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Short Intermolecular S...S Contacts in a Reaction Product from the Cyclic Sulfate Ester of Dimethyl *L*-Tartrate and 2-Thioxo-1,3--dithiole-4,5-dithiolate.

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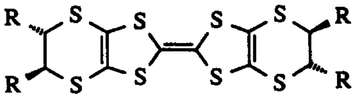
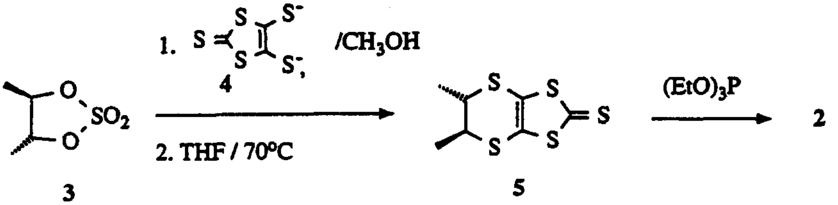
Abstract. Cyclic sulfate ester **6** reacts readily with dithiolate **4** to give *meso* and *dl* cyclic products **8** and **9**. The crystal structure of **9** shows two short S...S intermolecular interactions (< 3.4 Å) between trithiocarbonate groups, due to cooperative polarisations and the highly asymmetric shape of the bonded S atom. The latter effect is mainly responsible for the 'short' S...S contacts in ET's radical cation salts. In contrast to similar systems, the sp^3 C atoms of the six-membered ring in **9** are displaced to the *same* side of the dithiole plane.

Crystals of a range of radical cation salts of the polysulfur heterocycle "ET" **1** show superconductivity at very low temperatures, for example the κ-phase of the salt $\mathbf{1}_2$(Cu[N(CN)$_2$]Br) is superconducting from 0 to 12.8 K[1]. The appearance of superconductivity is controlled by the lattice vibrations in the material. In many of the radical cation salts of **1** and other simple derivatives, e.g. **2**[2], the solid-state packing arrangement is determined primarily by the organic cations, with the anions filling up holes bounded by the alkane portions of cations. There can be only weak electrostatic attractions between the anions and cations (whose charge is delocalised over eight sulfur atoms), and highly symmetrical anions tend to be disordered which inhibits



1 R = H
2 R = CH$_3$

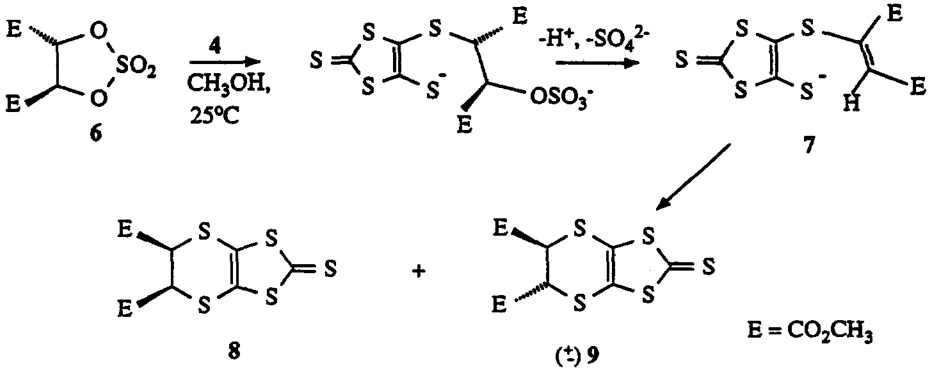
the development of the superconducting state. To produce more cohesive packing arrangements we are aiming to synthesize ET analogues capable of making specifically directed attractive interactions with the anions in their radical cation salts, for example utilising hydrogen bonding. This will promote a far better ordering of the solid-state packing. Earlier, we synthesized **2** by the reaction of the dithiolate **4** with the cyclic sulfate ester of 2*R*,3*R*-butane-2,3-diol **3**, to give **5** stereoselectively, followed by a coupling reaction (*Scheme 1*)[2]. We now report the results of extending this chemistry to the reaction of the dianion **4** with **6**, the cyclic sulfate ester of readily available dimethyl *L*-tartrate, with the goal of preparing ET derivatives bearing carboxylic acid substituents.



