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3,4-Bis[(4-methoxybenzoyl)methylsulfanyl]thiophene

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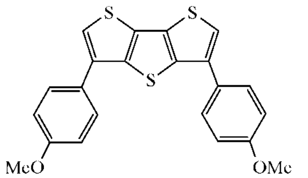
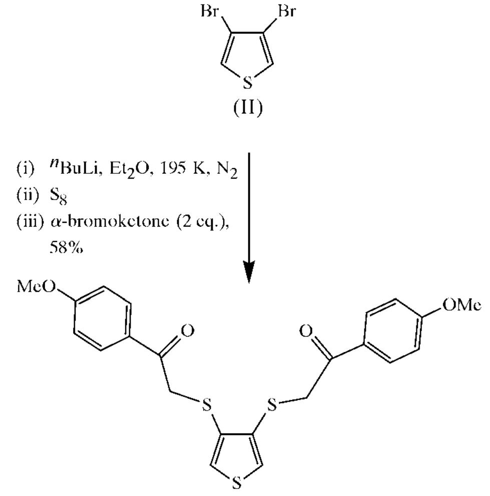
A new type of thiophene derivative having α-thioketone groups at the 3- and 4-positions, *viz.* the title compound, $C_{22}H_{20}O_4S_3$, has been prepared and studied by NMR spectroscopy and single-crystal X-ray diffraction techniques. The molecule is nearly planar, the dihedral angles between the essentially planar thiophene and benzene rings being 9.4 (1) and 10.6 (1)°. One of the thioketone O atoms is involved in an intermolecular C—H···O hydrogen-bonding interaction.

Comment

Dithieno[3,2-*b*;2′,3′-*d*]thiophenes (DTT), which consist of three fused thiophene heterocycles, are important compounds for the synthesis of a wide variety of materials for electronics and optical applications (Kim *et al.*, 2001, 1999; Osterod *et al.*, 2001; Ventelon *et al.*, 1999; Tsivgoulis & Lehn, 1995). Dimeric DTT systems, which have been employed in thin-film transistors, have been shown to have high mobilities and on/off ratios (Sirringhaus *et al.*, 1997; Morrison *et al.*, 1999; Li *et al.*, 1998). Their oxidized dioxide forms demonstrate interesting fluorescence properties and this creates important application opportunities, such as their use as labelling agents in biological systems (Sotgiu *et al.* 2003; Barbarella, 2002; Barbarella *et al.*, 2001), photovoltaic devices (Catellani *et al.*, 2002) and light-emitting diodes (Gigli *et al.*, 2001). Conducting polymers (Fujitsuka *et al.*, 1996; Lazzaroni *et al.*, 1989; Di Marco *et al.*, 1985), and organic acceptor and donor molecules for the preparation of different cationic radical salts and charge-transfer complexes (Mazaki & Kobayashi, 1992; Yui *et al.*, 1987; Hayashi *et al.*, 1992; Bertinelli *et al.*, 1984), have been prepared.



(I)



Although some methods have been developed for the synthesis of the DTT molecules (De Jong & Janssen, 1971; Mazaki & Kobayashi, 1989; Hellberg & Remonen, 1995; Schroth *et al.*, 1997; Frey *et al.*, 2002), new synthetic methods are still required, particularly to functionalize the system. Recently, we have reported an efficient and novel method (Ertas & Ozturk, 2004). During the application of this method

