

Spiro[1,3-dioxolane-2,4'-[8]phenyl-sulfonylbicyclo[4.2.0]octan-1-ol]

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Key indicators

Single-crystal X-ray study

T = 295 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.045

wR factor = 0.130

Data-to-parameter ratio = 17.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The structure of the title compound, $\text{C}_{16}\text{H}_{20}\text{O}_5\text{S}$, has been determined as part of an investigation into the synthesis of fused carbocyclic ring systems with functionality and containing a cyclobutanol ring. The conformational arrangement of the phenyl ring permits the formation of an infinite chain of intermolecular $\text{O}-\text{H}\cdots\text{O}-\text{S}$ hydrogen bonds. The dioxolane ring is removed from and does not participate in the chain of intermolecular hydrogen bonds.

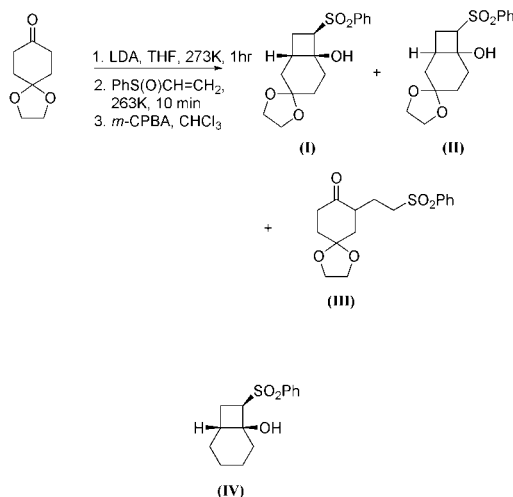
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Comment

We have recently shown that a novel cyclization reaction between the lithium enolates of simple unfunctionalized ketones and phenyl vinyl sulfoxide provides a simple and convenient route to the preparation of fused carbocyclic ring systems bearing a bridgehead hydroxy group (Loughlin & McCleary, 2003; Loughlin *et al.*, 2002). In the current study, reaction of the lithium enolate of 1,4-cyclohexanedione monoethylene ketal (obtained from lithium diisopropylamide, LDA) with phenyl vinyl sulfoxide and subsequent oxidation with *m*-chloroperoxybenzoic acid (*m*-CPBA), generated the first representative of a functionalized bicyclo[4.2.0]octan-1-ol, the novel spiro compound, (I).



The spiro compound can be perceived as a synthetic precursor to a bicyclo[4.2.0]octan-3-one, which is cognate with key structural components of, for example, benzocyclobutacarbazole antitumor agents (Graf-Christophe *et al.*, 2000; Christophe *et al.*, 1998), taxane precursors (Wender *et al.*, 1997) and products arising from Norrish type II photoreactions (Osuka *et al.*, 1987). Under the present reaction conditions, (I) was formed as the major bicyclo[4.2.0]octan-1-ol isomer in a 42:16:42 ratio of (I):(II):(III) from achiral 1,4-

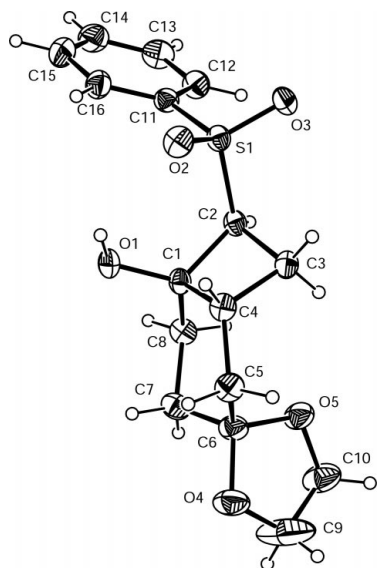


Figure 1
ORTEP-3 (Farrugia, 1997) plot, showing the atomic numbering scheme for a molecule of (I). Displacement ellipsoids for non-H atoms are drawn at the 30% probability level.

