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2,6-Bis(4-methoxyphenyl)-1,4-dithiine

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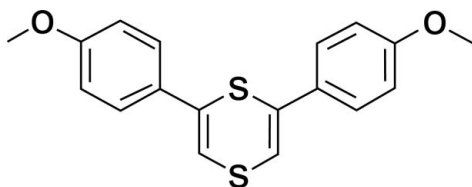
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.038; wR factor = 0.102; data-to-parameter ratio = 14.8.

The title molecule, $\text{C}_{18}\text{H}_{16}\text{O}_2\text{S}_2$, reveals crystallographic twofold rotation symmetry (with both S atoms lying on the axis) and one half-molecule defines an asymmetric unit. The dithiine ring is in a boat conformation. The aromatic ring and the C=C bond are nearly coplanar, with small torsion angles of -171.26 (19) and 8.5 (3)°. The two S—C bond lengths [1.7391 (19) and 1.7795 (18) Å] are shorter than single C—S bonds and longer than analogous C=S double bonds, which indicates a certain degree of conjugation between the lone pair on the S atom and π electrons of the C=C bond. The crystal packing only features van der Waals interactions.

Related literature

For a similar crystal structure, 2,6-diphenyl-1,4-dithiine, see: Piao *et al.* (2004). For background to 1,4-dithiine derivatives, see: Kobayashi & Gajurel (1986); Scott *et al.* (2000). For the synthesis of a similar compound, see: Nakayama *et al.* (1984). For standard bond lengths, see: Allen *et al.* (1987).



Experimental

Crystal data

$\text{C}_{18}\text{H}_{16}\text{O}_2\text{S}_2$	$V = 1533.6$ (3) Å ³
$M_r = 328.43$	$Z = 4$
Orthorhombic, <i>Pnma</i>	Mo $K\alpha$ radiation
$a = 10.1330$ (11) Å	$\mu = 0.35$ mm ⁻¹
$b = 27.318$ (3) Å	$T = 293$ K
$c = 5.5402$ (6) Å	$0.21 \times 0.18 \times 0.09$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	8513 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2001)	1541 independent reflections
$T_{\min} = 0.121$, $T_{\max} = 1.000$	1258 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.043$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	104 parameters
$wR(F^2) = 0.102$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.29$ e Å ⁻³
1541 reflections	$\Delta\rho_{\text{min}} = -0.16$ e Å ⁻³

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: KP2462).

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supplementary materials

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2,6-Bis(4-methoxyphenyl)-1,4-dithiine

Sha-Sha Zhao, Qiong Su, Zhi-Hong Peng and De-Lie An

1. Comment

1,4-Dithiine derivatives are very important intermediates in organic synthesis and can be used as versatile building blocks for a variety of chemical purposes (Kobayashi & Gajurel, 1986). In addition, some 1,4-dithiine derivatives have exhibited good biological activities, For example, Scott *et al.* showed that 2,3-dihydro-2-phenyl-1,4-dithiin-1,1,4,4-tetroxide could be used as nonpeptide antagonist of the human Galanin hGAL-1 receptor (Scott *et al.*, 2000). Unfortunately, there are very few acceptable methods to prepare 1,4-dithiine compounds thus far, and, in most cases, a successful protocol must use bis(arylethanonyl) sulfides compounds as precursors. Herein we report a new synthetic approaches and crystal structure of 2,6-bis(4-methoxyphenyl)-1,4-dithiine.

The molecular structure of the title compound(I) (Fig. 1) exhibits a twofold rotation axes symmetry. The dithiine ring is in a boat conformation. In the crystal, dominate columns of assembled molecules, however, their separation distances are larger than 5.5402 (13) Å (Fig. 2). The bond lengths of C1—C2 in heterocyclic ring presents a characteristic of the C=C double bond. An aromatic ring and the C=C bond are nearly coplanar, with small torsion angles of -171.26 (19)° and 8.5 (3)° for C1—C2—C3—C4 and C1—C2—C3—C8, respectively. The two characteristic bond lengths of S1—C2 and S2—C1 are shorter than C—S single bonds and longer than analogous C=S double bonds (Allen *et al.*, 1987), which indicates a certain degree of conjugation between the lone pair on the sulfur atom and π electrons of the C=C bond.

