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Novel organosulfur donors containing hydroxy functionalities: synthesis of bis[2,2-bis(hydroxymethyl)propane-1,3-diyldithio]-tetrathiafulvalene and related materials †

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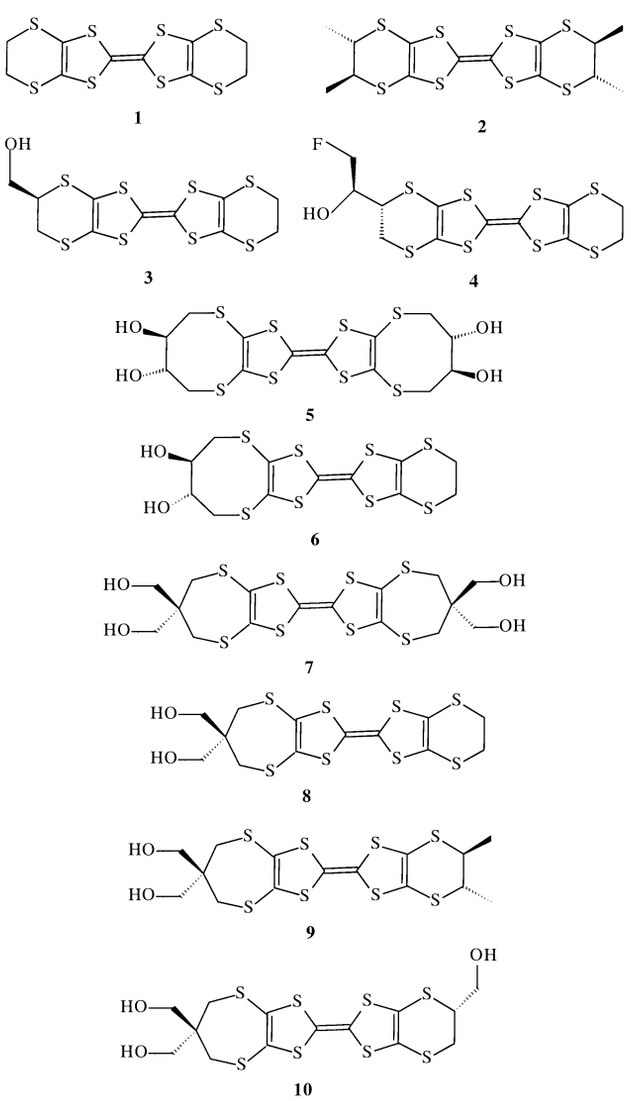
The synthesis of four novel organosulfur donors carrying two or more hydroxymethyl groups are described. TTF nuclei are fused to 1,4-dithiepine and/or 1,4-dithiine rings and in two cases both outer rings carry functionality capable of introducing hydrogen bonding; for the two chiral organosulfur donor molecules both racemic and enantiopure forms are prepared.

Introduction

Many radical cation salts of bis(ethylenedithio)tetrathiafulvalene 'ET', **1**, show electrical conductivity or semiconductivity,[1] and in some cases, at very low temperatures, superconductivity has been observed. The highest T_c for the onset of superconductivity on cooling a sample was observed at 12 K in $(ET)_2[Cu(N(CN)_2)Br]$.[2] A highly ordered crystal structure is needed in the superconducting state, yet in the radical cation salts of **1** there are only very weak hydrogen bonding interactions possible between the anions and the ethylene bridges of the cations.[3] This can result in the anion being orientationally disordered, and for the salts of the tetramethyl-substituted ET, **2**, positionally disordered.[4] Indeed, the lack of strong specific attractions may contribute to the polymorphism often observed among the radical salts of ET. To introduce the possibility of strong hydrogen bonding between the radical cation and the anion we have synthesised monosubstituted derivatives of ET which carry a hydroxy group, **3** and **4**;[5,6] the former is now available in enantiomeric and racemic forms. A second strategy was to prepare compounds **5** and **6**,[7] in which the ethylene bridges were replaced by butylene bridges which carried chirally disposed hydroxy groups on the central carbon atoms. Here we report the synthesis of the tetrol **7**, which has propylene bridges between the outer pairs of sulfur atoms, substituted with two hydroxymethyl groups on the central carbon, as well as hybrid materials **8**–**10**. Two of these materials carry hydroxy functionalities at both ends of the molecule designed to facilitate hydrogen bonding throughout the crystalline radical cation salt. Compounds **9** and **10** are prepared in both enantiomeric and racemic forms.

Achiral hydroxy-substituted derivatives of tetrathiafulvalene, such as **11**[8] and **12**[9] have been reported, and some tetrathiafulvalenes carrying alternative hydrogen bond donors, such as the phosphate salt **13**[10] and the thioamide **14**[11] have been prepared and studied. Use of a carboxylic acid group for this



† The synthetic details for the preparation of **34** are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p1/b0/b007660k/

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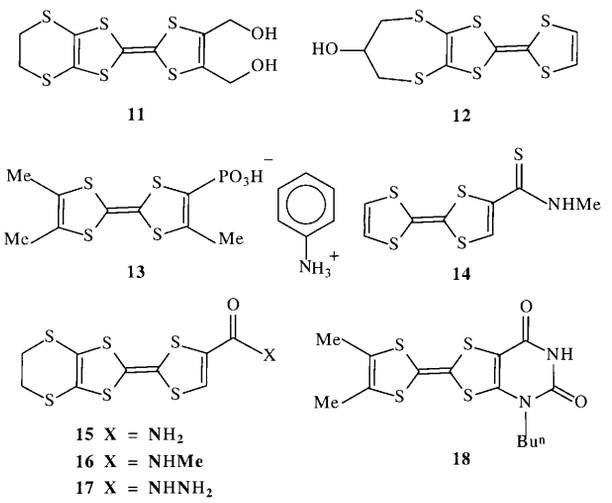


purpose is frustrated by anodic decarboxylation in the electrocrystallisation step.[12] A series of ethylenedithio-TTF derivatives carrying amide or hydrazide groups with hydrogen bonding potential on the TTF ring, **15**–**17**, have also been reported.[13] This approach has been extended by fusion of a pyrimidinedione ring to TTF to give **18** which can be bound to 2,6-diacetylaminopyridine by three hydrogen bonds with a concomitant increase of oxidation potential.[14] Installation of a hydroxymethyl functionality on to ET or ET-like molecules provides a 'handle' for attachment to other molecular systems to incorporate additional properties into the materials. In this way dendrimers containing up to twenty-one TTF systems have been constructed by Bryce and Becher and co-workers[15,16] and TTF's have been linked with phthalocyanines.[15,17] Linking TTF to appropriate molecular systems has seen a widening of its potential applications[18] with the production of liquid crystalline systems,[19] supramolecular switches[20–22] and polymeric systems.[23,24]

Results and discussion

The new series of tetrathio-TTF donors **7**–**10** reported here all contain at least one 2,2-bis(hydroxymethyl)propane-1,3-diyl bridge between sulfur atoms outside the TTF nucleus. The syntheses of these molecules use the di-MEM protected [1,3]dithiolo[4,5-*b*][1,4]dithiepin-2-one derivative **27** to introduce this structural feature by a self-coupling reaction, or cross-coupling reactions with other oxo compounds, in triethyl phosphite. Finally, a deprotection step reveals the hydroxy groups. The oxo compound **27** can be prepared in two high yielding steps from the bis(hydroxymethyl) thione **25**. Three routes to the preparation of this thione from the dithiolate[25] **23** were examined (Scheme 1): reaction with the spirobi[cyclic sulfate ester] **20**, with 2,2-bis(bromomethyl)propane-1,3-diol, and with the spirobi[oxetane][26] **21**. The first two approaches produce the diol in moderate yield, though the reagents required are readily available, but the reaction with the spirobi[oxetane] **21** was unsuccessful.

