

Synthesis and complexation of tetrathiafulvalene derivatives functionalised with [15]aneS₅ thioether crowns†

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Two new tetrathiafulvalene (TTF)-based molecules functionalised with [15]aneS₅ groups have been prepared by phosphite mediated coupling reactions. The [15]aneS₅-thione precursor has been characterised by X-ray crystallography. Cyclic voltammetry, spectroelectrochemistry and EPR studies of one of these TTF compounds with and without guest copper(II) ions have revealed binding of Cu^{II} and temperature dependent intramolecular electron transfer to give Cu^I and TTF⁺.

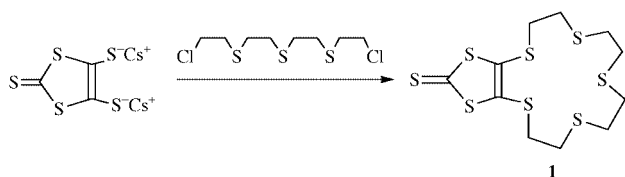
Introduction

The tetrathiafulvalene (TTF) family of molecules has been widely studied, mainly due to the utility of these species in molecular conductors and superconductors.¹ Systems which also incorporate the TTF molecule into crown ethers have been studied as potential sensors for metal ions² and as building blocks in supramolecular assemblies.^{2,3} The majority of such systems studied have focused on oxygen donor crown groups^{3,4} with fewer studies concerning soft donor atoms in the macrocyclic ring.^{5,6} The preparation of such molecules however offers the possibility of extending the study of metal-ion sensors to soft metals, the opportunity to build supramolecular assemblies where magnetic ions comprise part of the architecture and to study interactions of the TTF component with redox-active metals. We have prepared two TTF-based molecules incorporating [15]aneS₅ macrocyclic groups by phosphite mediated coupling of thione and ketone precursors including an unusual asymmetric derivative with alkyl chains for improved solubility. The latter compound has been studied in the presence of guest copper(II) ions. The precursor thione compound containing the [15]aneS₅ unit has been characterised by X-ray crystallography.

Results and discussion

Preparation

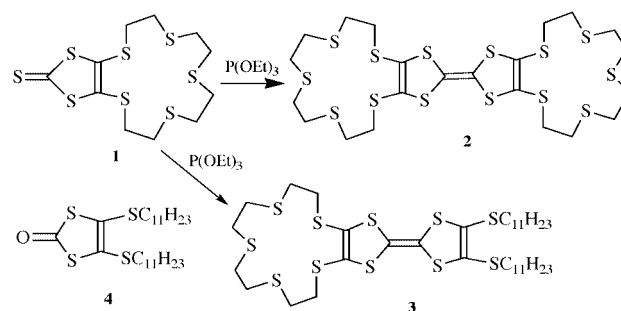
The preparation of the thione **1** is outlined in Scheme 1. The procedure used is modified from established methods for the



Scheme 1

preparation of thioether macrocycles which involve ring closure between a bis-halide and a bis-sulfide species. For the preparation of **1** the dicaesium salt of the dmit (4,5-disulfanyl-1,3-dithiole-2-thionate) dianion was utilised to incorporate the additional sulfur-containing unit onto the macrocycle.⁷ The

ring-closure reaction was carried out using the chloro derivative of the sulfur mustard compound in contrast to several literature reports⁸ where the bromo or tosyl (*p*-toluenesulfanyl) derivatives were used. Although the chloro compound has reduced reactivity and therefore is likely to lead to lower yields of the 1 : 1 cyclised product, it was found to be extremely convenient in its preparation requiring only the quantitative conversion of the hydroxy into the chloro compound with thionyl chloride followed by removal of volatile species under vacuum. This limits the danger of exposure to the highly toxic mustard compound. Phosphite mediated self-coupling of **1** yielded the TTF-based compound **2** which contains two [15]aneS₅ rings (Scheme 2).