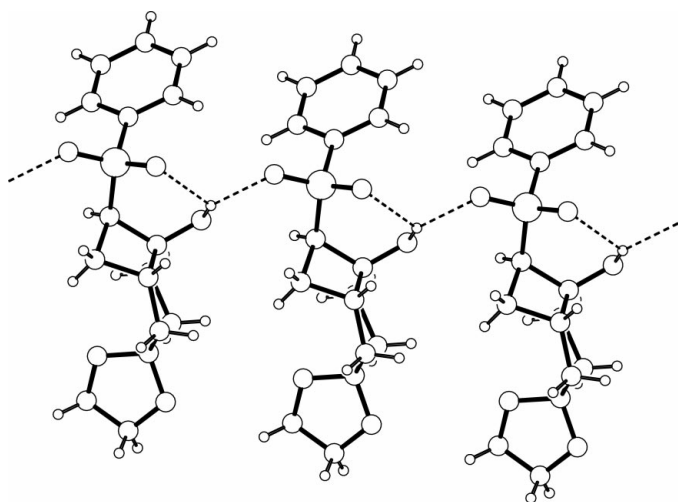


Figure 2
Hydrogen bonding scheme for (I).

cyclohexanedione mono-ethylene ketal and phenyl vinyl sulfoxide with less than 5% of other products observed. Here we report the synthesis, isolation and structural characterization of the novel bicyclo[4.2.0]octan-1-ol (I).

The crystal structure determination (Fig. 1 and Table 1) shows that the relative stereochemistry about the bicyclo[4.2.0]alkanol ring in (I) is the same as that found for the 'parent' compound 8-(phenylsulfonyl)bicyclo[4.2.0]octan-1-ol, (IV) (Loughlin *et al.*, 2002), with the C2–S bond *cis* to the bridgehead hydroxyl group and *trans* to the fused six-membered ring. As in the structure of (IV), this conformation is stabilized by three-centred 'bifurcated' intra- and intermolecular hydrogen bonds between the hydroxyl H and the sulfone O atoms (Fig. 2 and Table 2). These results indicate that the stereochemistry and molecular packing of this mol-

ecule are not significantly affected by the addition of the dioxolane ring to the system.

Experimental

1,4-Cyclohexanedione mono-ethylene ketal (0.5 g, 3.201 mmol) in THF (2 ml) was added to lithium diisopropylamide (1.4 M, 3.201 mmol, 2.30 ml) in THF (33 ml) at 273 K under nitrogen over 5 min and further reacted at 273 K for 1 h. Upon cooling to 263 K, rapid addition of phenyl vinyl sulfoxide (0.43 ml, 3.201 mmol) at 263 K, with the system shielded from light, a 10 min reaction time and workup, as described elsewhere (Loughlin *et al.*, 2002), gave the crude sulfoxide mixture (0.833 g). This was subsequently oxidized with *m*-CPBA (1 equivalent) in chloroform (30 ml). Work-up of the reaction mixture, as described elsewhere (Loughlin *et al.*, 2002), was followed by silica chromatography (hexane–ethyl acetate, 70:30). A mixture of compounds (I)–(III) (485 mg, 47%) was obtained. An analytically pure sample of compound (I) was obtained by semi-preparative HPLC (hexane–ethyl acetate, 50:50, retention time 12.9 min, 3 ml min⁻¹). Colourless crystals of (I) (m.p. 390.5–392.2 K) were isolated by slow evaporation of a hexane–ethyl acetate (50:50) solution of the compound. Analysis found: C 59.30, H 6.32, S 9.70%; calculated for C₁₆H₂₀O₅S: C 59.24, H 6.21, S 9.88%. ν_{\max} (KBr)/cm⁻¹: 3500 (OH), 1302 (SO₂), 1142 (SO₂). δ_{H} (400 MHz, CDCl₃, p.p.m.): 7.87–7.95 (2H, *m*, *o*-C₆H₅), 7.57–7.65 (1H, *m*, *p*-C₆H₅), 7.48–7.57 (2H, *m*, *m*-C₆H₅), 3.84–3.94 (4H, *m*, 2 × 4H, 2 × 5H), 3.52 (1H, *ddd*, J_{8',7'} 9, J_{8',7'} 3, J_{8',6'} 1, 8'-H), 3.03–3.13 (1H, *m*, 6'-H), 2.32 (1H, *ddd*, J_{7',7'} 10, J_{7',6'} 10, J_{7',8'} 3, 7'-H), 2.12 (1H, *ddd*, J_{7',7'} 11, J_{7',6'} 9, J_{7',8'} 9, 7'-H), 1.91–1.98 (2H, *m*, 2 × 3'-H), 1.85 (1H, *dd*, J_{5',5'} 15, J_{5',6'} 7, 5'-H), 1.68–1.77 (1H, *m*, 2'-H), 1.49–1.58 (2H, *m*, 2'-H, 5'-H), OH not observed. δ_{C} (50 MHz, CDCl₃) 139.8, (*i*-C₆H₅), 133.5, (*p*-C₆H₅), 129.2, (*m*-C₆H₅), 127.9, (*o*-C₆H₅), 108.4, (C-2,4'), 72.7, (C-1'), 67.3, (C-8'), 64.4, 63.9, (C-4, C-5), 43.8, (C-6'), 33.4, (C-2'), 32.8, (C-5'), 29.4, (C-3'), 20.4, (C-7'). ESMS⁺ 331 (M^{Li+}, 100%), 347 (M^{Na+}, 83%).

