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New Derivatives of Strained, Redox-Active 9,10-Bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene Systems

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Terry Finn BSc. (Hons.)

Department of Chemistry
University of Durham

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

February 2000
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Declaration

The work described in this thesis was carried out in the Department of Chemistry at the University of Durham between October 1996 and September 1999. All the work is my own, unless stated to the contrary, and it has not been submitted for a degree at this or any other university.
Acknowledgements

I would like to express my thanks to the following people who have helped, guided and supported me through my time at Durham: My supervisor, Professor Martin Bryce for his insight, discussions and pure enthusiasm towards all matters. Adrian Moore for his advice and problem solving skills. Andrei Batsanov and Judith Howard for performing the X-ray crystallography. Thomas Hansen for his preliminary work on the crown systems. Marta Kamenjicki, Igor Lednev and Sanford Asher for collaboration on the cation binding studies. Ritu Katak for some of the solution electrochemistry. Derek, for his cheerful and chirpy manner, Richard for extracurricular activities and Christian for his singing and banter. My thanks to the rest of the group, past and present for putting up with me, and my petty quirks. Thanks are also due to the technical staff for all their hard work and patience and the EPSRC, for financial support. Finally, thanks to my family for their unquestionable support.
Abstract

New Derivatives of Strained, Redox-Active 9,10-Bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene Systems

Terry Finn B.Sc. (Hons.)
University of Durham (February 2000)

The synthesis of new derivatives of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene has been achieved by three general routes. A variety of Horner-Wadsworth-Emmons reagents have been prepared from the corresponding 1,3-dithiolum cations; these have been shown to react in moderate yields to generate novel derivatives of the parent system. Alternative routes have also been developed for the preparation of unsymmetrical compounds, which were unattainable by Horner-Wadsworth-Emmons reagents. This was achieved via an addition/elimination reaction and provided a successful route to unsymmetrical derivatives. The use of lithiation chemistry has been extensively developed providing a direct route to a broad range of functionalities. This methodology has paved the way to a new range of crown ethers and sterically strained cyclophanes, some of which have been extensively studied by cyclic voltammetry and X-ray crystallography.

Solution electrochemistry of the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system displayed three redox waves, representing sequential formation of the dication, radical trication and tetracation species in an $E_aE_aE_a$ process. Detailed single crystal X-ray crystal studies have been performed on the neutral compounds and a TCNQ charge transfer complex. The neutral molecule adopts a saddle-like conformation; the bis(1,3-dithiole)benzoquinone system is U-shaped through an ‘accumulating bend’ comprising the boat conformation of the central (quinonoid) ring and folding of both 1,3-dithiole rings to generate a molecular cavity. Upon oxidation to the dication, the system becomes planar and aromatic with loss of the saddle shaped cavity. The development of this system as a potential sensor for metal cations has also been investigated.
Dedicated to my parents
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1.1 General Introduction

Various categories of organic conductors have now been described,\(^1,^2\) these include systems based upon molecular charge-transfer complexes, conjugated polymers, thiaarene systems and stacked organometallic species, where the metal atoms play no active role in conduction. In the quest to develop these systems various other interesting chemical and physical phenomena have come to light. It is on one such divergence that this work is based. The focus of this thesis is the development of a specific bis(1,3-dithiole) system, which undergoes a marked conformational change upon chemical and electrochemical oxidation. A diverse range of new 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivatives have been synthesised and the development of this methodology is described in detail, along with an exploration of the electrochemical and structural properties of these molecules.

1.2 Tetrathiafulvalene

![Tetrathiafulvalene (TTF)](image)

Tetrathiafulvalene (TTF) \(1\)

Tetrathiafulvalene (TTF) \(1\) first entered the spotlight when Wudl \textit{et al.}, in 1970, reported that TTF could be oxidised sequentially in the presence of chlorine gas to the radical cation, then to the dication, both of which could be isolated.\(^3\) The relatively high stabilities of the oxidised species lie in the accompanying gain in aromaticity. The neutral form of TTF consists of two \(7\pi\) non-aromatic systems. Upon oxidation each dithiole ring donates one electron allowing the formation of two, stable \(6\pi\) Hückel-type aromatic systems (Figure 1.1). The oxidation is reversible in a range of solvents and can be achieved electrochemically and monitored using cyclic voltammetry (CV), which reveals that the radical cation is formed at \(E^{1/2} = +0.34\) V followed by the dication at \(E^{1/2} = +0.71\) V vs Ag/AgCl (Figure 1.2).
Figure 1.1: Redox behaviour of TTF.

Figure 1.2: Cyclic Voltammogram of Tetrathiafulvalene 1.
1.3 Organic Metals

It is in the development of organic metals that TTF has made the greatest contribution, although TTF derivatives are now emerging as important building blocks in the wider context of supramolecular and materials chemistry. In 1973, it was discovered that TTF formed a 1:1 charge transfer complex with the electron acceptor tetracyano-p-quinodimethane (TCNQ).

Charge transfer (CT) complexes are often highly crystalline materials, prepared by the mixing of an acceptor and donor species in boiling solvents such as acetonitrile.

![7,7,8,8-Tetracyano-p-quinodimethane (TCNQ)](NC)\(^{\text{bN}}\)

The crystal structure of TTF-TCNQ illustrated one of the key requirements for conduction in a charge transfer complex, namely, that the crystal lattice consists of segregated stacks of planar TTF and TCNQ molecules. The geometry of each stack appears tilted relative to the stacking axis with the planes of donor and acceptor molecules lying in opposite directions producing a so-called ‘herringbone structure’ (Figure 1.3). Within each stack, TTF and TCNQ molecules align such that the exocyclic carbon-carbon double bond of one molecule lies directly over the ring of the molecule adjacent to it in the stack. This is referred to as “ring-over-bond” stacking. This arrangement maximises π-overlap within a stack.

A partial electron transfer of 0.59 electrons per molecule occurs between TTF and TCNQ. This has been elucidated using a range of spectroscopic and structural techniques. The formation of a mixed valence band is a prerequisite for conductivity in CT complexes. In 1:1 complexes, this is achieved by partial charge transfer; in complexes of different stoichiometry, e.g. 1:2 or 2:3, this can also be achieved by full charge transfer. In TTF-TCNQ, both donor and acceptor stacks contribute to the overall conductivity. Conductivity measurements showed unusually high electrical conductivity.
along the stacking axis ($\sigma_n = 500 \text{ Scm}^{-1}$) with little interaction between the stacks and conduction $10^3$-$10^4$ times lower along the other axis. These anisotropic charge transfer complexes have been termed ‘1-dimensional organic metals’.

Figure 1.3: Herringbone structure of TTF 1 and TCNQ 2, in the complex TTF-TCNQ.

1.4 Modification of the TTF Unit

In an effort to improve the conductivity of TTF containing charge transfer complexes various chemical modifications have been implemented and studied. One such modification concerns the exchange of sulfur for more polarisable atoms such as Se and Te. Both tetraselenafulvalene (TSF) and tetratellurafulvalene (TTeF) formed charge transfer complexes with TCNQ and exhibited higher conductivity than TTF-TCNQ. The increased conductivity has been attributed to increased intra- and inter- stack interactions.
Other approaches have utilised the sigma-bond framework by the addition of electron releasing groups such as alkyl groups, to lower the oxidation potential of TTF and thereby favour the charge transfer process.9

One important discovery not only utilised diffuse atoms and inductive alkyl groups but also inorganic closed-shell anions as the acceptors. These combined modifications paved the way to the first organic superconductors.10

1.5 Organic Superconducting CT Complexes

The attainment of superconductivity is one of the most competitive areas of materials research. When superconducting materials are cooled below a critical temperature, \( T_c \), their electrical resistance falls to zero; therefore these materials consume no current. Early examples required \( T_c \) temperature close to absolute zero, this rendered the materials impractical. Therefore, the search began to understand the processes involved and develop materials capable of superconducting at higher temperatures. The majority of this work became based on synthesised ceramics, which gradually showed improved \( T_c \) temperatures. Now materials with \( T_c \) temperatures well above the technologically important \(-196^\circ C\) (liquid nitrogen) have been prepared. Chemists continue to try and raise the \( T_c \) of organic superconductors. To date, no superconducting CT complexes have shown superconductivity at \( T_c \) comparable to ceramic superconductors.

\[
\text{Tetramethyltetraselenafulvalene (TMTSF) 3}
\]

The first example of a superconducting organic system was prepared by Bechgaard and coworkers in 1979-1980 and consisted of a series of \((\text{TMTSF})_2X\) salts \((X = \text{ClO}_4^-, \text{PF}_6^-, \text{AsF}_6^-, \text{FSO}_3^- \text{and ReO}_4^-)\).10 These CT salts exhibited metal-insulator transitions between 10 and 200 K. However, under hydrostatic pressure superconductivity was recorded. The first example \((\text{TMTSF})_2^{*}\text{PF}_6^-\) became
superconducting at 0.9 K, 12 kbar and became a cornerstone in the development of organic superconductors.

The X-ray crystal structure of (TMTSF)$_2$BrO$_4$ can be seen in Figure 1.4. Similarities can be drawn with one-dimensional metals; the molecules of TMTSF 3 are planar and form defined stacks. The charge compensating anions occupy the cavities created by ‘ring-over-bond’ stacking and exert negligible influence on the conductivity. The conduction pathway can be attributed to a mixed valence TMTSF stack and has been rationalised by band theory. An important aspect of the donor stacks is the relatively short and similar intrastack and interstack Se—Se contacts, which form an infinite sheet of interactions. It is these interactions which give rise to two-dimensionality, rather than the one-dimensionality of TTF-TCNQ. The formation of a three-dimensional array in (TMTSF)$_2$BrO$_4$ is disrupted by the presence of the BrO$_4$ counter ions.

Figure 1.4: X-ray structure of (TMTSF)$_2$BrO$_4$, interstack Se—Se distances are shown on the left, whilst the intrastack distances are shown on the right.
1.6 Extended TTF-Analogues

In an effort to break away from the basic tetrachalcogenofulvalene framework and perhaps provide new crystal packing motifs with improve conductivities, a range of extended π-systems have been prepared. One rationale behind the synthesis of extended TTF derivatives is to minimise the effects of coulombic repulsion within the dicationic state. The increased spatial separation of the 1,3-dithiolium cations was expected to lower the energy required for the second oxidation (radical cation to dication). The choice of spacer group is also important. The presence of the vinylic spacer serves to stabilise the intermediate radical cation by delocalisation between the dithiole rings.

In the majority of cases the spacer group can be subdivided into three general categories:

1) Those incorporating vinylic spacers \((n = 1, 2, 3, \text{ etc.})\).
2) Those including heteroaromatic groups (furan, thiophene and pyrrole).
3) Those based on quinonoidal systems.

1.6.1 Vinylic Redox Systems

The use of conjugated vinylic spacer units between 1,3-dithiole rings was first introduced by Yoshida et al. in 1982.\(^{12}\)

These compounds showed increased stability of the radical cation and dication, relative to TTF 1, as demonstrated by cyclic voltammetry (Table 1.1).
In comparison with TTF 1, donor 4 displayed lower first and second oxidation potentials. This has been rationalised on the basis that increased delocalisation results from the insertion of two sp\(^2\) hybridised carbon atoms and by the reduced through-space effects of increased separation of the dithiole rings. The formation of the radical cation is favoured as a more conjugated carbon skeleton effectively reduces the average charge per atom. The dication is also favoured as the through-space influence of one cation is reduced relative to the other. The difference between the consecutive redox waves (\(E_2^{1/2} - E_1^{1/2}\)) has been shown to decrease further with the inclusion of two additional vinylic carbon atoms (compound 5); in this example, the two redox waves coalesced into a single, two-electron, oxidation wave. The further incorporation of sp\(^2\) carbon atoms did not, however, lower the first redox potential from that of compound 5. This implies that delocalisation is already maximised with the insertion of one vinylic group. In compound 5, both 1,3-dithiole rings are now acting independently of one another. These studies proved that π-spacers suppress coulombic repulsion and promote the formation of the dication at a lower potential.

Longer polyalkenic spaced compounds have been synthesised by Nguyen et al., compounds 6-8.\(^{13}\) While extension of the spacer length does not further change the first oxidation potential, the direct formation of the dication species through a single two-electron transfer was observed for 7. It was reported that the replacement of the ester group by methyl groups 8, leads to a substantial decrease in stability, due to electron donation. This introduces a major limitation that requires extended vinylic systems to be counterbalanced by electron-withdrawing groups on the dithiole units.

To date, the longest vinylic spaced TTF analogue has been prepared by Markl et al.\(^{14}\) and incorporates 16 sp\(^2\) carbon atoms, compound 9. Again, the compound underwent

<table>
<thead>
<tr>
<th>Compound</th>
<th>(E_1^{1/2}) (V)</th>
<th>(E_2^{1/2}) (V)</th>
<th>(E_2^{1/2} - E_1^{1/2}) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.34</td>
<td>0.71</td>
<td>0.37</td>
</tr>
<tr>
<td>4</td>
<td>0.20</td>
<td>0.36</td>
<td>0.16</td>
</tr>
<tr>
<td>5</td>
<td>0.22 (2e)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1.1: Cyclic Voltammetric data for TTF 1 and vinylic bridged compounds 4 and 5.
a single, two-electron, oxidation. Interestingly, the compound incorporated cyano
substituents at the 4 and 5 positions of the 1,3-dithiole rings: again, an example of
increased stability arising from the presence of electron-withdrawing groups.

![Chemical structures](image.png)
1.6.2 Heteroaromatic Spacers

While polyalkenic spacers showed reduced coulombic repulsion upon oxidation, their major limitations lie in their limited stability and poor solubility. These problems were initially solved by the introduction of a heterocyclic spacer unit. TTF analogues incorporating five-membered heterocyclic spacers such as furan, thiophene and pyrrole have been well documented, 10-12.\(^\text{15-18}\)

\[
\begin{align*}
10 & \quad X = O \quad a \quad R = H \\
11 & \quad X = S \quad b \quad R = SMe \\
12 & \quad X = NMe \quad c \quad R = CO_2Me
\end{align*}
\]

All these compounds showed two reversible, one-electron oxidations by cyclic voltammetry. The introduction of a heterocyclic spacer reduced the potentials of both the first and second oxidations relative to TTF 1. Again, this can be understood on the grounds of increased delocalisation and reduced coulombic repulsion. However, contrary to expectations, the first oxidation potential decreased in the order thiophene > furan > pyrrole. Although the aromatic resonance energy of the heterocycle is important, this cannot be the only factor since furan should exhibit the lowest first oxidation potential. The lower oxidation of pyrrole has been attributed to pyrrole's ability to stabilise cationic structures with the positive charge localised on the nitrogen atom. The introduction of the heterocyclic spacer produced in every case a compound with reduced coulombic repulsion providing a small step in the right direction regarding improved conduction.

The next logical step in the development of a heterocyclic spaced donor was to further lower the oxidation potentials by the introduction of multiple spacer units analogous to the multi-vinylic systems previously described. Early examples of this approach were constructed around terthienyl and tetrathienyl cores, compounds 13 and 14, respectively.\(^\text{19}\)
The stepwise addition of thiophene rings to the spacer unit has provided a valuable insight into the structure-property relationship of heterocyclic systems. Elongation of the thiophene backbone produced unexpected changes in the CV and UV-vis spectroscopic data.

The cyclic voltammery of 13 showed two, consecutive, one-electron oxidations with a lowering of both first and second oxidations of the donor (relative to its vinylic equivalent). As previously described, the insertion of four sp\(^2\) carbon spacer units (compound 5) produced a single, two-electron oxidation wave. A similar phenomenon was observed for 13, with the two oxidation waves becoming almost coalesced, \((\Delta E^{1/2} = 90 \text{ mV})\). However, increasing the number of thiophene spacers to three, 14, lead to an increase in both oxidation potentials. This unexpected behaviour has been rationalised due to an increase in rotational disorder, which distorts the conjugated backbone between the dithiole rings leading to a poorer electron donor. As expected, the replacement of alkyl groups with electron-withdrawing ester groups lead to an increase in both oxidation potentials.

The effects of functionalisation has been studied for a similar thiophene system, compound 15, which was synthesised in an effort to improve solubility.\(^{20}\) This was achieved by derivatisation of both the vinylic and heterocyclic framework.
The UV-vis absorption measurements performed on compound 15 showed that the site of functionalisation played a pivotal role in modifying the conjugated pathway of the system. The introduction of solubilising chains on the medial thiophene produced significant red shifts (i.e. increased conjugation) of the $\lambda_{max}$ value in comparison with the unsubstituted terthienyl core. These shifts suggest a change in geometry of the terthienyl core. Whereas substitution of a methyl group on $R'$ produced a blue shift (i.e. less conjugation) attributed to a loss of planarity due to steric interactions.

A drawback with heterocyclic spacers lie in the steric effect of functionalisation, which contributes to rotational disorder around the core unit, leading to distorted intramolecular $\pi$-overlap. Furthermore, the use of additional heterocyclic spacers will probably be ineffective, as these systems seem to adopt an unfavourable twisted conformation. Therefore, more rigid spacer groups have been explored.

In an attempt to overcome these problems Takahashi et al. synthesised a range of heteroquinonoidal extended donors, compounds 16, 17 and 18.
Aryl and naphthyl spacer units have been incorporated into donor molecules to increase ring stability by hindering conformation changes. The extension of the donor π-system also contributed to increased stabilisation of the dication.

The cyclic voltammetry of compounds 16-18 revealed two, well-defined, reversible, one-electron oxidations. The first oxidation potential decreased in the order thiophene > furan > pyrrole, again, this can be rationalised by canonical forms and electronegativities. Table 1.2 shows a comparison of the electrochemistry of thiophene, benzothiophene and naphthothiophene functionalities.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}$ (V)</th>
<th>$E_{2/2}$ (V)</th>
<th>$E_{2/2} - E_{1/2}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16a</td>
<td>0.11</td>
<td>0.34</td>
<td>0.23</td>
</tr>
<tr>
<td>17b</td>
<td>0.31</td>
<td>0.55</td>
<td>0.24</td>
</tr>
<tr>
<td>18</td>
<td>0.36</td>
<td>0.65</td>
<td>0.29</td>
</tr>
</tbody>
</table>

*Table 1.2: Cyclic Voltammetric data for compounds 16a, 17b and 18.*

The CV data showed that increased aryl functionality on thiophene increased both the oxidation potentials and the difference between them. The explanation for this lies in the fact that aromaticity is lost in the aryl ring upon oxidation, providing a barrier to oxidation, which increases the oxidation potentials. The barrier to oxidation increases the greater the number of aromatic atoms are incorporated into the spacer unit, hence the oxidative potential is greater for the naphthyl derivative.

### 1.6.3 Quinonoidal Redox Systems

The use of a quinonoidal spacer group is in some respects similar to those of the heterocyclic systems discussed previously. Again, the 1,3-dithiole rings are separated by a conjugated pathway that increases π-delocalisation and reduces coulombic repulsion. The quinonoidal spacer group is a rigid spacer which fixes the geometry of the two dithiole rings thereby preventing rotational disorder and providing increased stability. However, in quinonoidal systems the spacer group gains aromaticity upon oxidation. This
provides a driving force, which lowers the difference between sequential oxidations (Figure 1.5).

Figure 1.5: The redox behaviour of quinonoidal spacer units.

Due to the gain in aromaticity and relative stability of the charged species, almost all quinonoidal spaced donors exhibit lower oxidations in the cyclic voltammetry than similar vinylic or heteroaromatic spaced moieties. These compounds are, therefore, very good electron donors. However, these redox processes are generally regarded as being quasi-reversible, the gained aromaticity being a barrier to reduction.

The preparation of compound 21 was first claimed, without experimental details, in an early patent by Miles et al.\textsuperscript{22}

This work was later continued by Cava et al, who prepared the bis(benzo-1,3-dithiole) derivative 22 and its dication tetrafluoroborate salt 23.\textsuperscript{23} By using differential pulse polarography the dication 23 could be sequentially reduced back to the monodithiolium radical cation, $E_{1/2} = +0.330$ V and the neutral compound, $E_{2/2} = \ldots$
+0.057 V (no reference stated). The low value for the second reduction illustrates that the effects of coulombic repulsion are negated by the driving force to aromatise.

Yamashita et al. repeated the work of Miles et al. in 1989,\textsuperscript{24} believing that quinonoidal spaced systems represented good electron donors, but that they were flawed by poor stability. Yamashita prepared a wide range of quinonoidally spaced systems in an attempt to improve stability. Compound 21 was also prepared using an alternative synthetic approach. CV data showed that compound 21 exhibited two reversible, one-electron oxidations (-0.11 V and -0.04 V vs SCE). A range of other quinonodial donors incorporating various spacer units and dithiole functionalities were prepared (Figure 1.7).

Detailed investigations revealed that compounds containing either benzo (21) or naphthyl (27) spacers were air sensitive. These compounds showed two, reversible, one-electron oxidation waves by CV (vs SCE). The use of dibenzo-1,3-dithiole rings instead of 1,3-dithiole rings renders analogues 22, 24 and 25 stable towards air and these compounds show a reversible, two-electron oxidation wave. The use of a cyclopentadiene adduct of \textit{p}-benzoquinone as a spacer, 23 and 26, gave compounds which were stable to air and also produced a reversible, two-electron oxidation wave. The exception appeared to be compound 28; this incorporated an anthraquinone spacer group. This compound showed an irreversible oxidation at +0.25 V. Compounds 21, 22, 24 and 27 gave charge transfer complexes with TCNQ 2.
Figure 1.7: Quinoidal donors prepared by Yamashita et al.

