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rel-(1*S*,3a*R*,4*R*,7*S*,7a*R*)-5,6,7,7a-Tetrahydro-4,7-methano-1*H*-indene-1,3a(4*H*)-diol, $C_{10}H_{14}O_2$

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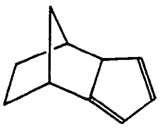
Abstract. $M_r = 166{\cdot}22$, monoclinic, $P2_1/c$, $a = 13{\cdot}657\,(3)$, $b = 6{\cdot}212\,(2)$, $c = 11{\cdot}069\,(3)$ Å, $\beta = 112{\cdot}42\,(3)°$, $V = 868{\cdot}0\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}272$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 7{\cdot}09$ cm^{-1}, $F(000) = 360$, room temperature, $R = 0{\cdot}043$ for 1056 unique reflections with intensities greater than $3\sigma(I)$. A planar cyclopentene ring is *cis* fused to a norbornane moiety. The two hydroxyl groups lie on the same side of the five-membered ring and participate in the formation of two intermolecular hydrogen bonds. π-system distortion and a short C=C distance are observed as in other strained ring systems.

Introduction. The three isomers of isodicyclopentadiene and their cycloaddition reactions have been studied (Subramanyam, Bartlett, Iglesias, Watson & Galloy, 1982; Paquette, Williams, Carr, Charumilind & Blount, 1982; Bartlett & Wu, 1983). The diene isomer (1) rapidly absorbs oxygen from the air even at low temperatures (253 K). When molecular oxygen is bubbled into a dilute solution of (1) in CH_2Cl_2 at 273 K and in the dark, a low-molecular-weight copolymer of (1) and O_2 is obtained (Wu, 1983). The polyperoxide, $(C_{10}H_{12}O_2)_n$, has a (1) to O_2 ratio of 1:1, a measured molecular weight of 1220 ($n = 7{\cdot}4$), and is stable up to 405 K where it decomposes with gas evolution.

When the polymer is reduced with $LiAlH_4$ in ether, a mixture of the diols (2) and (3) is obtained. Because an unambiguous determination of relative stereochemistry is essential for the understanding of stereoelectronic effects in these molecules, the structure was determined by X-ray diffraction techniques. The structural data are needed also for the development of suitable molecular mechanics parameters for norbornene and sesquinorbornene strained ring systems.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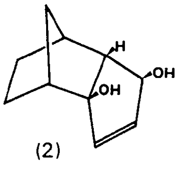

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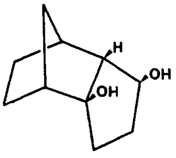

(3)

Experimental. Crystal of dimensions 0·4 × 0·33 × 0·25 mm, Syntex $P2_1$ diffractometer, $\theta{:}2\theta$ scan, variable scan rate, $2\theta_{\max} = 120°$, graphite-monochromated Cu $K\alpha$ radiation; lattice parameters from least squares of 15 medium-angle reflections, space group $P2_1/c$ (systematic absences $l = 2n+1$ for $h0l$ and $k = 2n+1$ for $0k0$); a monitored reflection showed no significant change in intensity; 1188 independent reflections ($0 \le h \le 14$, $0 \le k \le 6$, $-11 \le l \le 11$), 1056 with $I > 3\sigma(I)$; Lorentz and polarization, no absorption corrections; direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) located all heavy atoms, H atoms located in difference Fourier map but only positional parameters refined; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F_o)$, final $R = 0{\cdot}043$, $R_w = 0{\cdot}063$, $S = 0{\cdot}23$ (186 parameters), $(\Delta/\sigma)_{\rm av} = 0{\cdot}02$, $(\Delta/\sigma)_{\max} = 0{\cdot}09$, highest peak in final difference Fourier map 0·24 e Å^{-3}. Final calculations performed with *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Atomic scattering factors for C and O from Cromer & Mann (1968), those for H from Stewart, Davidson & Simpson (1965). Atomic positional parameters and $U_{\rm eq}$ values are listed in Table 1 while Table 2 gives bond lengths and valence angles.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39393 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic positional parameters* ($\times 10^4$, $\times 10^3$ *for* H) *and* U_{eq} *values* ($\text{Å}^2 \times 10^3$)

