New substrates for the preparation of electroactive materials: the syntheses of chiral tetrathiafulvalene derivatives with hydroxy-functionalised butane-1,4-dithio bridges

Graeme A. Horley,[a] Turan Ozturk,*[b] Figen Turksoy[b] and John D. Wallis *[a]

[a] Centre for Materials Research, School of Physical Sciences, University of Kent, Canterbury, UK CT2 7NH
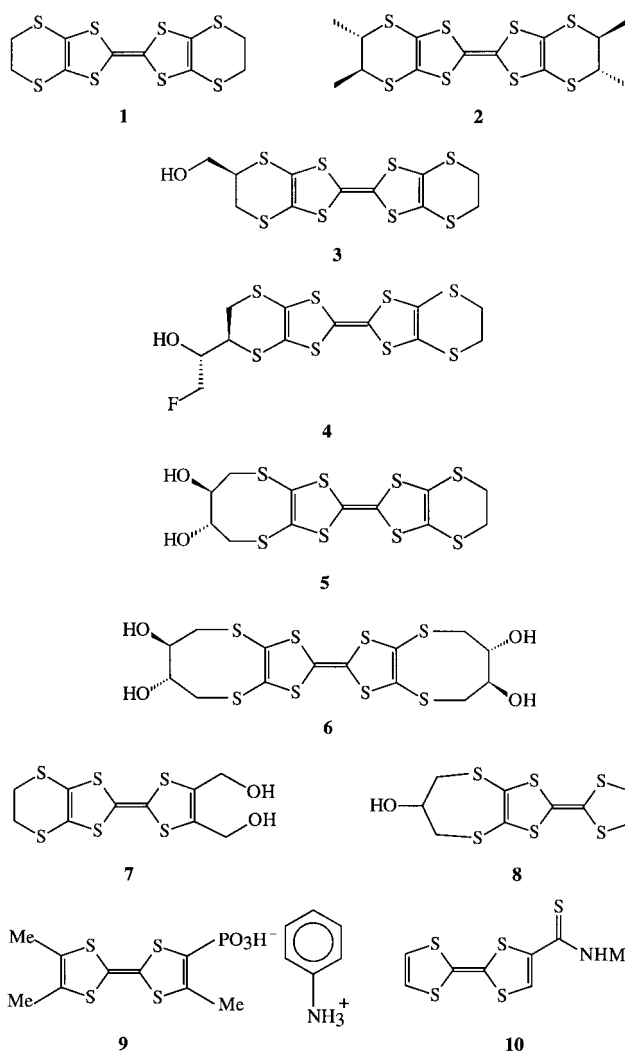[b] Department of Chemistry, TUBITAK—Marmara Research Centre, PO Box 21, 41470, Grebze-Kocaeli, Turkey
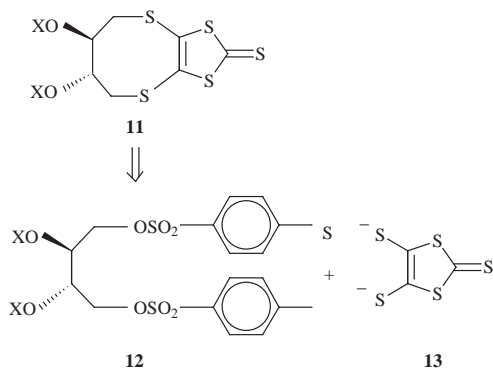
The syntheses of two derivatives of TTF containing (2R,3R)-2,3-dihydroxybutane-1,4-dithio bridges is described, for use in the preparation of chiral hydrogen bonded radical cation salts as potentially electroactive materials. The bridges are introduced by reaction of 2-thioxo-1,3-dithiole-4,5-dithiolate with 1,4-disubstituted derivatives of bis-O-protected butane-2,3-diol to give a bicyclic thione. The X-ray crystal structure of the isopropylidene ketal derivative shows that all four sp³ carbon atoms in the eight-membered ring are displaced to the same side of the dithiole plane. Ease of deprotection led to the use of methoxyethoxymethyl (MEM) protecting groups rather than the ketal. Treatment of the bis-MEM-protected bicyclic thione with mercuric acetate and acetic acid led not only to exchange of the exocyclic sulfur for oxygen but also to removal of just one of the MEM groups, which may have wider synthetic applications.

The different radical cation salts of bis(ethylenedithio)tetra-thiafulvalene 'ET', **1**, show a variety of electrical properties notably conducting and semi-conducting behaviour.[1] Moreover, in some cases, at very low temperatures superconducting behaviour has been observed. The highest T_c for onset of super-conductivity 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 ethylene bridges and the anions.[3] This results in the anion often being orientationally disordered, and in the case of salts of the chiral 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. Thus, we have embarked on the synthesis of ET derivatives carrying hydroxy groups to introduce the possibility of strong hydrogen bonding between the donor and the anion in the radical cation salts. We have reported already the synthesis of the enantiopure materials **3** and **4**.[5,6] We now report on the synthesis of two substances related to ET, **5** and **6**, in which one or both ethylene bridges are replaced by a saturated four carbon chain containing one hydroxy substituent on each of the central two carbon atoms arranged in a chiral fashion. The installation of two or four hydroxy groups will open up more possibilities for hydrogen bonding than in **3** or **4**, which just contain one hydroxy group per molecule. Some other achiral hydroxy-substituted derivatives of tetrathiafulvalene, such as **7**[7] and **8**[8] have been reported, and some tetrathiafulvalenes carrying alternative hydrogen bond donors, such as the phosphate salt **9**,[9] and the thioamide **10**[10] have been prepared and studied. Use of a carboxylic acid group for this purpose is frustrated by anodic decarboxylation in the electrocrystallisation step.[11]

The synthetic plan to prepare **5** and **6**, involved the synthesis of a bis-O-protected 1,3-dithiolo[1,4]dithiocine-2-thione deriv-ative of type **11**, which after exchange of the thione for an oxo group, could be self-coupled, or coupled with other oxo compounds such as the unsubstituted material **33** to give fused

Fig. 1 Molecular structure of **15** with atomic labels and anisotropic displacement parameters for non-hydrogen atoms drawn at the 50% level.

tetrathiafulvalenes. Removal of O-protecting groups would yield **5** or **6**. Structure **11** was to be synthesised from the dithiolate **13**[12] and a 2O,3O-protected derivative of the 1,4-ditosylate [1,4-bis(toluene-*p*-sulfonate)] of butane-1,2,3,4-tetrol **12**. The first choice for **12**, was the isopropylidene ketal **14**, which can be prepared from tartaric diesters, and is also commercially available (Scheme 1). Reaction of dithiolate **13** with
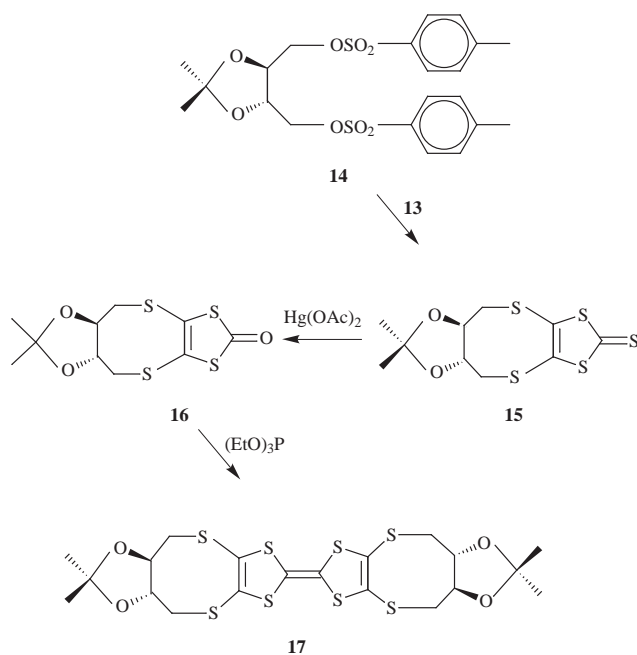
Scheme 1