1.7 Quinoidal Based Redox Systems

Although first synthesised by Akiba et al., many of the properties of anthraquinonoidal spaced systems, including their solid state structure and electrochemistry, have been elucidated by Bryce et al. Donor 29 was synthesised from anthraquinone.
The crystal structure shows the neutral donor 29 adopts a saddle-shape with the central quinonoid ring severely distorted into a boat conformation. Donor 29 also formed a highly conducting 1:4 charge transfer complex with TCNQ 2. The crystal structure of the CT salt showed that the central quinonoidal spacer was now a planar anthracene ring, with the attached 1,3-dithiolium rings almost orthogonal to this plane (Figure 1.8). The crystal structure showed that compound 29 formed a 1:4 CT salt with TCNQ 2. This is an example of a non-stoichiometric CT salt in which the dication plays no direct role in the conduction process: the observed high conductivity ($\sigma_n = 50$ S cm$^{-1}$) arises from a partially-filled band on the acceptor stacks (two electrons per four TCNQ molecules) as a consequence of the 1:4 stoichiometry.

The distorted structure of neutral donor 29 is attributed to peri-interactions between anthracene bound hydrogens and the large sulfur atoms of the dithiole rings. The cyclic voltammetry shows that on oxidation the system exhibits a quasi-reversible, two-electron oxidation, to the dication species. Again, the explanation for the two-electron oxidation lies in aromatisation of the central anthracene ring. The change in geometry of the donor upon oxidation creates a barrier to reduction of the dication rendering the redox system quasi-reversible.
Figure 1.8: The crystal structure of a) neutral donor 29 and b) its 1:4 TCNQ charge transfer salt.

To further elucidate the electrochemistry of these systems Bryce et al. synthesised compound 30, for which the pentyl substituents provided increased solubility for low temperature studies which allowed for the first time, the +3 and possibly the +4 oxidation states to be observed. The variable temperature CV data for compound 30 are shown in Figure 1.6.
The first redox wave ($E_{\text{ox}} = +0.28$ V vs Ag/AgCl) was a quasi-reversible, two-electron oxidation to yield the dication and is directly analogous to the other quinonoidal systems. Subsequently, there were two further, sequential, one-electron oxidations of the anthracene system. These afforded the trication radical and tetracation species, respectively. The first anthracene oxidation ($E_{\text{ox}} = +1.64$ V) is cleanly reversible, whereas the second anthracene oxidation ($E_{\text{ox}} = +2.2$ V) was at the limit of the solvent window for dichloromethane and was not cleanly observed. The data also revealed that the first oxidation process at +0.28 V was temperature independent; however, the coupled reductive peak of the dication to the neutral compound is shifted progressively to more negative potentials with decreasing temperature. This is undoubtedly due to a stabilisation within the $6\pi, 1,3$-dithiolium rings, at the dication stage. The marked conformational change that must occur on the reduction, accounts for the temperature dependence and the quasi-reversibility of this step.

![Figure 1.6: The variable temperature cyclic voltammetry of compound 30.](image)
Yamashita et al. have also prepared compounds incorporating naphtho[c]-1,2,5-thiadiazole spacers, compound 31. 

![Chemical structure of compound 31](image)

31a R = H  
31b R = Me  
31c R-R = SCH₂CH₂S  
31d R-R = benzo

These compounds contain only two hydrogen-sulfur peri interactions. A crystal structure of the neutral compound 31 revealed the formation of a distorted saddle conformation.

Only a limited number of aryl spaced redox systems have been prepared, some having benzannelated spacers.

![Chemical structures of compounds 32-34](image)

32  
33  
34

Martin et al., synthesised compounds 32-34 providing a systematic increase in the aryl π-spacer. Cyclic voltammetry studies of these compounds allowed a comparison of their oxidation potentials (Table 1.3). Compounds 32-34 showed a quasi-reversible first oxidation wave involving two electrons to form the corresponding
dication. An irreversible, second oxidation to the trication was also observed as a shoulder at 1.1-1.3 V.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{ox}}$ / V</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>0.28 (2e)</td>
</tr>
<tr>
<td>32</td>
<td>0.39 (2e)</td>
</tr>
<tr>
<td>33</td>
<td>0.50 (2e)</td>
</tr>
<tr>
<td>34</td>
<td>0.49 (2e)</td>
</tr>
</tbody>
</table>

Table 1.3: Cyclic Voltammetric data for compounds 28, 32-34 (vs. SCE).

The cyclic voltammetry data showed that increased π-extension on the central spacer increased the potential of the first oxidation. This is presumably due to difficulties in aromatising the extended system. Therefore, compounds 32-34 represent poorer donors than the anthracene bridged compound 28.

Investigations into mixed heteroatom quinonoidal systems have also been conducted by Bryce et al. 1,3-Selenathiole analogues, e.g. 35, were synthesised and their electrochemistry investigated.\(^\text{29}\)

The donor ability of the bis(1,3-dithiol)-9-10-dihydroanthracene system is significantly reduced by the incorporation of one selenium atom into the ring system (35a $E_{\text{ox}} = 0.45$ V, 35b $E_{\text{ox}} = 0.47$ V). This was consistent with known selenium analogues of TTF derivatives, and is attributed to selenium forming weaker π-bonds with carbon than

\[ 35a \text{ R = H} \\
\text{ b R = Me} \]
does sulfur. Thus, the selenium cations are less stable than their sulfur counterparts. Selenium atoms are less able to redistribute charge; this raises the overall energy required for ionisation of selenium donors.

Another development of quinonoidal spaced systems is the preparation of multistage redox donors, the rationale being the development of a donor capable of donating more than 4 electrons. Two groups have spearheaded this work, Bryce et al. prepared compounds 36-38 and Martin et al. prepared the first bis[bis(1,3-dithiole)-9,10-dihydroanthracene] system 39. The electrochemistry of compounds 36-37 revealed that functionalisation of the anthracene ring increased the oxidation potential for the first two-electron, quasi-reversible oxidation to between 0.50-0.61 V. The oxidation of the ferrocene rings occurred simultaneously to yield a cleanly reversible, one-electron oxidation per ferrocene. Compound 39a showed the formation of a bis-dication at 0.50 V (4e). Again this process was quasi-reversible.

Recently, Martin et al. reported the first bis(1,3-dithiol)-9-10-dihydroanthracene C₆₀-based, donor-acceptor system 40. Redox properties determined by cyclic voltammetry revealed the presence of four cathodically shifted reduction waves, relative to C₆₀, which correspond to the C₆₀ core, and a two-electron single oxidation wave to form a stable dication.
36

37

38

39

39a R = H
b R = SMe
c R-R = SCH₂CH₂S

40
1.8 Conclusion

The 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene molecule represents an interesting electron donor system, which adopts a saddle-shaped conformation created by peri-interations between sulfur and hydrogen atoms. This conformation creates a cavity between the two 1,3-dithiole units. These compounds readily donate two electrons (the dication is formed at a lower potential than TTF) and are capable of donating up to 4 electrons. On oxidation, a dramatic conformational change occurs which renders the anthracene spacer planar with loss of the cavity. At the outset of this project only a very limited number of derivatives had been synthesised. We recognised it was an interesting challenge to develop these systems with the aim of exploring chemical derivatisation, cavity properties, electrochemistry and structural conformations.
2.1 Introduction

Compound 28, has been independently studied by the groups of Bryce et al.$^{26,34-36}$ and Yamashita et al.$^{24}$ Studies have shown that compound 28, undergoes a two-electron oxidation, which was observable by cyclic voltammetry as a single quasi-reversible redox wave. However, the insolubility of the generated dication precluded further investigation into the higher oxidative states of the system.

![Chemical structure](image)

\[28 \ R^1 = R^2 = H \]
\[34 \ R^1 = \text{Me}; R^2 = \text{n-pentyl}\]

The oxidation of the more soluble compound 34 was studied by cyclic voltammetry in three different solvents (dichloromethane, acetonitrile and propylene carbonate) under rigorously anhydrous conditions.$^{27}$ Studies in dichloromethane at reduced temperature (-70°C) revealed three distinct oxidative steps. The first redox wave ($E_{\text{ox}} = +0.28 \text{ V}$) was a quasi-reversible, two-electron transfer to yield the dication species and was comparable to that of other similar donors at 20°C. The first anthracene oxidation ($E_{3^{1/2}} = +1.64 \text{ V}$) was cleanly reversible, a second anthracene oxidation ($E_{4^{1/2}} = \text{ca. +2.2 V}$) was also observed, but was at the limit of detection due to solvent masking.

This chapter aims to broaden our understanding of the electrochemistry and charge-transfer properties of the bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system by studying new derivatives with solubilising substituents. Initial experiments on the lithiation of this system are also described. This aspect is developed in detail in Chapter 3.
In general, bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene compounds have been prepared via Horner-Wadsworth-Emmons reactions onto anthraquinone in moderate yields. The required Horner-Wadsworth-Emmons reagents were first developed by Akiba et al, who described the reaction of benzo-1,3-dithiolium tetrafluoroborate salts 40, with trialkyl phosphites in dry acetonitrile to give the corresponding phosphonate ester 41, in > 90% yield. These phosphonates were then deprotonated with n-butyllithium in tetrahydrofuran at -78°C generating the reactive anion, 42, which proved to be more reactive than the analogous trialkylphosphine ylid. Wittig reagents fail to react with anthraquinone, however, the more reactive phosphonate anion reacted with anthraquinone and a range of heteroatom containing anthrones. In this example, Akiba quenched the anion 42 with 10H-9-thiaanthracen-10-one to give 43 (Scheme 2.1).

\[
\begin{align*}
\text{40} & \rightarrow \text{41} \\
\text{ii)} & \rightarrow \text{42} \\
\text{iii)} & \rightarrow \text{43}
\end{align*}
\]

*Scheme 2.1 Reagents and Conditions: i) NaI, P(OR)\text{3}, MeCN, rt. ii) n-BuLi, THF, -78°C. iii) 10H-9-thiaanthracen-10-one*
At the outset of this project, the literature contained only a limited range of functionalised bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene compounds, utilising either alkyl or aryl groups on the dithiole rings, or with the 2 and 6 positions of the anthracene spacer bearing substituents.\textsuperscript{30-32} We decided to use 2,6-dihydroxyanthraquinone (anthraflavic acid), 51, as a starting material for new derivatives, \textit{e.g.} 44.
2.2. Synthesis of 2,6-dibutoxy-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 44

The required phosphonate reagent 50 was described in the literature and prepared in seven steps, outlined in Scheme 2.2.36

Scheme 2.2 Reagents and Conditions: i) EtOH, rt, 5h. ii) (EtO)₂CHCH₂Br, EtOH, reflux, 24h. iii) C₆H₅SO₄, 70°C, 4d. iv) HPF₆, 0°C, 1h. v) NaBH₄, THF/PrOH, 0°C, 1h. vi) HPF₆, Ac₂O/Et₂O, 0°C, 1h. vii) NaI, Me₂CO, rt, 1h. viii) P(OMe)₃, MeCN, rt, 1h.
2,6-Dialkoxy-anthraquinones were prepared via Williamson ether synthesis from anthraflavic acid 51, which reacted with iodobutane and iodohexane in the presence of silver (I) oxide to afford derivatives 52 and 53 in 56% and 57% yields, respectively (Scheme 2.3).

![Scheme 2.3](image)

**Scheme 2.3 Reagents and Conditions:** i) iodobutane, Ag₂O, DMF, rt, 2d. ii) iodohexane, Ag₂O, DMF, rt, 2d

2,6-Dibutoxyanthraquinone 52 underwent Horner-Wadsworth-Emmons reaction with the carbanion generated from phosphonate ester 50, to yield the anthracenediyliidene derivative 44 in 51% yield, which proved to be soluble in a wide range of organic solvents (Scheme 2.4).
Scheme 2.4 Reagents and Conditions: i) LDA, THF, -78°C, 3h. followed by compound 52.

Using a similar procedure we synthesised analogue 55, from the literature dimethyl phosphonate ester 54, in 59% yield (Scheme 2.5).³⁷

Scheme 2.5 Reagents and Conditions: i) LDA, THF, -78°C, followed by compound 53.
2.3 Functionalisation of 2,6-dibutoxy-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 44

Having prepared the highly soluble compounds 44 and 55 we sought to expand the synthetic diversity of the system, via lithiation chemistry analogous to that of TTF 1; the transient anion could then be quenched with a range of electrophiles allowing the attachment of a range of functional groups.

Green first showed that formation of the TTF anion 56 could be accomplished with either n-butyl lithium (n-BuLi) or lithium disopropylamide (LDA) at -78°C and that the resulting anion could then be trapped with a wide range of electrophiles, to give mono-substituted derivatives in moderate yields (Scheme 2.6 and Table 2.1).^{38}

Temperature is critical for the success of TTF anion reactions. At temperatures above -78°C, disproportionation of the TTF monoanion occurs to give a range of multi-lithiated species, which lead to multi-substituted products and a substantial drop in reaction yield. These problems are avoided if the temperature is carefully controlled at -78°C.

\[
\begin{array}{c}
\text{1} \quad \overset{i) \quad \text{LDA or n-BuLi, THF or Et\textsubscript{2}O, -78°C.}}{\longrightarrow} \\
\text{56} \\
\end{array}
\]

**Scheme 2.6 Reagents and Conditions: i) LDA or n-BuLi, THF or Et\textsubscript{2}O, -78°C.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Electrophile</th>
<th>(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>(\text{Et}_3\text{OPF}_6)</td>
<td>Et</td>
</tr>
<tr>
<td>58</td>
<td>DMF, followed by H\textsubscript{2}O</td>
<td>CHO</td>
</tr>
<tr>
<td>59</td>
<td>Cl\textsubscript{2}CO\textsubscript{2}Et</td>
<td>CO\textsubscript{2}Et</td>
</tr>
<tr>
<td>60</td>
<td>CO\textsubscript{2} followed by HCl</td>
<td>COOH</td>
</tr>
</tbody>
</table>
Table 2.1: Electrophiles used in TTF anion reactions.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>61</td>
<td>MeC(O)Cl</td>
<td>C(O)Me</td>
</tr>
<tr>
<td>62</td>
<td>Me₂SO₄</td>
<td>Me</td>
</tr>
<tr>
<td>63</td>
<td>HCOH</td>
<td>CH₂OH</td>
</tr>
</tbody>
</table>

Efforts to employ lithiation chemistry on compound 44 proved problematic. Compound 44 was deprotonated at -78°C, using one equivalent of lithium diisopropylamide to generate the mono-anion. The lithium anion was then trapped with an excess of tosyl bromide. However, the reaction produced a range of substituted products, with the majority being the mono-substituted product (TLC evidence).

Attempts to tetra-lithiate the system also proved problematic. Compound 44 was lithiated using 5 equivalents of lithium diisopropylamide to generate the tetra-anion. This was then quenched with excess tosyl bromide to give tetrabromide 64 in low yield (12%, Scheme 2.7).

Scheme 2.7 Reagents and Conditions: i) LDA (5 equivalents), THF, -78°C, 3 h, followed by tosyl bromide.
Due to the formation of multiple products, which were difficult to separate by chromatography, and poor yields, this approach was abandoned and alternative precursors to functionalised derivatives were devised (Chapter 3).

2.4 Electrochemistry of the bis(1,3-dithiol-2-ylidene)-9,10-dihydro anthracene system

The solution electrochemistry of compounds 44 and 55 has been studied by CV and by square wave voltammetry (SQV) in acetonitrile. Both compounds displayed three redox waves at the following potentials: compound 44 $E^{ox}$ 0.320 V, 1.49 V and 1.64 V; compound 55 $E^{ox}$ 0.275 V, 1.47 V and 1.62 V (vs Ag/AgCl). The lower values of these potentials for the latter compound, especially $E^{ox}$, is consistent with the trend observed with compounds 28 and 29, arising from tetramethyl substitution on the 1,3-dithiole rings. Analysis of the data is consistent with an EqEqEq process (Eq = quasi-reversible). Figure 2.1 shows the SQV and CV for compound 44. The first wave is a two-electron process (neutral to dication, with aromaticity gain at the dication stage) and the second, reversible, one-electron wave is ascribed to oxidation of the anthracene unit (dication to radical trication) by analogy with previous work. Repeated recycling through the first wave resulted in no significant change in the CV, demonstrating that this is a chemically reversible redox process. The effect of the alkoxy substituents is to shift the second oxidation wave to lower potentials by ca. 150 mV (cf. compound 28 $E^{ox}_2$ 1.64 V, and 29 $E^{ox}_2$ 1.62 V, under the same conditions). The entirely new feature of compounds 44 and 55 is the presence of a third redox wave, which is also a quasi-reversible, one-electron process. This wave has not been unambiguously observed in previous derivatives of the system 28, (it was very tentatively seen for the 2,3-dipentylanthracene analogue 34 at ca. +2.2 V, i.e. at the limit of the solvent window) and we assign this process to the formation of the tetracation species $44^{4+}$ and $55^{4+}$ which could be stabilised by the electron-donating effect of the two alkoxy substituents. This assignment is further supported by comparison with the voltammetric data for 9,10-diphenylanthracene, which undergoes two, single-electron, oxidation waves ($E^{ox}_1$ 1.23 V,
and $E_{2}^{\text{ox}}$ 1.70 V, vs. SCE in MeCN) and these waves (especially $E_{2}^{\text{ox}}$) are cathodically shifted in 9,10-di(p-methoxyphenyl)anthracene ($E_{1}^{\text{ox}}$ 1.15 V, and $E_{2}^{\text{ox}}$ 1.37 V). This latter separation ($\Delta E^{\text{ox}}$ 220 mV) approaches the value ($\Delta E^{\text{ox}}$ 150 mV) which we observe for $E_{2}^{\text{ox}}$ and $E_{3}^{\text{ox}}$ for compounds 44 and 55. We eliminated the possibility that this third wave for 44 and 55 was derived from a different chemical species (e.g. a species in which the alkoxy groups had been cleaved in the electrochemical reaction) as recycling between 1.00V and 1.75 V for 50 cycles resulted in no significant change in the appearance of the CV.

![SQV and CV graphs](image)

*Figure 2.1: The SQV (top) and CV (bottom) for compound 44.*
2.5 Single Crystal X-ray Crystallography

The structure of compound 44 has been determined by single crystal X-ray analysis (Figure 2.2). Neutral molecule 44 adopts a saddle shaped conformation, in a similar manner to previously reported analogues. The anthracene system is folded along the C(7)...C(21) vector by 34.6°. The fold angle is slightly smaller than in previous systems, which vary from 38-45°, and the system actually comprises two isolated benzene π-systems, linked to C(7) and C(21) by single bonds. The bis(dithiol)benzoquinone system displays the usual ‘accumulating bend’ inward, with the dihedral angle of 91.5° between the S(1)...C(9)...C(10)...S(2) and S(3)...C(23)...C(24)...S(4) planes (literature 76-87°). Both dithiole rings are folded along the S(1)...S(2) and S(3)...S(4) vectors, by 6.6° and 10.0°, respectively. The crystal packing motif is a dimer, wherein the cavities of the bis(dithiol)benzoquinone systems engulf each other.

The molecular structure of 55 (Figure 2.3) is similar to that of 44. Folding of the anthracene moiety in 55 [44.8° along the C(7)...C(25) vector] is stronger, but folding of the dithiole rings [5.9° and 12.2° along the S(1)...S(2) and S(3)...S(4) vectors, respectively] means that the overall dihedral angle between the S(1)...C(9)...C(10)...S(2) and S(3)...C(27)...C(28)...S(4) moieties (90.0°) of the system are practically the same. From comparison with previous structures, and those described in Chapter 3, it is evident that a non-planar molecular conformation is, in principle, necessary to distance sulfur atoms from peri hydrogens of the anthracene moiety. However, non-planarity is achieved by a number of modes of distortion, which shows no obvious correlation with each other and with electronic properties of the substituents. Thus the actual degree of bending is rather flexible and can adjust to the demands of the crystal packing.
Figure 2.2: Single crystal X-ray structure of compound 44.

Figure 2.3: Single crystal X-ray structure of compound 55.
A charge transfer salt of compound 44 was prepared with TCNQ (Figure 2.4). The charge transfer salt comprised a 1:2 stoichiometry of donor: TCNQ and included two molecules of solvent acetonitrile. The asymmetric unit comprised a TCNQ anion radical and an acetonitrile molecule in general positions, and half of a dication 44\sup{2+} located at a crystallographic inversion centre (Figure 2.5). The dication has a structure similar to the literature examples incorporating methyl and thiomethyl substituted bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracenes.\textsuperscript{26,24} The anthracene system is planar and aromatic, bond distances therein are essentially the same as in the neutral anthracene.\textsuperscript{45} The dithiolium rings are also planar, their geometry is close to that of (TMTTF)(ClO\textsubscript{4})\textsubscript{2} and consistent with a charge of +1, or thereabouts, on each ring.\textsuperscript{46} The dithiolium and anthracene planes form a dihedral angle of 78°; the intervening C(7)...C(8) bond is essentially single. It is well known that charge transfer onto a TCNQ molecule results in lengthening of the carbon-carbon double bonds\textsuperscript{47} \(p\) and \(r\) and shortening of the single bonds \(q\) and \(s\), so that \(q \approx r \approx s\) for the charge of -1 (Figure 2.5). In the charge transfer salt the average distances are \(p = 1.371(2)\), \(q = 1.425(2)\), \(r = 1.423(2)\) and \(s = 1.423(2)\ \text{Å}\) which clearly indicate TCNQ to be mono-anion. Crystallographically parallel anions form a stack of dimers (Figure 2.6). The dication forms a stair-like stack, but perpendicular orientation of the dithiolium rings enforces a large interplanar separation of 3.97 Å. A notable feature of the structure is that both sulfur atoms of the dithiolium ring participate in short contacts with nitrogen atoms of the TCNQ: S(1)...N(1')(x, -1-y, -z) 2.959 (3) and S(2)...N(3) 2.865 (3) Å, cf. the standard van der Waals contact of 3.42 Å. In either case, the contacting nitrogen atom is nearly co-planar with the dithiolium ring and opposite to the C(8)-S bond, viz. the angles C(8)S(1)N(1) 173.1(2)° and C(8)S(2)N(3) 178.5(2)°. Short contacts of this kind are rather common in charge transfer complexes comprising TCNQ and TTF or their derivatives and could be expected, since the N and S atoms are the main centres of negative and positive charges, respectively. The single crystal conductivity of 44\sup{2+} (TCNQ -)\textsubscript{2} 2MeCN, measured using a two-probe technique is low (\(\sigma_{\text{rt}} = 10^{-8} \text{Scm}^{-1}\)), consistent with a fully anionic TCNQ stack. The C=N stretching frequencies in the IR spectrum (2172 and 2155 cm\textsuperscript{-1}) are consistent with a fully anionic TCNQ.\textsuperscript{6}
Figure 2.5: Identification of bonds for crystallographic analysis of TNCQ.

