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# (2*S*,*R*<sub>S</sub>)-6-Phenyl-1-(*p*-tolylsulfinyl)hexa-3(*E*),5(*E*)-dien-2-ol

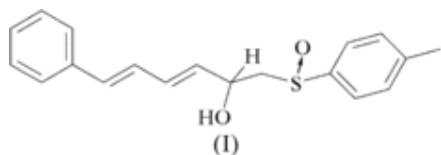
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The molecule of the title compound, C<sub>19</sub>H<sub>20</sub>O<sub>2</sub>S, corresponds to a chiral sulfinyldienol with two stereogenic centres, *viz.* the C atom substituted by the hydroxy group and the sulfinyl S atom. The molecule displays a V-shape in the solid state. The dihedral angle defined by the least-squares planes of the aromatic rings is 72.9 (1)°. The packing pattern exhibits the following intermolecular hydrogen bonds: one O-H...O [H...O = 1.98 Å, O...O = 2.785 (4) Å and O-H...O = 166°] and two C-H...O [H...O = 2.58 and 2.60 Å, C...O = 3.527 (5) and 3.347 (5) Å, and C-H...O = 164 and 134°]. These define a chain along *b*.

## Comment



Continuing our search for supramolecular synthons for the crystal engineering of substituted aromatic compounds (Araya-Maturana *et al.*, 2005<sup>➡</sup>), our group has focused on the crystalline properties of chiral sulfinyldienols, particularly in the packing patterns obtained by hydrogen bonding. Sulfinyl dienes have been used as an ideal substrate in Diels-Alder cycloadditions, where the presence of the sulfinyl group provides an extra element of stereocontrol (Carreño, 1995<sup>➡</sup>). The introduction of a hydroxyl group, bound next to the sulfinyl, to form the so-called sulfinyldienols, provides a new stereogenic centre which can be coordinated by a suitable dienophile through intermolecular hydrogen bonding in the transition state of Diels-Alder cycloadditions, thus providing a new diastereoselectivity control in the reaction, since the role of intermolecular hydrogen bonding in the regio- and stereochemical outcome of Diels-Alder reactions of dienes with hydroxyl groups has been well recognized (Araya-Maturana *et al.*, 1999<sup>➡</sup>; Fernández de la Pradilla *et al.*, 2005<sup>➡</sup>). The crystal structures of sulfinyldienols are unknown, but the X-ray crystal structure of the β-hydroxysulfoxide moiety of 2-(*p*-tolylsulfinyl)cyclohexanol has previously been established (García Ruano *et al.*, 1996<sup>➡</sup>). We now present the crystal structure of the title sulfinyldienol, (I)<sup>➡</sup>.



The molecule of (I)<sup>➡</sup> has a seven-atom chain connecting the phenyl and *p*-tolyl groups (Fig. 1<sup>➡</sup>). The chain contains two adjacent C=C double bonds (C12=C13 and C10=C11) and an S atom. It is important to note that both double bonds exhibit a *trans* arrangement. The chain is not planar but contains two planar segments of atoms, *viz.* C9-C14 and C9/C8/S/C1, including the aromatic ring C atom and with C9

as the common atom. In both cases, the atoms show small deviations from the corresponding least-squares planes. The chain is twisted at C9, with a dihedral angle of 56.8° between the two segments. Consequently, the C8-C9-C10-C11 torsion angle is -127.2 (4)° and the molecule is asymmetrically V-shaped, with one arm longer than the other. This is also reflected in the angle defined by the C17..C9 and C9..C4 vectors, with a value of 50.0°. The phenyl ring is not completely coplanar with the C14-C9 segment, with a dihedral angle of 19.6 (3)° between the two least-squares planes. The opposite is observed with the *p*-tolyl ring, which is almost perpendicular to the C9/C8/S/C1 segment, with a dihedral angle of 87.5 (1)°. The bent shape of the molecule is also reflected in the dihedral angle between the aromatic rings of 72.9 (1)°.

The packing structure of the molecule displays an intermolecular hydrogen-bonded chain along the *b* axis, in a 'concave-convex' arrangement (Fig. 2). Two adjacent molecules have their arms pointing towards opposite sides of the central C9 atom and they are separated by *b*/2, as they are related by the 2<sub>1</sub> screw axis of the space group. The hydrogen bond is then defined between hydroxy atom H2A and sulfinyl atom O1, with a distance of 1.724 Å. Thus, the molecular conformation precludes intramolecular H2A..O1 bonding, favouring the intermolecular interaction. This kind of intramolecular hydrogen bonding has previously been described for sulfinyl alcohols (Broutin & Colobert, 2003; 2005; Loughlin *et al.*, 2002; Satoh *et al.*, 2002). It has been pointed out (Fernández de la Pradilla *et al.*, 2005) that intermolecular hydrogen bonding plays a key role in the stereoselectivity of the Diels-Alders reaction of this type of diene.

