

1,2-Dimethoxy-4-methyl-3-[(*S*)-*p*-tolyl-sulfinyl]benzene

Virginia M. Mastranzo, José Luis Olivares, Rubén Sánchez-Obregón, Francisco Yuste and Rubén A. Toscano*

Instituto de Química, UNAM, Circuito Exterior, Ciudad Universitaria, Delegación Coyoacán, CP 04510, México, DF, Mexico
Correspondence e-mail: toscano@unam.mx

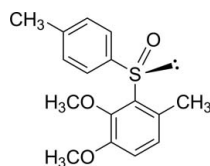
Received 29 September 2011; accepted 7 October 2011

Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.039; wR factor = 0.099; data-to-parameter ratio = 19.7.

In the title compound, $\text{C}_{16}\text{H}_{18}\text{O}_3\text{S}$, the dihedral angle between the benzene rings is $75.48(8)^\circ$. The absolute configuration at the stereogenic S-atom center was determined as *S*. The crystal structure is stabilized by intermolecular $\text{C}-\text{H}\cdots\text{O}$ contacts.

Related literature

For related sulfoxides, see: Brondel *et al.* (2010); Fuller *et al.* (2009). The title compound was prepared as a starting material for the synthesis of the tetrahydropyroberberine alkaloids (*S*)-(–)-tetrahydropalmatine and (*S*)-(–)-canadine following a synthetic strategy similar to that used for the synthesis of (*S*)-(–)-xylopinine (Mastranzo *et al.*, 2011).



Experimental

Crystal data

 $\text{C}_{16}\text{H}_{18}\text{O}_3\text{S}$
 $M_r = 290.36$

 Orthorhombic, $P2_12_12_1$
 $a = 7.4170(6)$ Å

 $b = 8.5406(7)$ Å

 $c = 24.0980(19)$ Å

 $V = 1526.5(2)$ Å³
 $Z = 4$

 Mo $K\alpha$ radiation
 $\mu = 0.22$ mm⁻¹
 $T = 298$ K
 $0.38 \times 0.37 \times 0.31$ mm

Data collection

 Bruker SMART APEX CCD diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
 $T_{\min} = 0.922$, $T_{\max} = 0.942$

 20418 measured reflections
 3645 independent reflections
 3380 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.099$
 $S = 1.06$
 3645 reflections
 185 parameters
 H-atom parameters not refined

 $\Delta\rho_{\text{max}} = 0.25$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.13$ e Å⁻³
 Absolute structure: Flack (1983),
 1534 Friedel pairs
 Flack parameter: 0.01 (6)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C8}-\text{H8B}\cdots\text{O3}^{\text{i}}$	0.96	2.58	3.366 (3)	139
$\text{C14}-\text{H14}\cdots\text{O1}^{\text{ii}}$	0.93	2.59	3.457 (2)	155
$\text{C15}-\text{H15}\cdots\text{O2}^{\text{ii}}$	0.93	2.55	3.3886 (18)	150
$\text{C12}-\text{H12}\cdots\text{O3}^{\text{iii}}$	0.93	2.56	3.406 (2)	152

 Symmetry codes: (i) $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINTE* (Bruker, 2006); data reduction: *SAINTE*; 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: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5660).

References

- Brondel, N., Moynihan, E. J. A., Lehane, K. N., Eccles, K. S., Elcoate, C. J., Coles, S. J., Lawrence, S. E. & Maguire, A. R. (2010). *CrystEngComm*, **12**, 2910–2927.
- Bruker (1999). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2006). *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Fuller, A. L., Aitken, R. A., Ryan, B. M., Slawin, A. M. Z. & Woollins, J. D. (2009). *J. Chem. Crystallogr.* **39**, 407–415.
- Mastranzo, V. M., Yuste, F., Ortiz, B., Sánchez-Obregón, R., Toscano, R. A. & García Ruano, J. L. (2011). *J. Org. Chem.* **76**, 5036–5041.
- Sheldrick, G. M. (2000). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supplementary materials