14 in THF gave the expected product **15** in 52% yield. The ^{13}C NMR showed the presence of the thione carbon resonance at δ 211.1, and two sets of ring sp^3 carbon atoms at δ 80.4 and 38.0, and the alkenyl carbon atoms at δ 141.0. The thione S atom in **15** was easily replaced by an O atom using the standard procedure of treatment with mercuric acetate in acetic acid–chloroform to give **16**. The ^{13}C NMR of **16** showed two main differences from **15**; the carbonyl carbon resonance was at δ 188.4 and the alkenyl carbons' resonance was at δ 132.5. Treatment of **16** with excess triethyl phosphite at 100 °C gave the coupled material **17** in 62% yield. The ^{13}C NMR spectrum showed the resonance of the central two alkenyl carbon atoms at δ 108.3, and that of those carbons at the fusion of the five and eight membered rings at δ 132.5. However, all attempts to cleanly deprotect **17** to furnish the tetrol **6** by various acidic treatments were unsuccessful. The difficulties are due in part to the low solubility of **17** in most organic solvents. Treatment with weakly acidic conditions are ineffective (*e.g.* aqueous acetic acid, reflux), but treatment with stronger acidic conditions leads to mixtures of several products, including some **6**. Bryce has reported that the diketal **18** needed unexpectedly vigorous conditions for its hydrolysis.[8] The stacking of the organo-
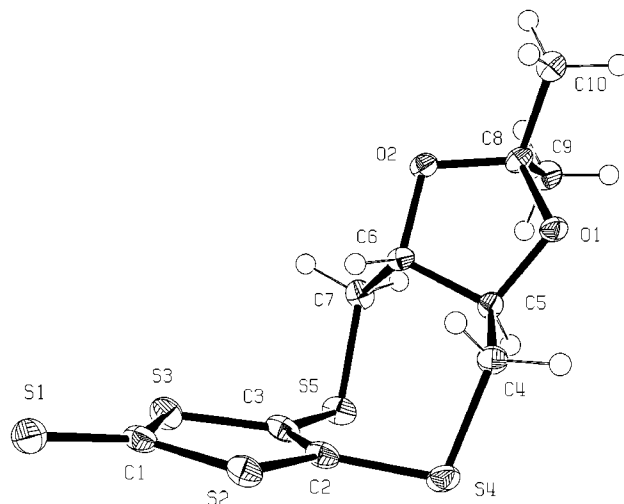
sulfur molecules with each other in solution may be a cause of their unexpected low reactivities. The structure **17** is related to the recently reported structures which have extra six-membered rings, formed by –X–CH$_2$CH$_2$–Y– (X, Y = S or O) units, fused to the outer rings of the ET framework.[13–15]

To investigate the conformation of the eight-membered ring in these substances the X-ray crystal structure of **15** was measured. (The coupled material **17** formed a crystalline chloroform solvate which lost solvent on the slightest mechanical disturbance and was unsuitable for measurement.) The molecular structure is shown in Fig. 1, and selected bond lengths and angles in Table 1. The eight-membered ring adopts a conformation, which displaces all of the ring sp^3 carbon atoms to the same side of the dithiole plane. Atoms C(4) and C(7) are displaced by 1.736(9) and 1.803(9) Å respectively from this plane. At the fusion of the five-membered ring the conformation about the C(5)–C(6) bond is nearly eclipsed; the O(1)–C(5)–C(6)–O(2) torsion angle is only 7.4(5)°, and the C(4)–C(5)–C(6)–C(7) torsion angle is 117.1(5)°. The ketal ring's conformation is near to a half chair with C(5), C(6) and O(2) coplanar. Surprisingly, the fusion of a dioxolane ring seems to have little influence on the conformation of the dithiocine ring, and thione **19**,[16] which lacks this structural feature, shows a very similar conformation in the eight-membered ring with eclipsing about the C(5)–C(6) bond (Table 2). Similar conformations are seen too in the related fused tetrathiafulvalene **20**[17] and in one of its 2 : 1 radical cation salts,[18] though the eight-membered ring in a 1 : 1 radical cation salt shows different conformations with one thioether group (sp^{3}C–S–sp^{2}C) near to coplanarity with the dithiole system and no eclipsed conformations about C,C bonds.[19]
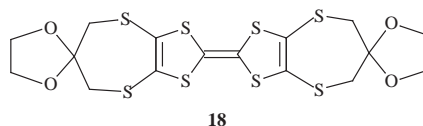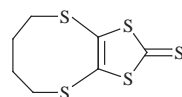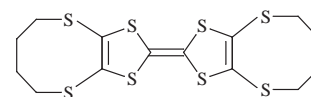

An alternative approach to the synthesis of **5** and **6** was to use methoxyethoxymethyl (MEM) groups for protection of the hydroxy groups (Scheme 2). This approach has the advantage that the MEM groups will confer solubility on the intermediate

Table 1 Selected bond lengths (Å) and angles (°) for **15** with estimated standard deviations in parentheses

Atom	Atom	Distance		Atom	Atom	Distance
S(1)	C(1)	1.640(6)		C(2)	C(3)	1.339(8)
S(2)	C(1)	1.736(6)		C(4)	C(5)	1.531(8)
S(2)	C(2)	1.752(5)		C(5)	C(6)	1.546(7)
S(3)	C(1)	1.735(6)		C(6)	C(7)	1.527(7)
S(3)	C(3)	1.746(6)		O(1)	C(5)	1.441(6)
S(4)	C(2)	1.765(6)		O(1)	C(8)	1.424(6)
S(4)	C(4)	1.810(5)		O(2)	C(6)	1.442(6)
S(5)	C(3)	1.756(5)		O(2)	C(8)	1.428(6)
S(5)	C(7)	1.815(5)				

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C(1)	S(2)	C(2)	97.9(3)	S(4)	C(4)	C(5)	114.7(4)
C(1)	S(3)	C(3)	98.2(3)	O(1)	C(5)	C(4)	105.5(4)
C(2)	S(4)	C(4)	102.2(2)	O(1)	C(5)	C(6)	103.9(4)
C(3)	S(5)	C(7)	100.9(2)	C(4)	C(5)	C(6)	115.8(5)
S(2)	C(1)	S(3)	111.8(3)	O(2)	C(6)	C(5)	104.4(5)
S(2)	C(2)	C(3)	116.1(5)	O(2)	C(6)	C(7)	109.8(4)
S(4)	C(2)	C(3)	127.2(4)	C(5)	C(6)	C(7)	115.2(4)
S(3)	C(3)	C(2)	116.0(4)	S(5)	C(7)	C(6)	113.8(4)
S(5)	C(3)	C(2)	124.7(5)				

