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8,9-Dimethoxybenzo[*b*]naphtho[2,3-*d*]thiophene

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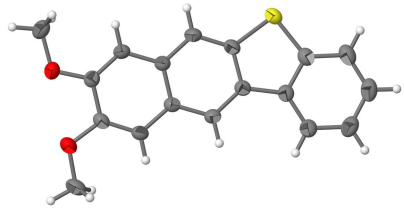
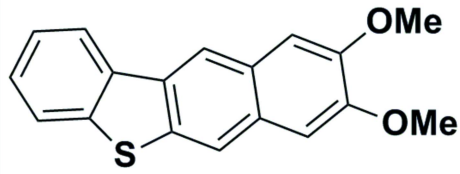
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{18}H_{14}O_2S$, the system of four fused rings is almost planar (r.m.s. deviation = 0.022 Å). The C atoms of the methoxy groups deviate from the mean plane of the ring system by 0.373 (2) and −0.104 (2) Å. In the crystal, very weak aromatic π–π stacking interactions [shortest centroid–centroid separation = 3.9286 (10) Å] may help to establish the packing.

3D view



Chemical scheme



Structure description

Thiophene and thiazole derivatives are known to possess interesting biological properties, such as anticancer activity (Bondock *et al.*, 2010; Al-Said *et al.*, 2011). As part of our studies in this area, we now describe the synthesis and structure of the title compound (Fig. 1).

As expected, the thiophene system is essentially planar and subtends dihedral angles with respect to the mean planes through the naphthalene ring system, *i.e.* the C7–C18 and C1–C6 phenyl rings, of 1.05 (9) and 1.53 (7)°, respectively. The C atoms of the methoxy groups are slightly displaced from their attached benzene ring, as indicated by the C15—C14—O1—C13 and C10—C11—O2—C12 torsion angles of −4.5 (2) and −9.1 (3)°, respectively. In the crystal, very weak aromatic π–π stacking interactions [shortest centroid–centroid separation = 3.9286 (10) Å between inversion-related C7–C9/C16–C18 rings] may help to establish the packing.

Synthesis and crystallization

To a solution of diethyl 2-[(2-(bromomethyl)benzo[*b*]thiophen-3-yl)methylidene]malonate (0.20 g, 0.50 mmol) and veratrole (1,2-dimethoxybenzene) (0.08 g, 0.55 mmol) in dry dichloroethane (5 ml) was added $ZnBr_2$ (0.03 g, 0.10 mmol). The reaction mixture was then stirred at room temperature under a nitrogen atmosphere for 4 h. After completion of the reaction (monitored by TLC), it was poured into ice water (30 ml). The

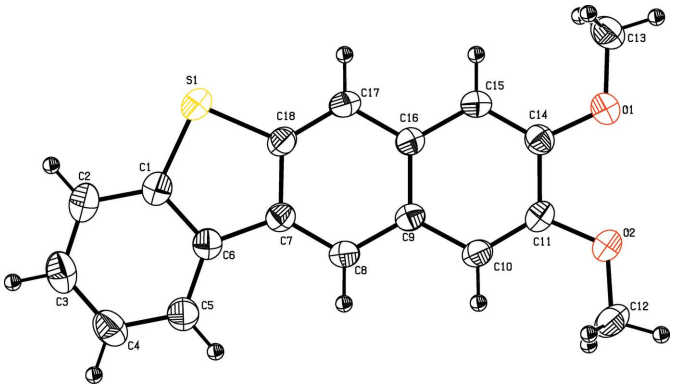


Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level.

organic layer was separated and the aqueous layer was extracted with DCM (2 × 20 ml). The combined organic layer was washed with water (2 × 20 ml) and dried (Na_2SO_4). Removal of the solvent followed by work-up and column chromatography (silica gel; 4% ethyl acetate in hexane) furnished the title compound (0.10 g, 30%) as a colourless solid (m.p. 463–465 K).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{18}H_{14}O_2S$
M_r	294.35
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	293
a, b, c (Å)	13.0062 (9), 5.9631 (4), 18.3801 (14)
β (°)	104.019 (7)
V (Å^3)	1383.05 (17)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.24
Crystal size (mm)	0.30 × 0.30 × 0.25
Data collection	
Diffractometer	Bruker SMART APEXII CCD
Absorption correction	Multi-scan
T_{min}, T_{max}	0.932, 0.943
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6823, 3192, 2344
R_{int}	0.028
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.684
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.119, 1.07
No. of reflections	3192
No. of parameters	192
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.26, −0.44

