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12-Bromo-1,2,3,4-tetrahydro-1,4-ethanoanthracen-11-ol

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.038
wR factor = 0.104
Data-to-parameter ratio = 15.5

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

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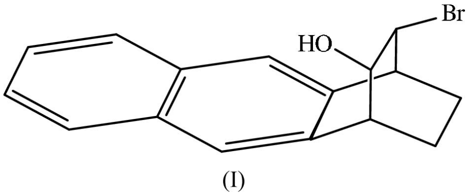
The title compound, $C_{16}H_{15}BrO$, contains two non-planar six-membered rings constituting a bicyclic system. One of these rings shares two C atoms with an ethanoanthracene moiety, while the second ring has bromo and hydroxy substituents. The bicyclic system has approximate D_3 symmetry. There are two molecules in the asymmetric unit. Two strong hydrogen bonds, with D···A distances of 2.765 (2) and 2.818 (2) Å, are observed between O atoms.

Comment

1*R*(*S*),2*R*(*S*),3*R*(*S*),10*S*(*R*),11*S*(*R*),12*S*(*R*)-3,10-Epoxytetracyclo[10.2.2.0^{2,11}.0^{4,9}]hexadeca-4,6,8,13-tetraene (Menzek *et al.*, 2004) was obtained from the cycloaddition reaction of oxobenzonorbornadiene with cyclohexadiene, and has one double bond and 1,4-epoxide as functional groups. These systems are important and undergo reactions such as rearrangement reactions (Menzek *et al.*, 1997; Altundaş *et al.*, 2000; Menzek, 2000; Daştan , 2001; Menzek & Gökmen, 2002; Menzek & Karakaya, 2004). 1*R*(*S*),2*R*(*S*),3*R*(*S*),10*S*(*R*),-11*S*(*R*),12*S*(*R*)-3,10-Epoxytetracyclo[10.2.2.0^{2,11}.0^{4,9}]hexadeca-4,6,8,13-tetraene was reacted with bromine in carbon tetrachloride at low temperature, and 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-oxa pentacyclo[8.7.0.0^{2,14}.0^{4,9}.0^{12,17}]heptadeca-4,6,8-trien-3-ol (Çoruh *et al.*, 2002) and the title compound, (I), were isolated from the reaction mixture as rearranged products. There are examples (Konaklieva *et al.*, 1992; Sharghi *et al.*, 2001) showing that 1,2-epoxides are opened in the presence of halogens. To explain the mechanisms of the rearrangement reactions, the structures of products such as (I) should be determined.



(I)

The crystal structure of (I) contains two independent molecules in the asymmetric unit, denoted *A* and *B* (Fig.1). The molecules contain a naphthalene ring system fused to a bicyclic system. As can be seen from the torsion angles (Table 1) and the puckering parameters (Cremer & Pople, 1975), the bicyclic system has approximate D_3 symmetry, but the presence of substituents, and the resulting intramolecular contacts and intermolecular hydrogen bonds, lead to some deviations from ideal geometry.

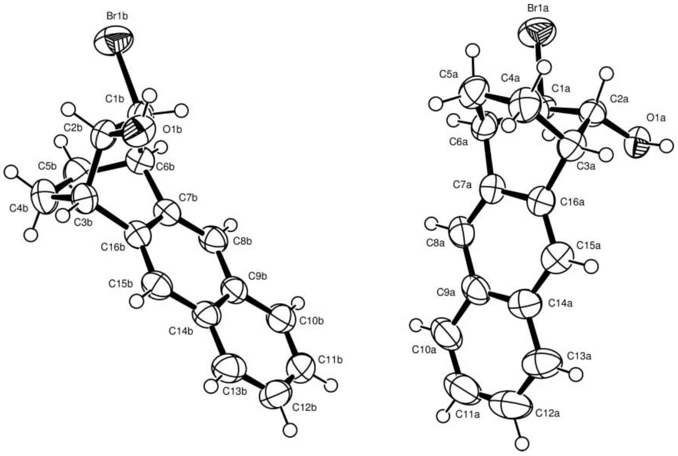


Figure 1
A view of the asymmetric unit of (I), with the atomic numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

