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meso-Bis(phenylsulfinyl)methane

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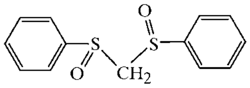
The title compound, *meso*-$C_{13}H_{12}O_2S_2$, is in an *anti* conformation, with *R* and *S* configurations around the S atoms. The two O atoms are *trans* to each other, and the same applies for the two benzene rings. The phenylsulfinyl groups are nearly orthogonal to the central dithiomethane group, and the orientation of the two phenyl rings are determined by the interactions in which they are involved. The packing is built from molecular columns stabilized by weak C—H···O interactions.

Comment

Bifunctional chelating ligands, such as carbamoyl methyl phosphonates (CMP), carbamoyl methyl phosphine oxides (CMPO), malonamides (MA) and *β*-diphosphine oxides, are known to be effective liquid–liquid extractants for lanthanide and actinide ions from acid media (Horwitz, Kalina & Muscatello, 1981; Horwitz, Muscatello *et al.*, 1981; Kalina *et al.*, 1981; Horwitz & Kalina, 1984; Musikas, 1987; Mathur *et al.*, 1991). The fundamental coordination chemistry of these ligands with lanthanide and actinide ions has been well established (Bowen *et al.*, 1982; Karthikeyan *et al.*, 1998; Kannan & Ferguson, 1997). This prompted us to synthesize the *β*-disulfoxide ligand bis(phenylsulfinyl)methane, and to study its coordination behaviour with actinide ions (Rajalakshmi *et al.*, 2003). Two isomeric forms of this ligand, *viz.* *meso* and *dl*, were separated by fractional crystallization and it was shown using ^{1}H NMR spectroscopy that the isomer having the lower melting point (391–393 K) is *meso* and that having the higher melting point (455–458 K) is *dl* (Geen Jun & Shevlin, 1971). Other data supporting this observation of two isomers have not yet been reported. We report here the crystal structure analysis of the *meso* isomer, (I).



(I)

The structure of (I) (Fig. 1) shows that the molecule is in an *anti* conformation. The two O atoms are *trans* to one another, and the same applies for the two benzene rings, as seen from the O1—S1···S2—O2 and Ph—S1···S2—Ph torsion angles of −178.0 (1) and 158.8 (1)°, respectively. The stereochemistries around the S atoms are *R* and *S*, which is expected for the *meso*-isomer. The bond lengths and angles of (I) (Table 1) show normal values (Allen *et al.*, 1987). The S=O, Csp^2—S and Csp^3—S bond lengths agree well with the corresponding values in previously reported *β*-disulfoxide compounds (Beckhaus *et al.*, 1979; Pelizzi, Coghi *et al.*, 1976; Pelizzi, Michelon & Bonivento, 1976). The bond angles at both the S atoms are in the range 98.0 (1)–107.3 (1)°, which corresponds to tetrahedral geometry. The dihedral angle between the two phenyl rings is 61.3 (1)°, and the torsion angles describing the conformation of the central chain joining the two benzene rings are listed in Table 1. The phenylsulfinyl groups are nearly orthogonal to the central dithiomethane S1—C7—S2 group, with dihedral angles of 88.4 (1) and 84.7 (1)° formed with that group by the weighted least-squares planes through C1–C6/S1/O1 and C8–C13/S2/O2, respectively. The two S=O groups are coplanar with their attached phenyl rings, as shown by the C5—C6—S1—O1 and C13—C8—S2—O2 torsion angles of 0.1 (2) and −6.4 (2)°, respectively. The difference is due to the C—H···O interactions in which these benzene rings are involved. This quasi-coplanar nature of the S=O groups with their phenyl rings is due to the conjugation between the sulfur lone pairs and the *π*-systems of the phenyl rings. This was also observed in the phenylsulfinyl derivative reported previously where the corresponding angle was −2° (Olivato *et al.*, 2000). The C—S (average 1.796 Å) and S=O (average 1.493 Å) bond distances are also indicative of *π*-conjugation along the phenylsulfinyl group.

The molecules are involved in seven C—H···O interactions (Table 2). Considering the intramolecular interactions, C5—H5···O1 and C13—H13···O2 appear to form similar approximately planar *S*(5) graph rings (Etter *et al.*, 1990), *viz.* O1—S1—C6—C5—H5 and O2—S2—C8—C13—H13, in the two chemically equivalent parts of the molecule. This is not observed for the *S*(7) graph ring, O2—S2—C7—S1—C6—C1—H1, generated by the C1—H1···O2 interaction, since the H9···O1 distance (4.11 Å) is too long to be an interaction. In the packing, the molecules are interconnected by three weak

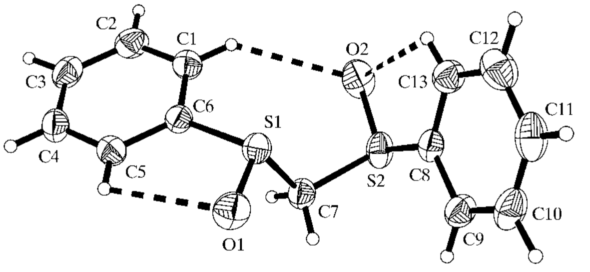


Figure 1
The structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

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C—H···O interactions (Table 2). C10—H10···O2^{iii} interactions link the molecules into chains parallel to the *a* direction and two adjacent chains are interconnected by C7—H7*B*···O1^{ii} and C9—H9···O1^{ii} interactions into columns (Fig. 2; see Table 2 for symmetry codes). It is noteworthy that the orientation of the C1–C6 benzene ring is determined by the C1—H1···O2 and C5—H5···O1 intramolecular interactions, together with the C4—H4···O2^{i} intermolecular interaction, while the orientation of the C8–C13 benzene ring is determined by the C13—H13···O2 intramolecular interaction, together with the C9—H9···O1^{ii} and C10—H10···O2^{iii} intermolecular interactions (see Table 2 for symmetry codes). This different structural situation is reflected in the conformation about the two S1—C7 and S2—C7 bonds, as shown by the remarkably different C6—S1—C7—S2 and C8—S2—C7—S1 torsion angles of 112.3 (1) and 53.4 (1)°, respectively.