2. Experimental

NaOEt (224 mg, 3.3 mmol) was dissolved in alcohol (10 mL), and then added to bis(4-methoxyphenylethynyl) sulfide (97.8 mg, 0.33 mmol). After the mixture was stirred at room temperature for 10 min, Na₂S·9H₂O (159 mg, 0.66 mmol) was added. The resulting mixture was then stirred at reflux temperature for 2 h. The reaction mixture was cooled to room temperature and quenched by water and extracted with dichloromethane. The extract was then washed with brine, dried over Na₂SO₄, and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed (SiO₂; eluent, ether/dichloromethane, 4: 1) to give 93 mg of compound **I** (85%) as a yellow solid: mp 401–403 K; ¹H NMR (400 MHz, CDCl₃): δ = 3.83 (s, 6H; OCH₃), 6.42 (s, 2H; CH), 6.89(d, *J* = 8.8 Hz, 4H; Ar—H), 7.58 (d, *J* = 8.8 Hz, 4H; Ar—H); ¹³C NMR (100 MHz, CDCl₃): δ = 55.50 (OCH₃), 114.07 (CH), 116.40 (CH), 128.45 (CH), 129.83 (C), 139.52 (C), 160.10 (C); IR (KBr): ν = 3020, 2959, 2914, 1607, 1508, 1457, 1258, 1191, 832 cm⁻¹; MS (EI): *m/z* (%): 328.2 (*M*⁺, 100), 313.1 (43); HRMS (EI): *m/z* Calcd for C₁₈H₁₆O₂S₂ 328.0584, Found 328.0586.

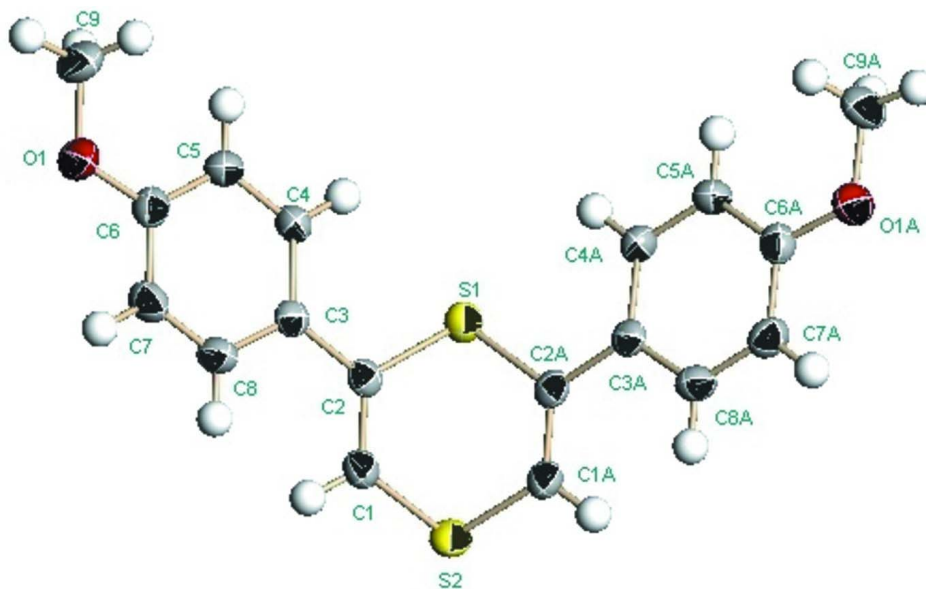
Single crystals of (I) suitable for X-ray diffraction analysis was obtained by slow diffusion of petroleum ether into a dichloromethane solution at 298 K.

3. Refinement

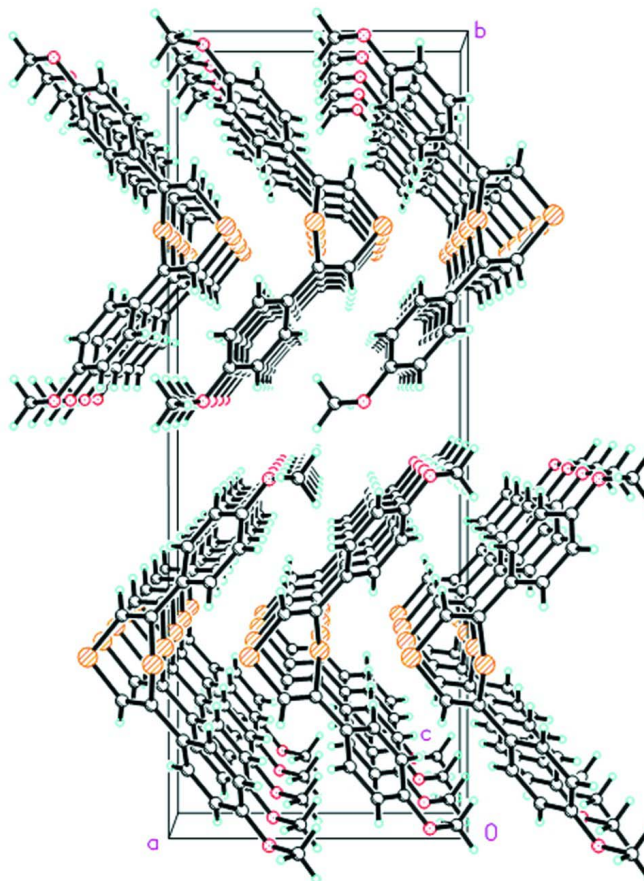
H atoms were refined with fixed individual displacement parameters [*U*_{iso} (H) = 1.2 *U*_{eq} (C) and *U*_{iso} (H) = 1.5 *U*_{eq} (C methyl)] using a riding model, with aromatic C—H = 0.93 Å, methyl C—H = 0.96 Å.