The spirobi[cyclic sulfate ester] **20** was prepared in two steps from pentaerythritol, starting by treatment with thionyl chloride and pyridine in THF to yield the spirobi[cyclic sulfite ester] **19** in 61% yield. The ^{1}H NMR of **19** shows four different hydrogen atom environments on account of the orientations of the two sulfinyl oxygen atoms (Fig. 1). The geminal coupling constants are *ca.* 12.0 Hz, and there is one longer range coupling of *ca.* 2.5 Hz probably between pairs of equatorial hydrogen atoms. The ^{13}C NMR spectrum shows two very close signals at δ 58.6 and 58.8 since the two methylene carbon atoms in one ring are differently oriented with respect to the sulfinyl group in the second ring.

This spirobi[cyclic sulfite ester] was converted into the spirobi[cyclic sulfate ester] **20** in high yield by oxidation with Ru(VIII) conducted catalytically using ruthenium trichloride and sodium periodate in acetonitrile and a small amount of water. Unlike many cyclic sulfate esters the product is water soluble, so it is isolated by evaporation of all solvents followed by extraction with THF. The more symmetrical structure is supported by the single methylene resonances in the ^{1}H and ^{13}C NMR spectra.

We have used cyclic sulfate esters of *vic*-diols in the preparation of substituted ET derivatives[5,6,27] by performing two substitution reactions with the dithiolate **23**. In contrast, this dithiolate reacts with the spirobi[cyclic sulfate ester] **20** by single

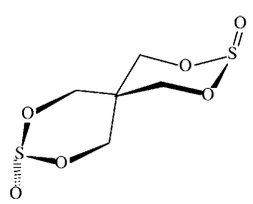
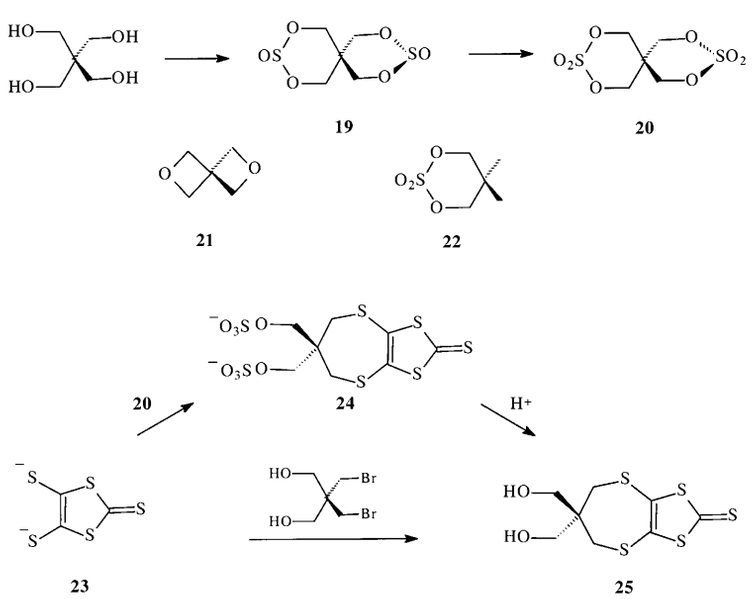


Fig. 1 Probable molecular conformation of **19**, with the two S=O bonds perpendicular to one another. Literature precedents suggest these bonds will prefer to be axial (see ref. 38 and 39).



Scheme 1

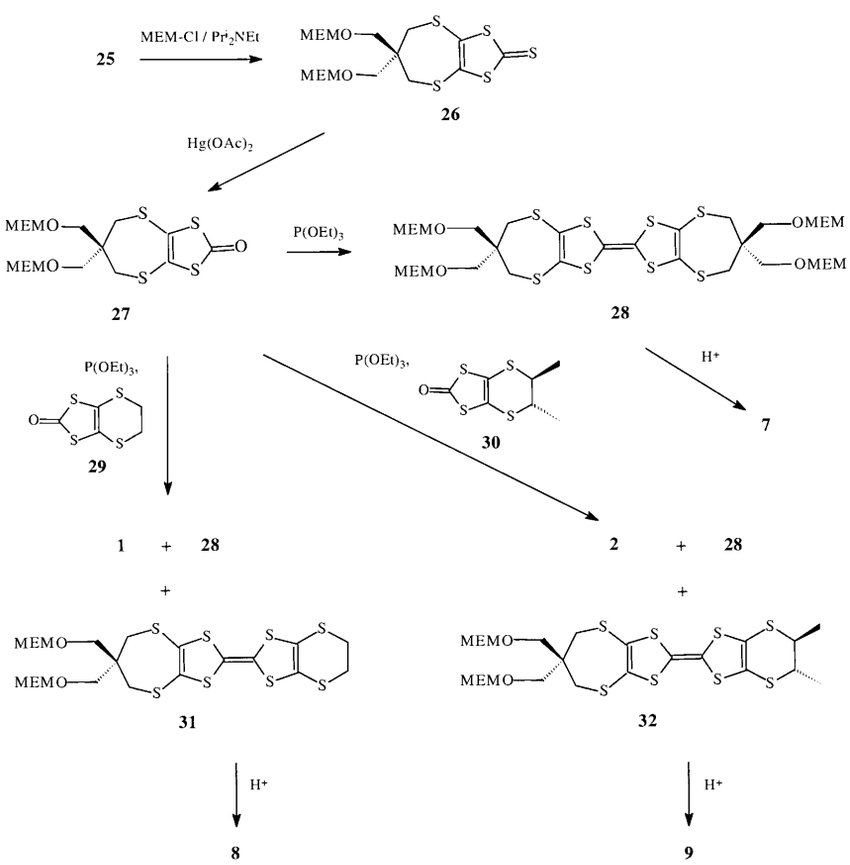
substitution reactions on each ring, leaving two hemi sulfate groups attached to the product. Thus, reaction of the bicyclic sulfate ester with the disodium salt of dithiolate **23** in THF at room temperature gave a 93% yield of the disulfate **24**. The hydrolysis of this material to dihydroxy thione **25** was not as successful, but could be conducted using a mixture of concentrated sulfuric acid and water (4 : 1) in THF over 2 days in 23% yield after chromatography. The side chain carbon atoms of **25** give a broad resonance centred at δ 62.3, and this feature is common to all other compounds prepared from this material, irrespective of whether the hydroxy groups are protected or not. This originates from dynamic conformational changes of the seven-membered ring which move the substituents between pseudo-equatorial and pseudo-axial positions.