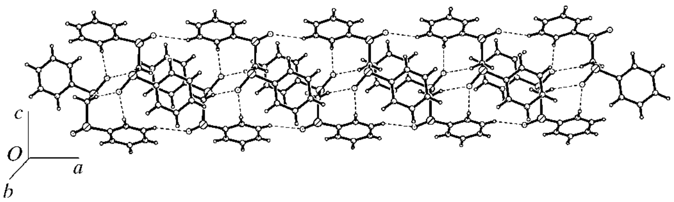

Figure 2
Packing diagram for the title compound, showing the molecular columns parallel to the *a* direction.

Experimental

The title compound was prepared according to a reported method using SeO_2/H_2O_2 (Drabowicz & Mikolajczyk, 1978). To a suspension of bis(phenylthio)methane (10 g, 0.043 mol) in methanol (100 ml) was added dropwise with stirring a solution of selenium dioxide (9.56 g, 0.086 mol) and H_2O_2 (9.8 ml of 30% H_2O, 2.94 g, 0.086 mol) in methanol. The resulting solution was stirred for a further 2 h, and was then left to evaporate in a fume hood overnight. The residue obtained after drying was extracted with chloroform (100 ml) and dried over anhydrous sodium sulfate and filtered. The volume of the solution was reduced to 40 ml on a hotplate and left to evaporate overnight. The paste-like solid obtained was suspended in ethanol (100 ml) and heated on a hotplate. The clear solution was filtered, the volume reduced to 50 ml and the resulting solution allowed to cool in a fume hood for 3 h, whereupon a white crystalline solid was deposited. This solid was filtered off, washed with cold ethanol (5 ml) and dried (yield: 3.5 mg, 39.5%). The resulting solid was recrystallized from chloroform/ethanol as the pure *dl* form. The ethanol-soluble part, on evaporation, yielded a white powder which was recrystallized from chloroform/dodecane as a white crystalline solid (yield: 6.5 mg, 57.2%). The ^{1}H NMR spectrum showed this solid to be a mixture of the *meso* and *dl* isomers. Repeating the crystallization three times yielded 98% pure *meso* form. The crystal used for X-ray analysis was obtained from a chloroform/dodecane mixture.

Crystal data

$C_{13}H_{12}O_2S_2$
$M_r = 264.35$
Triclinic, $P\overline{1}$
$a = 8.2540\ (9)$ Å
$b = 8.9037\ (10)$ Å
$c = 9.0690\ (10)$ Å
$\alpha = 106.875\ (2)°$
$\beta = 98.782\ (2)°$
$\gamma = 90.897\ (2)°$
$V = 629.05\ (12)$ Å^3
$Z = 2$
$D_x = 1.396$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2403 reflections
$\theta = 2.8$–$28.3°$
$\mu = 0.41$ mm^{-1}
$T = 293\ (2)$ K
Needle, yellow
0.60 × 0.20 × 0.14 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.792$, $T_{max} = 0.945$
3960 measured reflections
2936 independent reflections
2466 reflections with $I > 2\sigma(I)$
$R_{int} = 0.014$
$\theta_{max} = 28.3°$
$h = -10 \rightarrow 10$
$k = -9 \rightarrow 11$
$l = -12 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.094$
$S = 1.09$
2936 reflections
202 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 0.1734P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—O1	1.495 (2)	S2—O2	1.491 (2)
S1—C6	1.798 (2)	S2—C8	1.794 (2)
S1—C7	1.837 (2)	S2—C7	1.808 (2)
O1—S1—C6	107.3 (1)	O2—S2—C8	106.6 (1)
O1—S1—C7	105.2 (1)	O2—S2—C7	106.1 (1)
C6—S1—C7	98.0 (1)	C8—S2—C7	98.2 (1)
C7—S1—C6—C1	−74.8 (2)	O1—S1—C7—S2	−137.3 (1)
O2—S2—C7—S1	−56.6 (1)	C7—S2—C8—C9	69.4 (2)

Table 2
C—H···O interaction geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O2	0.95 (3)	2.58 (3)	3.363 (2)	140 (2)
C5—H5···O1	0.92 (2)	2.54 (2)	2.939 (2)	107 (2)
C13—H13···O2	0.91 (2)	2.44 (3)	2.904 (3)	112 (2)
C4—H4···O2^{i}	0.92 (3)	2.59 (3)	3.465 (2)	159 (2)
C7—H7*B*···O1^{ii}	0.92 (3)	2.56 (3)	3.441 (3)	162 (2)
C9—H9···O1^{ii}	0.95 (3)	2.45 (3)	3.360 (2)	158 (2)
C10—H10···O2^{iii}	0.95 (3)	2.54 (3)	3.255 (3)	132 (2)

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

All H atoms were located in difference Fourier maps and were refined isotropically [C—H = 0.85 (3)–0.98 (2) Å]. The highest peak and deepest hole are 0.93 Å from S2 and 1.15 Å from C4, respectively.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL, PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1603). Services for accessing these data are described at the back of the journal.

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