Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
10 634 measured reflections
6190 independent reflections
2899 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.054$
$\theta_{\rm max} = 28.30°$
$h = -12 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = 0 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.159$
$S = 0.906$
6190 reflections
366 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0678P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.33$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1997)
Extinction coefficient: 0.018 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

O1*A*—C15*A*	1.372 (3)	O1*B*—C15*B*	1.371 (4)
O1*A*—C2*A*	1.378 (3)	O1*B*—C2*B*	1.382 (3)
O2*A*—C4*A*	1.386 (3)	O2*B*—C17*B*	1.363 (3)
O2*A*—C17*A*	1.393 (3)	O2*B*—C4*B*	1.388 (3)
O3*A*—C6*A*	1.423 (3)	O3*B*—C6*B*	1.423 (3)
C9*A*—C10*A*	1.324 (4)	C9*B*—C10*B*	1.324 (3)
C15*A*—C16*A*	1.330 (3)	C15*B*—C16*B*	1.331 (4)
C8*A*—C14*A*—C11*A*	93.23 (18)	C11*B*—C14*B*—C8*B*	94.0 (2)
C17*A*—O2*A*—C4*A*—C3*A*	49.8 (4)		
C17*B*—O2*B*—C4*B*—C3*B*	−54.9 (4)		

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3*B*—H3*BA*···O2*A*	0.82	2.20	2.990 (3)	163
O3*A*—H3*AA*···O2*A*	0.82	2.48	2.978 (3)	120
O3*A*—H3*AA*···O2*B*	0.82	2.48	3.215 (3)	149
C8*A*—H8*AA*···O1*A*$^{\rm i}$	0.98	2.52	3.481 (3)	168
C15*A*—H15*A*···O3*A*$^{\rm ii}$	0.93	2.54	3.349 (4)	146
C15*B*—H15*B*···O3*B*$^{\rm iii}$	0.93	2.49	3.386 (4)	161

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

For both crystals, the data collection covered a hemisphere of reciprocal space by a combination of three sets of exposures, each with a different φ angle (0, 88 and 180°) for the crystal; the crystal-to-detector distance was 3 cm and the detector swing angle was −20°. The frame exposure time was 30 s for (I) and 10 s for (II). Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the intensity of duplicate reflections; it was found to be negligible. Both structures were solved by direct methods and refined by full-matrix least-squares techniques. After checking their presence in a difference map, all the H atoms were placed in geometrically calculated positions and a riding model was used for their refinement; rotating-group refinement was used for the methyl and OH groups.

For both compounds, data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structures: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

The authors thank the DST, New Delhi, for financial assistance. The authors also would like to thank the Malaysian Government and Universiti Sains Malaysia for the research grant R&D No. 190-9609-2801. KC thanks the Universiti Sains Malaysia for a Visiting Post-Doctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1407). Services for accessing these data are described at the back of the journal.

References

Beddoes, R. L., Gorman, A. A. & McNeeney, S. P. (1993). *Acta Cryst.* C**49**, 1811–1813.
Chinnakali, K., Fun, H.-K., Mal, D., Hazra, N. K., Ghorai, S. K. & Nigam, G. D. (1999). *Acta Cryst.* C**55**, 585–586.
Mal, D., Bandyopadhyay, M., Datta, K. & Murty, K. V. S. M. (1998). *Tetrahedron*, **54**, 7525–7538.
Nardelli, M. (1983). *Acta Cryst.* C**39**, 1141–1142.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Sheldrick, G. M. (1997). *SHELXTL. Structure Determination Software Programs*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Shim, S. C. (1984). In *CRC Handbook of Organic Photochemistry and Photobiology*, edited by W. M. Horspool & P. S. Song, pp. 1347–1356. New York: Plenum.
Siemens (1996). *SMART* and *SAINT*. *Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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6,11-Dihydroxy-1,4-methano-1,4,4a,12a-tetrahydronaphthacene-5,12-dione

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Abstract

The title compound, $C_{19}H_{14}O_4$, exists in the quinol form. The six-membered and five-membered rings of the norbornene moiety adopt boat and envelope conformations, respectively. The hydroxyl groups are involved in O—H···O intramolecular hydrogen bonds.

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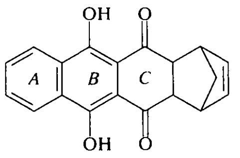
Comment

The title compound, (I), was prepared as a precursor to dimethoxy-1,4-anthraquinone (Majumdar *et al.*, 1994) en route to anthracycline antibiotics. It is also an important intermediate of the anticancer drug, mitoxantrone (Cheng & Cheng, 1978). The X-ray structural study was performed in order to establish the relative stereochemistry.