Figure 2.4: Single crystal X-ray structure of a charge transfer salt of $44^{2+} (\text{TCNQ}^-)_2$ 2MeCN.
Figure 2.6: A packing diagram of the charge transfer salt $44^{2+} \text{(TCNO}^-\text{)}_2 \text{2MeCN}$ (solvent molecules omitted for clarity). Interplanar separations $d_1 = 3.15 \text{ Å}, d_2 = 3.50 \text{ Å}, C...S contacts $r_1 = 3.289(2) \text{ Å}, N...S contacts $r_2 = 2.865(3) \text{ Å}.$
2.6 Conclusion

We have synthesised new derivatives of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene possessing flexible dialkoxy substituents. CV data establish increased $\pi$-donor strength with the detection of the tetracation oxidation state. X-ray crystal structures reveal the dramatic conformational change, which accompanies oxidation of the neutral molecule 44 to the dication. $44^{2+}$ (TCNQ')$_2$ 2MeCN is the third TCNQ complex of a 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene donor to be characterised crystallographically. Its stoichiometry is different from that of its two predecessors; a notable feature of the structure is that both sulfur atoms of the dithiolium ring participate in short intermolecular contacts with nitrogen atoms of a TCNQ moiety. This study further demonstrates that 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene is a very interesting $\pi$-electron rich system with unusual redox and structural properties.
3.1 Introduction

The design and synthesis of new anthracene bridged π-electron donor molecules is central to this thesis. In Chapter 2, we showed that functionalisation could be achieved via ether linkages to the central anthracene spacer. However, our attempts to functionalise the dithiole rings proved problematic. In this chapter, we reinvestigate the lithiation chemistry of the dithiole rings. We intended to synthesis a range of functional derivatives, which could later be utilised in target driven synthesis. We chose to functionalise the dithiole rings as substituents placed here were essentially unexplored and should afford reactive ‘handles’ for further transformations. It was also of interest to investigate how substituents affected the structural and electrochemical properties of the system.

3.2 Lithiation of the Dithiole Rings

Given the problems encountered with the lithiation of compound 44 (Chapter 2) we chose to prepare compound 65, which would possess only one acidic hydrogen. We anticipated that the methyl substituents would provide sufficient solubility (and indeed this proved to be the case).

![Diagram of compound 65]

One possible route to compound 65 was via two sequential, Horner-Wadsworth-Emmons reactions onto anthraquinone. However, initial investigations showed that the reactions of one equivalent of both anthraquinone and Horner-Wadsworth-Emmons
reagent 54 gave a mixture of mono- and di- substituted products, with the disubstituted product 29 predominating. It was decided that this methodology was impractical for the first stage of a multi-step synthetic route.

Our efforts then focused on the methodology of Gompper and Kutter who described the reaction of a benzo-1,3-dithiolium salt with anthrone 66, in an addition reaction followed by elimination of methylthiol under mildly basic conditions. Further investigation of this reaction in our laboratory had previously afforded compound 68 which provided a readily available starting material (Scheme 3.1).

![Scheme 3.1 Reagents and Conditions: i) Pyridine/acetic acid 3:1 v/v, 50-60 °C.]

The ketone 68 could then undergo a Horner-Wadsworth-Emmons reaction using the novel phosphonate ester reagent 75 to yield target 65. Compound 68 was synthesised as reported in the literature.

The new mono methyl Horner-Wadsworth-Emmons reagent 75 was prepared as shown in Scheme 3.2. Treatment of carbon disulfide with piperidine under basic conditions yields sodium piperidine-1-carbodithioate 69. Further reaction with 1-bromopropan-2-one in refluxing ethanol affords 2-oxopropylpiperidine-1-carbodithiolate 70. Sulfuric acid-induced cyclisation of 70 affords the desired imminium salt 71, which is isolated as the hexafluorophosphate salt. Reduction of the imminium salt 71 occurs with sodium borohydride to afford amine 72. The subsequent conversion of compound 72 was achieved by slow addition to anhydrous hexafluorophosphoric acid forming a white solid. Purification of salt 73 was most easily achieved by conversion to its iodide salt 74, reaction of which with trimethyl phosphite affords the phosphonate ester 75.
The reaction of compound 68 with the phosphonate anion obtained by deprotonation of reagent 75 using lithium diisopropylamide (LDA) in THF at -78°C afforded compound 65 in 55% yield (Scheme 3.3).
Scheme 3.3 Reagents and Conditions: i) LDA, THF, -78°C, 3h.

Our initial reaction to assess the lithiation of 65 was to perform a deuterium exchange, which was monitored by proton NMR spectroscopy (Scheme 3.4).

Scheme 3.4 Reagents and Conditions: i) LDA, THF, -78°C, 3h. ii) D₂O.

Deprotonation of 65 using LDA in THF at -78 °C followed by quenching with an excess of deuterium oxide gave a quantitative yield of the mono-deuterio derivative 76 (¹H NMR evidence) thus confirming the very efficient generation of the lithiated species. The results of the trapping of the metallated species 77 with a selection of electrophiles are shown in Table 3.1 (Scheme 3.5).
Scheme 3.5 Reagents and Conditions: i) LDA, THF, -78°C, 3h.

<table>
<thead>
<tr>
<th>Electrophilic Reagent</th>
<th>Reaction Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>78</td>
<td>13%</td>
</tr>
<tr>
<td>N-Methyl formanilide</td>
<td>78</td>
<td>0%</td>
</tr>
<tr>
<td>N-Methyl isothiocyanate</td>
<td>79</td>
<td>17%</td>
</tr>
<tr>
<td>Perfluorohexyl iodide</td>
<td>80</td>
<td>55%</td>
</tr>
<tr>
<td>Methyl chloroformate</td>
<td>81</td>
<td>83%</td>
</tr>
</tbody>
</table>

Table 3.1: Trapping of the lithium salt of compound 77 with various electrophiles.

The yields of the substituted products, 78 and 79, were consistently lower than those for the analogous trimethyl-TTF derivatives\textsuperscript{49} with the majority of unreacted compound 65 being easily recovered. The aldehyde and thioamide derivatives 78 and 79 were repeatably obtained in only 13% and 17% yields, respectively, with N,N-dimethylformamide and N-methylisothiocyanate as the electrophiles. For the synthesis of 78, N,N-dimethylformamide was preferable to N-methylformanilide as the formylating reagent, in direct contrast to the analogous reaction with TTF 1\textsuperscript{50} or trimethyl-TTF.\textsuperscript{49} A
considerably more efficient trapping of the lithiated species 77 occurred with methyl chloroformate, to yield the ester derivative 81 (83% yield).

Sulfur insertion into the lithiated species 77, followed by reaction of the transient thiolate anion with benzoyl chloride gave the thioester derivative 83 (53% yield). Compound 83 is a convenient shelf-stable precursor of mono-functionalised derivatives of 65. Saponification of 83 was readily achieved (sodium methoxide, room temperature) with the transient thiolate anion being regenerated and efficiently trapped with iodomethane and 6-bromohexan-1-ol to yield 84 and 85, respectively (80-93% yields, Scheme 3.6).

We established, therefore, that this lithiation approach provided a valuable route to some derivatives. The introduction of a methyl ester group should provide access to the alcohol allowing the formation of ester and ethers linkages, with the iodide derivative 80, providing a route to organometallic couplings. The development of a shelf stable protected thiolate, 83, increases the nucleophilicity of the anion and allows reactions to be performed at room temperature.
3.3 Functionalisation via Addition/Elimination Reactions

Having developed approaches for direct dithiole modification (Section 3.2) we now addressed other routes to different functionality. Here we describe a complimentary approach for the addition of functional groups directly to anthrone.

The starting point for our synthesis was 4,5-dithiolate-1,3-dithiole-2-thione 86, which was prepared via the chemical reduction of carbon disulfide in the presence of sodium. The mechanism of the reaction has been the focus of much debate since it was first reported by Fetkenhauser et al. The major product, trapped by the addition of chloromethane, was initially assigned as dimethyl tetrathioxalate 87, which is analogous
to the chemical reduction of carbon dioxide to oxalic acid performed by Kolbe in 1868 (Scheme 3.7).\textsuperscript{53}

\begin{equation}
\text{CS}_2 + \text{Na} \xrightarrow{\text{i)} \text{DMF, } 0^\circ \text{C followed by MeL}} \rightarrow \text{87}
\end{equation}

**Scheme 3.7 Reagent and Conditions: i) DMF, 0\textdegree C followed by MeL.**

This proposal was later disproved as the reaction produces 4,5-dithiolate-1,3-dithiole-2-thione 86, and 1,3-dithiolate-2-thione 88.\textsuperscript{51} The desired compound 86 can be separated from compound 88 by the addition of zinc chloride which selectively complexes with 86, precipitating 89 as a red solid (Scheme 3.8). Recently an improved procedure has been developed and a new mechanism for the formation of 86 proposed in our laboratory.\textsuperscript{54}

\begin{equation}
\text{CS}_2 + \text{Na} \xrightarrow{\text{i)} \text{DMF, 0\textdegree C. ii) ZnCl}_2, \text{Et}_4\text{NBr.}} \rightarrow \text{86} \xrightarrow{\text{ii)} \text{ZnCl}_2, \text{Et}_4\text{NBr.}} \rightarrow \text{89}
\end{equation}

**Scheme 3.8 Reagents and Conditions: i) DMF, 0\textdegree C. ii) ZnCl}_2, \text{Et}_4\text{NBr.**

It has been shown from TTF chemistry that sulfur insertion reactions can lead to products in higher yield than their lithium analogues.\textsuperscript{38} The use of zincate salt 89 provides an analogous dithiolate.
The literature contains a variety of protecting groups for thiolates ranging from thioesters to silyl reagents. Ideally, the protecting group should be stable towards strong bases which would allow conversion to the thiolate protected Horner-Wadsworth-Emmons reagent.

The problems experienced with various protecting groups were that they did not withstand the varied conditions of subsequent reactions. If a Horner-Wadsworth-Emmons approach was to be utilised then the protecting group would have to be stable against strong bases such as LDA and fluorine rich environments e.g. triflate salts, but also powerful electrophiles such as methyl triflate. The propionitrile group provided stability against the electrophilic methyl triflate but not strong bases. Therefore, a Horner-Wadsworth-Emmons type approach would fail, as strong bases would deprotect the thiolate. To overcome this problem we decided to introduce the protected thiolate via an addition-elimination type reaction. After experimentation we settled on the propionitrile-protecting group. The protecting group was applied directly to compound 89 affording 90 in a single step with an 85% overall yield, following the literature (Scheme 3.9).

![Scheme 3.9 Reagents and Conditions: i) 3-bromopropionitrile, toluene, reflux, 6h.](image)

This protecting group is stable to acid and weak bases but is easily removed by strong base. The system could then be deprotected and functionalised before performing a Horner-Wadsworth-Emmons reaction.

One of the advantages of the bis protected reagent 90 is that it may be mono-deprotected under certain conditions. If more basic conditions are imposed then the dithiolate is generated. In order to simplify our system we chose to selectively mono-deprotect at this stage, as this would reduce the number of potential products, simplifying
reaction monitoring. A methyl group was chosen as the blocking group for simplicity (Scheme 3.10).\textsuperscript{62}

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {90};
\node (b) at (2,0) {91};
\draw[->] (a) -- (b);\end{tikzpicture}
\end{center}

\textbf{Scheme 3.10 Reagents and Conditions:} i) CsOH.H\textsubscript{2}O, MeOH/THF, rt, 3h. ii) Mel

The methylation of thione 91 with methyl triflate gave the cation salt 92, which was reacted, without purification, with the anion of anthrone, 93 (generated using LDA at room temperature), to afford initially compound 94, which was converted into the desired compound 95 by treatment with p-toluene sulfonic acid (18\% yield, based on thione 91). The low yield occurred due to the competing deprotection of the cyanoethylthio group of 95 under these basic conditions. The thiolate anion derived from 95 was cleanly liberated using Becher’s conditions (caesium hydroxide at room temperature) and trapped \textit{in situ} with 6-bromohexan-1-ol to afford the alcohol derivative 96 in 89\% yield. Conversion of 96 into t-butyldiphenylsilyl ether derivative 97 (90\% yield) and subsequent Horner-Wadsworth-Emmons reaction with the anion derived from reagent 54, gave compound 98 (70\% yield) desilylation of which (tetrabutylammonium fluoride) gave alcohol derivative 99 (79\% yield). The suitability of compound 99 for further elaboration was established by reaction with benzoyl chloride in the presence of triethylamine, which gave the benzoyl ester derivative 100 in 50\% yield (Scheme 3.11).
Scheme 3.11 Reagents and Conditions: i) MeSO$_2$CF$_3$, DCM, 1h, rt. ii) LDA, $^1$PrOH, rt, 20min. iii) Compound 92 iv) p-TSA, PhMe, reflux. v) CsOH.H$_2$O, THF, 20°C, then Br(CH$_2$)$_6$OH vi) t-BuPh$_2$SiCl, imidazole, DMF, 20°C. vii) LDA, THF, -78°C. viii) TBAF, THF, 20°C ix) PhC(0)Cl, NEt$_3$, CH$_2$Cl$_2$, 20°C.
To capitalise on the protecting group’s ability to be selectively removed, we constructed compound 101 in a similar manner to that of ketone 95. Compound 101, represents the first building block for di-substituted systems and was prepared from compound 90 in 3 steps with an overall yield of 19%. We have not pursued reactions of 101 but it should prove to be a useful intermediate for other reactions.

![Chemical Structure of 101](image)
3.4 Electrochemistry

Solution electrochemical and UV-vis spectroscopic data for the new derivatives of the parent system 30 are entirely in accordance with their structures. Cyclic voltammetric data obtained in acetonitrile established that the redox properties are only slightly modified by the presence of the substituents: a predictable trend is that the two-electron oxidation wave is anodically shifted by an electron-withdrawing substituent on the 1,3-dithiole ring: cf. $E^{ox}$ values for compound 65 (0.320 V), compound 78 (0.450 V) and compound 81 (0.425 V). The lowest energy absorption in the UV-vis spectra is observed at $\lambda_{max}$ 420-430 nm, and is essentially unaffected by the substituents. Comparable data for the parent system 30 and benzoannulated analogues have been discussed recently by Martin et al. on the basis of theoretical calculations.

3.5 Single Crystal X-ray Structures of compounds 81 and 84.

Molecule 81 adopted a saddle-like conformation, relieving steric repulsion between sulfur atoms and hydrogen atoms in peri positions of the anthracene moiety (Figure 3.1) and incorporated one CDCl$_3$ molecule of crystallisation. The former being folded along the C(9)...C(10) axis by a dihedral angle ($\phi$) of 40.5°. The bis(1,3-dithiol)benzoquinone system is U-shaped through an ‘accumulating bend’ comprising the boat conformation of the central (quinonoid) ring, folding of both 1,3-dithiole rings along S...S vectors, and out-of-plane tilting of the exocyclic carbon-carbon double bonds, all in the same (inward) direction. Thus, the S(1)C(16)C(17)S(2) and S(3)C(22)C(23)S(4) moieties form an acute dihedral angle ($\theta$) of 75.6°. The C-S bonds in the methoxycarbonyl-substituted dithiole ring of 81 are asymmetrical, S(1)...C(16) shortened to 1.743(11) Å and S(1)...C(15) lengthened to 1.785(11) Å [(cf. S(2)...C(15) 1.757(10) and S(2)...C(17) 1.756(10) Å]. The crystal structure of thiocarbamoyl-TTF and thiocarbamoyl-Me$_2$TTF similarly reveals mesomeric effects (i.e. a contribution from canonical forms, Figure 3.2). In the other (dimethyl substituted) dithiole ring of 81, the
C(21)...S(3) and C(21)...S(4) bonds are equivalent (1.767(9) Å) as are the S(3)...C(22) and S(4)...C(23) bonds (1.749 (10) Å).

At this point it was also worth considering the questions of geometric isomers. Anthracene containing bis-dithiole compounds show a saddle shape in the solid state, if this geometry holds true for compound 65 in the solution state then two possible geometric isomers exist. These can be easily visualised as a saddle with the handle on either the left or right. These isomers were never separated and all reactions were performed on the mixture of geometric isomers.

Figure 3.1: Single crystal X-ray structure of compound 81.

Figure 3.2: The internal mesomeric CT of compound 81.

Crystal packing of 81 (Figure 3.3) showed the motif reported earlier for the tetra(thiomethyl) analogue, with pairs of inverted molecules engulfing each other’s dimethyl substituted dithiole moiety. These moieties contact face to face, but the interplanar separation of ca. 3.7 Å is rather long. CDCl₃ molecules occupy cavities between these pairs and are disordered.
Compound 84 exhibits a wider $\theta$ angle (86.9°) due to the more planar dithiole rings, and in spite of more pronounced folding of the anthracene moiety ($\phi = 45.1^\circ$). It has the same packing motif as 81, but without any solvent of crystallisation. The thiomethyl group is disordered over three positions, at C(16), C(17) and C(21), with occupancies of 80%, 15% and 5%, respectively. For the former two, the nearly overlapping positions of the sulfur and the methyl carbon atoms, S(5) and C(19), could not be resolved and were refined as a single atom; for the latter, the methyl group bound to sulfur was not located, the major position is shown in Figure 3.4.
3.6 Conclusion

Two routes have now been developed to gain access to unsymmetrical derivatives of the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system which contain a 'reactive handle' suitable for further chemical elaboration. We have also shown from electrochemical and UV-vis studies that functionalisation on the dithiole ring has little influence over the redox behaviour of the system. The single crystal X-ray studies confirm the presence of the cavity after functionalisation. The availability of these new derivatives in synthetically useful quantities paves the way for the development of this very interesting, strained ring system as a redox-active building block in supramolecular chemistry.
4.1 Introduction

Chapters 2 and 3 describe the synthesis and electrochemical properties of new 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivatives, with little emphasis on potential applications. In this chapter, we address molecular sensors based on the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system by virtue of annulated crown ether substituents.

Much of the groundwork on molecular sensors owes its origin to biological processes. Nature has long been using molecular sensors for catalysis, recognition, regulation and transport; it is from such well-developed systems that much can be learned. A molecular sensor is a system for which the physiochemical properties change upon interaction with a chemical species in such a way as to produce a detectable signal, e.g. binding of a guest analyte ion or molecule to a receptor (the host) is transduced to the signalling unit which responds by changing its electronic state, which is monitored spectroscopically or electrochemically. Interactions between host and guest range in complexity, and utilise a variety of interactions, such as hydrogen-bonding, ion-dipole, hydrophobic, π-π, or a combination of these. Such interactions are important as they determine the specificity of the sensor for the guest molecule. Specificity is defined as the degree of selectivity of the guest molecule when compared to other similar competitive guests. Many host molecules possess cavities or cyclic structures, which provide the site of interaction analogous to an 'antenna' (Figure 4.1).

![Figure 4.1: Components of a molecular sensor](image-url)
Crown ethers were first prepared by C. J. Pedersen in 1967, for which he later received the Noble prize along with Cram and Lehn. Pedersen synthesised dibenzo-18-crown-6, 102 and showed it selectively bound sodium ions in the presence of methanol.  

Crown ethers represent a simple antenna, and are well known for their ability to complex alkali metal ions. Further alkali ion selectivity can be achieved by varying the size of the crown, as larger crowns better accommodate larger ions. Measurements on the stability of these complexations show crowns prefer an optimum guest, that is a cation with a diameter closely fitting that of the cavity. The stability of complexation of alkali metals is also influenced by the choice of heteroatom. The complexation of “hard” alkali metal ions being preferential with “hard” oxygen crowns, due to similar orbital overlap. The ease of synthesis and well-understood principals of cation recognition using crown ethers made them a logical choice for our sensor system.

Several examples of macrocyclic systems based on crown ethers incorporating redox centres are contained in the literature. One example was prepared by Otsubo et al., who described the synthesis of TTF crown ether 104 (Scheme 4.1).
Compound 103 was prepared by direct alkylation via reaction of a tosylated crown ether with a crude mixture of 4,5-dithiolate-1,3-dithiole-2-thione 86, and 1,3-dithiolate-2-thione 88. The resulting thione 103 was then phosphite coupled to yield compound 104 in low yields.