Acta Cryst. (2011). E67, o2950 [doi:10.1107/S1600536811041420]

1,2-Dimethoxy-4-methyl-3-[(*S*)-*p*-tolylsulfinyl]benzene

V. M. Mastranzo, J. L. Olivares, R. Sánchez-Obregón, F. Yuste and R. A. Toscano

Comment

The compound (*S*)-1,2-dimethoxy-4-methyl-3-(*p*-tolylsulfinyl)benzene was prepared as starting material for the synthesis of the tetrahydroprotoberberine alkaloids (*S*)-(-)-tetrahydropalmatine and (*S*)-(-)-canadine following a synthetic strategy similar to that used for the synthesis of (*S*)-(-)-xylopinine (Mastranzo *et al.*, 2011). The absolute configuration of the levorotatory 1,2-dimethoxy-4-methyl-3-(*p*-tolylsulfinyl)benzene (I) was determined by X-ray structure analysis. Figure 1 clearly shows that has the (*S*) configuration at the stereogenic S1 center. The geometry at S1 conforms to that found for related *p*-tolyl sulfinyl derivatives, it adopts an asymmetric propeller-like conformation having the corresponding $C_{ortho}-C_{ipso}-S-O$ dihedral angles equal to -53.11 (15) and -28.07 (16) $^\circ$. The dihedral angle defined by the least-squares planes of the aromatic rings is 75.48 (8) $^\circ$. In the structure there are some intermolecular $C-H\cdots O$ contacts.

Experimental

1-(3,4-Dimethoxyphenyl)-*N,N*-dimethylmethanamine

To a stirred solution of dimethylamine hydrochloride (6.4 g, 78.48 mmol) in MeOH (100 ml) KOH (1.2 g, 21.38 mmol) was added. When the pellets were completely dissolved, 3,4-dimethoxybenzaldehyde (10.0 g, 60.17 mmol) was added in one portion. The resulting suspension was stirred at room temperature for 15 min. Then, a solution of $NaBH_3CN$ (1.5 g, 23.87 mmol) in MeOH (15 ml) was added dropwise over 30 min. After the addition was complete, the suspension was stirred for 5 h. Potassium hydroxide (15 g) was then added, and stirring was continued until the pellets were completely dissolved. The reaction mixture was filtered with suction, and the filtrate was reduced to approximately 50 ml with a rotary evaporator while the bath temperature was kept below 40 $^\circ C$. To this concentrate EtOAc (100 mL) and brine (25 ml) were added and the layers were separated. The aqueous layer was extracted with EtOAc (2x50 ml). The combined organic layers were washed with brine (10 ml), dried over anhydrous potassium carbonate and concentrated. The residue was purified by flash chromatography (98:2 EtOAc/Et₃N) to obtain a pale yellow liquid (8.21 g, 70% yield).

(*S*)-1-[3,4-Dimethoxy-2-(*p*-tolylsulfinyl)phenyl]-*N,N*-dimethylmethanamine

To a stirred solution of 1-(3,4-dimethoxyphenyl)-*N,N*-dimethylmethanamine (1.6 g, 8.20 mmol) in THF (30 ml) cooled at 0–5 $^\circ C$ a 2.3 *M* solution in hexanes of *n*-BuLi (4.1 ml, 9.02 mmol) was added dropwise. After 2 h, a solution of (*S*)-menthyl *p*-toluenesulfinate (2.9 g, 9.84 mmol) in THF (10 ml) was added *via* cannula. The resulting mixture was stirred at room temperature for 4 h. Then, the reaction mixture was quenched with of saturated NH_4Cl (10 ml) and extracted with EtOAc (3 x 20 ml). The combined organic layers were dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (99:1 EtOAc/Et₃N) to give a pale yellow oil (2.4 g, 88% yield), $[\alpha]_D -16.5$ (c 1, $CHCl_3$).