Crystal data

C ₁₆ H ₂₀ O ₅ S	Z = 2
<i>M_r</i> = 324.39	<i>D_x</i> = 1.397 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 5.736 (3) Å	Cell parameters from 25 reflections
<i>b</i> = 11.468 (5) Å	θ = 12.7–17.3°
<i>c</i> = 12.095 (4) Å	μ = 0.23 mm ⁻¹
α = 81.1 (6)°	<i>T</i> = 295 K
β = 98.83 (3)°	Needle, colorless
γ = 98.03 (3)°	0.60 × 0.20 × 0.15 mm
<i>V</i> = 771.2 (13) Å ³	

Data collection

Rigaku AFC-7R diffractometer	θ_{\max} = 27.5°
ω -2 θ scans	<i>h</i> = -7 → 3
Absorption correction: none	<i>k</i> = -14 → 14
4163 measured reflections	<i>l</i> = -15 → 15
3537 independent reflections	3 standard reflections
2637 reflections with <i>I</i> > 2 σ (<i>I</i>)	every 150 reflections
<i>R</i> _{int} = 0.052	intensity decay: 2.4%

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 0.277P]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.130$	(Δ/σ) _{max} = 0.001
<i>S</i> = 1.04	$\Delta\rho_{\max} = 0.32 \text{ e } \text{Å}^{-3}$
3537 reflections	$\Delta\rho_{\min} = -0.36 \text{ e } \text{Å}^{-3}$
200 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.034 (4)
OK?	

Table 1
Selected geometric parameters (Å, °).

S1—O2	1.4401 (19)	O4—C6	1.440 (3)
S1—O3	1.448 (2)	O4—C9	1.382 (5)
S1—C2	1.774 (2)	O5—C6	1.435 (3)
S1—C11	1.770 (2)	O5—C10	1.410 (4)
O1—C1	1.411 (3)		
O2—S1—O3	117.9 (6)	S1—C2—C1	118.1 (6)
O2—S1—C2	109.7 (6)	S1—C2—C3	111.1 (6)
O2—S1—C11	108.7 (6)	O4—C6—C5	109.7 (6)
O3—S1—C2	107.3 (6)	O4—C6—C7	110.9 (6)
O3—S1—C11	107.3 (6)	O4—C6—O5	105.1 (6)
C2—S1—C11	105.1 (6)	O5—C6—C7	110.4 (6)
C6—O4—C9	108.0 (6)	O5—C6—C5	109.9 (6)
C6—O5—C10	108.6 (6)	O4—C9—C10	109.4 (7)
O1—C1—C2	119.8 (6)	O5—C10—C9	104.1 (7)
O1—C1—C8	106.8 (6)	S1—C11—C12	118.9 (6)
O1—C1—C4	118.6 (6)	S1—C11—C16	119.8 (6)

Table 2
Hydrogen-bonding 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>
O1—H1...O2	0.85	2.43	3.022 (3)	127
O1—H1...O3 ⁱ	0.85	2.25	2.928 (3)	137

Symmetry code: (i) 1 + *x*, *y*, *z*.

H atoms were constrained as riding atoms, with C—H set to 0.95 Å. The hydroxy H atom was located from a difference Fourier map and the O—H bond length set to 0.85 Å. U_{iso} values for the H atoms were set at $1.2U_{eq}$ of the parent atom. Displacement parameters for atom C9 are indicative of potential disorder for this atom in the dioxolane ring.

Data collection: MSC/AFC-7 *Diffraction Control Software for Windows* (Molecular Structure Corporation, 1999); cell refinement:

MSC/AFC-7 *Diffraction 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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