Table 2 Torsion angles (°) about bonds A–G in the fused 1,4-dithiocine rings of compounds **15**, **19** and **20** indicating the very similar conformations
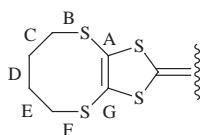
|	A	B	C	D	E	F	G
15	−92.9	47.9	56.3	−117.1	82.3	−72.5	81.4
19	−90.2	50.7	53.0	−113.0	80.1	−71.8	80.7
20	−92.4	44.0	59.4	−110.7	80.4	−77.7	82.9

products in the synthesis, and this protecting group has been used successfully in the preparation of enantiopure HMET **3**. Thus, dimethyl L-tartrate was reacted with MEM-Cl and diisopropylethylamine to give the bis-MEM protected diester **21**. Reduction of **21** with lithium aluminium hydride gave the corresponding diol **22**, which was converted to the ditosylate **23**. However, reaction of the ditosylate **23** with the dithiolate **13** in dry THF did not yield any of the expected thione **25**. This is probably due to the approach of the nucleophile to 1-C (or 4-C) being hindered by the MEM-O substituent at 3-C (at 2-C) and to some extent by the second MEM-O group. In the ditosylate **14**, the more constrained ketal group does not offer so much steric hindrance, and enforces a conformation which is preorganised for the formation of the eight-membered ring. To reduce the steric hindrance, the ditosylate **23** was converted to the diiodide **24** by treatment with sodium iodide in acetone. The crude product, which often contained a residue of starting material and monoiodinated material, was used without further purification since distillation led to decomposition (as referred to later), and chromatography was not satisfactory. The ^{13}C NMR spectrum showed a characteristic iodomethylene group at δ 4.7 and the resonance from the 2- and 3-C atoms was at δ 78.6. Reaction of crude **24** with dithiolate **13** in dry THF gave the desired product **25** in *ca.* 70% yield. The ^{13}C NMR spectrum showed the thione carbon atom at δ 211.2, ring sp^3 carbon atoms at δ 78.7 and 37.8, and the alkenyl carbons at δ 136.6, and chemical analysis and high resolution mass spectrometry confirmed the atomic composition of the material.

Treatment of **25** with mercuric acetate in acetic acid and chloroform and subsequent chromatography gave an inseparable 1:4 mixture of two oxo compounds **26** and **27**. The
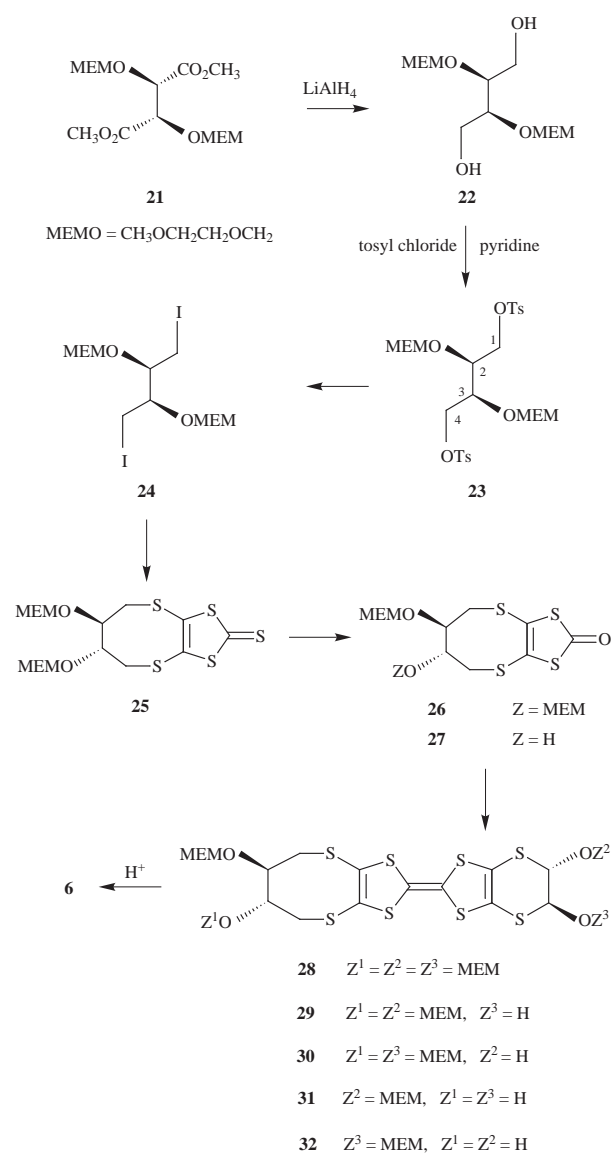

Scheme 2

expected bis-MEM protected material **26** is the minor component, but the major component is **27**, in which one MEM protecting group has been removed. Indeed these or similar reaction

conditions may provide the basis of a more general method for deprotection of one of a pair of MEM-protected *vic*-hydroxy groups. The compounds' identities are strongly supported by their ^{13}C NMR spectra. The asymmetry of **27** compared to **26** is indicated in the ^{13}C NMR resonances. For the ring sp^3 carbon atoms of **27** there are large peaks at δ 81.5, 72.7, 39.5 and 37.8 compared to much smaller peaks at δ 78.7 and 38.3 from **26**. Similarly for the ring sp^2 carbon atoms there are large peaks at δ 128.4 and 125.9, and a smaller peak at δ 127.6. The resonance of the isolated methylene hydrogens of the MEM groups in **26** occurs as an AB quartet, as observed in the bis-MEM substituted precursor thione **25**, but the resonance of the corresponding hydrogens of the MEM group in **27** is a singlet. The electron impact mass spectrum of the mixture shows peaks at *m/z* 356 and 444 corresponding to the molecular ions of **27** and **26** respectively, and the chemical ionisation mass spectrum shows peaks corresponding to both [M + NH$_4$]$^+$ ions, that for **27** being the base peak. The high resolution mass spectrum of the [M + NH$_4$]$^+$ ion for **26** confirms the atomic composition of that ion. The loss of a MEM-group most likely involves initial coordination of Hg^{2+} by both MEM-O groups, which promotes decomposition of the acetal link, or facilitates intermolecular attack by water present in the acetic acid (Scheme 3). Treatment


Scheme 3
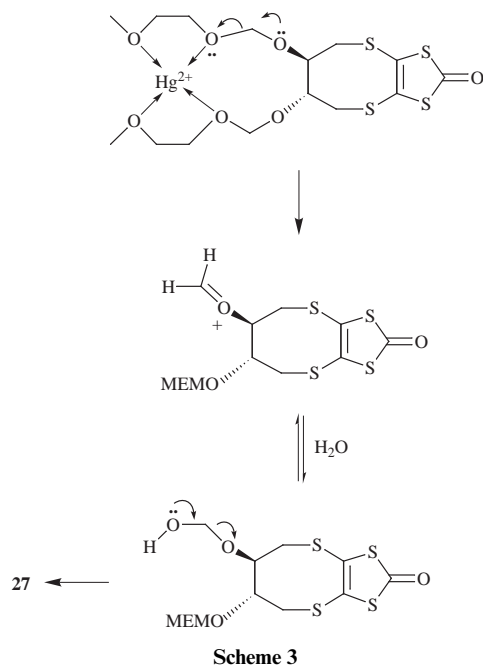
of the **26/27** mixture with triethyl phosphite at 120 °C gave a mixture of new tetrathiafulvalene derivatives **28–32**, derived from self-coupling of **26** or **27**, and cross coupling of **26** with **27**. Removal of the MEM groups from this mixture with aqueous HCl in THF yielded the single tetrahydroxy derivative **6**. Cross coupling of the **26/27** mixture with the unsubstituted dihydro-1,3-dithiole[1,4]dithiin-2-one **33** gave a mixture of **34** and **35** which was separated from 'ET' by chromatography (Scheme 4). Compounds **34** and **35** were distinguished by their ^{13}C NMR resonances in a very similar way to the precursor mixture of **26** and **27**, and by the difference in the ^{1}H NMR resonances from the isolated methylene hydrogens of the MEM groups. The latter mixture was deprotected as for **6**, to give the dihydroxy derivative **5**.