	<p><b>Figure 1</b></p> <p>The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.</p>
	<p><b>Figure 2</b></p> <p>A packing view of (I), showing the unit cell. [Symmetry codes: (i) <math>1 - x, y - \frac{1}{2}, 1 - z</math>; (ii) <math>1 - x, y + \frac{1}{2}, 1 - z</math>.]</p>

## Experimental

The stereoselective synthesis of compound (I) was carried out as follows. To a cooled solution (195 K, dry ice-acetone) of (*R<sub>C</sub>*)-6-phenyl-1-(*p*-tolylsulfinyl)-3(*E*),5(*E*)-hexadien-2-one (0.55 mmol) dissolved in dry tetrahydrofuran (5 ml), diisobutyl aluminium hydride (DIBALH; 1.4 ml) was added dropwise. After 60 min, methanol (1.5 ml) was added and the reaction mixture was allowed to reach ambient temperature. The solvent was then evaporated completely at reduced pressure and the resulting solid was resuspended and stirred into 5% sulfuric acid for 15 min. The mixture was then extracted with ethyl acetate. Concentration of the solution and purification by column chromatography (ethyl acetate-hexane 1:0.7 v/v) afforded a white solid (60% yield), which was recrystallized from a mixture of ethyl acetate and hexane (1:2 v/v) (m.p. 398-400 K).

### Crystal data

- C<sub>19</sub>H<sub>20</sub>O<sub>2</sub>S
- *M<sub>r</sub>* = 312.41
- Monoclinic, *P* 2<sub>1</sub>


- $a = 5.9765 (12) \text{ \AA}$
- $b = 7.9484 (16) \text{ \AA}$
- $c = 18.130 (4) \text{ \AA}$
- $\beta = 96.439 (4)^\circ$
- $V = 855.8 (3) \text{ \AA}^3$
- $Z = 2$
- $D_x = 1.212 \text{ Mg m}^{-3}$
- Mo  $K\alpha$  radiation
- $\mu = 0.19 \text{ mm}^{-1}$
- $T = 273 (2) \text{ K}$
- Plate, colourless
- $0.50 \times 0.23 \times 0.06 \text{ mm}$

#### Data collection

- Siemens SMART CCD area-detector diffractometer
- $\varphi$  and  $\omega$  scans
- Absorption correction: part of the refinement model ( $\Delta F$ ) (*SADABS* in *SAINT-NT*; Bruker, 1999)  $T_{\min} = 0.910$ ,  $T_{\max} = 0.989$
- 5368 measured reflections
- 2977 independent reflections
- 2232 reflections with  $I > 2\sigma(I)$
- $R_{\text{int}} = 0.033$
- $\theta_{\text{max}} = 25.1^\circ$
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#### Refinement

- Refinement on  $F^2$

- $R[F^2 > 2\sigma(F^2)] = 0.063$
- $wR(F^2) = 0.113$
- $S = 1.07$
- 2977 reflections
- 201 parameters
- H-atom parameters constrained
- $w = 1/[\sigma^2(F_o^2) + (0.0401P)^2]$  where  $P = (F_o^2 + 2F_c^2)/3$
- $(\Delta/\sigma)_{\max} < 0.001$
- $\Delta\rho_{\max} = 0.32 \text{ e } \text{\AA}^{-3}$
- $\Delta\rho_{\min} = -0.13 \text{ e } \text{\AA}^{-3}$
- Absolute structure: Flack (1983 ) , with 1346 Friedel pairs
- Flack parameter: -0.05 (12)

**Table 1**

Selected geometric parameters (Å, °)

S1-O1	1.497 (3)	
S1-C1	1.775 (4)	
S1-C8	1.782 (4)	
C9-O2	1.400 (4)	
O2-H2A	0.8200	
O1-S1-C1	106.92 (18)	
O1-S1-C8	104.34 (17)	
C1-S1-C8	99.82 (18)	
C1-S1-C8-C9		178.4 (3)
S1-C8-C9-C10		-176.1 (3)
C8-C9-C10-C11		-127.0 (4)
C9-C10-C11-C12		178.1 (4)
C11-C12-C13-C14		177.5 (4)

**Table 2**

Hydrogen-bond geometry (Å, °)

<i>D</i> -H... <i>A</i>	<i>D</i> -H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> -H... <i>A</i>
O2-H2A...O1 <sup>i</sup>	0.82	1.98	2.785 (4)	166
C8-H8A...O2 <sup>i</sup>	0.97	2.58	3.527 (5)	164
C8-H8B...O1 <sup>ii</sup>	0.97	2.60	3.347 (5)	134

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

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The H atoms of the organic skeleton were introduced in calculated positions and then allowed for using a riding model, with C-H = 0.93, 0.96 or 0.98 Å. Hydroxy atom H2A was located in a difference synthesis during the final stages of the structure completion. It was refined with O-H = 0.82 Å, C-O-H = 109.5° and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O2})$ .

Data collection: *SMART-NT* (Bruker, 2001 [↗](#)); cell refinement: *SAINT-NT* (Bruker, 1999 [↗](#)); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXTL-NT* (Bruker, 1999 [↗](#)); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *SHELXTL-NT*.

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