5,6-Diphenylthieno[2,3-*d*][1,3]-dithiole-2-thione

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The title compound, $C_{17}H_{10}S_4$, has two independent molecules in the asymmetric unit. In both molecules, the fused heterocycle is almost planar and the phenyl groups make dihedral angles of 42.88 (9) and 52.79 (8)° with the fused heterocycle in one molecule, and angles of 40.62 (9) and 52.28 (8)° in the other. The crystal packing is governed by short intermolecular S···S interactions, the shortest contact being 3.333 (1) Å.

Comment

It has recently been discovered that Lawesson's reagent (LR), (I), could be used to construct 1,4-dithiine (III) and/or thiophene heterocycles from 1,8-diketones (II) (Öztürk, 1996). The possible mechanism of this reaction involves a nine-membered-ring intermediate which then rearranges to the six-membered dithiine ring. Loss *in situ* of an S atom from the 1,4-dithiine ring leads to the formation of a thiophene ring. The dithiine/thiophene ratio depends on the electron-withdrawing or electron-releasing nature of the aromatic (Ar) substituent. While electron-donating groups make the loss of the S atom easier, electron-withdrawing groups make it more difficult.

Our previous and ongoing studies indicated that when the corresponding 1,8-diketone is treated with LR, dithiine (V) is obtained as a minor product (Öztürk, 1996; Öztürk & Türksoy, 1999). On the other hand, when the phenyl group of the 1,8-diketone is replaced by *para*-methoxyphenyl, thiophene rather than dithiine becomes a major product (Öztürk & Wallis, 1996).

In an effort to obtain new diphenyl-substituted dithiine (VIII) and thiophene (IX) heterocycles, which are useful building blocks for organic conducting/superconducting materials, the tetraphenyl-1,8-diketone (VII) was reacted overnight with LR in refluxing toluene under a nitrogen atmosphere. In accordance with the results obtained previously (Lee *et al.*, 1998), no product containing dithiine ring (VIII) was obtained. Diphenylthiophene (IX) was

isolated as the sole product and its X-ray crystal structure is reported here.

(I)

(II) → (III) + (IV)

Ar = Ph, 4-MeOPh, 4-BrPh

(V)   (VI)

(VII) → (VIII)   (IX)

LR, toluene, N₂, reflux
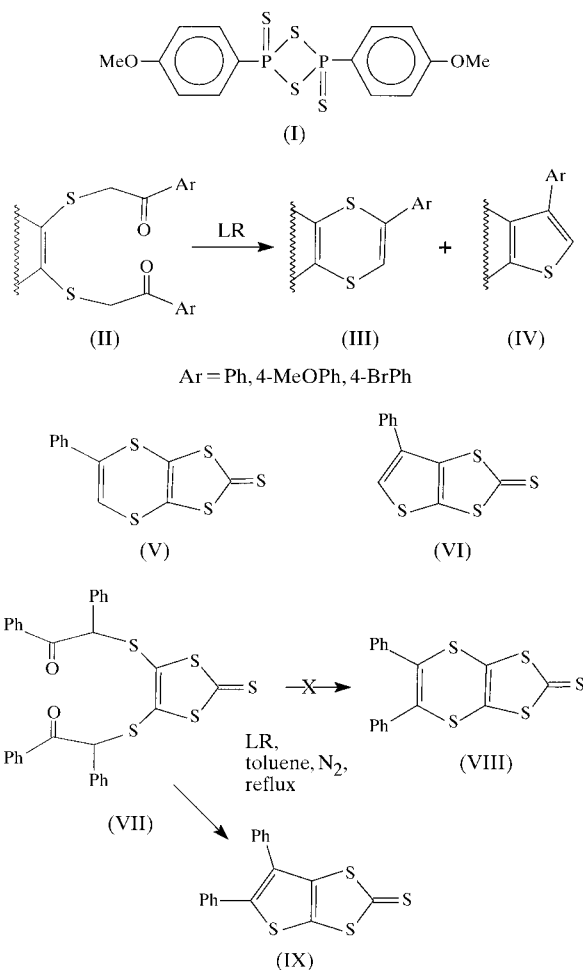
Compound (IX) crystallizes in $P2_1/c$ and has two crystallographically independent molecules in the asymmetric unit, labelled *A* and *B* (Fig. 1). Interatomic distances and angles are very similar in both molecules. The fused heterocyle in the molecules is nearly planar; the best planes of the two five-membered rings (thiophene and dithiole) form dihedral angles of 4.77 (8)° in molecule *A* and 5.35 (8)° in molecule *B*. These values are comparable with that found in 6-(4-methoxyphenyl)thieno[2,3-*d*][1,3]dithiole-2-thione [4.2 (1)°; Öztürk & Wallis, 1996]. The phenyl groups in (IX) are essentially planar, the maximum deviations being 0.007 (2) (C17*A* in molecule *A*) and −0.008 (3) Å (C15*B* in molecule *B*). The dihedral angles between the phenyl groups (C6–C11 and C12–C17) and the fused heterocycle are 42.88 (9) and 52.79 (8)°, while the dihedral angle between these two phenyl rings is 55.05 (11)° for molecule *A*; these values are slightly less for molecule *B*, *viz.* 40.62 (9), 52.28 (8) and 52.75 (11)°, respectively. The terminal C=S double bond [mean 1.648 (2) Å] is quite similar to that of other structures including the 1,3-thiole-2-thione moiety (Öztürk & Wallis, 1996; Parvez *et al.*, 1996; Lee & Noh, 1998). There is a marked asymmetry in the thiophene and dithiole rings. The S4—C5 bond distance [1.742 (2) Å in molecule *A* and 1.744 (2) Å in molecule *B*] is longer than the

