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1*S*(*R*),2*S*(*R*),3*S*(*R*),10*S*(*R*),12*R*(*S*),13*R*(*S*),-14*R*(*S*),17*S*(*R*)-13-Bromo-11-oxapentacyclo[8.7.0.0^{2,14}.0^{4,9}.0^{12,17}]heptadeca-4,6,8-trien-3-ol

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.043
wR factor = 0.118
Data-to-parameter ratio = 14.5

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

The title compound, $C_{16}H_{17}BrO_2$, exhibits C—H···O, C—H···Br and O—H···O hydrogen-bonding interactions. The molecule contains six-membered rings with twist and boat conformations in addition to the benzene ring.

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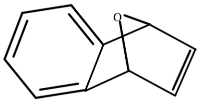
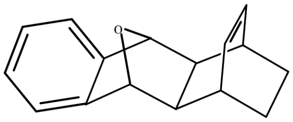
Comment

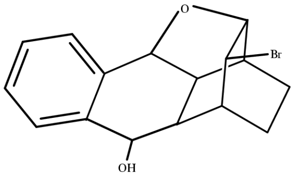
1,4-Dihydronaphthalene-1,4-epoxide, (1), is a reactive dienophile (Fieser & Haddadin, 1965). Compound (2) was obtained from a cycloaddition reaction of epoxide (1) with cyclohexadiene. These systems are important and undergo reactions such as rearrangements (Menzek *et al.*, 1997; Altundaş *et al.*, 2000; Menzek, 2000; Menzek & Gökmen, 2002). Compound (2) was reacted with bromine in carbon tetrachloride at low temperature, and compound (3) was isolated from the reaction mixture as a rearrangement product. There are examples (Konaklieva *et al.*, 1992; Sharghi *et al.*, 2001) showing that 1,2-epoxides are opened in the presence of halogens.



(1)



(2)



(3)

The title compound, (3), contains a central non-planar six-membered carbon ring with a twist conformation, which has a planar benzene ring on one side and two non-planar six-membered carbon rings constituting a bicyclic system on the other side. One of these non-planar carbon rings sharing two C atoms with the central ring has Br and O substituents, while the second has no substituents. The bicyclic system has approximate D_3 symmetry, but the presence of substituents, and the resulting intermolecular and intramolecular hydrogen bonds, lead to some deviations from the ideal geometry. This can be seen in the torsion angles (Table 2), and in the puckering parameters (Cremer & Pople, 1975). In the bicyclo fragment, all three six-membered rings adopt a boat conformation: q_2 = 0.925 (3) Å, q_3 = −0.094 (3) Å, φ_2 = 54.36 (15)°, θ_2 = 95.82 (18)° and Q_T = 0.929 (3) Å for the C8—C9—C16—C15—C12—C13 ring; q_2 = 0.805 (3) Å, q_3 = −0.078 (3) Å, φ_2 = −115.6 (2)°, θ_2 = 95.6 (2)° and Q_T = 0.809 (3) Å for the C8–C13 ring; q_2 = 0.787 (3) Å, q_3 = −0.031 (3) Å, φ_2 = 165.8 (2)°, θ_2 = 92.2 (2)° and Q_T = 0.787 (3) Å for the C9—C10—C11—C12—C15—C16 ring. The central twist-conformation ring also has OH and O substituents. In this ring, C1—C6—C7—C8—C13—C14, the dihedral angle between the planes which pass through atoms C1/C6/C7/C14 and through atoms C7/C8/C13/

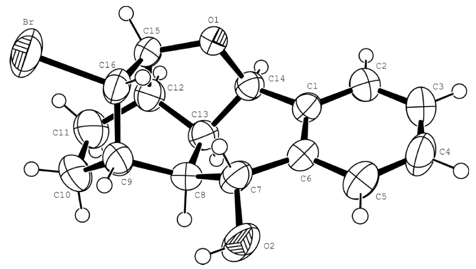


Figure 1
View of (3) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

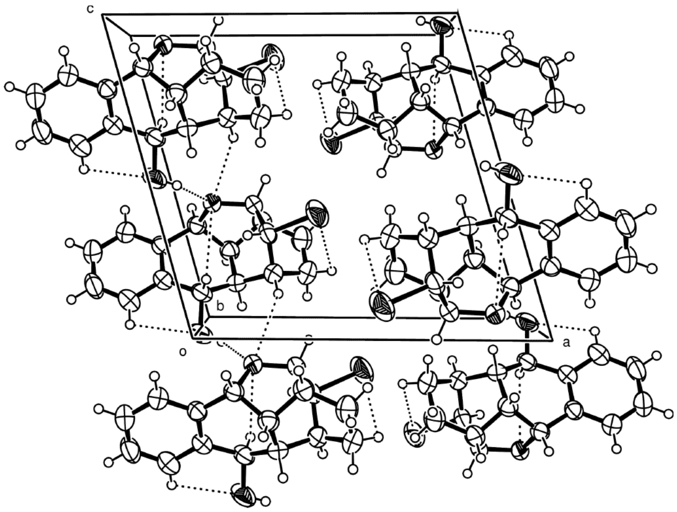


Figure 2
A packing diagram of (3), illustrating the close contact network. The view is along the *b* axis.

C14 is 143.1 (1)°. The benzene ring containing atoms C1–C6 is essentialy planar, with a maximum deviation of 0.009 (3) Å for atom C5. The five-membered ring, C12—C13—C14—C15—O1, has a half-chair conformation, as evidenced by the puckering parameters; q_2 = 0.504 (3) Å and φ_2 = 85.1 (2)°. The Br—C16 bond length is 1.974 (3) Å, compared with literature values of 1.942 (6) Å (Beddoes *et al.*, 1996) and 1.943 (12)–1.969 (11) Å (Ülkü *et al.*, 2002). The lengthening in (3) may be due to hydrogen bonding.

