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5-Benzyl-5-phenyl[1,3]dithiolo[4,5-*d*]-[1,3]dithiole-2-thione

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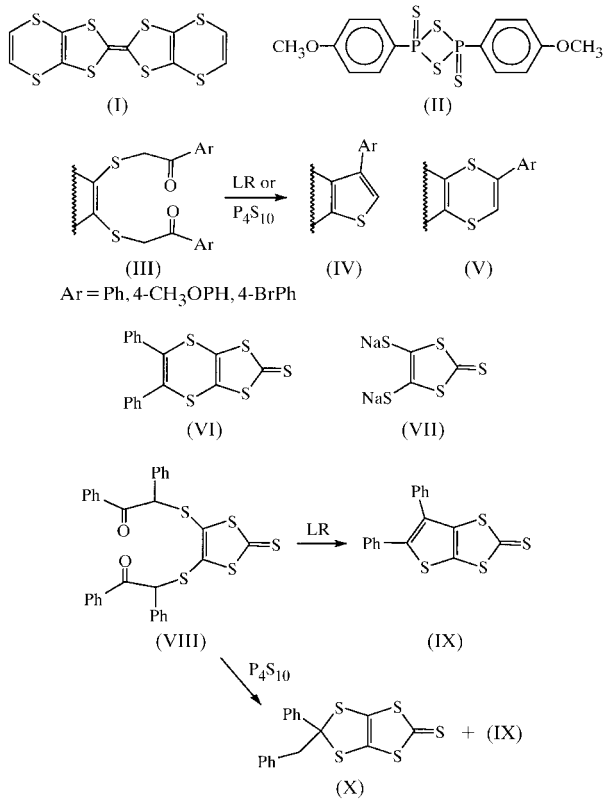
In the title compound, $C_{17}H_{12}S_5$, the dithiole ring bearing the aryl substituents assumes an envelope conformation with the maximum deviation from planarity being −0.053 Å. The phenyl and benzyl rings are twisted by 33.0 (1) and 31.1 (1)°, respectively, out of the dithiole plane. The crystal packing is governed by short S···S interactions, with the shortest being 3.550 (2) Å.

Comment

During the course of our studies on synthesizing new bis-(ethylenedithio)tetrathiafulvalene [BEDT–TTF or ET, (I)] derivatives, radical cation salts which show electrical conductivity and in some cases superconductivity (Williams *et al.*, 1985), we have focused on the recently developed reactions of Lawesson's reagent (LR), (II) (Öztürk, 1996; Öztürk & Wallis, 1996), or phosphorus pentasulfide, P_4S_{10}, with 1,8-diketones (III). These reactions have proved to be an efficient route to the synthesis of substituted thiophene (IV) and 1,4-dithiin (V) heterocyclic systems, which could be useful building blocks for new BEDT–TTF derivatives.

In an attempt to synthesize the 5,6-diphenyl derivative (VI) of BEDT–TTF, tetraphenyl-1,8-diketone (VIII), which was prepared from the reaction of readily available dithiolate (VII) (Svenstrup & Becher, 1995) with desyl chloride, was treated with both LR and P_4S_{10}. In accordance with the result obtained by Lee *et al.* (1998), diphenylthiophene (IX) rather than diphenyldithiin (VI) was isolated when the reaction was performed with LR. Surprisingly, when the reaction was carried out with P_4S_{10} under the same conditions, benzylphenyldithiole (X) ring formed along with (IX).

In the title compound, (X), with the exception of the C4 atom, the fused heterocycle is nearly planar, with a dihedral angle between the S5/C3/C2/S4 and C1/S2/C2/C3/S3 mean planes of 3.02 (8)°. The thiole ring which bears the aryl substituents deviates from planarity, while atom C4 is displaced from the S5/C3/C2/S4 mean plane by 0.736 (4) Å. The puckering parameters (Cremer & Pople, 1975) of this ring are Q = 0.469 (3) Å and φ = 321.8 (4)°, so the dithiole ring assumes an envelope conformation. The mean bond distances in the dithiole–thione ring are S=C = 1.640 (4) Å and S—Csp^2 = 1.732 (4) Å. These values are comparable with those found in the structures of both 6-(4-methoxyphenyl)-thieno[2,3-*d*][1,3]dithiole-2-thione (Öztürk & Wallis, 1996)