	x	y	z	$U_{\rm eq}$*
C(1)	1983 (2)	−46 (4)	10330 (2)	52 (1)
C(2)	3075 (2)	−147 (3)	10219 (2)	40 (1)
O(2)	3823 (1)	826 (3)	11384 (1)	48 (1)
C(3)	3469 (2)	−2283 (4)	9970 (2)	46 (1)
C(4)	3568 (2)	−2372 (4)	8829 (2)	48 (1)
C(5)	3251 (2)	−331 (4)	8076 (2)	45 (1)
O(5)	4141 (1)	483 (3)	7834 (1)	54 (1)
C(6)	2894 (2)	1135 (3)	8945 (2)	42 (1)
C(7)	1711 (2)	1758 (4)	8481 (2)	51 (1)
C(8)	1006 (2)	−220 (5)	8008 (3)	58 (2)
C(9)	1188 (2)	−1453 (5)	9293 (3)	62 (2)
C(10)	1625 (2)	2204 (4)	9788 (3)	56 (2)
H(1)	203 (2)	−55 (4)	1122 (3)	†
H(2)	450 (2)	27 (4)	1153 (3)	
H(3)	367 (2)	−340 (5)	1061 (3)	
H(4)	390 (2)	−357 (4)	856 (3)	
H(5*a*)	263 (2)	−60 (4)	719 (3)	
H(5*b*)	394 (2)	174 (5)	734 (3)	
H(6)‡	334 (2)	263	916 (2)	
H(7)	153 (2)	284 (5)	789 (3)	
H(8*a*)	25 (2)	32 (4)	758 (3)	
H(8*b*)	121 (2)	−115 (5)	742 (3)	
H(9*a*)	46 (2)	−161 (4)	948 (2)	
H(9*b*)	145 (2)	−299 (5)	927 (3)	
H(10*a*)	209 (2)	328 (5)	1033 (3)	
H(10*b*)	84 (2)	246 (4)	966 (3)	

* $U_{\rm eq} = (U_{11}U_{22}U_{33})^{1/3}$.

† Isotropic U values set to 0·075.

‡ y coordinate on H(6) not refined.

Table 2. *Interatomic distances* (Å) *and valence angles* (°)

C(1)–C(2)	1·543 (4)	C(4)–C(5)	1·489 (3)
C(1)–C(9)	1·520 (3)	C(5)–O(5)	1·432 (3)
C(1)–C(10)	1·526 (4)	C(5)–C(6)	1·534 (4)
C(2)–O(2)	1·438 (2)	C(6)–C(7)	1·545 (3)
C(2)–C(3)	1·496 (3)	C(7)–C(8)	1·525 (4)
C(2)–C(6)	1·554 (3)	C(7)–C(10)	1·521 (4)
C(3)–C(4)	1·322 (4)	C(8)–C(9)	1·550 (4)

C(2)C(1)C(9)	110·5 (2)	C(4)C(5)O(5)	108·6 (2)
C(2)C(1)C(10)	100·4 (2)	C(4)C(5)C(6)	104·4 (2)
C(9)C(1)C(10)	101·5 (2)	O(5)C(5)C(6)	113·8 (2)
C(1)C(2)O(2)	106·8 (2)	C(2)C(6)C(5)	106·6 (2)
C(1)C(2)C(3)	118·5 (2)	C(2)C(6)C(7)	102·4 (2)
C(1)C(2)C(6)	103·1 (2)	C(5)C(6)C(7)	118·8 (2)
O(2)C(2)C(3)	110·8 (2)	C(6)C(7)C(8)	110·8 (2)
O(2)C(2)C(6)	114·3 (2)	C(6)C(7)C(10)	100·3 (2)
C(3)C(2)C(6)	103·4 (2)	C(8)C(7)C(10)	101·8 (2)
C(2)C(3)C(4)	112·8 (2)	C(7)C(8)C(9)	103·0 (2)
C(3)C(4)C(5)	112·7 (2)	C(1)C(9)C(8)	103·1 (2)
		C(1)C(10)C(7)	94·5 (2)

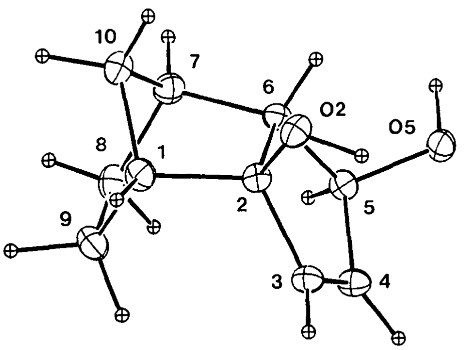

Fig. 1. *ORTEP* drawing of (2). Thermal ellipsoids are drawn at the 35% probability level.

Discussion. Fig. 1 is an *ORTEP* (Johnson, 1971) drawing of the title compound (2). The cyclopentene ring is planar [maximum deviation 0·011 (7) Å] and is *cis* fused to the norbornane system, interplanar angle 124 (1)°. The two hydroxyl groups lie on the same side of the five-membered ring. The interplanar angle between the cyclopentene ring and H(3)C(3)C(4)H(4) is 174 (1)° with the hydrogen atoms bent toward the hydroxyl-group side. Molecular mechanics calculations (Allinger & Yuh, 1980) do not reproduce accurately the π-system distortion or several specific interatomic distances; however, valence angles show remarkable agreement. The *MM*2 program relieves strain in the molecule by elongating bonds with only the C(8)–C(9) distance of 1·550 (4) being longer than the calculated value of 1·540 Å. The calculated structure shows a greater puckering around the five-membered ring with torsion angles falling between ±6° while the observed values range from −3 to +2°. To reflect the π-system distortion and the short C=C distance observed in this and other strained ring systems (Watson, Galloy, Bartlett & Roof, 1981), the C(sp^2)–C(sp^2) force constant must be increased and the 0 and 180° torsion angle minimum made shallower. Short intramolecular contacts are reasonably well reproduced: H(5*a*)···H(8*b*) = 2·08 (4), 2·25; H(8*a*)···H(10*b*) = 2·52 (4), 2·67; H(9*a*)···H(10*b*) = 2·57 (4) 2·57; H(6)···H(10*a*) = 2·54 (5), 2·56; H(9*b*)···C(3) = 2·60 (3), 2·57; and O(2)···H(10*a*) = 2·68 (3), 2·77 Å. Additional data must be obtained before general molecular mechanics parameters can be devised for these strained fused-ring systems.