The site of each substitution on the spirobi[cyclic sulfate ester] **20** is next to a quaternary centre and the reaction might have been expected to be quite difficult to achieve. Indeed, the related six-membered cyclic sulfate ester **22** which carries two methyl groups rather than the second ring does not react with dithiolate **23**. The greater reactivity of the spirobi[cyclic sulfate ester] **20** may be attributable to a sodium ion templating the reaction by coordinating both the dithiolate and a sulfonyl oxygen atom from the boat conformation of the ring not under attack. Attempts to substitute all four C–O(SO_2) groups in **20** with two equivalents of dithiolate **23** have been unsuccessful so far.

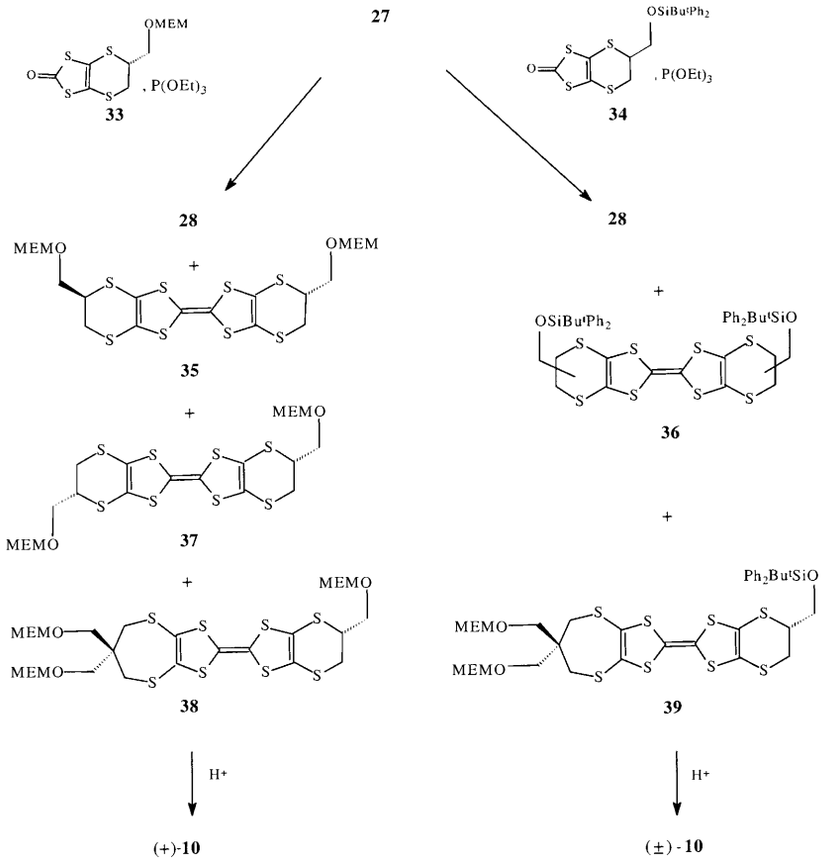
Alternatively, the dihydroxy thione **25** can be prepared in 25% yield by reaction of the disodium salt of the dithiolate **23** with 2,2-bis(bromomethyl)propane-1,3-diol. The reaction needs heat and is compromised by the thermal instability of the dithiolate. The product must be separated from unreacted starting material by crystallisation and chromatography. No product at all was detected when the dibromo reactant was replaced with the spirobi[oxetane] **21**.

The hydroxy functionalities of the thione **25** were protected with MEM ($CH_3OCH_2CH_2OCH_2$-) groups to give the thione **26** in 95% yield (Scheme 2). The exocyclic sulfur atom was then replaced with an oxygen by treatment with mercuric acetate and acetic acid in chloroform to give the oxo compound **27** in 97% yield. The chemical shifts of the sp^2 carbon atoms at the ring fusion are decreased by 9 ppm to δ 129.0 compared with the corresponding thione. The oxo compound **27** was self coupled by heating in triethyl phosphite to give **28**, a TTF derivative fused to two 1,4-dithiepine rings, as an orange oil in 82% yield. The ^{13}C NMR spectrum shows a signal at δ 112.7 for the central pair of sp^2 carbon atoms, and another signal at δ 129.2 for the sp^2 carbon atoms at the ring fusions. The hydroxy groups were deprotected by treatment with a 1 : 1 mixture of 20% HCl and THF over two days. After neutralisation with solid sodium carbonate, the deprotected product could be isolated from the THF layer to give the tetrol **7** in 78% yield after purification. The MEM protection strategy was preferable to forming an acetonide. Although the acetonide of **25** could be prepared and converted to the corresponding oxo compound in 91% overall yield, the self coupling product obtained on refluxing in triethyl phosphite was highly insoluble in all solvents, which meant that the deprotection step was not feasible.

Cross-coupling reactions of the MEM protected oxo compound **27** with dihydro-2*H*-[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-one **29** gave the cross-coupled product **31** in 43% yield after separation from self-coupled products ET and **28** by chromatography. The identity of the product is supported by the resonances of the sp^2 carbon atoms: δ 129.6 and 109.8 from the diethiepine containing 'half' of the structure and δ 114.6 and 114.1 from the dithiine containing 'half' of the molecule. The MEM groups were removed using 20% hydrochloric acid and THF as previously described for the tetrol to give the dihydroxy product **8** in 78% yield. In a similar way, cross-coupling of **30,** the enantiopure (5*S*,6*S*)-5,6-dimethyl analogue of **29**, with oxo compound **27** gave the dimethyl-di-MEM-protected material **32** which was deprotected in the usual way to give the dimethyl diol **9**. Racemic **9** was also prepared from the corresponding form of the dimethyl oxo compound **30.**



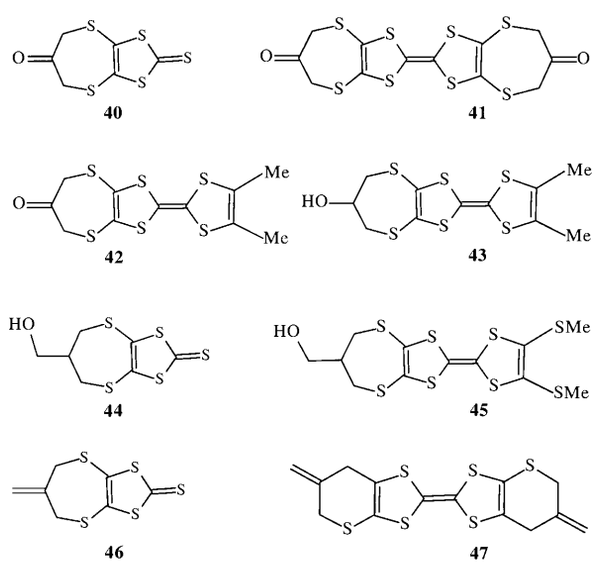
Scheme 2



Scheme 3

Finally, the non-symmetric tris(hydroxymethyl) substituted donor molecule **10** which has hydroxy functionalities at both "ends" of the organosulfur system was prepared by the cross-coupling method. Both the enantiopure and racemic triol were synthesized. The enantiopure and racemic oxo compounds **33** and **34** necessary for this synthesis have been prepared in this laboratory.† The former, **33**, which has a MEM-protected hydroxy group is available from reaction of dithiolate **23** with the cyclic sulfate ester of 1-*O*-MEM-propane-1,2,3-triol,[5] and the latter, **34**, with a diphenyl-*tert*-butylsilyl protected hydroxy group is available from the reaction of the dithiolate **23** with the *O*-protected 2,3-dibromopropanol.[28] The triprotected cross-coupled materials were prepared by heating in triethyl phosphite and separated from self-coupled materials by chromatography. Thus, for the enantiopure case the first band produces a mixture of two stereoisomers **35** and **37** from the self-coupling of **33** (Scheme 3), the second band is the desired cross-coupled material with three MEM-protected hydroxy groups and the final band gives the self-coupling product **28** described earlier. The racemic case behaves in a similar way, except that self-coupling of **34** gives a mixture of four stereoisomers (two racemic and two *meso* compounds). The yields of enantiopure and racemic materials **38** and **39** were 22 and 37%. There are now five resonances from sp^2 carbon atoms due to the lower symmetry of the dithiine containing 'half' compared with earlier examples. The deprotection of all three hydroxy groups in **38** and **39** was achieved in high yield with the 20% hydrochloric acid–THF mixture used previously.

