C2—C1—C7	119.7 (3)		
C6—C1—C7	119.5 (3)		
C1—C7—N1	177.8 (3)		
N1—C1—C2		118.7 (5)	119.4 (4)
N1—C1—C6		118.2 (5)	116.6 (4)
O1—N1—C1		117.6 (5)	118.2 (4)
O2—N1—C1		117.9 (5)	117.5 (4)
O1—N1—O2		124.6 (5)	124.3 (5)
C2—C1—C6	120.6 (3)	123.2 (5)	123.9 (5)
C1—C2—C3	118.5 (3)	116.8 (5)	116.8 (5)
C1—C2—C21	122.3 (3)	122.0 (5)	124.4 (5)
C3—C2—C21	119.1 (3)	121.3 (5)	118.7 (5)
C2—C3—C4	122.5 (3)	122.0 (5)	121.9 (5)
C3—C4—C5	117.2 (3)	118.8 (5)	118.6 (5)
C3—C4—C41	121.1 (3)	120.4 (5)	120.7 (5)
C5—C4—C41	121.7 (3)	120.8 (5)	120.7 (5)
C4—C5—C6	122.6 (3)	121.3 (5)	121.8 (5)
C1—C6—C5	118.5 (3)	118.0 (5)	116.9 (5)
C1—C6—C61	122.6 (3)	122.2 (5)	123.9 (5)
C5—C6—C61	119.0 (3)	119.7 (5)	119.2 (5)
C1—C2—C21—C22	−49.1 (4)	117.7 (6)	137.0 (6)
C1—C2—C21—C26	132.5 (3)	−63.1 (8)	−47.1 (8)
C3—C2—C21—C22	132.8 (3)	−61.1 (8)	−46.5 (7)
C3—C2—C21—C26	−45.6 (3)	118.2 (6)	129.4 (6)
C3—C4—C41—C42	−152.7 (3)	−40.4 (8)	−31.5 (8)
C3—C4—C41—C46	28.9 (4)	140.5 (6)	148.0 (5)
C5—C4—C41—C42	28.9 (3)	141.3 (6)	147.6 (6)
C5—C4—C41—C46	−149.6 (3)	−37.8 (8)	−32.9 (8)
C1—C6—C61—C62	−131.6 (3)	116.6 (6)	−56.3 (8)
C1—C6—C61—C66	49.3 (4)	−67.1 (8)	126.9 (6)
C5—C6—C61—C62	46.9 (3)	−68.0 (8)	125.8 (6)
C5—C6—C61—C66	−132.1 (3)	108.3 (7)	−51.0 (7)

For both compounds, the data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods. Full-matrix least-squares refinement minimizing $\Sigma w(|F_o|-|F_c|)^2$ was employed. Non-H atoms were refined anisotropically and all H atoms were placed in calculated positions and refined with isotropic displacement parameters. Calculations were carried out using the *SHELX*76 and *SHELXS*86 programs (Sheldrick, 1976, 1990). The final geometry calculations were performed with the *CSU* program (Vickovic, 1988).

We thank Professor T. M. Krygowski for helpful discussions.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1051). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5,6-Dihydro-5,6-diphenyl-1,3-dithiolo[4,5-*b*]-[1,4]dithiine-2-thione (DHPT-DTT), $C_{17}H_{12}S_5$

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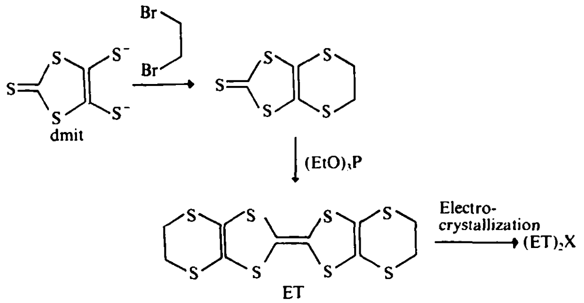
Abstract

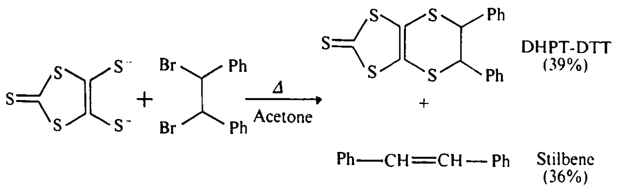
The DHPT-DTT molecule contains a conjugated 4,5-dimercapto-1,3-dithiole-2-thione plane and two phenyl planes, all of which are approximately perpendicular to one another. The crystal packing is stabilized by an S···S interaction between pairs of neighbouring molecules, which may account for the rather high thermal stability of the crystal.

