New precursors for preparing organic conducting materials: synthesis of (*R*)-hydroxymethylbis(ethylenedithio)tetrathiafulvalene, and the ring expansion of a cyclic sulfate ester

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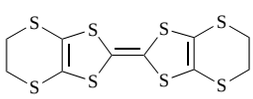
The chiral hydroxymethyl-substituted derivative of bis(ethylenedithio)tetrathiafulvalene, has been synthesized from D-mannitol *via* the cyclic sulfate ester of (2*R*)-3-(2-methoxyethoxymethoxy)propane-1,2-diol. The latter substance slowly decomposes at 45 °C and should be used when freshly prepared. In contrast, the cyclic sulfate ester of (2*R*)-3-benzoyloxypropane-1,2-diol containing a five-membered ring, undergoes clean rearrangement at room temperature to the cyclic sulfate ester of 2-benzoyloxypropane-1,3-diol, containing a six-membered ring.

The large number of radical cation salts prepared from bis(ethylenedithio)tetrathiafulvalene, 'ET', **1**,[1] have shown a



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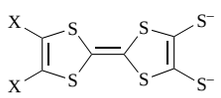
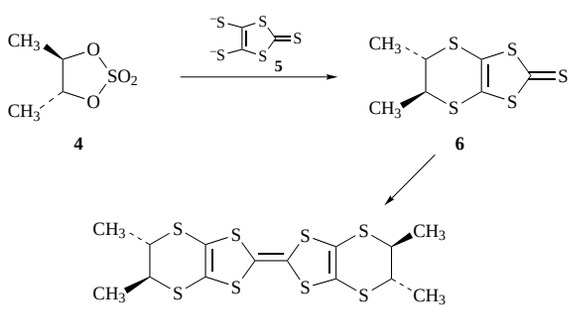


2 X = S^-
3 X,X = $-SCH_2CH_2S-$

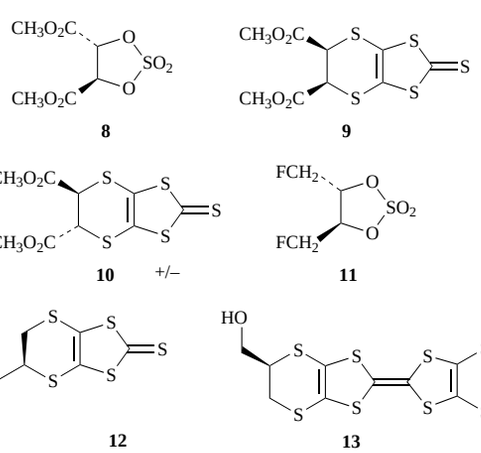
variety of electrical properties, including one-dimensional or two-dimensional, metallic or semiconducting, states at room temperature and pressure which often become insulating at lower temperatures. In some cases, however, superconducting states have been observed at temperatures below 12 K.[2] Indeed, among carbon based materials only the radical anion salts of buckminsterfullerene, C_{60},[3] have higher critical temperatures for the onset of the superconducting state. We have been preparing substituted derivatives of **1**,[4,5] and a particular focus is the inclusion of hydrogen bonding functionality to produce specific attractive interactions with the anions in the derived radical cation salts. This is designed to produce more ordered and cohesive crystalline states, and limit the problem of polymorphism encountered very commonly with the salts from ET. Attachment of a hydroxymethyl side chain is particularly attractive since it would provide a handle by which the ET unit could be attached to a polymer chain, or constructed into simpler oligomers.

Two main strategies to prepare substituted tetraalkylthio-TTF derivatives have been taken. One route is by direct alkylation of TTF-tetrathiolate **2** or a related dithiolate such as **3**, the thiolate groups having been protected in earlier synthetic steps by the use of the cyanoethyl[6] or 4-acetyloxybenzyl[7] groups or in other ways.[8] Alternatively, the same or two different 1,3-dithiol-2-ones (or -thiones) can be coupled together, with loss of two oxygen (sulfur) atoms, using triethyl phosphite. To prepare enantiopure ET derivatives carrying at least one substituent on the molecular framework, suitable chiral molecules with *vic*-leaving groups, at least one at a secondary centre, which will undergo stereospecific nucleophilic substitutions with dithiolates such as **3** or **5** are required. We have found cyclic sulfate esters to fulfil this role by reacting with dithiolate **5** and losing sulfate ion.[4] (Several other examples of such double displacement reactions of cyclic sulfate esters to form diamines and aziridines have been reported subsequently.[9,10]) Thus, the cyclic sulfate ester of (*R*,*R*)-butane-2,3-diol **4** gave stereo-