(*S*)-1-(Chloromethyl)-3,4-dimethoxy-2-(*p*-tolylsulfinyl)benzene

supplementary materials

To a slurry of (*S*)-1-[3,4-dimethoxy-2-(*p*-tolylsulfinyl)phenyl]-*N,N*-dimethyl methanamine (4.02 g, 11.98 mmol, 1 equiv) and K_2CO_3 (2.64 g, 19.17 mmol, 1.6 equiv) in THF (10 ml) cooled at $-78^\circ C$ ethyl chloroformate (2.08 g, 19.17 mmol, 1.6 equiv) was added. The reaction was stirred at room temperature for 12 h. The resulting mixture was quenched with water (10 ml) and extracted with EtOAc (3x15 ml). The combined organic layers were dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (70:30 hexane/EtOAc) to give a pale yellow solid (2.66 g, 68% yield), mp $77-78^\circ C$, $[\alpha]_D -132.4$ (c 1, $CHCl_3$).

(*S*)-1,2-Dimethoxy-4-methyl-3-(*p*-tolylsulfinyl)benzene (I)

A mixture of (*S*)-1-(chloromethyl)-3,4-dimethoxy-2-(*p*-tolylsulfinyl) benzene (1.72 g, 5.29 mmol) and $NaBH_4$ (1.2 g, 31.77 mmol) in THF (30 ml) was heated at reflux for 18 h. The reaction mixture was quenched with $Na_2SO_4 \cdot 10H_2O$ and filtered through Celite. The filtrate was evaporated under vacuum and the residue purified by flash chromatography (80:20 hexane/EtOAc) to obtain a white solid (1.03 g, 67%), mp $127-128^\circ C$, $[\alpha]_D -198.2$ (c 1, $CHCl_3$).

Refinement

H atoms were positioned geometrically and refined using a riding model with $C-H = 0.95-0.99 \text{ \AA}$ and with $U_{iso}(H) = 1.2$ (1.5 for methyl groups) times $U_{eq}(C)$.

Figures

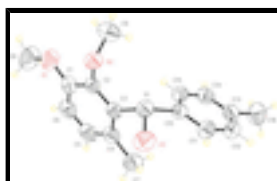


Fig. 1. The molecular structure of (I), with atom labels and 50% probability displacement ellipsoids for non-H atoms.

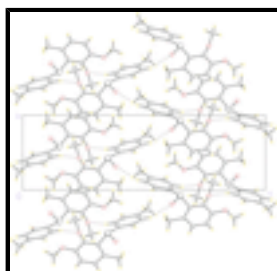


Fig. 2. The packing of the title compound, viewed down the **b** axis, showing one layer of molecules connected by $C-H \cdots O-C$ and $C-H \cdots O-S$ hydrogen bonds (dashed lines).

1,2-Dimethoxy-4-methyl-3-[(*S*)-*p*-tolylsulfinyl]benzene

Crystal data

$C_{16}H_{18}O_3S$

$M_r = 290.36$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 7.4170$ (6) \AA

$b = 8.5406$ (7) \AA

$D_x = 1.263 \text{ Mg m}^{-3}$

Melting point: 400 K

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 9922 reflections

$\theta = 2.5-27.6^\circ$

$\mu = 0.22 \text{ mm}^{-1}$

$c = 24.0980 (19) \text{ \AA}$
 $V = 1526.5 (2) \text{ \AA}^3$
 $Z = 4$
 $F(000) = 616$

$T = 298 \text{ K}$
 Prism, colourless
 $0.38 \times 0.37 \times 0.31 \text{ mm}$

Data collection

Bruker SMART APEX CCD diffractometer
 Radiation source: fine-focus sealed tube graphite
 Detector resolution: $0.661 \text{ pixels mm}^{-1}$
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2000)
 $T_{\min} = 0.922, T_{\max} = 0.942$
 20418 measured reflections