Comment

The ring closure of 4,5-dimercapto-1,3-dithiole-2-thione (dmit) with a dihalohydrocarbon to produce a suitable π-donor precursor is the first step of a three-stage procedure for the preparation of dmit-based organic electric conductors, such as the well known $(ET)_2X$ type of charge-transfer salts, where X^- is a charge-compensating monovalent anion (Williams *et al.*, 1987; Bryce, 1991).



During attempts to prepare new organic superconductors, many smaller precursors of dmit-based π donors have been synthesized, some of which represent significant advances in this field (Steimecke, Sieler, Kirmse & Hoyer, 1979; Nakamura, Iwasaka, Nakano, Inoue, Nogami & Mikawa, 1987; Jørgensen *et al.*, 1992). Larger precursors containing a phenyl group have also been reported (Varma *et al.*, 1989; Larsen *et al.*, 1991). The title compound, DHPT-DTT, which contains two phenyl groups, is the main product of a new type of dmit ring-closure reaction.



In DHPT-DTT, the C2=C3 and the terminal S1=C1 bonds are double bonds, although the latter is slightly longer than a typical C=S bond. The other C—S bonds in the dmit moiety have lengths which are approximately the average of typical single and double bond lengths. Thus, the dmit moiety in DHPT-DTT is conjugated to quite a high degree. It differs slightly from other dmit derivatives, as shown in Table 3. For compounds (1), (2), (3) and (4), the bonds of types *c* and *d* are very similar in length, but the *b*-type bonds are slightly shorter. The differences between the *b* and *c* (or *d*) bonds in compounds (1) and (2) are about 0.02 Å, while the differences between the corresponding bonds in the phenyl-containing compounds (3) and (4) are about 0.01 Å. In compound (5), in which the phenyl groups are linked directly to dmit, the *b*-type bond is the same length as the *c*-type bond within the e.s.d.'s. Furthermore, the *g*-type C—C bond of DHPT-DTT is obviously shorter than the corresponding bonds in compounds (1) and (2). These results indicate that dmit derivatives which contain phenyl groups are slightly more conjugated than those without phenyl groups.

The dmit plane and the two phenyl 'wing' planes are roughly perpendicular to one another and form a 'bird-like' DHPT-DTT molecule. The three conjugated subsystems of DHPT-DTT are relatively isolated, as the bridging bonds S4—C4, S5—C5, C4—C5, C4—C6 and C5—C12 which connect the three planes are all single bonds. Conducting crystals based on dmit are in general characterized by strong intermolecular interactions through short S···S contacts which are shorter than the sum of the van der Waals radii (3.70 Å; Pauling, 1960). Although there is only one S···S interaction between each pair of neighbouring DHPT-DTT molecules [S1′···S2, 3.62 (1) Å], the crystal packing is still considerably stabilized, as shown by the rather high melting point of 474 K.

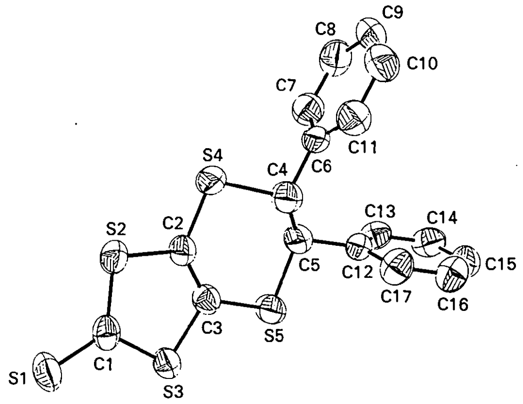


Fig. 1. View of a DHPT-DTT molecule showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

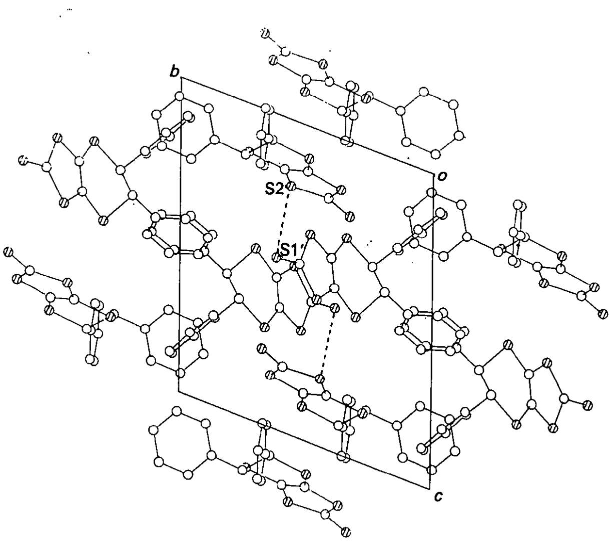


Fig. 2. View of the unit-cell contents projected on (100).