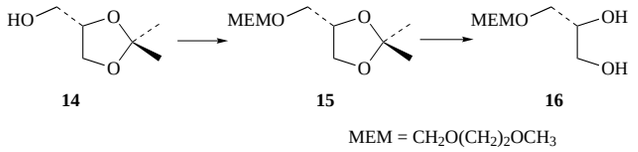
4 **5** **6** **7**

specifically the bicyclic thione **6** in 30% yield which was converted to the chiral tetramethyl-ET **7**.[4] (Reactions between cyclic sulfate esters and the di- and tetra-thiolates in which the TTF unit is already formed have not been successful.) For certain specific cyclic sulfate esters alternative products are formed with dithiolate **5**, thus **8** gave isomers **9** and **10**, and **11** gave **12**, the former two stereoisomers arising from elimination of hydrogen sulfate after the first substitution[11] and the latter product arising from substitution of the fluoride and not sulfate.[5] Here, we report the successful use of a cyclic sulfate ester to prepare the chiral hydroxymethyl-ET derivative **13**, and a novel rearrangement of cyclic sulfate esters discovered during this work.



8 **9** **10** +/– **11** **12** **13**

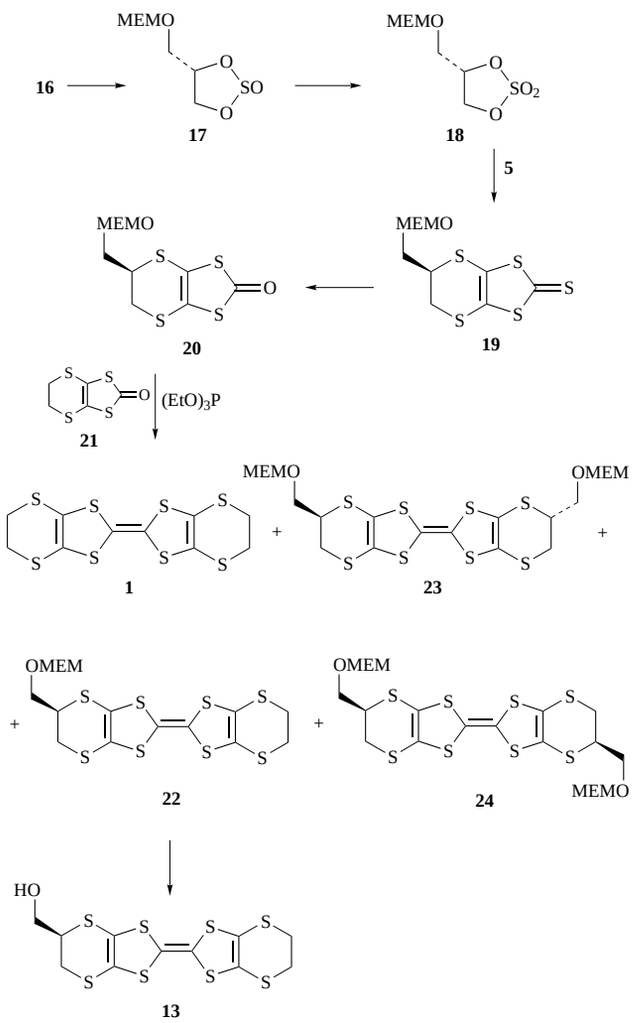
D-Mannitol was converted by known methods[12,13] to the *S*-enantiomer of the 1-*O*,2-*O*-acetonide of glycerol **14**. Reaction with 2-methoxyethoxymethyl chloride and a hindered base



14 **15** **16**

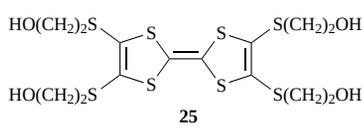
MEM = $CH_2O(CH_2)_2OCH_3$

yielded the MEM-protected material **15**, and hydrolysis of the ketal group with aqueous acetic acid gave the 1-*O*-MEM protected glycerol **16**.[14] This product was converted into its cyclic sulfite ester **17** (composed of a 2:1 mixture of diastereoisomers) by treatment with thionyl chloride and pyridine in ether at 0 °C, and purified by chromatography. Subsequent oxidation with ruthenium tetroxide, generated from sodium periodate and a catalytic quantity of ruthenium dioxide, in a vigorously stirred two phase system (dichloromethane–water) gave the corresponding cyclic sulfate ester **18** in 78% yield. The



