

Chalcogenation of Tetrathiafulvalene (TTF): Synthesis of Alkylthio-TTF and Alkylseleno-TTF Derivatives and X-Ray Crystal Structure of Ethylenediseleno-TTF (EDS-TTF)

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The reaction of mono-lithiated tetrathiafulvalene (TTF) with elemental sulfur or elemental selenium at $-78\text{ }^{\circ}\text{C}$ yields the transient species $\text{TTF-S}^{-}\text{Li}^{+}$ and $\text{TTF-Se}^{-}\text{Li}^{+}$, respectively, which have been trapped with a range of alkyl halides to yield new alkylthio- and alkylseleno-TTF derivatives. Reaction of the TTF-thiolate anion with 2-bromoethanol yields 4-(2-hydroxyethylthio)tetrathiafulvalene which is a particularly versatile building block for the synthesis of a range of new mono-functionalised TTF derivatives containing ether, ester, acrylate, urethane and vinylthio groups in the side chain. One-pot syntheses of ethylenedithio-TTF (EDT-TTF) and ethylenediseleno-TTF (EDS-TTF) from TTF are reported. The structure of EDS-TTF has been determined by single crystal X-ray analysis which reveals dimers with molecular planes orthogonal to each other.

Derivatives of TTF **1** are of considerable current interest because in the radical cation oxidation stage these molecules are components of organic metals.¹ Green first reported that TTF **1** could be metallated with butyllithium and with lithium diisopropylamide (LDA) in ether at $-78\text{ }^{\circ}\text{C}$, and the resultant mono-anion, $\text{TTF}^{-}\text{Li}^{+}$, could be trapped with electrophiles, *e.g.* CO_2 , ClCO_2Et , MeC(O)Cl , Me_2SO_4 and $\text{Et}_3\text{O}^{+}\text{PF}_6^{-}$, to yield mono-substituted TTF derivatives in reasonable yield. The reactions were complicated by the fact that $\text{TTF}^{-}\text{Li}^{+}$ readily disproportionates at temperatures above $-78\text{ }^{\circ}\text{C}$ to afford di- and multi-substituted products.² Reactions of mono-lithiated TTF have been used subsequently in the synthesis of other TTF derivatives.³

It has been shown that all four protons of TTF **1** are removed by reaction with 4 equivalents of LDA at $-78\text{ }^{\circ}\text{C}$, and the resultant tetra-anion can be treated with elemental sulfur, selenium or tellurium, followed by alkyl halides, to yield TTF derivatives substituted with four thioalkyl, selenoalkyl or telluroalkyl chains.⁴ This work established that the TTF-chalcogenate anions, *e.g.* **2**, are considerably more reactive towards electrophiles than are lithiated TTF species; for example, metallated TTF will not react with alkyl halides, whereas TTF-chalcogenate anions are readily alkylated. Tetrathiolate anion **2** can also be generated by ring opening of compound **3**⁵ or by deprotection of tetrakis(benzoylthio)TTF **4**,⁶ both reactions occurring under basic conditions.

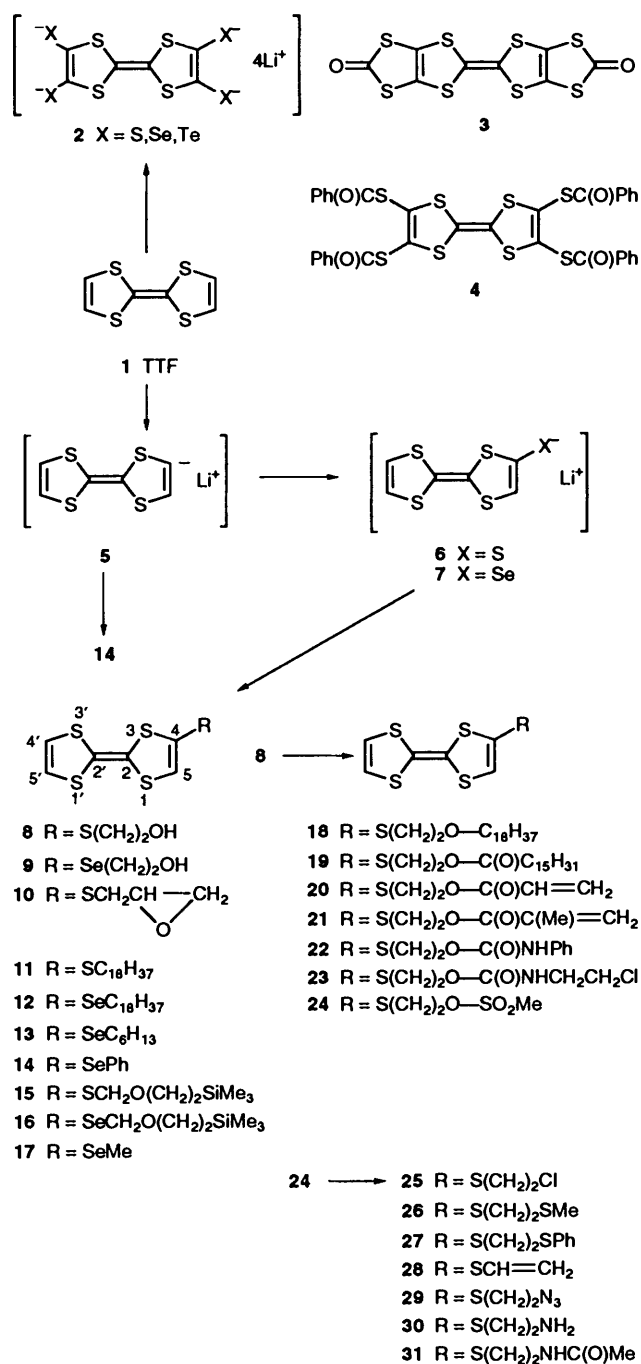
We now report that mono- and di-chalcogenation of lithiated TTF species can be readily achieved under carefully controlled conditions, and used as a key step in the synthesis of new functionalised TTF derivatives.⁷

Results and Discussion

Preparation and Trapping of Anions 6 and 7.—Mono-lithiated TTF **5** was generated as described previously^{2,3d} and treated with 1 equivalent of elemental sulfur or selenium at $-78\text{ }^{\circ}\text{C}$. The resulting thiolate or selenolate anions, **6** and **7**, respectively, were treated *in situ* with a range of electrophiles. The reaction with 2-bromoethanol is especially efficient yielding derivatives **8** and **9**, respectively (65 and 53% yields, based on TTF **1**). Compound **8** could also be obtained in considerably lower yield

(18%) by reaction of thiolate anion **6** with oxirane. Addition of 1,3-dibromopropan-2-ol to the solution containing thiolate anion **6** gave the epoxide **10** (38% yield) resulting from dehydrobromination, which could have occurred either before, or after, alkylation of anion **6**. Thiolate and selenolate anions, **6** and **7**, reacted with octadecyl iodide to yield the amphiphilic TTF derivatives **11** and **12** in 13–15% yields;⁸ the low yields of these reactions are probably due to the poor solubility of the alkyl iodide at low temperatures, possibly combined with steric factors associated with the conformational flexibility of the long-chain alkylating agent. With a view to improving the yield of amphiphilic derivatives, we explored the use of a tosylate leaving group; however, when selenolate anion **7** was treated with hexyl tosylate, hexylseleno TTF **13** was obtained in only modest yield, which discouraged us from using long-chain tosylates. [A small amount of the di-substituted product **37** was also isolated from this reaction (see below)]. Selenolate anion **7** reacted with iodobenzene to yield 4-phenylseleno-TTF **14** (67%, based on TTF). Tetrathiafulvalenyl lithium **1** was also monoselenated upon reaction with diphenyl diselenide, which yielded 4-phenylseleno-TTF **14** (45% yield).