Several other TTF derivatives containing a fused 1,4-dithiepine ring have been reported by other groups. Reaction of the zinc complex of dithiolate **23** with 1,3-dichloropropanone gave the bicyclic ketone **40**[29,30] which was converted to the tetrathio-TTF derivatives **41** and **42** by a route which involved protection of the carbonyl function prior to the coupling reaction.[27] Ketone **42** could be reduced to the hydroxy-substituted material **43**. The hydroxymethyl substituted thione **44** was



obtained from reaction of the zinc complex of dithiolate **23** with 1-bromo-2-(bromomethyl)propanol in high yield, and converted to the TTF derivative **45** which has been used in the construction of dendrimers.[31] In contrast, self-coupling of the thione **46**, which contains an exocyclic alkene, in triethyl phosphite gave the TTF derivative **47** which has unexpectedly lost a sulfur atom from each outer ring,[32] a problem not experienced in the syntheses of **7**–**10**.

The first two oxidation potentials of the new organosulfur donors **7** and **8** as well as those for the enantiopure and racemic forms of **9** and **10** were measured by cyclic voltammetry, and are compared with data for ET in Table 1. The first oxidation potentials fall in the range 0.42–0.51 V, and the second oxidation potentials fall in the range 0.70–0.80 V. The values obtained for ET also lie in these ranges. The first oxidation step

Table 1 Cyclic voltammetry data[a]

	$E^1_{1/2}$/V	$E^2_{1/2}$/V
1	0.50	0.77
7	0.40	0.70
8	0.42	0.70
(−)-**9**	0.48	0.75
(±)-**9**	0.48	0.75
(+)-**10**	0.45	0.72
(±)-**10**	0.51	0.80

[a] Data are measured in *ca.* 1 mM acetonitrile solutions containing sodium perchlorate (0.1 M), with sweep rates of 100 mV s^{-1}, and quoted relative to Ag/AgCl.

for ET is believed to involve the formation of dimeric species $(ET)_2^+$. Materials **7** and **8** are more easily oxidized than ET, and this might be due to hydrogen bonding in the dimer. The oxidation potentials for **9**, which differs from **8** by the presence of two methyl groups in the six-membered ring, are *ca.* 0.05 mV higher than those for **8**. The addition of four methyl groups to ET led also to a rise in oxidation potentials (by 0.11 V for $E_1^{1/2}$ and 0.07 V for $E_2^{1/2}$).[28] Although the oxidation potentials of enantiopure and racemic **9** are identical, those for the corresponding forms of **10** differ. Thus, enantiopure **10** has lower oxidation potentials than the racemate. In the case of the racemic material, the dimeric species $(\mathbf{10})_2^+$ can have three compositions, two composed of identical enantiomers, and one composed of mirror related enantiomers, and the stability of these two forms need not be the same. This may be particularly so when hydrogen bonding at each end of the molecule can play a role in the formation of the dimers. A more detailed study of the cyclic voltammetries and electrocrystallisations of compounds **7**–**10** is planned.

Chiral organosulfur donor molecules such as **3**, **9** and **10** are of particular interest for investigating whether novel electrical properties can arise through conduction in a chiral environment, for example in the presence of magnetic field. There has been very little investigation into this due to a lack of suitable materials. Recent studies on the radical cation salts of achiral ET with $MHg(SCN)_4$ (M = K or Tl) as the counterions suggest that in a magnetic field a chiral surface metal may form, since the electrons can only move in one direction under these conditions. Further results from these materials have been interpreted as due to a Quantum Hall Effect.[33]

The first reports of a ET radical cation salt with a chiral anion (β''-$(ET)_2SF_5CHFSO_3$) have appeared recently, in this case on the racemic material.[34] The two configurations of the anion have similar shapes, and are disordered among the anion sites, so that on cooling this material undergoes a metal to insulator transition. In contrast the analogue with the similar $SF_5CF_2SO_3^-$ anion becomes a superconductor on cooling. This suggests that for a chiral ET derivative it may be preferable to use the single enantiomer to form the radical cation salt, especially where the difference in overall shape of the two enantiomers is very small, to avoid disordering of the donor molecules in the racemic radical cation salts with deleterious effects on the electrical properties. This is likely to be more important for **9** than for **10** since the latter can use directional hydrogen bonding to order the racemate.

For a single enantiomer of a substituted ET, if the substituent at the stereogenic centre is not capable of making significant intermolecular interactions the packing of the central C_6S_8 regions of the ET may well be pseudocentrosymmetric, and so not provide a good system for investigating the role of chirality in electrical properties. The packing arrangement itself needs to be chiral, such that the packing arrangements of the two enantiomeric forms are nowhere near superimposable. Alternative approaches under investigation in other groups use molecules whose conjugated π-systems are themselves chiral, for example Miyamoto *et al.* have made a theoretical study of conduction through chiral nanotubes,[35] and Rajca and coworkers have synthesized chiral octaphenylenes and dimers of 1,1′-binaphthyl.[36] These are early days for investigating the electrical properties of chiral systems.

Experimental

NMR spectra were measured on a JEOL GX 270 machine at 270 MHz for ^1H and at 67.8 MHz for ^{13}C using $CDCl_3$ as solvent and tetramethylsilane (TMS) as standard, and measured in ppm downfield from TMS, unless otherwise stated. Coupling constants (*J*) are given in Hz. IR spectra were recorded on a ATI Mattson Genesis Series FTIR machine as liquid films or Nujol mulls. Mass spectra were recorded at the EPSRC Mass Spectrometry Centre. Optical rotations were recorded at 589 nm on a Perkin-Elmer 241 polarimeter using a 1 dm cell, and $[a]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. Flash chromatography was performed on 40–63 silica gel (Merck).