organic compounds

S4—C3 bond distance [1.709 (2) and 1.710 (2) Å for molecules *A* and *B*, respectively]. The mean bond angle at the S4 atom, 91.29 (8)°, is significantly smaller than the angles at the S2 and S3 atoms, which have mean values of 96.57 (8) and 95.89 (8)°, respectively.

As usual in this type of compound, packing appears to be governed by S⋯S interactions. Some intermolecular S⋯S contact distances are S1*A*⋯S3*A*^{i} 3.333 (1), S1*A*⋯S4*A*^{i}
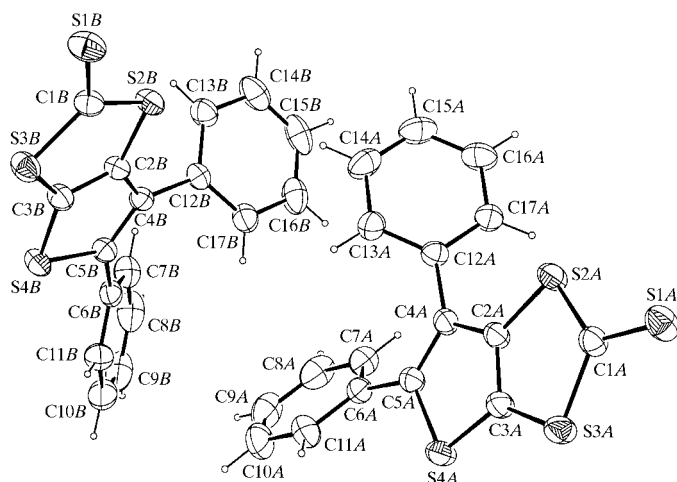
Figure 1
ORTEP (Johnson, 1965) drawing of the asymmetric unit of (IX), showing the atomic numbering scheme and displacement ellipsoids at the 40% probability level.

3.372 (1), S1*A*⋯S1*A*^{ii} 3.555 (1), S2*A*⋯S3*A*^{i} 3.427 (1), S1*B*⋯S3*B*^{iii} 3.344 (1), S1*B*⋯S4*B*^{iii} 3.355 (1), S1*B*⋯S1*B*^{iv} 3.570 (1) and S2*B*⋯S3*B*^{iii} 3.447 (1) Å, and contribute to the formation of chains along the *b* direction [symmetry codes: (i) $2 - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$; (ii) $2 - x$, $1 - y$, $2 - z$; (iii) $1 - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$; (iv) $1 - x$, $1 - y$, $2 - z$]. These chains, in turn, are held together by van der Waals interactions.