The structures of **5** and **6** were confirmed by their spectral data. High-resolution mass spectrometry confirmed the composition of their molecular ions. The ^{13}C NMR spectrum of **6** showed just four signals at δ 127.9, 111.1, 74.3 and 39.7, and the data for **5** included corresponding resonances at δ 128.0, 114.5, 74.3 and 39.7, as well as one at δ 30.9 for the carbons of the ethylene bridge. The ^{1}H NMR spectrum of **6** shows four reson-

Scheme 4
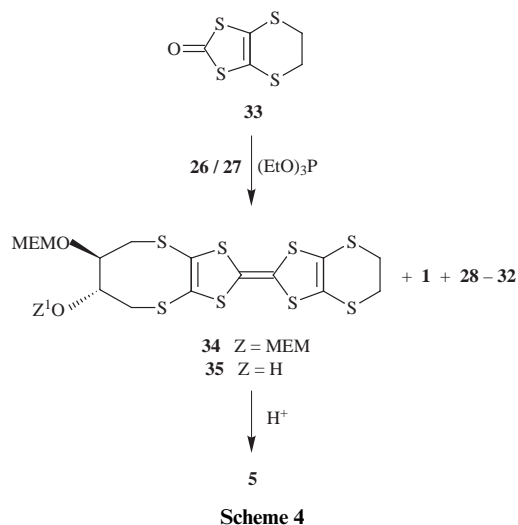
ances; the resonance for the hydroxy groups is a doublet, the resonances for the four diastereotopic methylene groups occur at δ 3.65 and 2.85 as double doublets, and the resonances for the four methine hydrogens give a multiplet at δ 3.89. Both **5** and **6** were stable to oxidation in the air. The selective removal of only one MEM group observed in the conversion of **25** to **27** allows the two substituents to be distinguished chemically, and so opens up a route to derivatives of **5** in which one hydroxy group is functionalised.

Scheme 5
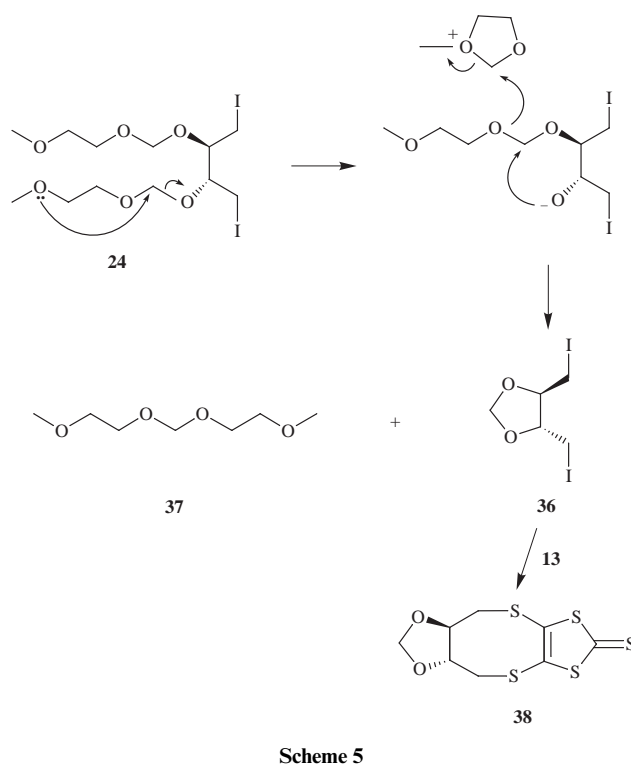
Distillation of the crude bis-MEM-protected 1,4-diiodo-butane-2,3-diol **24**, used in the previous preparation, leads to decomposition. The main products are assigned to be the bis-(iodomethyl)dioxolane **36** along with the polyether **37** on the basis of NMR spectra and chemical behaviour. Thus, direct reaction of this distilled mixture with dithiolate **13** yielded the thione **38**, containing a methylene acetal link. The identity of the thione was supported by the chemical analysis and the very close similarity of its NMR spectra with those of thione **15** apart from the lower shift of the acetal carbon atom which does not carry any methyl substituents (**38**, δ 94.1, **15**, δ 110.1). The ^{13}C NMR spectra of the mixture of **36** and **37** shows resonances

at δ 94.9 and δ 80.2 assigned to ring carbon atoms of **36**, and very similar to the corresponding shifts for thione **38**, and also a characteristic resonance at δ 5.2 for iodomethylene groups. A proposal for the thermal decomposition of **24** to **36** and **37** is given in Scheme 5.

Experimental

NMR spectra were measured on a JEOL GX 270 machine at 270 MHz for ^{1}H and at 67.8 MHz for ^{13}C using CDCl$_3$ as solvent and tetramethylsilane (TMS) as standard, and measured in ppm downfield from TMS, unless otherwise stated. Coupling constants (J) are given in Hz. IR spectra were recorded on an 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 mesh silica gel (Merck).

(5aR,8aR)-7,7-Dimethyl-5,5a,8a,9-tetrahydro-1,3-dithio-[4′,5′:2,3]dithiocino[6,7-d][1,3]dioxole-2-thione 15

A solution of ditosylate **14** (2.69 g, 5.72 mmol) in THF (25 ml) was added to a stirred suspension of the disodium salt of dithiolate **13** (1.38 g, 5.70 mmol) in THF (100 ml) under nitrogen, and stirred for 5 days. The solvent was evaporated, and the residue separated by column chromatography eluting with hexane–diethyl ether (7:3), to give **15** as yellow crystals (0.97 g, 52%), mp 143–145 °C (from acetone); Found: C: 37.0, H: 3.5%. C$_{10}$H$_{12}$O$_2$S$_5$ requires C: 37.0, H: 3.7%; δ_H: 4.20 (2H, J = 12.4, 3.8, $J_{5a,8a}$ = 5.3, 5a-,8a-H), 3.30 (2H, dd, J = 13.1, 3.8, 5-,9-H$_\alpha$), 2.69 (2H, dd, J = 13.1, 12.4, 5-,9-H$_\beta$), 1.39 (6H, s, 2 × CH$_3$); δ_C: 211.1 (2-C), 141.0 (3a-,10a-C), 110.1 (Me$_2$C), 80.4 (5a-,8a-C), 38.0 (5-,9-C), 26.8 (2 × CH$_3$); v_{max}: 1261, 1198, 1157, 1059, 1051, 1040, 1030, 875, 863, 517 cm^{-1}, $[a]_D$: +185.7 (c = 0.62, CH$_2$Cl$_2$).

