Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

5,6-Diphenyl[1,3]dithiolo[4,5-*b*]-dithiine-2-thione

F. Betül Kaynak,[a] Süheyla Özbey,[a]* Turan Öztürk[b] and Erdal Ertaş[b]

[a]Department of Engineering Physics, Hacettepe University, Beytepe 06532, Ankara, Turkey, and [b]Marmara Research Center, Department of Chemistry, 41470 Gebze, Kocaeli, Turkey
Correspondence e-mail: sozbey@hacettepe.edu.tr

Received 1 February 2001
Accepted 20 April 2001

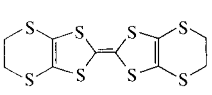
In the title compound, $C_{17}H_{10}S_5$, the dithiine ring adopts a boat conformation while the dithiole ring has an envelope conformation. The phenyl groups are planar and make dihedral angles of 40.7 (2) and 59.8 (2)° with the best plane of the thiine ring. The shortest intermolecular S···S contact is 3.305 (2) Å.

Comment

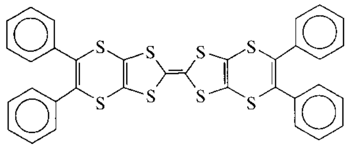
There has been wide interest in the introduction of increased conjugation to bis(ethylenedithio)tetrathiafulvalene [BEDT–TTF or ET, (I)], which is an electron-donating molecule. Its radical cation salts show electrical conductivity and, in some cases, superconductivity at lower temperatures (Williams *et al.*, 1985). Although the introduction of conjugation has been achieved in the middle of the molecule (Bryce, 1995), there are limited examples of the introduction of conjugation at the peripheral ethylene groups (Inoue *et al.*, 1986; Yamada *et al.*, 1996; Skabara *et al.*, 1999). This is mainly due to the limited availability of methodology in the literature.

In this context, attempts to synthesize a fully unsaturated ET analogue with peripheral phenyl groups, (II), have so far failed (Noh *et al.*, 1996; Lee *et al.*, 1998; Lee & Noh, 1998). On the other hand, we recently reported a concise synthesis of 5,6-diphenyl[1,3]dithiolo[4,5-*b*]dithiine-2-thione, (VII), and its coupling product, a fully unsaturated and tetra-phenyl-substituted ET analogue, (II) (Ertaş & Öztürk, 2000), by employing 1,8-diketone ring formation using P_4S_{10} in the dark (Öztürk, 1996), which proved that the 1,8-diketone ring formation reaction is an efficient procedure for the synthesis of fused and substituted 1,4-dithiine rings.

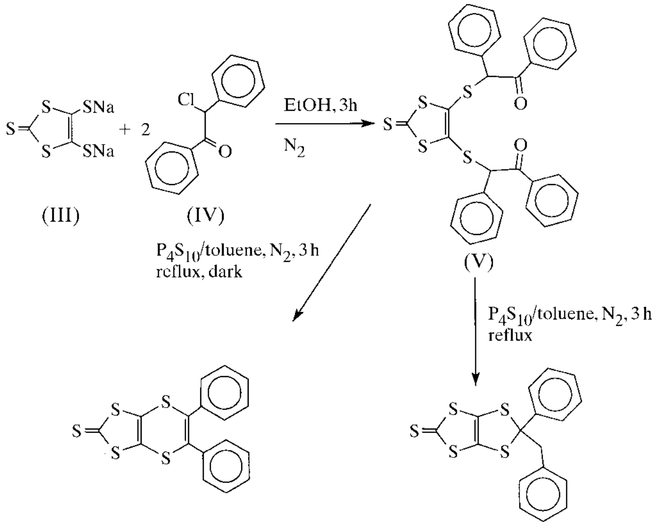
Diketone (V) was prepared from the reaction of the readily available dithiolate (III) (Svenstrup & Becher, 1995), with desyl chloride in ethanol under a nitrogen atmosphere. Surprisingly, when diketone (V) was refluxed in toluene, the benzylphenyldithiole ring (VI) was obtained rather than the desired dithiine ring (VII). The crystal structure of (VI) was determined and has been published (Kaynak *et al.*, 2001). In the light of this result, it was suggested that the reaction proceeds *via* a radical mechanism, which led us to repeat the reaction in the dark. Thus, the diphenyldithiine (VII) was obtained in 65% yield.