Lee^{4d} and Kini *et al.*^{4e} have shown that TTF-tetraselenolate ion **2** (X=Se) can be tetra-alkylated with the trimethylsilyl-ethoxymethyl (SEM) protecting group, which can then be removed upon treatment with fluoride ion under mild conditions to regenerate species **2** (X=Se). We have examined analogous reactions of the monothiolate and monoselenolate anions **6** and **7** with the aim of obtaining shelf-stable equivalents of these anions. Reactions proceeded cleanly with SEM chloride to afford compounds **15** and **16** (48–57% yield) as oils which were purified by column chromatography. Treatment of compound **16** with tetrabutylammonium fluoride in THF, in the presence of an excess of methyl iodide, cleanly afforded 4-methylseleno-TTF **17** (84% yield). Compound **16** is, therefore, a shelf-stable equivalent of selenolate anion **7**. We were dismayed, therefore, when the reaction of the SEM-protected TTF-thiolate **15**, under identical conditions, resulted in the quantitative recovery of unchanged compound **15**, with no evidence that thiolate anion **6** had been generated. [We have reported elsewhere⁹ that the benzoate ester TTF-S-C(O)Ph is a shelf-stable equivalent of thiolate anion **6**.]

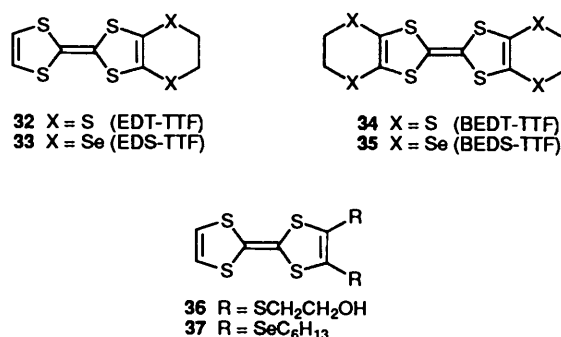


Reactions of 4-[2-(Hydroxyethyl)thio]tetrathiafulvalene 8.— We have reported elsewhere that alcohol **8** has been used in the synthesis of bis- and tris-TTF systems.⁹ Compound **8** is also a most attractive building block for a wide range of new TTF derivatives that are decorated with one highly functionalised side chain. We now report that alcohol **8** is readily converted into ether, ester, acrylate, sulfonate and urethane derivatives, using straightforward procedures. Deprotonation of alcohol **8** was achieved by treatment with sodium metal in toluene; the sodium salt of compound **8**, thus generated, reacted with octadecyl iodide to yield amphiphilic ether derivative **18** (79% yield) which provides a more efficient method of attaching a long thioalkyl chain to TTF than direct reaction with the thiolate anion **6** (*cf.* compound **11**).

Reaction of alcohol **8** with pentadecanoyl chloride in the presence of pyridine, and acryloyl chloride and methacryloyl chloride in the presence of triethylamine, gave ester derivatives

19–21, respectively, in >80% yields. Acrylate and methacrylate derivatives **20** and **21** are of particular interest as monomers that should be suitable for the preparation of new polymeric TTF systems. Phenyl isocyanate and 2-chloroethyl isocyanate reacted with alcohol **8** to afford the urethane derivatives **22** and **23**, respectively (56–63% yield). Mesylate **24**, which was obtained in 95% yield from alcohol **8** and methanesulfonyl chloride, underwent nucleophilic displacement with sodium chloride, sodium thiomethoxide and sodium thiophenoxide to give chloride and sulfide derivatives **25–27**, respectively. Alongside sulfides **26** and **27**, a small amount (*ca.* 10% yield) of thiovinyl derivative **28** was obtained, resulting from a competing elimination reaction. Both mesylate **24** and chloride **25** served as efficient precursors to thiovinyl derivative **28** upon treatment with sodium ethoxide in ethanol. Mesylate derivative **24** was converted into amine **30** *via* azide **29** using standard procedures (70% yield for the two steps) and thereby providing a new approach to amine-functionalised TTF systems, which are of current interest.^{3e,10b} Methylamide derivative **31** was readily obtained from amine **30**. These straightforward reactions of the alcohol group of compound **8** have established this compound to be by far the most versatile TTF derivative reported to date for the synthesis of a range of mono-substituted TTF derivatives containing side chain functionality.¹⁰

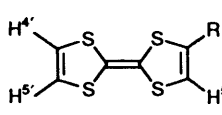
Preparation of Di-alkylchalcogeno-TTF Derivatives.— Reactions of TTF mono-anion **5**, with elemental sulfur or selenium (1.5 equivalents), followed by addition of 1,2-dibromoethane (0.5 equivalents) yielded the known donors EDT-TTF **32** and EDS-TTF **33**, respectively, in optimised yields of 10–20%. The



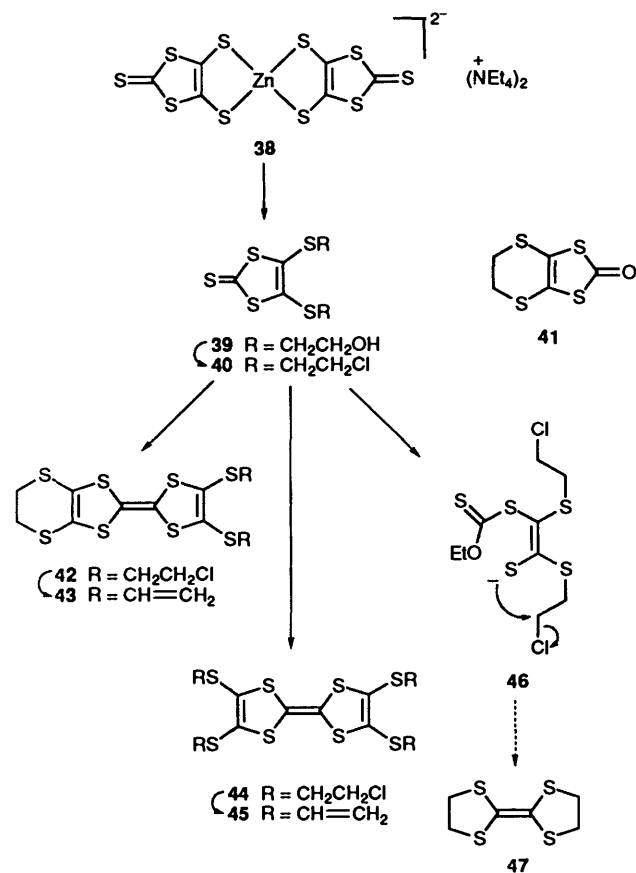
yield of EDT-TTF **32** could not be raised by varying the molar ratio of either LDA, sulfur or dibromoethane. For example, the use of TTF, LDA, sulfur and dibromoethane in a molar ratio 1:1:2:1 gave no EDT-TTF **32**; a mixture of unchanged TTF **1** and BEDT-TTF **34** was obtained instead. This is a new, one-pot, route to the unsymmetrical donors **32** and **33**, that although the yield is very low, is considerably shorter than the previous method which involved phosphite-mediated cross-coupling of the two 1,3-dithiole half units.^{11,*}

Similarly, the 4,5-disubstituted TTF derivative **36** was obtained in 20% yield from TTF, using 2-bromoethanol as the electrophile: regioisomeric disubstituted products were not detected in the reaction mixture (TLC and NMR evidence). The structure of **36** as the 4,5-isomer was inferred from the ¹H NMR spectrum, which showed a singlet for the two TTF protons at δ 6.35, whereas the proton adjacent to the same substituent group on TTF derivative **8** (and chloro analogue **25**) is shifted downfield to *ca.* δ 6.45 (*N.B.* We have found that an alkylthio substituent on TTF does not always shift the adjacent proton downfield: indeed, the single proton singlet of methylthio-TTF

* Since submission of this manuscript, a new efficient synthesis of EDT-TTF **32** has been reported: M. Fourmigué, F. C. Krebs and J. Larsen, *Synthesis*, 1993, 509.