Crystal structure determination for 15

Crystal data. C$_{10}$H$_{12}$O$_2$S$_5$, M_r = 324.5, a = 4.974(1), b = 16.357(2), c = 8.309(1) Å, β = 92.31(2)°, V = 675.5(2) Å^3, $P2_1$, Z = 2, D_c = 1.595 g cm^{-3}, μ(Mo-Kα) = 0.84 mm^{-1}, T = 150 K, 1699 unique reflections, R_1 = 0.042 for 1642 reflections with $F > 4\sigma(F)$, R_w = 0.105. X-Ray diffraction intensities were collected on an Enraf Nonius FAST system. The structure was solved using SHELXS-86,[20] and refined by full-matrix least-squares with SHELXL-93.[21] Positions of hydrogen atoms were calculated. An absorption correction was estimated using DIFFABS.[22] The absolute configuration is supported by a Flack parameter of 0.10(14).

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web pages (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/254.

(5aR,8aR)-7,7-Dimethyl-5,5a,8a,9-tetrahydro-1,3-dithio-[4′,5′:2,3]dithiocino[6,7-d][1,3]dioxol-2-one 16

Mercuric acetate (2.21 g, 6.95 mmol) was added to a solution of **15** (0.90 g, 2.78 mmol) in CHCl$_3$ (40 ml) and acetic acid (10 ml) and stirred for 1 h. The almost colourless mixture was filtered, and the filtrate washed with aqueous sodium hydrogen carbonate and then water, and dried over sodium sulfate. Filtration and evaporation gave **16** (0.69 g, 81%), mp 165–166 °C; Found: C: 38.9, H: 4.0%. C$_{10}$H$_{12}$O$_3$S$_4$ requires C: 38.9, H: 3.9%; δ_H: 4.19

(2H, m, 5a-,8a-H), 3.29 (2H, dt, J = 13.7, 1.7, 5-,9-H$_\alpha$), 2.67 (2H, dd, J = 13.7, 10.2, 5-,9-H$_\beta$), 1.39 (6H, s, 2 × CH$_3$); δ_C: 188.4 (2-C), 132.4 (3a-,10a-C), 110.0 (Me$_2$C), 80.6 (5a-,8a-C), 37.8 (5-,9-C), 26.8 (2 × CH$_3$); v_{max}: 1658, 1650, 1598, 1259, 1211, 1160, 1047, 1022, 1004, 879, 726 cm^{-1}; $[a]_D$: +72.2 (c = 0.4, CH$_2$Cl$_2$).

(5aR,5a′R,8aR,8a′R)-7,7-Dimethyl-2-(7′,7′-dimethyl-5′,5a′,8a′,9′-tetrahydro-1,3-dithiolo[4′,5′:2,3]dithiocino[6,7-d][1,3]-dioxol-2′-ylidene)-5,5a,8a,9-tetrahydro-1,3-dithiolo[4′,5′:2,3]dithiocino[6,7-d][1,3]dioxole 17

Oxo compound **16** (0.51 g, 1.66 mmol) was dissolved in triethyl phosphite (10 ml) under nitrogen and heated to 100 °C and stirred for 24 h. The precipitate was collected and washed with copious amounts of diethyl ether to yield **17** (0.42 g, 62%), as an orange powder giving orange–red needles (from toluene), mp 286–288 °C; Found: C: 41.2, H: 4.1%. C$_{20}$H$_{24}$O$_4$S$_8$ requires C: 41.1, H: 4.1%; δ_H: 4.22 (4H, m, 5a-,5a′-,8a-,8a′-H), 3.25 (4H, dd, J = 13.4, 3.3, 5-,5′-,9-,9′-H$_\alpha$), 2.63 (4H, dd, J = 13.4, 10.1, 5-,5′-,9-,9′-H$_\beta$), 1.39 (12H, s, 4 × CH$_3$); δ_C: 132.5 (3a-,3a′-,10a-,10a′-C), 109.8 (2 × Me$_2$C), 108.3 (2a-,2a′-C), 80.6 (5a-,5a′-,8a-,8a′-C), 37.3 (5-,5′-,9-,9′-C), 26.8 (4 × CH$_3$); v_{max}: 1262, 1210, 1160, 1048, 876, 724 cm^{-1}, m/z: (EI) 584 (M$^+$, 52%), 43 (100); $[a]_D$: +109 (c = 0.1, CH$_2$Cl$_2$).

Dimethyl (2R,3R)-2,3-bis(2-methoxyethoxymethoxy)butane-1,4-dioate 21

To a solution of dimethyl L-tartrate (10.0 g, 0.056 mol) and diisopropylethylamine (18.0 g, 0.14 mol) dissolved in dry dichloromethane (250 ml) was added 2-methoxyethoxymethyl chloride (17.4 g, 0.14 mol) dropwise as the temperature of the solution was kept at 0 °C in an ice bath. The solution was then stirred at room temperature for a further 4 h and extracted with 0.5 M HCl (2 × 100 ml) and then with H$_2$O (2 × 100 ml). The organic layer was dried over MgSO$_4$, filtered and the solvent was evaporated to give **21** (14.4 g, 72%), a viscous colourless liquid, which was sufficiently pure for use in the next step. Found: C: 47.1, H: 7.6%. C$_{14}$H$_{26}$O$_{12}$ requires C: 47.4, H: 7.3%; δ_H: 4.81 (2H, dd, J = 7.3, 2-,3-H), 4.75 (4H, s, 2 × OCH_2O), 3.78 (6H, s, 2 × CO$_2$CH_3), 3.67 (4H, m, 2 × CH$_3$OCH$_2$CH_2), 3.51 (4H, m, 2 × CH$_3$OCH_2), 3.37 (6H, s, 2 × CH$_2$OCH_3); δ_C: 169.2 (2 × C=O), 95.3 (2 × OCH$_2$O), 75.5 (2-,3-C), 71.5 (2 × CH$_3$-OCH$_2$CH$_2$), 67.7 (2 × CH$_3$OCH$_2$), 58.9 (2 × CH$_2$OCH$_3$), 52.3 (2 × CO$_2$CH$_3$); v_{max}: 1741, 1455, 1438, 1275, 1208, 1173, 1134, 1097, 1046, 1024, 935, 851, 814, 702 cm^{-1}; m/z (CI): 372 ([M + NH$_4$]$^+$, 100%); HRMS: 372.1870. C$_{14}$H$_{26}$O$_{10}$ + NH$_4^+$ requires: 372.1870; $[a]_D$: +115.8 (c = 2.5, THF).