(I)



(II)



We report here the crystal structure of 5,6-diphenyl[1,3]-dithiolo[4,5-*b*]dithiine-2-thione, (VII). The structure predicted from chemical and spectral analysis is confirmed. The molecular structure is shown in Fig. 1. Structural results show that the six-membered ring adopts the boat conformation having spherical polar set values (Cremer & Pople, 1975) Q = 0.770 (3) Å, θ = 91.6 (3)° and φ = 178.9 (3)°. Atoms S4 and S5 are displaced from the C2/C3/C4/C5 mean plane by −0.697 (2) and −0.636 (2) Å, respectively. The dithiole ring fused to the six-membered ring also deviates from planarity, while atom C1 is displaced from the S2/C2/C3/S3 mean plane by 0.122 (5) Å. The puckering parameters of this ring are Q = 0.077 (4) Å and φ = 36 (3)°, so the dithiole ring assumes an envelope conformation. The dihedral angle between the S2/C2/C3/S3 and C2/C3/C4/C5 mean planes is 31.5 (2)°. No structure determinations of molecules containing this heterocyclic system have been reported previously. However, it has been stated that a trace amount of the title compound was occasionally separated as needle-shaped crystals and identified by crystal structure analysis (Lee & Noh, 1998).

The bonds in the dithiole ring are very similar to those for 5-benzyl-5-phenyl[1,3]dithiolo[4,5-*d*][1,3]dithiole-2-thione (Kaynak *et al.*, 2001). The six-membered ring of the fused heterocycle (dithiine, hereafter) is affected by the presence of the phenyl substituents. The increase in the electron density of the dithiine ring due to the phenyl groups has made the S5—C4 and S4—C5 bond distances in (VII) [1.776 (4) and

1.802 (4) Å, respectively] longer than the values of S5—C3 and S4—C2 [1.750 (5) and 1.741 (5) Å, respectively]. In the molecule, the double-bond distances are S1═C1 1.639 (5), C2═C3 1.341 (6) and C4═C5 1.337 (6) Å. Similar bond lengths have been reported for the crystal structures of 4,5-(1′,2′-diphenylethylenedithio)-1,3-dithiole-2-thione (Lee & Noh, 1998) and 5-benzyl-5-phenyl[1,3]dithiolo[4,5-*d*][1,3]-dithiole-2-thione (Kaynak *et al.*, 2001). The phenyl rings are essentially planar [maximum deviations of −0.013 (6) and 0.006 (5) Å for C9 and C16, respectively] and twisted out of the C2/C3/C4/C5 mean plane of the dithiine ring with torsion angles of 53.6 (5) and −139.7 (4)° for S5—C4—C12—C17 and S4—C5—C6—C7, respectively; the dihedral angle between phenyl groups is 59.1 (2)°.

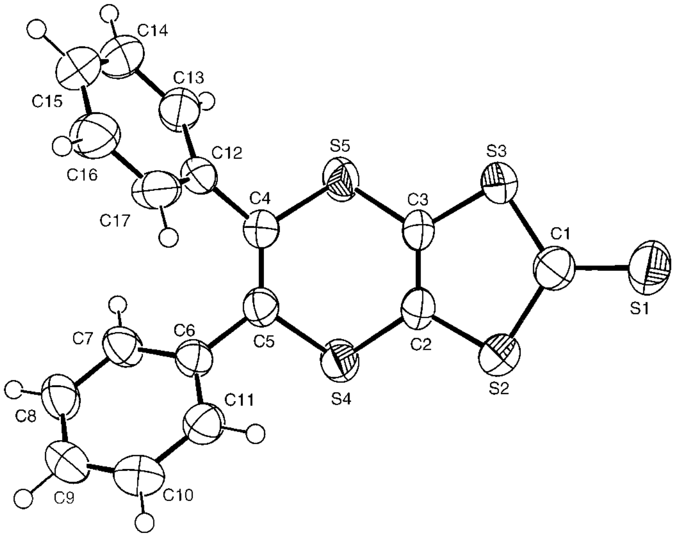


Figure 1
*ORTEP*III (Johnson & Burnett, 2000) drawing of the asymmetric unit of the title compound with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

In the title molecule, the shortest intermolecular contact is S2···S2(1 − *x*, −*y*, −*z*) 3.305 (2) Å, which is shorter than the sum of the van der Waals radii. Of particular note is the short non-bonding intramolecular distances observed for H11···S4 and H7···C12 of 2.77 and 2.74 Å, respectively.