Other sensors incorporating various crown ethers annulated to TTF have been prepared by Becher et al. who prepared compound 104 using an alternative synthetic route in good yields and went on to show that compound 104 showed a marked response to 250 equivalents of sodium in the cyclic voltammetry (Figure 4.2). The cyclic voltammetry of compound 104 exhibited a marked shift in the first oxidation potential ($E_{1^{os}}$) in the presence of Na$^+$, with little change in the second oxidation potential ($E_{2^{os}}$). The electrochemistry can be explained, as the sensors will bind metal ions in the neutral state by ion-dipole interactions. The first oxidation of the TTF will be hindered by the presence of the metal ion due to coulombic repulsion, increasing the first oxidation potential relative to the uncomplexed crown system.
Upon oxidation, repellent ion-ion interactions overpower the weaker ion-dipole interactions resulting in the ejection of the metal ion. The cavity is now empty in the radical cation state and is then oxidised to the dication without metal ion interference (Figure 4.3).

Figure 4.2: CV of compound 104 with 250 eq. NaPF₆ (solid line) and without sodium (dashed line). Recorded versus a SCE electrode in MeCN at a scan rate of 100 mV s⁻¹ with 0.2M Bu₄NClO₄.⁷⁸
More recently, Bryce et al. have prepared a range of unsymmetrical TTF-S$_2$O$_4$ crowns, e.g. compound 105, and studied their cation binding properties by UV/vis spectroscopy and cyclic voltammetry.\textsuperscript{77}

The effects of complexation with sodium, barium and silver were studied: monocrown 105 formed a 1:1 complex with sodium resulting in an anodic shift of 25-35 mV in the CV. Complexation with silver and barium produced the greatest shift in oxidation potential with an anodic shift 70-75 mV for silver. These results are consistent with silver binding primarily at the sulfur sites, inducing a large perturbation in the electronic
structure of the TTF moiety. The stability constant for these systems was estimated to be
$\log K = 2.26$ by electrochemical and spectroscopic measurements.

These examples led us to suggest that anthracene spaced bis-dithiole system 106
could be a potential sensor. Due to the high percentage of diffuse (soft) sulfur orbitals
present in our system we decided to tailor the sensor toward silver, which possesses
equally diffuse orbitals. Silver is a larger cation than sodium and requires a slightly larger
crown. We set the goal of preparing and studying target compound 106.

\begin{center}
\includegraphics[width=0.5\textwidth]{structure.png}
\end{center}

\textbf{4.2 Synthesis}

Pentaethylene glycol was utilised as the starting reagent for the crown
functionality and was treated with two equivalents of phosphorus tribromide to generate
the dibromo intermediate 107, in 51\% yield (Scheme 4.2), which was used without
further purification.\textsuperscript{78}

\begin{equation}
\begin{align*}
\text{HO(CH}_2\text{CH}_2\text{O)}_3\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{Br(CH}_2\text{CH}_2\text{O)}_3\text{CH}_2\text{CH}_2\text{Br}
\end{align*}
\end{equation}

\textbf{Scheme 4.2 Reagents and conditions: i) PBr}_3, \text{ py, 0}\degree\text{C.}

Saponification of compound 108 with sodium ethoxide generated the dithiolate
109, which precipitated from solution and was collected by Schlenck filtration.
Alkylation with glycol 107 generated thione 110 in 79\% yield. The thione was then
methylated using methyl triflate to afford compound 111 in 84\% yield. Reduction was
achieved with sodium cyanoborohydride to give compound 112, as an off-white solid.
Conversion to the Horner-Wadsworth-Emmons reagent 114 was achieved via the triflate salt 113 (Scheme 4.3).

Scheme 4.3 Reagents and Conditions: i) PhC(O)Cl, Me₂O, 6 h, rt. ii) NaOEt/EtOH, 20 min, rt. iii) Compound 99 iv) MeSO₂CF₃, DCM, 1 h, rt. v) NaBH₃CN, EtOH, 1 h, 0°C. vi) CF₃SO₃H, MeCN, 10 min, rt. vii) P(OEt)₃, NaI, MeCN, 30 min, rt.
Phosphonate ester 114 was stirred in dry THF at -78°C and treated with one equivalent of lithium diisopropylamide to give a white opaque solution containing the reactive anion. Half an equivalent of anthraquinone was then added and the reaction allowed to warm to 20°C, to yield the highly soluble bis-crown compound 106 in 67% yield.

In a similar procedure, compound 114 was stirred in dry THF at -78°C and treated with one equivalent of lithium diisopropylamide to generate the reactive anion. This was then quenched with one equivalent of compound 68 to yield the mono-crown compound 115 in 53% yield (Scheme 4.4).

![Scheme 4.4 Reagents and Conditions](image)

Scheme 4.4 Reagents and Conditions i) LDA, THF, -78°C, 1h followed by anthraquinone. ii) LDA, THF, -78°C, 1h followed by compound 68.
Unlike the previous Homer-Wadsworth-Emmons reaction detailed, the reaction of crown reagent 114, with anthraquinone allowed the isolation of the ketone 116 as a red oil, that solidified on standing.

4.3 Cation Binding Studies.

The cation binding properties of 106 and 115 were initially assessed by $^1$H NMR titration studies in CDCl$_3$. In the presence of Na$^+$ and Ag$^+$ the resonances due to the -SCH$_2$CH$_2$O- protons of the crown [(SCH$_2$)$_3$ δ 3.020; (OCH$_2$)$_3$ δ 3.650] shifted downfield (maximum shift ca. 0.07 ppm in the presence of 10 equiv. of Ag$^+$) while the anthracenediylidene resonances were essentially unaffected, confirming that cation binding occurs at the crown site. In contrast to this, Li$^+$ and K$^+$ cations had essentially no effect on the $^1$H NMR spectrum.

UV-vis absorption spectroscopic studies were performed on compounds 106 and 115. These spectra are very similar and show only ~2 nm differences in the wavelength of the main absorption peaks. These results indicate that although the sulfur atoms within the crown ether groups are conjugated into the chromophore part of the molecule, the perturbation of the chromophore electronic system due to the crown ether presence is relatively weak.

Investigations into complex formation with soft and hard metal cations in acetonitrile with compound 115 failed due to precipitation. Compound 106 showed normal chromonionophore behaviour, the absorption spectra in acetonitrile in the presence of sodium perchlorate and silver perchlorate are shown in Figures 4.5 and 4.6 respectively.
Figure 4.4: The absorption spectra attributed to the formation of the $LM^+$ complex.

Figure 4.5: The absorption spectra attributed to the formation of the $L(M^+)\_2$ complex.

In both cases, no isosbestic points were found, indicating that, most probably, more than one species are formed due to the complexation reaction and the absorption spectra of these species are different. Such behaviour is typical for bis(crown)
chromoionophores and may be attributed to the formation of 1:1 (LM') and 1:2 [L(M')₂] ligand:metal cation complexes. It was evident from absorption spectra (Figures 4.4 and Figures 4.5) that the formation of both LM' and L(M')₂ complexes occur for similar metal cation concentrations. Alternatively, one would expect the presence of isosbetric points for certain concentrations regions, where the formation of one type of complex dominates.

In agreement with reaction Scheme 4.5 the absorbance $A$ of chromoionophore solution at any wavelength $\lambda$ depends on metal cation concentration $M_0$ as described by Equation 4.1, where $A_0$, $A_1$, and $A_\infty$ are the absorbances of the free ligand $L$ and the complexes LM' and L(M')₂, respectively; $K_1$ and $K_2$ are the equilibrium constants for complex formation.

$$A = A_0 + \frac{K_1 \cdot M_0 (A_1 - A_0)}{1 + K_1 \cdot M_0 + K_2 \cdot M_0^2} + \frac{K_2 \cdot M_0^2 (A_\infty - A_0)}{1 + K_1 \cdot M_0 + K_2 \cdot M_0^2}$$

*Equation 4.1:*

The equation was found to fit compound 106 well ($R^2 > 0.98$). The estimated values for the equilibrium constants $K_1$ and $K_2$ are presented in Table 4.1. Although the fitting presented in Figure 4.4 is good, the equilibrium constants $K_1$ and $K_2$ cannot be accurately determined because of absorption overlap; additional measurements clearly distinguishing the formation of the LM' and L(M')₂ complexes would be required for a more accurate estimation.
Table 4.1: Stability constants for 106 with Na\(^+\) and Ag\(^+\) cations in acetonitrile.

The observed stability constant, $K_{obs}$, may be wavelength dependent because of the different relative absorptivity of compound 106 and its complexes at different wavelengths. The fitting of the absorbance data taken at a fixed wavelength gave estimated $K_{obs}$ values of 2.5 ± 0.2 and 2.4 ± 0.2, for sodium and silver cations, respectively. For comparison, the log $K_{obs}$ for compound 106, Na\(^+\) is very close to that reported for TTF-bis(crown), Na\(^+\) complexation in acetonitrile.\(^{77}\)

Cyclic voltammetry and square wave voltammetry (SQV) showed that, as expected, both compounds display a two-electron oxidation wave: $E_{1}^{ox}$ +0.405 V (compound 106) and $E_{1}^{ox}$ +0.345 V (compound 115); the lower oxidation potential of the latter compound being consistent with the electron donating effect of the methyl substituents. As observed for previous derivatives, a second reversible one-electron wave, ascribed to oxidation of the anthracene system (i.e. radical trication formation) was seen at $E_{2}^{ox}$ +1.62 V for both compounds [CV data was recorded vs Ag/AgCl, electrolyte Bu\(_4\)N^+ClO\(_4^−\) (0.1 M), acetonitrile, room temperature, scan rate 100 mV s\(^{-1}\)]. The reproducibility between different samples was ± 2 mV. The progressive addition of aliquots of metal triflate salts resulted in a positive shift of $E_{1}^{ox}$, while $E_{2}^{ox}$ remained unchanged, thereby acting as a convenient internal reference. This is consistent with expulsion of the metal cation from the ionophore prior to the second oxidation wave. The maximum positive shifts ($\Delta E_{1}^{ox}$) are as follows: Li\(^+\) (15-20 mV), Na\(^+\) (100 mV), K\(^+\) (15-20mV) and Ag\(^+\) (115 mV). The value of $\Delta E_{1}^{ox}$ is essentially the same for the mono- and bis-crown systems 115 and 106, respectively, whereas in the TTF series, e.g. compound

<table>
<thead>
<tr>
<th></th>
<th>log $K_{obs}$</th>
<th>Simultaneous Complexation</th>
<th>1:1 and 1:2 Complexes</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+)</td>
<td>2.5 ± 0.2</td>
<td>log $K_1$</td>
<td>~ 2.6</td>
<td>0.982</td>
</tr>
<tr>
<td></td>
<td></td>
<td>log $K_2$</td>
<td>~ 4.3</td>
<td></td>
</tr>
<tr>
<td>Ag(^+)</td>
<td>2.4 ± 0.2</td>
<td>log $K_1$</td>
<td>~ 3.4</td>
<td>0.992</td>
</tr>
<tr>
<td></td>
<td></td>
<td>log $K_2$</td>
<td>~ 5.5</td>
<td></td>
</tr>
</tbody>
</table>
104, a larger shift is observed for bis-crowns. This could be a consequence of intramolecular steric interactions between the crown rings of 115, and/or sandwich complexation between two crowns, favoured by the rigid saddle conformation. A comparison with related S$_2$O$_4$-crowned TTF systems shows two important advantages of system 106 and 115. (1) The positive shifts for Na$^+$ and K$^+$ are significantly larger, and (2) the system is significantly more sensitive, with saturation being achieved with <10 equivalents of cation (cf. 200 equivalents for 104). 78

We suggest that these results are a consequence of the unique combination of structural and redox properties of the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene transducer unit. The saddle-shape folding of the anthracenediyldiene system places the crown ring(s) of 106 and 115 in relatively close proximity to the redox-responsive moiety, and we believe, more significantly, the E$_1$ redox process which is monitored is a two-electron oxidation (cf. the one-electron wave of TTF, ferrocene etc.) thereby enhancing the electrostatic repulsion with the adjacent bound metal cation(s) leading to a increase in $\Delta E_{1}^{\text{ox}}$.

4.4 Single Crystal X-ray Crystallography of compounds 115 and 116

An X-ray crystallographic study of compound 115 (Figure 4.6), showed the same structural motif as previous derivatives; the molecules are saddle-shaped with each molecule engulfing each other's dimethyldithiole ends. The anthracenediyldiene moiety is folded along the C(9)--C(10) vector, the two benzene rings forming a dihedral angle of 39° (cf. 21° in 116, Figure 4.7). The dithiole rings are folded along the S(1)--S(2) and S(3)--S(4) vectors by 15.5° and 8.7°, the S(1)C(16)C(17)S(2) and S(3)C(19)C(20)S(4) planes form an acute dihedral angle of 81°. No solvent molecules are within the macrocyclic or saddle cavity (Figure 4.6).
Figure 4.6: Single crystal X-ray structure of compound 115.

Figure 4.7: Single crystal X-ray structure of compound 116.
4.5 Conclusion

In summary, using prototype ligands 106 and 115 we have exploited for the first time the redox properties of the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene transducer system to provide efficient and controllable cation recognition within appended crown ether units. These studies pave the way for the spectroscopic and electrochemical monitoring of supramolecular interactions in new derivatives of this system.
5.1 Introduction

Chapters 2-4 have described the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system in some detail and established through crystallographic studies that intramolecular steric interactions enforce a folding of the central anthracenediylidene ring of the system into a boat conformation, which forces the molecule to adopt a saddle shape.26

The focus of this chapter is the development of a new range of related electron donor molecules, incorporating a cyclic structure. These systems differ from those of the crown ethers (Chapter 4) in that the chain bridges the two dithiole rings, increasing strain to the system. The rational was to observe the effects of increased strain on the cavity in solution and in the solid state using cyclic voltammetry and single crystal X-ray crystallography.

In 1992 Misaki et al. succeeded in the preparation of bis(2-methylidene-1,3-dithiole[4,5])tetrafluorovalene (BDT-TTF), compound 122 (Scheme 5.1).79 The zinc complex 89 was reacted with α,α'-dichloromethyl methyl ether in acetone to afford 117 in 73% yield. Treatment of compound 117 with aqueous 42% hydrofluoroboric acid in dichloromethane/acetic anhydride (5:1, v/v) at 0°C gave the corresponding 1,3-dithiolium salt 118, which was converted to the phosphonate ester 119 with triethyl phosphite and sodium iodide in 88% yield. Treatment of 119 with various ketones and equimolar amounts of lithium diisopropylamide (LDA) in tetrahydrofuran (THF) at -78°C, gave the corresponding 2-methylidene-1,3-dithiole(4,5)1,3-dithiole-2-thione 120a-d (47-99% yields), which were converted to the corresponding ketones 121a-d, by reaction with mercury (II) acetate in chloroform/acetic acid (1:1, v/v) in 79-97% yields. The target BDT-TTF derivatives, 122a-d, were obtained by phosphite induced coupling at 100-110°C in moderate yields.
The phosphonate ester 119, represented an extremely interesting compound which could undergo two independent reactions. Misaki et al. demonstrated the ability of compound 119 to undergo a Horner-Wadsworth-Emmons type coupling to various ketones, and it was plausible that this reactivity could be extended to anthraquinones. The system also exhibited the ability to self-couple via the 2-oxo-1,3-dithiole functionality.

The use of phosphite induced couplings has provided one of the fundamental reactions in the preparation of TTF derivatives and was originally discovered by Corey, Corey and Winters. The mechanism of this reaction is still debated but is thought to proceed via a Wittig type mechanism as outlined in Scheme 5.2.
Scheme 5.2

Initial attack of one molecule of trialkylphosphite on the chalcogen of the C=X group polarises the bond making the carbon nucleophilic, allowing attack of a second equivalent containing C=X, forming a five membered ring. At high temperatures the cyclic structure collapses, eliminating one equivalent of trialkylphosphate and forming an epoxide. The epoxide is then ring opened by a second equivalent of trialkylphosphite, which proceeds through a four membered transition state, analogous to that of a Wittig reaction. Further elimination results in the formation of the double bond with elimination of another equivalent of trialkylphosphate. The reaction is thermodynamically driven by the formation of the P=X bond.

In Mizaki’s example, the thione 120a-d was converted to the ketone 121a-d prior to phosphite induced coupling. There are no clear guidelines governing the outcome of cross coupling reactions; the decision to use the ketone, as opposed to the thione, may have been based on improved yields or ease of separation of the products.
Summation of this information led us to propose the synthesis of compound 123 (with butoxy chains to ensure solubility).

5.2 Synthesis

Reaction of compound 52 with the anion generated from the phosphonate ester 119 gave the expected product 123 in 43% yield (Scheme 5.3).

\[
\begin{align*}
\text{Scheme 5.3: Reagents and conditions i) LDA, THF, -78^\circ C, 3h.}
\end{align*}
\]

With the aim of synthesising a cyclic derivative by intramolecular coupling, compound 123 was subjected to the standard phosphite-induced coupling reaction under high dilution, however, no coupled product was obtained. We believed the failure of the reaction might have been due to several factors. These factors may, include the failure of the phosphite to react with the thione present, the formation of multiple oligomers or the steric limitation imposed on intramolecular coupling. To further investigate the coupling reaction, compound 124 was prepared, as this compound could only undergo a single intermolecular coupling.

Reaction of compound 68 with the anion generated from phosphonate ester 119 gave the expected product 124 in 60% yield. Compound 124 was subjected to the
standard phosphite coupling conditions. No coupled product was obtained; the only isolated product was the unexpected compound 125 (50% yield) in which the 1,3-dithiole-2-thione ring has been transformed into two ethylsulfanyl substituents (Scheme 5.4).

![Chemical structures](image)

**Scheme 5.4** Reagents and conditions: i) LDA, THF, -78°C, 3 h. ii) P(OEt)₃, reflux.

The structures of both compounds 124 and 125 were established unequivocally by single crystal X-ray analysis. The conversion of 124 into 125 under these conditions appears to proceed via an unprecedented reaction of the 1,3-dithiole-2-thione system. Reactions of trialkylphosphite reagents with cyclic trithiocarbonates are generally assumed to proceed via an initial thiophilic addition, although a carbophilic mechanism has been considered. It is not readily apparent how a thiophilic addition can explain the formation of compound 125; we propose initial opening of the 1,3-dithiole-2-thione ring of 124 induced by carbophilic addition of triethylphosphite, to form the zwitterionic intermediate 126. Ethylation of 126 then occurs by a transfer of an ethyl group from triethyl phosphite to yield 127. This is more likely to be an intermolecular transfer than...
an intramolecular process. Generation of a second thiolate anion, and ethylation then gives product 125 (Scheme 5.5).

Scheme 5.5: The Proposed mechanism for the thioalkylation of 125.

The ethylation of compound 125 prevented the formation of a cyclic system. It was now apparent that an alternative synthetic approach to bridged systems was required.
5.3 Synthesis of the First Anthracenediylidene Cyclophanes

In 1995, Lorcy et al. reported the synthesis of a novel bis-Horner-Wadsworth-Emmons reagent 129 in the course of the preparation of tetrathiafulvalenophanes 130. This communication lacked experimental detail but clearly showed the capability of this new reagent to form cyclic systems by reaction with bis-ketones (Scheme 5.6).

We sought to apply reagents analogous to 129 to the synthesis of a new class of anthracenediylidene cyclophane compounds.

The preparation of the bis-imminium salts 135 and 136 had been described previously en route to symmetrically substituted TTFs. Reduction of bis(dithiolium) salts 135 and 136 with sodium borohydride followed by reaction of the bis(aminodithiole) intermediates with tetrafluoroboric acid afforded 139 and 140, which reacted with triethylphosphite in the presence of sodium iodide to give the corresponding bis(phosphonates), 141 and 142, in moderate yields. The synthesis of anthracenediylidene cyclophanes, 143 and 144, was achieved by a two-fold olefination reaction, under high dilution conditions, with anthraquinone and the anions generated from 141 and 142 respectively, [lithium diisopropylamide (LDA) at -78°C] following literature precedents for other 1,3-dithiole phosphonate ester reagents (Scheme 5.7). Compounds 143 and 144 were isolated as single isomers, and the cis configuration was confirmed by X-ray structural analysis.
Scheme 5.7 Reagents and conditions i) H₂O ii) Et₃N, Ac₂O, CS₂, Me₂CO. iii) dibromoalkane, Me₂CO. iv) NaBH₄, EtOH 0°C. v) HBF₄, DCM, 0°C. vi) NaI, P(OEt)₃, MeCN. vii) LDA, THF, -78°C, anthraquinone.
5.4 Electrochemistry

The solution electrochemistry of compounds 143 and 144 was studied by cyclic voltammetry and differential pulse voltammetry. Both compounds displayed an irreversible two-electron oxidation wave at $E^{\text{ox}} +0.69 \, \text{V}$ (compound 144) and $E^{\text{ox}} +0.74 \, \text{V}$ (compound 143) [vs Ag/AgCl, electrolyte Bu$_4$N$^+$ClO$_4^-$ (0.1 M), acetonitrile, room temperature, scan rate 100 mV/s] i.e. The oxidation wave of the bridged system 144 and 143 showed a significant positive shift ($\Delta E^{\text{ox}}$ ca. 300 mV) compared to the non-bridged analogue. This is explained by the rigidity of 143 and 144 (imparted by the bridge) restricting the conformational change which is known to accompany oxidation of the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system.$^{26}$ The slightly higher oxidation potential of 143 compared to 144 ($\Delta E^{\text{ox}}$ 50 mV) is also consistent with oxidation becoming progressively harder as the strain in the system increases. A second oxidation wave is observed at $E^{\text{ox}} +1.0 \, \text{V}$. Simulation of the data suggest an $ECE$ process where dication formation is followed by a chemical reaction to form a new electroactive species, which gives rise to the oxidation wave at a more positive potential.