Scheme 1

RESULTS AND DISCUSSION

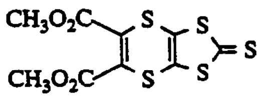
Cyclic sulfate ester **6** is much more reactive than **3** to the dianion **4**, producing cyclic products at room temperature in methanol (containing ammonium acetate), rather than requiring subsequent refluxing in THF, and in higher yield. However, the reaction is no longer stereospecific producing both *meso* and *dl* isomers **8** and **9** in the ratio 1 : 3. The latter have very similar chromatographic behaviours. An X-ray crystal structure on the material moving slightly faster on flash chromatography (silica, hexane/dichloromethane 1:3) showed it to be the racemic *trans* isomer **9**.



Scheme 2

The lack of stereospecificity in the reaction of **4** with **6** is probably due to initial ring opening of the cyclic sulfate ester by attack of the dianion (as observed for attack of a single nucleophile[3]) being followed by elimination of HSO_4^- to give the alkene **7**. The second thiolate then adds to **7** either with *trans* protonation to give **8**, or with *cis* protonation to give **9** (*Scheme 2*). Thus, the chemistry of **6** shows some similarity to that of dimethyl but-2-ynedioate (which adds two equivalents of thiols[4]), and both compounds produce the same product, **12**, with thiourea. Indeed, this alkyne reacts with **4** to give **8** and **9**.

Attempts to produce analogues of ET bearing carboxylate substituents from **8** and **9** either by self-coupling or by mixed couplings with **13** (e.g. using $(EtO)_3P$ or $Co_2(CO)_8$) have been unsuccessful to date. When the reaction of **4** with **6** was carried out in air and in the absence of ammonium acetate, a third product **10** was isolated in 15% yield. Indeed, treatment of a mixture of **8** and **9** with DDQ in refluxing THF led to partial conversion to **10**. However, attempts to couple this material to produce the unsaturated ET analogue **11** have also been unsuccessful. In a previous report **10** (prepared from C_6S_{10} (a product of oxidative dimerisation of **4**), dimethyl but-2-ynedioate and tributyl phosphine) was converted to its ketone analogue but on treatment with triethyl phosphite[5] this gave tetra(ethylthio)tetrathiafulvalene and not **11**.



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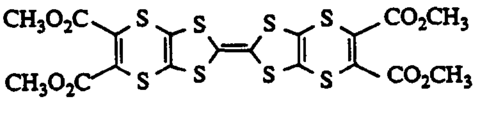

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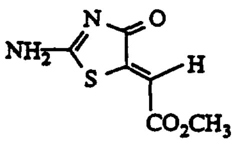

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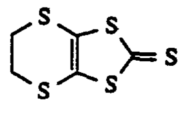

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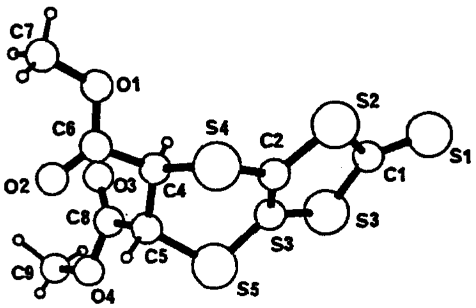


Figure 1. Structure of 9, molecule A, with atomic numbering scheme (PLUTON[20]).

Table. Selected geometry for 9, molecules A and B, distances in Å and angles in °.

Bond	A	B	Angle	A	B
S(1)-C(1)	1.635(4)	1.637(4)	C(1)-S(2)-C(2)	96.9(2)	96.9(2)
S(2)-C(1)	1.736(4)	1.724(3)	C(1)-S(3)-C(3)	97.0(2)	96.9(2)
S(2)-C(2)	1.728(3)	1.731(4)	C(2)-S(4)-C(4)	94.6(2)	95.0(2)
S(3)-C(1)	1.725(3)	1.742(4)	C(3)-S(5)-C(5)	103.0(2)	104.1(2)
S(3)-C(3)	1.728(4)	1.737(3)	S(2)-C(1)-S(3)	113.0(2)	113.0(2)
S(4)-C(2)	1.740(4)	1.745(3)	S(2)-C(2)-C(3)	116.3(3)	117.0(3)
S(4)-C(4)	1.829(3)	1.829(4)	S(4)-C(2)-C(3)	121.1(3)	122.6(3)
S(5)-C(3)	1.740(3)	1.738(4)	S(3)-C(3)-C(2)	116.6(3)	115.9(3)
S(5)-C(5)	1.835(4)	1.844(3)	S(5)-C(3)-C(2)	123.7(3)	125.2(3)
C(2)-C(3)	1.347(4)	1.344(4)	S(4)-C(4)-C(5)	114.4(2)	114.1(3)
C(4)-C(5)	1.523(4)	1.500(5)	S(5)-C(5)-C(4)	114.5(2)	115.4(3)