Experimental

Preparation of 2-[5-(2-oxo-1,2-diphenylethylsulfanyl)-2-thioxo-1,3-dithiol-4-ylsulfanyl]-1,2-diphenyl-1-ethanone, (V). To a solution of dithiolate (III) (0.26 g, 1 mmol) in dry ethanol (10 ml) and under a nitrogen atmosphere was added desyl chloride, (IV) (0.5 g, 2 mmol), dropwise and the solution was then stirred at room temperature for 3 h. The yellow precipitate was filtered and washed with ethanol (5 ml), and 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, (VI). A solution of 1,8-diketone (V) (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 the starting material had been consumed, which took approximately 3 h. The solvent was then evaporated under reduced pressure and the remaining viscous material was chromatographed, eluting with hexane–dichloromethane (3:1); 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$_3$): δ 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: λ_{max} (CH$_3$CN, nm) 426.

Preparation of 5,6-diphenyl[1,3]dithiolo[4,5-*b*][1,4]dithiine-2-thione, (VII). The same reaction as for (VI) was repeated in the dark. The crude material was purified by column chromatography (3:1, hexane/CH$_2$Cl$_2$), which gave 65% of (VII); m.p. 386–387 K. ^{1}H NMR (250 MHz, CDCl$_3$): δ 7.09–7.34 (*m*, 10 H); ^{13}C NMR (67.8 MHz, CDCl$_3$): δ 213.9 (C═S), 136.2 (C-*q*), 134.7 (C-*q*), 129.9 (C-*q*), 129.5 (C-*t*), 128.7 (C-*t*), 128.6 (C-*t*); HRMS: *m*/*z* calculated 373.9386; measured 373.9397 for $C_{17}H_{10}S_5$; found C 54.44, H 2.66%: calculated C 54.5, H 2.69%; IR: ν 1080 cm^{-1} (C═S); UV: λ_{max} (CH$_3$CN, nm) 391.

Crystal data

$C_{17}H_{10}S_5$
$M_r = 374.55$
Monoclinic, $P2_1/n$
$a = 12.343$ (2) Å
$b = 5.273$ (1) Å
$c = 26.029$ (7) Å
$\beta = 101.54$ (2)°
$V = 1659.8$ (6) Å^3
$Z = 4$

$D_x = 1.499$ Mg m^{-3}
Cu *Kα* radiation
Cell parameters from 19 reflections
$\theta = 15.5$–42.6°
$\mu = 6.36$ mm^{-1}
$T = 295$ K
Prismatic, light brown
0.48 × 0.20 × 0.12 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/2θ scans
Absorption correction: empirical *via* ψ scans (Fair, 1990)
$T_{min} = 0.272$, $T_{max} = 0.466$
3865 measured reflections
3393 independent reflections
2125 reflections with $I > 2\sigma(I)$

$R_{int} = 0.075$
$\theta_{max} = 74.2$°
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 6$
$l = -32 \rightarrow 31$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.149$
$S = 1.06$
2125 reflections
209 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0945P)^2 + 0.0036P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—S1	1.639 (5)	C3—S3	1.731 (5)
C1—S2	1.732 (5)	C3—S5	1.750 (5)
C1—S3	1.742 (5)	C4—C5	1.337 (6)
C2—C3	1.341 (6)	C4—S5	1.776 (4)
C2—S2	1.739 (4)	C5—S4	1.802 (4)
C2—S4	1.741 (5)		
S1—C1—S2	123.9 (3)	C5—C4—S5	122.4 (3)
S2—C1—S3	112.6 (3)	C4—C5—C6	127.1 (4)
C3—C2—S2	116.0 (4)	C6—C7—C8	121.0 (5)
C3—C2—S4	122.3 (3)	C1—S2—C2	97.1 (2)
C2—C3—S3	117.1 (3)	C3—S3—C1	96.7 (2)
C2—C3—S5	121.2 (4)	C2—S4—C5	99.6 (2)
C5—C4—C12	125.6 (4)	C3—S5—C4	100.39 (19)

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H atoms were placed geometrically 0.93 Å from their parent atoms and their displacement parameters were refined.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993); data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SIR* (Burla *et al.*, 1989) in *MolEN*; program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Johnson & Burnett, 2000); software used to prepare material for publication: *PLATON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1325). Services for accessing these data are described at the back of the journal.

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