(2S,3S)-2,3-Bis(2-methoxyethoxymethoxy)butane-1,4-diol 22

To a suspension of lithium aluminium hydride (2.28 g, 0.06 mmol) in dry diethyl ether (100 ml) was added a solution of **21** (15 g, 0.042 mol) in dry diethyl ether (50 ml) from a dropping funnel as the temperature of the solution was kept at ∼0 °C. The mixture was left stirring in an ice-bath for 1 h and then at room temperature overnight. Water (2.5 ml), aqueous sodium hydroxide (5%, 2.5 ml) and water (15 ml) were added successively to the reaction mixture from the dropping funnel. The formed cake was filtered and washed with ethyl acetate. The filtrate was dried over MgSO$_4$, filtered and the solvent was evaporated to give **22** (7.86 g, 62.3%) as a viscous colourless liquid. The crude product was sufficiently pure for use in the next step. δ_H: 4.82 (4H, AB quartet, J = 7.1, 2 × OCH_2O), 3.74 (8H, m, 2 × CH$_3$-OCH$_2$CH_2, 1-,4-H$_2$, 2-,3-H), 3.56 (4H, m, 2 × CH$_3$OCH_2), 3.38 (6H, s, 2 × OCH_3); δ_C: 96.0 (2 × OCH$_2$O), 79.8 (2-,3-C), 71.7 (2 × CH$_3$OCH$_2$CH$_2$), 67.4 (2 × CH$_3$OCH$_2$), 61.3 (1-,4-C), 58.9 (2 × -CH$_3$); v_{max}: 3442, 2933, 1456, 1369, 1245, 1201, 1104, 1016, 817 cm^{-1}; m/z (CI): 299 ([M + 1]$^+$, 100%), 240 ([M + 1 − CH$_3$-

O(CH$_2$)$_2$]$^+$, 34); HRMS: 299.1706, C$_{12}$H$_{26}$O$_8$ + H$^+$ requires: 299.1706; [a]$_D$: −16.9 (c = 2, THF).

(2S,3S)-2,3-Bis(2-methoxyethoxymethoxy)-1,4-bis(4′-methyl-phenylsulfonyloxy)butane 23

To a solution of diol **22** (7.86 g, 0.026 mol) dissolved in dry pyridine (75 ml) and cooled in an ice-bath, was added portion-wise toluene-4-sulfonyl chloride (9.90 g, 0.052 mol). The mixture was stirred for 4 h and then extracted with CH$_2$Cl$_2$ (2 × 100 ml). The organic extract was washed with 0.5 M HCl (4 × 100 ml) and then with H$_2$O (2 × 100 ml). The organic layer was dried over MgSO$_4$, filtered and the solvent was evaporated. The crude product was chromatographed (ethyl acetate–dichloromethane, 1:4) to give **23** (6.04 g, 37%) as an amorphous white solid, mp 59–61 °C; Found: C: 51.4, H: 6.4%. C$_{26}$H$_{38}$O$_{12}$S$_2$ requires C: 51.1, H: 6.3%; δ_H: 7.76 (4H, d, J = 8.4, 2 × 2′-,6′-H), 7.35 (4H, d, J = 8.5, 2 × 3′-,5′-H), 4.64 (4H, AB quartet, J = 7.0, 2 × OCH_2O), 4.19 (2H, dd, J = 10.3, 4.0, 1-,4-H$_a$), 4.08 (2H, dd, J = 10.4, 5.4, 1-,4-H$_\beta$), 3.92 (2H, m, 2-,3-H), 3.58 (4H, m, 2 × CH$_3$OCH$_2$CH_2), 3.47 (4H, t, J = 4.3, 2 × CH$_3$OCH_2), 3.35 (6H, s, 2 × OCH_3), 2.46 (6H, s, 2 × 4′-CH_3); δ_C: 145.0 (2 × 1′-C), 132.6 (2 × 4′-C), 129.9 (2 × 2′-,6′-C), 127.7 (2 × 3′-,5′-C), 95.9 (2 × OCH$_2$O), 74.4 (2-,3-C), 71.5 (2 × CH$_3$OCH$_2$CH$_2$), 68.1 (1-,4-C), 67.5 (2 × CH$_3$OCH$_2$), 59.0 (2 × OCH$_3$), 21.7 (2 × 4′-CH$_3$); ν_{max}: 1199, 1180, 1173, 1073, 1056, 959, 842, 814, 772, 767, 661 cm^{-1}; m/z: 624 ([M + NH$_4$]$^+$, 28%), 298 ([M + NH$_4$ − 2(CH$_3$C$_6$H$_4$SO$_2$) − O]$^+$, 100), 210 (44); HRMS: 624.215. C$_{26}$H$_{38}$O$_{12}$S$_2$ + NH$_4$$^+$ requires: 624.215; [a]$_D$: −10 (c = 0.3, CHCl$_3$).

(2R,3R)-1,4-Diiodo-2,3-bis(2-methoxyethoxymethoxy)butane 24

Ditosylate **23** (1.27 g, 2.0 mmol) and sodium iodide (1.72 g, 11.5 mmol) were refluxed in dry acetone (50 ml) overnight under a nitrogen atmosphere. The precipitated salts were filtered off and washed with acetone (15 ml). The combined acetone portions were evaporated and the oily solid residue was washed with aqueous sodium thiosulfate and then with water. The crude material was used directly in the next reaction. Attempts to effect further purification by chromatography or distillation were not successful. The material contains about 65% **24**, along with the mono-iodinated material and starting material. δ_H: 4.85 (4H, s, 2 × OCH_2O), 3.98 (2H, m, 2-,3-H), 3.81–3.44 (12H, m, 2 × OCH_2CH$_2$O and 1-,4-H$_2$), 3.37 (6H, 2 × CH_3); δ_C: 96.2 (OCH$_2$O), 78.6 (2-,3-C), 71.4 (2 × CH$_3$OCH$_2$CH$_2$), 67.5 (2 × CH$_3$OCH$_2$), 58.8 (2 × CH$_3$), 4.7 (1-,4-C); m/z (CI): 518 ([M]$^+$, 2%), 416 (18), 354 ([M − (CH$_3$OCH$_2$CH$_2$O)$_2$CH$_2$]$^+$, 50), 320 (40), 262 (58), 244 (64), 217 (55), 164 (69), 106 (100).

(6R,7R)-6,7-Bis(2-methoxyethoxymethoxy)-5,6,7,8-tetrahydro-1,3-dithiolo[4,5-b][1,4]dithiocine-2-thione 25

To a suspension of the disodium salt of the dithiolate **13** (0.38 g, 1.6 mmol) in dry THF (4.0 ml) was added crude **24** (0.83 g, containing *ca.* 1.0 mmol of **24**) dissolved in dry THF (20 ml) dropwise at room temperature under a nitrogen atmosphere. The bath temperature was brought up to ~74 °C and the mixture was kept stirring for two days during which time, the colour turned to brown. A precipitate was filtered off and the solvent was evaporated to give a brown viscous oil which was partitioned between water and dichloromethane. The organic phase was dried over MgSO$_4$, filtered and the solvent was evaporated. The crude product was chromatographed (hexane–ethyl acetate, 1:1) to yield **25** (0.34 g, *ca.* 70%) as a yellow solid, mp 82–84 °C (from ethanol); Found: C: 39.2, H: 5.3%. C$_{15}$H$_{24}$O$_6$S$_5$ requires C: 39.1, H: 5.2%; δ_H: 4.81 (4H, AB quartet, J = 7.1, OCH_2O), 4.21 (2H, m, 6-,7-H), 3.77 (4H, m, 2 × CH$_3$OCH$_2$-CH_2), 3.65 (2H, m, 5-,8-H$_a$), 3.55 (4H, m, 2 × CH$_3$OCH_2), 3.39 (6H, s, 2 × CH_3), 3.18 (2H, dd, J = 15.0, 6.5, 5-,8-H$_\beta$); δ_C: 211.2

(2-C), 136.6 (3a-,9a-C), 96.1 (OCH$_2$O), 78.7 (6-,7-C), 71.7 (CH$_3$OCH$_2$CH$_2$), 67.5 (CH$_3$OCH$_2$), 59.1 (2 × CH$_3$), 37.8 (5-, 8-C); ν_{max}: 1280, 1242, 1199, 1181, 1174, 1156, 1135, 1097, 1073, 1058, 1017, 967, 943, 888, 851, 812, 724 cm^{-1}; m/z (EI): 460 ([M]$^+$, 67%), 296 ([M − (CH$_3$OCH$_2$CH$_2$O)$_2$CH$_2$]$^+$, 21), 101 (100); HRMS: 461.0254. C$_{15}$H$_{24}$O$_6$S$_5$ + H$^+$ requires: 461.0255; [a]$_D$: +22.0 (c = 2, THF).