Computer programs: *APEX2* (Bruker, 2008), *SAINT* (Bruker, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015), *ORTEP-3* (Farrugia, 2012), *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

Acknowledgements

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full crystallographic data

IUCrData (2018). **3**, x181257 [https://doi.org/10.1107/S2414314618012579]

8,9-Dimethoxybenzo[*b*]naphtho[2,3-*d*]thiophene

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Crystal data

$C_{18}H_{14}O_2S$
M_r = 294.35
Monoclinic, $P2_1/n$
a = 13.0062 (9) Å
b = 5.9631 (4) Å
c = 18.3801 (14) Å
β = 104.019 (7)°
V = 1383.05 (17) Å^3
Z = 4
$F(000)$ = 616
D_x = 1.414 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2344 reflections
θ = 3.8–29.1°
μ = 0.24 mm^{-1}
T = 293 K
Colourless, block
0.30 × 0.30 × 0.25 mm

Data collection

Bruker SMART APEXII CCD diffractometer
ω and φ scans
Absorption correction: multi-scan
T_{min} = 0.932, T_{max} = 0.943
6823 measured reflections
3192 independent reflections
2344 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 29.1°, θ_{min} = 3.8°
h = −17→17
k = −8→7
l = −23→22

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.119
S = 1.07
3192 reflections
192 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0564P)^2 + 0.0382P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
S1	0.71269 (4)	0.65668 (8)	0.07885 (3)	0.04428 (18)

C7	0.63867 (13)	1.0145 (3)	0.13423 (9)	0.0299 (4)
C8	0.56269 (13)	1.1552 (3)	0.15027 (9)	0.0307 (4)
H8	0.583331	1.286299	0.177266	0.037*
O1	0.13171 (9)	0.9465 (2)	0.05384 (7)	0.0436 (3)
O2	0.18546 (9)	1.2955 (2)	0.13568 (8)	0.0448 (3)
C16	0.42315 (13)	0.9019 (3)	0.08384 (9)	0.0306 (4)
C6	0.75384 (13)	1.0333 (3)	0.15487 (9)	0.0311 (4)
C17	0.50106 (13)	0.7594 (3)	0.06797 (10)	0.0361 (4)
H17	0.481504	0.627975	0.040908	0.043*
C15	0.31383 (13)	0.8491 (3)	0.05877 (10)	0.0344 (4)
H15	0.293603	0.720126	0.030484	0.041*
C14	0.23822 (13)	0.9833 (3)	0.07530 (9)	0.0321 (4)
C9	0.45404 (13)	1.1018 (3)	0.12604 (9)	0.0296 (4)
C10	0.37291 (13)	1.2380 (3)	0.14356 (9)	0.0322 (4)
H10	0.391553	1.368253	0.171457	0.039*
C18	0.60588 (13)	0.8151 (3)	0.09257 (10)	0.0324 (4)
C11	0.26907 (14)	1.1807 (3)	0.12021 (10)	0.0324 (4)
C1	0.80319 (13)	0.8525 (3)	0.12815 (10)	0.0352 (4)
C4	0.92672 (15)	1.1857 (3)	0.20944 (11)	0.0456 (5)
H4	0.968898	1.296438	0.237431	0.055*
C2	0.91295 (14)	0.8391 (3)	0.14075 (11)	0.0442 (5)
H2	0.944654	0.718409	0.122655	0.053*
C5	0.81721 (14)	1.1985 (3)	0.19670 (10)	0.0387 (4)
H5	0.786216	1.317639	0.216149	0.046*
C13	0.09704 (14)	0.7594 (3)	0.00580 (11)	0.0457 (5)
H13A	0.127027	0.768290	−0.036975	0.069*
H13B	0.021131	0.760951	−0.010592	0.069*
H13C	0.119651	0.622921	0.032647	0.069*
C12	0.21008 (15)	1.4723 (3)	0.18900 (12)	0.0471 (5)
H12A	0.251238	1.414300	0.235742	0.071*
H12B	0.145632	1.536265	0.196376	0.071*
H12C	0.249993	1.585695	0.170861	0.071*
C3	0.97356 (15)	1.0083 (4)	0.18057 (11)	0.0475 (5)
H3	1.046885	1.003689	0.188240	0.057*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0379 (3)	0.0404 (3)	0.0547 (3)	0.0074 (2)	0.0116 (2)	−0.0117 (2)
C7	0.0330 (9)	0.0315 (9)	0.0252 (8)	0.0021 (7)	0.0070 (7)	0.0002 (7)
C8	0.0342 (9)	0.0275 (8)	0.0298 (9)	−0.0006 (7)	0.0067 (7)	−0.0033 (7)
O1	0.0292 (6)	0.0453 (7)	0.0542 (8)	−0.0016 (5)	0.0062 (6)	−0.0118 (6)
O2	0.0354 (7)	0.0431 (7)	0.0573 (9)	0.0049 (6)	0.0137 (6)	−0.0145 (6)
C16	0.0314 (9)	0.0294 (8)	0.0309 (9)	0.0008 (7)	0.0074 (7)	−0.0027 (7)
C6	0.0319 (9)	0.0365 (9)	0.0252 (8)	0.0014 (7)	0.0078 (7)	0.0023 (7)
C17	0.0375 (10)	0.0306 (9)	0.0390 (10)	0.0019 (8)	0.0067 (8)	−0.0104 (8)
C15	0.0347 (9)	0.0319 (9)	0.0353 (9)	−0.0012 (7)	0.0063 (8)	−0.0081 (7)
C14	0.0307 (9)	0.0327 (9)	0.0316 (9)	−0.0003 (7)	0.0053 (7)	0.0016 (7)