Table 1 pK_a Values of hydrogen atoms in TTF derivatives, calculated using the computer program CAMEO


| R | 5-H | 4'-H | 5'-H |
|--------------------|-----|------|------|
| H | 48 | 48 | 48 |
| Me | 48 | 48 | 48 |
| CO ₂ Me | 45 | 48 | 48 |
| C(O)Me | 45 | 48 | 48 |
| Br | 47 | 48 | 48 |
| SMe | 47 | 48 | 48 |



is slightly upfield of the two proton singlet in that compound.)⁹ Further evidence in favour of structure **36** was provided by the marked inequivalence of the central alkene carbon atoms of the TTF frame in the ¹³C NMR spectrum (δ_c 116.9 and 104.5). The disubstituted by-product obtained during the formation of **13** (see above) was, likewise, assigned structure **37**. The mass spectroscopic fragmentation pattern of compounds **36** and **37** was also consistent with the two substituents being on the same 1,3-dithiole ring. Conclusive proof of structure **36** came from an unambiguous synthesis: the cross-coupling reaction of the half-units, 1,3-dithiole-2-thione and the bis(*tert*-butyldiphenylsilyl)-protected derivative of compound **39**, followed by removal of the silyl groups, gave a product in low yield that was identical with compound **36** obtained above (m.p. and NMR comparison).

The sequence of events leading to the formation of the disubstituted products **32**, **33**, **36** and **37** is unclear. Disproportionation of lithiated TTF **5** and chalcogenated TTF

anions **6** and **7** may occur to yield transient dianion species. An alternative, and perhaps more likely, mechanism does not involve dianion species, but, instead, alkylation of species **6** and **7** occurs prior to the second deprotonation and chalcogenation of the TTF system. The directing influence of an alkylthio- or alkylseleno-substituent on further substitution onto the TTF ring has not been investigated previously, although Becker *et al.* assigned a different disubstitution pattern, namely the 4,4' or 4,5' regioisomer (*i.e.* one substituent on each ring) to a bis(ethyltelluro-TTF) derivative.¹² In early work, Green established that attachment of an electron withdrawing substituent (*e.g.* an ester group) to TTF activated the adjacent position to metallation, affording 4,5-disubstituted products, while an electron donating substituent (*e.g.* a methyl group) directed a second substitution into the 4' or 5' positions, although the situation was complicated by temperature dependency in some cases.^{2b} This substitution pattern has been supported by recent experiments on halogenation of lithiated TTF species, which yield the 4,5-disubstituted isomers,¹³ with X-ray crystallographic proof of structure.^{13a} The formation of the 4,5-disubstituted compounds **32**, **33**, **36** and **37** is, therefore, consistent with other work on the di-substitution of TTF. It is also likely that lithium coordination to the mono-chalcogenated species **6** and **7** plays a role in directing the second metallation to the adjacent site.

We have used the computer program CAMEO to examine the effect that a range of substituents on the TTF frame has on the pK_a values of the remaining TTF protons. It has been shown previously that there is agreement to within 1–2 pK_a units between calculated and experimental values for protons on unsaturated sites adjacent to sulfur.¹⁴ The calculated data for TTF derivatives are collated in Table 1. It can be seen that attachment of an electron withdrawing ester or acyl substituent increases the acidity of the adjacent proton by 3 pK_a units; a bromine atom or a methylthio group has less effect, but, nonetheless, the data for these compounds are consistent with deprotonation being favoured at the adjacent site, giving rise to the observed 4,5-disubstituted products. A methyl substituent on TTF does not change any of the pK_a values of the remaining ring protons.

To obtain substituted derivatives of EDT-TTF **32**, we have adopted standard phosphite-mediated cross-coupling methodology.¹⁵ Zincate salt **38** reacted with 2-bromoethanol in refluxing acetone to give the 4,5-disubstituted 1,3-dithiole-2-thione derivative **39**, which was converted into the chloride derivative **40**, by reaction with thionyl chloride (63% yield for the two steps). Cross-coupling of the thione and ketone half-units **40** and **41**, in the presence of triethyl phosphite under standard conditions, gave the functionalised EDT-TTF system **42** in 27% yield, after separation of self-coupled products by column chromatography. Base-induced elimination of HCl from **42** gave the di(vinylthio) derivative **43** (91% yield) by analogy with the preparation of **28**. Self-coupling of the 1,3-dithiole system **40**, proceeded cleanly to give the tetra-functionalised TTF derivative **44**, from which the tetra(vinylthio) derivative **45** was readily obtained.

Treatment of dihalogeno compound **40** with sodium ethoxide gave tetrahydro-TTF **47** (92%) presumably *via* initial attack of ethoxide ion at the thione group of **40**, followed by ring opening to form intermediate **46**, which cyclises as shown. Analogous reaction of a second ethoxide ion, loss of diethyl thiocarbonate and ring closure, would form product **47**. Related ring opening of 4,5-di(alkylthio)-1,3-dithiol-2-one derivatives upon reaction with sodium methoxide has been reported.¹⁶

X-Ray Crystal Structure of EDS-TTF 33.—The molecular structure of compound **33**, confirmed by a single crystal X-ray diffraction study, is shown in Fig. 1. The TTF framework of

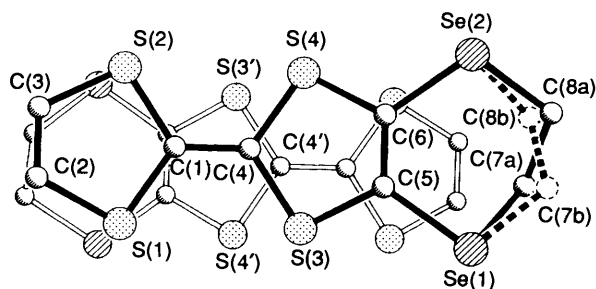


Fig. 1 Dimer of molecule **33** in the crystal (projection on the mean molecular plane; hydrogen atoms are omitted). For the basic molecule, both positions of the disordered atoms are shown; atoms generated *via* the inversion centre (1/2, 1/2, 1/2) are primed

