions between the three chromium electrons (spin 3/2) and the electron residing on the HMET molecule (spin ½).

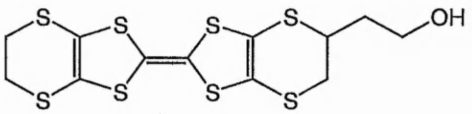
An investigation into a series of radical cation salts of HMET with $[Cr(NCS)_4(X)]^-$, (where X= bipym, bpy, phen) has commenced. These anions were chosen due to the Royal Institutions previous experience of these anions where bulk magnetic order had been observed in the salts of $[Cr(NCS)_4(Phen)]^-$ with TTF, TMTTF and TMTSF.[15] Salts obtained were black and micro-crystalline in form. Raman spectroscopy has been the only analysis carried out with these novel magnetic salts, but a full investigation into their magnetic and conducting properties is far from being complete.

4. The preparation of Hydroxyethyl- ET, HEET, 19.

The preparation of hydroxyethyl- ET **19**[4] was important as this provided another compound with a linker arm that could be used to append the ET molecule to polymer backbones. The arm could also be used to incorporate the ET moiety in molecular devices, or into supramolecular systems. Earlier work to derivatise the hydroxy function of **1** has proved troublesome, possibly due to intramolecular reaction of the oxy-anion with the nearest C-S bond, and the increase in chain length between the hydroxy function and ET framework in **19** may help to overcome these difficulties.

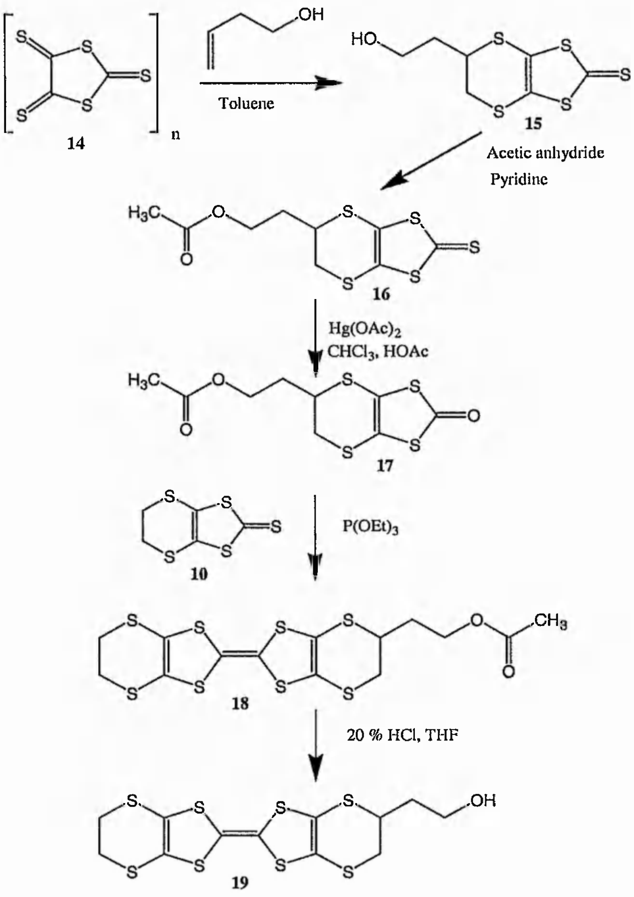


1



19

The preparation of **19** was achieved in five synthetic steps in an overall yield of 14 %.



Scheme 4. Synthesis of compound **19**.

The trithione **14** was prepared from zinc complex **7** in what appeared to be > 100 % yield. [17] This is due to the product being impure, data to prove the structure of the compound being difficult to obtain due to the high insolubility of the product in all solvents tested. Oxidation of zinc complex **7** in acetone by treatment with a solution of 2 eq. of iodine in ethanol, at -50°C, gave a mustard-yellow solid with composition $(C_3H_5)_X$. This was collected, washed extensively with water and ethanol until washings were colourless, and then dried in a warm (40-50°C) vacuum oven for 4-5h. A possible impurity is zinc iodide.

The trithione is reported to react with alkenes[17], but in variable yield, only the higher boiling solvents such as benzene, water and dioxane were used as solvents. Reaction of trithione **14** with 3-buten-1-ol in toluene at reflux for 5h. followed by chromatography afforded **15** in 85 % yield as an orange oil which solidified on standing. The ^{13}C NMR of **15** shows the *C*=S at δ: 207.7, the sp^2 carbon atoms at δ: 121.0, and the exocyclic carbon atoms (1- & 2- *C*) of the sidechain at δ: 59.3 and δ: 34.9. Subsequent protection of the hydroxy functionality as an acetate by reaction of **15** with acetic anhydride in pyridine at 70°C for 12h. resulted in **16** being obtained as a brown oil in 86 % yield.

Replacement of the exocyclic sulfur atom for oxygen by treatment of **16** with mercuric acetate in chloroform and acetic acid furnished the oxo compound **17** as a light brown solid in 68 % yield. A ^{1}H, ^{13}C NMR correlation experiment of **17** was carried out in order to correctly assign the positions of the hydrogen atoms on the molecule. The two hydrogen atoms connected to CH_2O (δ: 60.8) were found as a multiplet at δ: 4.23. The hydrogen atom connected to 5*C* (δ: 41.2) was found as a multiplet at δ: 3.74. The two hydrogen atoms connected to 6*C* (δ: 35.8) were each found as a double doublet, $6H_\alpha$ at δ: 3.45 and $6H_\beta$ at δ: 3.20. The two hydrogen atoms connected to 5-CH_2 (δ: 41.2) were found as a multiplet at δ: 2.14. From the correlation experiment the NMR spectra for the whole series of compounds leading to **19** could be assigned with confidence. The diagram below indicates the numbering scheme used to assign **17**.

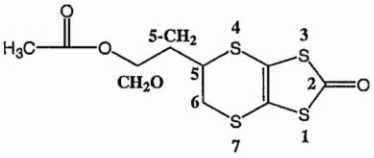


Figure 6. Numbering scheme used to assign **17**.

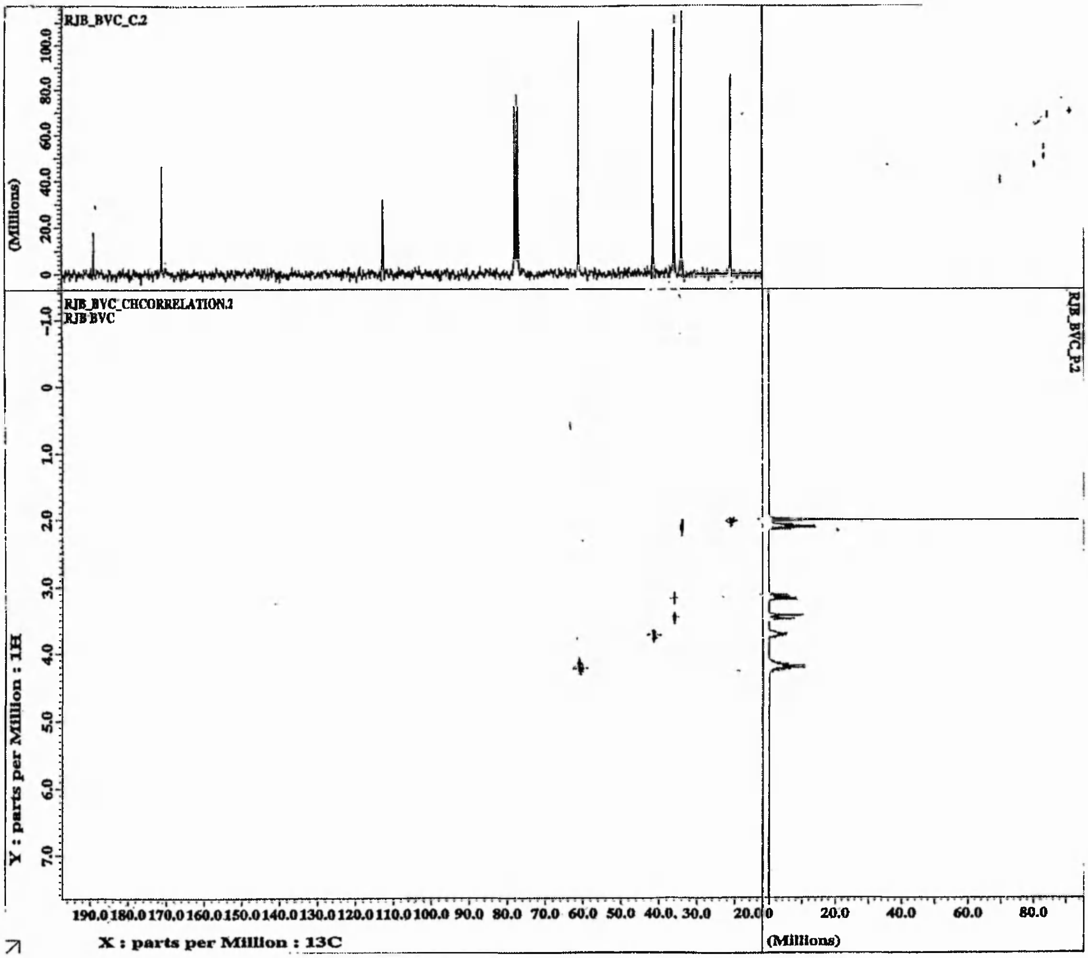


Figure 7. ^{1}H, ^{13}C NMR correlation experiment spectrum of **17**.

The structure of **17** is further supported by the ^{13}C NMR spectrum with shifts at δ: 188.3 for S_2C=O and δ: 170.7 for CH_3C=O. Sp^2 resonances were observed at δ: 112.4 and δ: 112.3. Absorptions for the carbonyl functions were present in the infrared spectrum at 1729 cm^{-1} for CH_3C=O and 1670 cm^{-1} for S_2C=O.

Cross coupling of **17** with excess thione **10** in triethyl phosphite at 80°C for 5h. followed by chromatography to separate the desired compound from ET and a mixture of isomeric disubstituted ET's, led to the cross coupled product **18** being obtained as a red/ orange solid in 55% yield. Removal of the protecting group was carried out by treatment of **18** in THF and 20% HCl solution to afford the product **19** after chromatography as a bright orange powdery solid in 51% yield. The ^1H NMR spectrum of **19** shows two multiplets at δ: 3.55 and δ: 1.84 corresponding to the side chain methylene hydrogen atoms, (1- H_2 and 2- H_2). The hydrogen atoms of the unsubstituted ethylene bridge (5'- & 6'- H_2) are observed as a singlet at δ: 3.38. The ^{13}C NMR indicated three different chemical environments for the sp^2 carbon atoms, shifts being observed at δ: 115.1, δ: 115.0 and δ: 114.4.

This approach to preparing HEET **19** will be adapted to the synthesis of HMET **1**, to provide a cheaper route not requiring expensive protecting groups.

Cyclic voltammetry data for HEET 19

The solution redox chemistry of the novel ET derivative **19** was studied by cyclic voltammetry (cv) and compared to ET **5**. **19** shows two, single-electron, reversible redox waves over a number of scan rates at the expected potentials for ET; the oxidation potentials of the novel donor is not affected by the presence of the hydroxyethyl function. Table 1 gives data measured in dichloromethane containing 0.1M tetrabutylammonium hexafluorophosphate under nitrogen, with a scan rate of 100mV s^{-1}, and quoted relative to Ag/AgCl.

Initial electrocrystallisation experiments were carried out in DCM, in which donor **19** is quite soluble. However, no crystalline products were obtained with PF_6^- and BF_4^- as counter-ions. The flexible spacer between the ET core and the hydroxy function of **19** increases the solubility but also introduces extra degrees of freedom to the molecule, which may hinder crystallisation of the radical cation salts. However, only a few sets of conditions have been investigated. Preliminary work from a co-worker has recently produced a $(HEET)_3(I_3)_2$ salt, by diffusion of iodine into a HEET solution.

Table 5. Oxidation Potentials (V, relative to Ag/AgCl electrode)

	$E_1^{1/2}$	$E_2^{1/2}$
ET	0.48	0.89
19	0.49	0.90

5. Experimental.

General Experimental Techniques:

NMR spectra were measured on a JEOL EX 270 machine at 270 MHz for ^{1}H and at 67.8 MHz for ^{13}C using $CDCl_3$ as solvent and tetramethylsilane (TMS) as standard, and measured in p.p.m. downfield from TMS, unless otherwise stated. Coupling constants (J) are given in Hz. IR spectra were recorded on a Perkin-Elmer 1600 Series FTIR machine as liquid films, nujol mulls, or KBr discs. Reflective Raman spectra were measured with a Renishaw System 1000 Ramascope using a He-Ne laser (λ = 632.8 nm) with 10 micron slits and x50 objective lens. Mass spectra were recorded at the EPSRC Mass Spectrometry Centre. Elemental analyses were performed at the Microanalysis Centre, University of Nottingham and the Microanalysis Laboratory, University of Manchester. Optical rotations were recorded at 589nm on a Perkin-Elmer 241 polarimeter using a 1dm cell, and $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. Conductivity measurements were carried using an Oxford Instruments Mag lab 2000 with EP probe, capable of measurements in the range 1.8- 400K. Magnetisation experiments were made with a Quantum Design MPSM7 SQUID magnetometer using randomly oriented polycrystalline material encased in a gel capsule. Capillary melting points were taken on a Gallenkamp melting point apparatus and are uncorrected. Flash chromatography was performed on 40-63 silica gel (Merck).

Bis (tetraethylammonium) bis(2-thioxo-1,3-dithiole -4,5-dithiolato)zincate, 7

Following the method of Bryce,[6] CS_2 (240ml) was added to degassed DMF (480ml) and the mixture cooled to 0°C under N_2. Sodium metal (14.5g, 0.6mol) was cut into fine pieces under cyclohexane, then added in one portion to the solution. Stirring was continued for 8h. until all the sodium was consumed (any unreacted sodium at this stage was destroyed by the addition of methanol). Separate solutions of (i) $ZnCl_2$

(21.3g) dissolved in 35% NH_3 (360ml) and water (100ml) and (ii) Et_4NBr (66.0g) in water (500ml) were added consecutively in approximately equivolume portions over 20 min. A red precipitate formed during the addition. The mixture was stirred overnight, and the product isolated by filtration *in vacuo* and washed sequentially with isopropanol (3x250ml) and ether (250ml) to afford the product **7** as a red powdery solid (84.6g, 76 %).

4,5-Bis(benzoylthio)-1,3-dithiole-2-thione, 8[18]

Benzoyl chloride (10.0ml, 83.5mmol) was added dropwise with stirring to a solution of zinc complex **7** (15.0g, 20.9mmol) in acetone AR (100ml). After the addition was complete and stirring had continued for 5 min. the orange precipitate was collected by filtration *in vacuo*. To the crude material was added $CHCl_3$ (100ml) and the mixture stirred for 10min. before filtration. The solid was slurried with further portions of $CHCl_3$ until the washings ran clear. Combined washings and filtrate were concentrated *in vacuo* to 150ml and the solution refluxed. After 5min. methanol (150ml) was added via the condenser to precipitate the product from solution. The product was isolated by filtration *in vacuo* and washed with cold methanol (50ml) to afford the product **8** as a bright yellow solid (14.9g, 88 %); ^{1}H NMR δ: 7.91 (2H, m, Ar- H_2), 7.64 (1H, m, Ar- H), 7.48 (2H, m, Ar- H_2); ^{13}C NMR δ: 212.3 (C=S), 185.3 (C=O), 134.9, 133.6, 129.1, 127.9 (Ar- C_{12}).

5,6-Dihydro-1, 3-dithiolo[4,5-b]1,4-dithiin-2-thione, 10[7]

The dibenzoylated thione **8** (30.0g, 73.9mmol) was added to a solution of sodium metal (3.7g, 160mmol) in dry methanol (450ml) under N_2. The reaction mix was stirred for 1h. at room temperature. 1,2- Dibromoethane (6.4ml, 73.9mmol) was added to the cold (0°C) reaction mix in one portion. Stirring was continued overnight at room temperature under N_2. The precipitate was collected by filtration and washed with cold methanol. The solid was dried *in vacuo* to yield **10** as a yellow solid (13.9g, 84 %); ^{1}H NMR δ: 3.36 (4H, s, 5-, 6- H_2); ^{13}C NMR δ: 207.9 (*C*=S), 122.8 (3a-, 7a- *C*), 29.6 (5-, 6- *C*).

5,6-Dihydro-1, 3-dithiolo[4,5-b]1,4-dithiin-2-one, 2[5]

To a solution of thione **10** (2.4g, 10.6mmol) in $CHCl_3$ (50ml) and glacial acetic acid (10ml) was added mercuric acetate (8.6g, 26.5mmol). After 2 h. stirring at room temperature the mix was filtered. The filtrate was washed consecutively with saturated $NaHCO_3$ solution (3x100ml) and H_2O (50ml), dried (Na_2SO_4) and evaporated to afford the product **2** as a pale brown solid (2.1g, 95 %); ^{1}H NMR δ: 3.42 (4H, s, 5-, 6- H_2); ^{13}C NMR δ: 188.9 (*C*=O), 113.2 (3a-, 7a- *C*), 31.0 (5-, 6- *C*).

3-(t-Butyldiphenylsilyloxy)prop-1-ene, 11[1]

To a solution of allyl alcohol (0.5g, 9.0mmol) in dry DMF (20ml) was added sequentially imidazole (6.8g, 100mmol) and t-butyldiphenylsilyl chloride (2.8g, 10mmol). After stirring at room temperature for 20h., water (90ml) and dichloromethane (40ml) were added, the dichloromethane layer separated, and the aqueous layer extracted with dichloromethane (2x40ml). The combined organic solution was washed sequentially with ice-cold HCl (3M, 3×50ml) and water (50ml) and dried over $MgSO_4$. Removal of the solvent under reduced pressure afforded the silylated product **11** (2.6g, 96 %) as a colourless oil; ^1H NMR δ: 7.65 (4H, m, Ar-H_4), 7.38 (6H, m, Ar- H_6), 5.91 (1H, ddt, J = 17.0, 10.4, 4.3 Hz, 2- *H*), 5.38 (1H, ddt, J = 17.0, 1.9, 1.9 Hz, 1-*H* (trans to 2-H)), 5.11 (1H, ddt, J = 10.4, 1.9, 1.9 Hz, 1- *H* (cis to 2-H)), 4.20 (2H, m, 3- H_2), 1.07 (9H, s, 3×CH_3); ^{13}C NMR δ: 136.9, 135.5, 129.6 & 127.6 (Ar- C_{12}), 133.6 (2- *C*), 113.8 (1- *C*), 64.6 (3- *C*), 26.8 (3×CH_3), 19.3 ($C(CH_3)_3$); ν_{max}/cm^{-1} (evaporated film) 3470, 3070, 2934, 1590, 1468, 1428, 1112, 822; found C, 77.4; H, 8.4%, $C_{19}H_{24}OSi$ requires C, 77.0; H, 8.2%; m/z (CI): 314 ($[M+NH_3+H]^+$, 65), 297 ($[M+H]^+$, 100), 239 ($M-C(CH_3)_3$, 19%); HRMS: (CI) found $[M+H]^+$ 297.1684, $[C_{19}H_{24}OSi + H]^+$ requires 297.1675.

3-(t-Butyldiphenylsilyloxy)-1,2-dibromopropane, 12[1]

To a stirred solution of 3-(t-butyldiphenylsilyloxy)prop-1-ene **11** (14.0g, 47.3mmol) in chloroform (100ml) maintained at 0°C was added slowly, dropwise, a solution of bromine (2.4ml, 47.3mmol) in chloroform (40ml). The resultant mixture was stirred for a further 30 min. at that temperature, and then allowed to warm to room temperature and stirred for a further 3 h. The solution was washed with aqueous sodium thiosulfate solution (2 x 30ml) and water (2 x 30ml), dried ($MgSO_4$), and the solvent removed *in vacuo* to afford the product **12** as a pale yellow oil (20.5 g, 95 %); ^1H NMR δ: 7.68 (4H, m, Ar- H_4), 7.39 (6H, m, Ar- H_6), 4.20 (1H, m, 2- *H*), 4.09 (1H, dd, J = 11.3, 3.8 Hz, 3- H_α), 4.00-3.91 (2H, m, 3- H_β & 1- H_α), 3.83 (1H, dd, J = 10.2, 4.7 Hz, 1- H_β), 1.09 (9H, s, 3 × CH_3); ^{13}C NMR δ: 135.6, 135.5, 129.8 & 127.8 (Ar-C_{12}), 64.6 (3- *C*), 51.5 (2- *C*), 32.6 (1- *C*), 26.7 (3×CH_3), 19.3 ($C(CH_3)_3$); ν_{max}/cm^{-1} (evaporated film) 3070, 2934, 2860, 1468, 1428, 1112, 702; found C, 49.9; H, 5.2%,

$C_{19}H_{24}Br_2OSi$ requires C, 50.0; H, 5.3%; HRMS: (CI) found $[M + NH_3 + H]^+$ 472.0307, $[C_{19}H_{24}OSiBr_2 + NH_3 + H]^+$ requires 472.0307.

Disodium- 2- thioxo- 1, 3- dithiolo- 4, 5- dithiolate, 9[7]

Dibenzoylated thione **8** (16.2g, 40.0mmol) was added to a solution of sodium metal (1.8g, 80.0mmol) in dry ethanol (60ml) under N_2. The reaction mix was stirred for 20 min. at room temperature. Dry ether (1.5L) was added and stirring was continued for a further 30min. under N_2. The precipitate was collected by filtration under an inert atmosphere and washed with dry ether (50ml). The product was dried *in vacuo* to afford a red solid **9** (9.2g, 95 %) that was stored under N_2 prior to its use.

5-(t-Butyldiphenylsilyloxy)methyl-5,6-dihydro-1,3-dithiolo[4,5-b]1,4-dithiin-2-thione, 13[1]

To a stirred solution of dithiolate **9** (4.6g, 18.8mmol) in dry THF (60ml) under N_2 at 0°C was added a solution of 3-(t-butyldiphenylsilyloxy)-1,2-dibromopropane **12** (8.6g, 18.8mmol) in THF (20ml) at room temperature. After stirring for 12 h., the solvent was removed under reduced pressure and the residue was extracted with dichloromethane (100ml), washed with water (3 x 50ml), dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by flash chromatography (hexane/ethyl acetate (10:1)) to afford **13** (5.0 g, 54 %) as a yellow solid; mp 100-102°C; ^1H NMR δ: 7.66 (4H, m, Ar- H_4), 7.37 (6H, m, Ar- H_6), 3.98-3.75 (3H, 2 × m, CH_2OSiR_3 & 5- H), 3.31 (1H, dd, J = 13.5, 5.8 Hz, 6- H_α), 3.19 (1H, dd, J = 13.5, 2.8 Hz, 6- H_β), 1.08 (9H, s, $3\times CH_3$); ^{13}C NMR δ: 207.1 (C=S), 135.3, 132.3, 129.9 & 127.7 (Ar- C_{12}), 123.7 & 121.9 (3a-, 7a- C), 64.6 (CH_2OSiR_3), 45.1 (5- C), 31.1 (6- C), 26.7 ($3\times CH_3$), 19.1 ($C(CH_3)_3$); ν_{max}/cm^{-1} (evaporated film) 1109, 1062, 1025, 893, 821, 737, 704, 604; m/z: (CI) 493 ([M + H]$^+$, 20), 492 (M$^+$, 20), 435 (65), 239 (35), 161 (100), 117 (43), 105 (29), 77 (25%); HRMS: (CI) found [M + H] $^+$ 493.0278, [$C_{22}H_{24}OS_5Si$ + H]$^+$ requires 493.0278.

5-(t-Butyldiphenylsilyloxy)methyl-5,6-dihydro-1,3-dithiolo[4,5-b]1,4-dithiin-2-one, 3[1]

To a solution of **13** (9.2g, 18.7mmol) in chloroform (160ml) and glacial acetic acid (35ml) was added mercuric acetate (6.0g, 18.7mmol) . The reaction mixture was stirred at room temperature for 2 h. during which the solution lightened in colour and a white precipitate was obtained. The mixture was filtered, and the filtrate washed sequentially with water (200ml), aqueous $NaHCO_3$ (4 x 200ml) and again with water (50 ml) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. to afford the product **3** as a pale yellow oil (8.2 g, 93 %); ^{1}H NMR δ: 7.67 (4H, m, Ar-H_4), 7.39 (6H, m, Ar- H_6), 3.99 (1H, dd, J = 12.1, 9.9 Hz, $CH_\alpha OSiR_3$), 3.83 (1H, m, 5-*H),* 3.82 (1H, dd, J = 12.1, 5.7 Hz, $CH_\beta OSiR_3$), 3.32 (1H, dd, J = 13.3, 5.5 Hz, 6- H_α), 3.23 (1H, dd, J = 13.3, 3.2 Hz, 6- H_β), 1.07 (9H, s, 3×CH_3); ^{13}C NMR δ: 188.7 (*C*=O), 135.5, 132.7, 130.0 & 127.9 (Ar- C_{12}), 114.4 & 112.7 (3a-, 7a- *C*), 64.9 (*C*H_2OSiR_3), 47.1 (5- *C*), 32.3 (6- *C*), 26.8 (3×*C*H_3), 19.3 (*C*$(CH_3)_3$); ν_{max}/cm^{-1} (evaporated film) 2958, 2858, 1678, 1590, 1468, 1262, 1112, 868 and 704 cm^{-1}; HRMS: (CI) found [M + NH_3 + H]$^+$ 494.0772, [$C_{22}H_{24}O_2S_4Si$ + NH_3 + H]$^+$ requires 494.0772.

5-(t-Butyldiphenylsilyloxy)methyl-ET, 4[1]

A mixture of protected oxo compound **3** (1.6g, 3.36mmol) and oxo compound **2** (1.4g, 6.7mmol) were heated in triethyl phosphite (30ml) to 90°C under N_2 for 5 h. to give an orange solution. Triethyl phosphite was removed by distillation *in vacuo* and the residue purified by flash chromatography (hexane/ethyl acetate 5:1), collecting the band with R_f 0.52 to give **4** (0.4 g, 39 %), as an orange solid; mp 54-56°C; ^{1}H NMR δ: 7.62 (4H, m, Ar- H_4), 7.41 (6H, m, Ar- H_6), 3.94 (1H, dd, J = 10.4, 11.8 Hz, CH_{α}OSiR$_3$), 3.76 (2H, m, CH_{β}OSiR$_3$ & 5- H), 3.29 (4H, s, 5'-, 6'- H_2), 3.28 (1H, dd, J = 13.2, 4.7 Hz, 6- H_{α}), 3.18 (1H, dd, J = 13.2, 3.3 Hz, 6- H_{β}), 1.06 (9H, s, 3×CH_3); ^{13}C NMR δ: 135.3, 132.6, 129.8 & 127.7 (Ar- C_{12}), 114.6, 113.6 & 113.2 (3a-, 3a'- ,7a-, 7a'- C), 111.7 (2a-, 2a'- C), 64.9 (CH$_2$OSiR$_3$), 45.6 (5- C), 31.8 (6- C), 30.0 (5'-, 6'- C), 26.7 (3×CH$_3$), 19.1 (C(CH$_3$)$_3$); ν_{max}/cm^{-1} 1284, 1106, 1001, 915, 820, 770, 737, 700, 608; m/z (CI): 653 ([M+H]$^+$, 4), 387 (7), 297 ([$Ph_2SiC(CH_3)_3OCH_2CH{=}CH_2$+H]$^+$, 54), 256 ([$Ph_2SiC(CH_3)_3OH$]$^+$, 51), 239 (36), 236 (42), 196 (83), 45 (100%). found C, 49.6; H, 4.3 %. $C_{27}H_{28}OSiS_8$ requires C, 49.7; H, 4.3 %.

(±) Hydroxymethyl- ET, HMET, 1[1]

Hydrochloric acid (18.0 ml, 20%) was added dropwise to a solution of **4** (0.20 g, 0.3 mmol) in THF (30 ml) under nitrogen and stirred for 24 h. After neutralisation with sodium hydrogen carbonate, the organic phase was separated, dried over Na_2SO_4, and evaporated. The residue was purified by chromatography on silica eluting with dichloromethane to give racemic HMET **1** (0.1 g, 75 %) as a light orange solid; mp 151 °C (from ethanol): ^{1}H NMR δ: 3.74 (3H, m, CH_2OH & 5- H), 3.32 (4H, s, 5'-, 6'- H_2), 3.30 (1H, dd, J = 13.5, 5.0 Hz, 6- H_{α}), 3.22 (1H, dd, J = 13.5, 3.4 Hz, 6- H_{β}), 1.58

(1H, br, s, O*H*); ^{13}C NMR δ: 114.5, 113.5, 113.0 (3a-, 3a'-, 7a-, 7a'- *C*), 111.2 & 111.1 (2-, 2'- *C*), 63.9 (*C*H$_2$OH), 45.5 (5- *C*), 31.7 (6- *C*), 30.1 (5'-, 6'- *C*); ν_{max}/cm^{-1} 3400, 2860, 1405, 1260, 1020 and 802 cm^{-1}; found C, 32.0; H, 2.6%. $C_{11}H_{10}S_8O$ requires C, 31.9; H, 2.4%; *m/z* (CI): 415 ([M+H]$^+$, 40), 385 (48), 207 (100), 151 (75%).

Radical cation salts of (±) HMET, 1_2 BF$_4$, 1_2Cl, 1_2 PF$_6$.

Radical cation salts were prepared by constant current electrocrystallisation of dichloromethane solutions (50 ml) containing **1** (10 mg) and the appropriate tetrabutylammonium salt (100 mg), at a current flow of 1μA.

1_2.BF$_4$: Raman υ_4: 1464.0 cm^{-1}; found C, 29.1; H, 2.2; S, 56.4; F, 8.1%. $C_{22}H_{20}O_2S_{16}BF_4$ requires C, 28.8; H, 2.2; S, 56.0; F 8.3%.

1_2Cl: Raman υ_4: 1466.7 cm^{-1}; found C, 30.6; H, 2.4; Cl, 4.2%. $C_{22}H_{20}O_2S_{16}Cl$ requires C, 30.6; H, 2.3; Cl, 4.1%

1_2PF$_6$: IR υ_{max}(KBr) 3436, 2919, 2837, 2355, 1731, 1625, 1414, 1335, 1267, 1173, 1120, 1079, 843, 668, 556 cm^{-1}; Raman υ_3: 1501.9, υ_4: 1464.0, cm^{-1}; found C, 27.6; H, 2.0; F, 11.0%. $C_{22}H_{20}O_2S_{16}PF_6$ requires C, 27.1; H, 2.1; F 11.7%.

5,6- Dihydro-1,3-dithiole-2,4,5-trithione, 14[17]

Bis(tetraethylammonium) bis(2-thioxo-1,3-dithiole-4,5-dithiolato)-zincate **7** (5.0g, 6.9 mmol) was dissolved in acetone (35ml) and cooled to -78°C by means of a CO$_2$/acetone bath. Iodine (3.6g, 14.2 mmol) dissolved in ethanol (100ml) was added dropwise to the cooled solution with stirring over 1.5 h. The reaction mixture was allowed to warm to room temperature, and the solid mustard yellow precipitate was filtered on a large glass sinter funnel. The solid was washed sequentially with large volumes of acetone (300ml), H_2O (300ml) and ethanol (300ml) and dried in a warm vacuum oven for 2h, to give a mustard yellow fine solid (3.2g, 118 %), (There clearly must be some impurity within the product. NMR investigation is very difficult due to the insolubility of the product in a wide range of solvents).

5- Hydroxyethyl- 5, 6- dihydro-1, 3- dithiolo [4, 5-b]-1, 4- dithiin- 2- thione, 15[4]

3-Buten-1-ol (7.0g, 104.4mmol) and trithione **14** (8.0g, 40.8mmol) in toluene (400ml) were heated to 130°C for 4 h. After cooling to room temperature the reaction mix was filtered, and the solid washed with ethanol. Combined washings and filtrate were evaporated and the residue purified by flash chromatography (SiO_2, EtOAc) to furnish the product **15** as an orange oil (8.8g, 83 %), which solidified on standing; m.p. 52-53°C; ^1H NMR δ: 3.88 (3H, m, 2'- H_2 & 5- *H*), 3.46 (1H, dd, J = 13.4, 2.8 Hz, 6- H_α), 3.22 (1H, dd, J = 13.4, 6.7 H_z, 6- H_β), 2.02 (2H, m, 1'- H_2), 1.52 (1H, s, O-*H*); ^{13}C NMR δ: 207.7 (*C*=S), 121.9 (3a-, 7a- *C*), 59.3 (2'- *C*), 39.8 (5- *C*), 37.1 (6- *C*), 34.9 (1'- *C*); ν_{max}/cm^{-1} (thin film) 3386, 2924, 1483, 1412, 1293, 1057, 890; found C, 31.3; H, 2.9 %, $C_7H_8OS_5$ requires C, 31.3; H, 3.0 %.

5- Acetyloxyethyl- 5, 6- dihydro-1, 3- dithiolo [4, 5-b]-1, 4- dithiin- 2- thione, 16[4]

To a solution of **15** (8.8g, 33.9mmol) in pyridine (50ml) at room temperature was added acetic anhydride (4.0ml, 36.3mmol). The stirred mixture was heated to 70°C for 12 h. Water (300ml) was added and the mixture extracted with CH_2Cl_2 (3x100ml). The organic solution was washed consecutively with 0.5M HCl solution (3x100ml) and H_2O (100ml), then dried (Na_2SO_4) and evaporated to yield **16** as a brown oil (8.9g, 86 %); ^1H NMR δ: 4.25 (2H, m, 2'- CH_2O), 3.73 (1H, m, 5- *H*), 3.43 (1H, dd, J = 13.3, 3.0 Hz, 6- H_α), 3.20 (1H, dd, J = 13.3, 6.8 H_z, 6- H_β), 2.14 (2H, m, 1'- H_2), 2.05 (3H, s, CH_3); ^{13}C NMR δ: 207.7 (*C*=S), 170.7 (*C*=O) 122.0 & 121.7 (3a-, 7a- *C*), 60.8 (2'- *C*), 39.7 (5 - *C*), 34.6 (6 - *C*), 33.8 (1'- *C*), 20.9 (*C*H_3); ν_{max}/cm^{-1} (thin film) 2955, 1737, 1485, 1426, 1384, 1364, 1236, 1062, 890; found C, 34.8; H, 3.1 %, $C_9H_{10}O_2S_5$ requires C, 34.8; H, 3.3 %.