Reaction of 25 with mercuric acetate

Mercuric acetate (0.43 g, 1.3 mmol) and glacial acetic acid (5 ml) were added to a solution of thione **25** (0.25 g, 0.54 mmol) in chloroform (37.5 ml), and stirred together for 3 h during which time the yellow colour disappeared. The mixture was filtered through Celite, extracted with aqueous sodium hydrogen carbonate (2 × 75 ml) and then water (2 × 75 ml), and dried over magnesium sulfate. The crude product was chromatographed (hexane–ethyl acetate, 1:1), to give a yellow viscous oil (0.41 g) which was a mixture (*ca.* 1:4) of **26** and **27**. *(6R,7R)-6,7-bis-(2-methoxyethoxymethoxy)-5,6,7,8-tetrahydro-1,3-dithiolo[4,5-b][1,4]dithiocin-2-one* **26**, δ_H: 4.82 (4H, AB quartet, J = 7.0, OCH_2O), 4.12 (2H, m, 6-,7-H), 3.72 (6H, m, 2 × CH$_3$OCH_2CH_2 and 5-,8-H$_a$), 3.56 (4H, m, 2 × CH$_3$OCH_2), 3.39 (6H, s, 2 × CH_3), 3.16 (2H, dd, J = 14.5, 6.2, 5-,8-H$_\beta$); δ_C: 189.2 (C=O), 127.6 (3a-,9a-C), 95.9 (OCH$_2$O), 78.8 (6-,7-C), 71.7 (2 × CH$_3$-OCH$_2$CH$_2$), 67.3 (2 × CH$_3$OCH$_2$), 58.9 (2 × CH$_3$), 38.3 (5-,8-C); *(6R,7R)-6-hydroxy-7-(2-methoxyethoxymethoxy)-5,6,7,8-tetrahydro-1,3-dithiolo[4,5b][1,4]dithiocin-2-one* **27**, δ_H: 4.83 (2H, s, OCH_2O), 4.12 (2H, m, 6-,7-H), 3.86 (1H, dd, J = 14.7, 2.6, 5-H$_a$), 3.77 (2H, m, CH$_3$OCH$_2$CH_2), 3.70 (1H, dd, J = 14.6, 2.7, 8-H$_a$), 3.56 (2H, m, CH$_3$OCH_2), 3.48 (1H, br, OH), 3.39 (3H, s, CH_3), 3.01 (2H, dd, J = 14.5, 6.7, 5-,8-H$_\beta$); δ_C: 189.2 (C=O), 128.4 and 125.9 (3a-,9a-C), 96.0 (OCH$_2$O), 81.5 (7-C), 72.7 (6-C), 71.6 (CH$_3$OCH$_2$CH$_2$), 67.9 (CH$_3$OCH$_2$), 59.0 (CH$_3$), 39.5 and 37.8 (5-,8-C). Mass spectral data for **26–27** mixture: m/z (EI): 444 ([M$_{26}$]$^+$, 1%), 356 ([M$_{27}$]$^+$, 18), 101 (100); (CI) 462 ([M$_{26}$ + NH$_4$]$^+$, 8%), 374 ([M$_{27}$ + NH$_4$]$^+$, 100), 267 (17), 226 (18), 210 (16), 94 (17); HRMS: 462.0749. C$_{15}$H$_{24}$O$_7$S$_4$ (=M$_{26}$) + NH$_4$$^+$ requires: 462.0749.

(6R,7R)-2-(5′,6′-Dihydro-1,3-dithiolo[4,5-b][1,4]dithiin-2′-yl-idene)-5,6,7,8-tetrahydro-1,3-dithiolo[4,5-b][1,4]dithiocine-6,7-diol 5

The mixture of **26** and **27** from the previous reaction (0.52 g, *ca.* 1.38 mmol) and **33** (0.37 g, 1.8 mmol) were heated with triethyl phosphite (50 ml) to 120 °C under nitrogen overnight. Triethyl phosphite was removed *in vacuo*, and the residue dissolved in dichloromethane, and 'ET' **1** removed by filtration. The evaporated filtrate was purified by chromatography eluting with hexane–ethyl acetate (1:1). The first fraction gave more 'ET', and the second fraction gave a mixture of cross-coupled materials **34** and **35** (0.23 g, 33%) (elution with ethyl acetate–methanol (15:1) gave homo-coupled materials **28–32**). **34**, δ_H: 4.81 (4H, AB quartet, J = 7.0, 2 × OCH_2O), 4.10 (2H, m, 6-,7-H), 3.80–3.55 (9H, 2 × CH$_3$OCH_2CH_2 and 5-,8-H$_a$), 3.39 (6H, s, 2 × CH_3), 3.29 (4H, s, 5′-,6′-H), 3.08 (2H, br dd, 5-,8-H$_\beta$); δ_C: 127.7 (3a-,9a-C), 113.8 (br, 2-,2′-,3a′-,7a′-C), 95.9 (OCH$_2$O), 79.4 (6-,7-C), 71.6 (2 × CH$_3$OCH$_2$CH$_2$), 67.3 (2 × CH$_3$OCH$_2$), 59.1 (2 × CH$_3$), 38.6 (5-,8-C), 30.2 (5′-,6′-C). **35**, δ_H: 4.83 (2H, s, OCH_2O), 4.10 (2H, m, 6-,7-H), 3.85–3.55 (6H, 2 × CH$_3$OCH_2CH_2 and 5-,8-H$_a$), 3.40 (3H, s, CH_3), 3.29 (4H, s, 5′-,6′-H), 2.94 (1H, dd, J = 14.5, 6.3, 5-H$_\beta$), 2.93 (1H, dd, J = 14.5, 7.2, 8-H$_\beta$); δ_C: 128.5 and 125.8 (3a-,9a-C), 113.8 (br, 2-,2′-,3a′-,7a′-C), 96.0 (OCH$_2$O), 81.8 (7-C), 72.9 (6-C), 71.6 (CH$_3$OCH$_2$CH$_2$), 68.0 (CH$_3$OCH$_2$), 59.0 (CH$_3$), 38.6 and 37.6 (5-,8-C), 30.2 (5′-,6′-C). Mass spectral data for **34–35** mixture: m/z (EI): 620 ([M$_{34}$]$^+$, 11%), 532 ([M$_{35}$]$^+$, 62), 236 (100); HRMS: 619.9650. C$_{20}$H$_{28}$O$_6$S$_8$ (=M$_{34}$) requires: 619.9652.