In the crystal structure of **9**, the asymmetric unit contains two independent molecules (A & B) which adopt similar conformations. The molecular structure of A is shown in *Figure 1*, and selected molecular geometry for both A and B is given in the *Table*. The out of plane displacements of the two ring sp^3 C atoms in **9** are substantially larger than those in **13** or in radical cation salts of ET. Furthermore, these two atoms lie to the *same* side of the best plane through the other seven atoms of the fused ring system (the 'ring plane') with C(4) displaced further out of this plane than C(5) (A, C(4): 1.477(3), C(5): 1.159(3) Å; B C(4): 1.351(3), C(5): 0.960(4) Å). The ring is twisted about the C(4)-C(5) bond so that the endocyclic torsion angle is 36.8(3)° (A) or -44.2(3)° (B) . The H atoms at C(4) and C(5) are oriented almost *antiperiplanar*, while the ester groups lie *gauche* to one another (torsion angles C(6)-C(4)-C(5)-C(8): A: -75.5(3), B: 68.7°). The planes of the two ester groups lie at 88.7(2)° (A) or 78.4(3)° (B) to each other. An unusual feature is the significant difference in the angles at S in the six-membered rings, the angles at S(5) are 8-10° larger than those at S(4). This style of conformation is only rarely seen in ET's radical cation salts, though it does occur for one ring of ET[6]. The unsubstituted analogue **13** adopts an envelope conformation.[7] For the *trans* 5,6-dimethyl analogue **5** the two sp^3 C atoms of the six-membered ring are displaced to opposite sides of the molecular plane, though by smaller amounts (ca. 0.6 & -0.2 Å), and both methyl groups take up pseudoequatorial positions[8]. Similar conformations are seen in the radical cation salts of **2**[9].

The molecules of **9** are packed together in stacks, each of which is composed of molecules A and B packed alternately (*Figure 2*). Neighbours within a stack are enantiomers, but their conformations are not symmetry related. Between stacks there are two sets of close interactions, (**a**) and (**b**), (*Figure 3*). These

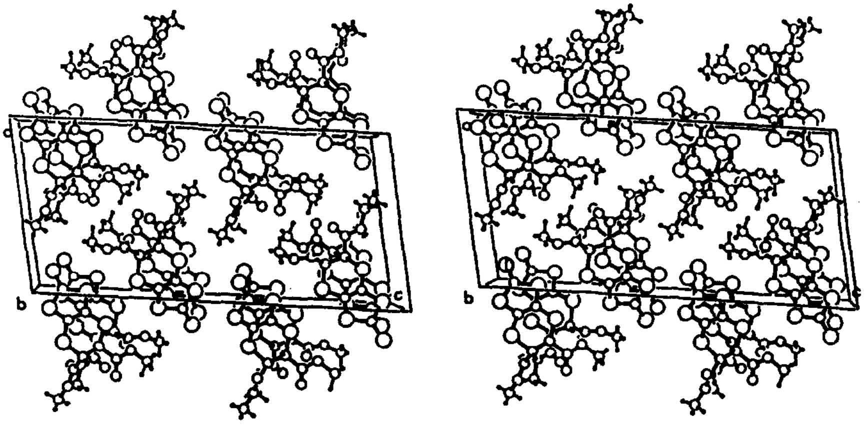


Figure 2. Stereoview of molecular packing of 9 along the b axis (PLUTON[20])

include two especially short S...S contacts, S(1A)...S(3A,-x,1-y,-z) 3.356(2) Å, and S(3A)...S(2B,-x,1-y,-z) 3.394(2) Å, which are significantly less than that (3.6 Å) predicted from traditional Van der Waals radii[10]. Interaction (**a**) between centrosymmetrically related A molecules may be accounted for by cooperative polarisations of the trithiocarbonate groups, the thiocarbonyl S atoms receiving electron density from the ring S(3A) atoms leaving these atoms with slight negative and positive charges respectively. Interaction (**b**), between molecules A and B in neighbouring stacks can be explained in the same way (S(1A)...S(2B) 3.735(2) Å, S(3A)...S(1B) 3.694 Å), however the molecules are pushed further past one another than in (**a**)