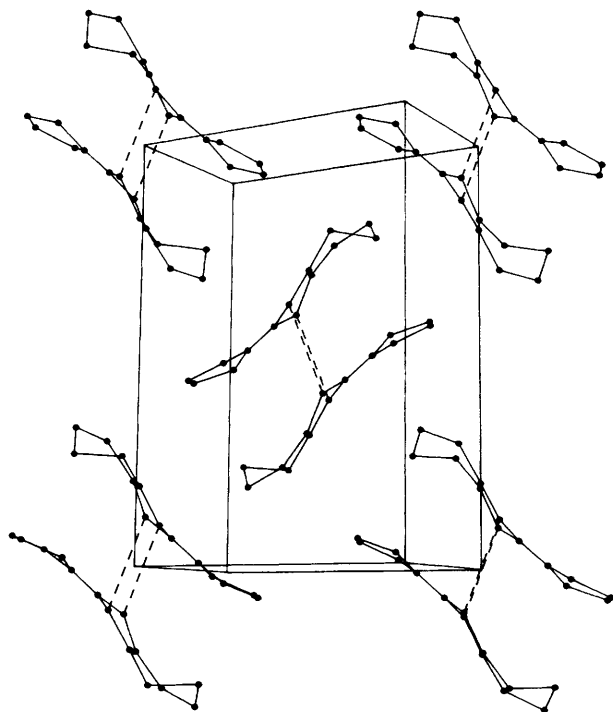


Fig. 2 Crystal packing of compound **33** within a layer of dimers (the disorder in the ethylene group is not shown)

compound **33** adopts a non-planar, boat-like conformation: the central tetrathioethane fragment is planar, but both five-membered heterocycles are folded in the same direction in an envelope mode, by 18.9° along the $S(1) \cdots S(2)$ axis, and by 23.7° along the $S(3) \cdots S(4)$ axis. A similar conformation (with rings folded by $12\text{--}18^\circ$) has been observed in neutral BEDT-TTF **34**¹⁷ and BEDS-TTF **35**,¹⁸ whereas the corresponding cation radicals are almost planar.^{19,20} However, the TTF conformation seems to be governed by intermolecular interactions (see below) rather than the outer six-membered rings, as neutral TTF **1** is shown to adopt a chair-like conformation with much smaller folding of the heterocycles.²¹

Within the six-membered ring of compound **33**, atoms $C(7)$ and $C(8)$ are disordered over two positions (A and B) each with equivalent occupancies. While the $Se(1)$, $C(5)$, $C(6)$, $Se(2)$ moiety is planar, atoms $C(7A)$, $C(8A)$, $C(7B)$ and $C(8B)$ deviate from that plane by 1.47, 1.06, 0.78 and 1.45 Å, respectively, to the same side. Thus, in both cases, this ring adopts a conformation intermediate between boat and twist.

Bond distances in the TTF part of structure **33** are similar to the equivalent distances in compounds **34** and **35**. The average $Se-C(sp^2)$ and $Se-C(sp^3)$ distances in **33** (although the latter are of poor accuracy due to the disorder) are 1.90(1) and 1.97(6) Å, respectively, *i.e.* they are essentially the same as in compound **35**

(1.90 and 1.94 Å) and its cations (1.89 and 1.96 Å).²⁰ The difference between these values is slightly larger than between the $C(sp^2)$ and $C(sp^3)$ covalent radii (0.03 Å)²² indicating some degree of lone pair- π orbital interaction between the selenium atoms and the TTF system. This is supported by the fact that the $S(3)\text{--}C(5)$, $S(4)\text{--}C(6)$ and $C(5)\text{--}C(6)$ bonds in structure **33** are slightly longer than the corresponding bonds in the unsubstituted half of the TTF system.

Crystal packing of TTF derivatives receives much attention in the search for correlations between structure and conductivity in these compounds.²³ The structure of compound **33** presents an unusual type of packing. Pairs of molecules related *via* an inversion centre (1/2, 1/2, 1/2 for the basic molecule) can be regarded as dimers with a ring-over-bond overlap (Fig. 1) favoured by the unsymmetrical shape of the molecule. Within the dimer, interplanar separation between the tetrathioethane moieties is rather short (3.35 Å) providing intermolecular contacts $C(4) \cdots C(4')$ 3.44 Å, $S(3) \cdots S(4')$ and $S(4) \cdots S(3')$ 3.57 Å, *i.e.* essentially double the Van der Waals radii of C (1.70 Å) and S (1.80 Å).²⁴ However, the sterically more bulky parts of the molecules are bent away from these central 'close contacts'.

The packing of dimers of **33** (Fig. 2) resembles to some extent the κ -type structures of $(BEDT\text{-}TTF)_2X$ salts.²⁵ Dimers with molecular planes orthogonal to each other, are arranged in a chess-board order to form a layer parallel to the (1 0 $\bar{1}$) plane. However, in the κ -phase structures the longer axes of the molecules lie perpendicular to a layer (and parallel to each other) while in **33** they lie within the layer, and perpendicular to each other. Neighbouring layers in **33** overlap in a molecule-over-gap fashion, with few contacts: notably, $Se(1) \cdots Se(2)$ 3.69 Å and $Se(1) \cdots S(4)$ 3.71 Å, are marginally shorter than the sums of the Van der Waals radii (1.80 Å for sulfur and 1.92 Å for selenium).²⁴ The crystal packing of compound **33** is similar to EDT-TTF **32**, the X-ray structure of which was reported while the present work was in progress.²⁶

Experimental

General.—Details are the same as those reported recently.²⁷

X-Ray Structure Determination of EDS-TTF 33.—*Crystal data.* $C_8H_6S_4Se_2$, $M = 388.3$, monoclinic, $a = 6.536(2)$, $b = 16.020(4)$, $c = 11.366(3)$ Å, $\beta = 92.95(2)^\circ$, $U = 1188.5(5)$ Å³ (from 24 reflections with $26 < 2\theta < 30^\circ$, including all symmetrical equivalents for each), space group $P2_1/n$ (no. 14), $Z = 4$, $D_c = 2.17$ g cm⁻³, $F(000) = 744$, λ (Mo-K α) = 0.710 73 Å (graphite-monochromated), $\mu = 6.88$ cm⁻¹.

A dark yellow needle-like crystal of compound **33** with dimensions $0.08 \times 0.10 \times 0.42$ mm was obtained from dichloromethane-hexane solution. The X-ray diffraction experiment was carried out using a Siemens R3m/V four-circle computer-controlled diffractometer at room temperature. 2114 Independent reflections with $2\theta \leq 52^\circ$ were measured by $\theta/2\theta$ scan technique, of which 1521 with $I \geq 2 \sigma(I)$ were used in calculations, after semi-empirical absorption correction (based on 360 ψ -scans from 10 reflections, minimum and maximum transmission 0.0393 and 0.0641, respectively). The structure was solved by direct methods and refined by full-matrix least squares using SHELXTL PLUS programs.²⁸ All the ordered non-hydrogen atoms were refined anisotropically. For the disordered atoms $C(7)$ and $C(8)$ both A and B positions were finally refined independently in isotropic approximation with 50% occupancy factors. All hydrogen atoms were included in the refinement in riding model. A weighting scheme $w^{-1} = \sigma^2(F) + 0.0004 F^2$ was used. The refinement converged at $R = 0.029$, $R_w = 0.033$ and $S = 1.02$ for 125 refined parameters, the final difference Fourier map showing features from +0.35 to -0.41 e Å⁻³. Bond distances are given in Table 2.

