

5,6-Diphenylthieno[2,3-*d*][1,3]-
dithiole-2-thioneF. Betül Kaynak,^{a*} Süheyla Özbey,^a Turan Öztürk^b and
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The title compound, C₁₇H₁₀S₄, 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.

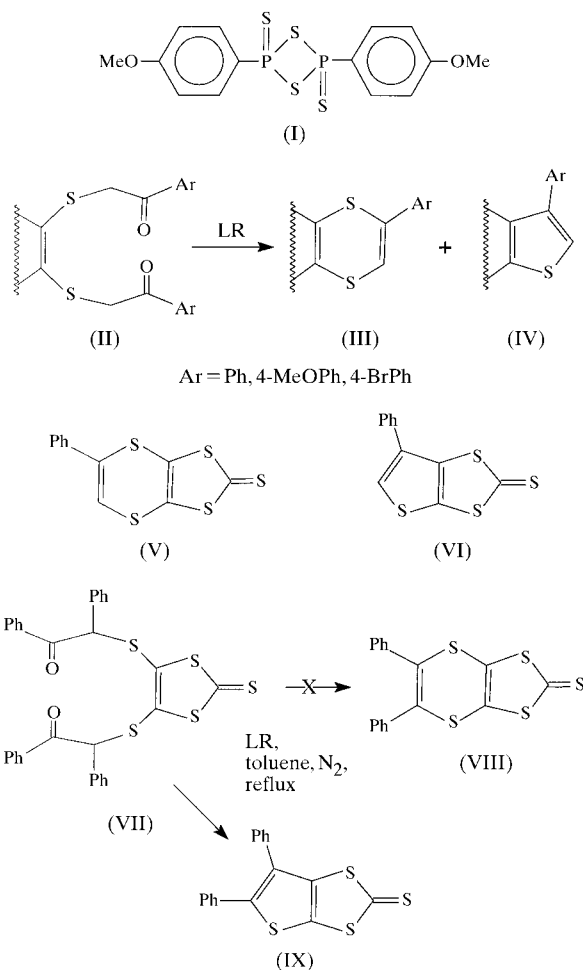
Comment

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 & Türksöy, 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.



Compound (IX) crystallizes in *P*₂₁/*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 heterocycle 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) Å (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

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 S1A··S3Aⁱ 3.333 (1), S1A··S4Aⁱ

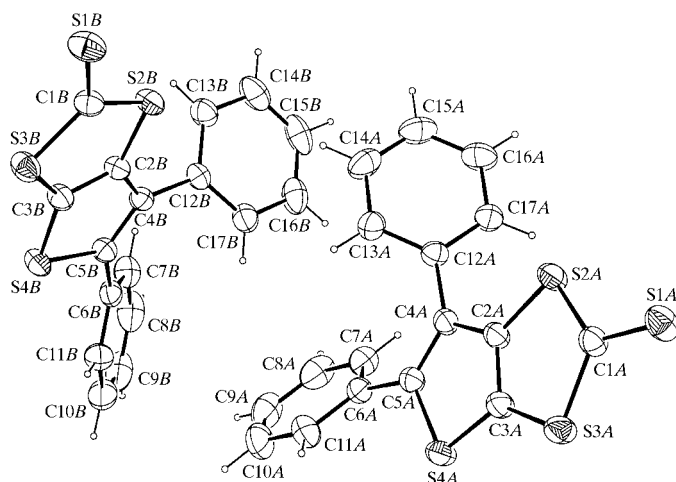


Figure 1
ORTEP (Johnson, 1965) drawing of the asymmetric unit of (IX), showing the atomic numbering scheme and displacement ellipsoids at the 40% probability level.