3645 independent reflections
 3380 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 $\theta_{\max} = 27.9^\circ, \theta_{\min} = 1.7^\circ$
 $h = -9 \rightarrow 9$
 $k = -11 \rightarrow 11$
 $l = -31 \rightarrow 31$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.099$
 $S = 1.06$
 3645 reflections
 185 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 not refined
 $w = 1/[\sigma^2(F_o^2) + (0.0693P)^2 + 0.0141P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.25 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.13 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983), 1534 Friedel pairs
 Flack parameter: 0.01 (6)

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	$U_{\text{iso}}^*/U_{\text{eq}}$
-----	-----	-----	----------------------------------

supplementary materials

S1	0.57970 (5)	0.27901 (5)	0.149352 (15)	0.04842 (12)
O1	0.77239 (19)	0.07949 (18)	0.33551 (5)	0.0664 (4)
O2	0.57075 (15)	0.25318 (11)	0.26763 (4)	0.0500 (3)
O3	0.6876 (2)	0.39213 (16)	0.11616 (5)	0.0671 (4)
C1	0.8129 (2)	0.0711 (2)	0.28050 (7)	0.0527 (4)
C2	0.7012 (2)	0.15921 (17)	0.24538 (6)	0.0447 (3)
C3	0.73064 (19)	0.15714 (18)	0.18847 (6)	0.0451 (3)
C4	0.8742 (2)	0.0726 (2)	0.16503 (7)	0.0544 (4)
C5	0.9821 (2)	-0.0114 (2)	0.20084 (9)	0.0621 (4)
H5	1.0779	-0.0684	0.1863	0.074*
C6	0.9531 (2)	-0.0143 (2)	0.25777 (8)	0.0621 (4)
H6	1.0278	-0.0736	0.2806	0.074*
C7	0.9144 (3)	0.0710 (3)	0.10365 (8)	0.0695 (5)
H7A	1.0391	0.0458	0.0979	0.104*
H7B	0.8892	0.1723	0.0882	0.104*
H7C	0.8403	-0.0062	0.0858	0.104*
C8	0.8723 (4)	-0.0178 (4)	0.37212 (9)	0.0968 (8)
H8A	0.8235	-0.0095	0.4089	0.145*
H8B	0.9962	0.0149	0.3724	0.145*
H8C	0.8649	-0.1245	0.3598	0.145*
C9	0.4070 (3)	0.1761 (2)	0.28212 (10)	0.0709 (5)
H9A	0.3163	0.2528	0.2903	0.106*
H9B	0.4267	0.1114	0.3141	0.106*
H9C	0.3679	0.1122	0.2517	0.106*
C10	0.49336 (19)	0.13539 (18)	0.10183 (6)	0.0454 (3)
C11	0.4650 (3)	0.1815 (2)	0.04729 (7)	0.0563 (4)
H11	0.4975	0.2815	0.0358	0.068*
C12	0.3884 (3)	0.0780 (2)	0.01049 (7)	0.0613 (4)
H12	0.3698	0.1089	-0.0261	0.074*
C13	0.3386 (2)	-0.0713 (2)	0.02686 (7)	0.0588 (4)
C14	0.3663 (2)	-0.1131 (2)	0.08149 (8)	0.0580 (4)
H14	0.3330	-0.2128	0.0931	0.070*
C15	0.4417 (2)	-0.01158 (18)	0.11920 (6)	0.0511 (3)
H15	0.4577	-0.0418	0.1560	0.061*
C16	0.2546 (4)	-0.1816 (3)	-0.01457 (11)	0.0911 (8)
H16A	0.3326	-0.1919	-0.0462	0.137*
H16B	0.1401	-0.1410	-0.0263	0.137*
H16C	0.2378	-0.2824	0.0023	0.137*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0537 (2)	0.04504 (19)	0.04650 (18)	0.00360 (16)	0.00099 (15)	-0.00251 (14)
O1	0.0699 (8)	0.0764 (9)	0.0528 (6)	0.0157 (7)	-0.0092 (5)	0.0025 (6)
O2	0.0525 (6)	0.0466 (6)	0.0509 (5)	0.0076 (5)	0.0038 (5)	-0.0048 (4)
O3	0.0840 (9)	0.0527 (7)	0.0645 (7)	-0.0127 (6)	0.0057 (7)	0.0006 (6)
C1	0.0492 (8)	0.0512 (9)	0.0576 (9)	-0.0011 (7)	-0.0075 (7)	-0.0026 (7)
C2	0.0422 (7)	0.0406 (7)	0.0513 (8)	-0.0022 (6)	-0.0032 (6)	-0.0052 (6)

