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4,5-Propylenedithio-1,3-dithiole-2-thione and 4,5-propylenedithio-1,3-dithiol-2-one

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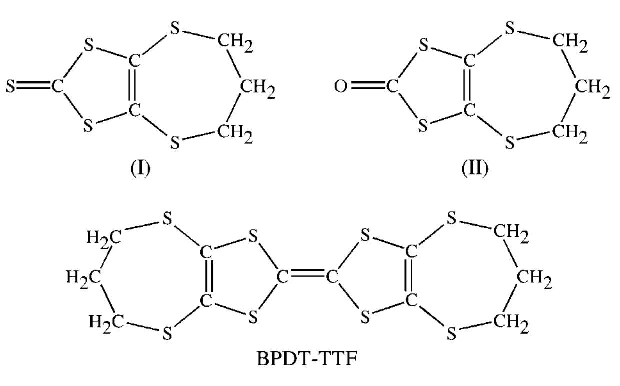
4,5-Propylenedithio-1,3-dithiole-2-thione, $C_6H_6S_5$, (I), crystallizes in the centrosymmetric space group $P2_1/c$. The molecular packing is characterized by pairs of S$\cdots$S intermolecular contacts between neighbouring molecules, which may account for the rather high thermal stablity of the crystal. 4,5-Propylenedithio-1,3-dithiol-2-one, $C_6H_6OS_4$, (II), in which an O atom replaces the terminal S atom of (I), crystallizes in the non-centrosymmetric polar space group *Cc*. The packing pattern of (II) indicates that the macropolarization direction is along [101]. Although the packing patterns are qualitatively significantly different, the molecular structures of (I) and (II) are similar, each exhibiting a chair conformation.

Comment

TTF (tetrathiafulvalene) and BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] derivatives and their charge-transfer salts have received a lot of attention because of their high electronic conductivity or superconductivity (Williams *et al.*, 1992). Replacement of the two ethylene units of BEDT-TTF by two propylene units gives another donor, namely BPDT-TTF [bis(propylenedithio)tetrathiafulvalene; Porter *et al.*, 1987]. In the course of synthesizing new BPDT-TTF-based molecular electronic conductors, we have determined the crystal structures of the title compounds, (I) and (II), which are the precursors of BPDT-TTF.


(I) (II)
BPDT-TTF

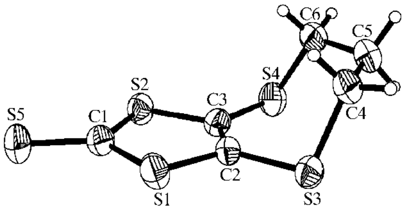


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

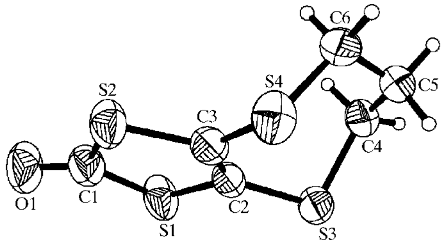


Figure 2
The molecular structure of (II). Displacement ellipsoids are drawn at the 50% probability level.

The molecular geometries of (I) and (II) are illustrated in Figs. 1 and 2, and bond lengths and angles are listed in Tables 1 and 2. In (I), the S5—C1 distance [1.652 (3) Å] is slightly longer than a typical C═S double bond. The C2═C3 distance [1.341 (4) Å] corresponds to a double bond. The bonds involving the methylene C atoms, S3—C4 and S4—C6, have lengths of 1.816 (3) and 1.814 (4) Å, respectively, characteristic of S—C single bonds. The remaining six S—C bonds are in the range 1.723 (3)–1.756 (3) Å, and lie between the typical values for single S—C and double S═C bonds. As a result of replacing the terminal S atom of (I) by an O atom, the terminal C═O bond length [1.228 (8) Å] in (II) is drastically shorter than the corresponding C═S bond length in (I). This shortening is accompanied by an apparent increase in the neighbouring C1—S1 and C1—S2 bond lengths, which average to 1.745 (6) Å [*cf.* 1.724 (3) Å for (I)]. This behaviour indicates that conjugation is more prominent in (I) than in (II). The other bond lengths in (II) are similar to their counterparts in (I).

Both (I) and (II) have planar five-membered rings (S1/C1/S2/C2/C3), with the maximum deviation from the least-squares plane being 0.011 (3) Å for atom C1 in (I) and 0.021 (7) Å for atom C1 in (II). In fact, as shown in Figs. 1 and 2, eight atoms (S5, C1, S1, S2, C2, C3, S3 and S4) in (I) are virtually coplanar. Three planes, *viz.* plane 1 (S5/C1/S1/S2/C2/C3/S3/S4), plane 2 (S3/C4/C6/S4) and plane 3 (C4–C6), form an overall chair conformation, with a dihedral angle between planes 1 and 2 of 65.9 (1)°. Compound (II) also adopts a chair conformation, with the dihedral angle between plane 1 (O1/C1/S1/S2/C2/C3/S3/S4) and plane 2 (S3/C4/C6/S4) being 61.2 (2)°.