Experimental

For the preparation of 5,6-diphenylthieno[2,3-*d*][1,3]dithiole-2-thione, (IX), a solution of 1,8-diketone (VII) (0.5 g, 0.85 mmol) and Lawesson's reagent, (I) (0.4 g, 0.99 mmol), in dry toluene (25 ml) was refluxed overnight under a nitrogen atmosphere. The solvent was evaporated and the residue purified by column chromatography, eluting with hexane–dichloromethane (2:1) (m.p. 429–430 K, 0.087 g, 30%). ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.5 (10H, *m*); ^{13}C NMR (50.32 Hz, CDCl$_3$): δ 207 (C=S), 143.8, 140.7, 133.9, 132.6, 129.06, 129, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4; *m/z* (EI): 342 (*M*$^+$); *m/z* (HRMS): 341.9665, C$_{17}$H$_{10}$S$_4$ requires 341.9684; UV (CH$_3$CN, nm) 392.

Crystal data

C$_{17}$H$_{10}$S$_4$	$D_x = 1.475$ Mg m^{-3}
$M_r = 342.53$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25
$a = 23.441$ (3) Å	reflections
$b = 10.1303$ (14) Å	$\theta = 11$–$18°$
$c = 13.5222$ (17) Å	$\mu = 0.60$ mm^{-1}
$\beta = 73.822$ (10)°	$T = 295$ K
$V = 3083.9$ (7) Å^3	Prismatic, yellow
$Z = 8$	$0.45 \times 0.24 \times 0.15$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.052$
$\omega/2\theta$ scans	$\theta_{max} = 27.9°$
Absorption correction: ψ scan (North *et al.*, 1983)	$h = -29 \rightarrow 30$
	$k = -13 \rightarrow 0$
$T_{min} = 0.840$, $T_{max} = 0.913$	$l = 0 \rightarrow 17$
7317 measured reflections	3 standard reflections
7013 independent reflections	frequency: 120 min
5657 reflections with $I > 2\sigma(I)$	intensity decay: 1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2$
$R(F) = 0.033$	$+ 0.6458P]$
$wR(F^2) = 0.099$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} = 0.001$
5657 reflections	$\Delta\rho_{max} = 0.25$ e Å^{-3}
379 parameters	$\Delta\rho_{min} = -0.36$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

C1*A*—S1*A*	1.6482 (18)	C1*B*—S1*B*	1.6485 (18)
C1*A*—S2*A*	1.7374 (18)	C1*B*—S2*B*	1.7359 (18)
C1*A*—S3*A*	1.7355 (19)	C1*B*—S3*B*	1.7373 (19)
C2*A*—S2*A*	1.7417 (17)	C2*B*—S2*B*	1.7398 (17)
C3*A*—S3*A*	1.7274 (18)	C3*B*—S3*B*	1.7257 (18)
C3*A*—S4*A*	1.7090 (18)	C3*B*—S4*B*	1.7104 (18)
C5*A*—S4*A*	1.7420 (18)	C5*B*—S4*B*	1.7437 (18)
S2*A*—C1*A*—S3*A*	114.37 (10)	S2*B*—C1*B*—S3*B*	114.40 (10)
C2*A*—C3*A*—S3*A*	117.75 (14)	C2*B*—C3*B*—S3*B*	117.93 (13)
C2*A*—C4*A*—C12*A*	122.62 (15)	C2*B*—C4*B*—C12*B*	122.59 (15)
C4*A*—C5*A*—S4*A*	112.40 (13)	C4*B*—C5*B*—S4*B*	112.16 (13)
C1*A*—S2*A*—C2*A*	96.47 (8)	C1*B*—S2*B*—C2*B*	96.67 (8)
C1*A*—S3*A*—C3*A*	95.95 (8)	C1*B*—S3*B*—C3*B*	95.84 (8)
C3*A*—S4*A*—C5*A*	91.22 (8)	C3*B*—S4*B*—C5*B*	91.37 (8)

Ring H atoms were placed geometrically 0.93 Å from their parent atoms and a riding model was used with U_{iso}(H) = 1.3U_{eq}(C).

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993); data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1965); software used to prepare material for publication: *PLATON* (Spek, 1990).

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