C3	0.0405 (7)	0.0431 (7)	0.0518 (8)	-0.0004 (6)	-0.0019 (6)	-0.0059 (6)
C4	0.0432 (7)	0.0558 (9)	0.0642 (9)	-0.0004 (7)	0.0034 (6)	-0.0108 (8)
C5	0.0406 (7)	0.0647 (10)	0.0808 (12)	0.0102 (7)	0.0022 (8)	-0.0110 (9)
C6	0.0455 (9)	0.0640 (10)	0.0766 (11)	0.0082 (8)	-0.0098 (8)	-0.0002 (9)
C7	0.0604 (10)	0.0814 (13)	0.0667 (10)	0.0081 (10)	0.0142 (9)	-0.0172 (9)
C8	0.1024 (18)	0.120 (2)	0.0680 (12)	0.0358 (17)	-0.0160 (12)	0.0157 (14)
C9	0.0540 (9)	0.0672 (11)	0.0915 (14)	0.0034 (8)	0.0160 (9)	-0.0008 (10)
C10	0.0431 (7)	0.0479 (8)	0.0452 (7)	0.0019 (6)	0.0009 (6)	-0.0012 (6)
C11	0.0641 (10)	0.0556 (9)	0.0493 (8)	-0.0001 (8)	-0.0012 (7)	0.0050 (7)
C12	0.0646 (11)	0.0735 (11)	0.0457 (7)	0.0000 (9)	-0.0038 (7)	-0.0004 (8)
C13	0.0483 (8)	0.0698 (11)	0.0583 (9)	-0.0012 (8)	-0.0009 (7)	-0.0117 (8)
C14	0.0550 (9)	0.0525 (9)	0.0665 (9)	-0.0093 (7)	0.0023 (7)	0.0003 (7)
C15	0.0505 (8)	0.0536 (8)	0.0490 (7)	-0.0021 (7)	0.0000 (6)	0.0049 (6)
C16	0.0964 (17)	0.0960 (17)	0.0808 (14)	-0.0243 (15)	-0.0147 (13)	-0.0228 (13)

Geometric parameters (Å, °)

S1—O3	1.4877 (13)	C8—H8A	0.9600
S1—C3	1.7959 (15)	C8—H8B	0.9600
S1—C10	1.7961 (15)	C8—H8C	0.9600
S1—O2	2.8595 (11)	C9—H9A	0.9600
O1—C1	1.361 (2)	C9—H9B	0.9600
O1—C8	1.421 (2)	C9—H9C	0.9600
O2—C2	1.3665 (18)	C10—C15	1.377 (2)
O2—C9	1.425 (2)	C10—C11	1.388 (2)
C1—C6	1.384 (2)	C11—C12	1.375 (2)
C1—C2	1.403 (2)	C11—H11	0.9300
C2—C3	1.389 (2)	C12—C13	1.385 (3)
C3—C4	1.405 (2)	C12—H12	0.9300
C4—C5	1.378 (3)	C13—C14	1.380 (3)
C4—C7	1.509 (3)	C13—C16	1.508 (3)
C5—C6	1.389 (3)	C14—C15	1.375 (2)
C5—H5	0.9300	C14—H14	0.9300
C6—H6	0.9300	C15—H15	0.9300
C7—H7A	0.9600	C16—H16A	0.9600
C7—H7B	0.9600	C16—H16B	0.9600
C7—H7C	0.9600	C16—H16C	0.9600
O3—S1—C3	108.86 (8)	O1—C8—H8B	109.5
O3—S1—C10	107.00 (7)	H8A—C8—H8B	109.5
C3—S1—C10	99.27 (7)	O1—C8—H8C	109.5
O3—S1—O2	126.76 (6)	H8A—C8—H8C	109.5
C3—S1—O2	56.39 (5)	H8B—C8—H8C	109.5
C10—S1—O2	125.07 (5)	O2—C9—H9A	109.5
C1—O1—C8	117.33 (16)	O2—C9—H9B	109.5
C2—O2—C9	115.36 (12)	H9A—C9—H9B	109.5
C2—O2—S1	68.76 (8)	O2—C9—H9C	109.5
C9—O2—S1	107.45 (11)	H9A—C9—H9C	109.5
O1—C1—C6	125.38 (15)	H9B—C9—H9C	109.5
O1—C1—C2	115.42 (15)	C15—C10—C11	120.28 (15)