2,4,8,10-Tetraoxa-3,9-dithiaspiro[5.5]undecane 3,9-dioxide, 19

Freshly distilled thionyl chloride (9.40 g, 79 mmol) was added dropwise over 10 min to a vigorously stirred solution of dry pyridine (12.0 g, 160 mmol) in dry THF (50 ml) containing a suspension of pentaerythritol (5.00 g, 36 mmol) at 0 °C. After 18 h the THF was evaporated *in vacuo* and the residue partitioned between water (30 ml) and dichloromethane (50 ml). The organic layer was separated, washed with hydrochloric acid (30 ml, 1.0 M) and water and dried over magnesium sulfate. Evaporation of the solvent gave **19** (5.10 g, 61%) as a white solid (recrystallised from acetone–petroleum ether), mp 128–130 °C (lit.[37] 130 °C) (Found C: 26.2, H: 3.4%. $C_5H_8O_6S_2$ requires C: 26.3, H: 3.5%); δ_H (DMSO-d_6): 4.86 (2H, d, *J* 12.1) and 4.54 (2H, d, *J* 11.9) (1α-, 7α-*H* and 5α-, 11α-*H*), 4.42 (2H, dd, *J* 11.9, 2.3, 1β-, 7β-*H*), 3.55 (2H, dd, *J* 12.0, 2.6, 5β-, 11β-*H*); δ_C (DMSO-d_6): 58.8 (2 × -CH_2), 58.6 (2 × -CH_2), 34.5 ($C(CH_2)_4$); ν_{max}: 1193, 1169, 1140, 1018, 1000, 962, 904, 758, 742, 676, 662, 580 cm^{-1}; *m*/*z*: (CI) 246 ($[M + NH_3]^+$, 28), 229 ($[M + H]^+$, 100%).

2,4,8,10-Tetraoxa-3,9-dithiaspiro[5.5]undecane 3,3,9,9 tetraoxide, 20

Sodium periodate (2.10 g, 9.6 mmol) dissolved in a minimum amount of water was added to a solution of the spirobi[bicyclic sulfite ester] **19** in acetonitrile (60 ml) which led to some sodium periodate precipitating. Ruthenium(III) trichloride (50 mg) was added to the mixture which was stirred for 15 min at room temperature. The solvents were removed *in vacuo*, the resultant solid extracted with THF (2 × 100 ml) and the combined extracts dried over magnesium sulfate. Evaporation of the THF gave **20** (1.01 g, 87%) as a white solid (recrystallised from THF–petroleum ether), mp 280 °C (Found C: 23.2, H: 2.9%. $C_5H_8O_8S_2$ requires C: 23.1 H: 3.1%); δ_H (CD_3COCD_3): 4.99 (8H, s, 4 × CH_2); δ_C (CD_3COCD_3): 73.2 (4 × CH_2), 33.1 ($C(CH_2)_4$); ν_{max}: 1398, 1212, 1197, 1144, 1031, 986, 977, 842, 830, 816, 774, 571, 528 cm^{-1}.

6,6-Bis(hydroxymethyl)-6,7-dihydro-5*H*-[1,3]dithiolo[4,5-*b*]-[1,4]dithiepine-2-thione, 25

Method 1. The spirobi[cyclic sulfate ester] **20** (5.44 g, 0.021 mol) was added to a stirred solution of the disodium salt of dithiolate **23**[25] (5.06 g, 0.021 mol) in dry THF (100 ml) under nitrogen. After 12 h a yellow precipitate was collected, washed with diethyl ether and dried to give crude *disodium 6,7-dihydro-2-thioxo-5H-[1,3]dithiolo[4,5-b][1,4]dithiepine-6,6-diyldimethyl disulfate* (as a THF solvate) **24** (9.75 g, 93%), a yellow powder which was used without further purification, δ_H (D_2O): 4.30 (4H, s, 6,6-CH_2O), 3.05 (4H, s, 5-, 7-H_2); δ_C (D_2O): 215.8 (*C*=S),

142.3 (3a-, 8a-*C*), 71.4 (br, 6,6-*C*H_2), 46.1 (5-, 7-*C*), 38.2 (6-*C*); ν_{max}: 1624, 1213, 1066, 1004, 858, 792, 721, 627, 582 cm^{-1}. The sulfate salt **24** (10.50 g, 20.1 mmol) was hydrolysed in THF (200 ml) containing a 4:1 mixture of conc. sulfuric acid and water (100 ml) for two days. The mixture was neutralised with sodium carbonate, filtered and the filtrate dried with magnesium sulfate. The evaporated filtrate was purified by flash chromatography on silica using diethyl ether as eluent to give diol **25** (1.43 g, 23%), light brown crystals mp 224–234 °C (dec.) (Found C: 32.1, H: 3.2%. $C_8H_{10}O_2S_5$ requires C: 32.4, H: 3.4%); δ_H (DMSO-d_6): 4.70 (2H, t, *J* 5.2 2 × O*H*), 3.52 (4H, d, *J* 5.0, 6,6-C*H*$_2$), 2.82 (4H, s, 5-,7-*H*$_2$); δ_C (DMSO-d_6): 210.5 (*C*=S), 138.5 (3a-, 8a-*C*), 62.3 (br, 6,6-*C*H_2), 44.9 (5-, 7-*C*), 36.0 (6-*C*); ν_{max} (KBr disk): 3340, 1426, 1395, 1393, 1310, 1106, 1079, 1029, 890, 857, 854, 568; *m*/*z*: (CI) 299 ([M + 1]$^+$, 100%).

Method 2. A solution of 2,2-bis(bromomethyl)propane-1,3-diol (0.92 g, 0.0038 mol) in absolute ethanol (20 ml) was added dropwise to a solution of the disodium salt of dithiolate **23** (1.0 g, 3.8 mmol) in absolute ethanol (50 ml). The mixture was refluxed overnight. The solvent was evaporated under reduced pressure, and the remaining solid was refluxed in toluene (25 ml) for 30 min, and the mixture was filtered hot after addition of charcoal. The light yellow precipitate formed on cooling was collected and recrystallised from toluene to obtain the diol **25** (15–25%).

6,6-Bis(methoxyethoxymethoxymethyl)-6,7-dihydro-5*H*-[1,3]-dithiolo[4,5-*b*][1,4]dithiepine-2-thione, 26

Methoxyethoxymethyl chloride (21 ml, 0.18 mol) dissolved in dry dichloromethane was added dropwise to a solution of the thione **25** (4.75 g, 0.016 mol) and diisopropylethylamine (42 ml) in dry dichloromethane (50 ml) at 0 °C. The mixture was left stirring at room temperature overnight and then extracted with water (50 ml), 0.05 M HCl (2 × 50 ml) and water (50 ml). The organic layer was dried over magnesium sulfate, filtered and the solvent was evaporated under reduced pressure to give the diprotected thione as a yellow solid **26** (7.20 g, 95%), mp 74–76 °C (from ethanol) (Found C: 40.5, H: 5.8%. $C_{16}H_{26}O_6S_5$ requires C: 40.5, H: 5.6%); δ_H: 4.60 (4H, s, 2 × OC*H*$_2$O), 3.55 (12H, m, 2 × OC*H*$_2$C*H*$_2$O- and 6,6-C*H*$_2$O), 3.39 (6H, s, 2 × C*H*$_3$), 2.90 (4H, s, 5-, 7-*H*$_2$); δ_C: 211.0 (2-*C*), 138.2 (br, 3a-, 8a-*C*), 95.9 (O-*C*H_2-O), 71.8 (2 × $CH_3OCH_2CH_2$), 69.5 (br, 6,6-*C*H_2O), 67.1 (2 × CH_3OCH_2), 59.1 (2 × O*C*H_3), 44.3 (5-, 7-*C*), 37.1 (6-*C*); ν_{max}: 1295, 1225, 1180, 1134, 1105, 1074, 1042, 1022, 955, 848, 722, 516; *m*/*z* (CI): 492 ([M + NH_3 + H]$^+$, 25), 491 ([M + NH_3]$^+$, 20), 476 ([M + NH_3 − CH_3]$^+$, 33), 475 ([M + H]$^+$, 70), 474 (M$^+$, 100), 473 ([M − H]$^+$, 67), 399 ([M − $OCH_2CH_2OCH_3$]$^+$, 29), 398 (M − $OCH_2CH_2OCH_3$-H]$^+$, 20%).