Table 2 Bond lengths (Å) for compound **33**

| | | | |
|-------------|----------|-------------|----------|
| Se(1)–C(5) | 1.905(5) | Se(1)–C(7A) | 2.00(1) |
| Se(1)–C(7B) | 1.95(1) | Se(2)–C(6) | 1.888(5) |
| Se(2)–C(8A) | 1.87(1) | Se(2)–C(8B) | 1.04(1) |
| S(1)–C(1) | 1.751(5) | S(1)–C(2) | 1.743(7) |
| S(2)–C(1) | 1.756(5) | S(2)–C(3) | 1.750(6) |
| S(3)–C(4) | 1.756(5) | S(3)–C(5) | 1.751(5) |
| S(4)–C(4) | 1.751(5) | S(4)–C(6) | 1.764(5) |
| C(1)–C(4) | 1.362(7) | C(2)–C(3) | 1.297(9) |
| C(5)–C(6) | 1.329(7) | C(7A)–C(8A) | 1.59(2) |
| C(7B)–C(8B) | 1.44(2) | | |

Additional material available from the Cambridge Crystallographic Data Centre comprises atomic coordinates, bond lengths and thermal parameters.*

4-(2-Hydroxyethylthio)tetrathiafulvalene † **8** was prepared as described.⁹

4-(2-Hydroxyethylseleno)tetrathiafulvalene **9**.—Into a stirred solution of TTF (500 mg, 2.5 mmol) in dry ether (100 cm³) at –78 °C under nitrogen was syringed a freshly prepared solution of LDA [obtained from diisopropylamine (0.37 cm³, 2.75 mmol) and butyllithium (1.7 cm³ of 1.6 mol dm⁻³ BuLi, 2.75 mmol) in dry ether (10 cm³) at –78 °C] over a period of 10 min. A yellow precipitate of monolithiated-TTF **5** began to form after ca. 10 min, and stirring was continued for a further 45 min at –78 °C. Elemental selenium (finely powdered 980 mg, 12.5 mmol) was then added in one portion against a positive pressure of nitrogen and stirring was continued at –78 °C for 7 h, to form the lithium salt of TTF-selenolate anion **7**. 2-Bromoethanol (2.0 cm³, 9.0 mmol) was then added. The mixture was stirred at –78 °C for 2 h and then slowly warmed to 20 °C over 12 h. Water (100 cm³) was added and the mixture extracted into dichloromethane (3 × 50 cm³), the combined extracts washed with water, dried (MgSO₄) and the solvent evaporated. Chromatography of the residue on a silica column eluting with cyclohexane gave **compound 9** (428 mg, 53%) as a viscous yellow oil that partially solidified at 0 °C (Found: C, 29.9; H, 2.4. C₈H₈OS₄Se requires C, 29.4; H, 2.5%; *m/z* (DCI) 328 (M⁺ + 1); δ_H(CDCl₃) 6.44 (1 H, s), 6.32 (2 H, s), 3.87 (2 H, t), 3.00 (2 H, t) and 2.18 (1 H, s).

4-(2,3-Epoxypropylthio)tetrathiafulvalene **10**.—This compound was prepared analogously to compound **8**⁹ using TTF (0.25 g, 1.2 mmol) in ether (30 cm³), LDA [from BuLi (1.6 mol dm⁻³, 1.6 cm³, 1.35 mmol) and diisopropylamine (0.2 cm³, 1.35 mmol)] in ether (10 cm³), sulfur (40 mg, 1.25 mmol) and 1,3-dibromopropan-2-ol (0.14 g, 0.62 mmol). Column chromatography on silica, eluent hexane–dichloromethane (1:1 v/v) gave **compound 10** (135 mg, 38%) as a yellow oil (Found: C, 36.8; H, 2.6. C₉H₈OS₅ requires C, 37.0; H, 2.7%; *m/z* (DCI) 293 (M⁺ + 1); δ_H(CDCl₃) 6.49 (1 H, s), 6.33 (2 H, s), 3.17 (1 H, m), 2.90 (1 H, m), 2.82 (2 H, m) and 2.66 (1 H, m).

4-Octadecylthiotetrathiafulvalene **11**. This compound was prepared analogously to compound **10** using 1-iodooctadecane (0.46 g, 1.35 mmol) and chromatography (eluent hexane) to give **compound 11** as a yellow solid (72 mg, 13%; m.p. 55–56 °C (Found: C, 59.2; H, 8.3; S, 32.9. C₂₄H₄₀S₅ requires C, 59.0; H, 8.2; S, 32.8%; *m/z* (EI) 488 (M⁺).

4-Octadecylselenotetrathiafulvalene **12**. This compound which was prepared analogously to compound **11**, using selenium (100 mg, 1.25 mmol) was isolated as a yellow solid (99 mg, 15%; m.p. 52 °C (Found: C, 53.9; H, 7.3. C₂₄H₄₀S₄Se requires C, 53.8; H, 7.5%; *m/z* (EI) 536 (M⁺, based on ⁸⁰Se).

4-Phenylselenotetrathiafulvalene **14**.—*Method 1*. This is analogous to the preparation of compound **12** using iodobenzene (0.15 cm³, 1.35 mmol) and hexane–dichloromethane (5:1) as the chromatography eluent, yielding **compound 14** (0.29 g, 67%) as a yellow solid; m.p. 78–79 °C (from acetonitrile) (Found: C, 40.0; H, 2.3. C₁₂H₈S₄Se requires C, 40.0; H, 2.2%; *m/z* (DCI) 361 (M⁺ + 1); δ_H(CDCl₃) 7.50 (2 H, m), 7.31 (3 H, m), 6.53 (1 H, s) and 6.29 (2 H, s).

Method 2. To an ethereal slurry of tetrathiafulvalenyllithium **5** (prepared as described above for compound **9**) was added diphenyl diselenide (0.42 g, 1.35 mmol) portionwise over 2 min. The reaction mixture was allowed to warm to 20 °C overnight. The resultant orange solution was poured onto distilled water (50 cm³) and the ether layer was separated. The aqueous layer was further extracted with dichloromethane (50 cm³) and the combined organic layers were dried (MgSO₄), filtered and evaporated to give the crude product. Purification, either as described in Method 1, or by preparative TLC (silica, eluent cyclohexane–dichloromethane 4:1 v/v) gave **compound 14** (0.20 g, 45%) identical (NMR and m.p.) with the sample prepared by Method 1.

Compounds 15 and 16.—*General procedure*. TTF-thiolate anion **6** and TTF-selenolate anion **7** were prepared as described for compounds **8**⁹ and **9** from TTF **1** (500 mg, 2.4 mmol). Trimethylsilyloxyethyl chloride (0.65 cm³, 3.7 mmol) was then syringed into the slurry over 5 min. Work-up as described for compound **9**, followed by chromatography on a silica column eluting with hexane–toluene (3:1 v/v) gave firstly unchanged TTF **1** (ca. 150 mg, 30%) and then the product. There was obtained:

4-(Trimethylsilyloxyethylthio)tetrathiafulvalene **15**. An orange oil (430 mg, 48%) (Found: C, 39.6; H, 4.5. C₁₂H₁₈OS₅Si requires C, 39.3; H, 4.9%; *m/z* (DCI) 366 (M⁺); δ_H(CDCl₃) 6.36 (1 H, s), 6.30 (2 H, s), 4.82 (2 H, s), 3.67 (2 H, t, *J* 8.1), 0.95 (2 H, t, *J* 8.1) and 0.30 (9 H, s).

4-(Trimethylsilyloxyethylseleno)tetrathiafulvalene **16**. An orange oil (580 mg, 57%) (Found: C, 35.0; H, 4.7. C₁₂H₁₈OS₄SeSi requires C, 34.8; H, 4.4%; *m/z* (DEI) 414 (M⁺); δ_H(CDCl₃) 6.37 (1 H, s), 6.30 (2 H, s), 5.18 (2 H, s), 3.66 (2 H, t, *J* 8.1), 0.96 (2 H, t, *J* 8.1) and 0.34 (9 H, s).

4-Methylselenotetrathiafulvalene **17**.—To a stirred mixture of compound **16** (200 mg, 0.5 mmol) and methyl iodide (0.5 cm³, 8.3 mmol) in dry THF (50 cm³) under nitrogen was added a solution of tetrabutylammonium fluoride (1 mol dm⁻³ in THF; 2 cm³, 2 mmol), and stirring was continued for 48 h. The solvent was evaporated and the residue chromatographed on a silica column eluting with hexane–toluene (3:1 v/v) to afford **compound 17** (120 mg, 84%) as a viscous yellow oil (Found: C, 27.9; H, 2.3. C₇H₆S₄Se requires C, 28.3; H, 2.0%; *m/z* (DCI) 299 (M⁺ + 1); δ_H(CDCl₃) 6.34 (1 H, s), 6.31 (2 H, s) and 2.30 (3 H, s). Continued elution of the column gave unchanged starting material **16** (24 mg, 12%).