5- Acetyloxyethyl -5, 6- dihydro-1, 3- dithiolo [4, 5-b]-1, 4- dithiin- 2- one, 17[4]

To a solution of **16** (8.9g, 29.2mmol) in $CHCl_3$ (100ml) and glacial acetic acid (30ml) was added mercuric acetate (15.0g, 47.1mmol). After 2 h. stirring at room temperature the mixture was filtered. The filtrate was washed consecutively with saturated $NaHCO_3$ solution (3x100ml) and water (100ml), dried (Na_2SO_4) and evaporated to afford **17** as a light brown solid (5.7g, 68 %); m.p. 46-47°C; ^{1}H NMR δ: 4.23 (2H, m, 2'- CH_2), 3.74 (1H, m, 5 - *H*), 3.45 (1H, dd, J = 13.3, 2.7 Hz, 6-H_α), 3.20 (1H, dd, J = 13.3, 6.7 Hz, 6- H_β), 2.14 (2H, m, 1'- *C*), 2.03 (3H, s, CH_3); ^{13}C NMR δ: 188.3 (S_2*C*=O), 170.7 (CH_3*C*=O) 112.4 & 112.3 (3a-, 7a- *C*), 60.8 (2' - *C*), 41.2 (5- *C*), 35.8 (6- *C*), 33.8 (1'- *C*), 20.8 (*C*H_3); ν_{max}/cm^{-1} (KBr) 2967, 1729, 1670, 1634, 1509, 1464, 1425, 1398, 1368, 1247, 1049, 895, 767, 469; found C, 36.7; H, 3.3 %, $C_9H_{10}O_3S_4$ requires C, 36.7; H, 3.4 %.

Acetyloxyethyl- ET, 18[4]

A mixture of oxo compound **17** (2.8g, 9.9mmol) and thione **10** (4.4g, 19.8mmol) were heated in triethyl phosphite to 80°C under N_2 for 5 h. to give an orange solution. Triethyl phosphite was removed by distillation *in vacuo* and the residue purified by flash chromatography (SiO_2, 5:1 cyclohexane/ EtOAc) to yield **18** as a red/orange solid (2.5g, 55 %); m.p.109-110°C; ^{1}H NMR δ: 4.23 (2H, m, CH_2O), 3.64 (1H, m, 5- *H*), 3.34 (1H, dd, J = 13.1, 3.2 Hz, 6- H_α), 3.32 (4H, s, 5'-, 6'- H_2), 3.32 (1H, dd, J =

13.1, 6.5 Hz, 6- H_{β}), 2.05 (5H, m, CH_3 & CH_2CH_2O); ^{13}C NMR δ: 170.7 (*C*=O) 113.9 & 113.0 (sp^2- *C*), 61.2 (CH_2O), 40.1 (5- *C*), 35.3 (6- *C*), 33.7 (CH_2CH_2O), 30.2 (5'-, 6'- *C*), 20.9 (CH_3); ν_{max}/cm^{-1} (KBr) 2955, 2920, 1731, 1365, 1239, 1039, 905, 772, 668; found C, 35.8; H, 3.0 %, $C_{14}H_{14}O_2S_8$ requires C, 35.7; H, 3.0 %.

(±) Hydroxyethyl- ET, HEET, 19[4]

A solution of acetyl compound **18** (0.7g, 1.4mmol) in THF (10ml) and 20% HCl solution (5.0ml) was stirred under N_2 for 48h. The solution was neutralised by the addition of solid $NaHCO_3$. The organic layer was collected, dried (Na_2SO_4) and purified by flash chromatography (SiO_2, 2:1 cyclohexane/EtOAc) to afford **19** (0.3g, 51 %) as a bright orange powdery solid; m.p.141-142°C; ^1H NMR (DMSO-d_6) δ: 4.69 (1H, t, J = 5.1 H_z, O*H*), 3.81(1H, m, 5- *H*), 3.55 (2H, m, CH_2O), 3.45 (1H, dd, J = 13.2, 3.0 Hz, 6-H_{α}), 3.38 (4H, s, 5'-, 6'- H_2), 3.27 (1H, dd, J = 13.2, 6.5 H_z, 6- H_{β}), 1.84 (2H, m, CH_2CH_2O); ^{13}C NMR (DMSO-d_6) δ: 115.1, 115.0 & 114.4 (sp^2-*C*), 59.8 (CH_2O), 42.5 (5- *C*), 39.5 (6- *C*), 36.9 (CH_2CH_2O), 31.2 (5'-, 6'- *C*); ν_{max}/cm^{-1} (KBr) 3450, 2922, 1652, 1458, 1280, 1046, 767.

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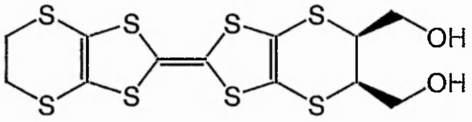
Chapter 3

Synthesis of poly hydroxy-functionalised ET donors

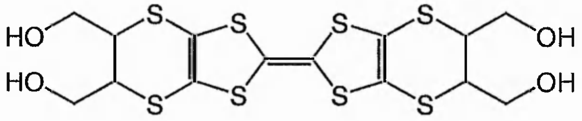
1. Introduction.

Some of the main criteria for high conductivity and superconductivity are good heteroatom orbital overlap and a well-ordered system. In order to achieve the latter, anion disorder has to be suppressed. Attaching strong hydrogen bonding functionalities to the ET core is expected to introduce donor – anion hydrogen bonding interactions, and in turn remove anion disorder. This chapter describes the preparation of novel ET derivatives functionalised with more than one hydroxyl substituent in order to introduce extra hydrogen bonding potential, and reports on some preliminary investigations into the formation of radical cation salts.

The only work to have been carried out in this area so far is for the *cis* isomer of **1**, reported by Zhang *et al.*[1], and a mixture of diastereoisomers of **2** reported by two groups.[2,3]



1



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Electrocrystallisations of **1** carried out by Zhang *et al.*[1] led to the formation of $(\mathbf{1})_2Cl$ and $(\mathbf{1})_2I$. Both were characterised as semiconductors with room temperature conductivities of 0.10 and 0.0071 S cm^{-1} respectively. The crystal structure of $(\mathbf{1})_2Cl$ was obtained. In the crystal structure, not only are there short side to side S···S contacts, but also short S···S contacts in the stack. So, the usual packing observed with ET salts remains. In a stack the molecules pack alternately with side chains to the left and then to the right etc up the stack. Thus there is an anion channel at both sides of the stack. The one axial side chain resides in this channel.

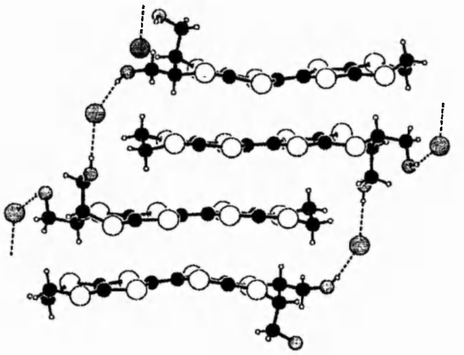
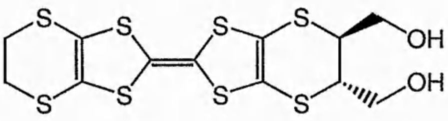


Figure 1. Crystal packing of $(\mathbf{1})_2$Cl, showing H- bonding network and axial – equatorial nature of substituents.

The salts of the corresponding *trans* isomer may be superior, since the two side chains can both lie pseudo equatorial and may lead to a more compact packing of the ET units. In principle, one can also make chiral radical cation salts from the *trans* isomer, by separation of the enantiomers on a chiral column.

Two groups have reported the synthesis of the tetraol **2** as a mixture of diastereoisomers. [2,3] The two strategies for the formation of **2** are identical, differing in the choice of protecting groups for the hydroxy functionalities. To date, no radical cation salts of **2** have been published. Preparation of the all- *trans* isomer of **2** would require access to an enantiopure thione precursor, if the triethyl phosphite coupling reaction was to give one product.

In this chapter, the preparation of **3**, the *trans* isomer of **1**, and **4**, a single diastereoisomer of **2**, with one *cis* and one *trans* arrangement of substituents are described along with related work.



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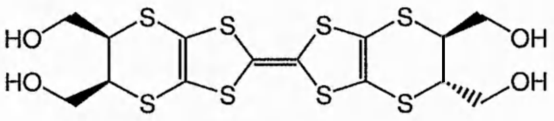

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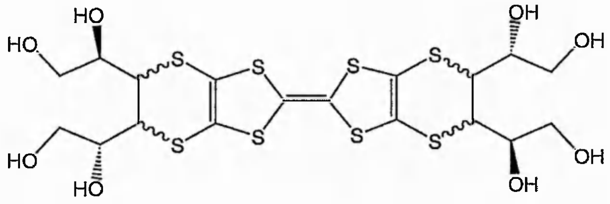
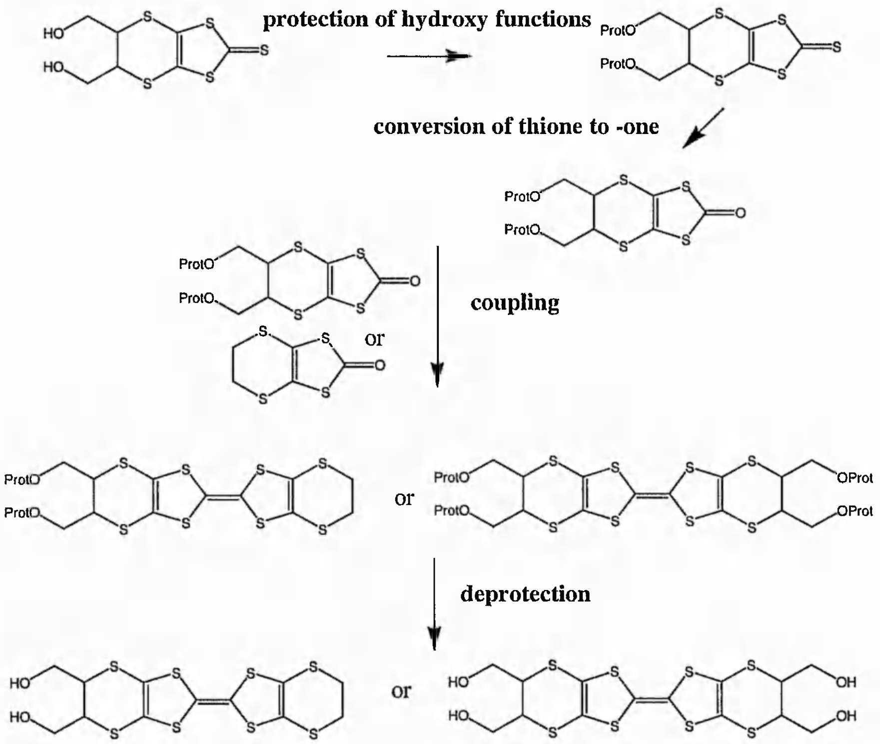
Progress in the synthesis of the enantiopure chiral donor shown below with eight hydroxy groups is also reported.



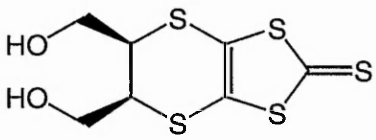
2. Synthesis of *trans*- ET diol 3 and the ET - tetrol 4.

These targets require good yielding syntheses of the *cis* and *trans* thiones, **5** and **6** which can be converted into the final compounds following the general scheme below.



Scheme 1. Synthetic methodology towards compounds **3** and **4**.

In the preparation of these and related organic donors, synthetic methodology followed two approaches to obtain the *cis* and *trans* thiones **5** and **6**:



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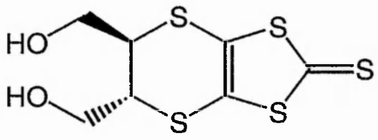
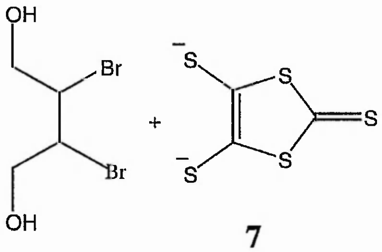


6

(1) Reaction of dithiolate **7** with *vic*- dibromo compounds, to give products by double nucleophilic substitution of bromide.

(2) 4+2 Cycloaddition reactions between *oligo*(1,3-dithiole-2,4,5-trithione) **8** and appropriate alkenes or alkynes.

The two strategies are illustrated below:



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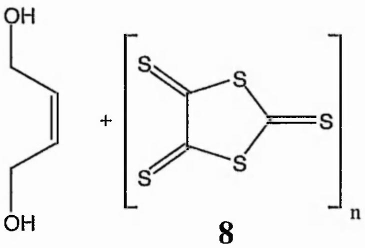

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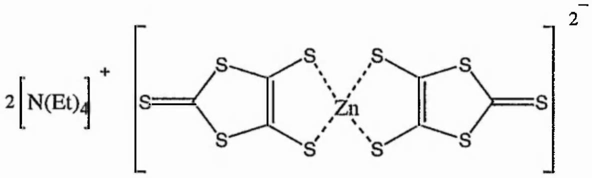
The preparation of *cis* 5,6-bis(hydroxymethyl)-5,6-dihydro-1,3-dithiolo[4,5-b]-1,4-dithiin-2-thione, 5

Three routes towards the synthesis of **5** were examined:

(1) Reaction of dithiolate **7** with *meso*- 2,3-dibromobutane-1,4-diol in methanol with stirring under nitrogen overnight led to no reaction occurring. The colour of the reaction mixture was deep red/ purple indicating that **7** was still present. Refluxing the reaction mixture for 5h. and analysing the mixture by tlc indicated no reaction had taken place.

(2) Overnight stirring of zinc complex **9** in acetone with *meso*- 2,3-dibromobutane-1,4-diol under nitrogen also led to no reaction being observed by tlc analysis. Changing the solvent used or more vigorous reaction conditions were not attempted, although literature precedents for the formation of thiones by direct nucleophilic substitution reactions of **9** with various compounds do exist.[4] Investigations were abandoned in favour of the third route.



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(3) The trithione **8** was reacted with 1.5 eq. of *cis* but-2-en-1,4-diol in 1,4-dioxane for 6 h. at an oil bath temp of 85°C. The reaction was worked up according to Neilands *et al.*[5] i.e. the mixture was filtered and the filtrate stirred over activated carbon for 30 min. to remove polymeric material. Chromatography of the crude material furnished the bis-hydroxymethyl compound **5** in low yield (25 %).

The yield was improved by employing toluene as solvent and heating the mixture to an oil bath temperature of 130°C for 5h. The workup procedure was also modified from that described above. Kugelrohr distillation to remove excess *cis* but-2-en-1,4-diol, followed by chromatography of the residue furnished **5** as a bright yellow solid in 38 % yield. The ^{1}H NMR spectrum of **5** shows a singlet at δ: 4.96 corresponding to the hydroxy functionalities, and two multiplets at δ: 4.06 and δ: 3.91. The ^{13}C NMR spectrum indicates the C=S carbon at δ: 209.9. The infrared spectrum shows the thione (C=S) stretch at 1069 cm^{-1} and broad OH peak at 3448cm^{-1}.

The preparation of *trans* 5,6-bis(hydroxymethyl)-5,6-dihydro-1,3-dithiolo[4,5-b]-1,4-dithiin-2-thione, 6

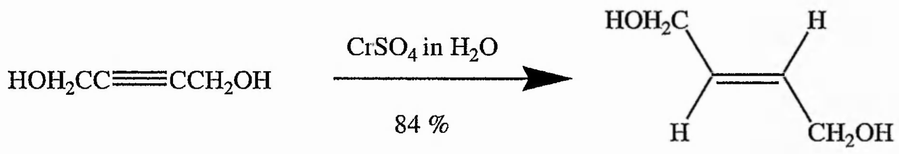
In principle **6** can be synthesised in the same manner as the *cis* analogue, i.e. the 4+2 cycloaddition of *trans* but-2-en-1,4-diol with trithione **8**. Indeed, Neilands and coworkers have succeeded in synthesising the compound, but in unspecified yield.[5] *trans*-But-2-en-1,4-diol **10** is not commercially available, therefore initial efforts were directed towards obtaining **10** by reduction of diethyl fumarate or the parent alkyne.

(1) Reduction of diethyl fumarate with diisobutylaluminiumhydride (DIBAL).

Diethyl fumarate is a *trans* diester. Reduction of the ester functionalities with four equivalents of DIBAL in toluene, under anhydrous conditions furnished the *trans*-diol **8** in 41 % yield.[6] However, further attempts to obtain **10** using this method resulted in mixtures of *cis* and *trans* products.

(2) Reduction of 2-butyne-1,4-diol with $Cr^{(II)}$.

The procedure by Castro[7] was found in 'Reagents for Organic Synthesis' by Feiser and Feiser, Vol. 1. The book states: 'Acetylenes are reduced by chromous sulfate in water or aq DMF to *trans* olefins in high yield'. In the example cited, the reaction was complete at room temperature in about 10 min.



10

The reaction was carried out following the experimental of Castro. Analysis of the reaction product, by NMR, showed the main compound to be *cis*-but-2-en-1,4-diol.

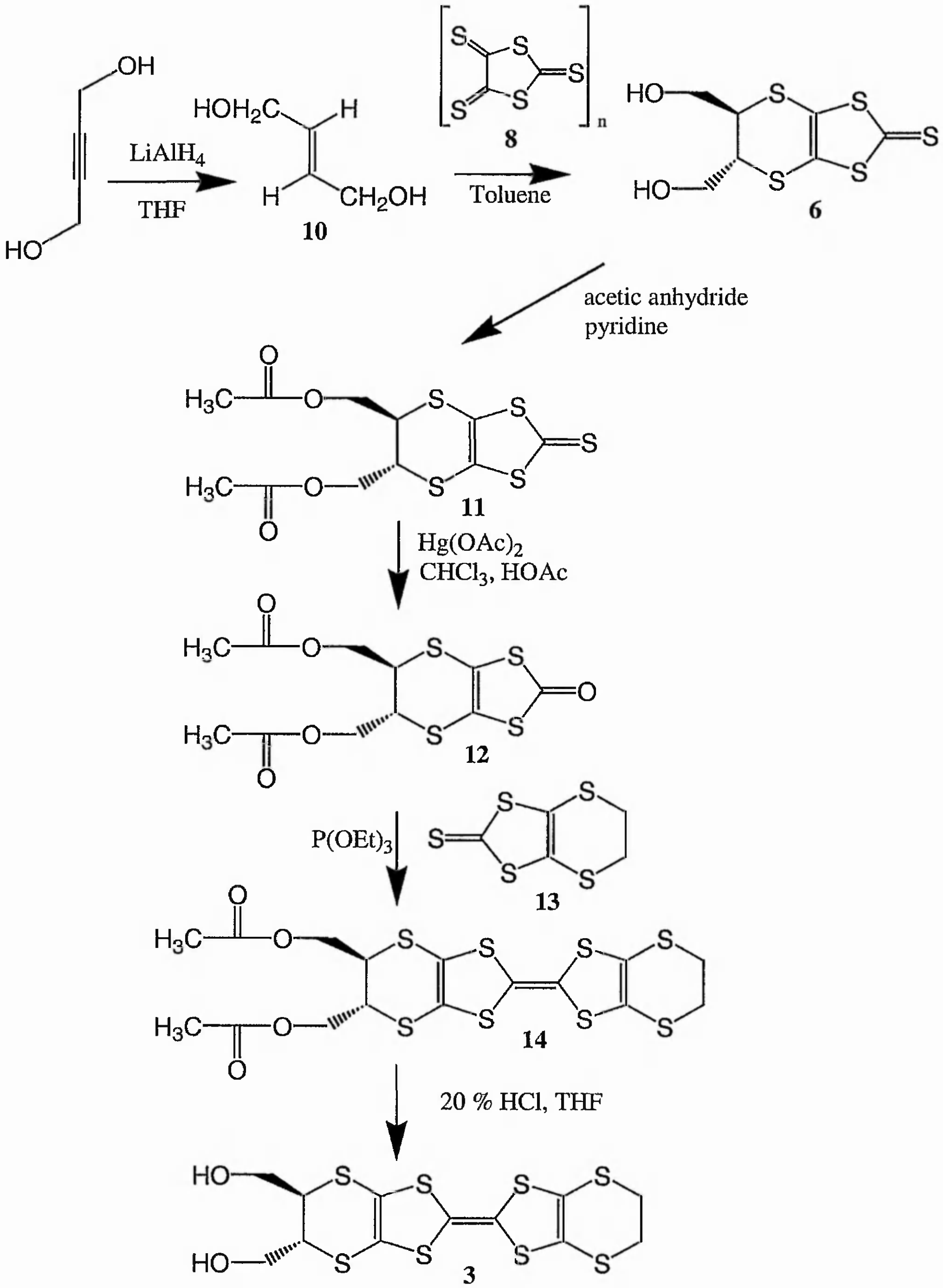
(3) Reduction of 2-butyne-1,4-diol with lithium aluminiumhydride ($LiAlH_4$).

A search of the literature found another method for preparing **10** using the reduction of 2-butyne-1,4-diol.[8] To a suspension of 4eq. of $LiAlH_4$ in THF was added a solution of 2-butyne-1,4-diol in THF and the reaction mixture refluxed for 1h. before the cautious dropwise addition of 0.1M HCl at room temperature to quench the reaction. After workup the reaction furnished the desired product, a pale yellow oil in 90 % yield and the method was reproducible. The ^{13}C NMR spectrum of **10** was identical to that obtained by the DIBAL reduction of diethyl fumarate (δ: 130.3 and δ: 61.9). Corresponding shifts for the *cis*-diol are found at δ: 131.4 and δ: 58.4.

Reaction of trithione **8** with 1.5eq. of **10** in toluene at an oil bath temperature of 130°C for 5h. followed by removal of excess **10** by Kugelrohr distillation and chromatography afforded **6** as a dark brown solid in 41% yield. The resonances of all H atoms occur together in a multiplet at δ: 3.80 in the ^{1}H NMR spectrum. The ^{13}C NMR spectrum indicates the C=S carbon at δ: 209.5. The CH_2 carbon atoms are observed at δ: 64.9 (cf. δ: 63.0 in the *cis* isomer). The infrared spectrum shows the thione (C=S) stretch at 1070 cm^{-1} and broad OH peak at 3260 cm^{-1}.

The preparation of *trans- vic-* bis(hydroxymethyl) ET, 3

With the thione **6** available, conversion to the disubstituted ET **3** was reasonably straightforward as shown in the scheme below. *trans- vic-* Bis(hydroxymethyl)ET, **3** is of importance since a more compact crystal packing in radical cation salts of **3** would be enhanced by the *trans* geometry of the hydroxymethyl groups, compared to the *cis* isomer.



Scheme 2. Synthesis of compound **3**.

Thus, six synthetic steps from 2-butyne-1,4-diol were employed to furnish the title compound. Protection of the hydroxy functionalities of **6** as acetates by reaction of **6** with acetic anhydride in pyridine at room temperature for 12h. afforded **11** as an orange/ brown oil in 94 % yield.

Replacement of the exocyclic sulfur atom for oxygen by treatment of **11** with mercuric acetate in chloroform and acetic acid furnished the oxo compound **12** as a light brown oil in 91 % yield. Cross coupling of **12** with thione **13** in triethyl phosphite at 90°C for 5h. followed by chromatography to separate the desired compound from ET and a mixture of isomeric tetra-substituted ET's, led to the cross coupled product **14** being obtained as an orange solid in 55% yield.

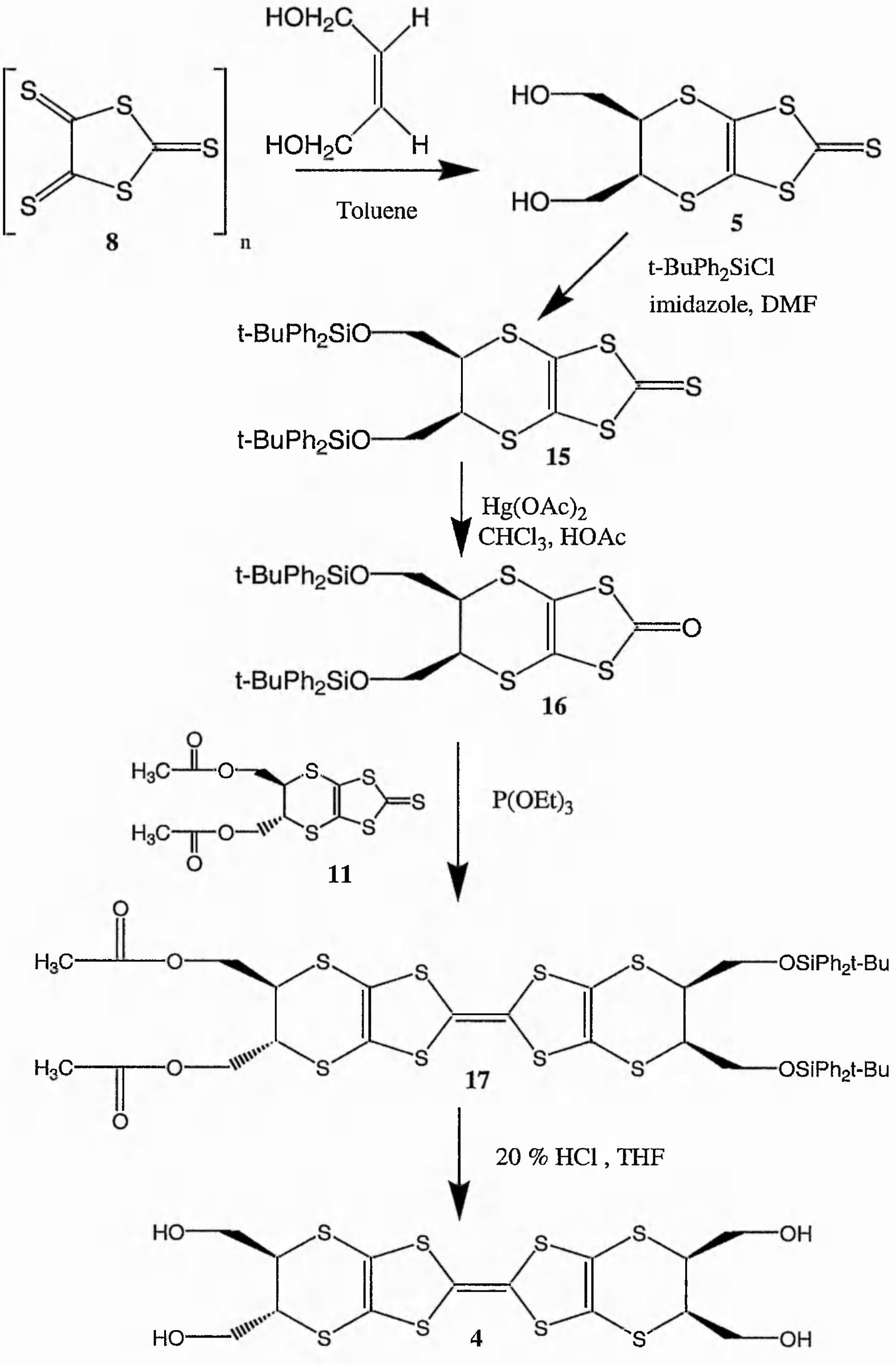
Removal of the protecting groups was carried out by treatment of **14** in THF with 20% HCl solution to afford the product **3** after chromatography as a bright orange powdery solid in 89 % yield. The two CH_2CH groupings were observed as a multiplet in the ^1H NMR spectrum, centred at δ: 3.65. The four protons of the unsubstituted ethylene bridge were observed as a singlet at δ: 3.25. ^{13}C NMR indicated two sp^2-*C* environments at δ: 114.8 and δ: 112.6, though up to four could be expected. However, these are the smallest peaks in the spectrum, and one cannot rule out accidental degeneracies. The infrared spectrum indicated the hydroxy absorption at 3401 cm^{-1}.

The preparation of a tetra(hydroxymethyl)-ET, 4

Tetra (hydroxymethyl)-ET **2** has been reported previously by two groups as a mixture of diastereoisomers[2,3] and has not been employed in the formation of radical cation salts. An ET molecule predisposed with four hydrogen bonding groups offers great potential for controlling the solid state by hydrogen bonding interactions. The aim of this investigation was to prepare one specific stereoisomer, **4** and begin work into the formation of radical cation salts. Since a very ordered crystalline radical cation salt is important for the electrical properties, it was essential to have access to just one diastereoisomer.

In the cross coupling of thiones or oxo compounds both with two hydroxymethyl functionalities it is important to take into consideration the stereochemical problems that could be encountered. For example coupling of two *cis* compounds together or two *trans* compounds leads to mixtures of diastereoisomers in each case that would be extremely difficult to separate by flash column chromatography. In light of this the stereoisomer **4** was prepared from coupling of the thione **11** bearing *trans* substituents with the oxo compound **16** bearing *cis* substituents. Only one possible pair of enantiomers can result from this coupling. Another key factor in designing the synthesis was to ensure efficient chromatographic separation of **17** from self coupled materials. This was achieved by employing different hydroxyl protecting groups for the *cis* and *trans* molecules, **16** and **11**.

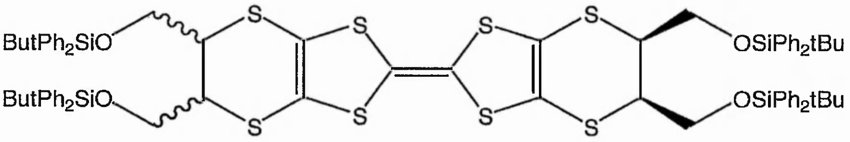
The synthetic scheme for the formation of **4** is shown below. Five synthetic steps were employed to furnish the title compound as an orange solid.



Scheme 3. Synthesis of compound 4.

Treatment of diol **5** with *t*-butyldiphenylsilyl chloride (2eq.) to protect the hydroxyl functions yielded **15** as an orange oil in 50 % yield. Replacement of the exocyclic sulfur atom for oxygen was achieved by treatment of **15** with mercuric acetate in chloroform and acetic acid to afford **16** as an orange oil in 97 % yield.

Cross coupling of **16** with thione **11** in triethyl phosphite for 5h. at an oil bath temperature of 90°C, followed by chromatography furnished **17** as a viscous orange oil in 20 % yield. Integration of the methyl peaks in the ^{1}H NMR spectrum of **17** show 2 x $COC\mathit{H}_3$ at δ: 2.10 and 2 x $SiC(C\mathit{H}_3)_3$ at δ: 1.01, helping to support the structure of **17**. Four chemical environments are shown for the sp^2 carbons in the ^{13}C NMR, these being found at: δ: 113.7, δ: 112.0, δ: 110.4 and δ: 109.3. The yield of **17** is low; a second fraction was also obtained as a viscous orange oil in ~20 % yield. NMR analysis of this second fraction indicated the self-coupled silylated compound **18**. In future work, better yields of **17** may be obtained by using an excess of the thione **11**, or by coupling the oxo derivative of **11** with the thione **15**.

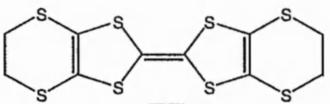


18

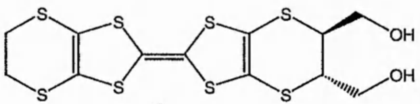
A solution of **17** in THF was treated with 20 % HCl solution and the mixture monitored by tlc analysis to indicate removal of the protecting groups. After 60h. the reaction mixture was worked up to afford **4** as an orange brown solid in 73 % yield. The ^{1}H NMR shows two multiplets at δ: 3.83 and δ: 3.64 corresponding to all twelve sp^3 protons, since the chemical environments at each end of the molecule are very similar. The ^{13}C NMR also highlights the similarities between the ends of the molecule, with signals at δ: 45.9, δ: 63.0 and δ: 65.0. There are two sp^2 shifts at δ: 113.1 and δ: 112.3. Assignment for the $\mathit{C}H_2$ carbons are tentatively based upon shifts observed for the *cis* and *trans* compounds (**16** and **11**). The *trans* CH_2's are assigned at δ: 65.0 and the *cis* CH_2's are assigned at δ: 63.0. The infrared spectrum shows a broad absorption at 3378 cm^{-1} corresponding to the hydroxy functions.

Cyclic voltammetry data for 3

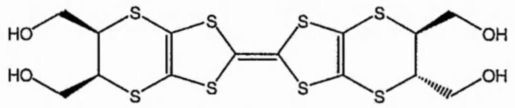
The solution redox chemistry of the novel ET derivatives **3** was studied by cyclic voltammetry (cv) and compared to ET. The novel donor shows two, single- electron, reversible redox waves over a number of scan rates at the expected potentials for ET; the oxidation potentials are not affected by the presence of the hydroxymethyl functions. Table 1 gives data measured in dichloromethane containing 0.1M tetrabutylammonium hexafluorophosphate under nitrogen, with a scan rate of 100mV s^{-1}, and quoted relative to Ag/AgCl. Attempted collection of cv data for **4** was hampered by the high insolubility of **4** in DCM and DMF.



ET



3



4

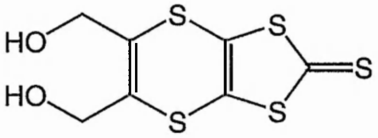
Table 1. Oxidation Potentials (V, relative to Ag/AgCl electrode)

	$E_1^{1/2}$	$E_2^{1/2}$
ET	0.48	0.89
3	0.50	0.88

As expected for the novel ET derivative **3**, the good electron donating ability makes it an ideal candidate for electrocrystallisation studies. Initial investigations into the formation of radical cation salts of **4** has commenced, but with little progress to date. **4** is completely insoluble in DCM and attempted electrocrystallisations using THF as solvent with BF_4^- and PF_6^- as counterions have failed to give any products. Gradually increasing the current through the cells from 1- 10 μA has also had no effect on crystal growth.

3. Related work in the preparation of novel ET derivatives bearing hydroxy functionalities.

The preparation of 5, 6- bis(hydroxymethyl)-1,3-dithiolo[4,5-b]-1,4-dithiin-2-thione, 19

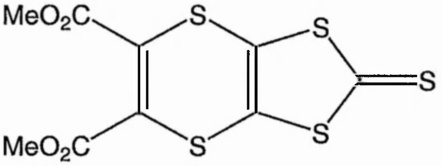


19

It was assumed that the formation of the title compound **19** could proceed in much the same fashion as the *cis* and *trans*-diols **5** and **6**, *i.e.*, by a 4+2 cycloaddition reaction but using an alkyne, not an alkene. Reaction of trithione **8** with 1.5 eq. of 2-butyne-1,4-diol in 1,4-dioxane at an oil bath temperature of 85°C for 5 h., and subsequent workup, gave starting material. Tlc analysis of the reaction mixture showed no presence of any product being formed. Changing the solvent to toluene and heating to an oil bath temperature of 130°C for 5 h. also failed to give any product.

A possible reason for the lack of reaction between the reagents could be due to the high energy of the π electrons in the alkyne bond. If the energy could be lowered, i.e., the loss of some electron density from the bond into neighbouring electron withdrawing groups, then reaction with the trithione may be energetically more favourable. With this in mind, it was decided to carry out reaction between **6** and dimethyl acetylenedicarboxylate (DMAD). The carbonyl functions of the esters are able to accept electron density from the electron-rich alkyne, so lowering the energy of the triple bond. Indeed, this substance is known for its exceptional reactivity with dienes and also nucleophiles. The reaction would lead to the formation of dimethyl 2-thioxo-1,3-dithiolo[4,5-b]1,4-dithiin-5,6-dicarboxylate **20**, which might then be reduced to the diol **19** with 4 eq. of DIBAL.