6,6-Bis(methoxyethoxymethoxymethyl)-6,7-dihyro-5*H*-[1,3]-dithiolo[4,5-*b*][1,4]dithiepin-2-one, 27

Acetic acid (39 ml) was added dropwise to a solution of the thione **26** (7.63 g, 16 mmol) and mercuric acetate (12.74 g, 49 mmol) in chloroform (150 ml) and the mixture was left stirring at room temperature for 3 h during which time a white precipitate was formed. The mixture was filtered through Celite and the filtrate extracted with water, aqueous sodium carbonate solution and finally water again. The organic layer was dried over magnesium sulfate, filtered and the solvent was evaporated under reduced pressure to give the oxo compound **27** as a viscous light brown oil which solidified slowly (7.19 g, 97%), mp 35–37 °C (Found C: 41.9, H: 5.8%. $C_{16}H_{26}O_7S_4$ requires C: 41.9, H: 5.7%); δ_H: 4.65 (4H, s, 2 × OC*H*$_2$O), 3.55 (8H, m, 2 × OC*H*$_2$-C*H*$_2$O), 3.70 (4H, s, 6,6-C*H*$_2$O), 3.53 (6H, s, 2 × OC*H*$_3$), 2.80 (4H, s, 5-, 7-*H*$_2$); δ_C: 189.5 (2-*C*), 129.0 (3a-, 8a-*C*), 95.8 (2 × O*C*H_2O), 71.7 (2 × $CH_3OCH_2CH_2$), 69.2 (br, 6,6-*C*H_2), 67.1 (2 × *C*H_3OCH_2), 59.0 (2 × *C*H_3), 43.2 (5-, 7-*C*), 37.2 (6-*C*); ν_{max}: 1667, 1623, 1413, 1304, 1238, 1174, 1136, 1098, 1043, 951, 898, 848, 750, 464; *m*/*z* (CI): 476 ([M + NH_3 + H]$^+$, 35), 458 (M$^+$, 50), 89 ($CH_3O(CH_2)_2OCH_2^+$, 44), 59 ($CH_3O(CH_2)_2^+$, 100), 45 ($CH_3OCH_2^+$, 58%).

2-[6′,6′-Bis(methoxyethoxymethoxymethyl)-6′,7′-dihydro-5′*H*-[1,3]dithiolo[4,5-*b*][1,4]dithiepin-2′-ylidene]-6,6-bis(methoxyethoxymethoxymethyl)-6,7-dihydro-5*H*-[1,3]dithiolo[4,5-*b*][1,4]-dithiepine, 28

Oxo compound **27** (1.50 g, 3.28 mmol) was heated in triethyl phosphite (40 ml) to 110 °C for 2 h during which time the colour of the reaction mixture changed from pale yellow to bright orange. The triethyl phosphite was distilled off *in vacuo* and the product was purified by flash chromatography using methanol–dichloromethane (5:95) as eluent to give the coupled material **28** (2.40 g, 82%) as an orange oil, δ_H: 4.70 (8H, s, 4 × OC*H*$_2$O), 3.72 (8H, br s, 6-, 6-, 6′-, 6′-C*H*$_2$O), 3.66 (8H, m, 4 × $CH_3OCH_2CH_2$), 3.55 (4 × CH_3OCH_2), 3.39 (12H, s, 4 × OC*H*$_3$), 2.75 (8H, s, 5-, 5′-, 7-, 7′-*H*$_2$); δ_C: 129.2 (br, 3a-, 3a′-, 8a-, 8a′-*C*), 112.7 (2-, 2′-*C*), 95.5 (4 × O*C*H_2O), 71.5 (4 × $CH_3OCH_2CH_2$), 69.4 (br, 6-, 6-, 6′-, 6′-*C*H_2), 66.8 (4 × CH_3OCH_2), 58.8 (4 × *C*H_3), 44.0 (5-, 5′-, 7-, 7′-*C*), 36.8 (6-, 6′-*C*); ν_{max} (thin film): 2923, 2853, 1453, 1410, 1364, 1302, 1251, 1173, 1106, 1040, 970, 898, 846, 771, 730, 546; *m*/*z* (FAB, NOBA matrix): 884 (M$^+$, 100%), 824 ([M − $CH_3O(CH_2)_2$ − H]$^+$, 11), 796 ([824-CO]$^+$, 6); HRMS (ES): 885.1306 for [M + H]$^+$, $C_{32}H_{52}O_{12}S_8$ requires 885.1303.

2-[6′,6′-Bis(hydroxymethyl)-6′,7′-dihydro-5′*H*-[1,3]dithiolo[4,5-*b*][1,4]dithiepin-2′-ylidene)-6,7-dihydro-5*H*-[1,3]dithiolo[4,5-*b*]-[1,4]dithiepine-6,6-dimethanol, 7

To the tetra-MEM protected material **28** (0.28 g, 0.32 mmol) dissolved in THF (10 ml) and cooled in an ice-bath was added dropwise 20% HCl (10 ml). The mixture was left stirring at room temperature for 2 days. It was then neutralised with solid sodium carbonate. The THF layer was decanted and the remaining material was extracted with THF (30 ml). The combined THF solutions were dried over magnesium sulfate, filtered and the solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane (10 ml) and hexane (50 ml) was added to give **7** as a fawn solid (0.13 g, 78%), mp 234 °C dec.; δ_H (DMSO-d_6): 4.71 (4H, t, *J* 5.2, 4 × O*H*), 3.53 (8H, br d, *J* 5.2, 2 × 6-C*H*$_2$, 2 × 6′-C*H*$_2$), 2.72 (8H, s, 5-, 5′-, 7-, 7′-*H*$_2$); δ_C (DMSO-d_6): 128.4 (3a-, 3a′-, 8a-, 8a′-*C*), 111.7 (2-, 2′-*C*), 62.3 (br, 2 × 6-*C*H$_2$, 2 × 6′-*C*H$_2$), 44.8 (5-, 5′-, 7-, 7′-*C*), 36.0 (6-, 6′-*C*); ν_{max} (KBr disk): 3350, 1100 cm^{-1}; *m*/*z* (EI) 532 (80%); HRMS: 531.9218, $C_{16}H_{20}O_4S_8$ requires 531.9127.