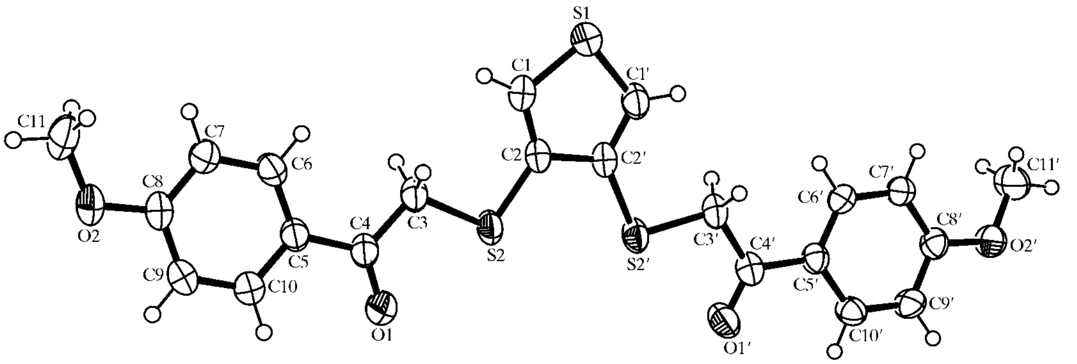


Figure 1
The molecular structure of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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to the synthesis of 3,5-bis(4-methoxyphenyl)dithieno[3,2-*b*;-2′,3′-*d*]thiophenes, (I), an intermediate was isolated, namely the title compound, (III), which was obtained in three steps starting from 3,4-dibromothiophene, (II) (see scheme). We report here the X-ray single-crystal structure of (III), which has α-thioketone groups at the 3- and 4-positions of the thiophene ring.

The molecular structure and atom-numbering scheme of (III) are shown in Fig. 1. Selected bond lengths and angles are listed in Table 1. Overall, the molecule is fairly flat; the dihedral angles between the essentially planar thiophene and benzene rings (C5–C10 and C5′–C10′) are 9.4 (1) and 10.6 (1)°, respectively, while the dihedral angle between these two benzene rings is 2.4 (1)°. The thioketone moieties attached to atoms C2 and C2′ of the thiophene ring adopt an extended conformation, with torsion angles close to 0 or 180°, *cf.* C1—C2—S2—C3 = −0.3 (2) and C1′—C2′—S2′—C3′ = −2.3 (2)°, C2—S2—C3—C4 = −176.4 (1) and C2′—S2′—C3′—C4′ = −179.2 (1)°, S2—C3—C4—O1 = 3.7 (2) and S2′—C3′—C4′—O1′ = 1.4 (2)°, and C3—C4—C5—C6 = 1.7 (3) and C3′—C4′—C5′—C6′ = −9.4 (3)°. The angles between the least-squares planes formed by the thioketone groups (S2/C3/C4/O1 and S2′/C3′/C4′/O1′) and the thiophene ring are 7.7 (1) and 0.7 (1)°, respectively. Thus, this part of the molecule is almost coplanar with the thiophene ring.

The S1—C1 and S1′—C1′ bond lengths [1.709 (2) and 1.709 (2) Å] are in good agreement with those found for other structures containing a thiophene ring (Kazak *et al.*, 2000; Rodinovskaya *et al.*, 2002). In the thioketone parts, the differences between the S2—C2/S2′—C2′ bond lengths [1.758 (2) and 1.762 (2) Å, respectively] and the S2—C3/S2′—C3′ bond lengths [1.799 (2) and 1.803 (2) Å, respectively] can be attributed to the different hybridization of the C*sp*^{3} and C*sp*^{2} atoms. Bonds C4—O1 and C4′—O1′ are found to have normal double-bond lengths.

There are no intramolecular hydrogen bonds in (III), but the O atoms of the ketone groups are involved in short contacts, forming a five-membered ring structure (Table 2). The interatomic distances S2···S2′ [3.169 (1) Å], S2···O1 [2.783 (2) Å] and S2′···O1′ [2.810 (2) Å] also indicate close contacts. There is a C—H···O-type intermolecular hydrogen bond between neighbouring molecules along the *b* axis. Molecules are stacked along the *a* direction with a mean interplanar distance of ≃ 3.45 Å; no hydrogen bonds are observed between these layers.

Experimental

To a solution of 3,4-dibromothiophene (0.96 g, 4 mmol) in dry ether (30 ml) was added *n*-BuLi (1.6 ml, 4 mmol, 2.5 *M*) by syringe at 351 K under a nitrogen atmosphere. The solution was stirred for 5 min and elemental sulfur (0.15 g, 4 mmol) was added portionwise. The solution was then stirred for 15 min and the addition of *n*-BuLi and elemental sulfur was repeated in the same ratios at the same temperature (351 K). The final solution was stirred for a further 30 min, then 2-bromo-4-methoxyacetophenone (2 g, 9 mmol) was added portionwise and the solution was allowed to come to room temperature. After the addition of ice, the mixture was extracted with ether (3 × 20 ml). The organic layer was dried over $MgSO_4$, filtered and the solvent evaporated under reduced pressure. The crude product was purified by column chromatography, eluting with hexane–ethyl acetate (5:1), to yield the title compound (m.p. 387–388 K; yield 1 g, 58%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.86 (4H, *d*, J = 8.3 Hz, Ph), 7.25 (2H, *s*, thiophene), 6.87 (4H, *d*, J = 8.3 Hz, Ph), 4.18 (4H, *s*, SCH_2), 3.83 (6H, *s*, OCH_3); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 192.7 (C═O), 163.7 (*q*, C), 132 (*q*, C), 130.1 (CH), 128.5 (*q*, C), 127.2 (CH), 113.8 (CH), 55.4 (OCH_3), 40.9 (SCH_2); *m*/*z* (EI): 444 (M^+).