4-Octadecyloxyethylthiotetrathiafulvalene **18**.—A stirred mixture of compound **8** (100 mg, 0.35 mmol) and sodium shavings (0.5 g) in dry toluene (100 cm³) was refluxed under nitrogen for 2 h, whereupon 1-iodooctadecane (140 mg, 0.36 mmol) was added and refluxing continued for a further 34 h. After cooling, water (100 cm³) was added and the toluene layer was separated,

* Full details of the CCDC deposition scheme are given in 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. I*, 1993, Issue 1.

† Throughout the paper the term tetrathiafulvalene is used to represent the 2,2'-bi(1,3-dithiolyliidene) group. The latter name is that recommended by IUPAC for such structures.

dried (MgSO_4) and evaporated. Chromatography of the residue on a silica column eluting with toluene–cyclohexane (1:3 v/v) afforded **compound 18** (147 mg, 79%) as a pale yellow oil (Found: C, 58.7; H, 8.1. $\text{C}_{26}\text{H}_{44}\text{OS}_5$ requires C, 58.6; H, 8.3%); m/z (DCI) 533 ($\text{M}^+ + 1$).

Compounds 19–21 and 24.—*General procedure.* Into a solution of alcohol **8** (250 mg, 0.9 mmol) and the appropriate acid chloride in dry dichloromethane (30 cm^3) at 20 °C under nitrogen, was syringed triethylamine (0.12 cm^3 , 0.9 mmol). The mixture was stirred at 20 °C for 2 h (24 h for compound **19**), whence water was added and the mixture extracted with dichloromethane (50 cm^3). The combined extracts were washed with water, dried (MgSO_4) and evaporated. Chromatography of the residue on a silica column eluting with cyclohexane–dichloromethane (1:1 v/v) afforded the products. There was obtained:

4-(Hexadecanoyloxyethylthio)tetrathiafulvalene **19** [from hexadecanoyl chloride (270 mg, 0.9 mmol)]: a brown wax (164 mg, 88%) (Found: C, 55.4; H, 7.3. $\text{C}_{24}\text{H}_{38}\text{O}_2\text{S}_5$ requires C, 55.6; H, 7.3%); m/z (DCI): 519 ($\text{M}^+ + 1$).

4-(Acryloyloxyethylthio)tetrathiafulvalene **20** [from acryloyl chloride (0.1 cm^3 , 1.2 mmol)]: a waxy orange oil (244 mg, 82%) (Found: C, 39.9; H, 3.1. $\text{C}_{11}\text{H}_{10}\text{O}_2\text{S}_5$ requires C, 39.5; H, 3.0%); m/z (DCI) 335 ($\text{M}^+ + 1$); $\delta_{\text{H}}(\text{CDCl}_3)$ 6.45 (1 H, s), 6.38 (2 H, s), 6.11, 5.86 and 5.82 (each 1 H, ABX, J_{ax} 17.27, J_{bx} 10.35, $J_{\text{ab}} < 1$), 4.35 (2 H, t, J 3.8) and 3.03 (2 H, t, J 3.8); $\delta_{\text{C}}(\text{CDCl}_3)$ 165.8, 131.5, 127.9, 125.6, 124.3, 119.0, 118.9, 113.4, 109.0, 62.8 and 34.0.

4-(Methacryloyloxyethylthio)tetrathiafulvalene **21** [from methacryloyl chloride (0.12 cm^3 , 1.2 mmol)]: an orange oil that partially solidified at 0 °C (258 mg, 83%) (Found: C, 41.1; H, 3.8. $\text{C}_{12}\text{H}_{12}\text{O}_2\text{S}_5$ requires C, 41.4; H, 3.5%); m/z (DCI) 349 ($\text{M}^+ + 1$); $\delta_{\text{H}}(\text{CDCl}_3)$ 6.44 (1 H, s), 6.32 (2 H, s), 6.12 and 5.56 (each 1 H, AB, $J_{\text{ab}} < 1$), 4.33 (2 H, t, J 3.9), 3.02 (2 H, t, J 3.9) and 1.93 (3 H, s); $\delta_{\text{C}}(\text{CDCl}_3)$ 167.0, 135.8, 126.3, 124.8, 124.3, 119.0, 118.9, 113.4, 109.1, 63.0, 34.0 and 18.2.

4-(Methylsulfonyloxyethylthio)tetrathiafulvalene **24** [from methanesulfonyl chloride (0.1 cm^3 , 1.2 mmol)]: an orange oil (302 mg, 95%) (Found: C, 30.6; H, 2.5. $\text{C}_9\text{H}_{10}\text{O}_3\text{S}_6$ requires C, 30.1; H, 2.8%); m/z (DCI) 359 ($\text{M}^+ + 1$); $\delta_{\text{H}}(\text{CDCl}_3)$ 6.50 (1 H, s), 6.33 (2 H, s), 4.37 (2 H, t, J 6.5), 3.06 (2 H, t, J 6.5) and 3.06 (3 H, s).

Compounds 22 and 23.—*General procedure.* To a solution of compound **8** in dichloromethane (30 cm^3) was added the isocyanate followed by triethylamine (0.25 cm^3 , excess). The reaction mixture was stirred at 20 °C for 24 h. Water was added and the organic layer was separated, dried (MgSO_4) filtered and evaporated under reduced pressure. The residue was chromatographed on a neutral alumina column with cyclohexane–dichloromethane (3:1 v/v) as eluent to afford the product which was recrystallised from methanol–ether. There was obtained:

4-[2-(N-Phenylcarbamoyloxy)ethylthio]tetrathiafulvalene **22** [from compound **8** (50 mg, 0.18 mmol) and phenyl isocyanate (0.018 cm^3 , 0.17 mmol)]: a yellow solid (40 mg, 56%) m.p. 86–88 °C (Found: C, 45.1; H, 3.3; N, 3.9. $\text{C}_{15}\text{H}_{13}\text{NO}_2\text{S}_5$ requires C, 45.0; H, 3.5; N, 3.8%); m/z (DCI) 400 ($\text{M}^+ + 1$); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.5–7.1 (5 H, m), 6.43 (1 H, s), 6.32 (2 H, s), 4.38 (1 H, s), 4.24 (2 H, t) and 3.03 (2 H, t); $\nu_{\text{max}}(\text{Nujol})/\text{cm}^{-1}$ 3345 (NH) and 1708 (C=O).

4-[2-[N-(2-Chloroethyl)carbamoyloxy]ethylthio]tetrathiafulvalene **23** [from compound **8** (80 mg, 0.29 mmol) and 2-chloroethyl isocyanate (0.025 cm^3 , 0.287 mmol)]: a yellow solid (70 mg, 63%) m.p. 74–77 °C (Found: C, 34.5; H, 2.6; N, 3.8. $\text{C}_{15}\text{H}_{12}\text{ClNO}_2\text{S}_5$ requires C, 34.3; H, 2.6; N, 3.6%); m/z (DCI) 388, 386 ($\text{M}^+ + 1$); $\delta_{\text{H}}(\text{CDCl}_3)$ 6.43 (1 H, s), 6.32 (2 H,

s), 5.13 (1 H, s), 4.27 (2 H, t), 3.59 (2 H, q), 3.52 (2 H, t) and 2.98 (2 H, t); $\nu_{\text{max}}(\text{Nujol})/\text{cm}^{-1}$ 3140 (NH) and 1700 (C=O).

