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4-Benzylidene-3,4-dihydro-1λ^4-cyclopenta-[2,1-*b*:3,4-*b*′]dithiophene at 120 K

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Key indicators

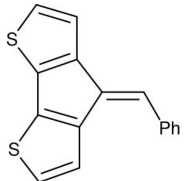
Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.048
wR factor = 0.114
Data-to-parameter ratio = 17.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

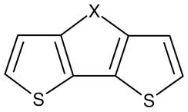
The title compound, $C_{16}H_{10}S_2$, is a further example of a 3,3′-bridged 2,2′-dithiophene. As in comparable members of this series of compounds, the monoatomic 3,3′-bridge constrains the tricyclic heterocyclic ring system to be essentially planar with, in this case, an S—C—C—S torsion angle of 2.3 (4)°.

Comment

The title compound, (I), was synthesized with a view to investigating its potential as a ligand. A search of the Cambridge Structural Database (Allen, 2002), accessed by means of the Chemical Database Service of the EPSRC (Fletcher *et al.*, 1996), revealed, however, the presence of known structures for a number of 3,3′-bridged 2,2′-dithiophenes, (II)–(VI) (Koster *et al.*, 1970; Pilati, 1995) analogous to (I). It is in relation to these, especially the series (II)–(VI) described by Pilati (1995), that the structure of (I) is discussed here.



(I)



(II): X = CH_2
(III): X = spirocyclo-C_5H_8
(IV): X = CH_2-O-CH_2
(V): X = CH_2-O-$(CH_2)_3$-O-CH_2
(VI): X = CH_2-O-$(CH_2)_2$-O-$(CH_2)_2$-O-CH_2

The molecule of (I) is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. In addition to the values given in the Table, and noting the C5—C6—C7 angle of 104.19 (19)°, the remaining internal C—C—C angles of the five-membered rings are in the range 108.3 (2)–112.4 (2)°. The C—C—S internal angles, in the range 112.15 (17)–113.09 (19)°, show less variation. The bond lengths and angles in the phenyl group in the ranges 1.380 (3)–1.395 (3) Å and 118.0 (2)–121.5 (2)°, respectively, are unexceptional. The torsion angles about the C1—C2 bond are a clear indication of the planar nature of the dithiophene ring system. The torsion angles about the C10—C11 bond, on the other hand, indicate a tilt of the phenyl group relative to the dithiophene group which amounts to a dihedral angle between their least squares planes of 44.38 (6)°.

A feature of the molecule of (I) is the difference between the S1—C1 and S2—C2 bond lengths [1.712 (2) and

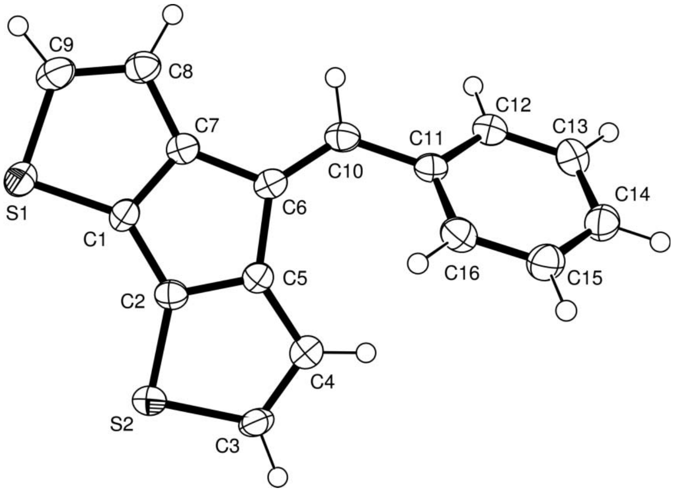


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

1.711 (2) Å, respectively] and the S1—C9 and S2—C3 bond lengths [1.734 (3) and 1.727 (3) Å, respectively]. Pilati (1995) has noted a similar disparity in S—C bond lengths, in the same sense for (II) and, although less marked, for (III) but in the opposite sense for (IV)–(VI) (see Table 2). Also evident from the torsion-angle data given in Table 2 is the planarity of the dithiophene ring system in the case of (II) and (III), now along with (I), which is not the case for (IV)–(VI). It is clear, therefore, that the monoatomic 3,3′ bridge in (I)–(III) as opposed to the polyatomic bridges in (IV)–(VI) is the key factor in creating the structural differences between the two classes of compound and is largely independent of the nature of the species providing the monoatomic bridge.