The mixture of **34** and **35** (0.075 g), was dissolved in THF (10 ml), cooled in an ice bath and aqueous HCl (10 ml, 20%) was

added dropwise. Stirring was continued at room temperature overnight. The mixture was cooled down to 0 °C and neutralised with solid sodium carbonate. The upper yellow THF phase was separated. The water phase was extracted with THF two more times and the THF phases were combined, dried over MgSO$_4$, filtered and the solvent was evaporated. The crude solid was recrystallised from methanol to give **5** (0.049 g, 82%), mp 170–172 °C; Found: C: 32.3, H: 2.7%. C$_{12}$H$_{12}$O$_2$S$_8$ requires C: 32.4, H: 2.7%; δ_H (THF-d$_8$): 4.60 (2H, d, J = 3.7, 2 × OH), 3.89 (2H, m, 6-,7-H), 3.64 (2H, dd, J = 14.1, 2.2, 5-,8-H$_\alpha$), 3.33 (4H, s, 5′-,6′-H$_2$), 2.86 (2H, dd, J = 14.2, 7.0, 5-,8-H$_\beta$); δ_C (THF-d$_8$): 128.0 (3a-,9a-C), 114.4 (3a′-,7a′-C), 108.4 (2-,2′-C), 74.3 (6-,7-C), 39.7 (5-,8-C), 30.9 (5′-,6′-C); ν_{max}: 3322, 1278, 1028, 888, 862, 771, 736, 723 cm^{-1}; m/z (EI): 444 (M$^+$, 3%), 416 ([M − (CH$_2$)$_2$]$^+$, 1), 88 (100); HRMS: 443.8603. C$_{12}$H$_{12}$O$_2$S$_8$ requires 443.8603; [a]$_D$: +26.6 (c = 0.15, THF).

(6R,6′R,7R,7′R)-2-(6′,7′-Dihydroxy-5′,6′,7′,8′-tetrahydro-1,3-dithiolo[4,5-b][1,4]dithiocin-2′-ylidene)-5,6,7,8-tetrahydro-1,3-dithiolo[4,5-b][1,4]dithiocine-6,7-diol 6

The mixture of **26** and **27** (0.17 g) was heated with triethyl phosphite (50 ml) to 120 °C under nitrogen for 16 h. After evaporation of the triethyl phosphite, the residue was chromatographed (methanol–ethyl acetate, 1:10) to give a red viscous oil (0.1 g). The oil was dissolved in THF (10 ml), cooled in an ice bath and aqueous HCl (10 ml, 20%) added dropwise. Stirring was continued at room temperature overnight. The mixture was cooled down to 0 °C and neutralised with sodium carbonate. The upper yellow THF phase was separated. The water phase was extracted with THF twice more and the THF phases were combined, dried over MgSO$_4$, filtered and the solvent was evaporated. The crude product was recrystallised from methanol to give **6** as a yellow powder (0.071 g, 61%), mp 227–229 °C; Found: C: 33.2, H: 3.1%. C$_{14}$H$_{16}$O$_4$S$_8$ requires C: 33.4, H: 3.2%. δ_H (THF-d$_8$): 4.60 (4H, d, J = 3.9, 4 × OH), 3.89 (4H, m, 6-,6′-,7-,7′-H), 3.65 (4H, dd, J = 14.0, 2.2, 5-,5′-,8-,8′-H$_\alpha$), 2.85 (4H, dd, J = 14.3, 6.8, 5-,5′-,8-,8′-H$_\beta$); δ_C (THF-d$_8$): 127.9 (3a-,3a′-,9a-,9a′-C), 111.1 (2-,2′-C), 74.3 (6-,6′-,7-,7′-C), 39.7 (5-,5′-,8-,8′-C); ν_{max}: 3369, 1260, 1237, 1170, 1103, 1014, 859, 806, 773, 759, 724, 699 cm^{-1}; m/z: (EI) 504 (M$^+$, 60%), 296 (C$_6$S$_7$$^+$, 100); m/z (CI) 505 (M + H$^+$, 100%); HRMS: FAB (PEG matrix) 503.8812. C$_{14}$H$_{16}$O$_4$S$_8$ requires 503.8814; [a]$_D$: +39.3 (c = 0.11, THF).

5,5a,8a,9-Tetrahydro-1,3-dithiolo[4′,5′:2,3][1,4]dithiocino[6,7-d][1,3]dioxole-2-thione 38

The crude product (1.05 g) from the reaction of ditosylate **23** with sodium iodide, which contained **24** as the main component, was distilled under vacuum (0.05 mmHg) at 110 °C. The distillate obtained (0.83 g) contained mainly *(4R,5R)-4,5-bis(iodomethyl)dioxolane* **36** and *2,5,7,10-tetraoxaundecane* **37**, whose identities are suggested by their NMR spectra and the chemical reactivity of the distillate, δ_H (**36**): 5.12 (2H, s, 2-H$_2$), 3.98 (2H, m, 4-,5-H), 3.34 (4H, m, (partially obscured), 4-,5-CH$_2$); δ_C (**36**): 94.9 (2-C), 80.2 (4-,5-C), 5.2 (4-,5-CH$_2$I); δ_H (**37**): 4.75 (2H, s, 6-H$_2$), 3.71 (4H, m, 4-,8-H$_2$), 3.56 (4H, m, 3-,9-H$_2$), 3.39 (6H, s, 1-,11-H$_3$); δ_C (**37**): 95.6 (6-C), 71.7 (4-,8-C), 66.7 (3-,9-C), 58.9 (1-,11-C). This distilled mixture of **36** and **37** (0.83 g) was mixed with the disodium salt of the dithiolate **13** (0.38 g) in dry THF (50 ml) under nitrogen at room temperature. The reaction mixture was heated to 70 °C for 12 h, and after cooling, the solvent was removed *in vacuo*, and the residue was extracted twice with dichloromethane. The organic extracts were dried over MgSO$_4$, filtered and evaporated, and the crude product recrystallised from ethanol to give **38** as a pale yellow solid (0.40 g, 86%); mp 205–207 °C; Found: C: 32.4, H: 2.8%. C$_8$H$_8$O$_2$S$_5$ requires C: 32.4, H: 2.7%; δ_H: 4.95 (2H, s, OCH_2O), 4.08 (2H, m, 6-,7-H), 3.28 (2H, dd,

J = 13.4, 3.3, 5-,8-H$_\alpha$), 2.70 (2H, dd, J = 13.4, 10.5, 5-,8-H$_\beta$); δ_C: 211.0 (2-C), 140.8 (3a-,9a-C), 94.1 (OCH$_2$O), 80.2 (6-,7-C), 36.4 (5-,8-C); ν_{max}: 1163, 1085, 1075, 1054, 1024, 1003, 975, 942, 875, 729 cm^{-1}; m/z (EI): 296 ([M]$^+$, 100%); HRMS: 295.9128. C$_8$H$_8$O$_2$S$_5$ requires: 295.9128; [a]$_D$: +92.7 (c = 0.55, CHCl$_3$).

Acknowledgements

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