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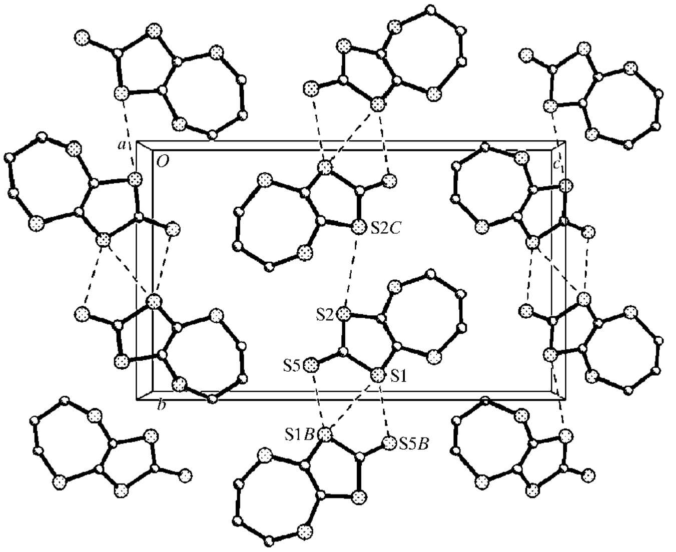

Figure 3
The packing in the structure of (I). The intermolecular S1$\cdots$S1*B*($1 - x$, $2 - y$, $1 - z$), S5$\cdots$S1*B*($1 - x$, $2 - y$, $1 - z$), S1$\cdots$S5*B*($1 - x$, $2 - y$, $1 - z$) and S2$\cdots$S2*C*($1 - x$, $1 - y$, $1 - z$) distances are 3.388 (2), 3.607 (2), 3.607 (2) and 3.637 (2) Å, respectively.

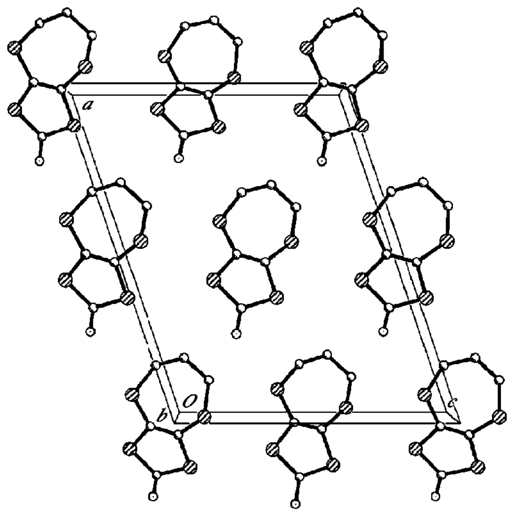

Figure 4
The packing of (II), showing the macropolarization direction along [101].

Compound (I) crystallizes in the centrosymmetric space group $P2_1/c$. As shown in Fig. 3, there are several intermolecular S$\cdots$S contacts shorter than 3.70 Å (the sum of the van der Waals radii). The S1$\cdots$S1*B*($1 - x$, $2 - y$, $1 - z$), S5$\cdots$S1*B*($1 - x$, $2 - y$, $1 - z$) and S2$\cdots$S2*C*($1 - x$, $1 - y$, $1 - z$) distances are 3.388 (2), 3.607 (2) and 3.637 (2) Å, respectively. Although there is also a short intermolecular S$\cdots$S contact in (II) [S3$\cdots$S4(x, $-y$, $-\frac{1}{2} + z$) = 3.685 (2) Å], the S$\cdots$S interactions in (II) are clearly less important than those in (I). The remarkable S$\cdots$S intermolecular interactions of (I) endow the crystal with extra thermal stability, and the measured melting point of (I) (432.6 K) is considerably higher than that of (II) (393.5 K). Another important factor contributing to the thermal stability of (I) is the antiparallel packing mode of the molecular dipole moments, which results in strong intermolecular dipole–dipole interactions. The interesting packing feature of (II) is that all molecular dipole moments are basically in the same direction (see Fig. 4); this parallel packing arrangement results in a non-centrosymmetric polar space group, *Cc*, with the macropolarization direction along [101]. Most polar molecules crystallize in centrosymmetric structures with an antiparallel packing motif, as is the case with (I). Moreover, the probability of polar molecules crystallizing with a non-centrosymmetric polar structure, such as in the case of (II), is quite small.

Experimental

Compound (I) was prepared according to the method of Kumasaki *et al.* (1998). $(Bu_4N)_2[Zn(dmit)_2]$ (dmit is the 2-thioxo-1,3-dithiole-4,5-dithiolate dianion, $C_3S_5^{2-}$) (57 g) was dissolved in acetonitrile (200 ml) and 1,3-dibromopropane (26 g) was added. The solution was stirred for 2 d at room temperature. The resulting orange precipitate was filtered off, chloroform was added to the residue and the solution was filtered. Activated charcoal was added to the filtrate and the solution was refluxed for 1.5 h, after which the solution was filtered and methanol was added. Compound (I) was obtained from this solution at room temperature. For the preparation of compound (II), compound (I) (2.4 g) and $Hg(CH_3COO)_2$ (8 g) were added to chloroform–acetic acid (3:1, 120 ml). The solution was stirred at room temperature for 2 h, and a white precipitate was obtained and filtered off. The filtered solution was washed with water and with a saturated aqueous $NaHCO_3$ solution. It was then filtered and methanol was added, yielding milky white crystals.