The molecules of (I) are found in layers parallel to (100) (Fig. 2) within which there are two significant intermolecular contacts. The first of these is a π–π interaction arising from the overlap of the dithiophene ring systems in pairs, creating interactions involving the rings with centroid *Cg*1 defined by C1/C2/C5–C7. For this interaction, $Cg1\cdots Cg1^{iii}$ [symmetry code: (iii) $-x$, y, $-z + \frac{1}{2}$], the distance between the ring centroids, the perpendicular distance of the centroid of one ring to the least-squares plane of the other ring of the pair and the lateral displacement or slippage of the rings relative to one another are 3.829, 3.467 and 1.625 Å, respectively. The second interaction is a C—H⋯π contact of the form $C8—H8\cdots Cg2^{i}$ where *Cg*2 is the centroid of the ring defined by C2/S2/C3–C5 [symmetry code: (i) $-x + \frac{1}{2}$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$]. Here the C—H, H⋯*Cg*, the perpendicular distance of the H atom from the l.s. plane of the ring and the C⋯*Cg* distances are 0.95, 2.750, 2.706 and 3.650 Å, respectively, and the C—H⋯*Cg* angle is 158°. Stacking of these layers in the direction of *a* produces a further π–π interaction between pairs of phenyl rings, C11–C16 with centroid *Cg*3, of the form $Cg3\cdots Cg3^{ii}$ (Fig. 3) [symmetry code: (ii) $-x + \frac{1}{2}$, $-y + \frac{1}{2}$, $-z$] for which the distance between the ring centroids, the perpendicular distance of the centroid of one ring to the least-squares plane of the other ring of the pair and the lateral displacement or slippage of the rings relative to one another are 3.617, 3.607 and 0.269 Å, respectively.

Experimental

To a solution of 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (2.0 g, 11.2 mmol), (II) (Kraak *et al.*, 1968), in Et_2O (25 ml) at 273 K was added dropwise by syringe a solution of BuLi (11.3 mmol) in hexane. The reaction mixture was stirred at 273 K for 1 h after addition was complete. A solution of PhCHO (1.3 g, 12 mmol) in Et_2O (10 ml) was then slowly added. The reaction mixture was refluxed for 20 min., saturated aqueous NH_4Cl solution (30 ml) added, the organic layer collected, washed with water and dried over $MgSO_4$, and rotary evaporated. The residue was recrystallized successively from EtOH and MeCN. The orange-red crystals used in the X-ray crystal structure determination were grown slowly from MeCN solution (m.p. 408–410 K).

Crystal data

$C_{16}H_{10}S_2$
$M_r = 266.36$
Monoclinic, *C*2/*c*
$a = 19.618$ (2) Å
$b = 10.4720$ (8) Å
$c = 12.0157$ (12) Å
$\beta = 91.525$ (4)°
$V = 2467.6$ (4) Å^3
$Z = 8$

$D_x = 1.434$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 2794 reflections
$\theta = 2.9$–27.5°
$\mu = 0.41$ mm^{-1}
$T = 120$ (2) K
Plate, orange–red
0.28 × 0.22 × 0.03 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.662$, $T_{\max} = 0.990$
11902 measured reflections

2815 independent reflections
1836 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.056$
$\theta_{\max} = 27.5°$
$h = -25 \rightarrow 25$
$k = -13 \rightarrow 12$
$l = -14 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.114$
$S = 1.03$
2815 reflections
163 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 1.7202P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.712 (2)	C4—C5	1.426 (3)
S1—C9	1.734 (3)	C5—C6	1.488 (3)
S2—C2	1.711 (2)	C6—C10	1.348 (3)
S2—C3	1.727 (3)	C6—C7	1.479 (3)
C1—C7	1.386 (3)	C7—C8	1.420 (3)
C1—C2	1.449 (3)	C8—C9	1.356 (3)
C2—C5	1.383 (3)	C10—C11	1.465 (3)
C3—C4	1.367 (3)		
C1—S1—C9	90.63 (12)	C4—C5—C6	139.2 (2)
C2—S2—C3	90.72 (11)	C7—C6—C5	104.19 (19)
C2—C1—S1	139.53 (18)	C8—C7—C6	138.1 (2)
C1—C2—S2	137.92 (19)	C6—C10—C11	127.7 (2)
C7—C1—C2—C5	−0.7 (3)	C6—C10—C11—C12	142.3 (2)
S1—C1—C2—S2	2.3 (4)	C6—C10—C11—C16	−40.9 (4)

Table 2
Summary of S—C distances (Å) and absolute values of selected torsion angles (°) for (I–VI).