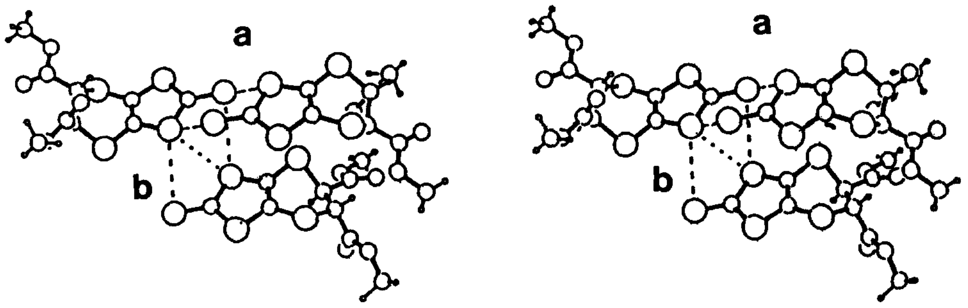
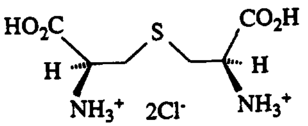


Figure 3. Stereoview[20] of short intermolecular interactions in the crystal structure of 9. Upper two molecules are both type A and the lower molecule is type B. Interaction (a) between A molecules, S...S 3.356 Å. Interaction (b) between left hand A molecule and the B molecule, shortest S...S contact, 3.394 Å, indicated by dotted line, for two dashed lines S...S contacts are 3.694 & 3.735 Å.

so that the shortest contact is between the ring S atoms. Support for these polarisations is found in the asymmetry in the bond lengths from ring S atoms to C(1) in molecules A and B: those bonds involved in polarisations are shorter than those that are not, i.e. S(3A)-C(1A) < S(2A)-C(1A) (by 0.011 Å) and S(2B)-C(1B) < S(3B)-C(1B) (by 0.018 Å). Short intermolecular S...S contacts have been observed before in both a 1,3-dithiole-2-thione[11] and a 1,2-dithiole-3-thione[12]. An analogy for the very short contact between ring S atoms in interaction (**b**) is found in *meso*-lanthionine dihydrochloride **14**[13]. The mutual orientation of neighbouring sulfide groups in crystalline 14 is shown in *Figure 4*, and resembles that between atoms S(3A) and S(2B) in interaction (**b**). Sulfur atoms in thioether groups can be described as having one lone pair occupying an orbital of high *p* character whose axis lies perpendicular to the plane of the CSC group, and an in-plane lone pair which has substantial *s* character and is therefore concentrated nearer to the S atom. Intermolecular interactions between in-plane S lone pairs are minimised in the C_{2h} arrangement shown in *Figure 4*, and the S atoms can approach one another closer than when the interaction involves two *p*-type lone pairs. The latter corresponds more closely to the traditional van der Waals radius of sulfur ca. 1.8 Å. Similarly, a survey of crystallographic data for intermolecular contacts between thiocarbonyl S atoms has indicated that this type of bonded sulfur atom has a larger effective shape perpendicular to the plane of the thiocarbonyl group than in the plane[14]. Short S...S contacts in radical cation salts of "ET" 1 are not necessarily indicators of specific attractions between molecules but rather a manifestation of the asymmetric shape of the bonded S atom[15]. A common feature of the (> 200) crystal structures of these radical cation salts is the occurrence of short side-to-side intermolecular S...S contacts (3.3-3.6 Å), while intermolecular face-to-face contacts are 'normal' (ca. >3.6 Å). However, the former involve interactions between the *s*-type sulfur lone pairs and the latter involve interactions between the *p*-type lone pairs. Great care needs to be taken in using traditional van der Waals radii as reference points for determining 'short' interactions. These radii were proposed nearly thirty years ago[10] on the basis of a limited set of crystallographic data. Furthermore, for some atoms at least, the assumption of spherical bonded atoms is not correct. This latter point was noted at the time[10] but has often been overlooked.



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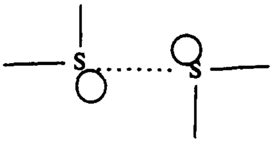

Figure 4. Mutual orientation of neighbouring sulfide groups in 14

EXPERIMENTAL

General. Melting points were measured on a Gallenkamp apparatus and are uncorrected. NMR spectra were recorded on a JEOL GX270 at 270 MHz (^{1}H) and 67.8 MHz (^{13}C), reported in δ relative to TMS, and using $CDCl_3$ as solvent unless otherwise stated. Infra-red spectra were recorded on a Perkin-Elmer 683 spectrometer. All solvents were dried before use.