Computing details

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

**Figure 1**

Structural unit of the title molecule with atom labelling scheme and 50% probability displacement ellipsoids. Symmetry code to generate the entire molecule: $x, -y+1/2, z$.

**Figure 2**

Crystal packing reveals a columns of molecules held together by van der Waals interactions, only.

2,6-Bis(4-methoxyphenyl)-1,4-dithiine

Crystal data

$C_{18}H_{16}O_2S_2$

$M_r = 328.43$

Orthorhombic, *Pnma*

Hall symbol: -P 2ac 2n

$a = 10.1330$ (11) Å

$b = 27.318$ (3) Å

$c = 5.5402$ (6) Å

$V = 1533.6$ (3) Å³

$Z = 4$

$F(000) = 688$

$D_x = 1.422$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1658 reflections

$\theta = 7.5\text{--}53.8^\circ$

$\mu = 0.35$ mm⁻¹

$T = 293$ K

Prismatic, yellow

$0.21 \times 0.18 \times 0.09$ mm

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

phi and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2001)

$T_{\min} = 0.121$, $T_{\max} = 1.000$

8513 measured reflections

1541 independent reflections

1258 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.043$

$\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -12 \rightarrow 12$

$k = -33 \rightarrow 32$

$l = -5 \rightarrow 6$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.102$
 $S = 1.04$
 1541 reflections
 104 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 0.3159P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.16 \text{ e } \text{\AA}^{-3}$

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.49280 (7)	0.2500	0.16602 (12)	0.0352 (2)
S2	0.70856 (7)	0.2500	-0.24173 (15)	0.0423 (2)
O1	0.14361 (14)	0.45648 (5)	0.0468 (3)	0.0484 (4)
C1	0.60102 (19)	0.29896 (6)	-0.2021 (4)	0.0364 (5)
H1	0.6115	0.3262	-0.3011	0.044*
C2	0.50486 (19)	0.29989 (6)	-0.0393 (3)	0.0307 (4)
C3	0.40701 (18)	0.33990 (6)	-0.0143 (3)	0.0296 (4)
C4	0.3199 (2)	0.34206 (7)	0.1786 (4)	0.0364 (5)
H4	0.3213	0.3172	0.2931	0.044*
C5	0.2311 (2)	0.38017 (7)	0.2059 (3)	0.0372 (5)
H5	0.1746	0.3808	0.3381	0.045*
C6	0.22660 (19)	0.41714 (7)	0.0376 (3)	0.0352 (5)
C7	0.31115 (19)	0.41530 (7)	-0.1595 (4)	0.0395 (5)
H7	0.3083	0.4399	-0.2753	0.047*
C8	0.3984 (2)	0.37754 (7)	-0.1841 (4)	0.0371 (5)
H8	0.4537	0.3769	-0.3180	0.044*
C9	0.0549 (2)	0.45883 (8)	0.2462 (5)	0.0556 (6)
H9A	0.0005	0.4301	0.2479	0.083*
H9B	0.0002	0.4874	0.2311	0.083*
H9C	0.1043	0.4606	0.3938	0.083*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0430 (4)	0.0328 (4)	0.0297 (4)	0.000	-0.0017 (3)	0.000
S2	0.0266 (4)	0.0405 (4)	0.0599 (5)	0.000	0.0101 (3)	0.000