supplementary materials

C6—C1—C2	119.19 (16)	C15—C10—S1	121.85 (11)
O2—C2—C3	120.42 (13)	C11—C10—S1	117.64 (13)
O2—C2—C1	119.74 (14)	C12—C11—C10	119.40 (16)
C3—C2—C1	119.74 (14)	C12—C11—H11	120.3
C2—C3—C4	121.52 (14)	C10—C11—H11	120.3
C2—C3—S1	114.39 (11)	C11—C12—C13	121.22 (15)
C4—C3—S1	123.99 (12)	C11—C12—H12	119.4
C5—C4—C3	117.11 (16)	C13—C12—H12	119.4
C5—C4—C7	119.62 (16)	C14—C13—C12	118.07 (16)
C3—C4—C7	123.27 (16)	C14—C13—C16	122.10 (19)
C4—C5—C6	122.54 (15)	C12—C13—C16	119.83 (18)
C4—C5—H5	118.7	C15—C14—C13	121.86 (16)
C6—C5—H5	118.7	C15—C14—H14	119.1
C1—C6—C5	119.86 (16)	C13—C14—H14	119.1
C1—C6—H6	120.1	C14—C15—C10	119.14 (14)
C5—C6—H6	120.1	C14—C15—H15	120.4
C4—C7—H7A	109.5	C10—C15—H15	120.4
C4—C7—H7B	109.5	C13—C16—H16A	109.5
H7A—C7—H7B	109.5	C13—C16—H16B	109.5
C4—C7—H7C	109.5	H16A—C16—H16B	109.5
H7A—C7—H7C	109.5	C13—C16—H16C	109.5
H7B—C7—H7C	109.5	H16A—C16—H16C	109.5
O1—C8—H8A	109.5	H16B—C16—H16C	109.5
O3—S1—O2—C2	-90.50 (11)	C2—C3—C4—C5	1.6 (2)
C3—S1—O2—C2	-1.18 (9)	S1—C3—C4—C5	177.80 (13)
C10—S1—O2—C2	75.52 (10)	C2—C3—C4—C7	-178.16 (17)
O3—S1—O2—C9	158.43 (11)	S1—C3—C4—C7	-2.0 (2)
C3—S1—O2—C9	-112.24 (11)	C3—C4—C5—C6	-0.1 (3)
C10—S1—O2—C9	-35.55 (12)	C7—C4—C5—C6	179.69 (19)
C8—O1—C1—C6	-5.7 (3)	O1—C1—C6—C5	-179.05 (18)
C8—O1—C1—C2	174.92 (19)	C2—C1—C6—C5	0.3 (3)
C9—O2—C2—C3	101.36 (18)	C4—C5—C6—C1	-0.9 (3)
S1—O2—C2—C3	1.47 (11)	O3—S1—C10—C15	157.47 (13)
C9—O2—C2—C1	-82.32 (19)	C3—S1—C10—C15	44.36 (14)
S1—O2—C2—C1	177.79 (15)	O2—S1—C10—C15	-10.85 (15)
O1—C1—C2—O2	4.2 (2)	O3—S1—C10—C11	-28.07 (16)
C6—C1—C2—O2	-175.16 (14)	C3—S1—C10—C11	-141.18 (14)
O1—C1—C2—C3	-179.42 (15)	O2—S1—C10—C11	163.61 (12)
C6—C1—C2—C3	1.2 (2)	C15—C10—C11—C12	-1.4 (3)
O2—C2—C3—C4	174.15 (14)	S1—C10—C11—C12	-175.92 (14)
C1—C2—C3—C4	-2.2 (2)	C10—C11—C12—C13	0.2 (3)
O2—C2—C3—S1	-2.40 (19)	C11—C12—C13—C14	0.6 (3)
C1—C2—C3—S1	-178.71 (12)	C11—C12—C13—C16	179.9 (2)
O3—S1—C3—C2	123.34 (12)	C12—C13—C14—C15	-0.3 (3)
C10—S1—C3—C2	-125.01 (12)	C16—C13—C14—C15	-179.6 (2)
O2—S1—C3—C2	1.19 (9)	C13—C14—C15—C10	-0.9 (3)
O3—S1—C3—C4	-53.11 (15)	C11—C10—C15—C14	1.7 (2)
C10—S1—C3—C4	58.54 (14)	S1—C10—C15—C14	176.01 (13)
O2—S1—C3—C4	-175.27 (16)		