Experimental

The title compound was prepared by refluxing 1.0 mmol of $(Bu_4N)_2[Zn(dmit)_2]$ with 2.0 mmol of 1,2-dibromo-1,2-diphenylethane in 20 ml of acetone under Ar for 2 h. The solvent was removed and the mixture of crude products was eluted with a chloroform–petroleum ether (1/4) eluent on a silica gel chromatographic column. The first component eluted was colourless platelet stilbene (36%). The second component yielded orange parallelepiped crystals of DHPT-DTT (39%) after slowly evaporating most of the solvent. Analysis: calculated for $C_{17}H_{12}S_5$, C 54.22, H 3.21%; found, C 54.31, H 3.34%; m.p. 474–476 K.

Crystal data

$C_{17}H_{12}S_5$	Mo $K\alpha$ radiation
$M_r = 376.58$	$\lambda = 0.71069$ Å

Triclinic
$P\bar{1}$
$a = 11.704$ (3) Å
$b = 12.141$ (4) Å
$c = 14.315$ (6) Å
$\alpha = 101.74$ (3)°
$\beta = 110.75$ (2)°
$\gamma = 106.96$ (2)°
$V = 1709$ (1) Å^3
$Z = 4$
$D_x = 1.46$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 2.0$–$12.5°$
$\mu = 0.65$ mm^{-1}
$T = 293$ K
Parallelepiped
0.25 × 0.23 × 0.18 mm
Orange

Data collection

Nicolet *R*3*m*/*E* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
6489 measured reflections
6342 independent reflections
4613 observed reflections [$I > 3\sigma(I)$]

$R_{\text{int}} = 0.015$
$\theta_{\text{max}} = 25.0°$
$h = 0 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -18 \rightarrow 18$
2 standard reflections monitored every 100 reflections
intensity variation: <5%

Refinement

Refinement on *F*
$R = 0.054$
$wR = 0.054$
$S = 1.254$
4613 reflections
397 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{\text{max}} = 0.396$
$\Delta\rho_{\text{max}} = 0.60$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.32$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

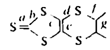
	x	y	z	U_{eq}
S1	−0.1693 (1)	0.3261 (1)	0.2375 (1)	0.069 (1)
S2	−0.0367 (1)	0.5607 (1)	0.2127 (1)	0.055 (1)
S3	0.0422 (1)	0.3608 (1)	0.1637 (1)	0.052 (1)
S4	0.1461 (1)	0.7320 (1)	0.1572 (1)	0.060 (1)
S5	0.2460 (2)	0.4902 (1)	0.1044 (1)	0.068 (1)
C1	−0.0616 (4)	0.4109 (4)	0.2059 (4)	0.052 (2)
C2	0.0851 (4)	0.5871 (4)	0.1670 (4)	0.050 (2)
C3	0.1234 (4)	0.4948 (4)	0.1455 (3)	0.049 (2)
C4	0.3099 (5)	0.7441 (4)	0.1684 (4)	0.062 (3)
C5	0.3067 (5)	0.6384 (4)	0.0897 (4)	0.059 (3)
C6	0.3732 (4)	0.8677 (4)	0.1598 (4)	0.052 (2)
C7	0.3279 (5)	0.8919 (5)	0.0671 (4)	0.062 (3)
C8	0.3900 (5)	1.0067 (5)	0.0630 (4)	0.071 (3)
C9	0.4941 (5)	1.0959 (5)	0.1499 (5)	0.075 (3)
C10	0.5408 (5)	1.0734 (5)	0.2422 (5)	0.078 (3)
C11	0.4811 (5)	0.9579 (5)	0.2478 (4)	0.065 (3)
C12	0.4399 (4)	0.6549 (4)	0.0895 (4)	0.049 (2)
C13	0.5482 (5)	0.6717 (5)	0.1795 (4)	0.068 (3)
C14	0.6691 (5)	0.6858 (5)	0.1778 (4)	0.071 (3)
C15	0.6814 (5)	0.6838 (5)	0.0876 (4)	0.069 (3)
C16	0.5761 (5)	0.6678 (5)	−0.0027 (4)	0.065 (3)
C17	0.4537 (5)	0.6522 (4)	−0.0018 (4)	0.058 (2)
S1′	0.9236 (1)	0.6186 (1)	0.4555 (1)	0.073 (1)
S2′	0.6318 (1)	0.4830 (1)	0.3417 (1)	0.059 (1)
S3′	0.7729 (1)	0.4556 (1)	0.5399 (1)	0.059 (1)
S4′	0.3628 (1)	0.3370 (1)	0.3086 (1)	0.066 (1)
S5′	0.5281 (1)	0.2990 (1)	0.5472 (1)	0.067 (1)
C1′	0.7851 (4)	0.5248 (4)	0.4473 (4)	0.053 (2)
C2′	0.5337 (4)	0.3967 (4)	0.3899 (4)	0.049 (2)
C3′	0.5986 (4)	0.3839 (4)	0.4821 (4)	0.050 (2)
C4′	0.2907 (5)	0.2347 (5)	0.3680 (4)	0.071 (3)
C5′	0.3771 (5)	0.1861 (5)	0.4341 (4)	0.066 (3)
C6′	0.1606 (4)	0.1379 (4)	0.2788 (4)	0.053 (2)
C7′	0.1569 (6)	0.0575 (5)	0.1949 (4)	0.074 (3)
C8′	0.0405 (8)	−0.0276 (6)	0.1165 (5)	0.097 (4)
C9′	−0.0752 (7)	−0.0360 (6)	0.1188 (6)	0.098 (4)
C10′	−0.0781 (6)	0.0430 (7)	0.2019 (6)	0.094 (4)
C11′	0.0450 (5)	0.1338 (5)	0.2838 (4)	0.069 (3)
C12′	0.3063 (4)	0.0954 (4)	0.4750 (3)	0.052 (2)
C13′	0.2965 (6)	−0.0223 (5)	0.4438 (4)	0.077 (3)
C14′	0.2239 (7)	−0.1101 (5)	0.4765 (5)	0.092 (4)
C15′	0.1691 (6)	−0.0728 (6)	0.5399 (5)	0.089 (3)
C16′	0.1805 (5)	0.0421 (6)	0.5710 (5)	0.080 (3)
C17′	0.2471 (5)	0.1266 (5)	0.5380 (4)	0.068 (3)