6,6-Bis(methoxyethoxymethoxymethyl)-2-(6′,7′-dihydro[1,3]-dithiolo[4,5-*b*][1,4]dithiin-2′-ylidene)-6,7-dihydro-5*H*-[1,3]-dithiolo[4,5-*b*][1,4]dithiepine, 31

Oxo compounds **27** (2.50 g, 5.4 mmol) and **29** (1.13 g, 5.4 mmol) were heated in triethyl phosphite at 110 °C for 3 h. The precipitated ET **1** was filtered and the triethyl phosphite was distilled under reduced pressure from the filtrate. The remaining red viscous material was chromatographed using first CH_2Cl_2–hexane (6:1) as eluent to remove the remaining ET (total yield: 0.51 g, 49%) and then ethyl acetate to separate the second and third fractions. The second fraction was characterised as the desired product **31** (1.46 g, 42.7%), orange–yellow solid, mp 83–84 °C (from ethanol). Found C: 39.7, H: 4.7%. $C_{21}H_{30}O_6S_8$ requires C: 39.6, H: 4.8%); δ_H: 4.70 (4H, s, 2 × OC*H*$_2$O), 3.71 (4H, br s, 6,6-C*H*$_2$O), 3.64 (4H, m, 2 × $CH_3OCH_2CH_2$O), 3.57 (4H, m, 2 × CH_3OCH_2), 3.39 (6H, s, 2 × C*H*$_3$), 3.28 (5′-, 6′-*H*$_2$), 2.75 (4H, s, 5-, 7-*H*$_2$); δ_C: 129.6 (br, 3a-, 8a-*C*), 114.6 and 114.1 (2′-, 3a′-, 7a′-*C*), 109.8 (2-*C*), 95.7 (O-*C*H_2-O), 71.7 (2 × $CH_3OCH_2CH_2$), 69.4 (br, 6,6-*C*H_2O), 66.9 (2 × CH_3-

OCH_2), 59.0 (2 × OCH_3), 44.2 (5-, 7-*C*), 37.0 (6-*C*), 30.1 (5′-, 6′-*C*); ν_{max}: 1300, 1244, 1197, 1172, 1137, 1098, 1040, 1012, 892, 864, 847, 837, 770, 722; *m*/*z* (EI): 634 (M^+, 100), 606 ([M − CH_2CH_2]$^+$, 18%). The third fraction gave the self-coupled material **28** (0.64 g, 27%).

2-(5′,6′-Dihydro[1,3]dithiolo[4,5-*b*][1,4]-dithiin-2′-ylidene)-6,7-dihydro-5*H*-[1,3]dithiolo[4,5-*b*][1,4]dithiepine-6,6-dimethanol, 8

To the di-MEM protected material **31** (0.02 g, 0.32 mmol) dissolved in THF (10 ml) and cooled in an ice-bath was added dropwise 20% HCl (10 ml). The mixture was left stirring at room temperature for two days. It was then neutralised with solid sodium carbonate. The THF layer was decanted and the remaining material was extracted with THF (30 ml). The combined THF solutions were dried over magnesium sulfate, filtered and the solvent was evaporated under reduced pressure. The red viscous material was chromatographed eluting with ethyl acetate–dichloromethane (1 : 1) to give **8** as a fawn powder (0.11 g, 78%), mp 127–129 °C; δ_H (THF-d_8): 4.72 (2H, br, 2 × O*H*), 3.39 (4H, s, 5′-, 6′-H_2), 3.52 (4H, br, 2 × 6-CH_2), 2.72 (4H, s, 5-, 7-H_2); δ_C (THF-d_8): 130.1 (br, 3a-, 8a-*C*), 115.0 and 114.4 (2′-, 3a′-, 7a′-*C*), 109.6 (2-*C*), 64.6 (br, 2 × 6-CH_2OH), 46.3 (5-, 7-*C*), 37.5 (6-*C*), 30.9 (5′-, 6′-*C*); ν_{max} (KBr disk): 3360, 1095 cm^{-1}; *m*/*z* (EI): 458 (M^+, 100%); HRMS: 457.8739. $C_{13}H_{14}O_2S_8$ requires 457.8760.

(5′*S*,6′*S*)-6,6-Bis(methoxyethoxymethoxymethyl)-2-(5′,6′-dihydro-5′,6′-dimethyl[1,3]dithiolo[4,5-*b*][1,4]dithiin-2′-ylidene)-6,7-dihydro-5*H*-[1,3]-dithiolo[4,5-*b*][1,4]dithiepine, 32

Oxo compounds **27** (0.19 g, 0.42 mmol) and **30** (0.100 g, 0.42 mmol) were heated in triethyl phosphite (10 ml) at 110 °C for 5 h. The triethyl phosphite was distilled under reduced pressure and the remaining red material was chromatographed using hexane–ethyl acetate (1 : 1) as eluent. The first fraction gave tetramethyl-ET **2**. The second fraction was characterised as the desired product **32** (0.081 g, 29%), yellow solid, mp 80–82 °C; δ_H: 4.66 (4H, s, 2 × OCH_2O), 3.69 (4H, s, 2 × 6-CH_2O), 3.57 (8H, m, 2 × $CH_3OCH_2CH_2O$), 3.36 (6H, s, 2 × CH_3), 3.15 (2H, m, 5′-, 6′-*H*), 2.72 (4H, s, 5-, 7-H_2), 1.38 (6H, d, *J* 6.3, 5′-, 6′-CH_3); δ_C: 129.4 (br, 3a-, 8a-*C*), 114.1 (3a′-, 7a′-*C*), 111.7 (2′-*C*), 109.9 (2-C), 95.6 (2 × O-CH_2-O), 71.6 (2 × CH_3OCH_2-CH_2), 69.4 (br, 2 × 6-CH_2O), 66.8 (2 × CH_3OCH_2), 58.9 (2 × OCH_3), 44.1 (5-, 7-, 5′-, 6′-*C*), 36.9 (6-*C*), 21.7 (5′-, 6′-CH_3); ν_{max}: 1239, 1172, 1138, 1105, 891, 850, 769, 721 cm^{-1}; *m*/*z* (EI): 662 (M^+, 100), 606; *HRMS:* 662.0099. $C_{23}H_{34}O_6S_8$ requires 662.0121. The third fraction gave the self-coupled material **28** (0.07 g, 38%).

(5′*S*,6′*S*)-2-(5′,6′-Dihydro-5′,6′-dimethyl[1,3]dithiolo[4,5-*b*]-[1,4]dithiin-2′-ylidene)-6,7-dihydro-5*H*-[1,3]dithiolo[4,5-*b*][1,4]-dithiepine-6,6-dimethanol, (−)-9

A solution of the di-MEM protected material **32** (0.090 g, 0.14 mmol) in THF (10 ml) was cooled in an ice-bath and treated dropwise with 20% HCl (10 ml). The mixture was left stirring at room temperature for two days. It was then neutralised with solid sodium carbonate. The THF layer was decanted and the remaining material was extracted with THF (30 ml). The combined THF solutions were dried over magnesium sulfate, filtered and the solvent was evaporated under reduced pressure. The residue was chromatographed eluting with ethyl acetate–dichloromethane (1 : 1) to give **9** as a fawn solid (0.047 g, 71%), mp 204–206 °C; δ_H (THF-d_8): 3.95 (2H, t, *J* 5.0, 2 × O*H*), 3.68 (4H, br d, *J* ~4.3, 2 × 6-CH_2), 3.31 (2H, m, 5′-, 6′-H), 2.52 (4H, s, 5-, 7-H_2), 1.39 (6H, d, *J* 6.5, 5′-, 6′-CH_3); δ_C (THF-d_8): 130.0 (3a-, 8a-*C*), 114.5 (3a′-, 7a′-C), 112.0 (2′-*C*), 109.6 (2-*C*), 64.5 (br, 2 × 6-CH_2OH), 46.2 (5′-, 6′-*C*), 44.7 (5-, 7-*C*), 37.4 (6-*C*), 22.3 (5′-, 6′-CH_3); HRMS: 485.9065, $C_{15}H_{18}O_2S_8$ requires 485.9073; [*a*] −6.2 (*c* = 0.275 in THF).