and 5,6-diphenylthieno[2,3-*d*][1,3]dithiole-2-thione (Kaynak *et al.*, 2000). The other dithiole ring of the fused heterocycle is affected by the presence of the phenyl and benzyl substituents. The bond lengths are quite different from those of the adjacent dithiole ring; the mean S—Csp^2 and S—Csp^3 bond lengths are 1.748 (1) and 1.855 (14) Å, respectively. The shortening of the S5—C4 and C4—C5 distances *versus* S4—C4 and C4—C11 may be explained by the two short intramolecular contacts H10···S5 (2.58 Å) and H112···C6 (2.63 Å).

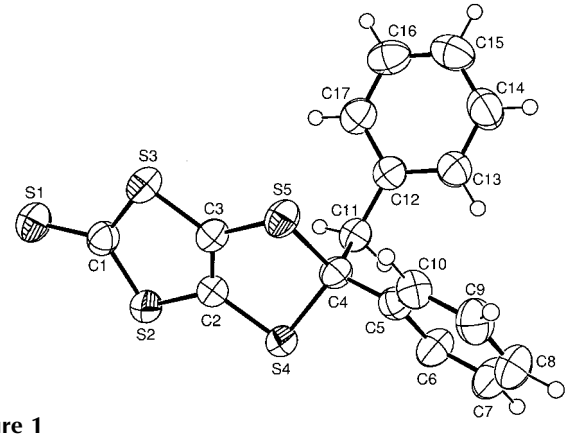


Figure 1
ORTEP (Johnson, 1965) drawing with the atomic numbering scheme. The displacement ellipsoids are drawn at the 30% probability level.

The substituted phenyl rings are essentially planar [maximum deviations of −0.002 (4) and −0.010 (4) Å for C8 and C14, respectively] and twisted slightly out of the plane of the fused heterocycle, with torsion angles of 175.4 (3) and 170.5 (3)° for S5—C4—C5—C6 and S4—C4—C11—C12, respectively. The dihedral angles between the phenyl groups (C5–C10 and C12–C17) and the S5/C3/C2/S4 mean plane are 33.0 (1) and 31.1 (1)°, respectively, while the dihedral angle between these two phenyl groups is 61.5 (1)°.

In the crystal, the molecules are packed in layers related by the translation [001]. The relevant S···S non-bonding contacts involved are S1···S2($2-x$, $\frac{1}{2}-y$, $\frac{1}{2}-z$) = 3.772 (2), S2···S3(x, $1+y$, z) = 3.601 (2), S3···S4(x, $-1+y$, z) = 3.630 (2) and S4···S5(x, $1+y$, z) = 3.550 (2) Å.

Experimental

Preparation of 2-[5-(2-oxo-1,2-diphenylethylsulfanyl)-2-thioxo-1,3-dithiol-4-ylsulfanyl]-1,2-diphenyl-1-ethanone, (VIII). To a solution of dithiolate (VII) (0.26 g, 1 mmol) in dry ethanol (10 ml) and under a nitrogen atmosphere, desyl chloride (0.5 g, 2 mmol) was added dropwise. The solution was then stirred at room temperature for 3 h. The yellow precipitate was filtered off and washed with ethanol (5 ml), which was sufficiently pure for use in the next step, m.p. 430–431 K (0.57 g, 90%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.8 (20H, *m*, Ph), 6.1 (H, *s*, PhCHS), 5.8 (H, *s*, PhCHS); *m*/*z* (EI): 587 M^+; found C 63.65, H 3.44%; $C_{31}H_{22}O_2S_5$ requires C 63.48, H 3.44%.