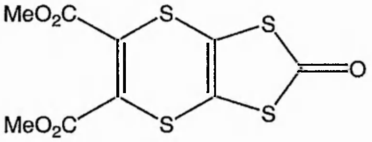
Reaction of trithione **8** with 1.5 eq. of DMAD in 1,4-dioxane at room temperature for 6 h. yielded no evidence of product formation by tlc analysis. The trithione, being very insoluble, was out of solution. Heating the reaction mixture to an oil bath temperature of 60°C for 6 hours, followed by subsequent workup and purification by flash column chromatography yielded a bright yellow powdery solid **20**, whose identity was confirmed by NMR analysis.



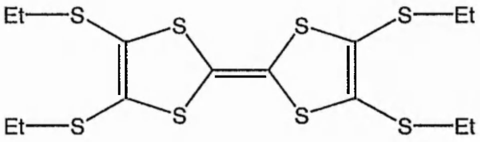
20

^{1}H NMR indicated a singlet for the six methyl protons at δ: 3.84. ^{13}C NMR showed the methyl shift at δ: 53.5 and the four sp^2 carbon atoms at δ: 128.2 (3'a-, 7'a- *C*) and δ: 135.9 (5'-, 6'- *C*). The carbonyls' shift was observed at δ: 161.7 and the thione resonance was at δ: 212.0.

Attempts to reduce the ester functionalities by DIBAL or $LiAlH_4$ reduction proved unsuccessful. However **20** was an interesting candidate for a self- or cross- coupling reaction. Firstly, the exocyclic sulfur atom was replaced with oxygen by treatment of **20** with mercuric acetate in chloroform and acetic acid to give oxo compound **21** as a pale yellow solid. ^{13}C NMR showed the new carbonyl shift (2- *C*) at δ: 190.8.

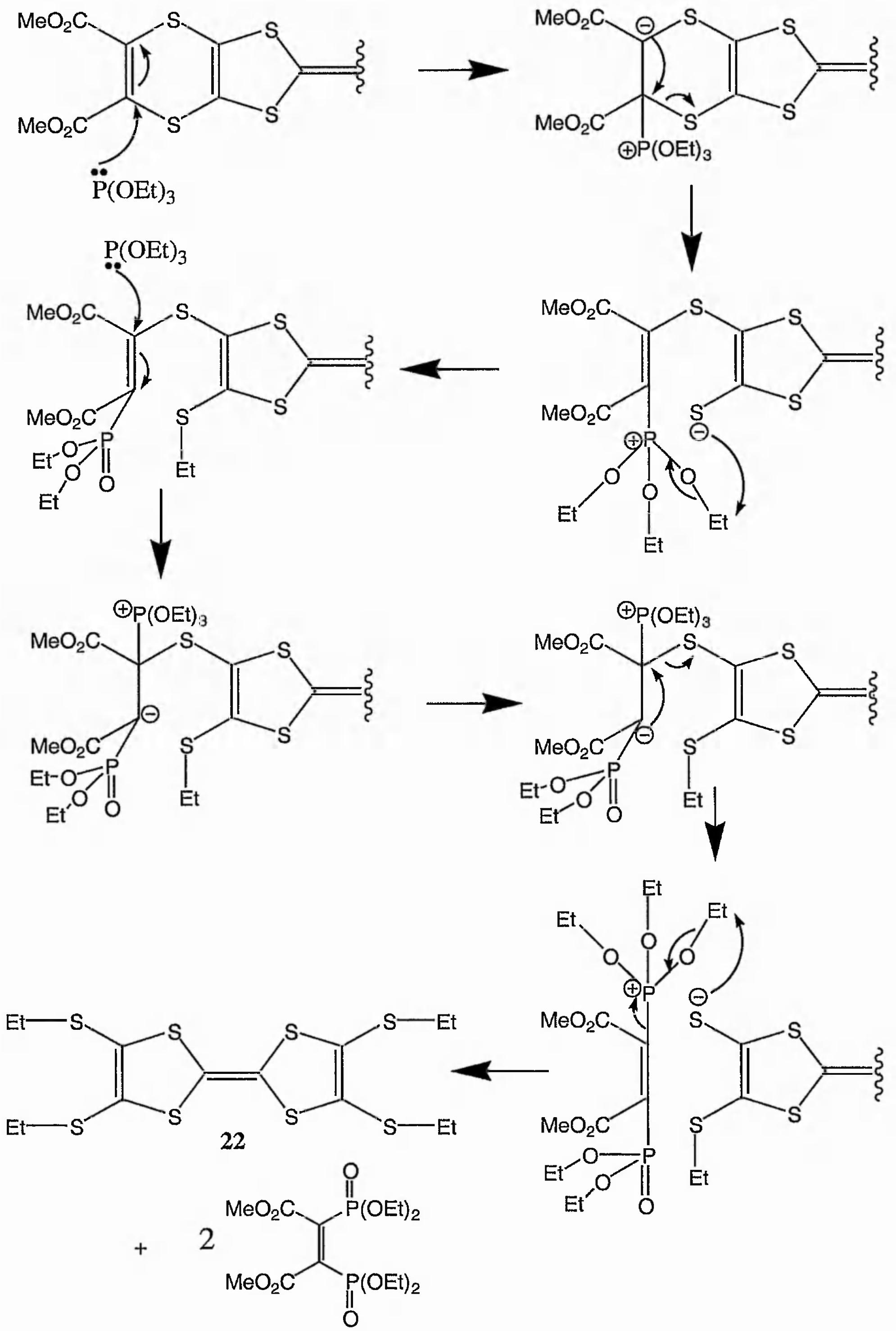


21



22

The triethyl phosphite mediated self coupling of **21** at an oil bath temperature of 90°C for 4h. followed by chromatography yielded an unexpected product. NMR analysis suggested that the reaction proceeded via an Arbusov rearrangement to yield **22** as an orange oil. Rauchfuss *et al.* [9] have also observed the rearrangement. ^{13}C NMR showed shifts at δ: 128.7 for the outer sp^2 carbon atoms, δ: 109.7 for the central sp^2 carbon atoms and δ: 40.7 & δ: 23.2 for the ethyl carbon atoms. Further investigations carried during the course of these studies with other bulkier phosphite reagents such as triisopropyl phosphite to try and prevent the rearrangement occurring were also unsuccessful. A proposed mechanism for the rearrangement is shown below:

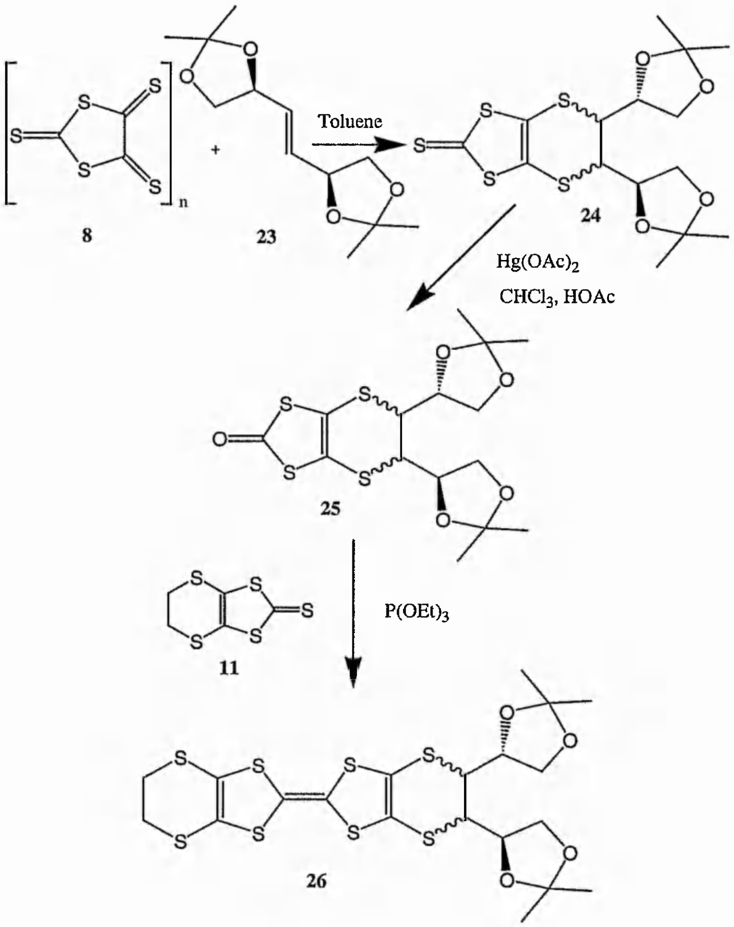


Scheme 4. Proposed mechanism for rearrangement product **22**.

The self-coupling of **21** using $Co_2(CO)_8$ was also investigated. After reaction the mixture was black in colour; tlc analysis using a number of solvents only indicated baseline material present.

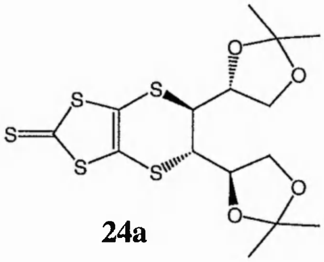
A diastereoselective 4+2 cycloaddition reaction of trithione 8 with chiral dienophile 23

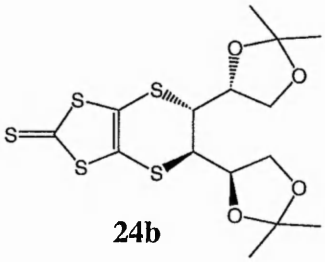
In the search for novel ET molecules bearing a number of hydroxyl substituents, the 4+2 cycloaddition reaction of trithione **8** with the enantiopure dienophile **23** was investigated. If the two diastereomeric products could be separated, then this would provide useful building blocks for preparing enantiopure organosulfur donors bearing four or eight hydroxy groups. This work has progressed so far to the production of **26**, which has four stereogenic centres. Dienophile **23** was derived from *D*- mannitol. Protection of the outer hydroxy functions as ketals, then removal of the two central hydroxy functions by conversion to mesylates and reduction with zinc furnished **23** as a pale solid. The approach to compound **26** followed the general scheme below:

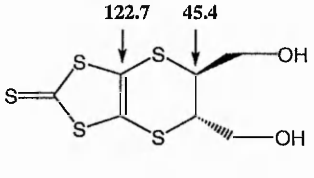


Scheme 5. Synthesis of compound **26**.

4+2 Cycloaddition reaction of trithione **8** with the *trans* dienophile **23** in toluene at an oil bath temperature of 130°C for 3h. followed by chromatography yielded two isomers of **24** which have quite distinct R_f values. The first isomer obtained from the column was a light brown solid (27 %) and the second, obtained after a second chromatographic separation from the starting material **23**, was an orange oil (4 %). ^1H NMR analysis of the isomers indicates very similar splitting patterns but subtle changes in the shift values of several protons on the dioxolane and dithiin rings. Mass spectral measurements however show the molecular masses to be 424 and 500 respectively. The molecular mass of **24b** indicates an extra 76 units, although there appears to be no extra C resonances in the NMR spectrum. A possible explanation is that this compound is indeed **24b**, but that in the mass spec it has formed a CS_2 adduct, with CS_2 formed by decomposition. It is notable that attempts in two laboratories to measure the high resolution mass spectrometry of the peak at 500 gave values of 534 which are totally incompatable with conceivable molecular structures.


24a


24b



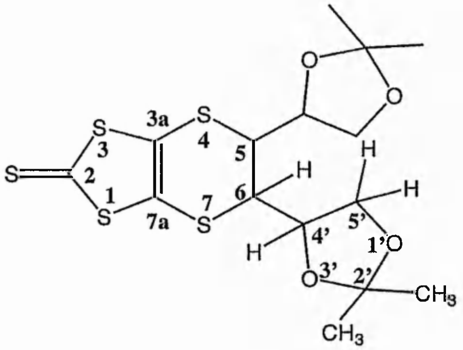
6

Isomer **24a** gave reasonable looking crystals, but no suitable unit cell could be found on examining several samples. In the ^{13}C NMR, 3a- and 7a- C resonates at δ: 118.9, and the 5- and 6- C atoms of the dithiin ring resonate at δ: 44.3. In comparison, the thione **6** shows comparable shifts at δ: 122.7 and δ: 45.4.

The preferred molecular conformation may have the two substituents both pseudo equatorial, or both pseudo axial, the latter may be the less crowded case. There is also some conformational freedom in the reduced dithiin ring, which often adopts an envelope conformation, but could also be in a half chair or even a pseudo boat.

Table 2:

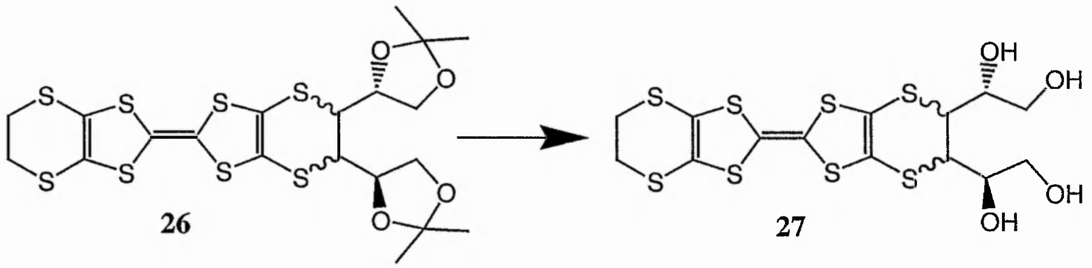
NMR data for isomers **24a** and **24b**.



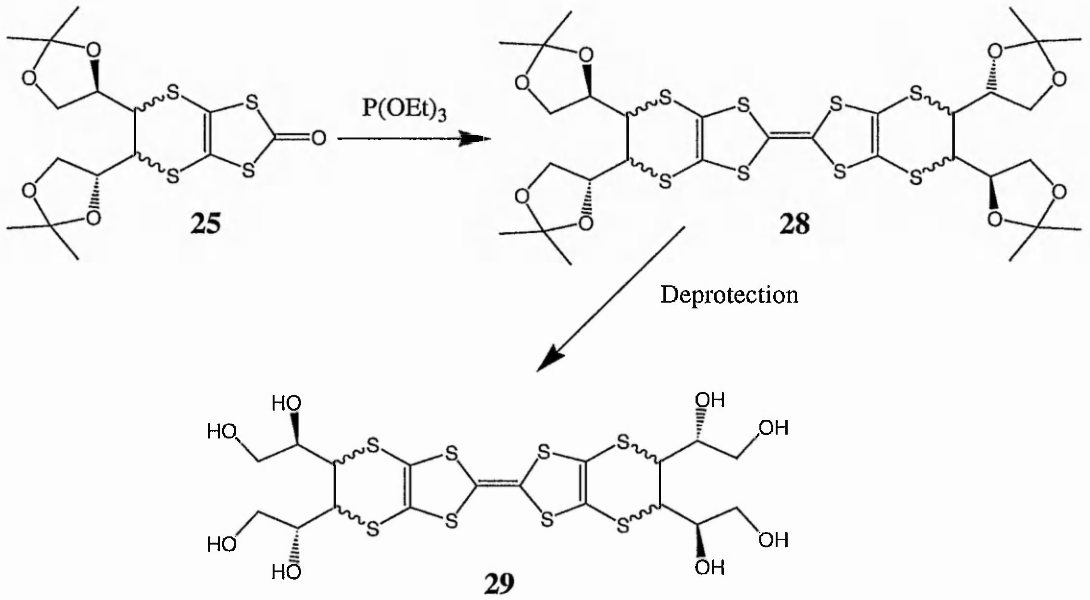
24A	24B		24A	24B	
1H NMR δ:		Assignment	13C NMR δ:		Assignment
4.45	4.42	4'- H	206.5	208.8	2- C
4.18	4.12	5'- H_α	118.9	128.3	3a, 7a- C
4.03	3.86	5'- H_β	110.6	110.3	2'- C
3.71	3.46	5-, 6- H	75.9	75.8	4'- C
1.41	1.44	CH_3	67.8	66.9	5'- C
1.33	1.33	CH_3	44.3	51.7	5-, 6- C
			27.1	26.4	CH_3
			25.3	25.0	CH_3

Compound **24** was used in further transformations. The stereochemistry of the dithiin ring is not indicated, but it is not expected to change in the subsequent synthetic steps. Replacement of the exocyclic sulfur atom of **24** by treatment with mercuric acetate in chloroform and acetic acid led to the oxo compound **25** being obtained as an orange solid in 84 % yield. Attempts to grow crystals of **25** were also unsuccessful, crystals obtained being poor in quality and not suitable for x-ray crystallography. ^{13}C NMR of **25** indicated the carbonyl resonance at δ: 188.9. The sp^2 carbon shifts were observed at δ: 110.6 and δ: 109.6, as would be expected for an oxo compound. The carbonyl absorption was observed in the infared spectrum at 1683 cm^{-1}.

Cross coupling of **25** with thione **11** in triethyl phosphite at an oil bath temperature of 90°C for 5h. followed by workup and purification by chromatography led to **26** being obtained as an orange solid in 35 % yield. Once again, attempts to grow crystals of **26** were unsuccessful. The synthetic work was halted at this point due to a lack of material. This synthesis needs to be repeated on a larger scale, so that the ketal groups of **26** can be hydrolysed to yield an ET derivative **27** with four hydroxy groups. Careful examination of this and previous intermediates will be necessary to ascertain whether there is a second diastereomeric product. If the material contains just one diastereomer, then the stereochemistry can be determined unambiguously by x- ray crystallography of the final tetrol, or a derivative, e.g. with 4-nitrobenzyl bromide to promote crystallinity.



An enantiopure ET derivative **29** functionalised with eight hydroxyl functions is also possible by self-coupling of a single diasteroisomer of **25** in triethyl phosphite, followed by deprotection of the ketal moieties, and would be the next step in the part of the project. The opposite enantiomer could be prepared from *L*- mannitol, and the racemate by combining equal amounts of the two enantiomers. These molecules will be of interest for investigating the influence of chirality in conduction. Furthermore, these molecules could be the core of novel dendrimers which had further 'ET' units in the branches.



4. Experimental.

E – But- 2- en- 1, 4- diol, 10[8]

$LiAlH_4$ (10.0g, 260.0mmol) was added to dry THF (70ml) under N_2. The mixture was refluxed for 1h. then allowed to cool to room temperature. A solution of 2-butyne-1, 4-diol (5.7g, 65.9mmol) in THF (50ml) was added dropwise over 45 min. When the addition was complete the reaction mix was heated to reflux for 1h., then quenched by the cautious dropwise addition of 0.1M HCl (56.0ml) at room temperature. The solid was filtered off and washed with THF (2x100ml). Combined washings and filtrate were stirred with Na_2SO_4 (100g) for 15 min. Removal of the solid by filtration and evaporation of the solvent afforded **10** as a light brown oil (5.2g, 90 %); ^{1}H NMR (MeOH-d_4) δ: 5.80 (2H, m, 2-, 3- *H*), 4.98 (2H, s, 2 x O*H*), 4.06 (4H, dd, J = 2.6, 1.1 Hz, 1, 4- H_2), ^{13}C NMR (MeOH-d_4) δ: 131.2 (2, 3- *C*), 63.0 (1-, 4- *C*); ν_{max}/cm^{-1} (thin film) 3324 (OH), 2932, 2865, 1420, 1675 (C=C), 1369, 1080, 990.

trans- 5, 6- Dihydro- 5, 6- di(hydroxymethyl)- 1, 3- dithiolo [4, 5-b]-1, 4- dithiin- 2- thione, 6

A mixture of *E*- but- 2- en- 1, 4- diol **10** (1.5g, 17.0mmol) and trithione **8** (2.2g, 11.3mmol) in toluene (220ml) was refluxed for 5h. The solvent was removed under reduced pressure and the residue purified by flash chromatography (SiO_2/1:1 EtOAc/cyclohexane) to give **6** as a brown powdery solid (1.3g, 41 %); m.p. 110-112°C; ^{1}H NMR (MeOH-d_4) δ: 3.80 (6H, m, 5-, 6- *H* & 2 x CH_2O); ^{13}C NMR (MeOH-d_4) δ: 209.5 (2- *C*), 122.7 (3a-, 7a- *C*), 64.9 (2 x *C*H_2OH), 45.4 (5-, 6- *C*); ν_{max}/cm^{-1} (KBr) 3260 (OH), 2931, 2872, 1485, 1459, 1070 (C=S), 1041, 1019; found C, 29.6; H, 2.8 %, $C_7H_8O_2S_5$ requires C, 29.6; H, 2.8 %.

trans- 5, 6- Dihydro- 5, 6- di(acetyloxymethyl)-1, 3- dithiolo [4, 5-b]-1, 4- dithiin-2- thione, 11

To a solution of **6** (1.0g, 3.7mmol) in pyridine (15.0ml) at 0°C was added acetic anhydride (0.7ml, 7.4mmol). The mixture was stirred at room temperature overnight. DCM (100ml) and water (30ml) were added. The mixture was shaken and the organic layer collected. This was washed sequentially with 1M HCl (3x100ml) and water (50ml), dried ($MgSO_4$) and evaporated to yield **11** as a dark orange/ brown oil (1.3g, 94 %); ^{1}H NMR δ: 4.32 (4H, m, 2 x CH_2O), 3.74 (2H, m, 5, 6- *H*), 2.07 (6H, s, 2 x OCH_3); ^{13}C NMR δ: 206.5 (*C*=S), 170.7 (*C*=O) 118.8 (3a-, 7a- *C*), 64.7 (2 x CH_2O), 40.1 (5-, 6- *C*), 20.7 (2 x CH_3); ν_{max}/cm^{-1} (thin film) 2923, 1743 (C=O), 1381, 1363, 1222, 1064 (C=S), 1034; HRMS (ES): Found: 368.9419 $(M+H)^+$, $C_{11}H_{12}O_4S_5$ requires: 368.9417 $(M+H)^+$.

trans- 5, 6- Dihydro-5,6-di(acetyloxymethyl)-1, 3- dithiolo [4, 5-b]-1, 4- dithiin- 2-one, 12

To a solution of **11** (0.2g, 0.4mmol) in $CHCl_3$ (10.0ml) and glacial acetic acid (3.0ml) was added mercuric acetate (0.2g, 0.6mmol). After 2h. stirring at room temperature the mix was filtered. The filtrate was washed consecutively with saturated $NaHCO_3$ solution (3x10ml) and H_2O (10ml), dried (Na_2SO_4) and evaporated to afford **12** as a light brown oil (0.1g, 91 %); ^{1}H NMR δ: 4.34 (4H, m, 2 x CH_2O), 3.72 (2H, m, 5-, 6- *H*), 2.04 (6H, s, 2 x CH_3); ^{13}C NMR δ: 187.2 (S_2C=O), 169.7 (O=CCH_3) 109.6 (3a-, 7a- *C*), 64.5 (2 x CH_2O), 41.2 (5-, 6- *C*), 20.4 (2 x CH_3); ν_{max}/cm^{-1} (thin film) 3025, 2943, 1744 (C=O), 1692 (C=O), 1507, 1440, 1381, 1364, 1222, 1035, 891, 755; HRMS (ES): Found: 369.9914 $(M+H)^+$, $C_{11}H_{12}O_5S_4$ requires: 369.9911 $(M+H)^+$.

trans- *vic*- Bis(acetyloxymethyl)- ET, 14

A mixture of oxo compound **12** (0.8g, 2.1mmol) and thione **13** (0.7g, 3.2mmol) were heated in triethyl phosphite (10.0ml) to 90°C under N_2 for 5h. to give an orange solution. Triethyl phosphite was removed by distillation *in vacuo* and the residue purified by flash chromatography (SiO_2, 3:1 cyclohexane/ EtOAc) to yield **14** as an orange solid (0.6g, 55 %); m.p.122-123°C; ^{1}H NMR δ: 4.27 (2H, dd, J = 11.2, 5.7 Hz, 2 x $CH_{\alpha}O$), 4.23 (2H, dd, J = 11.2, 8.0 Hz, 2 x $CH_{\beta}O$), 3.65 (2H, m, 5-, 6- *H*), 3.24 (4H, s, 5'-, 6'- H_2), 2.04 (6H, s, 2 x CH_3); ^{13}C NMR δ: 170.2 (*C*=O) 113.7, 110.2 (sp^2-*C*), 64.7 (5-, 6- CH_2O), 40.6 (5-, 6- *C*), 30.0 (5'-, 6'- *C*), 20.7 (2xCH_3); ν_{max}/cm^{-1} (KBr) 2931, 1740 (C=O), 1381, 1362, 1230, 1033, 909, 772; HRMS (ES): found: 528.8886 $(M+H)^+$, $C_{16}H_{16}O_4S_8$ requires: 528.8892 $(M+H)^+$.

trans- *vic*- Bis(hydroxymethyl)- ET, 3

A solution of **14** (0.2g, 0.4mmol) in THF (20ml) and 20% HCl solution (10.0ml) was stirred under N_2 overnight. The solution was neutralised by the addition of solid $NaHCO_3$. The organic layer was collected, dried (Na_2SO_4) and evaporated to afford **3** (0.2g, 89 %) as a bright orange powdery solid; m.p.150°C (dec); ^{1}H NMR (MeOH-d_4) δ: 3.65 (6H, m, 2 x $CHCH_2$), 3.25 (4H, s, 5'-, 6'- H_2); ^{13}C NMR (MeOH-d_4) δ: 114.8, 112.6 (sp^2- *C*), 65.0 (2 x CH_2O), 45.9 (5, 6- *C*), 31.1 (5'-, 6'- *C*); ν_{max}/cm^{-1} (KBr) 3401 (OH), 2919, 2861, 1451, 1417, 1298, 1167, 1026, 1005, 884, 773; HRMS (EI): Found: 443.8605, $C_{12}H_{12}O_2S_8$ requires: 443.8603.

cis- 5, 6- Dihydro- 5, 6-di(hydroxymethyl)-1, 3-dithiolo [4, 5-b]-1, 4- dithiin- 2-thione, 5

A mixture of *cis*- but- 2- en- 1, 4- diol (1.7ml, 20.4mmol) and the trithione **8** (2.0g, 10.2mmol) in toluene (200ml) was refluxed for 5h. The solvent was removed under reduced pressure and the residue purified by flash chromatography (SiO_2/1:1 EtOAc/cyclohexane) to give **5** as a bright yellow powdery solid (1.1g, 38 %); m.p.113-115°C (lit m.p. 125-126°C (from ethanol)[5]); ^1H NMR δ: 4.96 (2H, s, 2 x O*H*), 4.06 (4H, m, 5-, 6- *H* & 2 x $CH_\alpha O$), 3.91 (2H, m, 2 x $CH_\beta O$); ^{13}C NMR δ: 209.9 (2- *C*), 122.7 (3a-, 7a- *C*), 63.0 (2 x CH_2OH), 45.4 (5-, 6- *C*); ν_{max}/cm^{-1} (KBr) 3218 (OH), 2938, 2367, 1494, 1459, 1069 (C=S), 1041, 1017, 894.

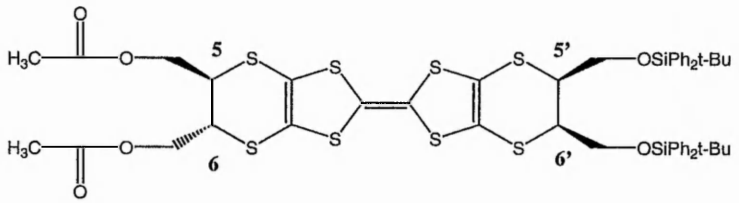
cis- 5, 6- Bis (t-butyldiphenylsilyloxymethyl)- 5, 6- dihydro-1, 3- dithiolo [4,5-b]1, 4- dithiin- 2- thione, 15

To a solution of **5** (2.0g, 7.0mmol) in dry DMF (120ml) was added sequentially imidazole (9.6g, 140.8mmol) and t-butyldiphenylsilyl chloride (4.5ml, 17.6mmol). After stirring at room temperature overnight, water (100ml) and dichloromethane (200ml) were added; the dichloromethane layer separated, and the aqueous layer extracted twice more with dichloromethane (2x40 ml). The combined organic solution was washed sequentially with ice-cold HCl (3M, 3×50 ml) and water (50 ml) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue purified by flash chromatography (SiO_2/ DCM) to afford **15** as an orange oil (2.7g, 50 %); ^1H NMR δ: 7.75 (8H, m, Ar- H_8), 7.50 (12H, m, Ar- H_{12}), 4.06 (6H, m, 2 x $CHCH_2$), 1.15 (18H, s, 6 x CH_3); ^{13}C NMR δ: 207.8 (*C*=S), 135.4, 132.4, 129.9, 127.8 (Ar- C_{24}), 121.4 (3a-, 7a- *C*), 63.5 (2 x CH_2O), 47.9 (5, 6- *C*), 26.7 (6 x CH_3), 19.0 (2 x $C(CH_3)_3$); ν_{max}/cm^{-1} (thin film) 2933, 2922, 2856, 1720 (C=O), 1470, 1427, 1273, 1113, 1067 (C=S), 823, 739, 701, 614; HRMS (EI): Found: 760.1473, $C_{39}H_{44}O_2S_5Si_2$ requires: 760.1483.

cis- 5, 6- Bis (t-butyldiphenylsilyloxymethyl)- 5, 6- dihydro- 1, 3- dithiolo[4, 5-b]1, 4- dithiin- 2- one, 16

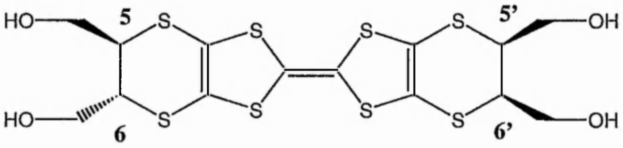
To a solution of **15** (2.5g, 3.3mmol) in $CHCl_3$ (60ml) and glacial acetic acid (20ml) was added mercuric acetate (1.6g, 4.9mmol). After 2h. stirring at room temperature the mixture was filtered. The filtrate was washed consecutively with saturated $NaHCO_3$ solution (3x100ml) and H_2O (100ml), dried (Na_2SO_4) and evaporated to afford **16** as an orange oil (2.4g, 97 %); ^{1}H NMR δ: 7.80 (8H, m, Ar- H_8), 7.49 (12H, m, Ar- H_{12}), 4.10 (6H, m, 2 x $CHCH_2$), 1.18 (18H, s, 6 x CH_3); ^{13}C NMR δ: 188.5 (C=O), 135.2, 132.3, 129.6, 127.5 (Ar- C_{24}), 111.3 (3a-, 7a- C), 63.5 (2 x CH_2O), 48.9 (5-, 6- C), 26.5 (6 x CH_3), 18.9 (2 x $C(CH_3)_3$); ν_{max}/cm^{-1} (thin film) 3075, 2955, 2932, 2856, 1682 (C=O), 1627, 1471, 1427, 1112, 823, 738, 700; found C, 62.5; H, 5.8 %, $C_{39}H_{44}O_3S_4Si_2$ requires C, 62.9; H, 6.0 %.

cis- *vic*- Bis (t-butyldiphenylsilyloxymethyl)- *trans*- *vic*- bis (acetyloxymethyl)-ET, 17



A mixture of oxo compound **16** (2.4g, 3.2mmol) and thione **11** (1.2g, 3.3mmol) were heated in triethyl phosphite (30ml) to 90°C under N_2 for 5 h. to give an orange solution. Triethyl phosphite was removed by distillation *in vacuo* and the residue purified by flash chromatography (SiO_2, 5:1 cyclohexane/ EtOAc) to yield **17** as an orange oil (0.7g, 20 %); ^{1}H NMR δ: 7.70 (8H, m, Ar- H_8), 7.40 (12H, m, Ar- H_{12}), 4.33 (2H, m, 5', 6'- *H*), 3.80 (10H, m, 5-, 6- *H*, 5-, 5'-, 6-, 6'- CH_2O), 2.10 (6H, s, 2 x COCH_3), 1.01 (18H, s, 6 x CH_3); ^{13}C NMR δ: 170.2 (*C*=O), 135.5, 132.5, 129.8, 127.7 (Ar- C_{24}), 113.7, 112.0, 110.4, 109.3 (sp^2- *C*), 64.8 (5, 6- *C*H$_2$O), 63.7 (5', 6'- *C*H$_2$O) 48.3 (5-, 6- C), 40.7 (5'-, 6'- C) 26.7 (6 x *C*H$_3$), 20.7 (2 x CO*C*H$_3$), 19.0 (2 x *C*(CH$_3$)$_3$); ν_{max}/cm^{-1} (thin film) 2955, 2922, 2856, 1721(C=O), 1462, 1428, 1380, 1273, 1224, 1114, 1073.0, 1034, 739, 701. HRMS (EI): found: 1065.1469, $C_{50}H_{56}O_6S_8Si_2$ requires: 1065.1459.

***cis- vic-* Bis- (hydroxymethyl)- *trans- vic-* bis (hydroxymethyl)- ET, 4**



A solution of **21** (0.2g, 0.2mmol) in a mixture of THF (20ml) and 20% HCl solution (10.0ml) was stirred under N_2 for 60h. The solution was neutralised by the addition of solid NaHCO$_3$. The organic layer was collected, dried (Na$_2$SO$_4$) and evaporated to afford **4** (0.1g, 73 %) as an orange brown solid; m.p.154-155°C; ^{1}H NMR (MeOH-d$_4$) δ: 3.83 (2H, m, 5'-, 6'- *H*), 3.64 (10H, m, 5-, 6- *H*, 5-, 5'-, 6-, 6'- CH_2O); ^{13}C NMR (MeOH-d$_4$) δ: 113.1, 112.3, (sp^2- *C*), 65.0 (5-, 6- *C*H$_2$O), 63.0 (5', 6'- *C*H$_2$O) 45.9 (5-, 5'- & 6-, 6'- *C*); ν_{max}/cm^{-1} (KBr) 3378 (OH), 2912, 2862, 1654, 1384, 1179, 1028; HRMS (EI): found: 503.8817, $C_{14}H_{16}O_4S_8$ requires: 503.8814.