end of this reaction is clearly indicated by a rapid colour change from brown to green after *ca.* 15 min. Although the neat product is stable at room temperature it is liable to decompose on heating; the ^{13}C NMR spectrum of a pure sample in deuteriochloroform held at 45 °C indicated some decomposition after 11 h. Nevertheless, freshly prepared material reacted successfully with the dithiolate **5** to furnish the bicyclic thione **19** in 54% yield. This latter reaction is accomplished in two stages: the first substitution on the cyclic sulfate ester **18** takes place readily at room temperature in dry methanol, but the second substitution only takes place in dry THF at 60 °C. (The solvents are removed after the first stage by room temperature evaporation.) Exchange of the exocyclic sulfur for oxygen using mercury(II) acetate gave **20**. Subsequent treatment with an excess of the unsubstituted dithiolodithiin-2-one **21** in triethyl phosphite gave a mixture of products which was separated by flash chromatography on silica (eluting with dichloromethane–ethyl acetate, 15:1) to give ET **1**, the monosubstituted ET **22** (36%), and a mixture of two disubstituted ET derivatives **23** and **24** (14%). (Most of **1** can be removed prior to chromatography due to its low solubility in chloroform.) Hydrolysis of **22** with 20% hydrochloric acid in THF gave the *R*-enantiomer of hydroxymethyl-ET, (*R*)-HMET, **13** (90%). The ^1H NMR spectrum of **13** in the presence of the chiral shift reagent (1*S*)-1-(9-anthryl)-2,2,2-trifluoroethanol, showed the presence of only one enantiomer, when compared to the corresponding spectrum for the racemic material (prepared by the same route). Interestingly the chiral and racemic modifications show significant differences in the cyclic voltammograms of acetonitrile solutions containing tetra(*n*-butyl)-ammonium hexafluorophosphate as supporting electrolyte. The oxidation peaks of the chiral material (524 and 805 mV relative to Ag/AgCl) are at higher potentials than for the racemate (515, 772 and 966 mV), and the former shows two oxidation peaks but the latter three. Further details are reported elsewhere.[15]

(*R*)-HMET, **13**, is an important intermediate for the preparation of many substituted ET derivatives, and by virtue of its chirality it will give only one stereoisomer when transformed into oligomeric and polymeric materials. Furthermore, the availability of both single enantiomers and corresponding racemic forms will allow investigation of the role of chirality in the solution electrochemistry and solid state electrical properties. Very few chiral metals have been reported.[16] Several TTF derivatives with hydrogen-bonding functionality have been prepared, for example tetrakis(hydroxyethylthio)TTF **25** which has been used as a core for the preparation of dendrimers containing several TTF molecules,[17] as well as **26**[18] and **27**.[19] However, none of these could be used to prepare chiral systems.



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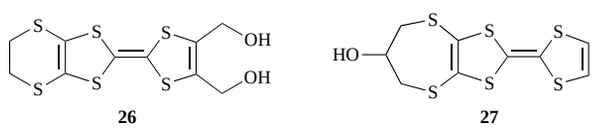
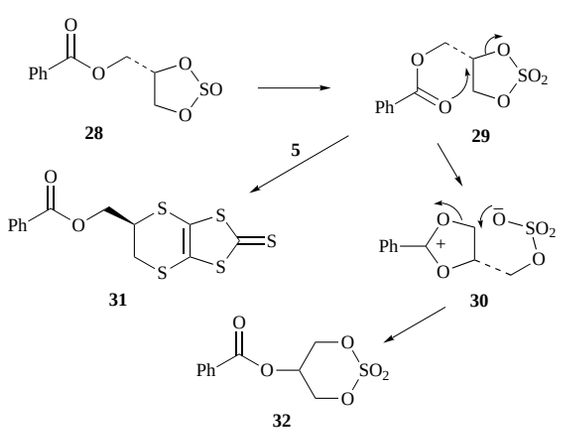


26 **27**

Five-membered cyclic sulfate esters are reasonably stable at ambient temperature, though Lowe has reported the thermal instability of phenyl substituted derivatives.[20,21] In **18**, the instability may originate from a side chain oxygen intramolecularly opening the cyclic sulfate ring. We have prepared the related cyclic sulfate ester of (2*R*)-3-benzoyloxypropane-1,2-diol **29** by oxidation of the corresponding cyclic sulfite ester **28**



with ruthenium tetroxide and found that it undergoes a clean rearrangement in chloroform at room temperature to the six-membered isomeric cyclic sulfate ester **32**. The former is characterised by signals in the ^{13}C NMR spectrum at δ 62.3, 69.5 and 79.9 for the sp^3 carbon atoms, while the latter shows just two signals at δ 63.3 and 75.6. Observation of the ^{13}C NMR spectrum in deuteriochloroform over a period of two days showed the disappearance of the first set of peaks and the appearance of the latter set. The ^1H NMR spectrum of the latter also shows a greater degree of symmetry. Nevertheless, reaction of freshly prepared cyclic sulfate ester **29** with the dithiolate **5** gave the expected thione **31**. In contrast, the six-membered cyclic sulfate ester **32** did not undergo displacement of sulfate ion by the dithiolate.

The rearrangement is proposed to proceed *via* intramolecular attack of the carbonyl O atom on the nearer ring carbon atom to give **30** which contains a dioxolanium cation and hemisulfate anion. Attack of the latter at the alternative ring sp^3 carbon atom yields the less strained cyclic sulfate ester **32**. Dioxolanium cations are well known intermediates in the reactions of carboxylic esters of 2-substituted alcohols where the substituent is a good leaving group,[22] for example in the acetolysis of the acetate of *trans*-2-tosylcyclohexanol to give the *trans*-diacetate.[23] The rearrangement reaction for the cyclic sulfate ester of (2*R*)-3-acetyloxypropane-1,2-diol proceeded with similar facility though not as cleanly.