Crystal data

$C_{22}H_{20}O_4S_3$
$M_r = 444.56$
Monoclinic, $P2_1/n$
$a = 10.4682$ (12) Å
$b = 10.9027$ (12) Å
$c = 18.4929$ (12) Å
$\beta = 101.390$ (7)°
$V = 2069.1$ (4) Å^3
$Z = 4$
$D_x = 1.427$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9.7$–18.1°
$\mu = 0.39$ mm^{-1}
$T = 293$ (2) K
Prism, yellow
0.6 × 0.6 × 0.48 mm

Data collection

Enraf-Nonius CAD-4 diffractometer
Non–profiled ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.802$, $T_{\max} = 0.837$
4417 measured reflections
4191 independent reflections
3279 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.026$
$\theta_{\max} = 26.3°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 13$
$l = -23 \rightarrow 22$
3 standard reflections
frequency: 120 min
intensity decay: 8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.100$
$S = 1.05$
4191 reflections
270 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 0.5012P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.358 (3)	C3—S2	1.7989 (18)
C1—S1	1.707 (2)	C4′—O1′	1.212 (2)
C1′—C2′	1.353 (3)	C4′—C5′	1.482 (2)
C1′—S1	1.708 (2)	C4—O1	1.218 (2)
C2—C2′	1.439 (2)	C4—C5	1.484 (2)
C2—S2	1.7575 (19)	C8—O2	1.360 (2)
C2′—S2′	1.761 (2)	C8′—O2′	1.356 (2)
C3′—C4′	1.514 (3)	C11′—O2′	1.426 (3)
C3′—S2′	1.8024 (17)	C11—O2	1.427 (3)
C3—C4	1.506 (3)		
C2—C1—S1	112.43 (14)	O2—C8—C9	115.31 (17)
C2′—C1′—S1	112.59 (14)	O2′—C8′—C9′	115.82 (16)
C1—C2—S2	128.65 (14)	C8—O2—C11	117.97 (16)
C1′—C2′—S2′	128.84 (14)	C8′—O2′—C11′	117.77 (16)
C4′—C3′—S2′	109.37 (13)	C1—S1—C1′	91.43 (10)
C4—C3—S2	109.26 (13)	C2′—S2′—C3′	99.89 (9)
C10′—C5′—C4′	119.05 (17)	C2—S2—C3	99.87 (9)
C10—C5—C4	118.32 (17)		
S2′—C3′—C4′—O1′	1.4 (2)	C2—C2′—S2′—C3′	−179.54 (14)
S2—C3—C4—O1	3.6 (2)	C4′—C3′—S2′—C2′	−179.19 (13)
O1′—C4′—C5′—C6′	169.74 (19)	C1—C2—S2—C3	−0.3 (2)
O1—C4—C5—C6	−178.31 (19)	C2′—C2—S2—C3	177.04 (14)
C1′—C2′—S2′—C3′	−2.3 (2)	C4—C3—S2—C2	−176.36 (13)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C10—H10···O1	0.93	2.47	2.778 (2)	99
C10′—H10′···O1′	0.93	2.53	2.811 (2)	98
C7—H7···O1^{i}	0.93	2.42	3.343 (2)	173

Symmetry code: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z-\frac{1}{2}$.

All H atoms were placed in idealized positions and refined using a riding model, with fixed C—H distances of 0.93 (aromatic), 0.96 (methyl) and 0.97 Å (ethyl), and with $U_{\rm iso}$(H) = 1.3$U_{\rm eq}$(C).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); 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) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1231). Services for accessing these data are described at the back of the journal.

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