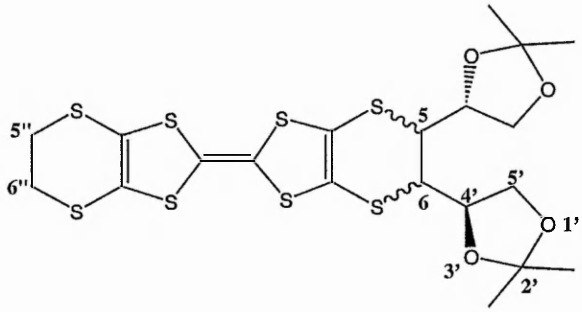
5, 6- bis((4'- R)- 2', 2"- dimethyl- 1, 3- dioxolan- 4'- yl)- 5, 6- dihydro- 1, 3- dithiolo [4, 5- b]1, 4- dithiin- 2- thione, 24

A mixture of the bis ketal **23** (0.5g, 2.2mmol) and the trithione **6** (0.2g, 1.1mmol) in toluene (25ml) was refluxed for 3h. The solvent was removed under reduced pressure and the residue purified by flash chromatography (SiO_2/5:1 cyclohexane/ EtOAc) to elute **24a** with R_f 0.45 as a light brown solid (0.1g, 27 %). Elution with 1:1 cyclohexane/ EtOAc gave crude **24b**. This material was further purified by flash chromatography (SiO_2/ DCM) to give a yellow oil (0.02g, 4 %); (**24a**) m.p. 164-165°C; ^{1}H NMR δ: 4.45 (2H, dd, J= 5.7, 4.2 Hz), 4.18 (2H, dd, J= 9.2, 5.9 Hz, 5''- H_α), 4.03 (2H, dd, J= 9.0, 4.2 Hz, 5''- H_β), 3.71 (2H, d, J= 9.9 Hz), 1.41 (6H, s, 2 x CH_3), 1.33 (6H, s, 2 x CH_3); ^{13}C NMR δ: 206.5 (*C*=S), 118.9 (3a-, 7a-*C*), 110.6 (2 x 2''- *C*), 75.9 (2 x 4''- *C*), 67.8 (2 x 5''- *C*), 44.3 (5, 6- *C*), 27.1 (*C*H_3), 25.3 (*C*H_3); ν_{max}/cm^{-1} (KBr) 2988, 2935, 1488, 1458, 1377, 1368, 1235, 1148, 1066 (C=S), 830; $^{293}[\alpha]_D$ = + 489 (c = 0.12, DCM). ^{1}H NMR (**24b**) δ: 4.42 (1H, m,), 4.12 (1H, dd, J= 8.7, 6.4 Hz), 3.86 (1H, dd, J= 8.8, 5.8 Hz), 3.46 (1H, dd, J= 3.5, 1.2 Hz), 1.44 (3H, s, CH_3), 1.33 (3H, s, CH_3); ^{13}C NMR δ: 208.8 (C=S), 128.3 (3a-, 7a- *C*), 110.3, 75.8, 66.9, 51.7, 26.4 (*C*H_3), 25.0 (*C*H_3).

5, 6- bis((4'- R)- 2', 2''- dimethyl- 1, 3- dioxolan- 4'- yl)- 5, 6- dihydro- 1, 3- dithiolo [4, 5- b]1, 4- dithiin- 2- one, 25

To a solution of **24a** (0.5g, 1.1mmol) in $CHCl_3$ (20ml) and glacial acetic acid (6ml) was added mercuric acetate (0.5g, 1.7mmol). After 2 h. stirring at room temperature the mix was filtered. The filtrate was washed consecutively with saturated $NaHCO_3$ solution (3x50ml) and H_2O (50ml), dried (Na_2SO_4) and evaporated to afford **25** as an orange solid (0.4g, 84 %); m.p.116-118°C; ^{1}H NMR δ: 4.51 (2H, m, 2 x 4'- *H*), 4.20 (2H, dd, J= 8.9, 6.1 Hz, 2 x 5'- H_α), 4.04 (2H, dd, J= 9.2, 4.2 Hz, 2 x 5'- H_β), 3.71 (2H, d, J= 9.9 Hz, 5-, 6- *H*), 1.42 (6H, s, CH_3), 1.34 (6H, s, CH_3); ^{13}C NMR δ: 188.9 (C=O), 110.6 (2', 2''- *C*), 109.6 (3a-, 7a-*C*), 76.1 (4', 4''- *C*), 68.0 (2 5', 5''- *C*), 45.7 (5, 6- *C*), 27.1 (2 x CH_3), 25.4 (2 x CH_3); ν_{max}/cm^{-1} (KBr) 2988, 2935, 1683 (C=O), 1381, 1372, 1260, 1245, 1229, 1214, 1074, 822; $^{293}[\alpha]_D = + 206$ (c = 0.14, DCM).

5, 6- Bis((4'- R)- 2'- dimethyl- 1', 3'- dioxolan- 4'- yl)- ET, 26



A mixture of oxo compound **25** (0.1g, 0.3mmol) and the thione **11** (0.1g, 0.4mmol) was heated in triethyl phosphite (5ml) to 90°C under N_2 for 5 h. to give an orange solution. Triethyl phosphite was removed by distillation *in vacuo* and the residue purified by flash chromatography (SiO_2, 3:1 cyclohexane/ EtOAc) to yield **26** as an orange solid (0.1g, 35 %); m.p.88-90°C; ^{1}H NMR δ: 4.37 (2H, m, 2 x 4'- *H*), 4.13 (1H, dd, J= 9.1, 5.9 Hz, 2 x 5'- H_α), 4.00 (1H, dd, J= 9.1, 4.4 Hz, 2 x 5'- H_β), 3.67

(2H, dd, J= 8.9, 1.0 Hz, 5-, 6- *H*), 3.26 (4H, s, 5'', 6''- H_2), 1.40 (6H, s, 2 x CH_3), 1.32 (6H, s, 2 x CH_3); ^{13}C NMR δ: 113.9, 112.3, 110.4 (sp^2- *C*), 109.9 (2 x 2''- *C*), 76.5 (2 x 4''- *C*), 68.0 (2 x 5''- *C*), 44.9 (5, 6- *C*), 30.2 (5', 6'- C), 27.1 (*C*H_3), 25.4 (*C*H_3); $^{293}[\alpha]_D$ = + 51.5 (c = 0.13, DCM).

5. References.

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Chapter 4

Synthesis of ester or amide - functionalised ET donors

1. Introduction.

In the search for new organic conductors and superconductors based on ET with the aim of controlling the solid state assembly by intra- and intermolecular hydrogen bonding, the preparation of ET derivatives functionalised with amide groups was an attractive area of investigation. The amide group can act as a hydrogen bond donor (N-H) and also as a hydrogen bond acceptor (through the oxygen atom of the carbonyl group). It is envisaged that the dual nature of the amide group will provide strong hydrogen bonding interactions from both donor to donor and also from donor to anion, leading to ordered packing arrangements and high conductivities.

The synthesis of ET derivatives bearing amide functionality directly attached to the ET molecule was avoided, Literature precedents[1,2] have shown that for the oxo compounds shown below, activation of 5- C by an ester group leads to the Arbusov rearrangement product when treated with triethyl phosphite rather than the expected coupled products.

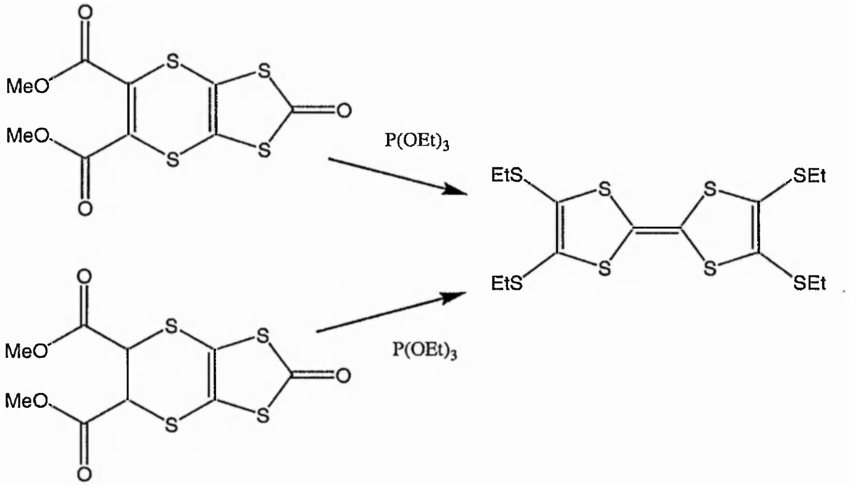
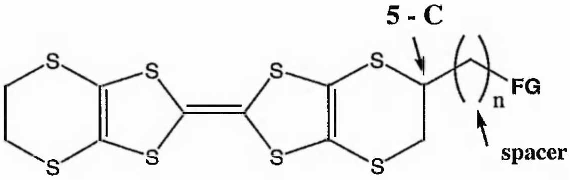
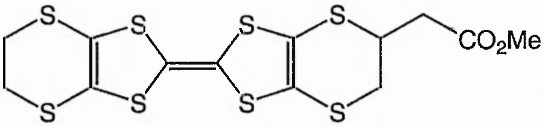


Figure 1. Arbusov rearrangement product.

However, introducing a spacer between the ET core and the functional group (FG) avoids activation of 5-C to nucleophilic attack by the phosphite.



It was initially envisaged that the synthetic route towards incorporating amide functionalities on to the ET framework would be through the hydrolysis of the racemic ester compound **1** to the carboxylic acid **2**, followed by known coupling routes of acids and amines to produce amides, such as the DCC coupling used in the formation of peptides.[3] The introduction of carbonyl functionality would open up further avenues for attaching the ET unit to supramolecular systems, dendrimers or polymers. In this case, the substituted ET would be the electrophile, in contrast to using the hydroxy derivatised ET's of the second chapter.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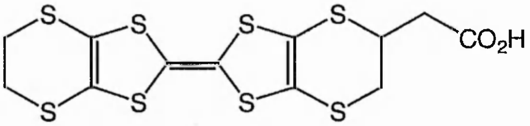
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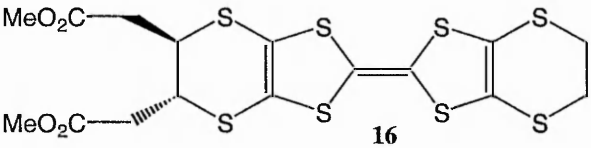
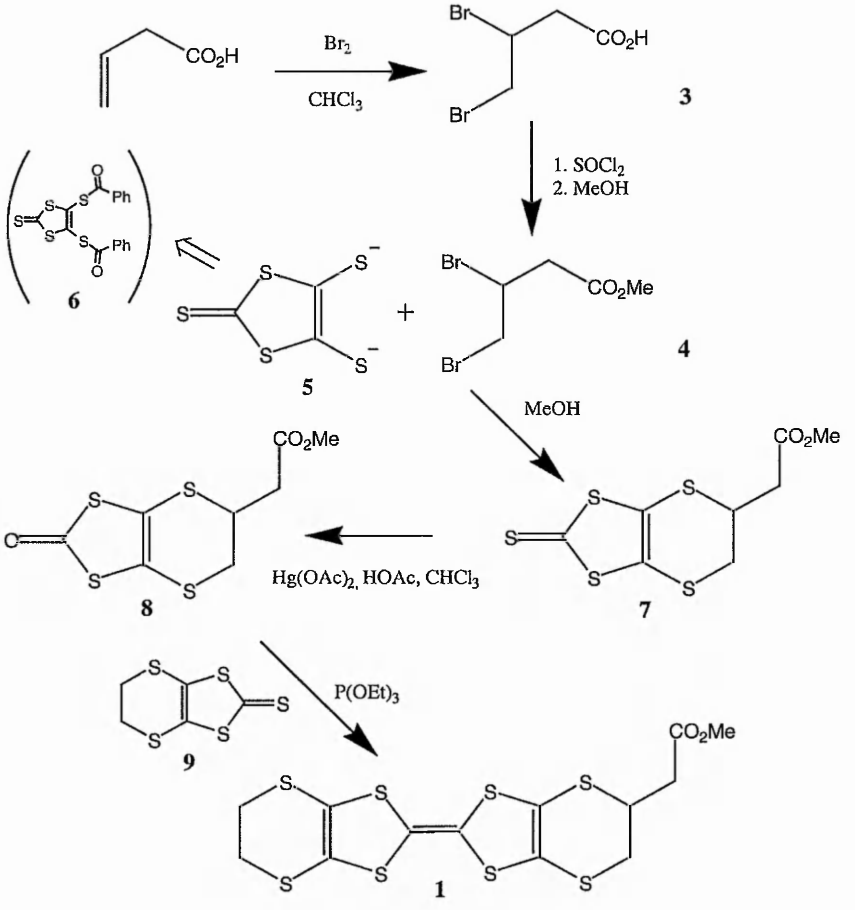
Investigations into the synthesis of both racemic and enantiomeric forms of the ET-ethanoate **1** were carried out successfully. The enantiomeric form and the racemate could be used as the basis of investigation into conductivity in a chiral environment, an area where very little research effort has taken place. However, the amide derivatives were finally prepared by installation of the amide functionality *before* formation of the ET unit by the coupling reaction in triethyl phosphite. The preparation of *trans*- ET-bis(ethanoate) **16** is also discussed; the compound offers potential for further derivatisation of the ester moieties to functionalities capable of taking part in intermolecular hydrogen bonding interactions.


16

2. Synthesis of ET- ethanoate esters.

The racemic form of methyl ET-ethanoate **1** was obtained through a five- step synthesis. The reactions were clean and efficient and chromatography was only required at the final step. This makes this a readily accessible molecule for the organic materials community.



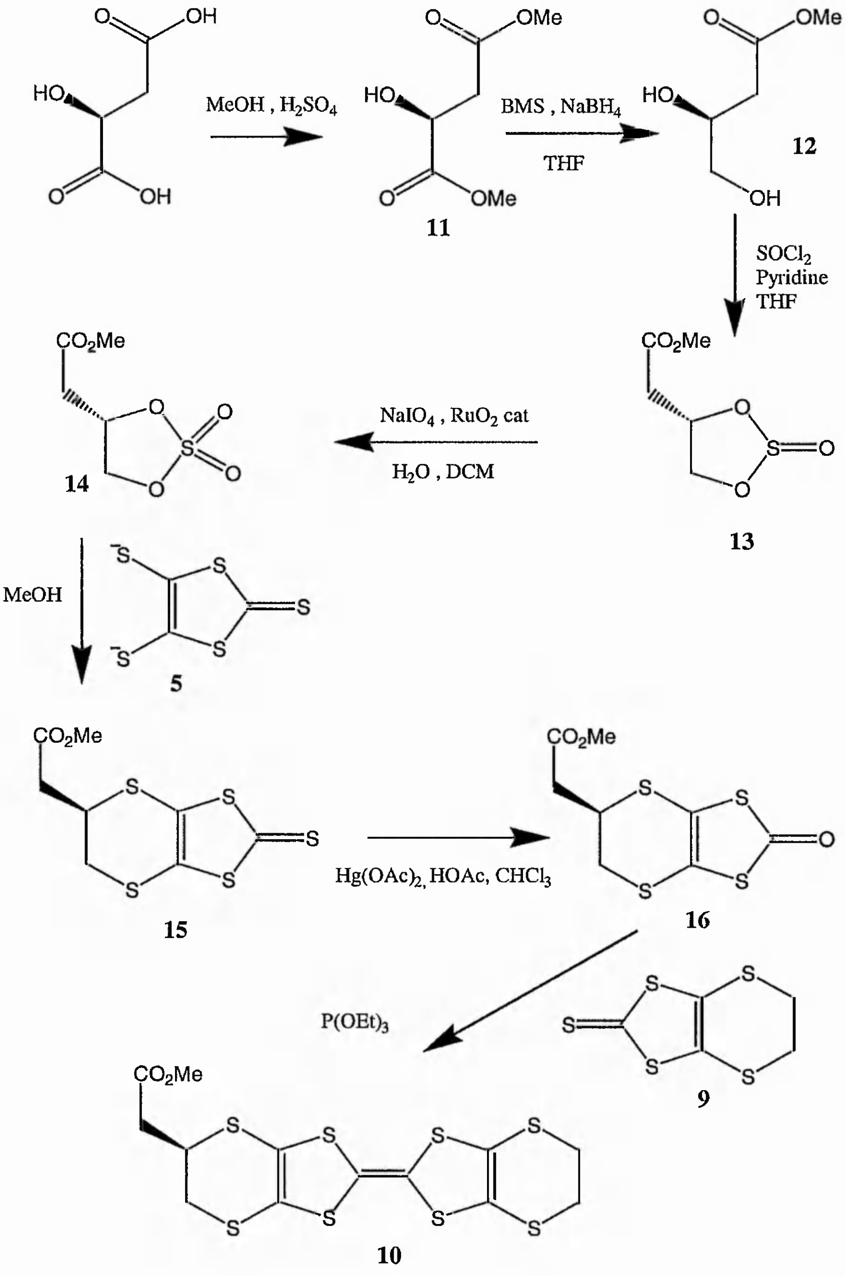
Scheme 1. Synthesis of compound **1**.

The synthetic route towards **1** began with the inexpensive starting material, vinylacetic acid. Treatment of a solution of vinylacetic acid in chloroform with 1eq. of bromine[4] and stirring overnight led to the dibromo compound **3** being obtained as a pale brown oil in 96 % yield. ^{13}C NMR for **3** showed three sp^3 carbon atoms at δ: 43.8, δ: 41.3 and δ: 35.0. Infrared spectroscopy indicated the carboxylic acid absorptions at 3032 cm^{-1} and 1715 cm $^{-1}$.

Conversion of the dibromoacid **3** to its acid chloride by treatment with thionyl chloride at reflux, followed by the immediate reaction of the crude acid chloride with methanol at 0°C, then refluxing for 1h. afforded the dibromoester **4** as an orange oil in 92 % yield.[4] The methyl group of **4** was present in the ^{1}H NMR at δ: 3.65 as a singlet and at δ: 52.0 in the ^{13}C NMR. Infrared spectroscopy showed the carbonyl absorption at 1740 cm $^{-1}$.

Overnight stirring of **4** with the disodium salt of dithiolate **5** led to the precipitation of thione **7** as a bright yellow solid in 72 % yield. The thione shift was present in the ^{13}C NMR at δ: 207.7 and the ester carbonyl observed at δ: 170.4. Sp^2 carbons were noted at δ: 122.7 and δ: 121.4. Infrared spectroscopy showed the carbonyl absorption at 1730 cm^{-1} and the thione stretch at 1061 cm $^{-1}$. Conversion of the exocyclic sulfur atom for oxygen in **7** was achieved by employing mercuric acetate in chloroform and acetic acid to furnish **8** as a brown oil in 83 % yield. ^{13}C NMR confirmed the presence of S_2C=O, the shift noted at δ: 188.4. The sidechain carbonyl was observed at δ: 170.4. Infrared spectroscopy showed the presence of two carbonyl functionalities, S_2C=O being noted at 1675 cm $^{-1}$ and the C=O at 1735 cm $^{-1}$.

Cross coupling of equimolar amounts of oxo compound **8** with unsubstituted thione **9** in triethyl phosphite at 90°C for 5h. followed by chromatography to remove ET and a mixture of disubstituted isomers afforded **1** as a bright orange solid in 42 % yield. The ^{1}H NMR spectrum of **1** showed a four hydrogen singlet at δ: 3.29, corresponding to 5'- & 6'- H_2, and the CH_2CHCCH_2 system at the other end of the molecule is described by a multiplet at δ: 4.03 which integrates for one hydrogen and is assigned as 5- *H*, and the two double doublets at δ: 3.33 and 3.14 which correspond to the two protons α. to the carbonyl function. These couple to each other with a *J* value of 13.2 Hz, and to 5- *H* with couplings of 5.6 and 3.1 Hz respectively. A doublet integrating for 2 hydrogens at δ: 2.84 with a *J* value of 6.9 Hz correspond to the two protons on 6- *C*. ^{13}C NMR indicated the carbonyl shift at δ: 170.8 and showed five different sp^2 carbon environments at δ: 113.8, δ: 113.5, δ: 112.7, δ: 112.0 and δ: 111.4. Infrared spectroscopy indicated the carbonyl absorption at 1730 cm $^{-1}$.



Scheme 2. Synthesis of compound **10**.

The enantiomeric form of methyl ET- ethanoate **10** was obtained through a seven step synthesis. The synthetic scheme employed cyclic sulfate ester chemistry, already utilized by Dunitz and Wallis in the formation of the chiral tetramethyl derivative.[5] The synthesis is more demanding than that used for the racemic alternative **1** but does lead to an enantiomerically pure compound. Future work will investigate the influence of chirality on the conductivity of radical cation salts.

The synthesis began from a molecule of known stereochemistry, namely *L*-malic acid. Refluxing a solution of *L*- malic acid overnight in methanol with a few drops of acid catalyst afforded the diester derivative **11** as a pale yellow oil in 72 % yield. ^{1}H NMR of **10** shows two singlets at δ: 3.63 and δ: 3.54 corresponding to the methyl functions. ^{13}C NMR shows the shifts of the two carbonyl functions at δ: 173.4 and δ: 170.7. Infrared spectroscopy indicates the hydroxy absorption at 3491 cm^{-1} and the carbonyl absorption at 1733 cm^{-1}.

The chemoselective reduction of the ester functionality of **11** directed by the adjacent hydroxy function was achieved by the application of borane dimethyl sulfide reagent (1eq.) and catalytic $NaBH_4$.[6] The reaction was worked up by the addition of tosic acid and after chromatography **12** was obtained as a pale yellow oil in 77 % yield. Only one singlet is present in the ^{1}H NMR of **12** at δ: 3.48 indicating reduction of one of the ester functions. One carbonyl function is present in the ^{13}C NMR spectrum at δ: 172.2. Infrared spectroscopy indicates a strong absorption due to the hydroxy functions at 3389 cm^{-1}. The carbonyl absorption is observed at 1732 cm^{-1}.

A solution of **12** in THF was treated with freshly distilled thionyl chloride and pyridine at 0°C to obtain the cyclic sulfite ester **13** as a pale yellow oil in 98 % yield. ^{1}H NMR of **13** indicates the product is a mixture of a major and a minor diastereomer, the S=O bond having two configurations relative to the CH_2CO_2Me substituent. Integration of the peaks suggests the ratio of the isomers is around 3:1, but the ratio varies between different experiments. The resonances due to 5'- H_α & H_β and 2- H_α & H_β of the major isomer all appear in the spectrum as double doublets. Analysis of the spectrum in detail indicates that each of these splitting patterns has a 'partner', the same splitting pattern due to the minor isomer. In total, the spectrum shows eight double doublets. 4'- H appears as a multiplet at the same position in the spectrum for both major and minor isomers at δ: 5.18. Every shift in the ^{13}C NMR spectrum has a 'shadow' due to the minor isomer.

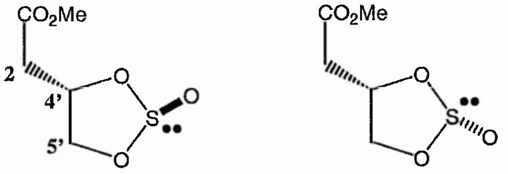


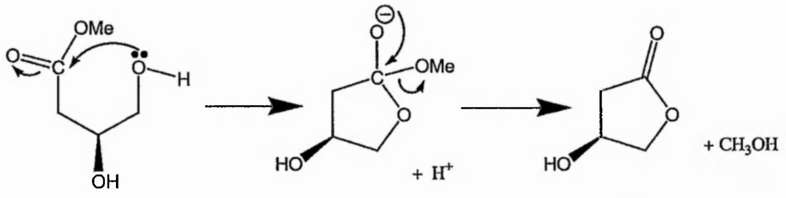
Figure 2. Sulfite isomers.

Further oxidation to the cyclic sulfate ester **14** was carried out by reaction of **13** with $NaIO_4$ and catalytic RuO_2 in a two phase system (DCM/ water). Stirring was continued until an apple-green appearance had been taken on by the contents of the flask. The reaction was worked up to afford **14** as an orange oil in 94 % yield. The ^{1}H NMR of **13** is much easier to assign due to only one isomer being possible. ^{13}C NMR indicates the positions of the sp^3 carbon atoms at δ: 77.9 (4'- *C*), 72.5 (5'- *C*) and 36.5 (2- *C*).

Treatment of cyclic sulfite ester **14** with the disodium salt of dithiolate **5** in methanol under nitrogen overnight, followed by removal of the solvent and refluxing the residue in THF for 5h. gave a brown/ black crude product. This was subjected to Kuglerohr distillation to remove methyl benzoate, a by-product of the reaction. Subsequent chromatography afforded the thione **15** as a yellow oil in 36 % yield. Spectral data for **15** is the same as for the racemic thione **7**, but the specific rotation [α] was + 182.67 for the Na D line.

The exocyclic sulfur atom of **15** was replaced with oxygen by reaction of **15** with mercuric acetate in chloroform and acetic acid. The oxo compound **16** was a brown oil and obtained in 86 % yield. Cross coupling of **16** with thione **9** in triethyl phosphite at 90°C for 5h. followed by chromatography to separate desired compound from ET and a mixture of isomeric disubstituted ET's afforded **10** as a bright orange solid in 47 % yield.

The synthesis of the enantiomeric ET-CH_2 ester **10** is essentially trouble free but care has to be taken with the second step. The diol **12** can undergo intramolecular cyclisation to give structure **12a**, which can be separated from **12** if chromatography is efficient. Fractions from a column containing both **12** and cyclic structure **12a** can be treated in a solution of methanol with tosic acid as catalyst to ring open the cyclic structure and obtain **12**.



12 12a

Figure 3. Mechanism of cyclisation.

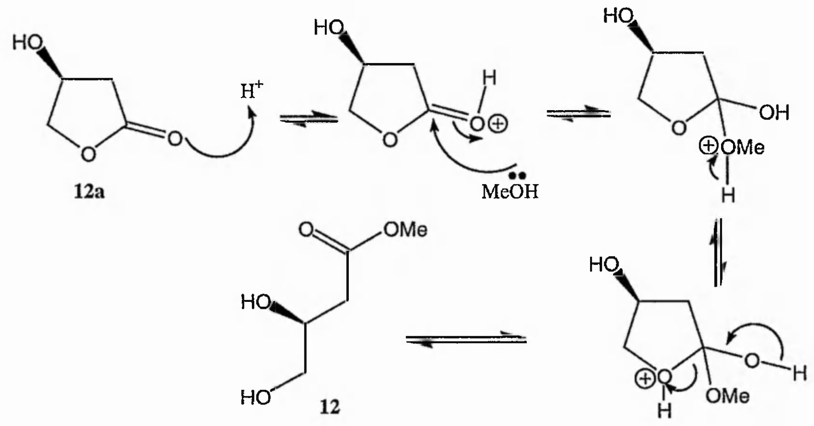
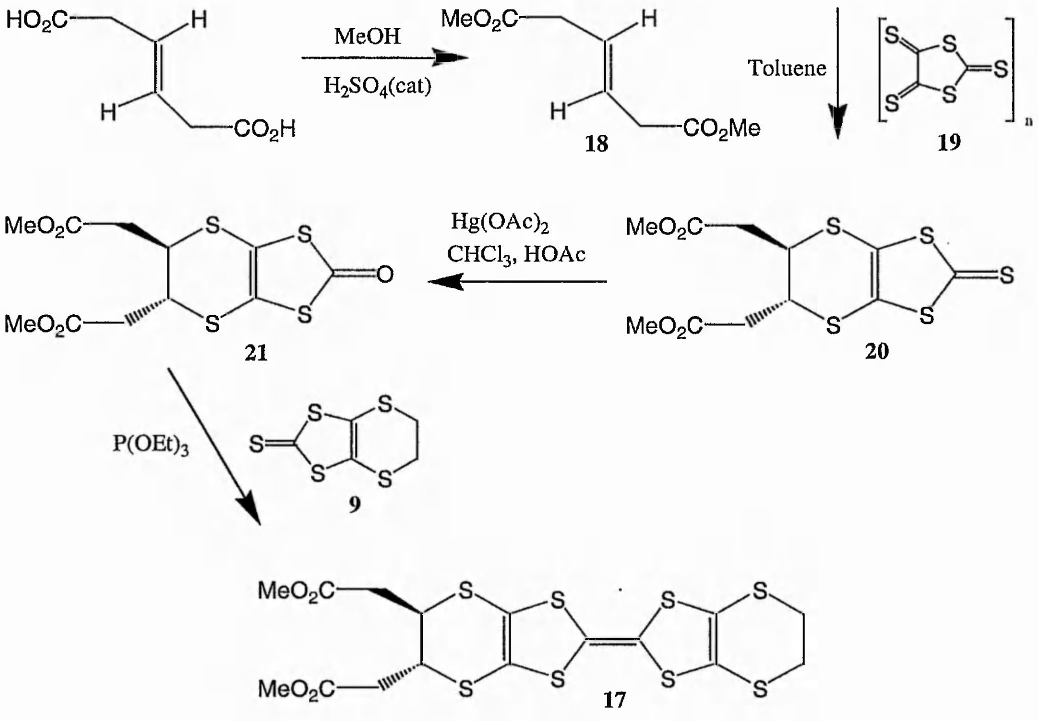


Figure 4. Retrieving the diol 12.

The synthesis of the ET derivative with two, trans oriented CH_2CO_2Me side chains, **17** was achieved in four synthetic steps from commercially available *trans*-hydromuconic acid. **17** offers potential for future derivatisation of the ester moieties to functions capable of taking part in intermolecular hydrogen bonding interactions.



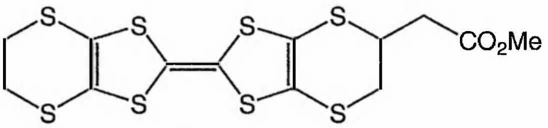
Scheme 3. Synthesis of compound **17**.

Trans- hydromuconic acid was converted to its diester **18** by reflux overnight in methanol with an acid catalyst. **18** was obtained as a pale yellow oil in 78 % yield. 2+4 Cycloaddition of **18** with trithione **19** in refluxing toluene for 5h. followed by collection of the precipitate and purification by chromatography afforded thione **20** as an orange solid in 55 % yield. ^{1}H NMR showed two multiplets at δ: 3.82 and 2.86 corresponding to 5'-, 6'- H and 2 x CH_2CO respectively. ^{13}C NMR indicated the thione shift at δ: 206.6 and the carbonyl shift at δ: 170.1. Sp^2 carbons were found at δ: 118.7. For most related thiones the sp^2 carbons are usually found between δ: 120.0 and δ: 125.0. Conversion of **20** to its oxo derivative **21** by treatment with mercuric acetate in chloroform and acetic acid furnished **21** as an orange oil in 92 % yield. ^{13}C NMR indicated the presence of $S_2C{=}O$ at δ: 187.7.

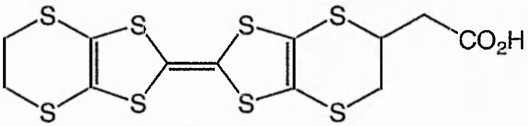
Cross coupling of **21** with 1.5 equivalents of unsubstituted thione **9** in triethyl phosphite at 90°C for 5h. followed by chromatography to remove ET and a mixture of disubstituted ET's furnished **17** as a bright orange solid in 29 % yield. Analysis of the ^{1}H NMR spectrum of **17** indicated two singlets, the first at δ: 3.65 corresponding to the two ester methyls and the second at δ: 3.23 assigned to the unsubstituted ethylene bridge. Two multiplets at δ: 3.70 and 2.75 corresponded to 5'-, 6'- H and 2 x CH_2CO respectively. Four sp^2 carbon environments were observed in the ^{13}C NMR spectrum, these being noted at δ: 113.8, 112.0, 110.4 and 109.6. The yield of the coupling is disappointing; the self- coupling of **21** in 20 % yield being responsible for this. Future work to prepare **17** could involve the cross coupling of substituted thione **20** with unsubstituted oxo compound **23**, thus restricting the formation of the tetra-substituted ET derivative.

3. Synthesis of ET- ethanamides.

It was initially envisaged that the synthetic route towards incorporating amide functionalities onto the ET framework would be through the hydrolysis of ester compound **1** to the carboxylic acid **2**, followed by known coupling routes of acids and amines to produce amides, such as the DCC coupling used in the formation of peptides.[3]



1



2

An investigation into the hydrolysis of **1** was undertaken. Hydrolysis of the ET-ethanoate **1** using bases such as NaOH or KOH was carried out. On workup of the reactions, NMR analysis could not identify the desired product. After further investigation, treatment of **1** by refluxing in aqueous THF and methanol in the presence of $KHCO_3$ led to the formation of the potassium salt of the carboxylic acid. Collecting the salt in the aqueous layer and acidifying with dilute HCl precipitated the acid **2** as a 'slimy' brown solid. The solid was very fine and was collected by gravity filtration before drying in a heated vacuum oven. Analysis of the product by NMR and infrared spectroscopy confirmed its identity.

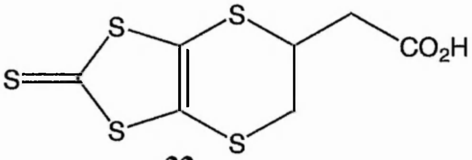
Attempted DCC couplings of **2** with simple amines such as ethylamine failed to give desired products. The attempted conversion of **2** to its acid chloride by reaction with thionyl chloride resulted in the solution turning a dark ink-blue in colour as soon as the two reagents were in contact with one another, indicating the possible oxidation of the ET system. Direct substitutions of ester **1** with amines such as ammonia were attempted. Stirring of **1** in DCM with a solution of ammonia in methanol for three days resulted in no new product being formed.

Reaction of **1** in THF with a solution of hydrazine in THF did however afford an ET-hydrazide. Upon addition of the hydrazine solution a precipitate formed rapidly. The reaction mixture was left to stir overnight at room temperature under nitrogen. Overnight the precipitate dissolved. Hexane was added and the product reprecipitated. The bright orange solid was collected by filtration. Tlc analysis (SiO_2/ EtOAc) showed one spot. NMR analysis indicated the hydrazide had indeed been formed. After leaving the sample on the bench for a few days it was observed that the bright orange colouration had been lost and the solid had turned orange-brown. Tlc analysis (SiO_2/ EtOAc) showed three spots indicating degradation of the product.

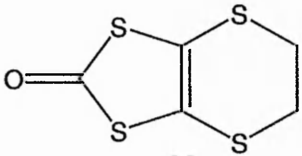
Following these setbacks it was decided to introduce the amide functionalities at an earlier stage in the reaction pathway. Introduction of the amide at the start of the synthesis proved impractical. Thus, direct reaction of amines with vinyl acetic acid or 3,4-dibromopropanoic acid **3** were unsuccessful, as was reaction of the acid chloride of **3** with ethylamine.

Reaction of vinylacetic acid with thionyl chloride and heating for 2h. to obtain the acid chloride resulted in an ink-red colouration being taken on by the reaction mixture. The reaction was abandoned. The intention was to react the acid chloride with amines to produce the desired amides by substitution. A 2+4 cycloaddition with trithione **19** would result in thiones being obtained, and from this, full ET derivatives would have been synthesised.

The alternative was to prepare the thione with -CH_2CO_2H side chain, **22,** and then derivatise the carboxylic acid group. This indeed proved a successful strategy.