For (II–IV), values and the associated su's have been averaged over all molecules in the asymmetric unit. In all cases S—C distances, according to type, have been averaged, in addition, over the two thiophene rings. Values for (II–VI) were obtained from the data of Pilati (1995).

Compound	S1—C1	S1—C9	S1—C1—C2—S2	C7—C1—C2—C5
(I)	1.712 (2)	1.730 (3)	2.3 (4)	0.7 (3)
(II)	1.713 (2)	1.726 (2)	4.4 (5)	0.2 (3)
(III)	1.709 (2)	1.716 (2)	2.6 (4)	0.9 (3)
(IV)	1.729 (1)	1.705 (2)	9.7 (2)	10.8 (3)
(V)	1.728 (1)	1.704 (2)	109.6 (1)	111.7 (2)
(VI)	1.728 (2)	1.708 (2)	56.8 (2)	61.3 (3)

In the final stages of refinement H atoms were placed in calculated positions, with C—H = 0.95 Å, and refined with a riding model, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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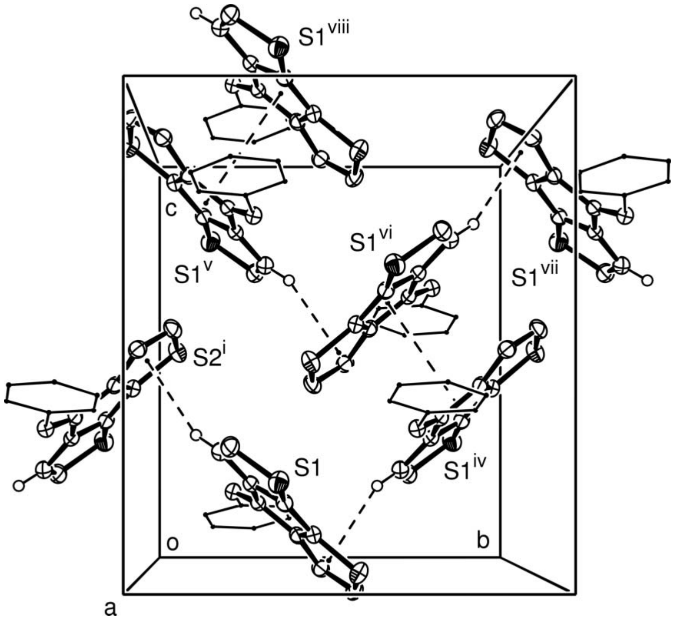

Figure 2
A layer of molecules of (I) parallel to (100) and centred on $x = \frac{1}{4}$. For clarity, the phenyl group (C11–C16) is shown in thin line outline and only the H atoms involved in C—H$\cdots\pi$ contacts are shown as small spheres of arbitrary radii. Dashed lines represent intermolecular contacts. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (v) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (vi) $x, -y+1, z+\frac{1}{2}$; (vii) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (viii) $x, y, z+1$.]

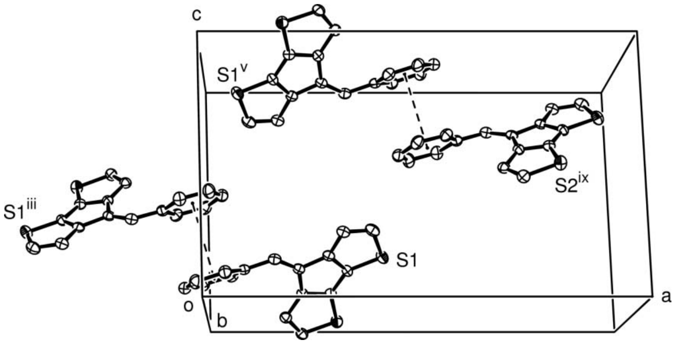

Figure 3
A section through the structure of (I) parallel to (010) and centred on $y = \frac{1}{4}$, showing interlayer $\pi\cdots\pi$ contacts (dashed lines). Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted. [Symmetry codes: (iii) $-x, y, -z+\frac{1}{2}$; (v) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (ix) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$.]