Preparation of the meso and dl stereoisomers of Dimethyl 2-Thioxo-5,6-dihydro-1,3-dithiolo[4,5-b]dithiin-5,6-dicarboxylates, 8 and 9.

Dimethyl 4*R*,5*R*-2,2-dioxo-1,3,2-dioxathiolane-4,5-dicarboxylate[16] **6** (0.28 g, 1.2 mmol) was added to a solution of the disodium salt of 2-thioxo-1,3-dithiole-4,5-dithiolate[17] **4** (0.30 g, 1.2 mmol) and ammonium acetate (3.00 g) in methanol (10 ml) under nitrogen at room temperature. A yellow precipitate of **8** and **9** rapidly appeared which, after standing overnight, was filtered off (0.20 g, 49%). Chromatography on silica eluting with hexane/dichloromethane (1:3) gave pure **9**, m.p. 98-101°, (Found C: 31.7, H: 2.2; expected C: 31.8, H: 2.4.) ^{1}H n.m.r.: 3.82 OCH_3, 4.72 5- & 6-H; ^{13}C n.m.r.: 50.2 5- & 6-C, 53.8 -OCH_3, 129.9 3a- & -7aC, 167.8 C=O, 208.5 C=S; IR: 1760 cm^{-1}; m/z (EI): 340(M^+,70%), 281(15%), 76(100%); (CI): 341 ($M+1^+$,100%), 145(40%). Subsequent fractions contained a mixture of **8** and **9** richer in the former, ^{1}H n.m.r.: 3.84 OCH_3, 4.70 5- & 6-H; ^{13}C n.m.r.: 46.8 5- & 6-C, 53.8 OCH_3, 133.3 3a- & 7a-C, 166.7 C=O, 207.4 C=S. (R_f's: **8**, 0.48, **9**, 0.51.)

Preparation of Dimethyl 2-Thioxo-1,3-dithiolo[4,5-b]dithiin-5,6-dicarboxylate 10.

(a) When the reaction described above was performed in the absence of ammonium acetate and in air, **8** and **9** were obtained in combined yield of 52 %, together with **10** (0.06 g, 15%) which was isolated as the first band on chromatography (conditions as above, R_f for **10**, 0.94), m.p. 198-200 °C, (Found C: 32.3, H: 1.8; expected C: 32.0, H: 1.8.) ^{1}H n.m.r.: 3.88 OCH_3; ^{13}C n.m.r.: 53.8 OCH_3, 128.2 2a- & 7a-C, 135.9 5- & 6-C, 161.7 C=O, 212.6 C=S; IR: 1710 cm^{-1}; m/z (EI) 338(M^+,60%), 88(100%); (CI) 339($M+1^+$,100%).

(b) A 1:3 mixture of **8** and **9** (0.30 g, 0.80 mmol) and 2,3-dichloro-4,5-dicyanoquinone (0.26 g, 1.14 mmol) in dry THF was refluxed for 48 h under nitrogen. Dichloromethane was added, and the mixture extracted successively with water, aqueous sodium hydroxide (5%) and water. The organic phase was dried with magnesium sulfate, and evaporated. Chromatography, eluting with hexane/dichloromethane (1:3), gave **10** (0.10 g, 35%).

X-Ray Crystal Structure of 9

Crystal data for 9: $C_9H_8S_5$, $M_r = 276.4$, $a = 12.465(3)$, $b = 8.540(7)$, $c = 26.071(7)$ Å, $\beta = 100.17(3)°$, $V = 2731.7$ Å^3, monoclinic, $P2_1/c$, $Z = 8$, $D_c = 1.66$ g cm^{-3}, Mo-Kα radiation, Enraf-Nonius CAD-4 diffractometer, $\mu = 8.2$ cm^{-1}, $T = 293$ K, 3569 reflections with $I > 3\sigma(I)$, max. $(\sin\Theta)/\lambda = 0.59$ Å^{-1}, F(000) = 1392. The structure was solved by 'direct methods' with SHELXS-86[18] and refined with SHELX-76[19]. All hydrogen atoms were located in difference Fourier maps and included in the refinement with isotropic displacement parameters. With weighting scheme $w = [\sigma(F)^2 + 0.0003F^2]^{-1}$ the structure converged with R = 0.038, $R_w = 0.042$. Fractional atomic coordinates, anisotropic displacement parameters and molecular dimensions have been deposited with the Cambridge Crystallographic Data Centre.

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