4-(2-Chloroethylthio)tetrathiafulvalene **25.**—A stirred solution of compound **22** (200 mg, 0.56 mmol) and sodium chloride (100 mg, 1.7 mmol) in dry acetone (20 cm^3) was refluxed under nitrogen for 6 h. After cooling, the solvent was evaporated and the residue chromatographed on a silica column eluting with cyclohexane–dichloromethane (2:1 v/v) to afford **compound 25** (143 mg, 86%) as a yellow oil (Found: C, 32.5; H, 2.6. $\text{C}_8\text{H}_7\text{ClS}_5$ requires C, 32.1; H, 2.4%); m/z (DCI) 299 and 301 ($\text{M}^+ + 1$); $\delta_{\text{H}}(\text{CDCl}_3)$ 6.47 (1 H, s), 6.33 (2 H, s), 3.67 (2 H, t, J 7.3) and 3.05 (2 H, t, J 7.3).

Compounds 26–28.—*General procedure.* Into a stirred solution of compound **24** (200 mg, 0.56 mmol) dissolved in dry THF (25 cm^3) at 20 °C under nitrogen was added either sodium thiomethoxide (58 mg, 0.7 mmol), sodium thiophenoxide (110 mg, 0.7 mmol) or sodium ethoxide (57 mg, 0.7 mmol) and the resulting mixture was stirred for 12 h. The solvent was then evaporated, water was added, and the mixture was extracted with dichloromethane. The organic layer was separated, dried (MgSO_4), evaporated and the residue was chromatographed on a silica column eluting with cyclohexane–dichloromethane (1:1 v/v) to afford the products. There was thus obtained:

4-[2-(Methylthio)ethylthio]tetrathiafulvalene **26.** A yellow oil (168 mg, 81%) (Found: C, 35.1; H, 2.8. $\text{C}_9\text{H}_{10}\text{S}_6$ requires C, 34.8; H, 3.2%); m/z (DCI) 311 ($\text{M}^+ + 1$); $\delta_{\text{H}}(\text{CDCl}_3)$ 6.41 (1 H, s), 6.32 (2 H, s), 2.91 and 2.76 (each 2 H, AA'XX') and 2.14 (3 H, s). [This reaction also yielded ca. 17 mg (10%) of compound **28** which was the first product to elute off the column.]

4-[2-(Phenylthio)ethylthio]tetrathiafulvalene **27.** An orange solid (190 mg, 76%) m.p. 71–73 °C (Found: 44.9; H, 3.3. $\text{C}_{14}\text{H}_{12}\text{S}_6$ requires C, 45.1; H, 3.2%); m/z (DCI) 373 ($\text{M}^+ + 1$); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.37–7.19 (5 H, m), 6.37 (1 H, s), 6.33 (2 H, s) and 3.10 and 2.93 (each 2 H, AA'XX').

4-Vinylthio)tetrathiafulvalene **28.** An orange oil (153 mg, 87%) (Found: C, 37.0; H, 2.1. $\text{C}_8\text{H}_6\text{S}_5$ requires C, 36.6; H, 2.3%); m/z (DCI) 263 ($\text{M}^+ + 1$); $\delta_{\text{H}}(\text{CDCl}_3)$ 6.46 (1 H, s), 6.32 (2 H, s) and 6.35, 5.39 and 5.38 (each 1 H, ABX, J_{AX} 16.52, J_{BX} 9.35, $J_{\text{AB}} < 1$); $\delta_{\text{C}}(\text{CDCl}_3)$ 130.2, 124.5, 123.7, 119.0, 118.9, 115.9, 113.2 and 109.2. Analogous reaction of compound **25** with 1.2 mol equiv. of sodium ethoxide also afforded compound **28** in 84% yield.

4-(2-Azidoethylthio)tetrathiafulvalene **29.**—A mixture of compound **24** (500 mg, 1.4 mmol), sodium azide (150 mg, 2.3 mmol) and trimethylcaprylammonium chloride (50 mg) in toluene (40 cm^3) and water (40 cm^3) was stirred at 80 °C for 24 h. After cooling the aqueous phase was removed and the organic layer washed with water, dried (MgSO_4), and evaporated to yield crude **compound 29** (392 mg, 92%) as a yellow oil. This was utilised in the next step without further purification. A TLC-pure sample was obtained by chromatography on a silica column eluting with dichloromethane; m/z (DCI): 306 ($\text{M}^+ + 1$); $\delta_{\text{H}}(\text{CDCl}_3)$ 6.47 (1 H, s), 6.32 (2 H, s), 3.50 (2 H, t, J 6.6) and 2.91 (2'-H, t, J 6.6).

4-(2-Aminoethylthio)tetrathiafulvalene **30.**—Lithium aluminium hydride (20 mg, 0.5 mmol) was added to a stirred solution of compound **29** (350 mg, 1.1 mmol) in dry ether (50 cm^3) under nitrogen and the mixture refluxed for 24 h. After cooling, the organic phase was washed with water. The organic phase was then extracted with 10% aqueous hydrochloric acid, and this aqueous phase washed with dichloromethane. Basification of the aqueous phase with dilute sodium hydroxide solution and extraction with dichloromethane, drying of the organic phase (MgSO_4) and evaporation afforded **compound 30** (243 mg, 76%)

as a yellow semi-solid (Found: C, 34.9; H, 2.9. $C_8H_9NS_5$ requires C, 34.4; H, 3.2%); m/z (DCI) 280 ($M^+ + 1$); δ_H ($CDCl_3$) 6.37 (1 H, s), 6.31 (2 H, s), 2.92 and 2.81 (each 2 H, AA'XX') and 1.48 (1 h, br s).

4-[2-(Methylamido)ethylthio]tetrathiafulvalene **31**.—Into a stirred solution of compound **30** (200 mg, 0.7 mmol) and acetyl chloride (0.1 cm^3 , 1.4 mmol) in dry dichloromethane (30 cm^3) at 20 °C under nitrogen was slowly added triethylamine (0.2 cm^3 , 1.4 mmol) and the mixture stirred for a further 2 h. The solvent was evaporated and the residue chromatographed on a silica column eluting with hexane–dichloromethane (2:1 v/v) to afford compound **31** (186 mg, 81%) as a yellow solid. M.p. 54–55 °C (Found: C, 37.6; H, 3.3. $C_{10}H_{11}NOS_5$ requires C, 37.4; H, 3.4%); m/z (DCI) 322 ($M^+ + 1$); δ_H ($CDCl_3$) 6.45 (1 H, s), 6.33 (2 H, s), 5.85 (1 H, br), 3.50 (2 H, q, J 6.0), 2.90 (2 H, t, J 6.0) and 2.00 (3 H, s).

Compounds 32 and 33.—General procedure. To an ethereal slurry of anion **5** [obtained from TTF **1** (250 mg, 1.2 mmol) as described above] at –78 °C was added either elemental sulfur (60 mg, 1.84 mmol) or elemental selenium (145 mg, 1.84 mmol) and the reaction mixture was maintained at –78 °C for 7 h. Then, 1,2-dibromoethane (0.1 cm^3 , 1.23 mmol) dissolved in ether (2 cm^3) was added dropwise over 2 min. The resulting orange solution was allowed to warm to room temperature overnight. Standard aqueous work-up, with extraction into toluene, followed by column chromatography on silica, eluted with cyclohexane–toluene (3:1 v/v) gave analytically pure products. There was obtained:

4,5-Ethylenedithiotetrathiafulvalene **32** (35–75 mg, 10–20%); m.p. 199 °C (lit.,¹¹ 200 °C).