Experimental

General

NMR Spectra were measured on a JEOL GX 270 machine at 270 MHz for ^1H and 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 $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. Flash chromatography was performed on 40–63 silica gel (Merck).

(2*R*)-3-(2-Methoxyethoxymethoxy)propane-1,2-diol 16

(4*S*)-2,2-Dimethyl-4-hydroxymethyl-1,3-dioxolane **14** was prepared from D-mannitol by protection of the terminal diol groups as their acetonides,[12] followed by cleavage with periodate and reduction with sodium borohydride as described.[13] Ketal **14** was treated with 2-methoxyethoxymethyl chloride (MEM-Cl) in dichloromethane in the presence of diisopropyl(ethyl)amine to give the corresponding MEM-protected ether **15** in almost quantitative yield as described.[14] Compound **15** (17.0 g, 77.3 mmol) was heated with 10% aqueous acetic acid (170 ml) at 60 °C for 1.5 h. After cooling, the mixture was neutralised with solid sodium carbonate, and the water removed by evaporation *in vacuo* at <50 °C. The resultant slurry was vigorously extracted with ethyl acetate (6 × 150 ml) and the combined organic fractions dried with sodium sulfate, evaporated and purified by flash chromatography on silica using hexane–ethyl acetate (5:95) as eluent (the product was observed by treatment of the TLC plate with a solution of vanillin in ethanol and sulfuric acid, and heating) to give diol **16** (8.1 g, 83%); δ_H 4.74 (2H, s, OCH_2O), 3.86 (1H, m, 2-*H*), 3.72 (2H, m, $CH_3OCH_2CH_2$), 3.63 (4H, m, 1-H_2 and 3-H_2), 3.57 (2H, m, CH_3OCH_2), 3.48 (2H, br, 2 × O*H*), 3.40 (3H, s, CH_3); δ_C 95.9 (OCH_2O), 71.8 ($CH_3OCH_2CH_2$), 70.9 (2-*C*), 69.9 (3-*C*), 67.1 (CH_3OCH_2), 63.7 (1-*C*), 58.9 (CH_3).

(2*R*,4*S*)-and(2*S*,4*S*)-4-(2-Methoxyethoxymethoxymethyl)-1,3,2-dioxathiolane 2-oxide 17

A stirred solution of diol **16** (4.8 g, 27 mmol) and pyridine (6.4 g, 81 mmol) in dry THF at 0 °C under a nitrogen atmosphere was treated dropwise with thionyl chloride (3.2 g, 31 mmol) and left to warm to room temperature over 8 h. After evaporation of the THF, the residue was partitioned between dichloromethane and water, the organic layer separated and the aqueous later was extracted twice more. The combined organic phase was washed with 0.5 M hydrochloric acid, water and brine, and dried over sodium sulfate. Chromatography of the evaporated solution using hexane–ethyl acetate (1:1) gave the product **17** (3.2 g, 53%), a colourless oil, as two diastereoisomers in the ratio 2:1 (Found: C, 36.9; H, 6.4. $C_7H_{14}SO_6$ requires C, 37.2; H, 6.2%), δ_H: major isomer 5.11 (1H, m, 4-*H*), 4.74 (2H, s, OCH_2O), 4.72 (1H, dd, *J* 8.5, 6.6, 5α-*H*), 4.32 (1H, dd, *J* 8.5, 5.2, 5β-*H*), 3.69 (4H, m, 4-CH_2 and $CH_3OCH_2CH_2$), 3.55 (2H, m, CH_3OCH_2), 3.39 (3H, s, OCH_3); minor isomer 4.72 (2H, s, OCH_2O), 4.69 (1H, m, 4-*H*), 4.56 (2H, m, 5-H_2), 3.92 (2H, m, 4-CH_2), 3.69 (2H, m, $CH_3OCH_2CH_2$), 3.55 (2H, m, CH_3OCH_2); δ_C(67.8 MHz, $CDCl_3$): major isomer 95.9 (OCH_2O), 78.6 (4-*C*), 71.7 ($CH_3OCH_2CH_2O$), 68.7 (5-*C*), 67.3 (CH_3OCH_2), 66.4 (4-CH_2), 59.0 (CH_3); minor isomer 95.8 (OCH_2O), 81.3 (4-*C*), 71.7 ($CH_3OCH_2CH_2O$), 69.0 (5-*C*), 67.3 (CH_3OCH_2), 67.8 (4-CH_2), 59.0 (CH_3); ν_{max}/cm^{-1} 1455, 1367, 1282, 1209, 1176, 1043, 966, 846, 749, 672; *m*/*z* (CI) 244 ($[M + NH_4]^+$, 100%), 227 ($[M + H]^+$, 10).