Scheme 2

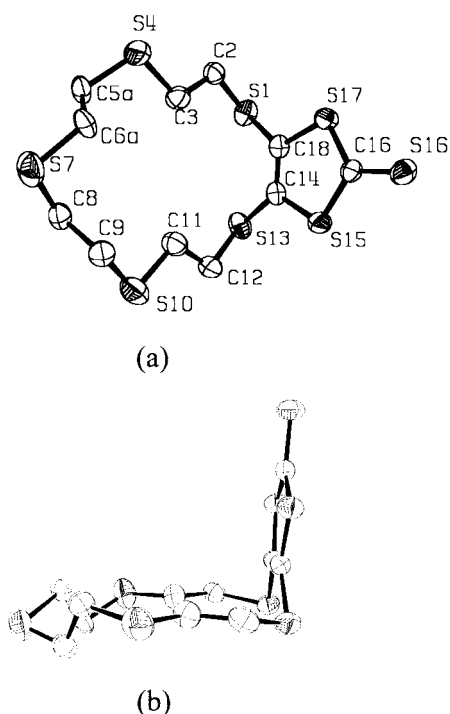
Compound **2** was characterised by elemental analysis and electrochemistry. Its suitability for study as a host for metal ions, however, was impaired by poor solubility in most solvents with the exception of slight solubility in chlorinated solvents.

In order to overcome the poor solubility of compound **2**, cross coupling of **1** with the ketone **4** (4,5-bis(alkylsulfanyl)-1,3-dithiol-2-one) was carried out to give the asymmetric TTF-based compound **3** with one [15]aneS₅ ring and two alkyl chains (Scheme 2). Such cross-coupling reactions typically give lower yields of the desired product because of formation of some of the related symmetric-coupling products. This can be minimised however by use of a thione and a ketone precursor which serves to maximise the cross-coupled product.⁹ Compound **3** is an unusual example of an asymmetric thioether functionalised TTF molecule and offers the considerable advantage of solubility in solvents such as THF where study of interactions with a variety of metal ions is more readily pursued than in chlorinated solvents. Further binding studies with Cu^{II} have therefore focused exclusively on the TTF compound **3**.

† Supplementary data available: rotatable 3-D crystal structure diagram in CHIME format. See <http://www.rsc.org/suppdata/dt/1999/3913/>

Table 1 Selected bond lengths (Å) and angles (degrees) for compound **1** with e.s.d.s in parentheses

S(1)–C(18)	1.752(2)	S(15)–C(16)	1.731(2)
S(13)–C(14)	1.749(2)	S(16)–C(16)	1.638(2)
C(14)–C(18)	1.346(3)	C(16)–S(17)	1.727(2)
C(14)–S(15)	1.751(2)	S(17)–C(18)	1.749(2)
C(18)–S(1)–C(2)	101.69(11)	S(16)–C(16)–S(15)	123.09(13)
C(14)–S(13)–C(12)	102.66(12)	S(17)–C(16)–S(15)	112.67(13)
C(18)–C(14)–S(13)	124.19(18)	C(16)–S(17)–C(18)	97.64(11)
C(18)–C(14)–S(15)	115.69(17)	C(14)–C(18)–S(17)	116.23(17)
S(13)–C(14)–S(15)	119.68(13)	C(14)–C(18)–S(1)	125.30(18)
C(16)–S(15)–C(14)	97.71(11)	S(17)–C(18)–S(1)	118.22(13)
S(16)–C(16)–S(17)	124.22(13)		

**Fig. 1** Crystal structure of macrocycle **1** showing atom labelling.

Crystal structure

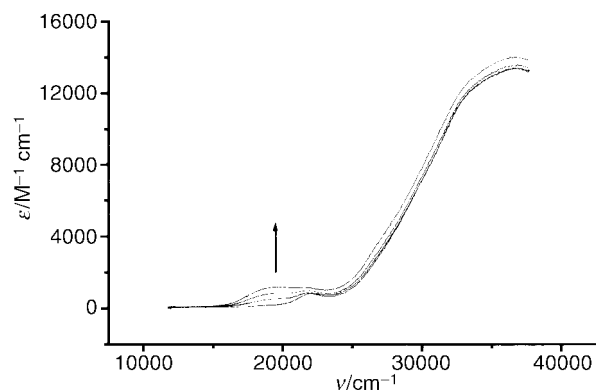
A structure determination was carried out of compound **1**·0.5CS₂ grown by slow evaporation of a CS₂–CH₂Cl₂ solution of **1** (Fig. 1a,b). Selected bond lengths and angles are given in Table 1.