4,5-Ethylenediselenotetrathiafulvalene **33** (83 mg, 18%); m.p. 194–197 °C (lit.,²⁹ 195 °C).

4,5-Bis(2-hydroxyethylthio)tetrathiafulvalene **36**.—To an ethereal slurry of anion **5** (obtained from tetrathiafulvalene **1** (250 mg, 1.23 mmol) at –78 °C was added elemental sulfur (120 mg, 3.75 mmol); the mixture was stirred at this temperature for 7 h, before the addition of 2-bromoethanol (1.0 cm^3 , 15 mmol). Work-up as described for compound **9** followed by chromatography on a silica column, eluted with dichloromethane–ethyl acetate (1:1 v/v) gave compound **36** as a yellow solid (87 mg, 20%); m.p. 98–101 °C (Found: C, 33.7; H, 3.4. $C_{10}H_{12}O_2S_4$ requires C, 33.7; H, 3.4%); m/z (DCI) 357 ($M^+ + 1$); δ_H ($CDCl_3$) 6.34 (2 H, s), 3.75 (2 H, q, J 4.5), 3.01 (2 H, t, J 3.0) and 2.90 (1 H, t, J 6.1); δ_C ($CDCl_3$) 128.2, 118.9, 116.9, 104.5, 59.8 and 39.2.

4,5-Bis(2-hydroxyethylthio)-1,3-dithiole-2-thione **39**.—A stirred mixture of compound **38**³⁰ (20 g, 0.03 mol) in acetone (200 cm^3) and bromoethanol (11.8 cm^3 , 0.17 mol) was refluxed for 12 h. After evaporation under reduced pressure the residue was chromatographed on a silica column eluting with dichloromethane–acetone (1:1 v/v) to afford compound **39** (12.1 g, 76%) as a yellow solid; m.p. 65–67 °C (from ethyl acetate–ether) (Found: C, 29.6; H, 3.3; S, 60.3. $C_7H_{10}O_2S_5$ requires C, 29.4; H, 3.5; S, 55.9); m/z (EI) 286 (M^+); δ_H ($CDCl_3$) 5.08 (2 H, t, J 6.1), 3.63 (4 H, q, J 6.1) and 3.09 (4 H, t, J 6.1).

4,5-Bis(2-chloroethylthio)-1,3-dithiole-2-thione **40**.—Into a stirred solution of compound **39** (5 g, 17 mmol) in dry dichloromethane (75 cm^3) at 0 °C under nitrogen was slowly added a solution of thionyl chloride (1.4 cm^3 , 18.7 mmol) in dry dichloromethane (20 cm^3), and the mixture stirred for 0.5 h at 0 °C, and then refluxed for a further 1 h. After evaporation, the residue was chromatographed on a silica column eluting with

hexane–dichloromethane (3:1 v/v) to afford compound **40** (4.7 g, 83%) as an orange solid; m.p. 58–59 °C (from hexane–dichloromethane) (Found: C, 25.8; H, 2.7; S, 49.5. $C_7H_8Cl_2S_5$ requires C, 26.0; H, 2.5; S, 49.6%); m/z (DCI) 323 ($M^+ + 1$); δ_H ($CDCl_3$) 3.68 (4 H, t, J 2.77) and 3.20 (4 H, t, J 2.77).

4,5-Bis(2-chloroethylthio)-4',5'-ethylenedithiotetrathiafulvalene **42**.—A stirred mixture of compound **40** (1.0 g, 3.1 mmol) and compound **41**³¹ (0.65 g, 3.1 mmol) in dry redistilled triethyl phosphite (15 cm^3) was heated at 100 °C for 4 h. After cooling to room temperature, and evaporation of the solvent under reduced pressure the mixture was chromatographed on a silica column eluting with hexane–dichloromethane (3:1 v/v) to give in order of elution: compound **44** (503 mg, 28%), compound **42** (403 mg, 27%) and compound **34**³¹ (404 mg, 34%).

Compound **42** was an orange solid, m.p. 65–66 °C (Found: C, 30.2; H, 2.2. $C_{12}H_{12}Cl_2S_8$ requires C, 29.8; H, 2.5%); m/z (DCI) 483 ($M^+ + 1$); δ_H ($CDCl_3$) 3.67 (4 H, t, J 7.1), 3.01 (4 H, s) and 3.14 (4 H, t, J 7.1).

4,4',5,5'-Tetrakis(2-chloroethylthio)tetrathiafulvalene **44**.—A stirred solution of compound **40** (0.5 g, 1.6 mmol) in dry redistilled triethyl phosphite (15 cm^3) was heated at 100 °C for 4 h. Work-up as described for compound **42**, gave compound **44** (342 mg, 76%) as an orange solid, m.p. 158–159 °C (from toluene) (Found: C, 30.0; H, 2.4. $C_{14}H_{16}Cl_4S_8$ requires C, 28.8; H, 2.8%); m/z (DCI) 581 ($M^+ + 1$); δ_H ($CDCl_3$) 3.68 (8 H, t, J 7.4) and 3.16 (8 H, t, J 7.4).

Compounds 43, 45 and 47.—General procedure. Into a stirred suspension of either compound **42** (240 mg, 0.5 mmol), **44** (290 mg, 0.5 mmol) or **40** (160 mg, 0.5 mmol) in dry ethanol (30 cm^3) at 20 °C under nitrogen was added a freshly prepared solution of sodium ethoxide (2 mol equiv. for compounds **40** and **42** and 4 mol equiv. for compound **44**) in dry ethanol. After stirring at 20 °C for 10 h, the solvent was evaporated off, water (50 cm^3) was added and the mixture was extracted with dichloromethane (3 × 30 cm^3). The combined extracts were dried ($MgSO_4$), evaporated under reduced pressure and the residue chromatographed on a silica column eluting with cyclohexane–dichloromethane (1:1 v/v) to afford the products. There was obtained:

Compound **47**. A yellow solid (95 mg, 92%); m.p. 174–176 °C (from toluene) [lit., yellow crystals, m.p. 172–176 °C (from light petroleum)^{16b} and colourless plates, m.p. 200–202 °C*]; m/z (EI) 208 (M^+); δ_H ($CDCl_3$) 3.47 (s).

4,5-(Ethylenedithio)-4',5'-bis(vinylthio)tetrathiafulvalene **43**. An orange solid (85 mg, 91%); m.p. 51 °C (Found: C, 34.9; H, 2.3. $C_{12}H_{10}S_8$ requires C, 35.1; H, 2.5%); m/z (EI) 410 (M^+); δ_H ($CDCl_3$) 6.37, 5.43 and 5.42 (6 H, 2 ABX, J_{AX} 16.47, J_{BX} 9.45, $J_{AB} < 1$) and 3.30 (4 H, s); δ_C ($CDCl_3$) 133.1, 129.2, 117.3, 113.9, 113.2, 110.2 and 30.2.

4,4',5,5'-Tetrakis(vinylthio)tetrathiafulvalene **45**. An orange solid (194 mg, 89%); m.p. 46 °C (Found: C, 38.6; H, 2.8. $C_{14}H_{12}S_8$ requires C, 38.5; H, 2.8%); m/z (EI) 436 (M^+); δ_H ($CDCl_3$) 6.38, 5.44 and 5.43 (12 H, 4 ABX, J_{AX} 16.45, J_{BX} 9.42, $J_{AB} < 1$); δ_C ($CDCl_3$) 129.2, 126.0, 117.4 and 111.4.

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* Coffen and Garret³² claim the preparation of compound **47**, although it should be noted that both the appearance and the melting point recorded for their product are very different from our results herein and those in ref. 16(b).

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