Compound (I)

Crystal data

$C_6H_6S_5$
$M_r = 238.41$
Monoclinic, $P2_1/c$
$a = 4.6572$ (13) Å
$b = 10.9765$ (14) Å
$c = 18.1026$ (17) Å
$\beta = 90.147$ (11)°
$V = 925.4$ (3) Å^3
$Z = 4$

$D_x = 1.711$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15 reflections
$\theta = 5.7$–12.5°
$\mu = 1.18$ mm^{-1}
$T = 293$ (2) K
Prism, Milky white
0.22 × 0.16 × 0.12 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: ψ scan (*XSCANS*; Bruker, 1996)
$T_{\min} = 0.791$, $T_{\max} = 0.868$
3160 measured reflections
2110 independent reflections
1331 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.026$
$\theta_{\max} = 27.5°$
$h = -6 \rightarrow 1$
$k = -14 \rightarrow 1$
$l = -23 \rightarrow 23$
3 standard reflections every 97 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.093$
$S = 1.03$
2110 reflections
101 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0330P)^2 + 0.1689P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0145 (13)

Table 1
Selected geometric parameters (Å, °) for (I).

S5—C1	1.652 (3)	S3—C2	1.756 (3)
S1—C1	1.726 (3)	S3—C4	1.816 (3)
S1—C2	1.739 (3)	S4—C3	1.750 (3)
S2—C1	1.723 (3)	S4—C6	1.814 (4)
S2—C3	1.743 (3)	C2—C3	1.341 (4)
C1—S1—C2	97.31 (15)	C3—C2—S1	116.6 (2)
C1—S2—C3	97.67 (15)	C3—C2—S3	125.6 (2)
C2—S3—C4	101.67 (15)	S1—C2—S3	117.83 (18)
C3—S4—C6	101.55 (16)	C2—C3—S2	115.6 (2)
S5—C1—S2	123.55 (19)	C2—C3—S4	126.1 (2)
S5—C1—S1	123.6 (2)	S2—C3—S4	118.21 (18)
S2—C1—S1	112.80 (18)	C5—C6—S4	116.0 (2)

Table 2
Selected geometric parameters (Å, °) for (II).

O1—C1	1.228 (8)	S3—C2	1.740 (5)
S1—C1	1.733 (6)	S3—C4	1.821 (6)
S1—C2	1.750 (6)	S4—C3	1.736 (6)
S2—C1	1.757 (6)	S4—C6	1.826 (7)
S2—C3	1.763 (6)	C2—C3	1.342 (7)
C1—S1—C2	96.6 (3)	C3—C2—S3	125.6 (4)
C1—S2—C3	96.2 (3)	C3—C2—S1	117.4 (4)
C2—S3—C4	101.6 (3)	S3—C2—S1	116.9 (3)
C3—S4—C6	103.4 (3)	C2—C3—S4	127.6 (4)
O1—C1—S1	123.7 (5)	C2—C3—S2	116.0 (4)
O1—C1—S2	122.6 (5)	S4—C3—S2	116.4 (3)
S1—C1—S2	113.7 (3)	C4—C5—C6	115.9 (5)

Compound (II)

Crystal data

$C_6H_6OS_4$
$M_r = 222.35$
Monoclinic, *Cc*
$a = 16.358$ (4) Å
$b = 4.5009$ (11) Å
$c = 13.066$ (3) Å
$\beta = 108.736$ (15)°
$V = 911.0$ (4) Å^3
$Z = 4$
$D_x = 1.621$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 40 reflections
$\theta = 8.9$–14.2°
$\mu = 0.98$ mm^{-1}
$T = 293$ (2) K
Plate, pale yellow
0.34 × 0.22 × 0.02 mm

Data collection

Bruker *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (*XSCANS*; Bruker, 1996)
$T_{\min} = 0.665$, $T_{\max} = 0.982$
1439 measured reflections
1150 independent reflections
925 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.035$
$\theta_{\max} = 27.5°$
$h = -1 \rightarrow 20$
$k = -5 \rightarrow 1$
$l = -16 \rightarrow 16$
3 standard reflections every 97 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.107$
$S = 1.04$
1150 reflections
100 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0612P)^2]$ where $P = (F_o^2 + 2F_o^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}
Absolute structure: Flack (1983), 112 Friedel pairs
Flack parameter = 0.3 (2)

The positions of the H atoms were located in a difference Fourier map and were then positioned geometrically and allowed to ride on their attached atoms [C—H = 0.93–0.97 Å and $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$]. For (II), the Flack (1983) parameter was refined but did not give a clear result. This structure does not involve an absolute configuration question, and the absolute structure determination does not influence the interpretation of the chemical structure.

For both compounds, data collection: *XSCANS* (Bruker, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1033). Services for accessing these data are described at the back of the journal.

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