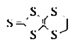
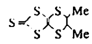
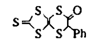
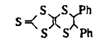
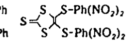
Table 2. *Selected geometric parameters* (Å, °)

The geometric parameters for the phenyl groups are not unusual, and have been deposited as supplementary material.

S1—C1	1.640 (6)	S5—C3	1.745 (6)
S3—C1	1.736 (6)	C4—C5	1.506 (8)
S4—C4	1.825 (6)	S2—C2	1.743 (6)
C2—C3	1.342 (8)	S4—C2	1.750 (5)
C5—C12	1.514 (8)	S5—C5	1.817 (6)
S2—C1	1.733 (6)	C4—C6	1.519 (7)
S3—C3	1.750 (5)		
C1—S2—C2	97.7 (3)	C1—S3—C3	97.5 (3)
C2—S4—C4	100.7 (3)	C3—S5—C5	104.0 (3)
S1—C1—S2	124.0 (4)	S1—C1—S3	123.6 (3)
S2—C1—S3	112.4 (3)	S2—C2—S4	116.4 (3)
S2—C2—C3	116.2 (4)	S4—C2—C3	127.4 (5)
S3—C3—S5	114.8 (3)	S3—C3—C2	116.1 (4)
S5—C3—C2	129.1 (4)	S4—C4—C5	114.1 (3)
S4—C4—C6	105.6 (4)	C5—C4—C6	113.6 (5)
S5—C5—C4	115.4 (5)	S5—C5—C12	105.5 (4)
C4—C5—C12	114.4 (3)		

Table 3. *Mean bond lengths for some typical dmit derivatives* (Å)



Bond	 (1)	 (2)	 (3)	 (4)	 (5)
a	1.656 (1)	1.636 (8)	1.670 (2)	1.637 (6)	1.630 (7)
b	1721 (1)	1.727 (8)	1.735 (2)	1.733 (6)	1.740 (7)
c	1.746 (1)	1.743 (5)	1.746 (2)	1.748 (5)	1.742 (6)
d	1.748 (1)	1.742 (5)	1.748 (2)	1.747 (5)	1.772 (7)
e	1.356 (2)	1.339 (8)	1.354 (3)	1.339 (8)	1.336 (9)
f	1.814 (6)	1.818 (6)	–	1.818 (6)	1.773 (7)
g	1.517 (2)	1.536 (8)	–	1.489 (9)	–

References: (1) Larsen *et al.* (1991); (2) Wallis & Dunitz (1988); (3) Larsen *et al.* (1991); (4) this work; (5) Fang Qi, Zheng, Yao & Xiao-Zeng (1992).

Data collection and cell refinement: Nicolet (1985) *R*3*m*/*E* software. Program used to solve the structure: *SHELXTL* (Sheldrick, 1984).

This work has been supported by a grant for the Key Research Project in Climbing Program from the State Science and Technology Commission of China.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data and complete geometry, and additional figures have been deposited with the IUCr (Reference: AB1108). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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