In the bicyclic fragments of molecules *A* and *B*, the three six-membered rings adopt boat conformations: Q_T = 0.837 (3) Å, $\varphi_2 = -66.4$ (2)° and θ_2 = 92.7 (2)° for the C1*a*–C6*a* ring, Q_T = 0.842 (3) Å, φ_2 = 125.86 (18)° and θ_2 = 92.7 (9)° for the C1*a*–C3*a*/C16*a*/C7*a*/C6*a* ring, Q_T = 0.795 Å, φ_2 = 2.9 (2)° and θ_2 = 89.6 (2)° for the C3*a*–C7*a*/C16*a* ring, Q_T = 0.839 (3) Å, $\varphi_2 = -62.94$ (19)° and θ_2 = 92.40 (19)° for the C1*b*–C6*b* ring, Q_T = 0.813 (13) Å, φ_2 = 123.08 (19)° and θ_2 = 92.15 (19)° for the C1*b*–C3*b*/C16*b*/C7*b*/C6*b* ring, and Q_T = 0.809 (3) Å, φ_2 = 0.1 (2)° and θ_2=90.1 (2)° for the C3*b*–C7*b*/C16*b* ring. The deviation from the ideal D_3 symmetry in the bicyclic rings can be seen by examination of the dihedral angles between the planes defining the three rings: in molecule *A*, C1*a*–C3*a*/C6*a* (plane *A*), C3*a*/C16*a*/C7*a*/C6*a* (plane *B*) and C3*a*–C6*a* (plane *C*) [*A*/*B* = 61.94 (14)°, *A*/*C* = 59.96 (12)° and *B*/*C* = 58.16 (14)°], and in molecule *B*, C1*b*–C3*b*/C6*b* (plane *D*), C3*b*/C16*b*/C7*b*/C6*b* (plane *E*) and C3*b*–C6*b* (plane *F*) [*D*/*E* = 60.15 (13)°, *D*/*F* = 60.51 (14)° and *E*/*F* = 59.35 (12)°].

Experimental

To a stirred solution of 1*R*(*S*),2*R*(*S*),3*R*(*S*),10*S*(*R*),11*S*(*R*),12*S*(*R*)-3,10-epoxytetracyclo[10.2.2.$0^{2,11}$.$0^{4,9}$]hexadeca-4,6,8,13-tetraene (200 mg, 0, 89 mmol) in CCl_4 (20 ml), Br_2 (158 mg, 0,99 mmol, in 1 ml of CCl_4) was added dropwise at 272 K for 5 min. The mixture was stirred for 30 min and the solvent was then evaporated. According to the NMR spectrum of the residue, 1*R*(*S*),2*R*(*S*),3*R*(*S*),10*S*(*R*),-11*S*(*R*),12*S*(*R*)-3,10-epoxytetracyclo[10.2.2.$0^{2,11}$.$0^{4,9}$]hexadeca-4,6,8,13-tetraene was absent from the reaction mixture. The residue was subjected to PLC (preparative thick-layer chromatography) with diethyl ether/hexane (1:1). 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 (Çoruh *et al.*, 2002) and compound (I) (56%, 150 mg) were isolated from the reaction mixture as rearranged products. For (I): m.p. 388–390 K (white crystals from diethyl ether/hexane); ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.83–7.78 (*AA* part of *AA BB* system, aromatic, 2H), 7.62 (*s*, aromatic, 1H), 7.56 (*s*, aromatic, 1H), 7.51–7.42 (*BB* part of *AA BB* system, aromatic, 2H), 4.22 (*dt*, *J* = 7.37 and 3.04 Hz, CHOH, 1H), 3.68 (*m*, CHBr, 1H), 3.33–3.29 (*m*, bridgehead, CH-CHBr, 1H), 3.01 (*m*, bridgehead, CH-CHOH, 1H), 2.34 (*brt*, *J* = 11.63 Hz, methylenic, 1H), 2.00 (*d*, *J* = 7.37 Hz, OH, 1H), 1.89 (*brt*, *J* = 9.17 Hz, methylenic, 1H), 1.59 (*dt*, *J* = 11.72 and 3.68 Hz, methylenic, *A* part of *AB* system, 1H), 1.51–1.36 (*m*, methylenic, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 141.01 (C), 137.62 (C), 135.08 (C), 135.03 (C), 129.88 (CH), 129.61 (CH), 127.70 (CH), 127.64 (CH), 126.87 (CH), 124.58 (CH), 81.76 (C—OH), 61.51 (C—Br), 44.97, 44.39, 25.22, 21.90; IR, ν_{max} (KBr): 3336, 3080, 3029, 2953, 2927, 1600, 1523, 1472, 1446, 1421, 1370, 1344, 1293 cm^{-1}.