O1	0.0487 (9)	0.0401 (8)	0.0563 (10)	0.0129 (7)	0.0112 (7)	0.0073 (7)
C1	0.0326 (10)	0.0306 (9)	0.0459 (12)	-0.0035 (8)	0.0042 (9)	0.0016 (8)
C2	0.0304 (9)	0.0287 (9)	0.0332 (11)	-0.0063 (8)	-0.0021 (8)	-0.0015 (7)
C3	0.0290 (10)	0.0274 (9)	0.0324 (10)	-0.0058 (8)	-0.0013 (8)	-0.0028 (7)
C4	0.0416 (11)	0.0314 (9)	0.0361 (11)	-0.0007 (8)	0.0067 (8)	0.0043 (8)
C5	0.0397 (11)	0.0362 (10)	0.0357 (11)	0.0002 (9)	0.0093 (9)	0.0000 (8)
C6	0.0333 (10)	0.0305 (10)	0.0420 (11)	-0.0001 (8)	-0.0015 (9)	-0.0015 (8)
C7	0.0421 (11)	0.0382 (10)	0.0381 (11)	0.0000 (9)	0.0019 (9)	0.0095 (9)
C8	0.0383 (11)	0.0397 (10)	0.0331 (11)	0.0004 (9)	0.0062 (8)	0.0030 (8)
C9	0.0548 (14)	0.0493 (13)	0.0627 (15)	0.0180 (11)	0.0168 (12)	0.0019 (12)

Geometric parameters (Å, °)

S1—C2	1.7795 (18)	C4—C5	1.384 (3)
S1—C2 ⁱ	1.7795 (18)	C4—H4	0.9300
S2—C1	1.7391 (19)	C5—C6	1.375 (3)
S2—C1 ⁱ	1.7391 (19)	C5—H5	0.9300
O1—C6	1.365 (2)	C6—C7	1.389 (3)
O1—C9	1.426 (3)	C7—C8	1.365 (3)
C1—C2	1.328 (3)	C7—H7	0.9300
C1—H1	0.9300	C8—H8	0.9300
C2—C3	1.482 (3)	C9—H9A	0.9600
C3—C4	1.387 (3)	C9—H9B	0.9600
C3—C8	1.397 (3)	C9—H9C	0.9600
C2—S1—C2 ⁱ	99.97 (12)	C4—C5—H5	120.0
C1—S2—C1 ⁱ	100.54 (13)	O1—C6—C5	124.98 (18)
C6—O1—C9	116.92 (16)	O1—C6—C7	115.96 (17)
C2—C1—S2	124.07 (15)	C5—C6—C7	119.06 (18)
C2—C1—H1	118.0	C8—C7—C6	120.36 (18)
S2—C1—H1	118.0	C8—C7—H7	119.8
C1—C2—C3	124.65 (16)	C6—C7—H7	119.8
C1—C2—S1	118.03 (15)	C7—C8—C3	121.97 (18)
C3—C2—S1	117.32 (14)	C7—C8—H8	119.0
C4—C3—C8	116.60 (17)	C3—C8—H8	119.0
C4—C3—C2	121.94 (16)	O1—C9—H9A	109.5
C8—C3—C2	121.46 (16)	O1—C9—H9B	109.5
C5—C4—C3	121.98 (17)	H9A—C9—H9B	109.5
C5—C4—H4	119.0	O1—C9—H9C	109.5
C3—C4—H4	119.0	H9A—C9—H9C	109.5
C6—C5—C4	120.00 (18)	H9B—C9—H9C	109.5
C6—C5—H5	120.0		
C1 ⁱ —S2—C1—C2	39.0 (2)	C3—C4—C5—C6	0.6 (3)
S2—C1—C2—C3	-175.75 (14)	C9—O1—C6—C5	-0.4 (3)
S2—C1—C2—S1	4.9 (2)	C9—O1—C6—C7	179.31 (19)
C2 ⁱ —S1—C2—C1	-48.1 (2)	C4—C5—C6—O1	-179.75 (18)
C2 ⁱ —S1—C2—C3	132.49 (11)	C4—C5—C6—C7	0.6 (3)
C1—C2—C3—C4	-171.26 (19)	O1—C6—C7—C8	179.64 (18)
S1—C2—C3—C4	8.1 (2)	C5—C6—C7—C8	-0.7 (3)

C1—C2—C3—C8	8.5 (3)	C6—C7—C8—C3	-0.5 (3)
S1—C2—C3—C8	-172.18 (14)	C4—C3—C8—C7	1.6 (3)
C8—C3—C4—C5	-1.7 (3)	C2—C3—C8—C7	-178.16 (18)
C2—C3—C4—C5	178.07 (17)		

Symmetry code: (i) $x, -y+1/2, z$.