5.5 Single Crystal X-ray Crystallography of Compounds 124, 125, 143 and 144.

The structure of compound 124 has been determined by single crystal X-ray analysis (Figure 5.1). The asymmetric unit 124 comprises two title molecules (A and B) and one severely disordered molecule of CDCl$_3$. Both molecules A and B have essentially planar S$_1$C$_2$S$_3$C$_2$C$_3$ systems, which form dihedral angles of 90.4° (A) and 94.1° (B) with the S$_6$C$_6$S$_7$C$_7$ moieties. Folding of the anthracene system along the C(10)...C(11) axis is unequal (35.9° in A, vs. 45.2° in B), while folding along the S(4)...S(5) vector is reversed (13.7° outward in A, vs. 7.6° in B). The crystal packing of 124 (Figure 5.2) is rather dissimilar from that of the other compounds studied herein. Molecules of A engulf each other's dimethylthiole ends, as does molecule B. In each dimer, the dithiole rings overlap in an antiparallel fashion, with interplanar
separations of 3.64 Å (A-A) and 3.55 Å (B-B) with the shortest contact being C...S at 3.66 Å in either case. These two dimers are orientated in mutually perpendicular planes and give rise to an unusual three-dimensional network of intermolecular contacts comparable to (or shorter than) the standard van der Waals distances S...S 3.60 Å and C...S 3.61 Å. Thus, dimethylthiole rings of the A-A dimer are sandwiched between dithiolethione systems of two adjacent B molecules (interplanar angle 7°, shortest S...S contact 3.63 Å). This tetramer is additionally strengthened by interactions between molecules A and B: S(2A)...S(2B) 3.66 Å and S(2A)...S(4B) 3.49 Å. However, no continuous stacks exist in the structure, and the forementioned stack is ‘underpinned’ at either end by the thione C(1A)=S(1A) bond of another A molecule. This bond is aligned perpendicular to the stacked plane and points towards the midpoint of the C(1B)...S(3B) bond (S(A)...S(3B) 3.52 Å, S(1A)...C(1B) 3.45 Å). The dimethylthiole rings of B dimer are contacted on the outside by dithiolethione moieties of adjacent A molecules, in an edge-to-face fashion. Thereby, S(3A) forms extremely short contacts with C(6B) and C(7B) 3.29 Å each, as well as rather close contact with S(6B) and S(7B) (3.61 Å and 3.62 Å respectively).

Figure 5.1: The single crystal X-ray structure of compound 124.
In compound 125 (Figure 5.3), one of the ethylthio substituents is disordered over two positions, S(6)C(19)C(20) and S(6')C(19')C(20'); their occupancies were refined to 61.2% and 38.8%, respectively. The conformation ($\phi = 40.6^\circ$, $\theta = 79.1^\circ$) is practically identical with that of 75, but here the ethylthio groups enter the intramolecular cavity of the opposing molecule (Figure 5.4).

Compound 144 gave a mixture of amber block- and needle- like crystals, which were characterised as monoclinic ($\alpha$) and orthorhombic ($\beta$) polymorphs, respectively, of cis-144. Two symmetrically independent molecules in the $\beta$-144 structure adopt very similar conformations (Figure 5.4), while that of $\alpha$-144 is significantly different. In each case, the conformation of the hexamethylene bridge is rather strained and asymmetric: torsion angles around the C-C bonds range from $144^\circ$ to $180^\circ$ in $\beta$-144 and from $58^\circ$ to
$176^\circ$ in $\alpha$-$144$, where two methylene groups are disordered. The bridge aggravates the U-bend of the bis(dithiolene)benzoquinone system: the dihedral angle between the outer $S(1)C(16)C(17)S(2)$ and $S(3)C(19)C(20)S(4)$ moieties is reduced from $77^\circ$ in non-bridge tetrathiomethyl molecule$^{43}$ to $54^\circ$ in $\beta$-$144$ and to only $46^\circ$ in $\alpha$-$144$, mostly through increased folding of both dithiole rings along the $S(1)...S(2)$ and $S(3)...S(4)$ vectors ($24^\circ$ and $13^\circ$ respectively in $\alpha$-$144$, $24^\circ$ and $20^\circ$ in $\beta$-$144$).

The structure of 143 contains two independent molecules, one of which shows disorder that can be rationalised as either a varying degree of molecular bending or a rocking of the molecule as a whole. In the other (ordered) molecule (Figure 5.5) the pentamethylene bridge adopts a nearly all trans conformation (C-C-C-C torsion angle $164^\circ$-$177^\circ$) and enhances the folding of the anthracene moiety by $43.4^\circ$ and both dithiole rings (by $29.4^\circ$ and $22.6^\circ$), thus narrowing the dihedral angle between the $S(1)C(16)C(17)S(2)$ and $S(3)C(19)C(20)S(4)$ planes to $34.7^\circ$. 

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Figure 5.4: The single crystal X-ray structure of compound β-144.

Figure 5.5: The single crystal X-ray structure of compound 143.
5.6 Conclusion

In summary, double olefination reactions of anthraquinone have afforded novel bridged 9,10-bis(methylene)-9,10-dihydroanthracenes, paving the way for studies on a new family of cyclophane molecules with interesting electrochemical and structural properties.
6.1 General Methods

Reactions were carried out under an inert atmosphere of argon, which was dried by passage through a column of phosphorus pentoxide. Diethyl ether, toluene and tetrahydrofuran were dried and distilled over sodium metal. Dichloromethane, acetone and acetonitrile were dried and distilled over calcium chloride. Ethanol and methanol were dried and distilled over magnesium. Anhydrous dimethyl formamide was obtained from Aldrich. All reagents were of commercial quality.

\(^1\)H and \(^{13}\)C Spectra were obtained on a Varian Unity 300, Oxford 200, Varian VXR 400s. Mass spectra were recorded on a Micromass Autospec spectrometer operating at 70eV. Infra-red spectra were recorded using a Golden Gate on a paragon 1000 FTIR spectrometer operated from a Grams Analyst 1600. Electronic absorption spectra were obtained using a Perkin-Elmer II UV-vis spectrometer operating with 1cm quartz cells. Melting points were obtained on a Philip Harris melting point apparatus and are uncorrected. Cyclic voltammometric data were measured with iR compensation using a BAS CV50 electrochemical analyser. The experiments were carried out with 5mL of ca. 10^{-4} M solution of the compound in acetonitrile containing 0.1M tetrabutylammonium hexafluorophosphate (Fluka, Puriss, electrochemical grade) as the supporting electrolyte, at a scan rate of 100 mV s\(^{-1}\). The potentials were measured \textit{versus} decamethylferrocene/decamethylferrocene\(^\ast\) by adding decamethylferrocene to the studied solution after the experiment, and referenced \textit{versus} Ag/AgCl.
6.2 Experimental Procedures For Chapter 2

2,6-Dibutoxyanthraquinone Acid 52.

To a solution of anthraflavic acid 51 (0.487 g, 1.15 mmol) in dry dimethylformamide (100 ml), was added silver (I) oxide (981 mg, 4.23 mmol) and iodobutane (0.7 ml, 6.15 mmol). After the mixture was stirred at 20°C for 48 h under an argon atmosphere, the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel with acetone/hexane (1:3, v/v) as the eluent to afford 52 as a yellow solid (205 mg, 56%). M.p. 109-111°C, MS (Cl) 353 m/z [M^+1]; (Found: C, 74.7; H, 6.9; C_{22}H_{24}O_{4} requires C, 75.0; H, 6.9); ^1H NMR (CDCl3) δ 1.00 (t, J = 7 Hz, 6H), 1.55 (m, 4H), 1.84 (m, 4H), 4.15 (t, J = 7 Hz, 4H), 7.26 (m, 2H), 7.69 (s, 2H), 8.19 (d, J = 9 Hz, 2H); ^13C NMR (CDCl3) δ 13.7, 19.1, 31.0, 68.4, 110.4, 120.8, 126.9, 129.5, 135.7, 163.9, 182.2 ppm. IR ν_{max} (Golden Gate): 2359, 2340, 1661, 1578, 1330, 1292, 1260, 1229 cm⁻¹.

2,6-Dihexoxyanthraquinone Acid 53.

To a solution of anthraflavic acid 51 (2.45 g, 10.2 mmol) in dry dimethylformamide (250 ml), was added silver (I) oxide (9.69 g, 40.7 mmol) and iodohexane (6 ml, 41.0 mmol). After the mixture was stirred for 48 h under an argon atmosphere, the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel with dichloromethane/hexane (1:3, v/v) as the eluent to afford 53 a yellow solid (2.31 g, 57%); M.p. 90-92°C; MS (Cl) 409 m/z [M^+1]; (Found: C, 76.0; H, 7.9; C_{26}H_{32}O_{4} requires C, 76.4; H, 7.9); ^1H NMR (CDCl3) δ 0.91 (t, J = 7.2 Hz, 6H), 1.36 (m, 8H), 1.49 (m, 4H), 1.83 (p, J = 7.0 Hz, 4H), 4.12 (t, J = 7.2 Hz, 4H) 7.19 (dd, J_{ab} = 2.0 Hz, J_{bc} = 7.0 Hz, 2H), 7.67 (d, J_{bc} = 2.0 Hz, 2H), 8.20 (d, J_{ab} = 9.0 Hz, 2H); ^13C NMR (CDCl3) δ 14.0, 22.6, 25.6, 29.0, 31.5, 68.8, 110.5, 120.8, 126.9,
129.6, 135.8, 164.0, 182.2 ppm; IR $\nu_{\text{max}}$ (Golden Gate) 956, 2936, 2919, 2855, 1662, 1586, 1492, 1469, 1425, 1387, 1310, 1259, 1236, 1149, 1078 cm$^{-1}$.

**2,6-Dibutoxy-9,10-bis(1,3-dithiol-2-yldene)-9,10-dihydroanthracene 44.**

Into a solution of 2-dimethoxyphosphinyl-1,3-dithiole 50 (1.0 g, 4.71 mmol) in dry tetrahydrofuran (50 ml) at $-78^\circ$C under argon, was added lithium diisopropylamide (3.6 ml of 1.5 M solution in cyclohexane, 5.4 mmol) over a period of 15 min. The reaction mixture was left for 3 h until a pale cloudy solution formed. Then a solution of 2,6-dibutoxyanthraquinone 52 (508 mg, 1.44 mmol) in dry tetrahydrofuran (10 ml) was added over 15 min. The reaction was stirred overnight under an argon atmosphere. The reaction mixture was evaporated in vacuo. The residue was purified by column chromatography on silica gel with hexane/dichloromethane (2:1 v/v) as the eluent to afford 44 as yellow solid (260 mg, 51%). A single crystal X-ray sample was recrystallized from anhydrous acetonitrile. M.p. 129-133°C, (Found: C, 63.7; H, 5.3; C$_{28}$H$_{28}$O$_2$S$_4$ requires C, 64.0; H, 5.3); MS (EI) 524 m/z [M$^+$]; $^1$H NMR (CDCl$_3$) $\delta$ 0.98 (t, $J = 7$ Hz, 6H), 1.50 (m, 4H), 1.80 (m, 4H), 4.03 (t, $J = 7$ Hz, 4H), 6.23 (s, 4H), 6.80 (dd, $J_{ab} = 3$ Hz, $J_{bc} = 9$ Hz, 2H), 7.26 (d, $J_{bc} = 3$ Hz, 2H), 7.50 (d, $J_{ab} = 9$ Hz, 2H). $^{13}$C NMR (CDCl$_3$) $\delta$ 13.8, 19.4, 31.2, 31.0, 31.3, 67.9, 68.5, 110.5, 110.9, 111.9, 117.1, 120.9, 122.2, 126.0, 126.9, 128.2, 129.6, 133.4, 125.8, 136.9, 157.1, 164.0, 182.3 ppm.

A charge transfer complex of compound 44 and TCNQ 2 was prepared by the mixing of 20 mg of both compounds in refluxing acetonitrile; yielding a black solid (21.7 mg) IR $\nu_{\text{max}}$ (Golden Gate): 2360, 2344, 2172, 2155, 1559, 1496 cm$^{-1}$.

**2,6-Dihexoxy-9,10-bis(1,3-dithiol-2-yldene-4,5-dimethyl)-9,10-dihydroanthracene 55.**

Into a solution of 2-dimethoxyphosphinyl-4,5-methyl-1,3-dithiole 54 (129 mg, 0.538 mmol) in dry tetrahydrofuran (50 ml) at $-78^\circ$C under argon, was added lithium
diisopropylamide (0.4 ml of 1.5 M solution in cyclohexane, 0.59 mmol). The reaction mixture was left for 3 h until a cloudy white solution formed. Then a solution of 2,6-dihexoxyanthraquinone 53 (97 mg, 0.24 mmol) was added. The reaction was stirred overnight under an argon atmosphere. The reaction mixture was evaporated in vacuo. The residue was purified by column chromatography on silica gel with hexane/dichloromethane (2:1 v/v) as the eluent to afford 55 as a yellow oil which solidified on standing (92 mg, 59%). M.p. 123-125°C; (Found: C, 67.6; H, 7.0; C_{36}H_{44}O_{2}S_{4} requires C, 67.9; H, 7.0); MS (EI) m/z [M+]; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \delta 0.92 (m, 6H) 1.37 (m, 12H) 1.82 (m, 4H) 1.92 (s, 12H) 4.03 (t, J = 6.6 Hz, 4H) 6.78 (dd, J = 2.6 Hz, J = 8.6 Hz, 2H) 7.14 (d, J = 2.4 Hz, 2H) 7.51 (d, J = 8.4 Hz, 2H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \delta 13.1, 14.1; 22.6, 25.7, 29.2, 31.6, 68.2, 105.4, 111.3, 111.6, 120.7, 121.4, 126.3, 128.1, 130.9, 136.8, 156.9 ppm.

2,6-Dibutoxy-9,10-bis(4,5-dibromo-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 64

Into a solution of 2,6-dibutoxy-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 44 (243 mg, 0.69 mmol) in dry tetrahydrofuran (50 ml) at −78°C under argon, was added lithium diisopropylamide (0.4 ml of 1.5 M solution in cyclohexane, 0.60 mmol) over a period of 15 min. The reaction mixture was left for 3 h until an orange solution formed. Then a solution of tosyl bromide (698 mg, 2.97 mmol) in dry tetrahydrofuran (20 ml) was added over 15 min. The reaction was stirred overnight under an argon atmosphere. The reaction mixture was evaporated in vacuo. The residue was purified by column chromatography on silica gel with hexane/dichloromethane (2:1 v/v) as the eluent to afford 64 as a red solid (45 mg, 12%). M.p. 85-87°C; MS (EI) m/z 524 [M+]; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \delta 0.99 (t, J = 7 Hz, 6H), 1.52 (m, 4H), 1.80 (m, 4H), 4.02 (t, J = 7 Hz, 4H), 6.23 (s, 4H), 6.80 (dd, J\textsubscript{ab} = 3 Hz, J\textsubscript{bc} = 9 Hz, 2H), 7.26 (d, J\textsubscript{bc} = 3 Hz, 2H), 7.50 (d, J\textsubscript{ab} = 9 Hz, 2H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \delta 13.9, 19.3, 31.2, 68.0, 100.0, 111.7, 112.3, 124.7, 126.5, 128.7, 135.5, 157.9 ppm.
6.3 Experimental Procedures For Chapter 3

2-Piperidino-2-methyl-1,3-dithiole 72.

To a stirred suspension of salt 71 (75.0 g, 217 mmol) in dry tetrahydrofuran/isopropanol (1:1 v/v, 1.0 l) at 0°C, finely-ground sodium borohydride (37.8 g, 1.0 mol) was added in portions over ca. 6 h. The reaction was then maintained at 0°C for a further 2 h, whereupon it was allowed to warm to room temperature and stirred for a further 40 h. After concentrating to ca. 150 ml, water (500 ml) was added cautiously and the mixture extracted with diethyl ether (4 x 125 ml). The combined extracts were washed with water (3 x 125 ml), dried (MgSO4) and evaporated in vacuo to afford compound 72 (40.6 g, 93%) as a yellow oil of high purity (1H NMR analysis) suitable for use in the next step without further purification. 1H NMR (CDCl3): δ 1.41 (m, 2H), 1.53 (m, 4H), 2.02 (s, 3H), 2.49 (t, J = 5.2 Hz, 4H), 5.72 (s, 1H), 6.18 (s, 1H).

4-Methyl-1,3-dithiolium Iodide 74.

To an ice-cooled, stirred solution of acetic anhydride (260 ml) was cautiously added hexafluorophosphoric acid (60 wt % in water, 115.0 g, 0.788 mol) over ca. 2 h. (CAUTION: vigorous exothermic reaction!). To the ice-cooled solution of anhydrous hexafluorophosphoric acid thus formed, was added dropwise over ca. 0.5 h a solution of compound 72 (38.0 g, 189 mmol) in dry diethyl ether (250 ml), precipitating immediately the salt 73. The mixture was diluted with dry diethyl ether (250 ml), stirred for a further 0.5 h, and the product was collected by filtration and washed with diethyl ether (125 ml) affording hexafluorophosphate salt 73 as an off-white solid. Purification was achieved by anion exchange to the iodide salt. To a stirred solution of the hexafluorophosphate salt in anhydrous acetone (125 ml) at 20°C was added a solution of sodium iodide (28.3 g, 189 mmol) in anhydrous acetone (50 ml) to precipitate iodide salt 74 as a bright yellow solid, which was collected by filtration and washed initially with cold anhydrous acetone (25 ml) and then anhydrous diethyl ether (100 ml) to afford 40.6 g (88%) of compound 74.
M.p. 98-101°C. 1H NMR (CD3)2SO: δ 2.91 (s, 3H), 9.09 (s, 1H), 11.47 (s, 1H). This salt can be stored under argon for 1 month or in a sealed ampule for several months without any observable decomposition.

4-Methyl-1,3-dithiole-2-dimethoxyphosphonate 75

To a stirred suspension of salt 74 (500 mg, 2.05 mmol) in dry acetonitrile (100 ml) at 20°C, was added trimethylphosphite (0.28 ml, 2.37 mmol) and the mixture was stirred for 1 h. The solvent was evaporated in vacuo to afford compound 75 (460 mg, 99%) as a light brown oil of high purity (1H NMR analysis) suitable for use in the next step without further purification. 1H NMR (CDCl3): δ 1.95 (s, 3H), 3.89 (d, J = 10.5 Hz, 6H), 4.97 (d, J = 4.2 Hz, 1H), 5.53 (s, 1H).

9-(4,5-Dimethyl-1,3-dithiole-2-ylidene)-10-(4-methyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 65.

Into a solution of reagent 75 (465 mg, 2.05 mmol) in dry tetrahydrofuran (150 ml) at -78°C, was added lithium diisopropylamide (1.5 ml of 1.5 M solution in cyclohexane, 2.25 mmol) over a period of 15 min. The reaction was stirred for 3 h at -78°C until a pale cloudy solution formed. Then compound 68 (725 mg, 2.25 mmol) was added portionwise over 15 min. The reaction was stirred overnight at 20°C. The reaction mixture was evaporated in vacuo and the residue was purified by column chromatography on silica gel with hexane/dichloromethane (2:1 v/v) as the eluent to afford 65 as a yellow solid (474 mg, 55%). M.p. 288-290°C (from hexane/dichloromethane). 1H NMR (CDCl3): δ 2.02 (s, 6H), 2.14 (s, 3H), 5.93 (s, 1H), 7.36 (m, 4H), 7.75 (m, 4H); 13C NMR (CDCl3): δ 13.8, 15.9, 111.0, 120.8, 121.2, 122.1, 125.1, 125.3, 129.3, 133.0, 135.1, 135.2, 136.0; UV (MeCN): λmax (log ε) = 360 nm (4.18), 430 (4.43); CV (Eox) 0.320 V; MS (EI); m/z (%) = 422 (37) [M+], 149 (50), 84 (100); HRMS: C23H18S4 (422.6): calcd. 422.0359; found 422.0359.
9-(4-Formyl-5-methyl-1,3-dithiol-2-ylidene)-10-(4,5-dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 78.

Into a solution of 65 (159 mg, 0.376 mmol) in dry tetrahydrofuran (50 ml) at -78°C, was added lithium diisopropylamide (0.26 ml of 1.5 M solution in cyclohexane, 0.39 mmol). The reaction was stirred for 3 h at -78°C to give a yellow solution containing anion 77. N,N-Dimethylformamide (0.055 ml, 0.71 mmol) was then added and the reaction was stirred overnight at 20°C. The reaction mixture was acidified with HCl (1M), and then extracted into dichloromethane (3 x 100 ml). The organic layer was separated and dried (MgSO4) and evaporated in vacuo and the residue was purified by column chromatography on silica gel with hexane/dichloromethane (2:1 v/v) as the eluent to afford 78 as an orange solid (22 mg, 13%). M.p. 160°C (dec); 1H NMR (CDCl3): δ = 1.93 (s, 6H), 2.40 (s, 3H), 7.26 (m, 4H), 7.64 (m, 4H), 9.67 (s, 1H); IR νmax (Golden Gate): 1635 (C=O) cm⁻¹; UV (MeCN): λmax (log ε) = 358 nm (3.90), 422 (4.08); CV (Eox) 0.450 V; MS (EI) m/z (%) = 450 (100) [M⁺], 306 (63), 252 (31) HRMS: C24H18OS4 (450.0): calcd. 450.0308; found 450.0308.

