(1RS,2RS,6SR,8SR)-2-methyl-8-(phenylsulfonyl)bicyclo[4.2.0]octan-1-ol

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The title compound, \( \text{C}_{15}\text{H}_{20}\text{O}_{3}\text{S} \), shows a conformational arrangement of the phenyl ring that permits hydrogen-bonded dimers to be disposed about a centre of symmetry.

**Comment**

The preparation of fused carbocyclic ring systems bearing a bridgehead hydroxyl group has been achieved by the reaction between the lithium enolates of simple unfunctionalized ketones and phenyl vinyl sulfoxide (Loughlin et al., 2002; Loughlin & McCleary, 2003; Healy et al., 2002; Loughlin et al., 2003). In the current study, reaction of the lithium enolate of 2-methylcyclohexan-1-one (obtained from lithium diisopropylamide, LDA) with phenyl vinyl sulfoxide and subsequent oxidation with \( \text{m}-\text{CPBA} \) generated a novel methylbicyclo[4.2.0]octan-1-ol, compound (I).

Bicyclo[4.2.0]octan-1-ols with a methyl substituent proximal to the bridgehead have been observed as key intermediates in synthetic and mechanistic studies (Blanchard & Burnell, 2001; Syah & Ghisalberti, 1998; Jamart-Gregoire et al., 1995). Under the present unoptimized reaction conditions, (I) was formed as the major bicyclo[4.2.0]octan-1-ol isomer in a 21:14:65 ratio of (I):(II):(III) and (IV) from 2-methylcyclohexan-1-one and phenyl vinyl sulfoxide (see Scheme). Here we report the synthesis, isolation and solid state structural characterization of the novel bicyclo[4.2.0]octan-1-ol, (I) (Fig. 1). The S—O3 bond in conjunction with the phenyl group is directed away from the bicyclo[4.2.0]alkan-1-ol ring, whereas the S—O2 bond is oriented towards this ring. The structure of (I) is stabilized by three-centred bifurcated intra- and intermolecular hydrogen bonds between the hydroxyl H and sulfone O atoms, forming a dimeric structure disposed about a crystallographic centre of symmetry (Table 2, Fig. 2). This differs from the chain-like intermolecular hydrogen-bonding pattern previously observed in the analogues of (I) that lack the C2 methyl group (Healy et al., 2002; Loughlin et al., 2003).
Experimental

2-Methylcyclohexanone (0.5 ml, 4.119 mmole) was reacted with lithium diisopropylamide (1.4 M, 2.95 ml, 4.119 mmol) in THF (44.5 ml) at 273 K under nitrogen over a period of 1 h. The reaction vessel was shielded from light. Rapid addition of phenyl vinyl sulf oxide (0.55 ml, 3.119 mmol) at 263 K with a 10 min reaction time and work-up as described elsewhere (Loughlin et al., 2002) gave the crude sulfoxide mixture (1.074 g). This was subsequently oxidized with m-CPBA (1 equiv) in chloroform (50 ml). Work-up of the reaction mixture as described elsewhere (Loughlin et al., 2002) was followed by silica chromatography (hexane:ethyl acetate, 60:40). A mixture of compounds (I)–(IV) (658 mg, 57%) was obtained. An analytically pure sample of compound (I) was obtained by semi-preparative HPLC (hexane–ethyl acetate, 80:20, retention time 11.8 min, 3 ml min⁻¹). Colourless crystals of compound (I) (m.p. 383.2–384.6 K) were isolated by slow evaporation of a hexane–ethyl acetate (80:20) solution of the compound. Analysis found: C 64.52, H 7.36, S 11.32%; calculated for C₁₅H₂₀SO₃: C 64.25, H 7.19, S 11.43%.

Crystal data

C₁₅H₂₀O₃S  
M_r = 280.38  
Monoclinic, P2₁/n  
a = 12.328 (6) Å  
b = 10.362 (4) Å  
c = 12.149 (2) Å  
β = 99.60 (3)°  
V = 1530.2 (10) Å³  
Z = 4  
D_x = 1.217 Mg m⁻³  
Mo Kα radiation  
Cell parameters from 24 reflections  
θ = 12.8–16.0°  
μ = 0.21 mm⁻¹  
T = 295 K  
Prism, colourless

Data collection

Rigaku AFC-7R diffractometer  
ω-2θ scans  
Absorption correction: none  
3987 measured reflections  
3516 independent reflections  
1717 reflections with I > 2σ(I)  
R_int = 0.067  
max = 27.5°  
h = −7 to 16  
k = 0 to 13  
l = −15 to 15  
3 standard reflections every 150 reflections  
intensity decay: none

Refinement

Refinement on F²  
R[F² > 2σ(F²)] = 0.053  
wR(F²) = 0.174  
S = 0.98  
3516 reflections  
173 parameters  
H-atom parameters constrained  
w = 1/[σ²(F²) + (0.0801P)²]  
where P = (F² + 2F*c)/3  
(Δ/σ)max = 0.001  
Δρ_max = 0.29 e Å⁻³  
Δρ_min = −0.35 e Å⁻³

Selected geometric parameters (Å, °).

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-S1-O2</td>
<td>1.441 (2)</td>
</tr>
<tr>
<td>C1-S1-O3</td>
<td>1.442 (2)</td>
</tr>
<tr>
<td>C1-S1-C8</td>
<td>1.765 (4)</td>
</tr>
<tr>
<td>O2-S1-O3</td>
<td>1.180 (14)</td>
</tr>
<tr>
<td>O2-S1-C8</td>
<td>1.099 (15)</td>
</tr>
<tr>
<td>O2-S1-C9</td>
<td>1.086 (15)</td>
</tr>
<tr>
<td>O3-S1-C8</td>
<td>1.067 (8)</td>
</tr>
<tr>
<td>O3-S1-C9</td>
<td>1.057 (5)</td>
</tr>
<tr>
<td>C8-S1-C9</td>
<td>1.057 (18)</td>
</tr>
<tr>
<td>O1-C1-C2</td>
<td>1.076 (3)</td>
</tr>
</tbody>
</table>

H-atom parameters constrained

Table 2

Hydrogen-bonding geometry (Å, °).

<table>
<thead>
<tr>
<th>D—H···A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
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</thead>
<tbody>
<tr>
<td>O1—H1···O2</td>
<td>0.96</td>
<td>2.44</td>
<td>3.036 (4)</td>
<td>120</td>
</tr>
<tr>
<td>O1—H1···O2’</td>
<td>0.96</td>
<td>2.02</td>
<td>2.918 (3)</td>
<td>154</td>
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</tbody>
</table>

Symmetry code: (i) 2 – x, 1 – y, 2 – z.

H atoms were positioned geometrically (C–H = 0.95 and O–H = 0.96 Å) and refined as riding, with U(eq)(H) = 1.2Ueq(parent atom).

Data collection: MSC/AFC-7 Diffractometer Control Software for Windows (Molecular Structure Corporation, 1999); cell refinement: MSC/AFC-7 Diffractometer Control Software for Windows; data reduction: TEXSAN for Windows (Molecular Structure Corporation, 1997–2001); program(s) used to solve structure: TEXSAN for...
Windows; program(s) used to refine structure: TExSAN for Windows and SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2001) and ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: TExSAN for Windows and PLATON.

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References