C9	0.0339 (9)	0.0283 (8)	0.0269 (8)	0.0011 (7)	0.0079 (7)	−0.0015 (7)
C10	0.0360 (9)	0.0288 (9)	0.0321 (9)	0.0021 (7)	0.0088 (7)	−0.0044 (7)
C18	0.0337 (9)	0.0308 (9)	0.0330 (9)	0.0048 (7)	0.0090 (7)	−0.0025 (7)
C11	0.0347 (9)	0.0313 (9)	0.0327 (9)	0.0063 (7)	0.0110 (7)	0.0008 (7)
C1	0.0349 (9)	0.0383 (10)	0.0332 (9)	0.0045 (7)	0.0099 (8)	0.0035 (8)
C4	0.0376 (10)	0.0595 (13)	0.0368 (10)	−0.0082 (9)	0.0033 (8)	−0.0015 (9)
C2	0.0377 (10)	0.0525 (12)	0.0444 (11)	0.0104 (9)	0.0138 (9)	0.0041 (9)
C5	0.0364 (10)	0.0482 (11)	0.0311 (9)	0.0016 (8)	0.0074 (8)	−0.0031 (8)
C13	0.0369 (10)	0.0452 (11)	0.0494 (11)	−0.0032 (9)	−0.0007 (9)	−0.0052 (10)
C12	0.0516 (12)	0.0414 (11)	0.0515 (12)	0.0096 (9)	0.0185 (10)	−0.0096 (9)
C3	0.0324 (9)	0.0685 (14)	0.0403 (11)	0.0019 (10)	0.0066 (8)	0.0068 (10)

Geometric parameters (Å, º)

S1—C1	1.7475 (18)	C15—H15	0.9300
S1—C18	1.7481 (17)	C14—C11	1.438 (2)
C7—C8	1.382 (2)	C9—C10	1.429 (2)
C7—C18	1.422 (2)	C10—C11	1.358 (2)
C7—C6	1.458 (2)	C10—H10	0.9300
C8—C9	1.411 (2)	C1—C2	1.392 (2)
C8—H8	0.9300	C4—C5	1.388 (2)
O1—C14	1.3631 (19)	C4—C3	1.389 (3)
O1—C13	1.427 (2)	C4—H4	0.9300
O2—C11	1.3720 (19)	C2—C3	1.377 (3)
O2—C12	1.422 (2)	C2—H2	0.9300
C16—C17	1.406 (2)	C5—H5	0.9300
C16—C15	1.420 (2)	C13—H13A	0.9600
C16—C9	1.426 (2)	C13—H13B	0.9600
C6—C5	1.391 (2)	C13—H13C	0.9600
C6—C1	1.403 (2)	C12—H12A	0.9600
C17—C18	1.369 (2)	C12—H12B	0.9600
C17—H17	0.9300	C12—H12C	0.9600
C15—C14	1.358 (2)	C3—H3	0.9300
C1—S1—C18	91.32 (8)	C7—C18—S1	112.60 (12)
C8—C7—C18	119.06 (15)	C10—C11—O2	125.90 (15)
C8—C7—C6	129.84 (15)	C10—C11—C14	120.35 (15)
C18—C7—C6	111.08 (14)	O2—C11—C14	113.74 (14)
C7—C8—C9	120.59 (15)	C2—C1—C6	121.58 (17)
C7—C8—H8	119.7	C2—C1—S1	125.64 (14)
C9—C8—H8	119.7	C6—C1—S1	112.78 (13)
C14—O1—C13	116.85 (13)	C5—C4—C3	120.30 (18)
C11—O2—C12	117.09 (13)	C5—C4—H4	119.9
C17—C16—C15	120.92 (15)	C3—C4—H4	119.9
C17—C16—C9	119.72 (15)	C3—C2—C1	118.58 (17)
C15—C16—C9	119.35 (15)	C3—C2—H2	120.7
C5—C6—C1	118.54 (16)	C1—C2—H2	120.7
C5—C6—C7	129.23 (15)	C4—C5—C6	120.05 (17)