(4*S*)-4-(2-Methoxyethoxymethoxymethyl)-1,3,2-dioxathiolane 2,2-dioxide 18

A solution of cyclic sulfite ester **17** (2.00 g, 8.84 mmol) in dichloromethane (20 ml) containing ruthenium dioxide (5 mg) was stirred vigorously with aqueous sodium periodate (3.80 g, 17.7 mmol) at room temperature. After 15 min the brown mixture suddenly turned to pale green. The organic layer was separated, and stirred with several drops of propan-2-ol for 15 min. After drying with sodium sulfate, the solution was filtered through a pad of Celite, and the colourless solution evaporated *in vacuo* at room temperature to give the cyclic sulfate ester **18** (1.68 g, 78%) as an oil (Found: C, 34.6; H, 5.8. $C_7H_{14}O_7S$ requires C, 34.7; H, 5.8%), δ_H 5.14 (1H, m, 4-*H*), 4.76 (1H, dd, *J* 8.8, 7.6, 5α-*H*), 4.76 (2H, s, OCH_2O), 4.63 (1H, dd, *J* 8.8, 7.1, 5β-*H*), 3.88 (2H, d, AB system, *J* 11.2, 4.0, 4-CH_2), 3.71 (2H, m, $CH_3OCH_2CH_2$), 3.55 (2H, m, CH_3OCH_2), 3.39 (3H, s, CH_3); δ_C 95.9 (OCH_2O), 80.0 (4-*C*), 71.7 ($CH_3OCH_2CH_2$), 69.8 (5-*C*), 67.5 (CH_3OCH_2), 65.6 (4-CH_2), 59.0 (CH_3); ν_{max}/cm^{-1} 2894, 1454, 1386, 1210, 1178, 1123, 1044, 982, 822, 650; *m*/*z* (CI) 260 ($[M + 18]^+$, 100%); $[\alpha]_D$ −8.1 (*c* 0.8 in CH_2Cl_2).

(5*R*)-5,6-Dihydro-5-(2-methoxyethoxymethoxymethyl)[1,3]-dithiolo[4,5-*b*][1,4]dithiine-2-thione 19

A solution of disodium 2-thioxo-1,3-dithiole-4,5-dithiolate[24] **5** (1.60 g, 6.6 mmol) in dry methanol (30 ml) under a nitrogen atmosphere was treated with cyclic sulfate ester **18** (1.60 g, 6.6 mmol) at room temperature. The deep purple solution turned orange–red over several minutes, and the mixture stirred at room temperature overnight. The solvent was removed *in vacuo* at room temperature, and replaced with dry THF, and the solution heated to 60 °C for 36 h. The mixture was filtered and the solids washed with further THF, and the combined filtrates evaporated. The residue was partitioned between dichloromethane and water, the organic layer separated, and washed again with water, and dried with sodium sulfate. Chromatography on silica using dichloromethane eluted the product **19** (1.23 g, 54%) as a reddish oil (Found: C, 34.9; H, 4.1. $C_{10}H_{14}O_3S_5$ requires C, 35.1; H, 4.1%), δ_H 4.76 (2H, s, OCH_2O), 3.92 (2H, m, 5-CH_2), 3.78 (1H, m, 5-*H*), 3.71 (2H, m, $CH_3OCH_2CH_2$), 3.57 (2H, m, CH_3OCH_2), 3.40 (3H, s, CH_3), 3.35 (2H, d, *J* 4.8, 6-H_2); δ_C 207.8 (2-*C*), 123.5 and 122.2 (3a-, 7a-*C*), 95.9 (OCH_2O), 71.7 ($CH_3OCH_2CH_2$), 68.8 (5-CH_2), 67.4 (CH_3OCH_2), 59.0 (CH_3), 42.9 (5-*C*), 31.3 (6-*C*); ν_{max}/cm^{-1} 2920, 2881, 2813, 1486, 1450, 1409, 1265, 1199, 1168, 1112, 1062, 952, 919, 894, 848, 736, 705; *m*/*z* (CI) 343 ($[M + 1]^+$,

60%), 236 ([M − $C_4H_{10}O_3$]$^+$, 55), 234 ([M − CS_3]$^+$, 90), 94 (98), 89 ([$C_4H_9O_2$]$^+$, 100); [*a*]$_D$ +129.9 (*c* 2.25 in CH_2Cl_2).