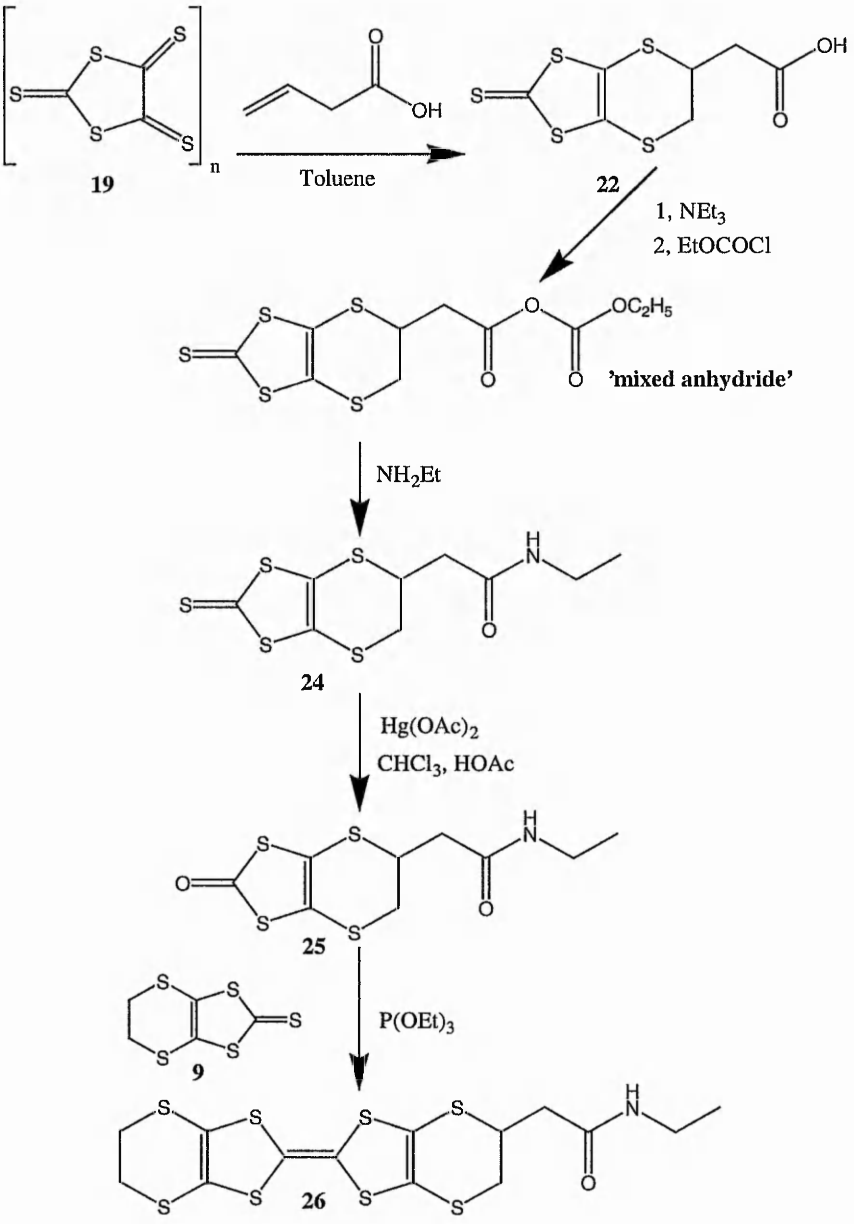


22



23

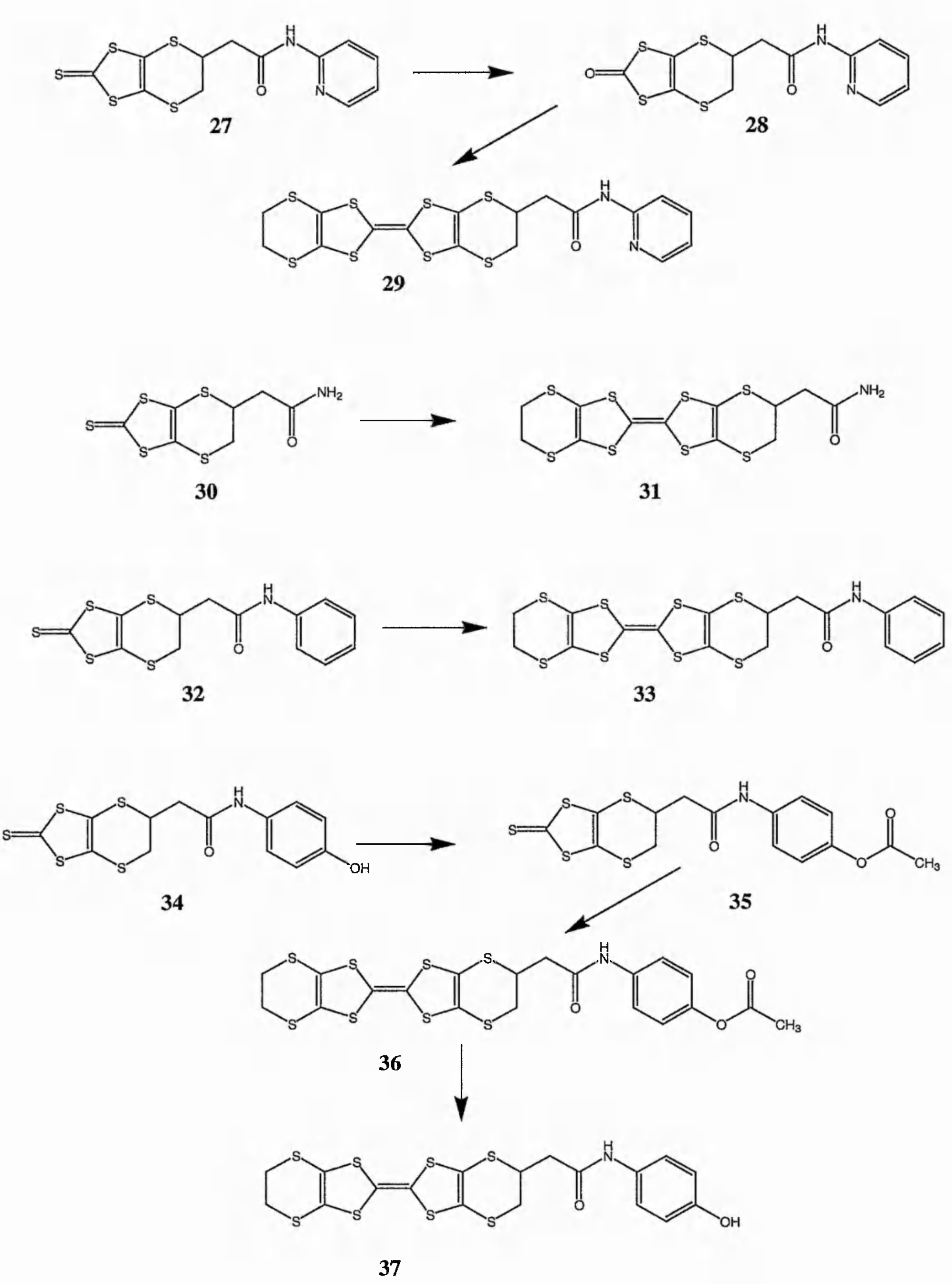
A 2+4 cycloaddition beween vinyl acetic acid and trithione **19** carried out in toluene at an oil bath temperature of 130°C, followed by chromatography afforded **22** as a brown solid in low yield. However, refining the workup procedure in subsequent reactions led to **22** being obtained as a brown solid in 56 % yield. Cross coupling of **22** with oxo compound **23** in triethyl phosphite at 90°C to obtain ET-CH_2CO_2H **2** was unsuccessful. On a positive note however, a clean efficient route had been identified to furnish the acid thione **22** in acceptable yield. ^{13}C NMR of **22** showed the thione shift at δ: 209.7 and the carbonyl shift at δ: 173.4. Infrared spectroscopy clearly showed the carboxylic acid (3448 and 1694 cm^{-1}) and thione groups (1066cm^{-1}). The alternative approach to **22** by reaction of 3,4-dibromopropanoic acid **3** and the disodium salt of dithiolate **5** proved unsuccessful.



Scheme 4. Formation of **26** using mixed anhydride synthetic methodology.

The amides were prepared from the acid thione **22** using mixed anhydride chemistry. To a solution of the acid thione **22** in THF under nitrogen at 0°C was added 1eq. of triethylamine, followed by 1eq. of ethyl chloroformate to obtain the mixed anhydride. Treatment with 1eq. of ethylamine followed by stirring overnight at room temperature yielded a mixture of compounds by tlc analysis. Chromatography of the crude mixture afforded the amide **24** as a yellow solid. Refining the experimental procedure in subsequent reactions led to **24** being obtained in 49 % yield. The amide group was evident in the ^{13}C NMR (δ: 168.3) and infrared spectra (1639 cm^{-1}). Reaction of **24** with mercuric acetate in chloroform and acetic acid afforded the oxo derivative **25** as a pale brown solid in 87 % yield. Cross coupling of **25** with 1.5 equivalents of thione **9** in triethyl phosphite at an oil bath temperature of 90°C, followed by chromatography to remove ET and a mixture of disubstituted ET's, furnished **26** as a pale orange solid in 23 % yield.

Using the same synthetic methodology as used above to obtain **26**, but changing the amine used in the reaction, a series of ET- ethanamides have been produced. Thus, amides **26** and **33** contain one H- bond donor and one H- bond acceptor. It could be expected that H- bonding in the radical cation salts might occur only between donors. In contrast, the amide **31** has two H- bond donors and just one H- bond acceptor, thus one donor is available for interaction with the anion. The same idea lies behind the synthesis of **37**, where the phenolic OH may interact with the anion in a radical cation salt. Amide **29** was prepared since it offers for the first time, a metal binding ligand attached to an ET system. The latter would be interesting for introducing magnetic metal ions into radical cation salts to produce materials with both electronic and magnetic properties.



Scheme 5. Synthesis of compounds **29, 31, 33** and **37**.

ET- ethanamides **26** and **29** were obtained by coupling of oxo derivatives **25** and **28** with thione **9**, whereas **31**, **33** and **36** were obtained by coupling of the thiones **30**, **32** and **35** with oxo compound **23**. The synthesis of **36** required the hydroxy group of the thione **34** to be protected as an acetate to give **35** before the cross coupling reaction. Removal of the protecting group to furnish final product **37** was achieved with 20 % HCl in THF.

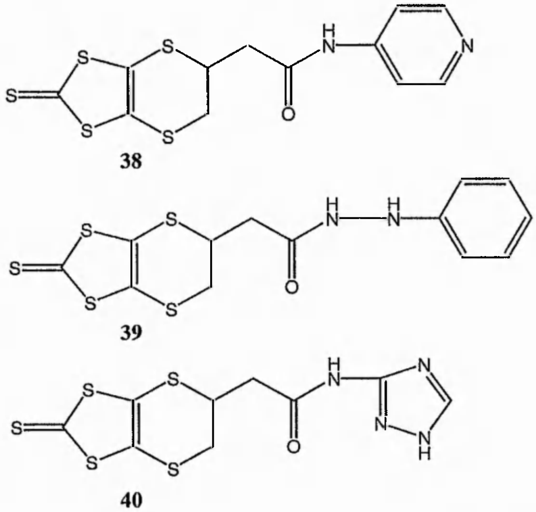
Thione **27** was obtained by reaction of acid **22** with 2- aminopyridine using mixed anhydride chemistry. Reaction of **27** with mercuric acetate in chloroform and acetic acid afforded the oxo derivative **28** as a pale brown solid in 69 % yield. Cross coupling of **28** with thione **9** in triethyl phosphite at an oil bath temperature of 90°C, followed by chromatography to remove ET and a mixture of disubstituted ET's furnished **29** as an orange solid in 36 % yield. ^{1}H NMR of **29** showed the four pyridine protons at δ: 8.27 (6''- H), δ: 8.23 (3''- H), δ: 8.18 (4''- H) and δ: 7.04 (5''- H). ^{13}C NMR indicated four sp^2 carbon environments for the ET unit between δ: 113.9 and δ: 112.1, and the sp^3 carbon resonances at δ: 42.2 (5– *C*H_2), δ: 37.9 (5- *C*), δ: 35.2 (6- *C*) and δ: 30.2 (5'-, 6'- *C*).

Thione **30** was obtained by reaction of acid **22** with a 1,4-dioxane solution of ammonia, using mixed anhydride chemistry. Cross coupling of **30** with oxo compound **23** in triethyl phosphite at an oil bath temperature of 90°C, followed by chromatography to remove ET and a mixture of disubstituted ET's furnished **31** as a red/ orange solid in 44 % yield. A broad singlet was observed in the ^{1}H NMR spectrum of **31** at δ: 6.04 and was assigned as N-*H*. The singlet at δ: 2.60 and integrating for four hydrogens was assigned as 5'-, 6'- H_2. ^{13}C NMR of **31** indicated three sp^2 environments, these being observed at δ: 112.4, δ: 111.7 and δ: 110.4. Infrared spectroscopy indicated the N-H absorptions at 3379 cm^{-1} and 3180 cm^{-1} and the carbonyl absorption at 1655 cm $^{-1}$.

Thione **32** was obtained by reaction of acid **22** with aniline using mixed anhydride chemistry. Cross coupling of **32** with oxo compound **23** in triethyl phosphite at an oil bath temperature of 90°C, followed by chromatography to remove ET and a mixture of disubstituted ET's furnished **33** as a pink/ orange solid in 34 % yield. Evidence for **33** was given by the ^{1}H NMR spectrum. A singlet was observed corresponding to 5'-, 6'- H_2 at δ: 3.32. Aromatic protons were present between δ: 7.57 and δ: 7.04. ^{13}C NMR indicated the carbonyl shift at δ: 167.7. Infrared spectroscopy showed an N-H absorption at 3049 cm^{-1} and the carbonyl absorption at 1654 cm^{-1}.

Thione **34** was obtained by reaction of acid **22** with 4- aminophenol using mixed anhydride chemistry. Protection of the hydroxy function of **34** as an acetate was achieved by reaction of **34** with acetic anhydride in pyridine to furnish **35**. Cross coupling of **35** with oxo compound **23** in triethyl phosphite at an oil bath temperature of 90°C, followed by chromatography to remove ET and a mixture of disubstituted ET's furnished **36** as a pink solid. Deprotection of **36** using THF and 20% HCl solution with stirring under N_2 for 48h. afforded **37** as an orange/ brown solid in 65 % yield. ^{1}H NMR indicates the amide and hydroxy protons at δ: 9.84 and δ: 9.18 respectively. The aryl protons were observed as two doublets at δ: 7.32 and δ: 6.69. ^{13}C NMR indicated the positions of the sp^3 carbon atoms at δ: 39.4 (5- *C*), 34.3 (6- *C*) and 29.5 (5'-, 6'- *C*).

Thiones **38**, **39** and **40** were also prepared using the mixed anhydride methodology but failed to undergo the cross coupling reaction.



38

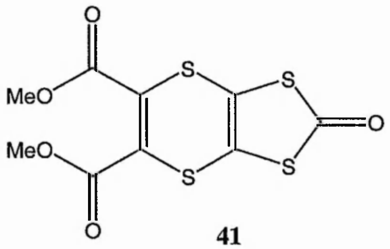
39

40

Figure 5. Thiones that failed to give cross- coupled materials.

The thiones structures are supported by their spectroscopic data. The phosphite reagent may be substituting the N- linked substituent at the heterocycle in **38** and **40**, and breaking the weak N,N bond in **39**. Future work here should examine whether the corresponding oxo compounds, which in general couple more rapidly than thiones, can be be used in the coupling reactions. Otherwise, these particular amides will have to be made from ET- ethanoic acid.

An attempt was made to determine whether it might be possible to build an ET-carboxamide. Although it was known that diester derivatives **41** and **42** did fail self-couple in triethyl phosphite[1,2], it was considered worth testing that just one, slightly less electron attracting group, might not divert the reaction to the Arbusov product **45**.



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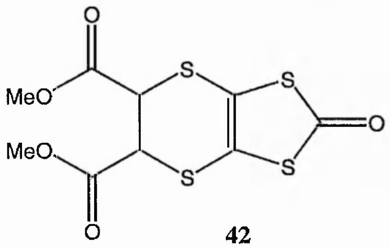

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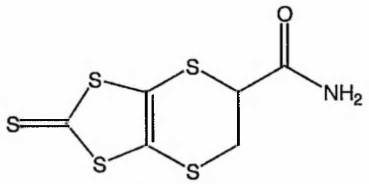

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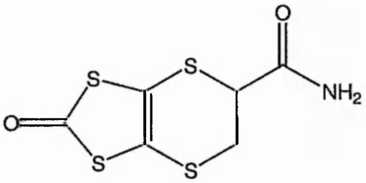
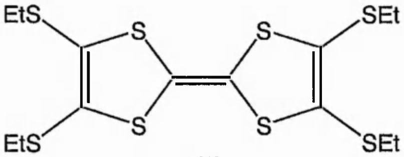


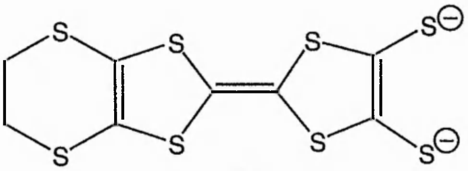
44

Reaction of acrylamide with trithione **19** in toluene at 130°C for 5h. followed by cooling to room temperature precipitated a yellow-green solid. Kuglerohr distillation to remove excess acrylamide gave thione **43**. ^{1}H NMR showed two broad N-H shifts at δ: 7.80 and δ: 7.55. 5- *C* and 6- *C* were observed at δ: 47.4 and δ: 32.7 respectively. ^{13}C NMR showed the thione shift at δ: 207.9 and the carbonyl resonance at δ: 168.7. Converting **43** to its oxo derivative **44** was achieved by treatment of **43** with mercuric acetate in chloroform and acetic acid. **44** was obtained as a beige solid. ^{1}H NMR showed two broad N-H shifts at δ: 7.79 and δ: 7.54. ^{13}C NMR showed the S_2C=O shift at δ: 188.5 and the NH_2C=O resonance at δ: 168.9. However, the attempted cross coupling of **44** with thione **9** in triethyl phosphite at 90°C for 5h. resulted in the Arbusov product **45** being obtained.



45

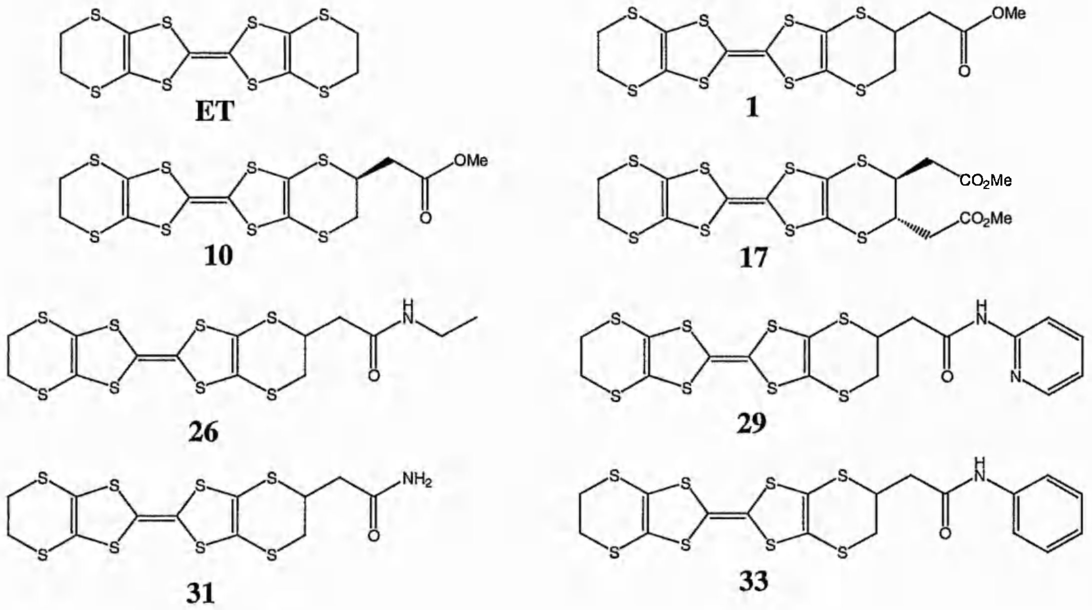
Synthesis of the ET- methanamide might be envisaged by reaction of dithiolate **46** with ethyl 2, 3- dibromopropionoate, followed by conversion of the ester to amide. However, preliminary studies (chapter 5) on the above reaction were unsuccessful.



46

4. Cyclic voltammetry data for the novel ET- ethanoates and – ethanamides.

The solution redox chemistry of the novel ET derivatives **1**, **10**, **17**, **26**, **29**, **31** and **33** were studied by cyclic voltammetry (cv) and compared to ET, which was also run. Each donor shows two, single-electron, reversible redox waves over a number of scan rates (50, 100, 200, 500 mV) at similar potentials for ET; the oxidation potentials of the novel donors are not affected by the electron withdrawing nature of the ester or amide functions. The cyclic voltammogram of **26** shown below is typical of the plots observed. Table 1 gives data measured in dichloromethane containing 0.1M tetrabutylammonium hexafluorophosphate under nitrogen, with a scan rate of 100mV s^{-1}, quoted relative to Ag/AgCl.



ET **1**

10 **17**

26 **29**

31 **33**

Figure 6. The novel ET esters and ethanamides.

Table 1. Oxidation potentials (V, relative to Ag/AgCl electrode)

	$E_1^{1/2}$	$E_2^{1/2}$
ET	0.48	0.89
1	0.50	0.91
10	0.50	0.91
17	0.52	0.94
26	0.48	0.88
29	0.48	0.89
31	0.48	0.88
33	0.48	0.88

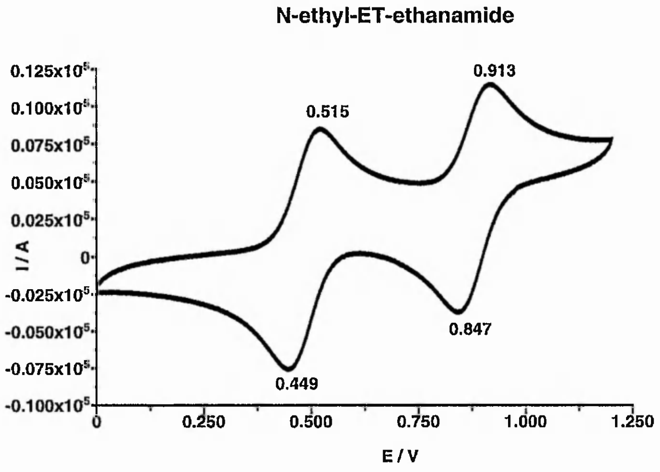


Figure 7. Cyclic voltammogram of N- ethyl- ET- ethanamide, **26**, representative of those in Table 1.

5. Formation of radical cation salts of 26 and 29.

Investigations into the formation of radical salts of the novel ET- amides have begun. Both **26** and **29** were used with the tetrabutylammonium (TBA) salts of PF_6^-, BF_4^-, ClO_4^- and Cl^-, to produce black micro- crystalline products. The conductivities of three of these salts have been measured, each being a semiconductor at 300K. The room- temperature conductivities of (**26**)ClO_4, (**29**)ClO_4 and (**29**)BF_4 are 1.8, 4.29 and 7.35 x 10^{-3} Scm^{-1} respectively. At present no other physical data is present for these or any other ET- amide salts.

(**26**)ClO_4 produced large plate- like crystals which appeared to be suitable for X-ray crystallography. Crystals of (**26**)ClO_4 were sent to the EPSRC service in Southampton. On analysis however, the crystal had smeared spots in one direction, and as such a crystal structure could not be obtained. The formation of large crystals is however hope for the future, and further work with these novel ET- amides to produce radical cation salts will continue.

6. Experimental.

3, 4- Dibromobutanoic acid, 3[4]

To a stirred solution of vinylacetic acid (5.0g, 58.1mmol) in chloroform (30ml) maintained at 0°C was added dropwise, a solution of bromine (3.0ml, 58.1mmol) in chloroform (20ml). The resultant mixture was left to stir overnight. The solution was washed with aqueous sodium thiosulfate solution (2 x 10ml) and with water (2 x 10ml), dried over $MgSO_4$, and the solvent removed *in vacuo* to afford the product **3** as a pale brown oil (13.5g, 96 %); ^1H NMR δ: 4.45 (1H, m, 3- *H*), 3.89 (1H, dd, J = 10.3, 4.5 Hz, 4- CH_α), 3.69 (1H, t, J = 10.3 Hz, 4- CH_β), 3.41 (1H, dd, J = 17.2, 3.7 Hz, 2- CH_α), 2.90 (1H, dd, J = 17.2, 9.2 Hz, 2- CH_β); ^{13}C NMR δ: 176.3 (*C*=O), 43.8 (2- *C*), 41.3 (3- *C*), 35.0 (4- *C*); ν_{max}/cm^{-1} (thin film) 3032 (OH), 1715 (C=O), 1433, 1305, 1223, 1153, 937, 839.

Methyl 3,4-dibromobutanoate, 4[4]

A solution of **3** (7.8g, 31.5mmol) in thionyl chloride (25ml) was heated to reflux with stirring for 2 h. Excess thionyl chloride was removed by distillation *in vacuo*. Methanol (80ml) was added dropwise to the residue at 0°C. After the addition was complete the mixture was heated to reflux for 2h. The solvent was removed under reduced pressure to afford the product **4** as an orange oil (7.6g, 92 %); ^1H NMR δ: 4.42 (1H, m, 3- *H*), 3.83 (1H, dd, J = 10.4, 4.2 Hz, 4- CH_α), 3.65 (1H, m, 4- CH_β), 3.65 (3H, s, OCH_3), 3.24 (1H, dd, J = 16.8, 4.0 Hz, 2- CH_α), 2.79 (1H, dd, J = 16.8, 9.1 Hz, 2- CH_β); ^{13}C NMR δ: 169.8 (*C*=O), 52.0 (OCH_3), 44.7 (2- *C*), 41.1 (3- *C*), 35.3 (4- *C*); ν_{max}/cm^{-1} (thin film) 3001, 2952, 1740 (C=O), 1437, 1379, 1308, 1211, 1022, 984, 936.

Methyl (5', 6'-dihydro- 2'-thioxo-1, 3-dithiolo [4, 5-b]-1, 4- dithiin- 5'- yl) ethanoate, 7

The dibenzoylated thione **6** (22.3g, 54.8mmol) was added to a solution of sodium metal (2.8g, 120.0mmol) in dry methanol (450ml) under N_2. The reaction mix was stirred for 1h. at room temperature. A solution of dibromo compound **4** (13.8g, 53.1mmol) in dry methanol (25ml) was added to the cold (0°C) reaction mix in one portion. Stirring was continued overnight at room temperature under N_2. The precipitate was collected by filtration and washed with cold methanol. The solid was dried *in vacuo* to yield **7** as a bright yellow solid (11.3g, 72 %); m.p.101-102°C; ^{1}H NMR δ: 4.08 (1H, m, 5'- *H*), 3.73 (3H, s, OCH_3), 3.43 (1H, dd, J = 13.6, 2.8 Hz, 2- CH_α), 3.24 (1H, dd, J = 13.6, 5.7 Hz, 2- CH_β), 2.89 (2H, d, J = 7.2 Hz, 6'- H_2); ^{13}C NMR δ: 207.7 (*C*=S), 170.4 (*C*=O), 122.7, 121.4 (3a'-, 7a'- *C*), 52.3 (OCH_3), 39.3 (5-CH_2O), 38.2 (5'- *C*) 34.0 (6'- *C*); ν_{max}/cm^{-1} (thin film) 2937, 1730 (C=O), 1485, 1434, 1360, 1242, 1220, 1172, 1061 (C=S); found C, 32.4; H, 2.7 %, $C_8H_8O_2S_5$ requires C, 32.4; H, 2.7 %.

Methyl (5', 6'- dihydro- 2'- oxo-1, 3-dithiolo [4, 5- b]-1, 4- dithiin-5-yl) ethanoate, 8

To a solution of **7** (5.0g, 16.9mmol) in $CHCl_3$ (100ml) and glacial acetic acid (30ml) was added mercuric acetate (8.1g, 25.3mmol). After 2 h. stirring at room temperature the mix was filtered. The filtrate was washed consecutively with saturated $NaHCO_3$ solution (3x100ml) and H_2O (100ml), dried (Na_2SO_4) and evaporated to afford **8** as a brown oil (3.9g, 83 %); ^{1}H NMR δ: 4.08 (1H, m, 5'- *H*), 3.68 (3H, s, OCH_3), 3.44 (1H, dd, J = 13.5, 3.0 Hz, 2- CH_α), 3.20 (1H, dd, J = 13.5, 5.8 Hz, 2- CH_β), 2.88 (2H, d, J = 7.2 Hz, 6'- H_2); ^{13}C NMR δ: 188.4 (*C*=O), 170.4 (5'- CH_2C=O), 113.2, 111.9

(3a'-, 7a'- *C*), 52.1 (O*C*H$_3$), 39.9 (5- *C*H$_2$O), 39.2 (5'- *C*) 35.0 (6'- *C*); ν_{max}/cm^{-1} (thin film) 2946, 1735 (C=O), 1675 (C=O), 1625, 1435, 1362, 1297, 1242, 1221, 1172, 891; found C, 34.2; H, 2.8 %, $C_8H_8O_3S_4$ requires C, 34.3; H, 2.9 %.

Methyl ET-ethanoate, 1

A mixture of **8** (3.7g, 13.1mmol) and the thione **9** (2.9g, 13.1mmol) was heated in triethyl phosphite (35ml) to 90°C under N_2 for 5 h. to give an orange solution. Triethyl phosphite was removed by distillation *in vacuo* and the residue purified by flash chromatography (SiO_2, 1:1 cyclohexane/ DCM) to yield **1** as a bright orange solid (2.5g, 42 %); m.p.149-150°C; ^{1}H NMR δ: 4.03 (1H, m, 5- *H*), 3.73 (3H, s, OC*H*$_3$), 3.33 (1H, dd, J = 13.2, 3.1 Hz, C*H*$_\alpha$C=O), 3.29 (4H, s, 5', 6'- *H*$_2$), 3.14 (1H, dd, J = 13.2, 5.6 Hz, C*H*$_\beta$C=O), 2.84 (2H, d, J = 6.9 Hz, 6- *H*$_2$); ^{13}C NMR δ: 170.8 (*C*=O), 113.8, 113.5, 112.7, 112.0, 111.4 (sp^2- *C*), 52.1 (O*C*H$_3$), 39.4 (*C*H$_2$CO), 38.6 (5- *C*) 34.7 (6- *C*), 30.2 (5'-, 6'- *C*); ν_{max}/cm^{-1} (KBr) 2947, 1730 (C=O), 1432, 1303, 1253, 1202, 1014, 772; found C, 34.3; H, 2.6 %, $C_{13}H_{12}O_2S_8$ requires C, 34.2; H, 2.7 %.

Dimethyl *L* - malate, 11

To a solution of malic acid (10.0g, 74.6mmol in dry methanol (100ml) was added 4-5 drops of concentrated H_2SO_4. A $CaCl_2$ guard tube was fitted to the apparatus and the mixture refluxed overnight. The mixture was neutralised by the addition of solid $NaHCO_3$ at room temperature. Evaporation of the solvent under reduced pressure gave a pale yellow oil. This was taken up in DCM (200ml) and washed sequentially with water (50ml), saturated $NaHCO_3$ solution (3x50ml) and water (50ml). The organic solution was dried ($MgSO_4$) and evaporated to yield **11** as a pale yellow oil

(8.7g, 72 %); ^1H NMR δ: 4.35 (1H, dd, J = 10.9, 5.4 Hz, 2- *H*), 3.63 (3H, s, CH_3), 3.54 (3H, s, CH_3), 2.67 (2H, m, 3- H_2); ^{13}C NMR δ: 173.4(1- *C*=O), 170.7(4- *C*=O), 66.9 (2- *C*), 52.3 (4- OCH_3), 51.5 (1- OCH_3), 38.1 (3- *C*); ν_{max}/cm^{-1} (thin film) 3491(OH), 2954, 1733 (C=O), 1438, 1365, 1275, 1222, 1169, 1105, 1042, 995, $^{293}[\alpha]_D = +3.50$ (c = 1.03, $CHCl_3$).

Dimethyl *S* - 3,4- dihydroxybutanoate, 12[6]

To a solution of **11** (3.1g, 21.6mmol) in THF (30ml) was added borane-dimethylsulfide complex (2.2ml, 22.2mmol) dropwise over 5 min. Stirring was continued until the evolution of hydrogen had ceased. The reaction mix was cooled to 0°C and stirred for 10 min. before the addition of $NaBH_4$ (0.04g, 5mol%), then stirred for 1h. at room temperature. Tlc analysis (SiO_2/EtOAc, $KMnO_4$ dip) indicated no starting material was present. A solution of tosic acid (0.2g, 5mol%) in ethanol (6.0ml) was added and the mix stirred for 30 min. Removal of the solvent under reduced pressure gave a thick white oily material. To the residue was added 1:1 toluene/methanol (40ml) and the solution was concentrated under reduced pressure to give a clear yellow oil. The washing/evaporation procedure was repeated with the 1:1 mix to remove $B(OEt)_3$, followed by a final wash and concentration with toluene (40ml) to give a crude oil. This was purified by flash chromatography (SiO_2/EtOAc) to furnish **12** as a pale yellow oil (2.0g, 77 %); ^1H NMR δ: 3.89 (1H, m, 3- *H*), 3.48 (3H, s, OCH_3), 3.40 (1H, dd, J = 11.4, 3.7 Hz, 4- H_α), 3.28 (1H, dd, J = 11.4, 6.4 Hz, 4- H_β), 2.29 (2H, d, J = 6.5 Hz, 2- H_2); ^{13}C NMR δ: 172.2 (*C*=O), 68.3 (4- *C*), 65.2 (3- *C*), 51.3 (OCH_3), 37.5 (2- *C*); ν_{max}/cm^{-1} (thin film) 3389 (OH), 2955, 1732, 1439, 1287, 1171, 1042, $^{293}[\alpha]_D = -24.91$ (c = 1.06, $CHCl_3$).

Methyl (2'-oxo-1, 3, 2- dioxathiolan-4'-yl)ethanoate, 13

To a solution of diol **12** (0.8g, 6.3mmol) in THF (25ml) at 0°C was added dropwise thionyl chloride (0.5ml, 6.9mmol). The mixture was allowed to warm to room temperature and left to stir overnight. Pyridinium hydrochloride was filtered off and washed with THF (20ml). The combined washing and filtrate was evaporated under reduced pressure to give a yellow oil. This was partitioned between DCM (50ml) and water (20ml). The organic phase was collected and washed consecutively with water (20ml) and 0.5M HCl (2 x 20ml), dried (Na_2SO_4), evaporated and the crude oil purified by flash chromatography (SiO_2, 1:1 EtOAc/cyclohexane) to afford **13** as a light yellow oil (1.1g, 98 %); ^{1}H NMR **major isomer** δ: 5.18 (1H, m, 4'- *H*), 4.32 (1H, t, J = 8.9 Hz, 5'- CH_α), 4.07 (1H, dd, J = 8.9, 5.6 Hz, 5'- CH_β), 3.60 (3H, s, OCH_3), 2.72 (1H, dd, J = 16.5, 6.3 Hz, 2- CH_α), 2.54 (1H, dd, J = 16.5, 7.3 Hz, 2- CH_β); ^{1}H NMR **minor isomer** δ: 5.18 (1H, m, 4'- *H*), 4.72 (1H, dd, J = 8.9, 6.2 Hz, 5'- CH_α), 4.60 (1H, dd, J = 8.9, 6.4 Hz, 5'- CH_β), 3.60 (3H, s, OCH_3), 2.99 (1H, dd, J = 16.8, 6.4 Hz, 2- CH_α), 2.79 (1H, dd, J = 16.8, 7.2 Hz, 2- CH_β); ^{13}C NMR **major isomer** δ: 169.4(*C*=O), 76.5 (4'- C), 71.0 (5'- C) 52.1 (OCH_3), 37.2 (2- *C*); ^{13}C NMR **minor isomer** δ: 169.7 (*C*=O), 76.0 (4'- *C*), 70.7 (5'- *C*) 51.7 (OCH_3), 38.7 (2- *C*); ν_{max}/cm^{-1} (thin film) 2955, 2860, 1734 (C=O), 1281, 1212, 1123, 1070, 954, 743; HRMS (ES): Found: 198.0432 $(M+H)^+$, $C_5H_8O_5S$ requires: 198.0431 $(M+H)^+$; $^{293}[\alpha]_D$ = - 7.92 (c = 1.06g, $CHCl_3$).