The conformation of the macrocycle shows two of the sulfur atoms are constrained to adopt a *syn* arrangement by the unsaturated C=C bond while the others adopt an *anti* arrangement. This contrasts with the structure of the parent saturated [15]aneS₅ compound where all the sulfur–sulfur arrangements are of an *anti* type leading to an *exo* conformation.¹⁰ This is anticipated to have an effect on the co-ordination chemistry of the ligand as a rearrangement energy is normally required to bring the sulfurs into an *endo* conformation such that co-ordination to a guest metal ion can take place. This requirement has clearly been modified for **1** and presumably also for **2** and **3**.

Some disorder around the CH₂CH₂ groups linking S7 with S4 and S10 has been determined giving two different conformations for each ethylene link. Bond lengths are comparable to those of other thioether crowns¹⁰ with the exception of those around the unsaturated C=C link. The structure around the C₃S₃ moiety is consistent with that of the related [9]aneS₃-containing compound.⁵ The bond lengths S(1)–C(18) and S(13)–C(14) at 1.752 and 1.749 Å respectively are shorter than typical C–S distances in thioether crowns and C(14)–C(18) is, as expected, considerably shorter than the other C–C bonds.

Table 2 Electrochemistry vs. Ag–AgCl

System	<i>E/V</i>	
2 in CH ₂ Cl ₂	+0.48	+0.78
3 in CH ₂ Cl ₂	+0.45	+0.75
3 in THF	+0.86	+0.96
3 + Cu ^{II} in THF (1:1)	+0.72	+0.83

**Fig. 2** Electrogeneration of cation **3**²⁺ followed by uv/vis spectrometry.

Complexation behaviour is also expected to be affected by the modified electronic nature of the two *cis*-sulfur atoms. The angles of 101.69° for C(18)–S(1)–C(2) and 102.66° for C(14)–S(13)–C(12) lead to the compound adopting an arrangement with two planes almost perpendicular to each other (Fig. 1b).

Electrochemistry

Cyclic voltammetry studies of compounds **2** and **3** have been carried out in CH₂Cl₂ and for **3** in THF and results are presented in Table 2. Both compounds show two reversible oxidations as expected for compounds based on TTF and those for **3** are at slightly less positive potential which reflects the electron donating alkyl groups. Both compounds, however, show more positive oxidation potentials than that of TTF, typical for species with four sulfur atoms substituted around the periphery. (Values for TTF itself are reported as 0.30–0.37 and 0.70–0.78 V vs. SCE for the first and second oxidations respectively.¹¹) The electrochemistry of **3** was also carried out in THF and shows both oxidations to be closely spaced, separated by only 100 mV. Separation of the waves by cyclic voltammetry was difficult to achieve but could clearly be determined by differential pulse voltammetry. Such redox behaviour has to the best of our knowledge not previously been reported and the experiments were carried out using both LiClO₄ and NBu₄PF₆ as electrolyte to eliminate the possibility of electrolyte as a factor in the oxidation potentials. The origin of these unusual potential shifts is not known but such behaviour has recently been observed for other, non-macrocylic TTF derivatives in THF.¹²

Coulometry was carried out on compound **3** in THF and this confirmed that the composite oxidation peak corresponded to a two electron process indicating that both closely spaced cyclic voltammetric waves involve one electron. Owing to the low solubility of **2** coulometry could not be reliably carried out but the two oxidation processes could be assigned as one-electron steps by analogy with **3** and with other TTF derivatives.

Spectroelectrochemistry was carried out on compound **3** by following the uv/vis spectrum as oxidation to the dication was undertaken and results are illustrated in Fig. 2. These data show the growth of a new broad absorption centred at 19230 cm⁻¹. Other bands centred at 21980 and 36700 cm⁻¹ were conserved during the oxidation. Owing to the close spacing of the first and second oxidations of **3** in THF, it was not possible independently to electrogenerate the monocation.