(5*R*)-5,6-Dihydro-5-(2-methoxyethoxymethoxymethyl)[1,3]-dithiolo[4,5-*b*][1,4]dithiin-2-one 20

Acetic acid (6 ml) and mercury(II) acetate (0.72 g, 2.2 mmol) were added to a solution of thione **19** (300 mg, 0.88 mmol) in chloroform (25 ml) and the mixture stirred at room temperature for 1 h. After 5 min the reaction mixture changed from yellow to almost colourless. After filtration of solids, the solution was extracted with aqueous sodium hydrogen carbonate twice, washed with water and dried over sodium sulfate. Chromatography on silica using hexane–ethyl acetate (1:1) as eluent gave the desired product **20** (256 mg, 89%) as a pale yellow–orange oil; δ_H 4.77 (2H, s, OCH_2O), 3.96 (1H, dd, *J* 13.1, 7.8, 5-CH_α), 3.96 (1H, m, 5-*H*), 3.80 (1H, dd, *J* 13.1, 7.8, 5-CH_β), 3.73 (2H, m, $CH_3OCH_2CH_2O$), 3.58 (2H, m, CH_3OCH_2), 3.40 (1H, dd, *J* 13.1, 3.0, 6-H_α), 3.40 (3H, s, CH_3), 3.33 (1H, dd, *J* 13.5, 5.1, 6-H_β); δ_C 188.7 (2-*C*), 114.0 and 112.9 (3a-, 7a-*C*), 95.9 (OCH_2O), 71.7 ($CH_3OCH_2CH_2$), 68.9 (5-CH_2), 67.3 (CH_3OCH_2), 59.0 (CH_3), 44.7 (5-*C*), 32.6 (6-*C*); ν_{max}/cm^{-1} 1679, 1623, 1506, 1457, 1199, 1168, 1114, 1095, 1045, 983, 952, 919, 890, 867, 763 (Found: M$^+$, 325.9775. $C_{10}H_{14}O_4S_4$ requires *M*, 325.9776); [*a*]$_D$ +95.2 (*c* 2.1 in CH_2Cl_2).

(5*R*)-5,6-Dihydro-2-(5′,6′-dihydro[1,3]dithiolo[4,5-*b*][1,4]-dithiin-2′-ylidene)-5-(2-methoxyethoxymethoxymethyl)[1,3]-dithiolo[4,5-*b*][1,4]dithiine 22

A mixture of compounds **20** (0.82 g, 2.5 mmol) and **21** (0.60 g, 3.0 mmol) and freshly distilled triethyl phosphite (15 ml) were warmed to 70 °C under nitrogen for 5 h during which time a precipitate of **1** was produced. The triethyl phosphite was distilled off *in vacuo* and the residue treated with dichloromethane (10 ml) and filtered. The filtrate was evaporated and separated into its components by chromatography on silica eluting with dichloromethane–ethyl acetate (15:1), to give ET, **1**, (total yield 0.16 g, 28%), followed by **22** (0.45 g, 36%) as an orange solid, mp 56–58 °C (Found: C, 35.6; H, 3.3. $C_{15}H_{18}O_3S_8$ requires C, 35.8; H, 3.6%), δ_H(CD_2Cl_2) 4.71 (2H, s, OCH_2O), 3.85 (2H, m, 5-CH_2), 3.69 (3H, m, 5-*H* and CH_3OCH_2-CH_2O), 3.51 (2H, m, CH_3OCH_2), 3.33 (3H, s, CH_3), 3.30 (4H, s, 5′- and 6′-H_2), 3.24 (2H, m, 6-H_2); δ_C(CD_2Cl_2) 115.0 and 114.1 (3a-, 7a-*C*), 114.4 (3a′-, 7a′-*C*), 112.0 and 111.7 (2-, 2′-*C*), 96.2 (OCH_2O), 72.2 ($CH_3OCH_2CH_2$), 69.4 (5-CH_2), 67.7 (CH_3OCH_2), 59.0 (CH_3), 44.1 (5-*C*), 32.8 (6-*C*), 30.8 (5′-, 6′-C); ν_{max}(evaporated film)/cm^{-1} 2922, 2886, 2813, 1457, 1406, 1285, 1212, 1197, 1167, 1110, 1093, 1043, 1032, 984, 773; *m*/*z* (EI) 502 ([M]$^+$, 12%), 356 ([M − $C_7H_{14}O_3$]$^+$, 8), 208 (10), 192 (9), 132 (14), 88 (46), 59 (48), 45 (100); [*a*]$_D$ +34.4 (*c* 0.75 in CH_2Cl_2).

Further elution of the column gave, as an orange oil (0.01 g, 14%), a 2:1 mixture of isomers **23** and **24** (or *vice versa*), to each of which the NMR data cannot be unambiguously assigned. δ_H(CD_2Cl_2) 4.64 and 4.43 (4H, 2 × s, OCH_2O), 3.77 (4H, m, CHCH_2O), 3.60 (6H, m, $CH_3OCH_2CH_2$ and SC*H*), 3.44 (4H, m, CH_3OCH_2), 3.27 and 3.26 (6H, 2 × s, CH_3), 3.17 and 3.15 (4H, 2 × s, SCH_2); δ_C(CD_2Cl_2) 114.99, 114.14 and 114.08 (3a-, 3a′-, 7a-, 7a′-*C*), 112.02 (2-, 2′-*C*), 96.25 (OCH_2O), 72.17 ($CH_3OCH_2CH_2O$), 69.44 (CHCH_2O), 67.10 (CH_3OCH_2), 59.06 (CH_3), 44.13 and 44.10 (S*C*H), 32.81 (SCH_2); *m*/*z* (EI) 620 (M$^+$, 100%), 576 (25), 476 (28), 474 (60), 327 (20) (Found: M$^+$, 619.9650. $C_{20}H_{28}O_6S_8$ requires *M*, 619.9653).