Methyl *S* - (2'-dioxo-1, 3, 2- dioxathiolan-4'-yl)ethanoate, 14

To a solution of **13** (0.5g, 2.8mmol) in DCM (10ml) at 0°C was added a solution of $NaIO_4$ (1.1g, 5.1mmol) in water (10ml). RuO_2 (2-3 mg) was added as catalyst, and the stirring set to maximum to ensure full mixing of the phases. Stirring was continued at room temperature until an apple-green colouration appeared. Tlc (SiO_2, $KMnO_4$) indicated no starting material present. The organic phase was collected and isopropanol (2-3ml) was added. After 10 min. stirring $MgSO_4$ was added and the mixture stirred for a further 10 min. Filtration of the reaction mixture through Celite to remove the fine catalyst and removal of the solvent under reduced pressure furnished **14** as an orange oil (0.6g, 94 %); ^{1}H NMR δ: 5.26 (1H, m, 4'- *H*), 4.85 (1H, dd, J = 9.2, 6.2 Hz, 5'- CH_α), 4.45 (1H, dd, J = 9.2, 7.2 Hz, 5'- CH_β), 3.70 (3H, s, OCH_3), 3.03 (1H, dd, J = 17.1, 6.4 Hz, 2- CH_α), 2.84 (1H, dd, J = 17.1, 7.4 Hz, 2- CH_β); ^{13}C NMR δ: 168.4(*C*=O), 77.9 (4'- *C*), 72.5 (5'- *C*) 52.3 (OCH_3), 36.5 (2- *C*); ν_{max}/cm^{-1} (thin film) 2912, 1719 (C=O), 1402, 1378, 1243, 1189, 1051, $^{293}[\alpha]_D$ = -18.89 (c = 0.27, MeOH).

Methyl *R* - (5', 6'-dihydro- 2'-thioxo-1, 3-dithiolo [4, 5-b]-1, 4- dithiin-5'-yl) ethanoate, 15

The dibenzoylated thione **6** (1.2g, 2.9mmol) was added to a solution of sodium metal (0.1g, 6.3mmol) in dry methanol (40ml) under N_2. The reaction mix was stirred for 1 h. at room temperature. A solution of **14** (0.6g, 2.9mmol) in dry methanol (5ml) was added to the cold (0°C) reaction mix in one portion. Stirring was continued overnight at room temperature under N_2. The solvent was removed *in vacuo* and replaced with dry THF (40ml). The mixture was heated to reflux for 5h. Removal of the solvent under reduced pressure gave a brown residue. This was partitioned between DCM

(100ml) and water (50ml). The organic phase was collected, washed with water (50ml), dried ($MgSO_4$) and evaporated to yield a brown oil. The oil was subjected to Kugelrohr distillation to remove methyl benzoate, then purified by flash chromatography (SiO_2, 2:1 chloroform/cyclohexane) to furnish **15** as a yellow oil (0.3g, 36 %); ^{1}H NMR δ: 4.12 (1H, m, 5'- *H*), 3.75 (3H, s, OC*H*$_3$), 3.45 (1H, dd, J = 13.5, 2.9 Hz, 2- C*H*$_\alpha$), 3.26 (1H, dd, J = 13.5, 5.7 Hz, 2- C*H*$_\beta$), 2.92 (2H, d, J = 7.2 Hz, 6'- *H*$_2$); ^{13}C NMR δ: 207.8 (*C*=S), 170.5 (*C*=O), 122.5, 121.3 (3a'-, 7a'- *C*), 52.3 (O*C*H$_3$), 39.3 (2- *C*), 38.2 (5'- *C*), 34.0 (6'- *C*); ν_{max}/cm^{-1} (thin film) 1732 (C=O), 1486, 1437, 1408, 1361, 1296, 1242, 1220, 1173, 1061 (C=S), 1032, 979, 891, 756, $^{293}[\alpha]_D$ = + 182.67 (c = 0.15, $CHCl_3$).

Methyl - *R* - (5', 6'-dihydro- 2'-oxo-1, 3-dithiolo [4, 5-b]-1, 4- dithiin-5'-yl) ethanoate, 16

To a solution of **15** (0.2g, 0.7mmol) in $CHCl_3$ (10ml) and glacial acetic acid (3ml) was added mercuric acetate (0.3g, 1.1mmol). After 2 h. stirring at room temperature the mixture was filtered. The filtrate was washed consecutively with saturated $NaHCO_3$ solution (3x20ml) and H_2O (20ml), dried (Na_2SO_4) and evaporated to afford **16** as a brown oil (0.2g, 86 %); ^{1}H NMR δ: 4.09 (1H, m, 5'- *H*), 3.75 (3H, s, OC*H*$_3$), 3.45 (1H, dd, J = 13.4, 3.0 Hz, 2- C*H*$_\alpha$), 3.20 (1H, dd, J = 13.4, 5.8 Hz, 2- C*H*$_\beta$), 2.89 (2H, d, J = 6.9 Hz, 6'- *H*$_2$); ^{13}C NMR δ: 188.6 (S_2*C*=O), 170.5 (*C*=O), 113.3, 112.1 (3a'-, 7a'- *C*), 52.2 (O*C*H$_3$), 40.0 (2- *C*), 39.3 (5'- *C*) 35.2 (6'- *C*); ν_{max}/cm^{-1} (thin film) 2955, 1733 (C=O), 1677 (C=O), 1625, 1505, 1436, 1410, 1363, 1298, 1222, 1171, 1013, 984, 892, 764, $^{293}[\alpha]_D$ = + 104.41 (c = 0.204, $CHCl_3$).

Methyl *R* - ET-ethanoate, 10

A mixture of **16** (0.1g, 0.5mmol) and the thione **9** (0.1g, 0.6mmol) was heated in triethyl phosphite (5.0ml) to 90°C under N_2 for 5 h. to give an orange solution. Triethyl phosphite was removed by distillation *in vacuo* and the residue purified by flash chromatography (SiO_2, 1:1 cyclohexane/ DCM) to yield **10** as an orange oil (0.1g, 47 %); ^{1}H NMR δ: 4.03 (1H, m, 5- *H*), 3.71 (3H, s, OCH_3), 3.31 (1H, dd, J = 13.3, 3.1 Hz, $CH_\alpha C{=}O$), 3.28 (4H, s, 5', 6'- CH_2), 3.13 (1H, dd, J = 13.3, 5.4 Hz, $CH_\beta C{=}O$), 2.84 (2H, d, J = 7.2 Hz, 6- CH_2); ^{13}C NMR δ: 170.7 (*C*=O), 113.8, 113.5, 112.7, 112.0, 111.3 (sp^2- *C*), 52.1 (OCH_3), 39.4 (5- $CH_2(CO)$), 38.6 (5- *C*) 34.7 (6- *C*), 30.1 (5', 6'- *C*); ν_{max}/cm^{-1} (KBr) 1733 (C=O), 1434, 1408, 1359, 1290, 1220, 1170, 1006, 979, 917, 888, 773, $^{293}[\alpha]_D = +12.50$ (c = 0.16, $CHCl_3$).

Dimethyl *E*- hex-3-endioate, 18

To a solution of *trans*-hydromuconic acid (5.0g, 34.7mmol) in dry methanol (25ml) was added 4-5 drops of concentrated H_2SO_4. The solution was allowed to reflux with stirring overnight under an N_2 atmosphere. The solvent was removed under reduced pressure to give a yellow oil. The oil was taken up in DCM (30ml) and washed sequentially with water (10ml), saturated $NaHCO_3$ solution (3 x 10ml) and water (10ml) before being dried ($MgSO_4$) and concentrated under reduced pressure to yield the product **18** as a pale yellow oil (4.6g, 78 %); ^{1}H NMR δ: 5.52 (2H, t, J = 3.8, 1.9 Hz, 3-,4- *H*), 3.51 (6H, s, 2 x CH_3), 2.93 (4H, dd, J = 3.8, 1.6 Hz, 2-, 5- H_2); ^{13}C NMR δ: 171.5 (*C*=O), 125.6 (3-, 4- *C*), 51.4 (2 x CH_3) 37.3 (2-, 5- *C*).

Dimethyl *trans*- (5', 6'-dihydro- 2'-thioxo-1', 3'-dithiolo [4, 5-b]-1, 4- dithiin-5'-yl) bis ethanoate, 20

18 (4.6g, 27.0mmol) and the trithione **19** (3.5g, 18.0mmol) in toluene (350ml) were heated to 130°C for 4 h. After cooling to room temperature the reaction mixture was filtered, and the solid was washed with ethanol. Combined washings and filtrate were evaporated and the residue purified by flash chromatography (SiO_2, EtOAc) to furnish **20** as an orange solid (3.7g, 55 %); m.p. 88-89°C; ^{1}H NMR δ: 3.82 (2H, m, 5'-, 6'-*H*), 3.72 (6H, s, 2 x -OC*H*$_3$), 2.86 (4H, m, 2 x C*H*$_2$O); ^{13}C NMR δ: 206.6 (*C*=S), 170.1 (2x *C*=O), 118.7 (3a'-, 7a'- *C*), 52.0 (2 x -O*C*H$_3$), 40.5 (5', 6'- *C*), 26.6 (2 x *C*H$_2$CO); ν_{max}/cm^{-1} (KBr) 2955, 1735 (C=O), 1485, 1437, 1370, 1251, 1209, 1170, 1065 (C=S); HRMS (ES): Found: 368.9414 $(M+H)^+$, $C_{11}H_{12}O_4S_5$ requires: 368.9417 $(M+H)^+$.

Dimethyl *trans* (5', 6'-dihydro- 2'-oxo-1', 3'-dithiolo [4', 5'-b]-1', 4'- dithiin-5'-yl) bis ethanoate, 21

To a solution of **20** (2.0g, 5.5mmol) in $CHCl_3$ (30ml) and glacial acetic acid (10ml) was added mercuric acetate (2.6g, 8.2mmol). After 2 h. stirring at room temperature the mixture was filtered. The filtrate was washed consecutively with saturated $NaHCO_3$ solution (3x50ml) and H_2O (50ml), dried (Na_2SO_4) and evaporated to afford **21** as an orange oil (1.8g, 92 %); ^{1}H NMR δ: 3.80 (2H, m, 5 & 6- *H*), 3.70 (6H, s, 2x -OC*H*$_3$), 2.89 (4H, m, 2 x C*H*$_2$O); ^{13}C NMR δ: 187.7 (S$_2$*C*=O), 171.8 (CH$_2$*C*=O), 170.4 (CH$_2$*C*=O), 109.4 (3a-, 7a-*C*), 52.1 (2 x -O*C*H$_3$), 41.9 (5-, 6- *C*H$_2$), 40.7 (5-, 6-*C*); ν_{max}/cm^{-1} (thin film) 2997, 2952, 2842, 1733 (C=O), 1628, 1436, 1365, 1252, 1214, 1169, 889; HRMS (ES): Found: 369.9910 $(M+NH_4)^+$, $C_{11}H_{12}O_5S_4$ requires: 369.9911 $(M+NH_4)^+$.

Dimethyl *trans*- ET- bis (ethanoate), 17

A mixture of oxo compound **21** (1.4g, 4.0mmol) and the thione **9** (1.3g, 6.0mmol) were heated in triethyl phosphite to 90°C under N_2 for 5 h. to give an orange solution. Triethyl phosphite was removed by distillation *in vacuo* and the residue purified by flash chromatography (SiO_2, 1:1 cyclohexane/ DCM) to yield **17** as a bright orange solid (0.6g, 29 %); m.p.149-151°C; ^{1}H NMR δ: 3.70 (2H, m, 5-, 6- *H*), 3.65 (6H, s, 2 x -OCH_3), 3.23 (4H, s, 5'-, 6'- H_2), 2.75 (4H, m, 2 x CH_2CO); ^{13}C NMR δ: 170.6 (*C*=O), 113.8, 112.0, 110.4, 109.6 (sp^2- *C*), 52.1, (2 x -OCH_3), 41.0 (2 x CH_2CO), 40.8 (5-, 6- *C*), 30.1 (5'-, 6'- *C*); ν_{max}/cm^{-1} (KBr) 2943, 2908, 1733 (C=O), 1435, 1359, 1287, 1214, 1169; HRMS (ES): Found: 528.8892 (M+H)$^+$, $C_{16}H_{16}O_4S_8$ requires: 528.8893 (M+H)$^+$.

(5', 6'- Dihydro- 2'-thioxo-1, 3-dithiolo [4, 5-b]-1, 4- dithiin-5'-yl)ethanoic acid, 22

Vinylacetic acid (4.3ml, 51.0mmol) and the trithione **19** (5.0g, 25.5mmol) in toluene (500ml) were heated to 130°C for 5h. After cooling to room temperature the reaction mix was filtered through a short plug of SiO_2. The filtrate was evaporated under reduced pressure and the residue subjected to Kugelrohr distillation to remove unreacted vinylacetic acid. The product **22** was obtained as a brown solid (4.1g, 56 %); m.p.133-134°C; ^{1}H NMR (MeOH-d_4) δ: 4.07 (1H, m, 5'- *H*), 3.38 (1H, dd, J = 13.7, 3.0 Hz, CH_αCO), 3.26 (1H, dd, J = 13.7, 5.8 Hz, CH_βCO), 2.80 (2H, m, 6'- H_2); ^{13}C NMR (MeOH-d_4) δ: 209.7 (*C*=S), 173.4 (*C*=O), 125.2, 123.4 (3a'-, 7a'- *C*), 40.8 (CH_2CO), 40.8 (5' - *C*), 30.1 (6' - *C*); ν_{max}/cm^{-1} (KBr) 3448 (OH), 1694 (C=O), 1432, 1399, 1302, 1249, 1205, 1066 (C=S); HRMS (EI): Found: 281.8969, $C_7H_6O_2S_5$ requires: 281.8971.

N-Ethyl- (5’, 6’-dihydro- 2’-thioxo-1, 3-dithiolo [4, 5-b]-1, 4- dithiin-5’-yl) ethanamide, 24

To a solution of **22** (0.5g, 1.8mmol) in THF (15ml) at 0°C under N_2 was added sequentially triethylamine (0.3ml, 1.8mmol) and ethyl chloroformate (0.2ml, 1.8mmol). The mixture was stirred for 5 min. before the addition of ethylamine (2.0M solution in THF) (2.0ml, 4.0mmol), then allowed to warm to room temperature and stirred overnight under N_2. The following day the reaction mix was concentrated and the residue purified by flash chromatography (SiO_2, 1:1 EtOAc,cyclohexane) to yield **24** as a yellow solid (0.3g, 49 %); m.p.148-149°C; ^{1}H NMR δ: 5.60 (1H, br.s, N*H*), 4.20 (1H, m, 5’- *H*), 3.46 (1H, dd, J = 13.3, 2.7 Hz, CH_{α}CO), 3.29 (1H, dd, J = 13.3, 7.2 Hz, CH_{β}CO), 3.16 (2H, q, J = 7.3 Hz, NH-CH_2CH$_3$), 2.71 (2H, dd, J = 7.1, 3.1 Hz, 6’- H_2), 1.14 (3H, t, J = 7.3 Hz, NH-CH$_2$CH_3); ^{13}C NMR δ: 168.3 (*C*=O), 121.2 (3a’-, 7a’- *C*), 41.5 (NH-CH$_2$), 38.4 (*C*H$_2$CO), 34.7 (5 - *C*), 34.1 (6- *C*), 14.8 (CH$_2$*C*H$_3$); ν_{max}/cm^{-1} (KBr) 3313, 2986, 2922, 1639 (C=O), 1549, 1405, 1255, 1064 (C=S); found C, 34.6; H, 3.5; N, 4.2 %, $C_9H_{11}ONS_5$ requires C, 34.9; H, 3.6; N, 4.5 %.

N-Ethyl- (5’, 6’- dihydro- 2’- oxo- 1, 3- dithiolo [4, 5-b]-1, 4- dithiin-5’-yl) ethanamide, 25

To a solution of **24** (0.8g, 2.4mmol) in $CHCl_3$ (30ml) and glacial acetic acid (6ml) was added mercuric acetate (1.2g, 3.6mmol). After 2 h. stirring at room temperature the mix was filtered. The filtrate was washed consecutively with saturated $NaHCO_3$ solution (3x30ml) and H_2O (30ml), dried (Na_2SO_4) and evaporated to afford **25** as a pale brown solid (0.6g, 87 %); m.p.139-141°C; ^{1}H NMR δ: 5.65 (1H, br.s, N*H*), 4.20 (1H, m, 5’- *H*), 3.50 (1H, dd, J = 13.5, 2.9 Hz, CH_{α}CO), 3.31 (2H, q, J = 6.9 Hz, NH-CH_2CH$_3$), 3.21 (1H, dd, J = 13.5, 5.4 Hz, CH_{β}CO), 2.72 (2H, dd, J = 7.1, 3.6 Hz, 6’-

H_2), 1.13 (3H, t, J = 7.3 Hz, NH-CH_2CH_3); ^{13}C NMR δ: 188.7 (S_2C=O), 168.5 (CH_2C=O), 113.1, 111.6 (3a'-, 7a'- *C*), 41.5 (NH-CH_2), 40.1 (CH_2CO), 35.2 (5 - *C*), 34.6 (6- *C*), 14.8 ($NHCH_2CH_3$); ν_{max}/cm^{-1} (KBr) 3281, 3091, 2975, 2922, 1634 (C=O), 1610, 1566, 1496, 1411, 1257, 900, 668, 575; HRMS (ES): Found: 293.9748 $(M+H)^+$, $C_9H_{11}O_2NS_4$ requires: 293.9751$(M+H)^+$.

N-Ethyl-ET-ethanamide, 26

A mixture of **25** (0.6g, 2.2mmol) and the thione **9** (0.7g, 3.3mmol) was heated in triethyl phosphite (20ml) to 90°C under N_2 for 5 h. to give an orange solution. Triethyl phosphite was removed by distillation *in vacuo* and the residue purified by flash chromatography (SiO_2, 3:1 cyclohexane/ EtOAc) to yield **26** as a pale orange solid (0.2g, 23 %); m.p.170-171°C; ^1H NMR δ: 5.55 (1H, br.s, N*H*), 4.10 (1H, m, 5-*H*), 3.31 (2H, m, CH_2CO), 3.29 (4H, s, 5'-, 6'- H_2), 3.13 (2H, dd, J = 13.4, 5.0 Hz, NH-CH_2CH_3), 2.61 (2H, dd, J = 7.2, 3.3 Hz, 6- H_2), 1.13 (3H, t, J = 7.3 Hz, NH-CH_2CH_3); ^{13}C NMR δ: 168.5 (*C*=O), 113.9, 111.3 (sp^2- *C*), 41.6 (NH- CH_2), 38.5 (CH_2CO), 34.8 (5 - *C*), 34.6 (6- *C*), 30.2 (5'-, 6'- *C*), 14.8 ($NHCH_2CH_3$); ν_{max}/cm^{-1} (KBr) 3424, 3281, 2972, 2922, 1633 (C=O), 1560, 1408, 1284, 1253, 1105, 774; found C, 35.5; H, 3.2; N, 2.9 %, $C_{14}H_{15}ONS_8$ requires C, 35.8; H, 3.2; N, 3.0 %.

N- (2’’- Pyridyl)- (5’, 6’- dihydro- 2’- thioxo-1, 3-dithiolo [4, 5-b]-1, 4- dithiin-5-yl)ethanamide, 27

To a solution of **22** (1.5g, 5.3mmol) in THF (20ml) at 0°C under N_2 was added sequentially triethylamine (0.7ml, 5.3mmol) and ethyl chloroformate (0.5ml, 5.3mmol). The mix was stirred for 5 min. before the addition of a solution of 2-aminopyridine (0.5g, 5.3mmol) in THF (10ml), and then allowed to warm to room temperature and stirred overnight under N_2. The following day the reaction mix was concentrated and the residue purified by flash chromatography (SiO_2, 2:1 cyclohexane, EtOAc) to yield **27** as a brown/yellow solid (0.4g, 23 %); m.p. 170-172°C; ^{1}H NMR δ: 9.17 (1H, br.s, N*H*), 8.27 (1H, m, 6’’- *H*), 7.75 (1H, m, 3’’- *H*), 7.26 (1H, m, 4’’- *H*) 6.92 (1H, m, 5’’- *H*), 4.32 (1H, m, 5’- *H*), 3.44 (1H, dd, J = 13.4, 3.0 Hz, $CH_\alpha CO$), 3.24 (1H, dd, J = 13.4, 5.6 Hz, $CH_\beta CO$), 2.95 (2H, d, J = 7.0 Hz, 6’-H_2); ^{13}C NMR δ: 208.8 (*C*=S), 172.4 (*C*=O), 150.9, 147.5, 138.9, 120.3, 114.5 (Ar–C_5), 113.7, 112.6 (3a’-, 7a’-*C*), 42.2 (CH_2CO), 38.0 (5’- *C*), 34.1 (6’- *C*); ν_{max}/cm^{-1} (KBr) 3228, 3176, 3112, 3038, 2912, 1657 (C=O), 1574, 1542, 1435, 1303, 1061 (C=S), 982, 780; HRMS (ES): Found: 358.9475 $(M+H)^+$, $C_{12}H_{10}ON_2S_5$ requires: 358.9475 $(M+H)^+$.

N- (2’’- Pyridyl)- (5’, 6’- dihydro- 2’- oxo- 1’, 3’- dithiolo [4, 5-b]-1, 4- dithiin-5’-yl)ethanamide, 28

To a solution of **27** (0.5 g, 1.4mmol) in $CHCl_3$ (20ml) and glacial acetic acid (6ml) was added mercuric acetate (0.7g, 2.1mmol). After 2 h. stirring at room temperature the mix was filtered. The filtrate was washed consecutively with saturated $NaHCO_3$ solution (3x20ml) and H_2O (20ml), dried (Na_2SO_4) and evaporated to afford **27** as a pale brown solid (0.3g, 69 %); m.p.177-178°C; ^{1}H NMR (DMSO-d_6) δ: 10.69 (1H, br.s, N*H*), 8.36 (1H, d, J = 3.7 Hz, 6''- *H*), 8.08 (1H, d, J = 8.2 Hz, 3''- *H*), 7.78 (1H, t, J = 8.0 Hz, 4''- *H*), 7.10 (1H, m, 5''- *H*), 4.32 (1H, m, 5'- *H*), 3.58 (1H, dd, J = 13.3, 2.7 Hz, $CH_{\alpha}CO$), 3.44 (1H, dd, J = 13.3, 5.4 Hz, $CH_{\beta}CO$), 3.05 (2H, m, 6'- H_2); ^{13}C NMR (DMSO-d_6) δ: 188.5 (*C*=O), 168.7 (CH_2C=O), 151.7, 148.0, 138.2, 119.5, 113.6 (Ar – *C*), 113.7, 112.6 (3a'-, 7a'-*C*), 41.1 (CH_2CO), 38.0 (5'- *C*), 35.3 (6'- *C*); ν_{max}/cm^{-1} (KBr) 3259, 3114, 3041, 2979, 1690 (S_2C=O), 1677 (C=O), 1580, 1538, 1435, 1408, 1299, 1217, 1142, 897, 871, 787; found C, 42.2; H, 3.0 %, $C_{12}H_{10}O_2N_2S_4$ requires C, 42.1; H, 2.9 %.

N- (2''- Pyridyl)- ET- ethanamide, 29

A mixture of **28** (0.4g, 1.2mmol) and the oxo compound **23** (0.5g, 2.5mmol) was heated in triethyl phosphite (20ml) to 90°C under N_2 for 5 h. to give an orange solution. Triethyl phosphite was removed by distillation *in vacuo* and the residue purified by flash chromatography (SiO_2, 3:1 cyclohexane/ EtOAc) to yield **29** as an orange solid (0.2g, 36 %); m.p.129-131°C; ^{1}H NMR δ: 8.87 (1H, br.s, N*H*), 8.27 (1H, dd, J = 5.0, 1.0 Hz, 6''- *H*), 8.19 (1H, dd, J = 8.2, 0.5 Hz, 3''- *H*), 7.72 (1H, dt, J = 8.2, 1.8 Hz, 4''- *H*), 7.07 (1H, ddd, J = 7.3, 5.0, 0.8 Hz, 5''- *H*), 4.20 (1H, m, 5- *H*), 3.41 (1H, dd, J = 13.4, 2.9 Hz, $CH_{\alpha}CO$), 3.29 (4H, s, 5' & 6'- H_2), 3.21 (1H, dd, J = 13.4, 2.9 Hz, $CH_{\beta}CO$), 2.92 (2H, d, J = 7.0 Hz, 6- H_2); ^{13}C NMR δ: 168.2 (*C*=O), 151.3, 147.6, 138.7, 120.2, 114.7 (Ar– *C*), 113.9, 113.8, 112.4, 112.1 (sp^2- *C*), 42.2 (CH_2CO), 37.9 (5- *C*), 35.2 (6- *C*), 30.2 (5'-, 6'- *C*); ν_{max}/cm^{-1} (KBr) 2967, 2920, 2850, 1684, 1654, 1577, 1434, 1302, 774. HRMS (ES): Found: 518.8949 (M+H)$^+$, $C_{17}H_{14}N_2OS_8$ requires: 518.8950 (M+H)$^+$.

(5’, 6’- Dihydro- 2’- thioxo-1, 3-dithiolo [4, 5-b]-1, 4- dithiin-5’-yl)ethanamide, 30

To a solution of **22** (0.5g, 1.8mmol) in THF (ml) at 0°C under N_2 was added sequentially triethylamine (0.3ml, 1.8mmol) and ethyl chloroformate (0.2ml, 1.8mmol). The mix was stirred for 5 min. before the addition of ammonia (2.0M solution in dioxane) (5.0ml, 2.5mmol), then allowed to warm to room temperature and stirred overnight under N_2. The following day the reaction mix was concentrated and the residue purified by flash chromatography (SiO_2, EtOAc) to yield **30** as a yellow solid (0.3g, 62 %); m.p.158-159°C; ^{1}H NMR (MeOH-d_4 & DMSO-d_6) δ: 4.28 (1H, m, 5’- *H*), 3.56 (1H, dd, J = 13.5, 5.6 Hz, CH_{α}CO), 3.44 (1H, dd, J = 13.5, 3.2 Hz, CH_{β}CO), 2.83 (2H, d, J = 7.1 Hz, 6’- H_2); ^{13}C NMR (MeOH-d_4 & DMSO-d_6) δ: 173.2 (*C*=O), 125.6 (3a’-, 7a’- *C*), 41.3 (CH_2CO), 41.2 (5’- *C*), 35.6 (6’- *C*); ν_{max}/cm^{-1} (KBr) 3449, 3283, 3237, 3184, 2924, 1678 (S_2C=O), 1657 (C=O), 1480, 1404, 1068 (C=S), 893, 741.

ET- ethanamide, 31

A mixture of thione **30** (0.2g, 0.6mmol) and the oxo compound **23** (0.2g, 1.1mmol) was heated in triethyl phosphite (10ml) to 90°C under N_2 for 5 h. to give an orange solution. Triethyl phosphite was removed by distillation *in vacuo* and the residue purified by flash chromatography (SiO_2, 3:1 cyclohexane/ EtOAc) to yield **31** as a red/orange solid (0.1g, 44 %); m.p.184-185°C (dec); ^{1}H NMR ($CDCl_3$ & DMSO-d_6) δ: 7.49 (1H, br.s, N*H*), 6.84 (1H, br.s, N*H*), 4.14 (1H, m, 5- *H*), 3.31 (4H, s, 5’-, 6’- H_2), 3.30 (1H, dd, J = 13.4, 5.7 Hz, CH_{α}CO), 3.20 (1H, dd, J = 13.4, 3.2 Hz, CH_{β}CO), 2.62 (2H, d, J = 7.2 Hz, 6- H_2); ^{13}C NMR ($CDCl_3$ & DMSO-d_6) δ: 169.5 (*C*=O), 112.4, 111.7, 110.4 (sp^2- *C*), 39.3 (CH_2CO), 33.1 (6- *C*), 28.3 (5’-, 6’- *C*); ν_{max}/cm^{-1}

(KBr) 3379, 3180, 2918, 2855, 1655, 1625, 1407, 1264, 908, 770, 609, HRMS (EI): Found: 440.8613 $(M+H)^+$, $C_{12}H_{11}NOS_8$ requires: 440.8606 $(M+H)^+$.

N- (Phenyl)- (5', 6'- dihydro- 2'- thioxo-1, 3-dithiolo [4, 5-b]-1, 4- dithiin-5'-yl) ethanamide, 32

To a solution of **22** (0.5g, 1.8mmol) in THF (20ml) at 0°C under N_2 was added sequentially triethylamine (0.3ml, 1.8mmol) and ethyl chloroformate (0.2ml, 1.8mmol). The mix was stirred for 5 min. before the addition of aniline (0.2ml, 1.8mmol), then allowed to warm to room temperature and stirred overnight under N_2. The following day the reaction mix was concentrated and the residue purified by flash chromatography (SiO_2, 3:1 cyclohexane/ EtOAc) to yield **32** as a yellow solid (0.4g, 64 %); m.p.163-164°C; ^1H NMR δ: 9.42 (1H, br.s, N*H*), 7.41(2H, d, J = 7.2 Hz, Ar-H_2), 7.12 (2H, m, Ar- H_2), 6.91 (1H, t, J = 6.6 Hz, Ar- *H*), 4.11 (1H, m, 5'- *H*), 3.35 (1H, dd, J = 13.7, 1.7 Hz, $CH_\alpha CO$), 3.16 (1H, dd, J = 13.4, 1.5 Hz, $CH_\beta CO$), 2.78 (2H, m, 6'- H_2); ^{13}C NMR δ: 207.4 (*C*=S), 167.1 (*C*=O), 138.0, 128.4, 123.6, 119.5 (Ar-*C*), 122.8, 121.3 (3a'-, 7a'- *C*), 41.4 (CH_2CO), 38.5 (5'- *C*), 34.0 (6'- *C*); ν_{max}/cm^{-1} (KBr) 3313, 3057, 2923, 1655 (C=O), 1600, 1535, 1443, 1408, 1362, 1312, 1254, 1066 (C=S), 691; found C, 43.3; H, 3.1; N, 3.5 %, $C_{13}H_{11}ONS_5$ requires C, 43.7; H, 3.1; N, 3.9 %.

N- (Phenyl)- ET- ethanamide, 33

A mixture of thione **32** (0.2g, 0.6mmol) and the oxo compound **23** (0.3g, 1.2mmol) were heated in triethyl phosphite (10ml) to 90°C under N_2 for 5 h. to give an orange solution. Triethyl phosphite was removed by distillation *in vacuo* and the residue purified by flash chromatography (SiO_2, 3:1 cyclohexane/ EtOAc) to yield **33** as a pink/orange solid (0.1g, 34 %); m.p.196-197°C; ^{1}H NMR (DMSO-d_6) δ: 7.57 (2H, d, J = 8.4 Hz, Ar- H_2), 7.29 (2H, m, Ar- H_2), 7.04 (1H, m, Ar- *H*), 4.23 (1H, m, 5- *H*), 3.38 (2H, d, J = 4.2 Hz, CH_2CO), 3.32 (4H, s, 5'-, 6'- H_2), 2.88 (2H, m, 6- H_2); ^{13}C NMR (DMSO-d_6) δ: 167.7 (C=O), 138.8, 128.7, 123.3, 119.1 (Ar- C_6), 112.8 (sp^2- *C*), 41.5 (*C*H_2CO), 34.4 (6- *C*), 29.5 (5'-, 6'- *C*); ν_{max}/cm^{-1} (KBr) 3049, 2966, 2920, 2849, 1654 (C=O), 1596, 1522, 1497, 1442, 1410, 1311, 1284, 1256, 888, HRMS (EI): Found: 516.8930 $(M+H)^+$, $C_{18}H_{15}NOS_8$ requires: 516.8919 $(M+H)^+$.

N- (4''- Hydroxyphenyl)- (5', 6'- dihydro- 2'- thioxo-1, 3-dithiolo [4, 5-b]-1, 4-dithiin-5'-yl)ethanamide, 34

To a solution of **22** (1.5g, 5.3mmol) in THF (40ml) at 0°C under N_2 was added sequentially triethylamine (0.7ml, 5.3mmol) and ethyl chloroformate (0.5ml, 5.3mmol). The mix was stirred for 5 min. before the addition of a solution of 4-aminophenol (0.6g, 5.3mmol) in dioxane (5ml), then allowed to warm to room temperature and stirred overnight under N_2. The following day the reaction mix was concentrated and the residue purified by flash chromatography (SiO_2, 3:1 cyclohexane/ EtOAc) to yield **34** as a brown solid (1.1g, 57 %); m.p.185-186°C; ^{1}H NMR (DMSO-d_6) δ: 9.87 (1H, br.s, O*H*), 9.18 (1H, br.s, N*H*), 7.35 (2H, d, J = 8.9 Hz, Ar- H_2), 6.69 (2H, d, J = 8.9 Hz, Ar- H_2), 4.30 (1H, m, 5'- *H*), 3.47 (2H, d, J = 4.0 Hz, CH_2CO), 2.87 (2H, d, J = 6.4 Hz, 6'- H_2); ^{13}C NMR (DMSO-d_6) δ: 207.7 (*C*=S), 166.8 (*C*=O), 153.4, 130.5, 120.9, 115.1, (Ar- C_6), 124.3, 122.8 (3a'-, 7a'- *C*), 41.1 (CH_2CO), 40.4 (5'- *C*), 34.2 (6'- *C*); ν_{max}/cm^{-1} (KBr) 3403, 3304, 2921, 2525, 1666 (C=O), 1532, 1516, 1245, 1062 (C=S), 833. HRMS (EI): Found: 372.9391, $C_{13}H_{11}NO_2S_5$ requires: 372.9388.