9-(4-Methylthiocarbamoyl)-5-methyl-1,3-dithiol-2-ylidene)-10-(4,5-dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 79.

Into a solution of 65 (102 mg, 0.241 mmol) in dry tetrahydrofuran (50 ml) at -78°C was added lithium diisopropylamide (0.17 ml of 1.5 M solution in cyclohexane, 2.55 mmol). The reaction was stirred for 3 h, then methyl isothiocyanate (0.10 ml, 1.46 mmol) was added and the reaction was stirred overnight at 20°C. Workup and purification as described for 78, gave 79 as an orange solid (20 mg, 17%). M.p. 197-200°C; 1H NMR (CDCl3): δ = 1.92 (s, 6H), 2.03 (s, 3H), 2.99 (d, J = 4.8 Hz, 3H), 7.30 (m, 4H), 7.52 (m, 2H), 7.66 (m, 2H), (NH not observed); 13C NMR (CDCl3): δ = 13.1, 15.0, 32.6, 120.9, 125.3, 125.3, 125.5, 125.6, 125.8, 125.9, 126.2, 127.3, 129.3, 131.1, 134.0, 134.3, 134.4, 135.1 ppm; UV (MeCN): λmax (log ε) = 362 nm (4.11), 430 (4.32);
CV ($E^{ox}$) 0.365 V; MS (EI) $m/z$ (%) = 495 (100) [M$^+$], 447 (36), 350 (40); HRMS: 
C$_{25}$H$_{21}$NS$_5$ (495.8): calcd. 495.0362; found 495.0362.

9-(4-Iodo-5-methyl-1,3-dithiol-2-ylidene)-10-(4,5-dimethyl-1,3-dithiol-2-ylidene)-
9,10-dihydroanthracene 80.

Into a solution of 65 (200 mg, 0.47 mmol) in dry tetrahydrofuran (150 ml) at
−78°C was added lithium diisopropylamide (1.0 ml of 1.5 M solution in cyclohexane,
1.50 mmol) over a period of 15 min. The reaction was stirred for 3 h, then perfluorohexyl
iodide (0.511 ml, 2.37 mmol) was added over 15 min and the reaction was stirred
overnight at 20°C. Workup and purification as described for 78, with
hexane/dichloromethane (3:1 v/v) as the eluent to afford 80 as a brown solid (141 mg,
55%). $^1$H NMR (CDCl$_3$): δ = 1.92 (s, 6H) 2.03 (s, 3H) 7.26 (m, 4H) 7.52 (m, 2H) 7.63
(m, 2H); $^{13}$C NMR (CDCl$_3$): δ = 13.3, 14.4, 19.1, 22.9, 27.2, 31.8, 62.0, 121.1, 123.5,
125.3, 125.6, 125.7, 125.9, 126.1, 126.4, 130.4, 134.2, 134.6, 134.8, 135.0, 135.4, 135.5
ppm; MS (EI) $m/z$ (%) = 548 (100) [M$^+$]; C$_{23}$H$_{17}$I$_4$ (548): calcd. C 50.36, H 3.12;
found C 50.20, H 3.30.

9-(4-Methoxycarbonyl-5-methyl-1,3-dithiol-2-ylidene)-10-(4,5-dimethyl-1,3-dithiol-
2-ylidene)-9,10-dihydroanthracene 81.

Into a solution of 65 (504 mg, 1.19 mmol) in dry tetrahydrofuran (150 ml) at
−78°C was added lithium diisopropylamide (0.87 ml of 1.5 M solution in cyclohexane,
1.30 mmol) over a period of 15 min. The reaction was stirred for 3 h, then methyl
chloroformate (0.27 ml, 3.54 mmol) was added over 15 min and the reaction was stirred
overnight at 20°C. Workup and purification as described for 78, with
hexane/dichloromethane (3:1 v/v) as the eluent afforded 81 as a yellow solid (475 mg,
83%). M.p. 218-220°C; $^1$H NMR (CDCl$_3$): δ = 1.83 (s, 6H), 2.28 (s, 3H), 3.69 (s, 3H),
7.20 (m, 4H), 7.51 (m, 2H), 7.57 (m, 2H); $^{13}$C NMR (CDCl$_3$): δ = 13.4, 15.7, 52.4,
117.2, 121.0, 121.2, 123.7, 125.4, 125.5, 125.7, 125.9, 126.1, 126.4, 129.5, 134.2, 134.8,
135.5, 145.8, 160.9 ppm; IR (powder) ν\textsubscript{max} 1714 (C=O) cm\textsuperscript{-1}; UV (MeCN): λ\textsubscript{max} (log ε) = 358 nm (4.18), 426 (4.40); CV (E\textsuperscript{OX}) 0.425 V; MS (EI) m/z (%) = 480 (100) [M\textsuperscript{+}], 306 (37), 175 (35); C\textsubscript{25}H\textsubscript{20}O\textsubscript{2}S\textsubscript{4} (480.0): calcd. C 62.47, H 4.19; found C 62.40, H 4.12; Crystals for X-ray analysis were grown from CDCl\textsubscript{3}.

9-(4-Benzoylsulfanyl-5-methyl-1,3-dithiol-2-ylidene)-10-(4,5-dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 83.

Into a solution of compound 68 (199 mg, 0.471 mmol) in dry tetrahydrofuran (50 ml) at -78°C was added lithium diisopropylamide (0.38 ml of 1.5 M solution in cyclohexane, 0.57 mmol) over a period of 15 min. The reaction was stirred for 3 h at -78°C. Finely powdered, elemental sulfur (78 mg, 2.37 mmol) was added and the reaction was stirred for a further 2 h at -78°C before benzoyl chloride (0.275 ml, 2.37 mmol) was added. The colour of the solution turned a darker yellow, and the reaction was stirred overnight at 20°C. Workup and purification as described for 78, gave 83 as a yellow solid (138 mg, 53%). M.p. 160°C (dec.); 1H NMR (CDCl\textsubscript{3}): δ = 1.84 (s, 6H), 1.97 (s, 3H), 7.19 (m, 4H), 7.39 (t, J = 7.5 Hz, 2H), 7.53 (m, 5H), 7.86 (d, J = 7.9 Hz, 2H); 13C NMR (CDCl\textsubscript{3}): δ = 13.1, 14.9, 108.1, 120.8, 120.9, 121.0, 123.0, 125.1, 125.2, 125.4, 125.5, 125.7, 125.8, 126.0, 126.1, 126.8, 126.9, 131.3, 133.9, 134.2, 134.7, 134.9, 135.3, 135.4, 135.7, 139.3, 187.7; IR (powder) ν\textsubscript{max} 1737 (C=O) cm\textsuperscript{-1}; UV (MeCN): λ\textsubscript{max} (log ε) = 364 nm (4.16), 430 (4.38); CV (E\textsuperscript{OX}) 0.420 V; MS (EI) m/z (%) = 558 (5) [M\textsuperscript{+}], 84 (100), 64 (71); C\textsubscript{30}H\textsubscript{22}O\textsubscript{2}S\textsubscript{5} (558.0): calcd. C 64.48, H 3.97; found C 64.29, H 4.25.

9-(4-Methylsulfanyl-5-methyl-1,3-dithiol-2-ylidene)-10-(4,5-dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 84.

Into a solution of compound 65 (97 mg, 0.174 mmol) in dry tetrahydrofuran (35 ml) at 20°C was added sodium methoxide (0.39 ml of 0.5 M solution in methanol, 0.195 mmol). The reaction was stirred for 1 h until a dark red solution formed. Then
iodomethane was added (0.10 ml, 1.61 mmol) and the reaction was stirred overnight at 20°C. The reaction mixture was evaporated in vacuo and the residue was purified by column chromatography on silica gel with hexane/dichloromethane (2:1 v/v) as eluent to afford 84 as a yellow solid (65 mg, 80%). M.p. 220°C (dec.); 1H NMR (CDCl3): δ = 1.86 (s, 6H), 2.03 (s, 3H), 2.20 (s, 3H), 7.20 (m, 4H), 7.51 (m, 2H), 7.59 (m, 2H); 13C NMR (CDCl3): δ = 13.1, 14.5, 19.3, 118.3, 120.8, 125.2, 125.3, 125.4, 125.6, 125.8, 125.9, 132.0, 134.8, 135.0, 135.2, 197.9; UV (MeCN): λmax (log ε) = 360 nm (3.89), 432 (4.38); CV (E⁰X) 0.355 V; MS (EI) m/z (%) = 468 (100) [M⁺], 350 (50), 57 (60); C24H20S5 (468.0): calcd. C 61.50, H 4.30; found C 61.30, H 4.26; Crystals for X-ray analysis were grown from CS2/CH2Cl2.

9-[4-(6-Hydroxyhexylsulfanyl)-5-methyl-1,3-dithiol-2-yldene]-10-(4,5-dimethyl-1,3-dithiol-2-yldene)-9,10-dihydroanthracene 85.

Into a solution of compound 65 (100 mg, 0.179 mmol) in dry tetrahydrofuran (50 ml) at 20°C was added sodium methoxide (0.39 ml of 0.5 M solution in methanol, 0.195 mmol). The reaction was left for 1 h before 6-bromohexan-1-ol was added (0.07 ml, 0.535 mmol), and the reaction was stirred overnight at 20°C. The reaction mixture was evaporated in vacuo and excess 6-bromohexan-1-ol was removed by Kugelrohr distillation at 140°C at ca. 0.1 mm Hg, and the distillate was discarded. The residue was purified by column chromatography on silica gel with ethyl acetate/dichloromethane (1:4 v/v) as the eluent to afford 85 as a red oil (93 mg, 93%). 1H NMR (CDCl3): δ = 1.37 (m, 4H), 1.55 (m, 4H), 1.92 (s, 6H), 2.09 (s, 3H), 2.66 (m, 2H), 3.60 (t, J = 6.6 Hz, 2H), 7.26 (m, 4H), 7.58 (m, 2H), 7.64 (m, 2H), (OH not observed); 13C NMR (CDCl3): δ = 13.1, 14.7, 25.2, 28.1, 28.9, 29.6, 32.5, 35.9, 62.8, 117.1, 120.8, 122.3, 125.2, 125.3, 125.6, 125.8, 125.9, 131.3, 133.0, 133.1, 134.8, 135.0, 135.2 ppm; UV (MeCN): λmax (log ε) = 366 nm (4.14), 432 (4.39); CV (E⁰X) 0.380 V; MS (EI) m/z (%) = 554 (100) [M⁺], 350 (76), 220 (31); HRMS: C29H30OS5 (554.0) calcd. 554.0985; found 554.0985.
2-Methylsulfanyl-4-(2-cyanoethylsulfanyl)-5-methylthio-1,3-dithiolium trifluoromethylsulfonate 92.

Into a solution of thione 91 (1.029 g, 4.10 mmol) in dry dichloromethane (100 ml) at 20°C, was added methyl trifluoromethylsulfonate (0.90 ml, 7.97 mmol). The reaction was left for 1 h until a dark yellow solution formed. The reaction mixture was concentrated in vacuo to ca. 10 ml and the resulting suspension washed with dry diethyl ether (50 ml), which was then decanted off and discarded. The reaction mixture was then evaporated in vacuo affording 92, as an unstable red oil which was quickly used without further purification; 1H NMR (CDCl3): δ = 2.85 (s, 3H), 2.92 (t, J = 6.6 Hz, 2H), 3.22 (s, 3H), 3.33 (t, J = 6.4 Hz, 2H).

10-[4-(2-Cyanoethyisulfanyl)]-5-methylsulfanyH3-dithioi-2-yIdene)-anthracene-9-(10H)-one 95.

Into a solution of anthrone 93 (773 mg, 3.98 mmol) in dry isopropanol (50 ml) at 20°C was added lithium diisopropylamide (2.65 ml, of 1.5 M solution in cyclohexane, 3.98 mmol). The reaction was stirred for 15 min until a bright yellow solution formed. Then salt 92 (1.653 g, 3.98 mmol) in dry tetrahydrofuran (50 ml) was added and the reaction mixture was stirred overnight. The mixture was evaporated in vacuo and the residue was purified by column chromatography on silica gel with hexane/dichloromethane (1:1 v/v) as the eluent to afford crude compound 94 as a red solid. 1H NMR (CDCl3): δ = 2.00 (s, 3H), 2.26 (s, 3H), 2.47 (m, 2H), 2.73 (m, 2H), 4.91 (s, 1H), 7.51 (m, 4H), 7.69 (m, 2H), 8.15 (m, 2H). This solid (398 mg, 0.889 mmol) was dissolved in dry toluene (100 ml) at 20°C and p-toluene sulfonic acid (100 mg, 0.526 mmol) was added. The reaction mixture was refluxed for 16 h to give a dark red solution. The mixture was evaporated in vacuo and the residue purified by column chromatography on silica gel with dichloromethane as eluent to afford 95 as a red solid (293 mg, 18% based on 91). M.p. 142-145°C; 1H NMR (CDCl3): δ = 2.04 (s, 3H), 2.24 (t, J = 6.8 Hz, 2H), 2.58 (t, J = 6.8 Hz, 2H), 7.04 (t, J = 7.8 Hz, 2H), 7.26 (m, 4H), 7.85
(d, J = 7.4 Hz, 2H); $^{13}$C NMR (CDCl$_3$): $\delta$ = 18.7, 18.1, 31.3, 117.4, 119.6, 120.3, 126.1, 127.2, 127.3, 130.7, 131.9, 134.1, 138.2, 138.4, 183.4 ppm; IR (powder) $\nu_{\text{max}}$ 1635 (C=O) cm$^{-1}$; MS (EI) m/z (%) = 425 (61) [M$^+$], 236 (100), 91 (66); C$_{21}$H$_{15}$NOS$_4$ (425.6) calcd. C 59.27, H 3.55, N 3.29; found C 59.51, H 3.70, N 3.28.

10-[4-(6-Hydroxyhexylsulfanyl)-5-methylsulfanyl-1,3-dithiol-2-ylidene]-anthracene-9-(10H)-one 96.

Into a solution of 95 (200 mg, 0.471 mmol) in dry tetrahydrofuran (50 ml) at 20°C was added cesium hydroxide monohydrate (94 mg, 0.528 mmol). The reaction was stirred for 1 h until a dark red solution formed. 6-Bromohexan-1-ol (0.2 ml, 1.53 mmol) was added and the reaction was stirred overnight at 20°C then evaporated in vacuo and excess 6-bromohexan-1-ol was removed by Kügelrohr distillation at 140°C at ca. 0.1 mm Hg, and the distillate was discarded. The residue was purified by column chromatography on silica gel with hexane/dichloromethane (1:1 v/v) as eluent to afford 96 as a red oil (198 mg, 89 %); $^1$H NMR (CDCl$_3$): $\delta$ = 1.47 (m, 8H), 2.41 (s, 3H), 2.79 (t, $J$ = 7.2 Hz, 2H), 3.60 (t, $J$ = 7.2 Hz, 2H), 7.44 (t, $J$ = 7.8 Hz, 2H), 7.65 (t, $J$ = 7.8 Hz, 2H), 7.77 (d, $J$ = 7.8 Hz, 2H), 8.26 (d, $J$ = 7.8 Hz, 2H); $^{13}$C NMR (CDCl$_3$): $\delta$ = 19.2, 25.1, 28.0, 29.4, 32.4, 36.2, 62.6, 119.0, 125.1, 126.1, 127.1, 127.6, 129.0, 130.5, 131.8, 138.5, 140.3, 183.4; IR (Powder) $\nu_{\text{max}}$ 1649 (C=O) cm$^{-1}$; MS (EI) m/z (%) = 472 (100) [M$^+$], 236 (58), 55 (79); HRMS: C$_{24}$H$_{24}$O$_2$S$_4$ (472.7): calcd. 472.0659; found 472.0644.

10-[4-(6-tert-Butyldiphenylsilyloxyhexylsulfanyl)-5-methylsulfanyl-1,3-dithiol-2-ylidene]-anthracene-9-(10H)-one 97.

Into a solution of compound 96 (305 mg, 0.646 mmol) in dry dimethylformamide (50 ml) was added tert-butylchlorodiphenylsilane (0.18 ml, 0.692 mmol) and imidazole (345 mg, 5.07 mmol). The reaction was stirred overnight at 20°C and then evaporated in vacuo and the residue was purified by column chromatography on silica gel with hexane/dichloromethane (1:1 v/v) as eluent to afford 97 as a red oil (413 mg, 90 %); $^1$H
NMR (CDCl3): δ = 1.06 (s, 9H), 1.37 (m, 4H), 1.55 (m, 4H), 2.40 (s, 3H), 2.79 (t, J = 7.6 Hz, 2H) 3.65 (t, J = 6.4 Hz, 2H), 7.42 (m, 8H), 7.67 (m, 6H), 7.79 (m, 2H), 8.29 (d, J = 7.6 Hz, 2H); 13C NMR (CDCl3): δ = 19.5, 25.6, 27.2, 28.4, 29.8, 32.6, 36.7, 64.0, 119.3, 125.6, 126.5, 127.5, 129.3, 129.8, 130.9, 132.1, 134.3, 135.8, 138.9, 140.7, 183.7. IR (Powder) νmax 1653 (C=O) cm⁻¹; MS (EI) m/z (%) = 710, (100) [M⁺], 653 (99), 135 (79); HRMS: C40H42O2S4Si (711.1) calcd. 710.1904; found 710.1902.

9-[4-(6-tert-Butyldiphenylsilyloxyhexylsulfanyl)-5-methylsulfanyl-1,3-dithiol-2-ylidene]-10-(4,5-dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 98.

Into a solution of 54 (117 mg, 0.488 mmol) in dry tetrahydrofuran (150 ml) at -78°C was added lithium diisopropylamide (0.34 ml of 1.5 M solution in cyclohexane, 0.506 mmol) over a period of 15 min. The reaction was stirred for 3 h until a pale cloudy solution formed. Then compound 97 (171 mg, 0.241 mmol) was added over 15 min and the reaction was stirred overnight at 20°C and then evaporated in vacuo and the residue purified by column chromatography on silica gel with hexane/dichloromethane (2:1 v/v) as eluent to afford 98 as a yellow oil (138 mg, 70%); 1H NMR (CDCl3) δ 1.05 (s, 9H), 1.36 (m, 4H), 1.56 (m, 4H), 1.93 (s, 6H), 2.36 (s, 3H), 2.76 (m, 2H), 3.65 (t, J = 6.6 Hz, 2H), 7.30 (m, 4H), 7.41 (m, 6H), 7.54 (m, 2H), 7.66 (m, 6H); 13C NMR (CDCl3) δ 13.1, 19.2, 25.3, 26.9, 28.1, 29.6, 31.6, 32.3, 34.6, 36.2, 63.7, 120.8, 120.9, 123.7, 124.2, 125.8, 126.1, 127.6, 129.5, 130.4, 133.5, 134.0, 134.6, 135.2, 135.5; MS (EI) m/z (%) = 824 (100) [M⁺], 350 (89), 220 (66); HRMS: C45H48O3S4Si (825.3): calcd. 824.1900; found 824.1900.

9-[4-(6-Hydroxyhexylsulfanyl)-5-methylsulfanyl-1,3-dithiol-2-ylidene]-10-(4,5-dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 99.

Into a solution of compound 98 (137 mg, 0.167 mmol) in dry tetrahydrofuran (50 ml) was added tetrabutylammonium fluoride (0.5 ml of 1.0 M solution in water, 0.5 mmol). After stirring for 1 h at 20°C a dark red solution had formed. The reaction
mixture was stirred at 20°C overnight and then evaporated in vacuo and the residue was purified by column chromatography on silica gel with dichloromethane as eluent to afford 99 as a yellow oil (77 mg, 79%); \(^1\)H NMR (CDCl\(_3\)): δ = 1.39 (m, 4H), 1.56 (m, 4H), 1.93 (s, 6 H), 2.37 (s, 3H), 2.77 (m, 2H), 3.61 (t, J = 6.5 Hz, 2H), 4.35 (t, J = 7.0 Hz, 1H), 7.28 (m, 4H), 7.52 (m, 2H), 7.66 (m, 2H); \(^1^3\)C NMR (CDCl\(_3\)): δ = 13.1, 19.1, 25.2, 28.1, 29.6, 32.5, 36.0, 60.4, 62.8, 120.9, 123.8, 124.0, 125.3, 125.7, 126.1, 127.7, 130.2, 133.5, 134.5, 135.2; MS (EI) m/z (%): 586 (21) [M\(^+\)], 350 (100), 220 (100); HRMS: C\(_{29}\)H\(_{30}\)OS\(_6\) (586.9) calcd. 586.0621; found 586.0634.

9-[4-(6-Carboxobenzoxyhexylsulfanyl)-5-methylsulfanyl-1,3-dithiol-2-ylidene]-10-(4,5-dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 100.