(5*R*)-5,6-Dihydro-2-(5′,6′-dihydro[1,3]dithiolo[4,5-*b*][1,4]-dithiin-2′-ylidene)[1,3]dithiolo[4,5-*b*][1,4]dithiine-5-methanol 13

A solution of **22** (0.15 g, 0.3 mmol) in THF (10 ml) was stirred with 20% aqueous HCl (10 ml) overnight at room temperature. The mixture was neutralised with solid sodium carbonate, the upper organic layer separated and the solvent evaporated. Recrystallisation of the residue from ethanol gave **13** (0.10 g, 83%), fawn solid, mp 138 °C (decomp.) (Found: C, 31.9; H, 2.5. $C_{11}H_{10}OS_8$ requires C, 31.9; H, 2.4%); δ_H(400 MHz) 3.70–3.90 (3H, m, 5-CH_2 and 5-*H*), 3.28 (4H, s, 5′-, 6′-H_2), 3.27 (1H, dd, *J* 13.4, 3.6, 6-H_α), 3.21 (1H, dd, *J* 13.4, 5.5, 6-H_β), 1.58 (1H, br, O*H*); δ_C(100 MHz) 113.80, 113.73 and 113.70 (3a-, 7a-, 3a′-, 7a′-*C*), 112.06 and 111.30 (2-, 2′-*C*), 63.85 (5-CH_2), 45.47 (5-*C*), 31.72 (6-*C*), 30.05 6′-*C*); *m*/*z* (CI) 415 [M$^+$ + 1]; (FAB) 414; ν_{max}(Nujol)/cm^{-1} 3150–3550 (OH); [*a*]$_D$ +72 (*c* 0.08 in THF). The product should be stored under nitrogen to prevent oxidation.

(2*R*,4*S*)- and (2*S*,4*S*)-4-Benzoyloxymethyl-1,3,2-dioxathiolane 2-oxide 28

Dry pyridine (3.3 g, 42 mmol) was added to a stirred solution of (2*R*)-3-benzoyloxypropane-1,2-diol (4.2 g, 21 mmol) (prepared as described[13]) in dry THF (50 ml) and the mixture cooled to 0 °C, and a solution of thionyl chloride (2.8 g, 23 mmol) in dry diethyl ether (30 ml) added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 6 h. The mixture was filtered and the solids washed with further diethyl ether. The combined organic phase was evaporated and the residual oil dissolved in dichloromethane (50 ml), washed with water (15 ml), dilute hydrochloric acid (0.5 M, 15 ml) and dried over magnesium sulfate. Evaporation of the solvent and chromatography on silica eluting with dichloromethane gave the product **28**, as a mixture of two diastereoisomers, as a colourless oil (3.11 g, 61%) (Found: C, 49.7; H, 4.1. $C_{10}H_{10}O_5S$ requires C, 49.6; H, 4.2%), δ_H 8.04 (2H, m, 2′-, 6′-*H*), 7.54 (1H, m, 4′-*H*), 7.41 (2H, m, 3′-, 5′-*H*), 5.25 (1H, m, 4-*H*), 4.87–4.36 (4H, m, 5-H_2 and 4-CH_2); δ_C 165.87 and 165.85 (*C*=O), 133.49 and 133.42 (4′-*C*), 129.77 and 129.68 (2′-, 6′-*C*), 129.24 and 129.16 (1′-*C*), 128.54 and 128.49 (3′-, 5′-*C*), 80.31 and 78.12 (4-*C*), 68.47 and 68.02 (5-*C*), 63.09 and 62.91 (5-CH_2); ν_{max}(Nujol)/cm^{-1} 1718, 1602, 1452, 1384, 1316, 1276, 1212, 1120, 1070, 1028, 974, 950, 870, 828, 712; *m*/*z* (CI) 260 ([M + NH_4]$^+$, 100%), 179 (55), 105 (82).

(4*S*)-4-Benzoyloxymethyl-1,3,2-dioxathiolane 2,2-dioxide 29

A solution of **28** (5.6 mmol) in dichloromethane (5 ml) at 0 °C was vigorously stirred with ruthenium dioxide (10 mg) and a solution of sodium periodate (11 mmol) in water (10 ml) for 2 h. The organic layer was stirred with propan-2-ol (1 ml) for 15 min, dried over $MgSO_4$, filtered and evaporated to give **29** (42%), as a colourless oil; δ_H 8.02 (2H, d, *J* 7.8, 2′-, 6′-*H*), 7.54 (1H, t, *J* 7.3, 4′-*H*), 7.39 (2H, t, *J* 7.5, 3′-, 5′-*H*), 5.28 (1H, m, 4-*H*), 4.84 (1H, m, 5-H_α), 4.65 (1H, dd, *J* 12.0, 2.7, 4-CH_α), 4.52 (1H, dd, *J* 12.9, 4.6, 4-CH_β), 4.40 (1H, m, 5-H_β); δ_C 166.0 (*C*=O), 133.8 (4′-*C*), 129.8 (4′-*C* and 2′-, 6′-*C*), 128.6 (3′-, 5′-*C*), 79.8 (4-*C*), 69.5 (5-*C*), 62.3 (4-CH_2O). This material steadily rearranged to the isomer **32**.