N- (4''- Acetyloxyphenyl)- (5', 6'- dihydro- 2'- thioxo-1, 3-dithiolo [4, 5-b]-1, 4-dithiin-5'-yl)ethanamide, 35

To a solution of **34** (0.3g, 0.7mmol) in pyridine (3ml) was added acetic anhydride (0.1ml, 1.mmol). The mixture was stirred at room temperature overnight. DCM (30ml) and water (20ml) were added. The mixture was shaken and the organic layer collected. This was washed sequentially with 1M HCl (2x30ml) and water (20ml), dried ($MgSO_4$) and evaporated to yield **35** as a yellow/brown solid (0.3g, 94 %); m.p.185-186°C; ^1H NMR (DMSO-d_6) δ: 10.20 (1H, br.s, N*H*), 7.58 (2H, d, J = 8.9 Hz, Ar- H_2), 7.05 (2H, d, J = 8.9 Hz, Ar- H_2), 4.32 (1H, m, 5'- *H*), 3.49 (2H, d, J = 4.1 Hz, CH_2CO), 2.93 (2H, d, J = 3.2 Hz, 6'- H_2), 2.24 (3H, s, -CH_3); ^{13}C NMR (DMSO-d_6) δ: 207.7 (*C*=S), 169.3 (CH_3C=O), 167.6 (N*C*=O), 145.9, 136.4, 122.0, 120.0 (Ar- C_6), 124.2, 122.8 (3a'-, 7a'- *C*), 41.3 (CH_2CO), 39.5 (5'- *C*), 34.1 (6'- *C*), 20.8 (-CH_3); ν_{max}/cm^{-1} (KBr) 3373, 2924, 1732 (OC=O), 1682 (NC=O), 1540, 1508, 1409, 1368, 1234, 1192, 1070 (C=S); found C, 43.4; H, 3.2; N, 3.1 %, $C_{15}H_{13}O_3NS_5$ requires C, 43.4; H, 3.2; N, 3.4 %.

N- (4''- Acetyloxyphenyl)- ET- ethanamide, 36

A mixture of thione **35** (0.2g, 0.4mmol) and the oxo compound **23** (0.2g, 0.8mmol) were heated in triethyl phosphite (10ml) to 90°C under N_2 for 5 h. to give an orange solution. Triethyl phosphite was removed by distillation *in vacuo* and the residue purified by flash chromatography (SiO_2, 3:1 cyclohexane/ EtOAc) to yield **36** as a pink solid (0.1g, 50.0 %); m.p.198-199°C; ^{1}H NMR (DMSO-d_6) δ: 10.18 (1H, br.s, N*H*), 7.58 (2H, d, J = 8.9 Hz, Ar- H_2), 7.05 (2H, d, J = 8.9 Hz, Ar- H_2), 4.23 (1H, m, 5- *H*), 3.39 (2H, d, J = 4.0 Hz, CH_2CO), 3.30 (4H, s, 5'-, 6'- H_2), 2.91 (2H, m, 6- H_2), 2.24 (3H, s, -CH_3); ^{13}C NMR (DMSO-d_6) δ: 169.3 (CH_3*C*=O), 167.7 (N*C*=O), 145.9, 136.4, 122.0, 120.0 (Ar- C_6), 112.9, 112.8 (sp^2- *C*), 41.4 (*C*H_2CO), 39.4 (5- *C*), 34.3 (6- *C*), 29.5 (5'-, 6'- *C*), 20.8 (-CH_3); ν_{max}/cm^{-1} (KBr) 3376, 2924, 2849, 1750 ($CH_3C=O$), 1674 (NHC=O), 1541, 1508, 1407, 1368, 1221, 1193, 668, HRMS (ES): Found: 575.9045 $(M+H)^+$, $C_{20}H_{17}NO_3S_8$ requires: 575.9047 $(M+H)^+$.

N- (4''- Hydroxyphenyl)- ET- ethanamide, 37

A solution of **36** (0.1g, 0.2mmol) in THF (20ml) and 20% HCl solution (10ml) was stirred under N_2 for 48h. The solution was neutralised by the addition of solid $NaHCO_3$. The organic layer was collected, dried (Na_2SO_4) and evaporated to afford **37** (0.1g, 65 %) as an orange brown solid; ^{1}H NMR (DMSO-d_6) δ: 9.84 (1H, br.s, N*H*), 9.18 (1H, br.s, O*H*), 7.32 (2H, d, J = 8.9 Hz, Ar- H_2), 6.69 (2H, d, J = 8.9 Hz, Ar- H_2), 4.20 (1H, m, 5- *H*), 3.39 (4H, s, 5'-, 6'- H_2), 3.36 (2H, d, J = 4.0 Hz, CH_2CO), 2.91 (2H, m, 6- H_2); ^{13}C NMR (DMSO-d_6) δ: 167.1 (*C*=O), 145.9, 136.4, 122.0, 120.0 (Ar- C_6), 112.9, 112.8 (sp^2- *C*), 41.4 (*C*H_2CO), 39.4 (5- *C*), 34.3 (6- *C*), 29.5 (5'-, 6'- *C*).

N- (4''- Pyridyl)- (5', 6'- dihydro- 2'- thioxo-1, 3-dithiolo [4, 5-b]-1, 4- dithiin-5'-yl)ethanamide, 38

To a solution of **22** (0.5g, 1.8mmol) in THF (20ml) at 0°C under N_2 was added sequentially triethylamine (0.3ml, 1.8mmol) and ethyl chloroformate (0.2ml, 1.8mmol). The mix was stirred for 5 min. before the addition of 4-aminopyridine (0.2g, 1.8mmol), then allowed to warm to room temperature and stirred overnight under N_2. The following day the reaction mix was concentrated and the residue purified by flash chromatography (SiO_2, EtOAc) to yield **38** as a brown/yellow solid (0.3g, 44 %); m.p.163-164°C; ^{1}H NMR ($CDCl_3$ & DMSO-d_6) δ: 9.88 (1H, br.s, N*H*), 7.99 (2H, dd, J = 5.0, 1.5 Hz, 2''-, 6''- *H*), 7.14 (2H, dd, J = 5.0, 1.5 Hz, 3''-, 5''- *H*), 3.88 (1H, m, 5'- *H*), 3.10 (1H, dd, J = 13.5, 2.9 Hz, CH_αCO), 2.96 (1H, dd, J = 13.5, 5.3 Hz, CH_βCO), 2.57 (2H, m, 6'- H_2); ^{13}C NMR ($CDCl_3$ & DMSO-d_6) δ: 206.5 (*C*=S), 167.8 (*C*=O), 149.3, 144.6, 112.6 (Ar- C_6), 122.1, 120.7 (3a'-, 7a'-*C*), 40.8 (*C*H_2CO), 37.5 (5'- *C*), 33.3 (6'- *C*); ν_{max}/cm^{-1} (KBr) 1707, 1592, (C=O), 1521, 1417, 1374, 1328, 1296, 1066 (C=S), 826, HRMS (ES): Found: 358.9476 $(M+H)^+$, $C_{12}H_{10}N_2OS_5$ requires: 358.9469 $(M+H)^+$.

N- (5', 6'- dihydro- 2'- thioxo-1, 3-dithiolo [4, 5-b]-1, 4- dithiin-5-yl)ethanoyl- N'-phenyl hydrazine, 39

To a cold (0°C) solution of **22** (1.5g, 5.3mmol) in THF (20ml) under N_2 was added sequentially triethylamine (0.7ml, 5.3mmol) and ethyl chloroformate (0.5ml, 5.3mmol). The mix was stirred for 5 min. before the addition of phenylhydrazine (0.5ml, 5.3mmol), then allowed to warm to room temperature and stirred overnight under N_2. The following day the reaction mix was concentrated and the residue purified by flash chromatography (SiO_2, 2:1 cyclohexane/ EtOAc) to yield **39** as a yellow solid (0.5g, 39 %); ^{1}H NMR ($CDCl_3$ & DMSO-d_6) δ: 9.62 (1H, br.s, N*H*), 7.02 (2H, m, Ar- H_2), 6.65 (3H, m, Ar- H_3), 6.33 (1H, br.s, N*H*), 4.02 (1H, m, 5'- *H*), 3.30 (1H, dd, J = 13.5, 2.9 Hz, CH_αCO), 3.09 (1H, dd, J = 13.5, 5.7 Hz, CH_βCO), 2.65 (2H, m, 6'- H_2); ^{13}C NMR ($CDCl_3$ & DMSO-d_6) δ: 207.4 (*C*=S), 168.5 (*C*=O), 147.9, 128.6, 120.2, 112.9 (Ar- C_6), 122.1, 121.4 (3a'-, 7a'-*C*), 38.3 (CH_2CO), 38.2 (5'- *C*), 33.9 (6'- *C*).

N- (1'', 2'', 4''- Triazol- 3''- yl)- (5', 6'- dihydro- 2'- thioxo-1, 3-dithiolo [4, 5-b]-1, 4- dithiin-5'-yl)ethanamide, 40

To a cold (0°C) solution of **22** (1.5g, 5.3mmol) in THF (20ml) under N_2 was added sequentially triethylamine (0.7ml, 5.3mmol) and ethyl chloroformate (0.5ml, 5.3mmol). The mix was stirred for 5 min. before the addition of a solution of 3-amino-1,2,4-triazole (0.5g, 5.3mmol) in dry MeOH (5ml), then allowed to warm to room temperature and stirred overnight under N_2. The following day the reaction mix was concentrated and the residue purified by flash chromatography (SiO_2, 1:1 cyclohexane/ EtOAc) to yield **40** as a brown solid (0.7g, 39 %); ^{1}H NMR (DMSO-d_6) δ: 7.58 (3H, br.s, 2 x N*H* & 5''- *H*), 4.40 (1H, m, 5'- *H*), 3.49 (4H, m, CH_2CO & 6'-H_2); ^{13}C NMR (DMSO-d_6) δ: 209.1 (*C*=S), 172.0 (*C*=O), 158.3 (3''- *C*), 152.9 (5''-*C*), 126.3, 124.7 (3a'-, 7a'-*C*), 45.8 (CH_2CO), 44.0 (5'- *C*), 39.5 (6'- *C*); ν_{max}/cm^{-1} (KBr) 3425, 2926, 1723 (C=O), 1639, 1522, 1397, 1323, 1256, 1200, 1149, 1060 (C=S), 742; found C, 30.9; H, 2.2 %, $C_9H_8ON_4S_5$ requires C, 31.0; H, 2.3 %.

(5', 6'- Dihydro- 2'- thioxo-1, 3-dithiolo [4, 5-b]-1, 4- dithiin-5'-yl)methanamide, 43

A mixture of acrylamide (3.6g, 51.0mmol) and the trithione **19** (5.0g, 25.5mmol) in toluene (500ml) was refluxed for 5h. then left to stir overnight at room temperature. The solid was collected by filtration under reduced pressure and purified by distillation *in vacuo* to remove starting material. The product **43** was obtained as a yellow / brown solid; m.p.175-177°C; ^{1}H NMR (DMSO-d_6) δ: 7.80 (1H, s, N- *H*), 7.55 (1H, s, N- *H*), 4.42 (1H, dd, J= 7.8, 2.8 Hz, 5'- *H*), 3.69 (1H, dd, J= 12.9, 2.8 Hz, 6'- H_α), 3.50 (1H, dd, J= 12.9, 8.6 Hz, 6'- H_β); ^{13}C NMR (DMSO-d_6) δ: 207.9 (*C*=S), 168.7 (*C*=O), 125.7, 124.8 (3a'-, 7a'- *C*), 47.4 (5'- *C*), 32.7 (6'- *C*); found C, 26.8; H, 1.7; N, 4.9 %, $C_6H_5ONS_5$ requires C, 27.0; H, 1.9; N, 5.2 %.

(5', 6'- Dihydro- 2'- oxo-1, 3-dithiolo [4, 5-b]-1, 4- dithiin-5'-yl)methanamide, 44

To a solution of **43** (0.3g, 0.9mmol) in $CHCl_3$ (20ml) and glacial acetic acid (6ml) was added mercuric acetate (0.5g, 1.4mmol). After 2 h. stirring at room temperature the mix was filtered. The filtrate was washed consecutively with saturated $NaHCO_3$ solution (3x20ml) and H_2O (20ml), dried (Na_2SO_4) and evaporated to afford **44** as a beige solid (0.1g, 43 %); ^{1}H NMR (DMSO-d_6) δ: 7.79 (1H, s, N- *H*), 7.54 (1H, s, N-*H*), 4.42 (1H, dd, J= 8.5, 3.7 Hz, 5'- *H*), 3.70 (1H, dd, J= 12.9, 3.7 Hz, 6'- H_α), 3.52 (1H, dd, J= 12.9, 8.5 Hz, 6'- H_β); ^{13}C NMR (DMSO-d_6) δ: 188.5 (S_2C=O), 168.9 (NH_2C=O), 115.6, 114.6 (3a'-, 7a'- *C*), 48.9 (5'- *C*), 34.1 (6'- *C*).

7. References.

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Chapter 5

Further investigations into novel organosulfur donors related to ET

1. Approaches to ET-CO_2H derivatives.

Introduction.

The previous chapter described the synthesis of carbonyl derivatives of ET, in which a methylene group separated the ET and carbonyl groups. Preliminary attempts to prepare related systems in which the carbonyl group (as an ester) is directly attached to the ET system are discussed here. It is already known[1,2] that coupling of oxo or thione molecules appended with such groups, using triethyl phosphite leads to decomposition of the outer rings, due to the electrophilic nature of the carbon bearing the ester functionality. Thus, the organosulfur network needs to be constructed first, and a functionalised bridge subsequently added.

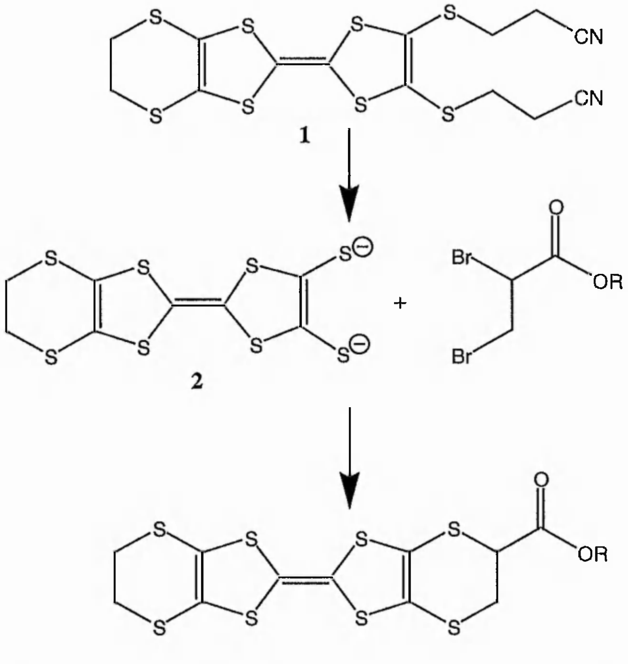
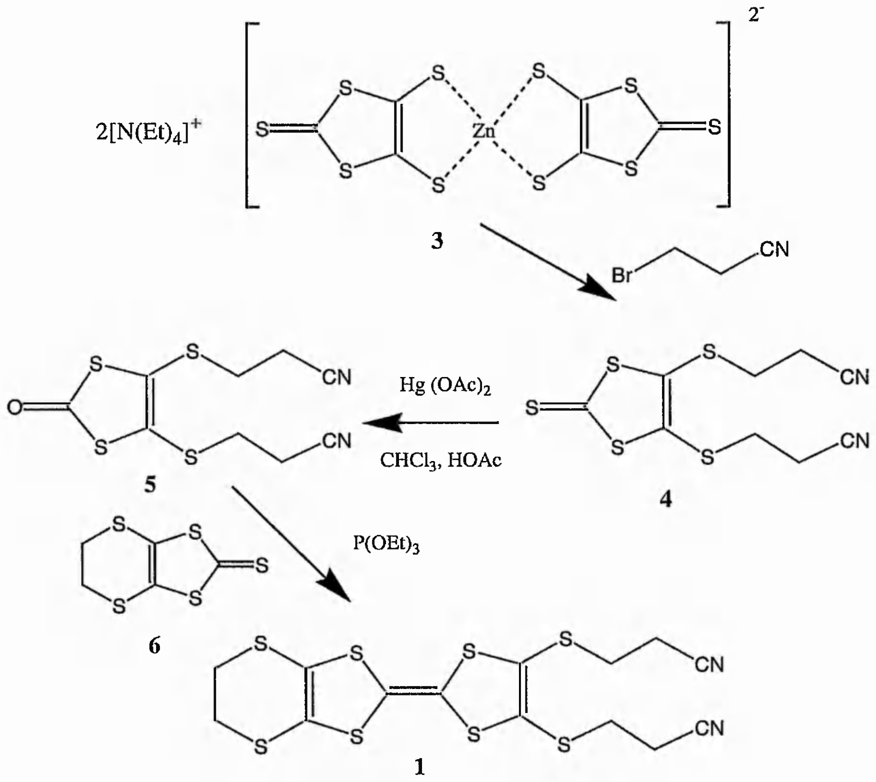


Figure 1. Synthetic methodology towards novel functionalised ET compounds.

An investigation into the chemistry of dithiolate **2** was carried out in order to ascertain whether it was possible to obtain ET-CO_2R derivatives as shown in figure 1 above. With the central bond of the sulfur system already being present in the case of **1**, it was envisaged that reactions between dithiolate **2** and functionalised dibromo compounds would lead to desired products by two nucleophilic substitutions of bromide.

Preparation of 1.

The preparation of **1** was through a three-step synthesis originally reported by Becher *et al.*[3] Reaction of zinc complex **3** in acetonitrile with an excess of 3-bromopropionitrile at an oil bath temperature of 100°C, afforded thione **4** as a brown solid in 91 % yield. Replacement of the exocyclic sulfur atom for oxygen by treatment of **4** with mercuric acetate furnished the oxo compound **5** as a yellow/ brown solid in 86 % yield. Cross coupling of **5** with thione **6** in triethyl phosphite at an oil bath temperature of 90°C for 4h., followed by purification by chromatography to remove ET and disubstituted material afforded **1** as a bright orange solid in 69 % yield.

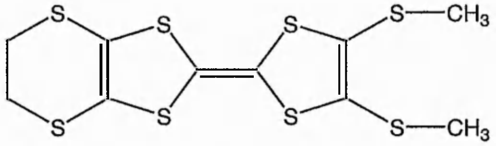


Scheme 1. Synthesis of compound **1**.

Deprotection of 1.

An efficient method for deprotecting **1** was sought. The use of ethoxide or sodium hydride in DMF[3] failed to cleave the cyanoethyl groups from the molecule. Treatment of a solution of **1** in THF under nitrogen with 2.2eq. or 4eq. of $CsOH.H_2O$ in methanol and then, after 1h. stirring, adding an excess of methyl iodide to obtain **7** also failed to yield the desired compound.

However, a procedure to remove the protecting groups sequentially was found.[4] After 1h. stirring of **1** in THF under nitrogen with 1eq. of $CsOH.H_2O$ in methanol followed by an addition of an excess of methyl iodide and stirring for 30 min. a second portion of $CsOH.H_2O$ (1eq.) was added and the mixture stirred for 1h. before the addition of an excess of methyl iodide. After stirring overnight the known bis(methylthio) derivative **7** was collected by filtration as an orange solid.



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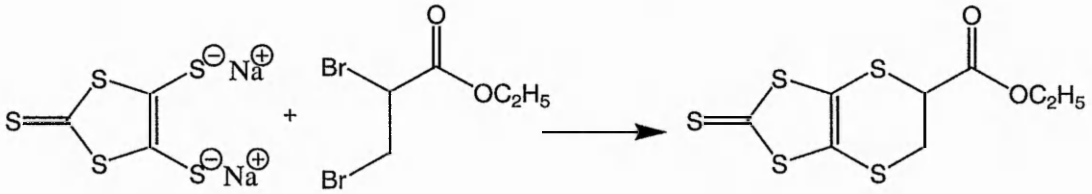
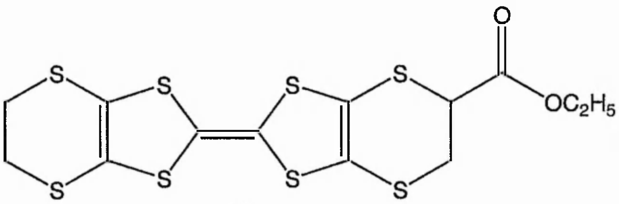
Reaction of 1 with ethyl 2, 3- dibromopropionate.



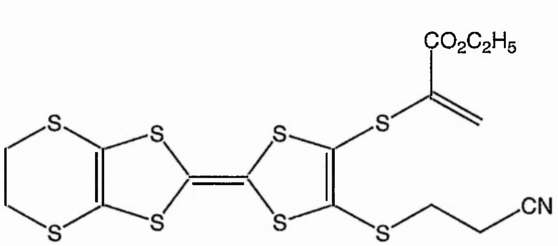
8 **9**

Following the successful reaction of the disodium salt of dithiolate **8** with ethyl 2,3-dibromopropionate to afford the thione **9**, an investigation into the reaction of **1** with ethyl 2, 3- dibromopropionate was carried out. It was envisaged that ET-CO_2Et **10** would be obtained.



10

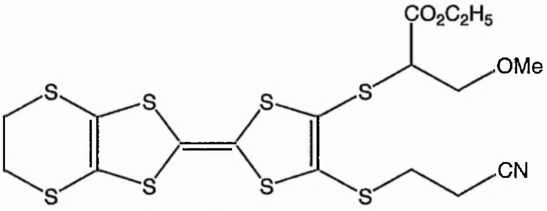
After 1h. stirring of **1** in THF under nitrogen with 1eq. of $CsOH.H_2O$ in methanol, 1eq. of ethyl 2, 3- dibromopropionate was added. A precipitate formed and the mixture stirred for 1h. 1eq. of $CsOH.H_2O$ in methanol was added and the mixture stirred overnight. Workup of the reaction mixture and purification by chromatography afforded an unexpected product **11** in 23 % yield, which was characterised by NMR. The first substitution of bromine α to the carbonyl group must have occurred, followed by base catalysed loss of HBr to give the alkene, rather than removal of the second cyanoethyl protecting group.



11

The presence of the ethyl and cyanoethyl groups is clear from the NMR spectra and the alkenyl group showed two proton singlets at δ: 6.53 and δ: 5.80 and two carbon resonances at δ: 134.7 and δ: 126.4. Attempts to prepare ET-CO_2Et **10** from **11** by reacting a solution of **11** in THF with 2eq. of $CsOH.H_2O$ in methanol to remove the protecting group and stirring at room temperature or heating failed to bring about the cyclisation to afford **10**.

A second attempt to obtain ET-CO_2Et **10** was carried out. After stirring a solution of diprotected ET **1** in THF under nitrogen with 1eq. of $CsOH.H_2O$ in methanol, 1eq. of ethyl 2, 3- dibromopropionate was added. A precipitate formed and the mixture stirred for 1h. 2eq. of $CsOH.H_2O$ in methanol was added and the mixture stirred overnight. Workup of the reaction mixture and purification by chromatography afforded three products: the alkenyl derivative **11** (9 %), the unexpected product **12** (13 %), and surprisingly, starting material **1** (20 %).



12

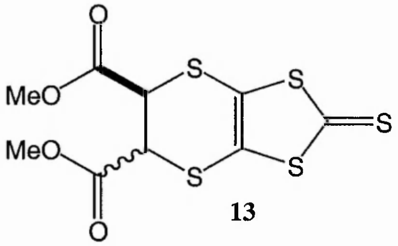
Due to the extra equivalent of $CsOH.H_2O$ used in the reaction compared to the previous reaction, methoxide (generated from MeOH + $CsOH.H_2O$) has displaced bromine from the original substitution product **11** to give the β- methoxy ester **12**. The ^1H NMR supports the structure of **12**. A multiplet at δ: 3.80 integrating for three protons is assigned as (CH_2OMe) and ($CHCO_2Et$). A singlet at δ: 3.39 corresponds to the shift of the methyl protons. ^{13}C NMR shows new peaks compared to **11** with shifts observed at δ: 51.1 (OCH_3), δ: 71.7 (CH_2OMe) and δ: 59.3 ($CHCO_2Et$).

A final attempt was carried out to synthesise ET-CO_2Et **10**. To a solution of **1** in THF under nitrogen at an oil bath temperature of 65°C was added 2eq. of $CsOH.H_2O$ in methanol. After stirring for 3h. 1eq. of ethyl 2, 3-dibromopropionoate was added and the mixture stirred overnight at 65°C. Workup of the reaction mixture and purification by chromatography afforded trace amounts of **10** and **11**.

The work was discontinued at this point but needs further investigation. The important issue is to find conditions, which generate exclusively the dithiolate **2** in solution. Isolation of this material as a salt would allow reactions to be performed in non- basic media.

A novel reaction of the disodium salt of dithiolate 8 with electron deficient vinyl alkyne 14.

Dimethyl acetylenedicarboxylate (DMAD) is known to react with the disodium salt of dithiolate **8** to give the bicyclic thione **13** as a mixture of cis and trans isomers[2], though it was not possible to couple **13** to form ET derivatives. The vinyl alkyne dimethyl hex- 2- en- 4- yne- 1, 6- dioate (DMHD) **14** is another possible substrate for the reaction, which could ultimately be extended to reaction of dithiolate **2**, to form ET derivatives with ester functionality directly attached.



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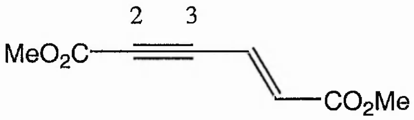
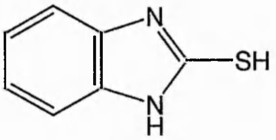


14

Alkyne **14** is known to react with amines[5] by reaction at either sp C atom, and reacts with thiol **15** in a similar way, to give addition at 3- C followed by amide formation to give **16**, or by addition at 2- C to give **17**.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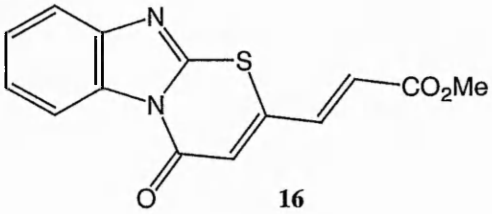
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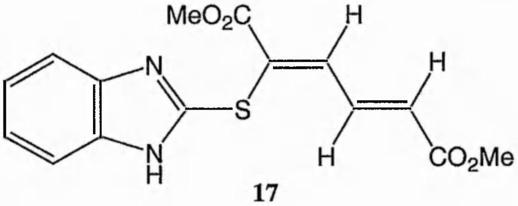
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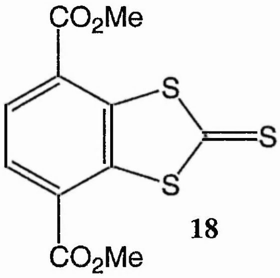
Alkyne **14** was obtained by dimerisation of methyl propiolate with *N*-methyl piperidine at 0°C.[5] Reaction of dithiolate **8** with vinyl alkyne **14** in methanol, gave only one, rather unexpected product **18** in 12 % yield. ^{1}H NMR shows just two singlets at δ: 8.15 and δ: 4.03. The ^{13}C NMR shows six resonances, including the thione carbon at δ: 218.8 and three benzenoid carbon resonances in the range δ: 145.4 – δ: 126.6. Mass spectrometry confirms the molecular mass of 360 g mol^{-1}, and the relative height of the [m+2] peak suggests the presence of just three sulfur atoms.


18

Two possible mechanisms for the formation of **18** are given below.

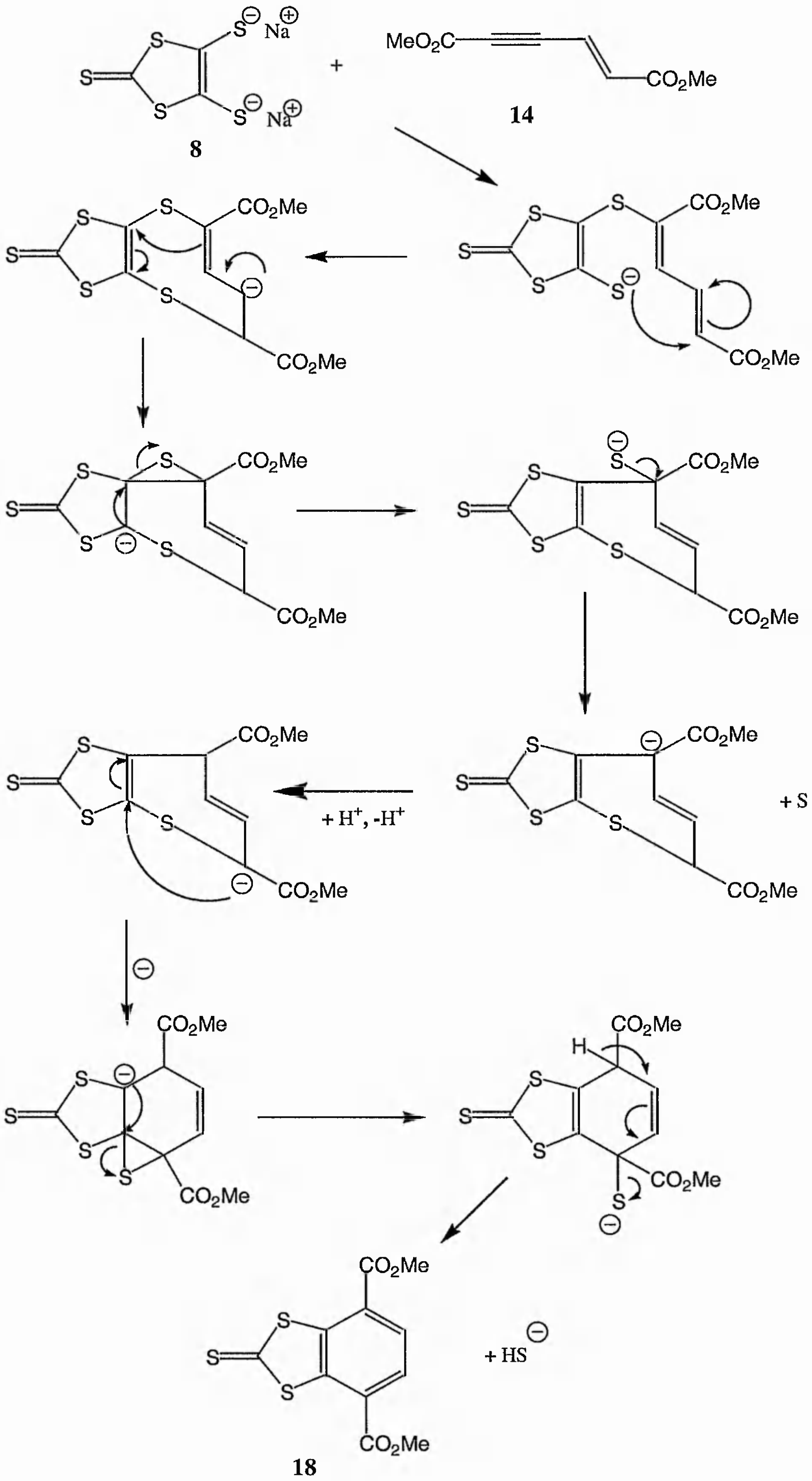
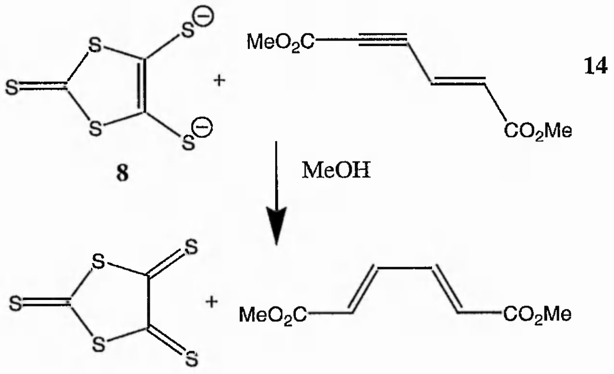


Figure 2. Possible mechanism for the formation of **18**.



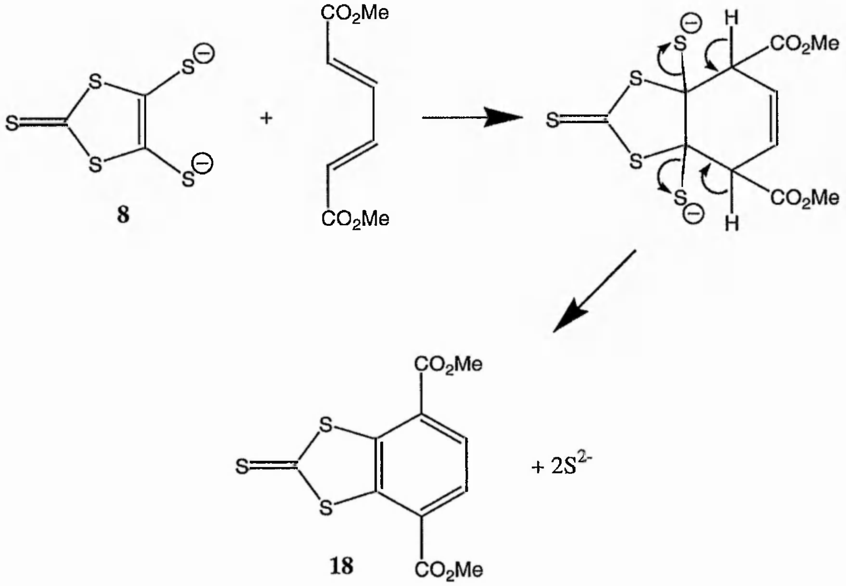
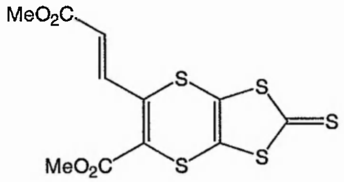


Figure 3. Possible mechanism for the formation of **18**.

To moderate the reactivity of dithiolate **8** it was converted to the corresponding monothiolate with one equivalent of benzoic acid, and the subsequent reaction buffered with sodium hydrogen carbonate, since addition of the thiolate to the alkyne **14** would consume a proton, and increase the basicity of the reaction mixture. Reaction with vinyl alkyne **14** now gave two products, assigned as **19** and **20**, both in 8 % yield.



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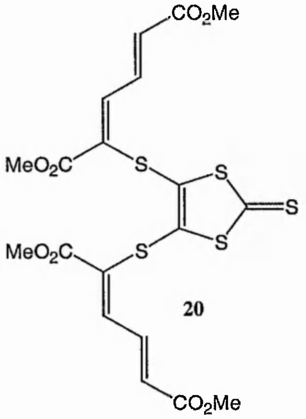
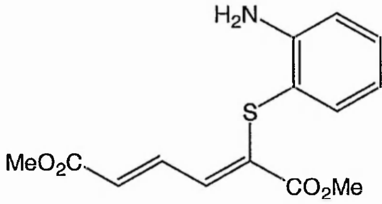


20

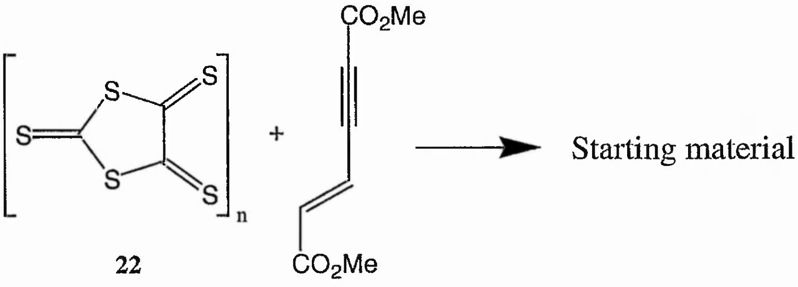
The structure of thione **19** is supported by the presence of only two methyl resonances and two doublets (J = 15.4 Hz) in the ^{1}H NMR. The mass spectrum shows a molecular ion at 364. The second product **20** is a 1: 2 addition product, as supported by a molecular ion at 534. The ^{1}H NMR shows three coupled protons attached to three consecutive protons, at δ: 7.91 (dd, J = 11.4, 15.3 Hz), δ: 7.71 (dd, J = 0.5, 11.4 Hz) and δ: 6.35 (dd, J = 0.5, 15.3 Hz), whose shifts are similar to that of the trans addition product **21** of the vinyl alkyne **14** with 2- aminobenzenethiol.[5] Reaction of thiols to electron deficient alkynes in protic solvents are predominantly by trans addition.