Into a solution of compound 99 (74 mg, 0.127 mmol) in dry dichloromethane (50 ml) was added triethylamine (1 ml, excess) and benzoyl chloride (0.20 ml, 1.72 mmol). The reaction was stirred overnight at 20°C and then evaporated in vacuo and the residue purified initially by column chromatography on silica gel with hexane/dichloromethane (1:1 v/v) as the eluent, and then further purified by column chromatography on silica gel with acetone/hexane (1:3 v/v) as eluent, to afford 100 as a yellow oil (44 mg, 50%); \(^1\)H NMR (CDCl\(_3\)): δ = 1.38 (m, 4H), 1.56 (m, 2H), 1.67 (m, 2H), 1.84 (s, 6H), 2.28 (s, 3H), 2.70 (m, 2H), 4.21 (t, J = 6.5 Hz, 2H), 7.20 (m, 4H), 7.35 (t, J = 8.0 Hz, 2H), 7.45 (m, 3H), 7.59 (m, 2H), 7.95 (d, J = 8.0 Hz, 2H); \(^1^3\)C NMR (CDCl\(_3\)): δ = 13.1, 19.1, 25.6, 28.0, 28.5, 29.5, 36.0, 64.9, 120.8, 120.9, 123.8, 123.9, 125.3, 125.3, 125.8, 126.1, 127.9, 128.3, 129.5, 130.2, 130.4, 132.8, 133.5, 134.6, 135.2, 166.6; UV (MeCN): λ\(_{\text{max}}\) (log e) = 366 nm (4.09), 434 (4.33); CV (E\(^{0x}\)) 0.375 V; MS (DCI) m/z (%): 691 (49) [M\(^{+}\)+1], 322 (100), 105 (63); HRMS: C\(_{36}\)H\(_{34}\)O\(_2\)S\(_6\) (691.0) calcd. 690.0985; found 690.0988.
10-{4,5-bis(2-Cyanoethylsulfanyl)-1,3-dithiol-2-ylidene}-anthracene-9-(10H)-one

Into a solution of anthrone 93 (1.41 g, 7.26 mmol) in dry isopropanol (50 ml) at 20°C was added lithium diisopropylamide (4.83 ml, of 1.5 M solution in cyclohexane, 7.24 mmol). The reaction was stirred for 15 min until a bright yellow solution formed. Then the triflate salt of 90 (3.08 g, 6.58 mmol) in dry tetrahydrofuran (50 ml) was added and the reaction mixture was stirred overnight. The mixture was evaporated in vacuo and the residue was purified by column chromatography on silica gel with hexane/dichloromethane (1:1 v/v) as the eluent to afford crude compound 101 as a red solid. This solid (1.51 g) was dissolved in dry toluene (100 ml) at 20°C and p-toluene sulfonic acid (100 mg, 0.526 mmol) was added. The reaction mixture was refluxed for 16 h to give a dark red solution. The mixture was evaporated in vacuo and the residue purified by column chromatography on silica gel with dichloromethane as eluent to afford 101 as a red solid (590 mg, 19% based on 90). M.p. 138-141°C; 1H NMR (CDCl3): δ 2.69 (m, 4H) 3.06 (m, 4H) 7.48 (m, 2H) 7.66 (m, 4H) 8.25 (m, 2H); 13C NMR (CDCl3): δ = 18.8, 19.0, 31.3, 31.6, 117.3, 121.2, 126.0, 127.1, 127.4, 130.7, 132.0, 136.9, 138.2, 183.4, 197.9 ppm; IR (powder) ν_max 1635 (C=O) cm⁻¹; MS (EI) m/z (%) = 464 [M⁺]; C23H16N2OS4 (464.0) calcd. C 59.46, H 3.47, N 6.03; found C 59.18, H 3.35, N 6.19.
6.4 Experimental Procedures For Chapter 4

1,10-Dibromo pentaethylene 107.

Into a mechanically stirred solution of pentaethylene glycol (35.7 g, 0.15 mmol) in pyridine (4 ml) was added phosphorus tribromide (33.9 g, 0.13 mmol) at 0°C for 7 h to give a cloudy white solution. The reaction mixture was extracted into dry diethyl ether (6 x 100 ml). The organic layer was separated and dried (MgSO4) and evaporated in vacuo and the residue was purified by column chromatography on silica gel with ethylacetate as the eluent to afford 107 as a colourless oil (28.2 g, 51%) of high purity (1H NMR analysis) suitable for use in the next step without further purification; 1H NMR (CDCl3): δ = 3.81 (t, J = 6.3 Hz, 4H) 3.67 (s, 12H) 3.48 (t, J = 6.3 Hz, 4H).

1,3-Dithiole-2-thione Crown 110.

Into a solution of 4,5-bis(thiobenzoyl)-1,3-dithiole-2-thione 108 (2.00 g, 4.93 mmol) in dry ethanol (40 ml) was added sodium methoxide (20 ml of 0.5 M in methanol, 10.0 mmol) at 0°C for 30 min to give a dark red solution. After 30 min, the solution was poured into dry diethyl ether (1 l) and stirred for 1 h. The red solid was then collected by Schlenk filtration. The red solid was transferred to a flask containing dry tetrahydrofuran (150 ml) and compound 107 (1.81 g, 4.97 mmol) and stirred for 12 h. Then the solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel with ethylacetate as the eluent to afford 110 as a yellow oil, which solidified on standing (1.56 g, 79%). 1H NMR (CDCl3): δ = 3.07 (t, J = 6.0 Hz, 4H) 3.64 (s, 12H) 3.75 (t, J = 6 Hz, 4H); C13H20O4S5 (400.0): calcd. C 38.98, H 5.03; found C 38.82, H 5.19.
Triflate salt 111.

Into a solution of 110 (2.7 g, 6.8 mmol) in dry methylene chloride (50 ml) was added methyl triflate (1.2 g, 7.3 mmol) at 20°C for 5 h to give a dark brown solution. Then the solvent was partially evaporated in vacuo (5 ml) and dry diethyl ether added (100 ml) and stirred for 30 min. Next, the solvent was decanted off and the oil dried in vacuo to afford 111, as a brown oil (3.2 g, 84%) of high purity suitable for use in the next step without further purification. C_{13}H_{23}F_{2}O_{3}S_{6} (564.0): calcd. C 31.91, H 4.08; found C 31.64, H 4.27.

1,3-Dithiole crown 112.

Into an ice cooled solution of 111 (120 mg, 1.9 mmol) in dry ethanol (75 ml) was added sodium cyanoborohydride portionwise (1.0 g, 1.8 mmol) at 0°C for 1 h. Then the solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel with ethylacetate as the eluent to afford 112, as a pale reddish oil (0.72 g, 98%). The oil was recrystallized from hot ethyl acetate with cooling in acetone/dry ice to yield an off-white solid. 1H NMR (CDCl3): δ = 5.77 (s, 1H) 3.71 (t, J = 2.6 Hz, 4H) 3.70 (s, 12H) 2.98-3.16 (m, 4H) 2.24 (s, 3H). C_{14}H_{24}O_{4}S_{5} (416.0): calcd. C 40.38, H 5.76; found C 40.25, H 5.84.

Triflate salt 113.

Into a solution of 112 (0.5, 1.2 mmol) in dry acetonitrile (5 ml) was added triflic acid (1 ml, 10 mmol) at 20°C for 10 min to give a deep red-orange solution. Then the solvent was partially evaporated in vacuo (5 ml) and dry diethyl ether added (100 ml) and stirred for 30 min. Next the solvent was decanted off and the oil dried in vacuo to afford 113, as a brown oil (3.2 g, 84%) of high purity (1H NMR analysis) suitable for use in the next step without further purification. 1H NMR (CD_{3}CN): δ = 3.38 (s, 12H) 3.55 (t, J = 4.5 Hz, 4H) 3.85 (t, J = 4.5 Hz, 4H) 9.22 (s, 1H).
Horner-Wadsworth-Emmons reagent \(114\).

To a stirred suspension of salt \(113\) (540 mg, 1.0 mmol) in dry acetonitrile (5 ml) at 20°C, was added triethylphosphite (0.17 ml, 1.0 mmol) and the mixture was stirred for 1 h. Then the solvent was evaporated \textit{in vacuo} and extracted into ethylacetate (2x50 ml). The organic layer was separated and dried (MgSO\(_4\)) and evaporated \textit{in vacuo} and the residue was purified by column chromatography on silica gel with ethylacetate as the eluent to afford \(114\) as a colourless oil (0.40 g, 75%) of high purity (\(^1\)H NMR analysis) suitable for use in the next step without further purification; \(^1\)H NMR (CDCl\(_3\)): \(\delta = 1.30\) (t, \(J = 7.0\) Hz, 6H) 2.86-2.96 (m, 2H) 2.99-3.12 (m, 2H) 3.62 (s, 4H) 3.64 (s, 8H) 3.74 (t, \(J = 6.2\) Hz, 2H) 3.75 (t, \(J = 6.8\) Hz, 2H) 4.18 (p, \(J_p = J_H = 7.0\) Hz, 2H) 4.63 (s, 1H).

Bis-Crown 106 and Mono-crown 116.

Into a solution of \(114\) (558 mg, 1.10 mmol) in dry tetrahydrofuran (70 ml) at -78°C, was added lithium diisopropylamide (0.74 ml of 1.5 M solution in cyclohexane, 1.11 mmol). The reaction was stirred for 3h at -78°C until a cloudy solution formed. Then anthraquinone (115 mg, 0.552 mmol) was added, the reaction was allowed to warm overnight to 20°C. The reaction mixture was evaporated \textit{in vacuo} and the residue was purified by column chromatography on silica gel with ethyl acetate as eluent. The first product to elute was \(116\) as a red oil which solidified on standing (178 mg, 29%). M.p. 123-124°C. C\(_{27}\)H\(_{28}\)O\(_5\)S\(_4\) (560) calcd. C 56.9, H 5.1; found C 56.7, H 5.0; \(m/z\) (EI) 560 [M\(^+\)]; \(^1\)H NMR (CDCl\(_3\)): \(\delta = 3.04\) (t, \(J = 6.0\) Hz, 4H) 3.58 (m, 16H) 7.46 (t, \(J = 7.6\) Hz, 2H) 7.76 (d, \(J = 7.6\) Hz, 2H) 8.27 (m, 2H). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta = 35.8, 69.6, 70.4, 70.6, 119.5, 126.3, 126.9, 127.2, 127.3, 130.6, 131.9, 138.6, 140.1, 197.9\) ppm. \(\nu_{\text{max}}\) (Golden Gate): 2853, 1646, 1591, 1482, 1429, 1291, 1105, 1087, 770.

Ethyl acetate/acetone (3:1 v/v) as the eluent followed by recrystallization from dichloromethane/hexane afforded \(106\) as a yellow solid (335 mg, 67%). M.p. 216-218°C; C\(_{40}\)H\(_{48}\)O\(_8\)S\(_8\) (912) calcd. C 52.1, H, 5.3; found C 51.9, H 5.4; \(m/z\) (EI) 912 [M\(^+\)]; \(^1\)H
NMR (CDCl₃): δ = 3.05 (m, 8H) 3.66 (m, 32H) 7.33 (m, 4H) 7.56 (m, 4H). ¹³C NMR (CDCl₃): δ = 19.4, 26.5, 116.1, 116.4, 120.4, 120.9, 126.2, 127.8, 128.7, 129.8, 131.3, 132.9, 135.5, 135.7, 136.6, 153.2 ppm.

Mono Crown 115.

Into a solution of 114 (250 mg, 0.494 mmol) in dry tetrahydrofuran (50 ml) at -78°C, was added lithium diisopropylamide (0.33 ml of 1.5 M solution in cyclohexane, 0.495 mmol). The reaction was stirred for 3 h at -78°C until a cloudy solution formed. Then compound 68 (159 mg, 0.494 mmol) was added, then the reaction was allowed to warm overnight to 20°C. The reaction mixture was evaporated in vacuo and the residue was purified by column chromatography on silica gel with ethyl acetate then ethyl acetate/acetone (3:1 v/v) as the eluent followed by recrystallization from dichloromethane/hexane to afford 115 as a yellow/orange solid (178 mg, 53%) M.p. 223-225°C; C₃₂H₃₄O₄S₆ requires HRMS 674.0883; found 674.0883; m/z [EI] 674 m/z; ¹H NMR (CDCl₃): δ = 1.94 (s, 6H) 3.00 (m, 4H) 3.58 (m, 16H) 7.29 (m, 4H) 7.52 (m, 2H) 7.68 (m, 2H). ¹³C NMR (CDCl₃): 13.1, 35.4, 53.4, 69.8, 70.4, 70.5, 70.6, 76.7, 77.0, 77.3, 120.8, 123.8, 125.3, 125.8, 126.1, 129.9, 133.4, 134.4, 135.1 ppm.
6.5 Experimental Procedures For Chapter 5

2,6-Dibutoxy-9,10-bis[(methylene-4,5-dithio)-1,3-dithiol-2-thione]-9,10-dihydroanthracene 123.

Into a solution of 119 (559 mg, 1.76 mmol) in dry tetrahydrofuran (50 ml) at -78°C, was added lithium diisopropylamide (1.0 ml of 1.5 M solution in cyclohexane, 1.5 mmol) over a period of 15 min. The mixture was stirred at -78°C for 3 h until a dark red solution formed. Then compound 52 (248 mg, 0.70 mmol) was added over 15 min and the mixture was stirred overnight at 20°C. The reaction mixture was evaporated in vacuo and the residue purified by column chromatography on silica gel with hexane/dichloromethane (2:1 v/v) as eluent to afford 123 as a red solid (220 mg, 43%). M.p. 106-108°C; ¹H NMR (CDCl₃): δ = 1.00 (t, J = 7 Hz, 6H) 1.51 (m, 4H), 1.80 (m, 4H), 4.04 (t, J = 7.6 Hz, 4H), 6.87 (dd, Jₕₑ = 3 Hz, Jbc = 9 Hz, 2H) 7.00 (d, J = 3 Hz, 2H) 7.39 (d, J = 9 Hz, 2H); ¹³C NMR (CDCl₃): δ = 13.9, 19.3, 31.3, 68.2, 112.2, 122.1, 126.5, 126.7, 127.2, 131.5, 135.5; 158.2, 211.5 ppm; MS (Cl) 738 m/z [M⁺]; C₃₀H₂₄O₂S₁₀ calcd. C 48.9, H 3.3; found C 49.5, H 3.6;

9-[(4-5-Methylenedisulfanyl)-1,3-dithiol-2-thione]-10-(4,5-dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 124.

Into a solution of 119 (216 mg, 0.63 mmol) in dry tetrahydrofuran (50 ml) at -78°C, was added lithium diisopropylamide (0.46 ml of 1.5 M solution in cyclohexane, 0.69 mmol) over a period of 15 min. The mixture was stirred at -78°C for 3 h until a dark red solution formed. Then compound 68 (198 mg, 0.61 mmol) was added over 15 min and the mixture was stirred overnight at 20°C. The reaction mixture was evaporated in vacuo and the residue purified by column chromatography on silica gel with hexane/dichloromethane (2:1 v/v) as eluent to afford 124 as a red solid (189 mg, 60%). M.p. 246-249°C; ¹H NMR (CDCl₃): δ = 1.93 (s, 6H) 7.27 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.42 (d, J = 7.6 Hz, 2H), 7.71 (d, J = 7.6 Hz, 2H); ¹³C NMR (CDCl₃): δ =
13.1, 29.7, 119.8, 121.0, 122.3, 125.2, 125.5, 125.8, 127.1, 128.8, 130.8, 133.7, 135.2, 135.9, 211.7; CV 0.430 V; MS (EI) m/z (%) = 514 (82) (M⁺), 350 (100), 220 (82); C₂₃H₁₄S₇ (514.8) calcd. C 53.66, H 2.74; found C 53.80, H 3.19. Crystals for X-ray analysis were grown from CDCl₃.

9-(4,5-DiethyIsulfanyI-1,3-dithiol-2-ylidene)-10-(4,5-dimethyI-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 125.

A solution of 124 (102 mg, 0.20 mmol) in triethylphosphite (10 ml) was heated at reflux for 3 h to give a pale orange solution. The reaction mixture was evaporated in vacuo and the residue was purified by column chromatography on silica gel with hexane/dichloromethane (2:1 v/v) as eluent to afford 125 as a yellow solid (46 mg, 50%). M.p. 255-258°C; ¹H NMR (CDCl₃): δ = 1.22 (t, J = 7.4 Hz, 6H), 1.87 (s, 6H), 2.75 (m, 4H), 7.21 (m, 4H), 7.47 (m, 2H), 7.60 (m, 2H); CV (E⁰) 0.345 V. MS (EI) m/z (%) = 528 (14) (M⁺), 350 (45), 468 (38); HRMS C₂₆H₂₄S₆ (528.8) calcd. 528.0304; found 528.0304. Crystals for X-ray analysis were grown from CDCl₃.

2-(Dimethylamino)-4-(pentylthio)-1,3-dithiolium Salt 135.

The mesoion 134 (3.00 g, 15.7 mmol) was mixed in dry acetone (250 ml) with 1,5-diiodopentane (1.59 ml, 7.9 mmol) and refluxed for 3 h until the solution turned pale yellow. After being cooled to room temperature, the salt was filtered and washed sequentially with acetone and ether to afford 135 as an off white solid (3.61 g, 65%). Compound 135 was used in the following reaction without further purification. M.p. 142-145°C (dec.); ¹H NMR (DMSO-d₆): δ = 1.49 (m, 2H) 1.60 (m, 4H) 2.50 (s, 6H) 2.95 (t, J = 7.2 Hz, 4H) 3.36 (s, 12H).
Bis[2-(dimethylamino)-4-(hexylthio)-1,3-dithiolium] Salt 136.

The mesoion 134 (0.956 g, 5.00 mmol) was mixed in dry acetone (100 ml) with 1,6-dibromohexane (0.38 ml, 2.47 mmol) and refluxed for 3 h until the solution turned pale yellow. After being cooled to room temperature, the salt was filtered and washed with acetone and ether to afford 136 as a pale yellow solid (1.29 g, 83%). Compound 136 was used in the following reaction without further purification. M.p. 188-191°C (dec); \(^1\)H NMR (DMSO-d\(_6\)): \(\delta = 1.38 \, (m, \, 4H) \, 1.57 \, (m, \, 4H) \, 2.50 \, (s, \, 6H) \, 2.93 \, (t, \, J = 7.6 \, Hz, \, 4H) \, 3.50 \, (s, \, 12H)\).

Bis[2-(dimethylamino)-4-(pentylthio)-1,3-dithiole] 137.

To a stirred solution of salt 135 (3.50 g, 4.96 mmol) in dry ethanol at 0°C under argon was portionwise added finely ground sodium borohydride (0.40 g, 10.6 mmol) over ca. 1 h and the reaction maintained at 0°C for a further 3 h, whereupon the reaction is allowed to come to 20°C and the mixture stirred for a further 15 h. The reaction mixture was evaporated \textit{in vacuo} and the residue dissolved in ethyl acetate (100 ml). Brine (200 ml) was added and the mixture extracted with ethyl acetate (3x75 ml), the combined extracts washed with water (2x100 ml), dried (MgSO\(_4\)) and evaporated \textit{in vacuo}. The residue was purified by column chromatography on silica gel with ethyl acetate/dichloromethane (1:4 v/v) as the eluent to afford 137 as a pale brown (2.14 g, 95%). MS (EI) 454 m/z [M+]; \(^1\)H NMR (CDCl\(_3\)): \(\delta = 1.59 \, (m, \, 6H) \, 2.12 \, (s, \, 6H) \, 2.27 \, (s, \, 12H) \, 2.71 \, (m, \, 4H) \, 5.94 \, (s, \, 2H)\). \(^1^3\)C NMR (CDCl\(_3\)): \(\delta = 15.4, \, 27.5, \, 28.9, \, 29.3, \, 35.5, \, 38.2, \, 115.6, \, 131.8 \, ppm\).

Bis[2-(dimethylamino)-4-(hexylthio)-1,3-dithiole] 138

To a stirred solution of salt 136 (1.02 g, 1.63 mmol) in dry ethanol at 0°C under argon is portionwise added finely ground sodium borohydride (0.16 g, 4.23 mmol) over ca. 1 h and the reaction maintained at 0°C for a further 3 h, whereupon the reaction is
allowed to come to 20°C and the mixture stirred for a further 15 h. The reaction mixture was evaporated
in vacuo and the residue dissolved in ethyl acetate (100 ml). Brine (200 ml) was added and the mixture extracted with ethyl acetate (3x75 ml), the combined extracts washed with water (2x100 ml), dried (MgSO4) and evaporated in vacuo. The residue was purified by column chromatography on silica gel with ethyl acetate/dichloromethane (1:4 v/v) as the eluent to afford 138, as a pale yellow oil which solidified on standing (0.610 g, 82%). M.p. 75-78°C (dec.); HRMS C18H32N2S6 (468.8) calcd: 468.0991; found 468.0991; 1H NMR (CDCl3): δ = 1.40 (m, 4H) 1.59 (m, 4H) 2.12 (s, 6H) 2.27 (s, 12H) 2.69 (m, 2H) 2.78 (m, 2H) 5.93 (s, 2H); 13C NMR (CDCl3): δ = 15.5, 28.1, 29.6, 35.7, 38.3, 115.8, 131.8 ppm.

Bis[2-(dimethylamino)-4-(pentylthio)-1,3-dithiolium tetrafluoroborate] 139.

To a stirred solution of 137 (1.77 g, 4.02 mmol) in dry dichloromethane (15 ml) at 0°C under argon was added dropwise 54% hydrofluoroboric acid in diethyl ether (2.20 ml, 16.1 mmol). After the reaction mixture was stirred for 1 h, dry diethyl ether was added (200 ml). The precipitate was collected by filtration, washed with dry diethyl ether to afford 139 as a grey powder. Due to instability of the tetrafluoroborate salt the product was reacted on without further purification.

Bis[2-(dimethylamino)-4-(hexathio)-1,3-dithiolium tetrafluoroborate] 140.