(I)

The asymmetric unit contains two molecules; the corresponding bond lengths and angles of these two molecules agree with each other and show normal values (Allen *et al.*, 1987). In both molecules, the six-membered rings in the norbornene moiety adopt the symmetrical boat conformation and the two five-membered rings are in the envelope conformation. In molecule *A*, the fused six-membered rings *A*, *B* and *C* are nearly coplanar; the dihedral angles formed by *B* with *A* and *C* are 1.29 (6) and 1.64 (4)°, respectively. In molecule *B*, the ring *C* adopts a flattened twist conformation and the mean planes through rings *A* and *C* make dihedral angles of 2.77 (9) and 6.42 (7)° with ring *B*. The C7/C9/C10/C12 plane of the norbornene moiety is nearly perpendicular to ring *C* [dihedral angle 89.19 (4)°] in molecule *A*, whereas in molecule *B* it forms an angle of 82.98 (8)° with ring *C*.

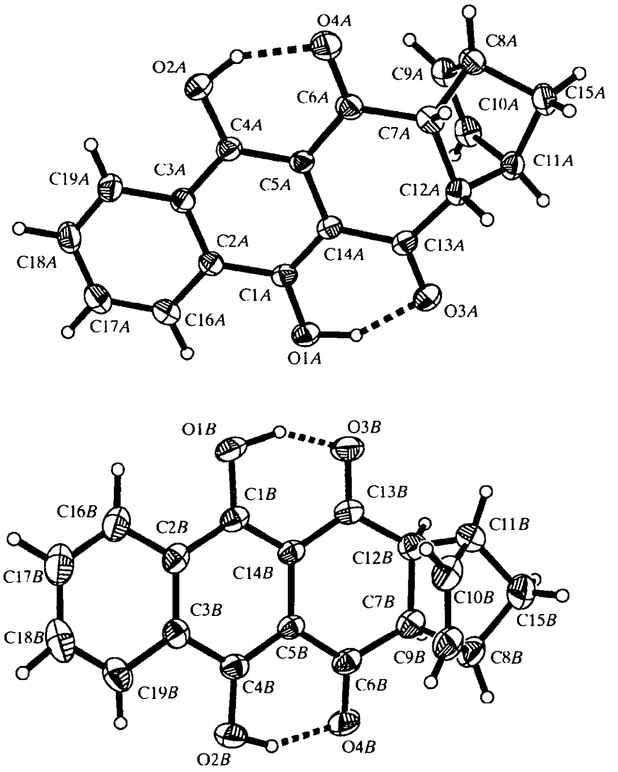


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.

The relative stereochemistry of C15, C12 and C7 in both molecules is found to be *cis* and the H atoms of C7 and C12 did not undergo epimerization under the conditions of the condensation reaction adopted for its preparation. Both molecules exist in the quinol form and the hydroxyl groups are involved in O—H···O intramolecular hydrogen bonds. In the solid state, short intermolecular C—H···O contacts exist between C9*A* and O4*B*($x-1$, $y-1$, $z-1$) [3.373 (3) Å] and also between C10*B* and O4*A*($2-x$, $-y$, $-z$) [3.340 (3) Å].

Experimental

To a stirred solution of lithium *tert*-butoxide (432 mg, 5.4 mmol) in tetrahydrofuran (THF) (20 ml) at 213 K ($CHCl_3$/liquid N_2 bath) under argon was added 3-phenylsulfonylphthalide (500 mg, 1.8 mmol). Stirring was continued for 20 min, after which a solution of 1,4,4a,8a-tetrahydronaphthalene (375 mg, 2.16 mmol) in THF (5 ml) was introduced into the reaction flask. The resulting mixture was stirred at 213 K for 30 min, allowed to come to ambient temperature and then stirred for another 16 h. The reaction mixture was quenched with 20% HCl solution and concentrated under reduced pressure. A solid appeared at this point, which was chromatographed (silica gel) to give 65% (429 mg) yield of the title compound. Single crystals were grown by slow evaporation of acetone solution of the compound.

Crystal data

$C_{19}H_{14}O_4$
$M_r = 306.30$
Triclinic
$P\bar{1}$
$a = 10.2782$ (1) Å
$b = 11.4269$ (2) Å
$c = 13.5079$ (2) Å
$\alpha = 96.11$ (1)°
$\beta = 99.224$ (1)°
$\gamma = 113.462$ (1)°
$V = 1410.85$ (4) Å^3
$Z = 4$
$D_x = 1.442$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 4919 reflections
$\theta = 2.74$–33.18°
$\mu = 0.101$ mm^{-1}
$T = 293$ (2) K
Parallelepiped
0.46 × 0.42 × 0.36 mm
Orange

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
11 615 measured reflections
8434 independent reflections