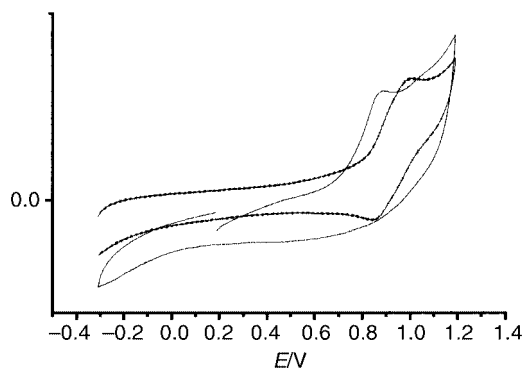


Fig. 3 Cyclic voltammety of compound **3** and **3** + Cu^{II} (1:1) (0.13 mM) in THF-0.4 M LiClO₄.

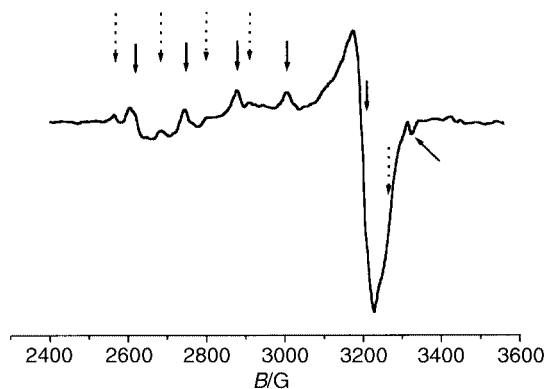


Fig. 4 The EPR spectrum of **3** + Cu^{II} (2:1) in THF as a frozen glass at 9.36 GHz showing parallel and perpendicular features for the complex [3·Cu^{II}]₂⁺ (solid arrows) and free Cu^{II} (dashed arrows) plus organic radical (oblique arrow).

Complexation with Cu^{II}

In order to assess the utility of the new compounds as hosts for metal ions and to investigate the nature of the resultant behaviour, Cu(BF₄)₂ was added to a THF solution of **3** in various ratios and the resulting solutions explored by electrochemical and spectroscopic methods. The cyclic voltammogram of a 1:1 solution showed some modification in comparison with that of the parent solution of **3** (Fig. 3) although shifts in the observed potentials were small and did not appear to increase upon addition of higher ratios of Cu^{II} up to ten equivalents. Again two closely spaced waves for the **3** + Cu^{II} solution could be resolved by differential pulse voltammetry (Table 2). In the case of a 1:1 solution, cycling the potential between -0.5 and +1.0 V at 100 mV s⁻¹ did not show peaks corresponding to free copper in THF. If, however, the potential was held at -0.5 V for longer periods, plating of copper on the electrode was evidenced by a characteristic desorption spike.

The EPR spectra were recorded for the monocation of compound **3** and for the complex formed between **3** and Cu^{II} and results are shown in Fig. 4 and Table 3 along with the EPR of TTF⁺ in THF for comparison. As expected the monocation of **3**, generated by electrochemical oxidation, shows a singlet with $g = 2.017$ typical of an organic based radical. We found no evidence of hyperfine structure on the signal and therefore conclude that the unpaired electron in **3**⁺ is localised on the TTF part of the molecule. The spectrum obtained for **3** + Cu^{II} however shows curious temperature dependent behaviour. At room temperature and a 1:1 ratio of species, the spectrum obtained is that of an organic radical with a singlet at $g = 2.012$. No indication of peaks associated with Cu^{II} is apparent. Upon freezing the solution to a glass, two different patterns typical of Cu^{II} are apparent and there is only a very slight indication of the

Table 3 The EPR parameters (g , A/G)

Sample	Organic radical	Cu ^{II}	
		parallel	perpendicular
Monocation of 3	2.017	—	—
Monocation of TTF	2.018	—	—
3 + Cu ^{II} at RT	2.012	—	—
3 + copper(II) glass	—	2.378, $A = 134$	2.09
		2.435, $A = 117$	2.097