To a stirred solution of 138 (1.01 g, 2.16 mmol) in dry dichloromethane (15 ml) at 0°C under argon was added dropwise 54% hydrofluoroboric acid in diethyl ether (1.17 ml, 8.55 mmol). Reaction and workup as described for 139 afforded 140 as a grey powder. Due to instability of the tetrafluoroborate salt the product was reacted on without further purification.
Bis[2-(dimethoxyphosphinyl)-4-(pentylthio)-1,3-dithiole] 141.

To a stirred solution of crude 139 (2.91 g, 4.72 mmol) and sodium iodide (2.83 g, 18.9 mmol) in dry acetonitrile (10 ml) at 20°C under argon was added trimethyl phosphite (2.2 ml, 18.9 mmol). After the reaction was stirred for 15 h, the solvent was evaporated in vacuo, the residue was dissolved in ethyl acetate (150 ml). Brine (100 ml) was added and the mixture extracted with ethyl acetate (3x50 ml); the combined extracts were washed with water (2x100 ml), dried (MgSO4) and evaporated in vacuo. The residue was purified by column chromatography on silica gel with ethyl acetate as the eluent to afford 141 as an unstable pale brown oil (1.48 g, 54%). 1H NMR (CDCl3): δ = 1.77 (m, 6H) 2.03 (s, 6H) 2.78 (m, 4H) 3.87 (m, 12H) 4.73 (d, J = 4.4 Hz, 2H).

Bis[2-(dimethoxyphosphinyl)-4-(hexathio)-1,3-dithiole] 142.

To a stirred solution of crude 140 (2.76 g, 4.72 mmol) and sodium iodide (1.28 g, 8.54 mmol) in dry acetonitrile (10 ml) at 20°C under argon was added trimethyl phosphite (1 ml, 8.48 mmol). Reaction and workup as described for 141 afforded 142 as a pale brown oil (681 mg, 53%). 1H NMR (CDCl3): δ = 1.42 (m, 4H) 1.64 (m, 4H) 2.02 (s, 6H) 2.71 (m, 4H) 3.88 (dd, J = 10.6 Hz, J = 2.6 Hz, 12H) 4.73 (d, J = 4.4 Hz, 2H).

9,10-Bis-(4-methyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracenocyclophane 143

Into a solution of 141 (1.33 g, 2.27 mmol) in dry tetrahydrofuran (100 ml) at -78°C, was added lithium diisopropylamide (3.0 ml of 1.5 M solution in cyclohexane, 4.50 mmol). The reaction was stirred for 3 h at -78°C to give a pale cloudy solution then, anthraquinone (0.473 g, 2.27 mmol) in dry tetrahydrofuran (100 ml) at -78°C was added. The mixture was then stirred for a further 1 h at -78°C and then allowed to slowly warm to 20°C over 6 h. The mixture was evaporated in vacuo and the residue was purified by column chromatography on silica gel with dichloromethane/hexane (1:2 v/v) as the eluent to afford 143 as a yellow solid (122 mg, 10%). Recrystallization was achieved by
dissolution in dichloromethane and addition of hexane. A single crystal was grown for X-ray crystallography from acetonitrile/dichloromethane. M.p. 270-273°C (dec > 160°C); (found: C, 59.8; H, 4.5; C₂₇H₂₄S₆ (540) requires C, 60.0 H, 4.5); m/z (EI) 540, 264, 220 [M⁺]; ¹H NMR (CDCl₃): δ = 0.85 (m, 4H) 1.12 (m, 4H) 1.97 (s, 6H) 2.17 (m, 4H) 2.61 (m, 4H) 7.30 (m, 6H) 7.36 (m, 2H). ¹³C NMR (CDCl₃): δ = ppm.

9,10-Bis-(4-methyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracenocyclophane 144.

Into a solution of 142 (681 mg, 1.14 mmol) in dry tetrahydrofuran (50 ml) at -78°C, was added lithium diisopropylamide (1.7 ml of 1.5 M solution in cyclohexane, 2.55 mmol). The reaction was stirred for 3 h at -78°C to give a pale cloudy solution then, anthraquinone (0.237 g, 1.14 mmol) in dry tetrahydrofuran (50 ml) at -78°C was added. Reaction and workup as described for 143 afforded 144 as a pale green/yellow solid (138mg, 22%). Recrystallisation, if required, may be achieved by dissolution in dichloromethane and addition of hexane. A single crystal was grown for X-ray crystallography from acetonitrile/dichloromethane. M.p. 286-288°C (dec.); (found: C, 60.33; H, 4.71; C₂₈H₂₆S₆ (554.9) requires C, 60.61 H, 4.72); m/z (EI) 554, 264, 220 [M⁺]; ¹H NMR (CDCl₃): δ = 1.11 (m, 4H) 1.32 (m, 4H) 2.10 (s, 6H) 2.23 (m, 2H) 2.68 (m, 2H) 7.35 (m, 6H) 7.49 (m, 2H). ¹³C NMR (CDCl₃): δ = 14.8, 29.0, 30.9, 35.2, 116.7, 125.7, 125.7, 126.0, 126.2, 126.3, 126.5, 132.1, 132.7, 134.3, 135.3, 148.8 ppm.
7.0 References


Appendix

X-Ray Crystallographic Data
2,6-Dibutoxy-9,10-bis(1,3-dithio-2-ylidene)-9,10-dihydroanthracene 44.

Crystal data and structure refinement

Empirical formula
C_{46}H_{68}O_{14}S_{4}

Formula weight
532.74

Temperature
130(2) K

Wavelength
1.34164 Å

Crystal system
Monoclinic

Space group
P2_1/a (No. 14)

Unit cell dimensions
a = 11.2587(12) Å
b = 17.0260(13) Å
\(c = 18.2364(11) Å, \beta = 90°\)

Volume
2137.1(6) Å³

Z
4

Density (calculated)
1.279 g/cm³

Absorption coefficient
3.644 mm⁻¹

\(\mu\) (Mo Kα)
1104

Crystal size
0.40 × 0.30 × 0.13 mm³

Range for data collection
3.85 to 25.00°

Least squares
1 2 4 6 8 10 12

Reflections collected
5801

Independent reflections
4545 (Rint = 0.02576)

Reflections with \(I > 2\sigma(I)\)
4020

Completeness to \(\theta = 75.00°\)
99.5 %

Absorption correction
\(\varphi\) scan

Max. and min. transmission
0.0000 and 0.6727

Refinement method
Full-matrix least-squares on \(F^2\)

Data / restraints / parameters
4645 / 6 / 419

Largest shift/error ratio of a.l. sites
0.001

Goodness-of-fit on \(F^2\)
1.057

Final R indices \([I > 2\sigma(I)]\)
R = 0.063, wR = 0.1867

Flack parameter \([\chi(I)\sigma(I)]\)
0.06(5), w = 0.004

Largest diff. peak and hole
0.443 and -0.335 e/Å³
2,6-Dihexoxy-9,10-bis(1,3-dithiol-2-ylidene-4,5-dimethyl)-9,10-
dihydroanthracene 55.

Crystal data and structure refinement:

Identification code: C26H24O4S
Empirical formula: C26H24O4S
Formula weight: 414.45
Temperature: 130(2) K
Wavelength: 0.71073 Å
Crystal system: Triclinic
Space group: P1 (No. 2)
Unit cell dimensions:
- a = 10.414(1) Å
- b = 11.407(1) Å
- c = 13.189(1) Å
- β = 113.45(1)°

Volume: 1605.10(4) Å³
Z: 2
Density (calculated): 1.218 g/cm³
Absorption coefficient: 9.333 mm⁻¹
F(000): 460
Crystal size: 0.30 x 0.15 x 0.07 mm³
θ range for data collection: 1.9 to 27.0°
Index ranges:
- h: -13 ≤ h ≤ 13
- k: -14 ≤ k ≤ 14
- l: -14 ≤ l ≤ 14

Reflections collected: 7551
Independent reflections: 2009
Completeness to θ = 27.0°: 98.3 %
Absorption correction: Integration
Max. and min. transmission: 0.9797 and 0.9772

Refinement method: Full-matrix least-squares on F²

Data / restraints / parameters: 7551 / 61 / 48

Final R indices [I > 2σ(I)]: 0.003
Goodness-of-fit on F²: 1.001
Final R indices [all data]: R = 0.0423, wR2 = 0.0459
R indices (all data): R = 0.0771, wR2 = 0.0961

Largest diff. peak and hole: 0.245 and -0.238 e Å⁻³

Symmetry: C2(h) and C2(d) with their hydrogens are disordered over 2 positions, A and B, with equal occupancies.

Bond lengths [Å] and angles [°]:

| S1(1-29) | 1.706(2) | C10(1-21) | 1.404(3) |
| S1(1-29) | 1.706(2) | C10(1-21) | 1.404(3) |
| S2(1-29) | 1.706(2) | C10(1-21) | 1.404(3) |
| S2(1-29) | 1.706(2) | C10(1-21) | 1.404(3) |
| S3(1-29) | 1.648(2) | C10(1-21) | 1.389(3) |
| S3(1-29) | 1.648(2) | C10(1-21) | 1.389(3) |
| S4(1-29) | 1.648(2) | C10(1-21) | 1.389(3) |
| S4(1-29) | 1.648(2) | C10(1-21) | 1.389(3) |
| S5(1-29) | 1.580(2) | C10(1-21) | 1.352(3) |
| S5(1-29) | 1.580(2) | C10(1-21) | 1.352(3) |
| S6(1-29) | 1.404(2) | C10(1-21) | 1.225(3) |
| S6(1-29) | 1.404(2) | C10(1-21) | 1.225(3) |
| S7(1-29) | 1.404(2) | C10(1-21) | 1.225(3) |
| S7(1-29) | 1.404(2) | C10(1-21) | 1.225(3) |
| S8(1-29) | 1.404(2) | C10(1-21) | 1.225(3) |
| S8(1-29) | 1.404(2) | C10(1-21) | 1.225(3) |

125
9-(4-Methoxycarbonyl-5-methyl-1,3-dithio-2-ylidene)-10-(4,5-dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 81.
9-(4-Methylsulfanyl-5-methyl-1,3-dithiol-2-ylidene)-10-(4,5-dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 84.

Crystal data and structure refinement

Identification code
| 9 postponed

Empirical formula
| Co-Ba

Formula weight
| 448.70

Temperature
| 120(2)K

Wavelength
| 0.71073 Å

Crystal system
| Triclinic

Space group
| P T (No. 2)

Unit cell dimensions
| a = 9.077(1) Å | α = 84.79(1)*
| b = 10.382(1) Å | β = 87.30(1)*
| c = 13.014(1) Å | γ = 76.02(1)*

Volume
| 1064.0(2) Å³

Z
| 2

Density (calculated)
| 1.434 g/cm³

Absorption coefficient
| 0.544 mm⁻¹

Radiation
| MoKα

Crystal data
| 0.30 x 0.10 x 0.06 mm

α range for data collection
| 1.7 to 27.2°

Index ranges
| h: -10 to 10, -10 ≤ k ≤ 10, -11 ≤ l ≤ 13

Reflections collected
| 3847

Reflections with > 0.1σ(F²)
| 3103

Completeness to 28.7°
| 94.6 %

Absorption correction
| Inherent

Max. and min. transmission
| 0.9664 and 0.8920

Refinement method
| Full-matrix least-squares on F²

Data / restraints / parameters
| 4910 / 0 / 588

Largest diff. peak and hole
| 0.42 and -0.38 eÅ⁻³

Table showing bond lengths [Å] and angles [°]

127
Mono-crown 115.
Mono-crown 116.

Crystal data and structure refinement

**Identification code**
99er0056

**Empirical formula**
C27 H28 O5 S4

**Formula weight**
560.77

**Temperature**
150(2) K

**Wavelength**
0.71073 Å

**Crystal system**
Orthorhombic

**Space group**
P2₁(1)2₁(1)2₁(1)

**Unit cell dimensions**

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<th>c (Å)</th>
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**Volume**
2595.6(4) Å³

**Z**
4

**Density (calculated)**
1.435 g/cm³

**Absorption coefficient**
0.404 mm⁻¹

**F(000)**
1176

**Crystal size**
0.55 x 0.12 x 0.08 mm

**Theta range for data collection**
1.54 to 26.37 deg.

**Index ranges**
-8 < h < 8, -22 < k < 22, -21 < l < 21

**Reflections collected**
10781

**Independent reflections**
4235 [R(int) = 0.0372]

**Observed reflections, I > 2\sigma(I)**
3920

**Absorption correction**
Integration

**Max. and min. transmission**
0.9808 and 0.9276

**Refinement method**
Full-matrix least-squares on \( F^2 \)

**Data / restraints / parameters**
4219 / 5 / 418

**Final R indices [I>2\sigma(I)]**
\( R1 = 0.0378, wR2 = 0.0743 \)

**R indices (all data)**
\( R1 = 0.0453, wR2 = 0.0827 \)

**Absolute structure parameter**
0.07(4)

**Largest shift/e.s.d. ratio**
0.001

**Largest diff. peak and hole**
0.278 and -0.213 e.A⁻³

**Bond lengths [Å] and angles [°]**

| S(1)-C(15) | 1.755(4) |
| S(1)-C(16) | 1.741(3) |
| S(2)-C(17) | 1.755(3) |
| S(2)-C(18) | 1.771(3) |
| S(3)-C(19) | 1.764(4) |
| S(4)-C(20) | 1.763(3) |
| O(1)-C(21) | 1.230(4) |
| O(2)-C(22) | 1.345(3) |
| O(3)-C(23) | 1.320(4) |
| O(4)-C(24) | 1.477(3) |
| O(5A)-C(25) | 1.477(3) |
| O(5B)-C(26) | 1.511(5) |
| O(8B)-C(27) | 1.504(4) |

**Bond lengths [Å]**

| S(l)-C(15) | 1.755(4) |
| S(l)-C(19) | 1.741(3) |
| S(2)-C(17) | 1.755(3) |
| S(2)-C(20) | 1.771(3) |
| S(3)-C(19) | 1.764(4) |
| S(4)-C(20) | 1.763(3) |
| O(1)-C(21) | 1.230(4) |
| O(2)-C(22) | 1.345(3) |
| O(3)-C(23) | 1.320(4) |
| O(4)-C(24) | 1.477(3) |
| O(5A)-C(25) | 1.477(3) |
| O(5B)-C(26) | 1.511(5) |
| O(8B)-C(27) | 1.504(4) |
9-{[4-5-Methylenedisulfanyl]-1,3-dithiol-2-thione}-10-(4,5-dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 124.
9-(4,5-Diethylsulfanyl-1,3-dithiol-2-ylidene)-10-(4,5-dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydroanthracene 125.

Crystal data and structure refinement

Identification code 98crv074
Empirical formula C32 H44 S4
Formula weight 576.44
Temperature 150(2) K
Wavelength 0.71073 Å
Crystal system Triclinic
Space group P-1
Unit cell dimensions

\[ a = 11.6822(8) \text{ Å}, \quad \alpha = 79.410(4) \text{ deg.} \]
\[ b = 11.4826(6) \text{ Å}, \quad \beta = 71.677(4) \text{ deg.} \]
\[ c = 17.7135(9) \text{ Å}, \quad \gamma = 99.285(4) \text{ deg.} \]

Volume 2475.3(2) Å³
Z 4
Density (calculated) 1.541 g/cm³
Absorption coefficient 0.311 mm⁻¹
\( \mu = 1.772 \text{ mm} \)

Crystal size 0.25 x 0.20 x 0.06 mm

Theta range for data collection 1.41 co 30.65 deg.

Index ranges
\[-14<=h<=16, -15<=k<=15, -24<=l<=24\]

Reflections collected 18705
Independent reflections 12287 (R(int) = 0.0208)

Observed reflections. 2σ(2σ) (2σ) 8292

Absorption correction Full-matrix least-squares on \( h^2 \)

Max. and min. transmission 0.9077 and 0.7860

Refinement method Full-matrix least-squares on \( F^2 \)

Goodness-of-fit on \( F^2 \) 1.125

Final R indices. ||σ(σ)| |
R1 = 0.0670, wR2 = 0.1259

Largest peak and hole

Largest diff. peak and hole

Bond lengths (Å) and angles (deg)

\begin{tabular}{|c|c|c|c|}
\hline
S(1A) - C(1A) & 1.73(1) & S(1A) - C(1A) & 1.79(1) \\
S(1A) - C(1A) & 1.79(1) & S(1A) - C(1A) & 1.79(1) \\
S(1A) - C(1A) & 1.79(1) & S(1A) - C(1A) & 1.79(1) \\
S(1A) - C(1A) & 1.79(1) & S(1A) - C(1A) & 1.79(1) \\n\hline
\end{tabular}
9,10-Bis-(4-methyl-1,3-dithiol-2-yldiene)-9,10-dihydroanthracenocyclophane 143.
Appendix Two

Publications
Publications

Part of the work presented in this thesis has been reported in the following publications.

Appendix Three

Research Colloquia
RESEARCH COLLOQUIA

The author attended the following colloquia.

1996

October 14  Professor A. R. Katritzky, University of Gainesville, University of Florida, USA
Recent Advances in Benzotriazole Mediated Synthetic Methodology

October 22  Professor B. J. Tighe, Department of Molecular Sciences and Chemistry, University of Aston
Making Polymers for Biomedical Application - can we meet Nature's Challenge?
Joint lecture with the Institute of Materials

October 23  Professor H. Ringsdorf (Perkin Centenary Lecture), Johannes Gutenberg-Universitat, Mainz, Germany
Function Based on Organisation

November 12 Professor R. J. Young, Manchester Materials Centre, UMIST
New Materials - Fact or Fantasy?
Joint Lecture with Zeneca & RSC

November 18 Professor G. A. Olah, University of Southern California, USA
Crossing Conventional Lines in my Chemistry of the Elements

November 19 Professor R. E. Grigg, University of Leeds
Assembly of Complex Molecules by Palladium-Catalysed Queueing Processes

November 27 Dr Richard Templer, Imperial College, London
Molecular Tubes and Sponges

December 11 Dr Chris Richards, Cardiff University
Sterochemical Games with Metallocenes

1997

January 15  Dr V. K. Aggarwal, University of Sheffield
Sulfur Mediated Asymmetric Synthesis

January 16  Dr Sally Brooker, University of Otago, NZ
Macrocycles: Exciting yet Controlled Thiolate Coordination Chemistry

January 21  Mr D. Rudge, Zeneca Pharmaceuticals
High Speed Automation of Chemical Reactions
February 4  Dr A. J. Banister, University of Durham
From Runways to Non-metallic Metals - A New Chemistry Based on Sulphur

February 5  Dr A. Haynes, University of Sheffield
Mechanism in Homogeneous Catalytic Carbonylation

February 19  Professor Brian Hayden, University of Southampton
The Dynamics of Dissociation at Surfaces and Fuel Cell Catalysts

February 25  Professor A. G. Sykes, University of Newcastle
The Synthesis, Structures and Properties of Blue Copper Proteins

February 26  Dr Tony Ryan, UMIST
Making Hairpins from Rings and Chains

March 4  Professor C. W. Rees, Imperial College
Some Very Heterocyclic Chemistry

October 23  Professor M R Bryce, University of Durham, Inaugural Lecture
New Tetrathiafulvalene Derivatives in Molecular, Supramolecular and Macromolecular Chemistry: controlling the electronic properties of organic solids

November 5  Dr M Hii, Oxford University
Studies of the Heck reaction

November 26  Professor R W Richards, University of Durham, Inaugural Lecture
A random walk in polymer science

December 2  Dr C J Ludman, University of Durham
Explosions

December 3  Professor A P Davis, Department of Chemistry, Trinity College Dublin.
Steroid-based frameworks for supramolecular chemistry

1998

January 28  Dr S Rannard, Courtaulds Coatings (Coventry)
The synthesis of dendrimers using highly selective chemical reactions

February 3  Dr J Beacham, ICI Technology
The chemical industry in the 21st century

February 4  Professor P Fowler, Department of Chemistry, Exeter University
Classical and non-classical fullerenes
February 24  Professor R Ramage, University of Edinburgh
The synthesis and folding of proteins

March 4  Professor T C B McLeish, IRC of Polymer Science Technology, Leeds
University
The polymer physics of pyjama bottoms (or the novel rheological
characterisation of long branching in entangled macromolecules)

October 9  Professor M F Hawthorne, Department Chemistry & Biochemistry,
UCLA, USA, RSC Endowed Lecture

October 27  Professor A Unsworth, University of Durham
What's a joint like this doing in a nice girl like you?
In association with The North East Polymer Association

October 28  Professor J P S Badyal, Department of Chemistry, University of
Durham
Tailoring Solid Surfaces, Inaugural Lecture

November 3  Dr C J Ludman, Chemistry Department, University of Durham
Bonfire night Lecture

November 11  Dr M Wills, Department of Chemistry, University of Warwick
New Methodology for the Asymmetric Transfer Hydrogen of Ketones

November 12  Professor S Loeb, University of Windsor, Ontario, Canada
From Macrocycles to Metallo-Supramolecular Chemistry

November 17  Dr J McFarlane
Nothing but Sex and Sudden Death!

December 1  Professor N Billingham, University of Sussex
Plastics in the Environment - Boon or Bane
In association with The North East Polymer Association.

December 2  Dr M Jaspers, Department of Chemistry, University of Aberdeen
Bioactive Compounds Isolated from Marine Invertebrates and
Cyanobacteria

1999

January 19  Dr J Mann, University of Reading
The Elusive Magic Bullet and Attempts to find it?

February 9  Professor D J Cole-Hamilton, St. Andrews University
Chemistry and the Future of life on Earth

February 23  Dr C Viney, Heriot-Watt
Spiders, Slugs And Mutant Bugs