Racemic 32 and 9

These materials were made as for the enantiopure materials. (±)-**32** 29%, mp 78–80 °C; HRMS: 662.0108, $C_{23}H_{34}O_6S_8$ requires 662.0121; (±)-**9** 75%, mp 208–210 °C, HRMS: 485.9075, $C_{15}H_{18}O_2S_8$ requires 485.9073.

(5′*R*)-6,6-Bis(methoxyethoxymethoxymethyl)-2-(5′,6′-dihydro-5′-methoxyethoxymethoxymethyl[1,3]dithiolo[4,5-*b*][1,4]dithiin-2′-ylidene)-6,7-dihydro-5*H*-[1,3]dithiolo[4,5-*b*][1,4]dithiepine, 38

Oxo compounds **27** (0.084 g, 0.184 mmol) and **33** (0.060 g, 0.184 mmol) were heated in triethyl phosphite (10 ml) at 110 °C for 2 h. The triethyl phosphite was distilled under reduced pressure and the residue was chromatographed using hexane–ethyl acetate (1 : 10) as eluent. The first fraction contained two stereoisomers, **35** and **37**, from self-coupling of oxo compound **33**. The second fraction gave the desired product **38** as an orange oil (0.03 g, 22%) (Found C: 41.8, H: 5.6%. $C_{26}H_{40}O_9S_8$ requires C: 41.5, H: 5.4%); δ_H: 4.72 and 4.68 (6H, 2 × s, 3 × OCH_2O), 3.83 (2H, m, 5′-CH_2), 3.69 (5H, m, 5′-*H* and 2 × 6-CH_2O), 3.59 (12H, m, 3 × OCH_2CH_2O), 3.39 and 3.37 (9H, 2 × s, 3 × OCH_3), 3.20 (2H, m, 6′-H_2), 2.73 (4H, s, 5-, 7-H_2); δ_C: 129.3 (3a-, 8a-*C*), 115.1, 114.1 and 113.3 (2′-, 3a′-, 7a′-*C*), 109.6 (2-*C*), 95.7 (3 × OCH_2O), 71.6 and 66.9 (3 × OCH_2CH_2O), 69.1 (2 × 6-CH_2O), 68.9 (5′-CH_2), 59.0 (3 × OCH_3), 44.1 (5′-*C*), 43.2 (5-, 7-*C*), 37.0 (6-*C*), 32.1 (6′-*C*); ν_{max}: 3398, 2922, 2880, 1729, 1257, 1170, 1112, 1044, 847, 771 cm^{-1}; *m*/*z* (ES): 753 ([M + 1]$^+$, 100). The final fraction yielded **28**.

(5′*R*)-2-(5′,6′-Dihydro-[1,3]dithiolo[4,5-*b*][1,4]dithiin-2′-ylidene)-6,7-dihydro-5*H*-[1,3]dithiolo[4,5-*b*][1,4]dithiepine-5′,6,6-trimethanol, (+)-10

To tri-MEM protected material **38** (0.16 g, 0.21 mmol) dissolved in THF (10 ml) and cooled in an ice-bath was added dropwise 20% HCl (10 ml). The mixture was left stirring at room temperature for two days. It was then neutralised with solid sodium carbonate. The THF layer was decanted and the remaining material was extracted with THF (30 ml). The combined THF solutions were dried over magnesium sulfate, filtered and the solvent was evaporated under reduced pressure. The residue was chromatographed eluting with ethyl acetate–dichloromethane (1 : 1) to give (+)-**10** as a fawn solid (0.070 g, 67%), mp 186 °C dec., δ_H (THF-d_8): 3.92 (3H, br, 3 × O*H*), 3.70 (7H, br m, 2 × 6-CH_2, 5′-*H*, 5′-CH_2), 3.25 (2H, d, *J* 4.1, 6′-H_2), 2.74 (4H, s, 5-, 7-H_2); δ_C (THF-d_8): 130.1 (3a-, 8a-*C*), 115.6 and 115.0 (3a′-, 7a′-*C*), 113.8 (2′-*C*), 109.9 (2-C), 64.6 (br, 2 × 6-CH_2OH), 64.4 (5′-CH_2OH), 47.3 (5′-*C*), 46.2 (5-, 7-*C*), 37.4 (6-*C*), 32.5 (6′-*C*); *m*/*z* (EI): 488 (M^+, 100%); HRMS: 487.8869. $C_{14}H_{16}O_3S_8$ requires 487.8868; [*a*] +68 (*c* = 0.026 in THF).

6,6-Bis(methoxyethoxymethoxymethyl)-2-(5′,6′-dihydro-5′-*tert*-butyldiphenylsilyloxymethyl[1,3]dithiolo[4,5-*b*][1,4]dithiin-2′-ylidene)-6,7-dihydro-5*H*-[1,3]dithiolo[4,5-*b*][1,4]dithiepine, 39

Oxo compounds **27** (0.25 g, 0.54 mmol) and **34** (0.26 g, 0.55 mmol) were heated in triethyl phosphite (15 ml) at 110 °C for 5 h. The triethyl phosphite was distilled under reduced pressure and the residue was chromatographed using ethyl acetate as eluent. The first fraction gave the self-coupling product **36** as a mixture of four stereoisomers (0.13 g, 26%), mp 48–50 °C. The second fraction gave the desired product **39** as an orange oil (0.18 g, 37%); δ_H: 7.43 (10H, m Ar-H_{10}), 4.61 (4H, s, 2 × OCH_2O), 3.91 (1H, m, 5′-CH_a), 3.67 (4H, m, 5′-*H*, 5′-CH_β and 6-CH_2O), 3.52 (8H, m, 2 × OCH_2CH_2O), 3.31 (6H, s, 2 × OCH_3), 3.14 (2H, m, 6′-H_2), 2.67 (4H, s, 5-, 7-H_2), 0.98 (9H, s, 3 × CH_3); δ_C: 135.3, 132.6 and 127.7 (Ar-C_8) 129.8 (3a-, 8a-*C* and Ar-C_4), 114.8 and 114.5 (3a′-, 7a′-*C*), 113.1 (2′-*C*), 109.7 (2-*C*), 95.6 (2 × OCH_2O), 71.5 and 66.8 (2 × OCH_2CH_2O), 69.3 (2 × 6-CH_2O), 64.8 (5′-CH_2O), 58.9 (2 × OCH_3), 45.5 (5′-*C*), 44.0 (5-, 7-*C*), 36.9 (6-*C*), 31.8 (6′-*C*), 26.7 (3 × CH_3), 19.1

(CMe_3); ν_{max}: 1670, 1587, 1302, 1258, 1172, 1110, 1045, 896, 823, 754, 701, 612 cm^{-1}; *m/z*: 902 (M^+, 100%). The third fraction gave **28**.

Racemic 10

Hydrolysis of **39** (0.16 g, 0.17 mmol) according to the method used for the tri-MEM derivative **38** after chromatography (ethyl acetate–dichloromethane 1 : 1) gave (±) **10** (0.070 g, 84%) mp 186 °C dec., identical in spectral characteristics to the enantiopure material.

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