3.372 (1), S1A··S1Aⁱⁱ 3.555 (1), S2A··S3Aⁱ 3.427 (1), S1B··S3Bⁱⁱⁱ 3.344 (1), S1B··S4Bⁱⁱⁱ 3.355 (1), S1B··S1B^{iv} 3.570 (1) and S2B··S3Bⁱⁱⁱ 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%). ¹H NMR (200 MHz, CDCl₃): δ 7.5 (10H, *m*); ¹³C NMR (50.32 Hz, CDCl₃): 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, C₁₇H₁₀S₄ requires 341.9684; UV (CH₃CN, nm) 392.

Crystal data

C₁₇H₁₀S₄
M_r = 342.53
 Monoclinic, *P*₂₁/*c*
a = 23.441 (3) Å
b = 10.1303 (14) Å
c = 13.5222 (17) Å
 β = 73.822 (10)°
V = 3083.9 (7) Å³
Z = 8
D_x = 1.475 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 25 reflections
 θ = 11–18°
 μ = 0.60 mm⁻¹
T = 295 K
 Prismatic, yellow
 0.45 × 0.24 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω/2θ scans
 Absorption correction: ψ scan (North *et al.*, 1983)
*T*_{min} = 0.840, *T*_{max} = 0.913
 7317 measured reflections
 7013 independent reflections
 5657 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.052
 θ_{max} = 27.9°
h = -29 → 30
k = -13 → 0
l = 0 → 17
 3 standard reflections
 frequency: 120 min
 intensity decay: 1%

Refinement

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

Table 1
Selected geometric parameters (Å, °).

C1A—S1A	1.6482 (18)	C1B—S1B	1.6485 (18)
C1A—S2A	1.7374 (18)	C1B—S2B	1.7359 (18)
C1A—S3A	1.7355 (19)	C1B—S3B	1.7373 (19)
C2A—S2A	1.7417 (17)	C2B—S2B	1.7398 (17)
C3A—S3A	1.7274 (18)	C3B—S3B	1.7257 (18)
C3A—S4A	1.7090 (18)	C3B—S4B	1.7104 (18)
C5A—S4A	1.7420 (18)	C5B—S4B	1.7437 (18)
S2A—C1A—S3A	114.37 (10)	S2B—C1B—S3B	114.40 (10)
C2A—C3A—S3A	117.75 (14)	C2B—C3B—S3B	117.93 (13)
C2A—C4A—C12A	122.62 (15)	C2B—C4B—C12B	122.59 (15)
C4A—C5A—S4A	112.40 (13)	C4B—C5B—S4B	112.16 (13)
C1A—S2A—C2A	96.47 (8)	C1B—S2B—C2B	96.67 (8)
C1A—S3A—C3A	95.95 (8)	C1B—S3B—C3B	95.84 (8)
C3A—S4A—C5A	91.22 (8)	C3B—S4B—C5B	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) = 1.3*U*_{eq}(C).

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1993); data reduction: MolEN (Fair, 1990); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP (Johnson, 1965); software used to prepare material for publication: PLATON (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1332). Services for accessing these data are described at the back of the journal.

References

- Enraf–Nonius (1993). CAD-4 EXPRESS. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
 Fair, C. K. (1990). MolEN. Enraf–Nonius, Delft, The Netherlands.
 Johnson, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
 Lee, H.-J., Kim, Y.-Y. & Noh, D.-Y. (1998). *Bull. Korean Chem. Soc.* **19**, 1011–1013.
 Lee, H.-J. & Noh, D.-Y. (1998). *Bull. Korean Chem. Soc.* **19**, 340–344.
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
 Öztürk, T. (1996). *Tetrahedron Lett.* **37**, 2821–2824.
 Öztürk, T. & Türksoy, F. (1999). Unpublished results.
 Öztürk, T. & Wallis, J. D. (1996). *Acta Cryst.* **C52**, 2552–2554.
 Parvez, M., Meshher, S. T. E. & Clark, P. D. (1996). *Acta Cryst.* **C52**, 1503–1505.
 Sheldrick, G. M. (1997). SHELXL97 and SHELXS97. University of Göttingen, Germany.
 Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.