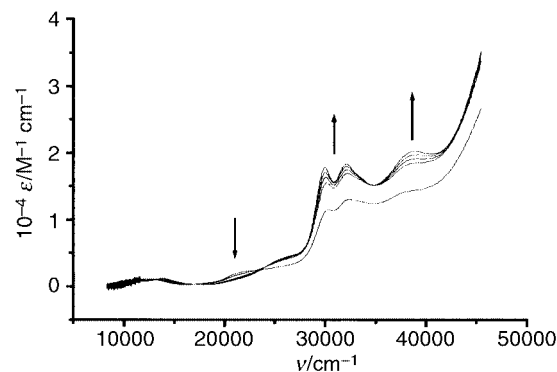


Fig. 5 Variation of the uv/vis spectrum of **3** + Cu^{II} (1:1) in THF with temperature at +25, -11, -27.5, -38.5 and -50 °C.

organic radical signal. These changes are found to be reversible upon warming and cooling the solution. Both copper signals show parallel and perpendicular features at $g = 2.378$ and 2.435 and $g = 2.090$ and 2.097 respectively. One of these pairs can be identified as that for free copper(II) ions in THF ($g_{\text{parallel}} = 2.435$, $g_{\text{perpendicular}} = 2.097$). The appearance of free copper ions in the EPR spectrum at 77 K is apparent with ratios as low as 4:1 (**3**:Cu^{II}) and the addition of a larger amount of Cu^{II} leads to a large increase in these signals such that they dominate the spectrum at 1:1 ratio. The observation of additional signals however which do not correspond to free Cu^{II} confirms that some complexation has occurred.

The temperature dependence of the **3** + Cu^{II} interaction was followed by uv/vis spectroscopy over the temperature range 298–223 K and the results are illustrated in Fig. 5. These indicate an increase in intensity for the bands observed at 40000, 31250, 28570 and the weak band at 13900 cm⁻¹ plus a decrease in intensity of the visible band at 23000 cm⁻¹ as the temperature of the solution is decreased. The spectral changes are accompanied by a clearly observable change in the solution from brown-green at room temperature to light green as it is cooled. Attempts to record spectra at lower temperatures were hampered by the onset of precipitation.

We interpret these results as an indication of complexation of Cu^{II} by the TTF species with an equilibrium involving binding of only some of the copper(II) ions, evidenced by the presence of two copper environments in the EPR spectrum of the frozen glass. Free Cu^{II} can be shown to display no EPR spectrum at room temperature in THF and it may therefore be reasonable to expect that copper species, although present, give no signal in the room temperature spectrum. Additionally, the small changes observed in the cyclic voltammetry suggest that uncomplexed **3** is present in solution, giving rise to oxidations little changed from those of the solution free of Cu^{II}.

Warming the solution leads to marked changes in the uv/vis spectrum and the EPR spectrum consistent with oxidation of the TTF molecule to a radical and presumably reduction of the Cu^{II} to Cu^I. This is illustrated by a comparison of the first three absorption bands in the variable temperature spectrum (Fig. 5) with those of the parent compound **3** (37450, $\epsilon = 13000$; 32500, $\epsilon = 13000$ and 30400 M⁻¹ cm⁻¹, $\epsilon = 11800$ M⁻¹ cm⁻¹). This

suggests that the bands which develop as the temperature is reduced have their origin in π - π transitions within the delocalised organic unit and indicate an increasing similarity with the neutral parent compound. The band at 23000 cm^{-1} can be associated with oxidised **3** as indicated by the spectroelectrochemistry on this compound (Fig. 2) and is seen to diminish in intensity at lower temperature in keeping with the presence of less Cu^{3+} . Furthermore, the weak absorption observed at 13900 cm^{-1} presumably arises from copper d-d transitions and is seen to increase at lower temperature consistent with the presence of a greater proportion of Cu^{II} rather than Cu^{I} .

The gradual nature of this process as illustrated by uv/vis spectroscopy (Fig. 5) is consistent with the population of a low lying charge-transfer excited state with an internal redox from $\text{Cu}^{\text{II}}\text{-TTF}$ to $\text{Cu}^{\text{I}}\text{-TTF}^+$. Consideration of the redox potentials of the TTF species **3** and Cu^{II} in THF suggests that this process would require stabilisation of the Cu^{I} formed to be feasible. Such stabilisation of Cu^{I} is a familiar feature of thioether macrocycle chemistry and is typified by the complex $[\text{Cu}^{\text{II}}(\text{[15]aneS}_5)]^{2+}$ which is highly redox labile affording $[\text{Cu}^{\text{I}}(\text{[15]aneS}_5)]^+$.¹³ This provides further evidence for the complexation of some of the copper(II) ions by the thioether host.