C1—C6—C7	112.22 (15)	C4—C5—H5	120.0
C18—C17—C16	119.64 (15)	C6—C5—H5	120.0
C18—C17—H17	120.2	O1—C13—H13A	109.5
C16—C17—H17	120.2	O1—C13—H13B	109.5
C14—C15—C16	121.27 (15)	H13A—C13—H13B	109.5
C14—C15—H15	119.4	O1—C13—H13C	109.5
C16—C15—H15	119.4	H13A—C13—H13C	109.5
C15—C14—O1	125.49 (15)	H13B—C13—H13C	109.5
C15—C14—C11	119.62 (15)	O2—C12—H12A	109.5
O1—C14—C11	114.88 (14)	O2—C12—H12B	109.5
C8—C9—C16	119.28 (15)	H12A—C12—H12B	109.5
C8—C9—C10	122.57 (14)	O2—C12—H12C	109.5
C16—C9—C10	118.13 (15)	H12A—C12—H12C	109.5
C11—C10—C9	121.20 (15)	H12B—C12—H12C	109.5
C11—C10—H10	119.4	C2—C3—C4	120.91 (18)
C9—C10—H10	119.4	C2—C3—H3	119.5
C17—C18—C7	121.70 (15)	C4—C3—H3	119.5
C17—C18—S1	125.70 (13)		

C18—C7—C8—C9	0.3 (2)	C8—C7—C18—S1	−179.18 (12)
C6—C7—C8—C9	−178.41 (16)	C6—C7—C18—S1	−0.24 (18)
C8—C7—C6—C5	0.4 (3)	C1—S1—C18—C17	−179.24 (17)
C18—C7—C6—C5	−178.38 (17)	C1—S1—C18—C7	−0.07 (14)
C8—C7—C6—C1	179.31 (17)	C9—C10—C11—O2	178.01 (15)
C18—C7—C6—C1	0.5 (2)	C9—C10—C11—C14	−1.7 (3)
C15—C16—C17—C18	179.70 (16)	C12—O2—C11—C10	−9.1 (3)
C9—C16—C17—C18	−0.6 (3)	C12—O2—C11—C14	170.64 (15)
C17—C16—C15—C14	178.51 (16)	C15—C14—C11—C10	2.6 (2)
C9—C16—C15—C14	−1.1 (3)	O1—C14—C11—C10	−178.48 (16)
C16—C15—C14—O1	−179.95 (16)	C15—C14—C11—O2	−177.11 (15)
C16—C15—C14—C11	−1.2 (3)	O1—C14—C11—O2	1.8 (2)
C13—O1—C14—C15	−4.5 (2)	C5—C6—C1—C2	−1.9 (3)
C13—O1—C14—C11	176.69 (15)	C7—C6—C1—C2	179.11 (15)
C7—C8—C9—C16	−0.8 (2)	C5—C6—C1—S1	178.45 (13)
C7—C8—C9—C10	177.72 (15)	C7—C6—C1—S1	−0.57 (18)
C17—C16—C9—C8	1.0 (2)	C18—S1—C1—C2	−179.29 (16)
C15—C16—C9—C8	−179.36 (15)	C18—S1—C1—C6	0.37 (14)
C17—C16—C9—C10	−177.62 (15)	C6—C1—C2—C3	0.1 (3)
C15—C16—C9—C10	2.0 (2)	S1—C1—C2—C3	179.73 (14)
C8—C9—C10—C11	−179.17 (16)	C3—C4—C5—C6	0.0 (3)
C16—C9—C10—C11	−0.6 (2)	C1—C6—C5—C4	1.8 (3)
C16—C17—C18—C7	0.1 (3)	C7—C6—C5—C4	−179.37 (17)
C16—C17—C18—S1	179.24 (13)	C1—C2—C3—C4	1.8 (3)
C8—C7—C18—C17	0.0 (3)	C5—C4—C3—C2	−1.8 (3)
C6—C7—C18—C17	178.97 (16)		