5411 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\rm max} = 31°$
$h = -14 \rightarrow 13$
$k = -16 \rightarrow 16$
$l = 0 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.150$
$S = 1.079$
8434 reflections
528 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 0.5786P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1996)
Extinction coefficient: 0.0196 (16)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1*A*—C1*A*	1.340 (2)	O1*B*—C1*B*	1.346 (2)
O2*A*—C4*A*	1.335 (2)	O2*B*—C4*B*	1.343 (2)
O3*A*—C13*A*	1.244 (2)	O3*B*—C13*B*	1.242 (2)
O4*A*—C6*A*	1.240 (2)	O4*B*—C6*B*	1.247 (2)
C9*A*—C10*A*	1.316 (3)	C9*B*—C10*B*	1.316 (3)
C8*A*—C15*A*—C11*A*	94.33 (15)	C8*B*—C15*B*—C11*B*	93.2 (2)

C12*A*—C7*A*—C8*A*—C9*A*	66.7 (2)
C12*A*—C7*A*—C8*A*—C15*A*	−37.2 (2)
C15*A*—C8*A*—C9*A*—C10*A*	32.1 (2)
C7*A*—C8*A*—C9*A*—C10*A*	−71.1 (2)
C8*A*—C9*A*—C10*A*—C11*A*	0.6 (2)
C9*A*—C10*A*—C11*A*—C15*A*	−32.9 (2)
C9*A*—C10*A*—C11*A*—C12*A*	70.4 (2)
C8*A*—C7*A*—C12*A*—C11*A*	0.7 (2)
C10*A*—C11*A*—C12*A*—C7*A*	−67.8 (2)
C15*A*—C11*A*—C12*A*—C7*A*	36.0 (2)
C9*A*—C8*A*—C15*A*—C11*A*	−48.6 (2)
C7*A*—C8*A*—C15*A*—C11*A*	59.0 (2)
C10*A*—C11*A*—C15*A*—C8*A*	49.0 (2)
C12*A*—C11*A*—C15*A*—C8*A*	−58.6 (2)
C12*B*—C7*B*—C8*B*—C9*B*	69.8 (2)
C12*B*—C7*B*—C8*B*—C15*B*	−34.7 (2)
C15*B*—C8*B*—C9*B*—C10*B*	34.1 (3)
C7*B*—C8*B*—C9*B*—C10*B*	−70.2 (2)
C8*B*—C9*B*—C10*B*—C11*B*	−0.7 (3)
C9*B*—C10*B*—C11*B*—C15*B*	−32.6 (3)
C9*B*—C10*B*—C11*B*—C12*B*	71.1 (2)
C8*B*—C7*B*—C12*B*—C11*B*	−3.2 (2)
C10*B*—C11*B*—C12*B*—C7*B*	−64.6 (2)
C15*B*—C11*B*—C12*B*—C7*B*	39.8 (2)
C9*B*—C8*B*—C15*B*—C11*B*	−49.9 (2)
C7*B*—C8*B*—C15*B*—C11*B*	58.3 (2)
C10*B*—C11*B*—C15*B*—C8*B*	49.4 (2)
C12*B*—C11*B*—C15*B*—C8*B*	−60.5 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1O*A*···O3*A*	0.99 (3)	1.63 (3)	2.526 (2)	148 (2)
O1*B*—H1O*B*···O3*B*	1.10 (4)	1.52 (4)	2.530 (2)	149 (4)
O2*A*—H2O*A*···O4*A*	0.96 (3)	1.64 (3)	2.514 (3)	148 (2)
O2*B*—H2O*B*···O4*B*	0.96 (4)	1.65 (3)	2.529 (3)	150 (3)

The data collection covered a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm ($2\theta_{\max} = 66.37°$) and the detector swing angle was −35°. Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the duplicate reflections, and was found to be negligible. Only reflections with $2\theta < 62°$ were used for the refinement.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. All H atoms were located from a difference Fourier map and refined isotropically. C—H distances range from 0.93 (2) to 1.02 (3) Å and $U_{\rm iso}$ values for H atoms range from 0.49 (6) to 0.15 (2) Å^2.

Data collection: *SMART* (Siemens, 1996*a*). Cell refinement: *SAINT* (Siemens, 1996*b*). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1996). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1163). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Cheng, R. K. Y. & Cheng, C. C. (1978). *J. Med. Chem.* **21**, 291–294.
Majumdar, G., Murty, K. V. S. N. & Mal, D. (1994). *Tetrahedron Lett.* **35**, 6139–6140.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Sheldrick, G. M. (1996). *SHELXTL Reference Manual.* Version 5.0. University of Göttingen, Germany.
Siemens (1996*a*). *SMART Software Reference Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1996*b*). *SAINT Software Reference Manual.* Version 4. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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5-Benzyloxy-1-phenyltetrazole: catalytic transfer hydrogenolysis of benzyl ethers

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Abstract

In contrast to the earlier reported inertness of 5-benzyloxy-1-phenyltetrazole, (1*a*), and 3-benzyloxy-1,2-benzisothiazole 1,1-dioxide, (2*a*), towards catalytic