(5*R*)-5-Benzoyloxymethyl-5,6-dihydro[1,3]dithiolo[4,5-*b*][1,4]-dithiine-2-thione 31

A solution of freshly prepared cyclic sulfate ester **29** (0.85 g, 3.3 mmol) in dry THF (20 ml) was added dropwise over 30 min to a stirred mixture of the disodium salt of dithiolate **5** (0.80 g, 3.3 mmol) in dry THF (10 ml) at 0 °C under nitrogen. After being left to warm to room temperature, the reaction mixture was refluxed for 12 h. The solvent was evaporated, the residue dissolved in dichloromethane, washed with water (3 × 20 ml) and dried over magnesium sulfate. Purification by chromatography on silica eluting with hexane–ethyl acetate (1:1) gave **31** as a yellow solid (0.30 g, 25%), mp 124–125 °C (from acetonitrile), δ_H(400 MHz, CD_2Cl_2) 8.06 (2H, dd, *J* 8.3, 1.3, 2′-, 6′-*H*), 7.64 (1H, tt, *J* 7.4, 1.7, 4′-*H*), 7.51 (2H, br t, *J* 7.7, 3′-, 5′-*H*), 4.67 (1H, dd, *J* 11.4, 7.9, 5-CH_α), 4.62 (1H, dd, *J* 11.4, 6.2, 5-CH_β), 4.19 (1H, m, 5-*H*), 3.49 (1H, dd, *J* 13.6, 3.2, 6-H_α), 3.42 (1H, dd, *J* 13.6, 5.8, 6-H_β); δ_C(100 MHz, CD_2Cl_2) 207.3 (*C*=S), 165.0 (*C*=O), 132.8 (4′-*C*), 128.9 (2′-, 6′-*C*), 128.6 (1′-*C*), 127.8 (3′-, 5′-*C*), 122.4 and 121.9 (3a-, 7a-*C*), 64.0 (CH_2O), 41.1

(5-*C*), 32.0 (6-*C*); *m*/*z* (EI) 358 (M^+, 20%), 236 ([M − $PhCO_2H]^+$, 25), 160 ([M − $PhCO_2H$ − $CS_2]^+$, 25), 120 (22), 105 (C_6H_5CO, 100); (CI) 359 ([M + H]$^+$, 100%); $[a]_D$ +48.8 (*c* 0.023 in CH_2Cl_2).

5-Benzoyloxymethyl-1,3,2-dioxathiane 2,2-dioxide 32

A chloroform solution of freshly prepared cyclic sulfate ester **29** was left at 37 °C for 48 h, after which time a ^{13}C NMR spectrum of a sample revealed that the rearrangement was complete. Evaporation of solvent gave the new cyclic sulfate ester **32** as white plates, mp 109–110 °C (Found: C, 46.2; H, 3.7. $C_{10}H_{10}O_6S$ requires C, 46.5; H, 3.9%); δ_H(270 MHz, CD_2Cl_2) 8.11 (2H, dd, *J* 8.3, 1.5, 2′-, 6′-*H*), 7.65 (1H, tt, *J* 7.4, 1.6, 4′-*H*), 7.50 (2H, t, *J* 7.5, 3′-, 5′-*H*), 5.20 (1H, tt, *J* 1.9, 1.6, 5-*H*), 5.10 (2H, ddd, *J* 13.2, 3.3, 1.9, 4-, 6-H_α), 4.78 (2H, ddd, *J* 12.9, 3.1, 1.5, 4-, 6-H_β); δ_C(67.8 MHz, CD_2Cl_2), 165.8 (*C*=O), 134.4 (4′-*C*), 130.3 (2′-, 6′-*C*), 130.0 (1′-*C*), 129.1 (3′-, 5′-*C*), 75.6 (4-, 6-*C*), 63.3 (5-*C*); *m*/*z* (CI) 259 ([M + 1]$^+$, 100%), 105 ([$C_6H_5CO]^+$, 40); ν_{max}-(evaporated film)/cm^{-1} 1708, 1452, 1394, 1276, 1196, 1122, 1108, 896, 884, 824, 710. (Small vicinal H,H coupling constants have also been observed in the ^1H NMR spectra of 5-hydroxydioxane and its benzoate ester.[25])

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