Crystal data

$C_{16}H_{15}BrO$
M_r = 303.20
Triclinic, $P\overline{1}$
a = 9.854 (1) Å
b = 12.316 (1) Å
c = 12.488 (1) Å
α = 79.928 (10)°
β = 77.248 (10)°
γ = 66.719 (10)°
V = 1351.3 (2) Å^3
Z = 4
D_x = 1.490 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 4542 reflections
θ = 1.7–25.6°
μ = 3.03 mm^{-1}
T = 293 (2) K
Prism, colourless
0.15 × 0.07 × 0.06 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
9387 measured reflections
5043 independent reflections
4542 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 25.6°
$h = -11 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.104$
S = 1.10
5043 reflections
325 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2 + 0.8183P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max}$ = 0.57 e Å^{-3}
$\Delta\rho_{min}$ = −0.96 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br1*a*—C1*a*	1.969 (2)	C2*a*—C1*a*	1.540 (3)
Br1*b*—C1*b*	1.977 (2)	C2*b*—C1*b*	1.541 (3)
O1*a*—C2*a*	1.430 (3)	C5*b*—C4*b*	1.534 (4)
O1*b*—C2*b*	1.420 (3)	C4*a*—C5*a*	1.540 (4)
C2*a*—O1*a*—H1*Aa*	109.5	C6*a*—C1*a*—Br1*a*	111.21 (16)
O1*a*—C2*a*—C3*a*	113.2 (2)	C2*a*—C1*a*—Br1*a*	111.26 (16)
O1*a*—C2*a*—C1*a*	106.81 (19)	C6*b*—C1*b*—Br1*b*	111.14 (16)
O1*b*—C2*b*—C3*b*	110.1 (2)	C2*b*—C1*b*—Br1*b*	111.28 (16)
O1*b*—C2*b*—C1*b*	110.42 (19)		
O1*a*—C2*a*—C1*a*—C6*a*	132.7 (2)	Br1*b*—C1*b*—C6*b*—C5*b*	−69.8 (2)
O1*a*—C2*a*—C1*a*—Br1*a*	−102.96 (19)	O1*b*—C2*b*—C3*b*—C16*b*	−68.5 (2)
O1*b*—C2*b*—C1*b*—C6*b*	127.1 (2)	O1*b*—C2*b*—C3*b*—C4*b*	174.76 (19)
O1*b*—C2*b*—C1*b*—Br1*b*	−108.38 (18)	C1*b*—C2*b*—C3*b*—C4*b*	−64.2 (2)
O1*a*—C2*a*—C3*a*—C16*a*	−67.5 (2)	Br1*a*—C1*a*—C6*a*—C7*a*	170.92 (16)
O1*a*—C2*a*—C3*a*—C4*a*	175.11 (19)	Br1*a*—C1*a*—C6*a*—C5*a*	−72.2 (2)
Br1*b*—C1*b*—C6*b*—C7*b*	174.22 (15)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*a*—H1*Aa*···O1*b*^{i}	0.82	2.05	2.765 (2)	145
O1*b*—H1*Bb*···O1*a*^{ii}	0.82	2.10	2.811 (2)	145

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

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All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 (aromatic), 0.97 (methylene) and 0.98 Å (other CH), and with $U_{iso}(H) = 1.2U_{eq}(C)$ and $1.5U_{eq}(O)$.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PARST95* (Nardelli, 1995), *PLATON* (Spek, 2003) and *WinGX* (Farrugia, 1999).

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