The fact that much of the Cu^{II} appears to remain unbound by the host species can be attributed to the unfavourable donor set of the ligand with five sulfur atoms. A comparison with the literature compound $[\text{15]aneS}_5$ indicates that this ligand has given rise to many fewer isolated complexes than related four- and six-donor thioether ligands¹⁴ and this can be correlated to the unfavourable co-ordination number five. Such restricted binding capabilities can be viewed as an important property when considered in the context of electrochemical sensors where some selectivity towards guest ions is desirable.

The observation of temperature dependent valence tautomerism for the $\text{3}\cdot\text{Cu}^{\text{II}}$ complex is reminiscent of behaviour previously observed in amine oxidases.¹⁵ Studies of the EPR spectra of such systems have revealed a low temperature Cu^{II} -reduced quinone state which at higher temperature is in equilibrium with a Cu^{I} -semiquinone state. It was speculated that similar effects might be present in other enzymes containing multiple redox centres with intramolecular electron transfer steps. In addition, related behaviour has also been observed in a nickel complex of a conjugated diimine macrocycle.¹⁶ In this species an equilibrium exists between the Ni^{II} -reduced macrocycle and the Ni^{I} -macrocycle complexes with the former favoured at lower temperatures.

Conclusion

We have prepared two new TTF compounds functionalised with thioether crowns and characterised a precursor $[\text{15]aneS}_5$ species by X-ray crystallography. The binding of guest copper(II) ions by the host TTF-based compound has been studied by electrochemistry, EPR and uv/vis spectroscopy and points toward incomplete complexation of the copper(II) ions and an unusual temperature-dependent intramolecular electron-transfer process to give Cu^{I} and TTF^+ .

Experimental

Triethyl phosphite was purchased from Aldrich and distilled prior to use. 4,5-Bis(benzoylsulfanyl)-1,3-dithiole-2-thione,¹⁷ the ketone **4**¹⁸ and 1,1'-[thiobis(ethylene)dithio]bis(2-chloroethane)⁷ were prepared by literature methods. Electrochemistry was carried out in THF, distilled from sodium-benzophenone and stored over Na or in CH_2Cl_2 distilled from CaH_2 and stored over 4A molecular sieve in which LiClO_4 or NBu_4PF_6 (0.1 M) and NBu_4PF_6 (0.4 M) respectively were used as supporting electrolyte. Cyclic voltammetry experiments were performed using an AUTOLAB/PSTATIO potentiostat, driven by the electrochemical software GPES (4.4), using a three elec-

trode cell. The working and counter electrodes were a platinum microdisc (0.5 mm diameter) and a large surface area platinum wire respectively. Potentials are quoted vs. a AgCl/Ag reference electrode against which the potential of the ferrocenium-ferrocene couple is measured as 0.55 V at room temperature. All solutions were purged with dry nitrogen for 15 min prior to electrochemical study. All cyclic voltammograms were recorded at a scan rate of 100 mV s^{-1} . The optically transparent thin-layer electrode (OTTLE) experiment was performed as described previously.¹⁹ Electronic spectra were recorded on a Perkin-Elmer $\lambda 9$ uv/vis/NIR spectrophotometer and EPR spectra on a Bruker ER200D X-band spectrometer.

Crystallography

Crystal data for 1·0.5CS₂, $\text{C}_{23}\text{H}_{32}\text{S}_{18}$, monoclinic, space group $P2_1/n$, $a = 35.970(3)$, $b = 9.9454(5)$, $c = 5.3287(3)$ Å, $\beta = 92.660(8)^\circ$, $U = 1904.2(2)$ Å³, $Z = 2$, $D_c = 1.544\text{ Mg m}^{-3}$, $\mu = 1.036\text{ mm}^{-1}$, $F(000) = 916$, $T = 293\text{ K}$.