Preparation of 5-benzyl-5-phenyl[1,3]dithiolo[4,5-*d*][1,3]dithiole-2-thione, (X). A solution of 1,8-diketone (VIII) (1 g, 1.7 mmol) and P_4S_{10} (0.8 g, 1.70 mmol) in dry toluene (30 ml) under a nitrogen atmosphere was refluxed until consumption of the starting material was complete, which took approximately 5 h. The solvent was then evaporated under reduced pressure and the remaining viscous material was chromatographed, eluting with hexane–dichloromethane (3:1). The first fraction yielded 5,6-diphenylthieno[2,3-*d*][1,3]dithiole-2-thione, (IX) (0.23 g, 40%), and the second fraction was characterized as (X), m.p. 401–402 K (0.17 g, 25%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.40–7.18 (8H, *m*, Ph), 6.92 (2H, *d*, J = 12 Hz, Ph), 3.76 (2H, *s*, $PhCH_2$); ^{13}C NMR (50.32 Hz, $CDCl_3$): 205 (C═S), 139, 134, 130, 128.8, 128.5, 127.8, 127.6, 127, 126, 86, 51; *m*/*z* (EI): 376 M^+; found C 54.28, H 3.21%; $C_{15}H_{12}S_5$ requires C 54.59, H 3.54%; UV: (CH_3CN, *nm*) 426.

Crystal data

$C_{17}H_{12}S_5$
M_r = 376.62
Monoclinic, $P2_1/c$
a = 14.178 (3) Å
b = 6.3433 (6) Å
c = 19.227 (3) Å
β = 101.538 (15)°
V = 1694.2 (5) Å^3
Z = 4
D_x = 1.48 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 22.2–42.7°
μ = 6.23 mm^{-1}
T = 295 K
Prismatic, brown
0.30 × 0.15 × 0.09 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North *et al.*, 1968)
T_{min} = 0.171, T_{max} = 0.571
3891 measured reflections
3448 independent reflections
2513 reflections with $I > 3\sigma(I)$
R_{int} = 0.048
θ_{max} = 74.4°
$h = -17 \rightarrow 17$
$k = 0 \rightarrow 7$
$l = -23 \rightarrow 0$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F
R = 0.047
wR = 0.054
S = 0.95
2513 reflections
199 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F) + (0.02F)^2 + 0.85]$, except $w = 0$ if $F^2 <$ cutoff × σ^2F, cutoff = 3.0
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.640 (4)	S5—C3	1.748 (4)
S2—C1	1.729 (4)	S5—C4	1.845 (3)
S2—C2	1.733 (4)	C2—C3	1.336 (5)
S3—C1	1.736 (4)	C4—C5	1.513 (5)
S3—C3	1.731 (4)	C4—C11	1.533 (4)
S4—C2	1.747 (4)	C11—C12	1.500 (5)
S4—C4	1.865 (4)		
C1—S2—C2	96.3 (2)	S4—C2—C3	116.9 (3)
C1—S3—C3	96.6 (2)	S3—C3—S5	125.7 (2)
C2—S4—C4	92.8 (2)	S3—C3—C2	116.3 (3)
C3—S5—C4	92.3 (2)	S5—C3—C2	117.9 (3)
S1—C1—S2	123.0 (2)	S4—C4—S5	105.0 (2)
S1—C1—S3	123.5 (3)	S4—C4—C5	106.9 (2)
S2—C1—S3	113.4 (2)	S4—C4—C11	108.7 (2)
S2—C2—S4	126.0 (2)	S5—C4—C11	109.5 (2)
S2—C2—C3	117.2 (3)	C4—C11—C12	115.0 (3)

Ring-H atoms were placed geometrically 0.95 Å from their parent atoms, while the positions of atoms H111 and H112 were taken from a difference map. A riding model was used for all ring-H atoms, with U_{eq}(H) = 1.3U_{eq}(C). The same model was also applied for the H atoms on C11 and after refining for a few cycles isotropically, they were fixed.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1993); data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SIR* in *MolEN*; program(s) used to refine structure: *LSFM* (Fair, 1990); molecular graphics: *ORTEP* (Johnson, 1965); software used to prepare material for publication: *MolEN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1309). Services for accessing these data are described at the back of the journal.

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