Other similar structures have been reported (Mostafa *et al.*, 1996; Buñuel *et al.*, 1996, 2000; Zuckermann-Schpector *et al.*, 2001; Jones *et al.*, 1997; Gable *et al.*, 1996). In (3), Br and O atoms are able to form hydrogen bonds with C atoms in the same molecule and with C and O atoms in symmetry-related molecules. C—H···O, O—H···O and C—H···Br interactions, by which the crystal structure is stabilized, are detailed in Table 2 and shown in Fig. 2.

Experimental

Br_2 (158 mg, 0.99 mmol, in 1 ml of CCl_4) was added dropwise to a stirred solution of compound (2) (200 mg, 0.89 mmol, in 20 ml CCl_4) at 273 K over a period of 5 min. The mixture was stirred for 30 min and the solvent was then evaporated. According to NMR spectroscopy, compound (2) was now absent. The residue was separated by preparative thick-layer chromatography, with ether/hexane (1:1). Compound (3) (31.4%, 90 mg) was isolated pure. Two compounds, whose structures have not yet been determined, were also isolated from this residue. Analytical data for (3): mp 450–452 K, white crystals were obtained from ethyl acetate; ^{1}H NMR (200 MHz, $CDCl_3$, p.p.m.): δ 7.54 (*d, J* = 7.33 Hz, aromatic, 1H), 7.46–7.29 (*m*, aromatic, 3H), 4.72–4.66 (*m*, 2H), 4.41 (*d, J* = 5.86 Hz, 1H), 4.12 (*m*, 1H), 2.41–1.89 (*m*, methylenic and OH, 7H), 166–1.53 (*m*, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, p.p.m.): δ 141.09 (C), 135.43 (C), 131.23 (2 CH), 129.23 (CH), 126.49 (CH), 85.50, 80.60, 70.34, 56.23, 46.36, 40.58, 39.40, 34.96, 25.62, 17.91; ν_{max} (KBr): 3336, 3080, 2953, 2927, 2902, 1497, 1472, 1395, 1319, 1268, 1242, 1063, 987, 782 cm^{-1}.

Crystal data

$C_{16}H_{17}BrO_2$
M_r = 321.21
Monoclinic, $P2_1/c$
a = 11.651 (5) Å
b = 10.835 (5) Å
c = 11.029 (5) Å
β = 105.801 (5)°
V = 1339.7 (10) Å^3
Z = 4
D_x = 1.593 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 2637 reflections
θ = 3.9–96.6°
μ = 4.14 mm^{-1}
T = 293 (2) K
Prism, colorless
0.20 × 0.15 × 0.06 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.484, T_{max} = 0.780
33118 measured reflections
2511 independent reflections
2209 reflections with $I > 2\sigma(I)$
R_{int} = 0.100
θ_{max} = 69.6°
$h = -14 \rightarrow 14$
$k = -13 \rightarrow 13$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.118$
S = 1.04
2511 reflections
173 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 0.6924P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0040 (5)

Table 1
Selected geometric parameters (Å, °).

Br—C16	1.973 (3)	O1—C14	1.467 (3)
O1—C15	1.450 (3)	O2—C7	1.422 (3)
C15—O1—C14	108.24 (17)	C16—C9—C10	111.0 (2)
C6—C1—C2	120.0 (2)	C16—C9—C8	107.62 (19)
C6—C1—C14	119.0 (2)	C10—C9—C8	107.5 (3)
C9—C16—C15	109.6 (2)	C15—C12—C11	113.7 (3)
C15—C16—Br	110.04 (16)	C15—C12—C13	97.96 (19)
O1—C14—C13	102.53 (17)	C11—C12—C13	114.8 (2)
O1—C15—C12	105.14 (19)	C11—C10—C9	109.0 (2)
O1—C15—C16	107.29 (19)	C12—C11—C10	110.4 (2)
C12—C15—C16	109.2 (2)		
C15—O1—C14—C13	−20.5 (2)	C14—C1—C6—C7	−7.0 (3)
O1—C14—C13—C12	44.0 (2)	C15—C16—C9—C10	−67.7 (3)
C12—C13—C8—C9	−2.9 (3)	Br—C16—C9—C10	54.5 (3)
C14—C13—C8—C7	−20.3 (3)	C15—C16—C9—C8	49.7 (3)
C14—O1—C15—C12	−11.9 (2)	C13—C8—C9—C16	−57.5 (3)
C14—O1—C15—C16	104.3 (2)	C7—C8—C9—C16	72.2 (3)
C9—C16—C15—O1	−95.9 (2)	C5—C6—C7—O2	−23.4 (3)
Br—C16—C15—O1	140.95 (16)	C14—C13—C12—C15	−49.9 (2)
C9—C16—C15—C12	17.6 (3)	C9—C10—C11—C12	12.1 (4)

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Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7···O1	0.98	2.95	3.145 (3)	92
C5—H5···O2	0.93	2.43	2.748 (4)	100
C10—H10B···Br	0.97	2.83	3.202 (4)	104
C9—H9···O1^{i}	0.98	2.99	3.893 (3)	153
O2—H2···O1^{i}	0.82	2.12	2.824 (3)	144
C4—H4···Br^{ii}	0.93	2.93	3.808 (3)	157

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

All H atoms were positioned geometrically at distances of 0.82, 0.93, 0.97 and 0.98 Å for hydroxyl O—H, aromatic C—H, methylene group C—H and methine C—H bonds, respectively, and allowed to ride on their attached atoms.

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *PARST*95 (Nardelli, 1995), *PLATON* (Spek, 1990) and *WinGX* (Farrugia, 1999).

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