Data were collected at RT on a Stoe IPDS image plate system using Mo-K α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods (SHELXS 97)²⁰ and refined on F^2 by full matrix least squares (SHELXL 97)²¹ using all 3573 unique data to final wR (on F^2) = 0.0951 and R (based on F and 2926 data with $F > 4\sigma(F)$) = 0.0407 [H atoms in riding model]. There is 50:50 conformational disorder in the S4-S10 region.

CCDC reference number 186/1675.

See <http://www.rsc.org/suppdata/dt/1999/3913/> for crystallographic files in .cif format.

Preparations

Compound 1. 4,5-Bis(benzoylsulfanyl)-1,3-dithiole-2-thione (2.29 g, 5.64 mmol) was treated with Cs_2CO_3 (3.58 g, 10.98 mmol) in methanol (100 ml, distilled) at room temperature for 1 h then this mixture refluxed with 1,1'-[thiobis(ethylene)dithio]bis(2-chloroethane) (5.57 mmol) (**CAUTION:** this compound is a sulfur mustard and the utmost care must be taken to avoid contact) in a total of 700 ml of dry methanol for 1 h. This was allowed to cool overnight then the yellow precipitate was filtered off and washed with methanol. The crude product (1.82 g) was stirred in 60 ml of $\text{CS}_2\text{-CH}_2\text{Cl}_2$ (3:2) and filtered to remove undissolved solid (ca. 0.5 g). The solution was eluted through a silica column (50 ml silica) with $\text{CS}_2\text{-CH}_2\text{Cl}_2$ (3:2) using about 200 ml of the solvent to obtain all the desired product. The eluent was evaporated to dryness then the yellow solid was recrystallised from $\text{CH}_2\text{Cl}_2\text{-MeOH}$. Yield = 0.475 g, 1.18 mmol, 21% (Found: C, 32.4; H, 4.1; N, 0.0. $\text{C}_{11}\text{H}_{16}\text{S}_8$ requires C, 32.7; H, 4.0; N, 0.0%). ¹H NMR (CDCl_3): δ 2.7-3.2 (multiplet). EIMS: m/z 404 (M^+). IR: 1424 (C=C) and 1063 cm^{-1} (C=S).

Compound 2. Compound **1** (0.64 g, 1.58 mmol) was heated in freshly distilled triethyl phosphite (25 ml) at 100°C for 4 h and allowed to cool overnight. The orange solid was collected by filtration and washed with methanol and THF. Yield = 0.373 g, 0.50 mmol, 63% (Found: C, 34.8; H, 4.3; N, 0.0. $\text{C}_{11}\text{H}_{16}\text{S}_7$ requires C, 35.5; H, 4.3; N, 0.0%). ¹H NMR (CDCl_3): δ 2.8-3.1 (multiplet). IR: 1425 and 1466 cm^{-1} (C=C).

Compound 3. Thione **1** (0.190 g, 0.47 mmol) was heated with ketone **4** (0.364 g, 0.74 mmol) in triethyl phosphite (5 ml) at 90°C for 17 h and the resultant orange solid filtered off and washed with hexane by stirring for several hours. The hexane insoluble product was recovered by filtration, dissolved in CH_2Cl_2 , filtered, and the filtrate eluted through a silica column (15 × 2 cm) with CH_2Cl_2 and recrystallised from $\text{CH}_2\text{Cl}_2\text{-methanol}$. Yield = 0.038 g, 0.045 mmol, 9.5% (Found: C, 49.6; H, 7.3; N, 0.0. $\text{C}_{36}\text{H}_{62}\text{S}_{11}\cdot 0.5\text{CH}_2\text{Cl}_2$ requires C, 49.3; H, 7.1; N, 0.0%). ¹H NMR (CDCl_3): δ 0.87 (t, CH_3 , 6 H), 1.2 (br, CH_2 , 32 H), 1.6 (q, CH_2 , 4 H) and 2.7-3.1 (m, $\text{SCH}_2\text{CH}_2\text{S} + \text{SCH}_2$, 20 H). FAB MS: m/z 846 (M^+). IR 1469 and 1417 cm^{-1} (C=C).

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