The interplanar angles involving C(1)C(2)C(6)C(7) *A*, C(7)C(8)C(9)C(1) *B* and C(1)C(10)C(7) *C* are *AC* = 121·7 (6), *BC* = 123·8 (6) and *AB* = 115·1 (8)°. Two intermolecular hydrogen bonds are formed: O(2)–H(2) = 0·94 (3), H(2)···O(5$^{\rm i}$) ($1-x,-y,2-z$) = 1·78 (3), O(2)···O(5$^{\rm i}$) = 2·703 (2) Å, O(2)–H(2)···O(5$^{\rm i}$) = 166·6 (6)° and O(5)–H(5*b*) = 0·93 (3), H(5*b*)···O(2$^{\rm ii}$) ($x,0{\cdot}5-y,z-0{\cdot}5$) = 1·82 (3), O(5)···O(2$^{\rm ii}$) = 2·737 (2) Å, O(5)–H(5*b*)···O(2$^{\rm ii}$) = 168·2 (6)°.

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rel-(1*S*,2*S*,3*S*,3a*R*,4*R*,7*S*,7a*R*)-1,2,3,4,5,6,7,7a-Octahydro-1,3a-etheno-4,7-methano-3a*H*-indene-2,3-dicarboxylic Anhydride, $C_{14}H_{14}O_3$

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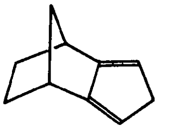
Abstract. $M_r = 230{\cdot}26$, monoclinic, $P2_1/n$, $a = 6{\cdot}387\,(2)$, $b = 10{\cdot}216\,(3)$, $c = 16{\cdot}897\,(7)$ Å, $\beta = 100{\cdot}27\,(3)^\circ$, $V = 1084{\cdot}9\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}41$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}06$ cm^{-1}, $F(000) = 488$, room temperature, $R = 0{\cdot}055$ for 1357 unique reflections with intensities greater than $3\sigma(I)$. The six-membered ring of the norbornane system is in a skew-boat conformation owing to the fusion of two five-membered rings and a methylene bridge. There are two short intramolecular contacts, H(10)-*endo*···H(5) = 2·20 (4) and H(8)-*endo*···H(2) = 2·17 (5) Å; H(8)-*endo* may also interact with the C(2) π system.

Introduction. Isodicyclopentadiene (1) is prepared by dehydration of the tricyclic alcohol (4) over alumina at 573 K (Alder, Flock & Janssen, 1956). Loss of water does not yield (1) directly, but the reaction passes through (3) and (2) by two consecutive 1,5-sigmatropic hydrogen shifts. Since isomers (2) and (3) have not been detected in this reaction system, the rearrangements must be rapid. In the reaction of (1) with inactive dienophiles at elevated temperatures (453 K) only cycloadducts of (2) are obtained (Subramanyam, Bartlett, Iglesias, Watson & Galloy, 1982; Paquette, Williams, Carr, Charumilind & Blount, 1982). Isomer (1) shows *endo* Diels–Alder stereoselectivity toward certain dienophiles, but isomer (2) has a norbornene-type double bond and shows *exo* selectivity. Isomer (3) can be prepared by the careful quenching of (5) with water in tetrahydrofuran or ether (Bartlett & Wu, 1983). Although (3) isomerizes to (1) on heating to 353 K, it can be purified from a mixture by the selective reaction of (1) with maleic anhydride at 273 K. The Diels–Alder reactivities of the three isomers are in the order (2) > (1) > (3).

The slow reaction of (3) with maleic anhydride at 273 K yielded the title compound (6) as the only adduct. The structure of (6) confirms the structure of (3) and the *exo*-face selectivity.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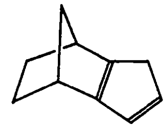
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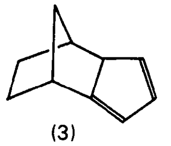
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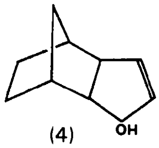

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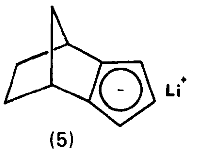

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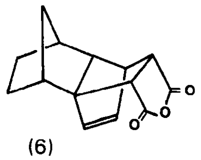

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