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C8—H8B \cdots O3 ⁱ	0.96	2.58	3.366 (3)	139.
C14—H14 \cdots O1 ⁱⁱ	0.93	2.59	3.457 (2)	155.
C15—H15 \cdots O2 ⁱⁱ	0.93	2.55	3.3886 (18)	150.
C12—H12 \cdots O3 ⁱⁱⁱ	0.93	2.56	3.406 (2)	152.

Symmetry codes: (i) $-x+2, y-1/2, -z+1/2$; (ii) $-x+1, y-1/2, -z+1/2$; (iii) $x-1/2, -y+1/2, -z$.

Fig. 1

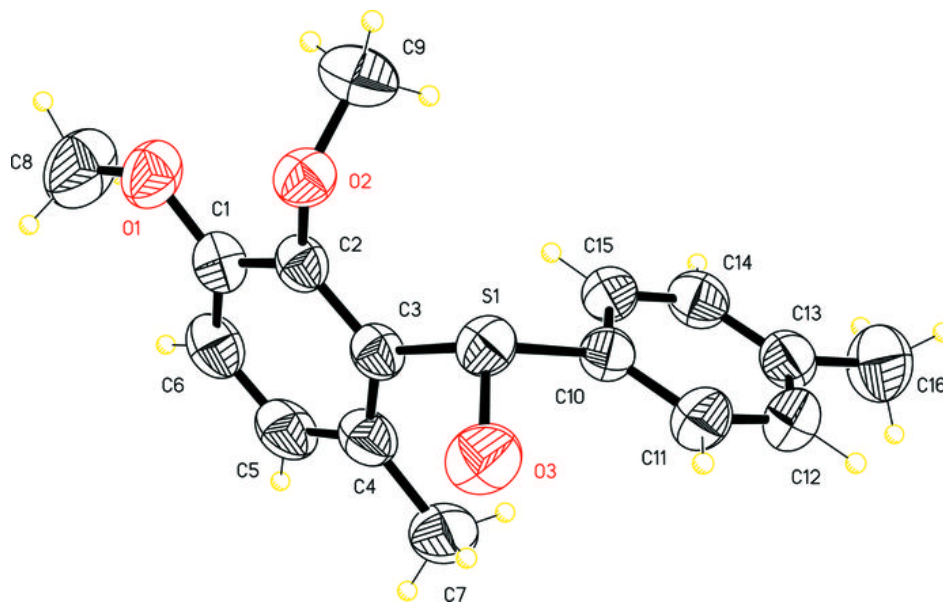


Fig. 2