21

The 1: 2 adduct **20** is formed by addition to 2- C of the alkyne **14**. The thione **19** is formed by addition of both thiol groups to opposite ends of the alkyne, followed by loss of hydrogen to give a conjugated product. The source of this oxidation is not clear, but could be due to hydride transfer to the unreacted alkyne. (The adduct **13** is known to be oxidised by DDQ to the corresponding dithiin). The low yields of **19** and **20** mean that this chemistry is of little application. The majority of the crude reaction mixture did not move on chromatography.

Reaction of alkyne **14** with trithione **22** in refluxing dioxane for 4 h. led only to isolation of unreacted alkyne after chromatography. This is quite surprising as both alkyne and alkene groups present in **14** would be expected to react with the trithione. Further work could explore the use of alternative solvents for the reaction.

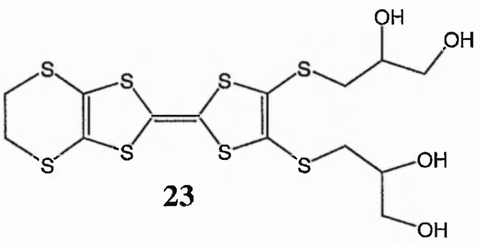


22 **14**

2. Approaches to polyhydroxy chiral TTF donors.

An investigation into the reactivity of dithiolate 8 with solketal derivatives 25-28.

An extension of the work described in chapters 2 and 3 would be to prepare TTF derivatives such as **23** and **24**. As well as providing substrates for investigating the influence of chirality on conductivity, they could act as cores for chiral dendrimers containing further TTF or ET derivatives. An investigation into the reactions of the disodium salt of dithiolate **8** and racemic solketal derivatives **25-28** were carried out in order that the first step towards the novel organosulfur donors **23** and **24** may be obtained.



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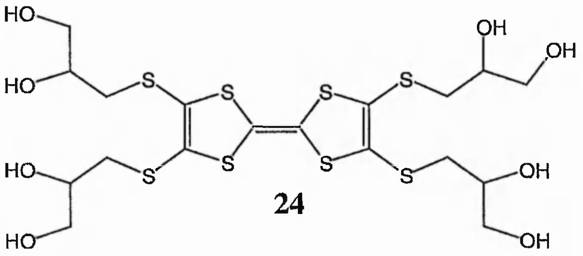
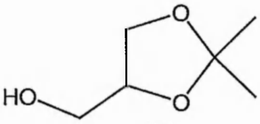


24

The investigation centred on the application of different leaving groups to promote the reaction between the disodium salt of dithiolate **8** and solketal derivatives. The hydroxy function of solketal **25** was converted to a tosylate **26**, triflate **27**[6] or replaced by an iodide **28**.[6]



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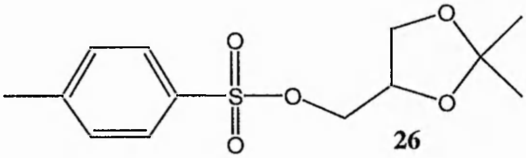

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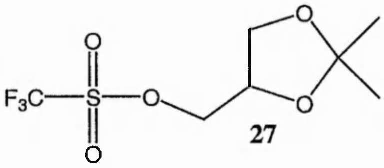

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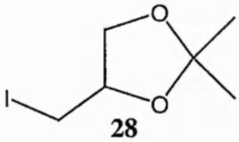
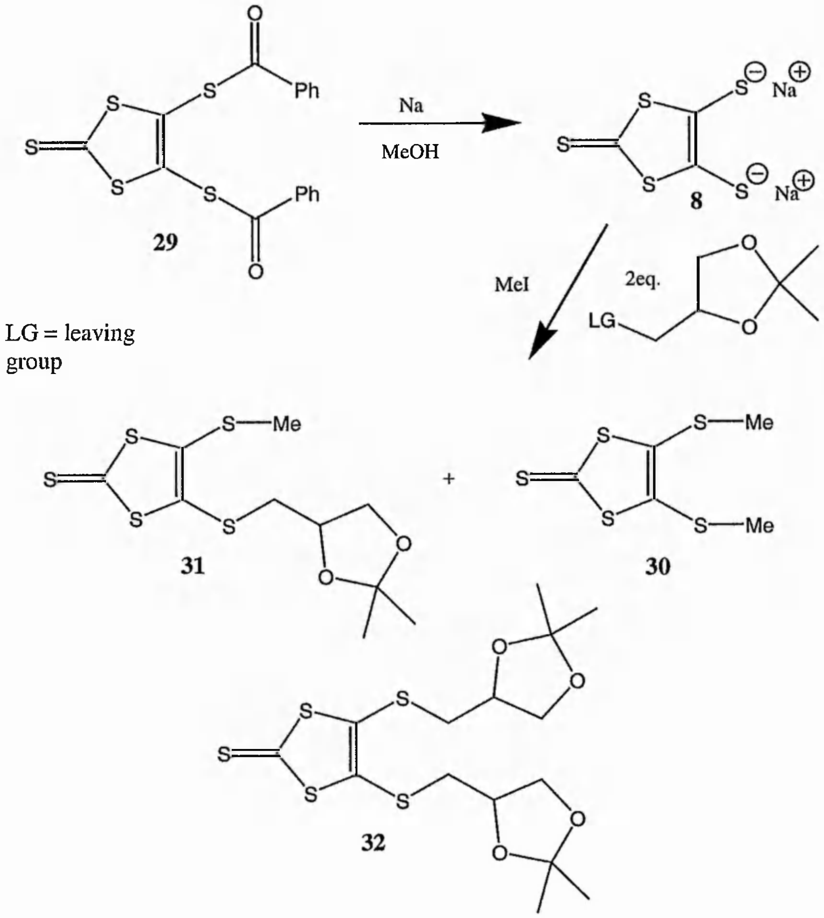


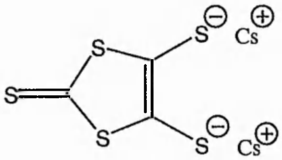
28

Treatment of dibenzoylated compound **29** with 2.2eq. of sodium methoxide furnished **8** *in situ.* Reaction of **8** with 2eq. of the activated solketals shown above, and stirring overnight under nitrogen, gave mainly baseline material on tlc analysis, indicating that dithiolate or thiolate was still present. Refluxing the reaction mixture to bring the reaction to completion was unsuccessful. The reactions were worked up by the addition of methyl iodide and generally gave, in variable yields, the dimethylated thione **30**, and the thione **31** in which one solketal moiety and a methyl group have been added. In one reaction using **26**, a trace of the desired compound **32** was formed.



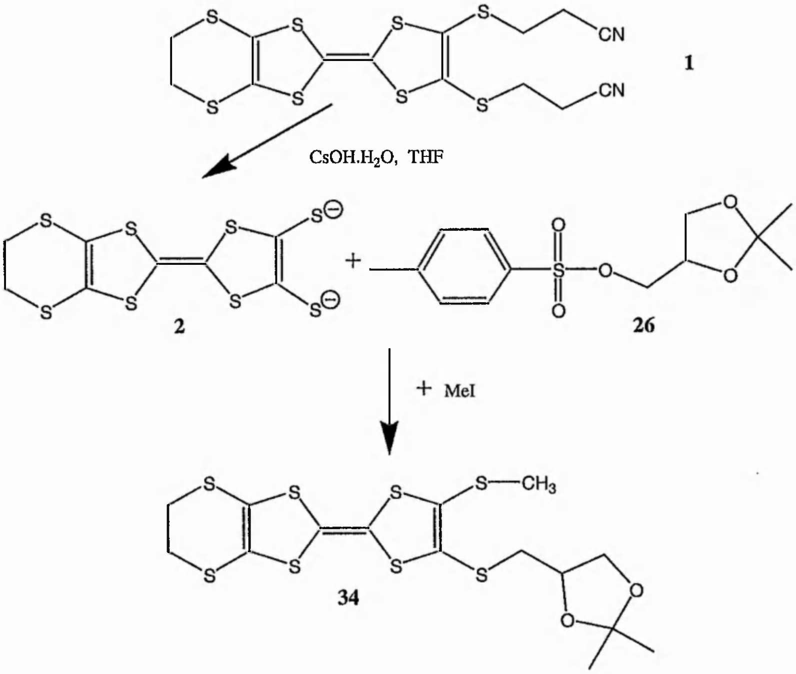
Scheme 2. Products obtained from reaction of **8** with solketal.

From the results obtained it was clear that the addition of one solketal moiety to **8** could be achieved. It was thought that the second nucleophilic substitution could not take place due to the presence of the small sodium cation being coordinated to the thiolate and an oxygen in the solketal moiety, leaving the thiolate sterically hindered and not able to carry out reaction with the second equivalent of the solketal derivative. Thus, the dicesium salt of dithiolate, **33**, was prepared as a purple solid.[7] The cesium cation, being a lot larger and less coordinating than the sodium cation, should leave the thiolate ‘naked’ and able to carry out the second nucleophilic substitution. However, reaction of tosylate **26** with the dicesium salt **33,** followed by the addition of excess methyl iodide failed to give desired product **32**. Mixtures of **30** and **31** were obtained.



33

As an alternative approach to polyhedral donors, the TTF- dithiolate **2** was also reacted with the tosylate **26** and then excess methyl iodide, with the aim of producing **34**.

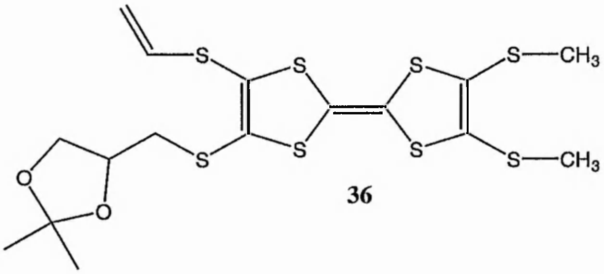


Scheme 3. Synthesis of compound **34**.

After 1h. stirring of **1** in THF under nitrogen with 4eq. of $CsOH.H_2O$ in THF, 2eq. of tosylate **26** were added and the mixture stirred overnight. An excess of methyl iodide was then added and after 10 min. the colour of the reaction mixture was bright orange. The reaction mixture was stirred for 30 min. Workup of the reaction mixture and purification by chromatography afforded two compounds, mono- and dimethylated materials **34** (15 %) and **7** (41 %), which were characterised by NMR.

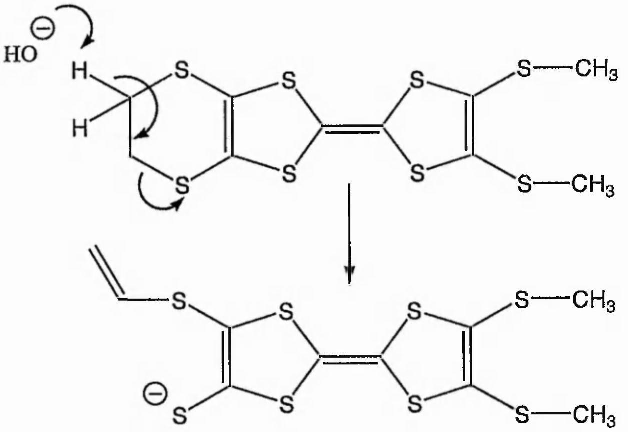
^{1}H NMR of **34** indicates four singlets at δ: 3.24, δ: 2.37, δ: 1.36 and δ: 1.28 corresponding to S*C**H*$_3$, 5'-, 6'-*H*$_2$, and 2 x C(C*H*$_3$) respectively. ^{13}C NMR indicates the three carbon atoms of the dioxolane ring at δ: 109.8 (*C*(CH$_3$)), δ: 74.9 and δ: 68.6 . The shift for 5'-, 6'-*C* is observed at δ: 30.2 and S*C*H$_3$ at δ: 19.1.

The experimental procedure was modified for a further reaction between dithiolate **2** and tosylate **26**. After 1h. stirring of **1** in THF under nitrogen with 2.2eq. of CsOH.H$_2$O in methanol, 5eq. of methyl iodide was added. A bright orange precipitate formed and the mixture stirred for 1h. The solvent was removed from the reaction mixture *in vacuo*. To the residue was added THF and 2.2eq. of CsOH.H$_2$O in methanol. After 1h. stirring 2.2eq. of **26** was added and the reaction mixture stirred overnight. Workup of the reaction mixture and purification by chromatography led to the unexpected product **36** as an orange oil which was characterised by NMR and low resolution mass spectrometry.



36

^{1}H NMR of **36** indicates the alkenyl protons at δ: 6.30 (4- SC*H*) and δ: 5.38 (4-SCH=C*H*$_2$). Three singlets are present at δ: 2.36, δ: 1.36 and δ: 1.28 corresponding to SC*H*$_3$, and 2 x C(C*H*$_3$) respectively. ^{13}C NMR indicates the vinyl carbon atoms at δ: 129.3 and δ: 117.1. We tentatively propose that dimethylated compound **7** formed in the first step has been opened at the ethylene bridge by base in the second step to give thiolate **35**, which then reacted with the solketal tosylate **26** to afford **36**. This is highly unusual and requires further investigation.



7

35

The following conditions failed to furnish anything more than starting material **1**, and the dimethyl compound **7**. After 1h. stirring of **1** in THF under nitrogen with 4eq. of $CsOH.H_2O$ in methanol, 1eq. of **26** was added and the mixture stirred overnight. An excess of methyl iodide was added. After 10 min. the colour of the reaction mixture was bright orange. The reaction mixture stirred for 4h. Workup of the reaction mixture and purification by chromatography afforded the two compounds **1** and **7**, which were characterised by NMR.

3. Experimental.

4, 5- Di(cyanoethylthio)- 1, 3- dithiole- 2- thione, 4[3]

To a solution of zinc complex **3** (10.0g, 13.9mmol) in acetonitrile (175ml) was added 3-bromopropionitrile (6.0ml, 69.5mmol). The reaction mixture was heated to reflux for 1h. then cooled to room temperature and filtered *in vacuo*. The filtrate was concentrated under reduced pressure and the residue taken up in DCM (200ml). The organic solution was washed with water (4 x 150ml), dried ($MgSO_4$) and concentrated *in vacuo* to afford **4** as a brown solid (7.8g, 91 %); ^{1}H NMR δ: 3.14 (4H, t, J= 6.9 Hz, CH_2CH_2CN), 2.79 (4H, t, J= 6.8 Hz, CH_2CH_2CN); ^{13}C NMR δ: 209.3 (*C*=S), 135.9 (3a-, 7a- *C*), 117.2 (*C*≡N), 31.8 (CH_2CH_2CN), 19.0 (CH_2CH_2CN).

4, 5- Di(cyanoethylthio)- 1, 3- dithiole- 2- one, 5[3]

To a solution of dinitrile **4** (3.8g, 12.5mmol) in $CHCl_3$ (200ml) and glacial acetic acid (50ml) was added mercuric acetate (6.0g, 18.8mmol). After 2 h. stirring at room temperature the mix was filtered. The filtrate was washed consecutively with saturated $NaHCO_3$ solution (3 x 150ml) and H_2O (150ml), dried (Na_2SO_4) and evaporated to afford **5** as a light brown solid (3.1g, 86 %); ^{1}H NMR δ: 3.12 (4H, t, J= 6.6 Hz, CH_2CH_2CN), 2.78 (4H, t, J= 6.9 Hz, CH_2CH_2CN); ^{13}C NMR δ: 189.5 (*C*=O), 127.4 (3a-, 7a-*C*), 117.2 (*C*≡N), 31.7 (CH_2CH_2CN), 19.0 (CH_2CH_2CN).

4, 5- Di(cyanoethylthio)-4', 5'- (ethylenedithio)- tetrathiafulvalene, 1[3]

A mixture of **5** (0.6g, 2.2mmol) and thione **6** (0.5g, 2.2mmol) were heated in triethyl phosphite (15ml) to 100°C under N_2 for 1.5 h. to give an orange solution. Triethyl phosphite was removed by distillation *in vacuo* and the residue purified by flash chromatography (SiO_2, DCM) to yield **1** as an orange solid (0.7g, 69 %); ^{1}H NMR δ:

3.29 (4H, s, 5' & 6'- *H_2*), 3.06 (4H, t, J= 7.2 Hz, CH_2CH_2CN), 2.71 (4H, t, J= 7.2 Hz, CH_2CH_2CN); ^{13}C NMR δ: 117.4 (*C*≡N), 113.9 (3a-, 7a- *C*), 31.4 (CH_2CH_2CN), 30.2 (5' & 6'- *C*), 18.9 (CH_2CH_2CN).

(5, 6- Dihydro- 2- thioxo- 1, 3- dithiolo [4, 5- b]- 1, 4- dithiin- 5- yl) methanoate, 9

The dibenzoylated thione **29** (3.0g, 7.4mmol) was added to a solution of sodium metal (0.4g, 16.2mmol) in dry ethanol (75ml) under N_2 and the mix stirred for 1 h. at room temperature. Ethyl 2, 3- dibromopropionate (1.1ml, 7.4mmol) was added to the cold (0°C) reaction mix in one portion. Stirring was continued overnight at room temperature under N_2. The solvent was removed *in vacuo* and the residue partitioned between DCM (100ml) and water (50ml). The organic phase was collected, washed with water (50ml), dried ($MgSO_4$) and evaporated to yield an orange oil. The oil was purified by flash chromatography (SiO_2, 4:1 cyclohexane/ ethyl acetate) to furnish **9** as a red/ brown oil (1.1g, 51 %); ^1H NMR δ: 4.42 (1H, dd, J = 6.8, 4.4 Hz, 5- C*H*), 4.28 (2H, q, J = 14.2 Hz, OCH_2CH_3), 3.55 (1H, dd, J = 13.2, 6.8 Hz, 6- CH_α), 3.48 (1H, dd, J = 13.2, 4.4 Hz, 6- CH_β), 1.32 (3H, t, J = 7.2 Hz, OCH_2CH_3); ^{13}C NMR δ: 207.9 (C=S), 167.5 (*C*=O), 125.1, 124.2 (3a-, 7a- C), 63.0 OCH_2CH_3), 46.7 (5- *C*), 32.3 (6- *C*) 52.3 (OCH_2CH_3).

Reactions of dithiolate 2 with ethyl 2, 3- dibromopropionate.

(a)

To a solution of **1** (0.2g, 0.4mmol) in THF (10ml) under N_2 was added $CsOH.H_2O$ (0.1g, 0.4mmol) in MeOH (2ml). Upon addition the orange solution turned dark red. After 1h. stirring ethyl 2, 3- dibromopropionate (0.1ml, 0.4mmol) was added and the reaction mixture left to stir for 1h. at room temperature under N_2. A second equivalent of $CsOH.H_2O$ (0.1g, 0.4mmol) in MeOH (2ml) was added, and the reaction mixture left to stir overnight at room temperature under N_2. The solvent was removed under reduced pressure and the residue partitioned between DCM (30ml) and water (30ml). The organic phase was collected, washed with water (30ml), dried ($MgSO_4$) and evaporated to yield a red/ brown oil. Purification by flash chromatography (SiO_2, 2:1 cyclohexane/ ethyl acetate) furnished **11** as a red/ brown oil (0.1g, 23 % based on product obtained); ^{1}H NMR δ: 6.53 (1H) & 5.79 (1H), (2 x s, =C*H*$_2$) 4.28 (2H, q, J = 7.2 Hz, OC*H*$_2$CH$_3$), 3.30 (4H, s, 5' & 6'- *H*$_2$), 3.07 (2H, t, J= 7.1 Hz, CH$_2$C*H*$_2$CN), 2.73 (2H, t, J= 7.1 Hz, C*H*$_2$CH$_2$CN), 1.34 (3H, t, J = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR δ: 163.1 (*C*=O), 134.7 (4'- S*C*COCH$_2$CH$_3$), 126.4 (4'- S (CO*C*H$_2$CH$_3$)*C*CH$_2$), 129.7, 127.6, 114.0, 113.8 (sp^2-*C*), 117.4 (*C*≡N), 62.4 (O*C*H$_2$CH$_3$), 31.4 (CH$_2$*C*H$_2$CN), 30.2 (5' & 6'- *C*), 18.8 (*C*H$_2$CH$_2$CN), 14.1 (OCH$_2$*C*H$_3$).

(b)

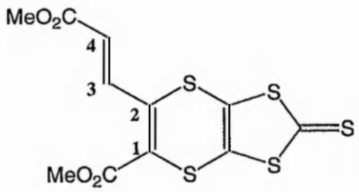
To a solution of **1** (0.2g, 0.4mmol) in THF (10ml) under N_2 was added $CsOH.H_2O$ (0.1g, 0.4mmol) in MeOH (2ml). Upon addition the orange solution turned dark red. After 1h. stirring ethyl- 2,3-dibromopropionate (0.1ml, 0.4mmol) was added and the reaction mixture left to stir for 1h. at room temperature under N_2. $CsOH.H_2O$ (0.1g, 0.9mmol) in MeOH (3ml) was added, and the reaction mixture left to stir overnight at room temperature under N_2. Tlc analysis indicated a number of compounds. The reaction mixture was heated at an oil bath temperature of 85° for 2.5 h., tlc analysis indicated no change in the composition of the mixture. The solvent was removed under reduced pressure and the residue partitioned between DCM (50ml) and water (30ml). The organic phase was collected, washed with water (20ml), dried ($MgSO_4$) and evaporated to yield a red/ brown oil. Purification by flash chromatography (SiO_2, 2:1 cyclohexane/ ethyl acetate) furnished three compounds, starting material **1** (0.04g, 20 %), the alkene **11** (0.02g, 9 %) and **12** (0.03g, 13 %) as red/ brown oils. ^{1}H NMR δ: 4.21 (2H, q, J = 7.2 Hz, OCH_2CH_3), 3.38 (1H, s, OCH_3), 3.29 (4H, s, 5' & 6'- H_2), 3.04 (2H, t, J= 7.1 Hz, CH_2CH_2CN), 2.72 (2H, t, J= 7.1 Hz, CH_2CH_2CN), 1.28 (3H, t, J = 7.2 Hz, OCH_2CH_3); ^{13}C NMR δ: 169.1 (*C*=O), 129.4, 128.4, 113.8, 111.5 (sp^2-*C*), 117.5 (*C*- N), 71.7 (*C*OCH$_3$), 62.1 (O*C*H$_2$CH$_3$), 59.3 (S*C*COCH$_2$CH$_3$), 51.1 (O*C*H$_3$), 31.5 (CH$_2$*C*H$_2$CN), 30.2 (5' & 6'- *C*), 18.7 (*C*H$_2$CH$_2$CN), 14.1 (OCH$_2$*C*H$_3$).

Reactions of dithiolate 8 with alkyne 14[5].

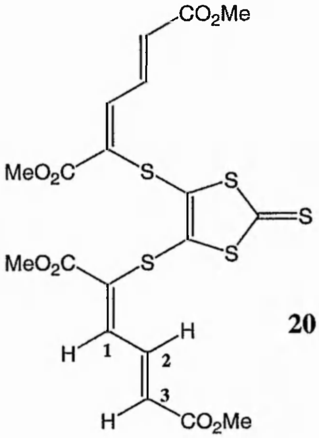
(a) Preparation of 2- Thioxo- benzo [1, 3] dithiole- 4, 7- dicarboxylic acid dimethyl ester, 18

The dibenzoylated thione **29** (1.2g, 3.0mmol) was added to a solution of sodium metal (0.1g, 5.9mmol) in dry methanol (30ml) under N_2. The reaction mix was stirred for 1 h. at room temperature. Alkyne **14** (0.5g, 3.0mmol) in methanol (15ml) was added to the cold (0°C) reaction mix in one portion. Stirring was continued overnight at room temperature under N_2. The precipitate was collected by filtration, washed with cold methanol (5ml), and dried *in vacuo* to furnish **18** as a yellow solid (0.1g, 12 %); ^{1}H NMR δ: 8.13 (2H, s, 5, 6- *H*), 4.01 (6H, s, 2 x CO$_2$C*H*$_3$); ^{13}C NMR δ: 218.8 (*C*=S), 164.6 (2 x *C*=O), 145.4 (3a-, 7a- *C*), 126.6 (4-, 7- *C*), 53.3 (O*C*H$_3$); LRMS (EI$^+$) (M+H)$^+$ 301 observed.

(b) Preparation of 19 and 20.



19



20

The dibenzoylated thione **29** (2.4g, 6.0mmol) was added to a solution of sodium metal (0.3g, 13.1mmol) in dry methanol (90ml) under N$_2$. The reaction mix was stirred for 1 h. at room temperature. Benzoic acid (0.7g, 6.0mmol) in methanol (10ml) was added and the reaction mixture stirred for 30 min. before the addition of solid sodium hydrogen carbonate (0.8g, 8.9mol). After stirring for 30 min. alkyne **14** (1.0g, 6.0mmol) in methanol (8ml) was added to the cold (0°C) reaction mix in one portion. A precipitate instantly formed. Stirring was continued overnight at room temperature under N$_2$. The precipitate was collected by filtration and the solid partitioned between DCM (20ml) and water (10ml). The organic phase was collected, washed with water (10ml), dried (MgSO$_4$) and evaporated to yield a yellow solid. The solid was purified by flash chromatography (SiO$_2$, 5:1 cyclohexane/ ethyl acetate) to furnish two compounds, *E*- 6- (2- Methoxycarbonylethen- 2- yl)- 2- thioxo- [1, 3]- dithiolo [4, 5-b] [1, 4]- dithiin- 5- carboxylic acid methyl ester **19** and 4,5((1Z, 3*E*) 1', 4'-di(methoxycarbonyl)buta- 1, 3- dien- 1- ylthio)1, 3- dithiole- 2- thione **20** as yellow solids (**19**, 0.2g, 8 %, **20**, 0.1g, 8 %); **19:** m.p. 191-192°C; ^{1}H NMR δ: 8.23 (1H, d, J = 15.4 Hz) & 6.56 (1H, d, J = 15.4 Hz) (C*H*=C*H*), 3.90 (3H, s, OC*H*$_3$), 3.80 (3H, s, OC*H*$_3$); ^{13}C NMR δ: 165.9 (*C*=O), 161.7 (*C*=O), 144.6 (2- *C*), 136.9 (3- *C*), 127.9 (1-

C), 126.0 (4- *C*), 53.8 (O*C*H$_3$), 52.4(O*C*H$_3$); HRMS (EI): Found: 363.9027, $C_{11}H_8NO_4S_5$ requires: 363.9021. **20:** m.p. 138-140°C; ^{1}H NMR δ: 7.91 (2H, dd, J = 11.4, 15.3 Hz, 2- *H*), 7.71 (2H, dd, J = 0.5, 11.4 Hz, 1- *H*), 6.35 (2H, dd, J = 0.5, 15.3 Hz, 3- *H*), 3.85 (6H, s, OC*H*$_3$), 3.78 (6H, s, OC*H*$_3$); ^{13}C NMR δ: 165.8 (2 x *C*=O), 163.8 (2 x *C*=O), 145.0 (1- *C*), 137.5 (2- *C*), 134.0 (S*C*CH), 131.3 (3- *C*), 130.1 (3a-, 7a- *C*), 53.6 (2 x O*C*H$_3$), 52.2(2 x O*C*H$_3$); LRMS (EI) MW 501 observed.

2, 2- Dimethyl- 4- tosyloxymethyl- 1, 3- dioxolane, 26

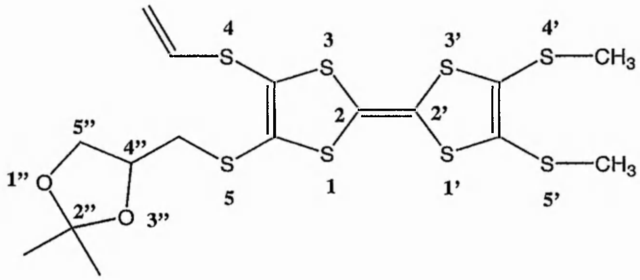
To a cold (0°C) solution of solketal 25 (4.3ml, 37.9mmol) in pyridine was added tosyl chloride (10.8g, 56.8mmol). The reaction mixture was allowed to stir for 3h. at room temperature. Ice-water (30ml) was added and stirring continued for 30min. DCM (50ml) was added and the mixture stirred for 5min. before collecting the organic phase and washing consecutively with 4M HCl solution (2 x 30ml) and water (30ml). The organic solution was dried ($MgSO_4$) and concentrated *in vacuo* to yield 26 as a pale yellow oil (8.7g, 83 %); ^{1}H NMR δ: 7.69 (2H, d, J = 8.2 Hz, Ar-*H*$_2$), 7.26 (2H, d, J = 8.4 Hz, Ar-*H*$_2$), 4.17 (1H, m, 4- *H*), 3.90 (3H, m, C*H*$_2$OTs & 5- H_α), 3.64 (1H, dd, J = 8.8, 5.3 Hz, 5- H_β), 2.33 (3H, s, Ar- C*H*$_3$), 1.23 & 1.20 (6H, 2 x s, 2 x C*H*$_3$); ^{13}C NMR δ: 144.8, 132.3, 129.7, 127.6, (Ar- C_6), 109.6 (2- *C*), 72.6 (*C*H$_2$OTs), 69.4 (4- *C*), 65.7 (1- *C*), 26.3 & 24.8 (2 x *C*H$_3$), 21.3 (Ar- *C*H$_3$).

Reaction of 1 with 26, conditions (1).

To a solution of donor **1** (0.5g, 1.1mmol) in THF (20ml) under N_2 was added $CsOH.H_2O$ (0.7g, 4.3mmol) in THF (5ml). Upon addition the orange solution turned dark red. After 2h. stirring a solution of tosylate **26** (0.6g, 2.2mmol) in THF (5ml) was added and the reaction mixture left to stir overnight at room temperature under N_2. Tlc analysis (SiO_2, 3:1 cyclohexane/ EtOAc) indicated 2 spots and baseline material. Methyl iodide (0.3ml, 5.4mmol) was added, the reaction mixture instantly lightened in colour. Stirring was continued for 5h. Tlc analysis (SiO_2, 3:1 cyclohexane/ EtOAc) indicated 3 spots, no baseline material was observed. The solvent was removed under reduced pressure and the residue purified by flash chromatography (SiO_2, 3:1 cyclohexane/ EtOAc) to yield starting material **1** (0.2g) and two compounds, **7** (0.2g, 41 %) and **34** (0.1g, 15 %); **7**, (*4', 5'- ethylenedithio- 4, 5- di (methylthio)-tetrathiafulvalene*) ^1H NMR δ: 3.26 (4H, s, 5' & 6'- H_2), 2.39 (6H, s, 2 x CH_3); ^{13}C NMR δ: 127.3, 119.3, 113.8, 109.1 (sp^2- *C*), 30.2 (5' & 6'- C), 19.4 (2 x CH_3); **34**, *(4(1, 3- Dioxolan- 4"- yl) methylthio- 4', 5'- ethylenedithio- 5- methylthio-tetrathiafulvalene*) ^1H NMR δ: 4.20 (1H, m, 4"- *H*), 4.11 (1H, dd, J = 8.6, 6.1 Hz, 5"- H_α), 3.75 (1H, dd, J = 8.6, 5.6 Hz, 5"- H_β), 3.27 (4H, s, 5' & 6'- H_2), 3.05 (1H, dd, J = 13.3, 5.2 Hz, SCH_α), 2.79 (1H, dd, J = 13.3, 7.4 Hz, SCH_β), 2.40 (3H, s, S-CH_3), 1.40 & 1.32 (6H, 2 x s, (2 x CH_3); ^{13}C NMR δ: 131.8, 123.3, 114.0, 113.8 (sp^2-*C*), 109.8 (2"- *C*), 74.9 (4"- *C*), 68.6 (5"- *C*), 38.9 (SCH_2), 30.2 (5' & 6'- *C*), 26.9 & 25.5 (2 x 2"- CH_3), 19.4 (S- CH_3).

Reaction of 1 with 26, conditions (2).

To a solution of donor **1** (0.5g, 1.1mmol) in THF (20ml) under N_2 was added $CsOH.H_2O$ (0.4g, 2.4mmol) in MeOH (5ml). Upon addition the orange solution became a little darker. After 1h. stirring methyl iodide (0.3ml, 5.4mmol) was added to the orange/red solution. A bright orange precipitate was obtained. Stirring was continued for 1h. The solvent was removed under reduced pressure and to the residue was added THF (20ml). $CsOH.H_2O$ (0.4g, 2.4mmol) in MeOH (5ml) was added to the solution. After 1h. stirring a solution of tosylate **26** (0.6g, 2.2mmol) in THF (5ml) was added and the reaction mixture left to stir overnight at room temperature under N_2.. The following day the reaction mix was refluxed for 5h. The solvent was removed under reduced pressure and the residue purified by flash chromatography (SiO_2, 2:1 cyclohexane/ EtOAc) to yield *4', 5'- Di(methylthio)- 4- ethenylthio 5- (1, 3 dioxolan-4"- yl) methylthio) tetrathiafulvalene*, **36** as a bright orange oil (0.1g, 24 %); ^{1}H NMR δ: 6.36 (1H, dd, J = 16.6, 9.4 Hz, 4- SC*H*), 5.39 (2H, m, 4- SCH=CH_2), 4.20 (1H, m, 4"- *H*), 4.10 (1H, dd, J = 8.5, 6.1 Hz, 5"-H_α), 3.76 (1H, dd, J = 8.5, 5.5 Hz, 5"- H_β), 3.07 (1H, dd, J = 13.3, 5.0 Hz, 5- SCH_α), 2.79 (1H, dd, J = 13.3, 7.9 Hz, 5- SCH_β), 2.40 (6H, s, 2 x S- CH_3), 1.40 & 1.32 (6H, 2 x s, (CH_3)$_2$); ^{13}C NMR δ: 129.3 (4'-S*C*H), 127.5, 127.4, 126.6, 112.0 (sp^2-*C*), 117.1 (4- SCH=*C*H$_2$), 109.8 (*C*(CH$_3$)$_2$), 74.8 (4"- *C*), 68.5 (5"- *C*), 38.8 (5- SCH_2), 26.9 & 25.4 (2 x 2"- CCH$_3$), 19.2 (2 x S-*C*H$_3$); LRMS (+ve APCI) (M+H)$^+$ 501 observed.



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