

Fig. 3. ORTEP drawing, with thermal ellipsoids at 20% probability level, of a fragment of (4) showing the two alternative dispositions, with 50% occupancy factors, around the peroxidic function.

(Table 5), a result in agreement with the general relationship between the signs of these angles, for both the *cis*- and *trans*-fused lactones (Cox & Sim, 1977; McPhail & Sim, 1973). The chirality of  $\omega_2$  matches the sign of the experimental value of the circular dichroism (CD:  $\theta_{260} = -1700^\circ$ ). The dihedral angle H(7)C(7)-C(11)C(13) is here  $-38(2)^\circ$  corresponding to a conformation of the pseudo-rotational *A* type, after Samek (1979), for the exomethylene lactone; this is in keeping with the very small value of  $J_{7,13}$  observed in the <sup>1</sup>H NMR spectrum of (3) (Appendino *et al.*, 1983).

The O(3)-O(4) length in the split model of (4) is longer than in (3) and several hydrogen peroxide complexes (1.46–1.47 Å; *e.g.* Fritchie & McMullan, 1981), but the O-C distances (Table 4) are normal and the torsion angles around the O-O bond (Table 5) approach the values of (3) whilst the torsion angle C(5)O(3)O(4)C(16) was  $-174.7(4)^\circ$ , refining the unsplit model.

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### 4 $\alpha\beta$ ,5,8,8 $\alpha\beta$ -Tetrahydronaphthoquin-1 $\alpha$ ,4 $\alpha$ -diol,\* C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>

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**Abstract.**  $M_r = 166.22$ , orthorhombic, *Pbca*,  $a = 20.479(4)$ ,  $b = 8.101(1)$ ,  $c = 21.375(3)$  Å,  $V = 3546(1)$  Å<sup>3</sup>,  $Z = 16$ ,  $D_m(\text{floatation}) = 1.22(1)$ ,  $D_x = 1.245$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 0.796$  cm<sup>-1</sup>,  $F(000) = 1440$ ,  $T = 295$  K,  $R = 0.048$  for

The pyrazoline ring of (4) is approximately planar [r.m.s.d. = 0.089 (2) Å] and it is almost orthogonal to the lactone ring. The torsion angle N(1)C(11)C(12)O(2) is negative,  $-86.0(3)^\circ$ , and this steric disposition gives rise to a strongly positive Cotton effect ( $\theta_{327} = +22,000^\circ$ ;  $\theta_{238} = +5640^\circ$ ) from the azochromophore. The sign of this effect complies with the empirical rule relating the junction type of an exomethylene- $\gamma$ -lactone to the CD of the azochromophore of its corresponding pyrazoline adduct (Suchý, Doleiš, Herout, Šorm, Snatzke & Himmelreich, 1969).

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1953 observed data. Extensive hydrogen bonding links molecules in a three-dimensional network. The two crystallographically independent molecules adopt a similar conformation, half-chair cyclohexene ring *cis*-fused to a half-chair cyclohexenediol moiety. The OH configurations in each molecule are both *anti* with respect to the bridgehead H atoms; one is pseudo-equatorial, the other is pseudo-axial.

\* IUPAC name: 1,4,4 $\alpha\beta$ ,5,8,8 $\alpha\beta$ -hexahydronaphthalene-1 $\alpha$ ,4 $\alpha$ -diol.

**Introduction.** The solid-state  $^{13}\text{C}$  NMR spectra of the tetrahydronaphthoquinones (McDowell, Naito, Schefler & Wong, 1981) indicated that chemically equivalent C atoms, which appear as singlets in solution, appear as doublets in the solid state. However, the complex solid-state  $^{13}\text{C}$  NMR spectrum of the tetrahydronaphthoquindiol (I) suggests the presence of more than one independent molecule in the crystal structure. The present crystallographic study was undertaken to establish the presence of structurally independent

molecules, and to determine the molecular conformations.

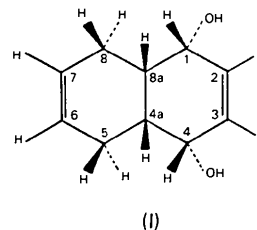


Table 1. Atomic coordinates ( $\times 10^4$ ) and thermal parameters ( $\text{\AA}^2 \times 10^3$ ) with e.s.d.'s in parentheses

	Molecule A				$U_{\text{eq}}^*$	Molecule B			
	x	y	z			x	y	z	$U_{\text{eq}}^*$
O(1)	417 (1)	3114 (2)	1957 (1)	42	9369 (1)	774 (2)	2153 (1)	42	
O(4)	2116 (1)	4855 (2)	296 (1)	49	8051 (1)	2102 (2)	232 (1)	46	
C(1)	395 (1)	3426 (3)	1294 (1)	38	8680 (1)	1077 (3)	2096 (1)	39	
C(2)	632 (1)	5154 (3)	1199 (1)	44	8622 (1)	2748 (3)	1796 (1)	44	
C(3)	1099 (1)	5555 (3)	808 (1)	47	8338 (1)	3014 (3)	1257 (1)	43	
C(4)	1460 (1)	4318 (3)	419 (1)	38	8013 (1)	1698 (2)	884 (1)	38	
C(4a)	1467 (1)	2650 (2)	738 (1)	34	8306 (1)	19 (2)	1030 (1)	33	
C(5)	1905 (1)	2567 (3)	1312 (1)	41	8985 (1)	-258 (3)	769 (1)	36	
C(6)	1816 (1)	956 (3)	1652 (1)	46	9260 (1)	-1868 (3)	990 (1)	45	
C(7)	1310 (1)	9 (3)	1575 (1)	50	9038 (1)	-2638 (3)	1490 (1)	49	
C(8)	748 (1)	395 (3)	1155 (1)	46	8505 (1)	-2011 (3)	1900 (1)	45	
C(8a)	767 (1)	2153 (2)	890 (1)	37	8294 (1)	-247 (3)	1741 (1)	38	
				$U_{\text{iso}}$				$U_{\text{iso}}$	
H(O1)	99 (14)	2397 (31)	2030 (12)	78 (10)	9439 (13)	-81 (32)	2436 (13)	85 (9)	
H(O4)	2093 (13)	5684 (33)	111 (12)	69 (9)	7752 (13)	1505 (32)	27 (12)	87 (11)	
H(1)	-65 (11)	3402 (23)	1167 (9)	42 (6)	8500 (9)	1138 (24)	2534 (10)	43 (6)	
H(2)	399 (10)	5988 (29)	1447 (10)	56 (7)	8847 (10)	3598 (26)	2012 (9)	45 (6)	
H(3)	1227 (13)	6628 (33)	738 (12)	68 (9)	8316 (10)	4073 (28)	1057 (10)	48 (7)	
H(4)	1240 (9)	4217 (23)	3 (10)	34 (6)	7556 (11)	1709 (23)	992 (8)	30 (5)	
H(4a)	1643 (9)	1886 (24)	441 (8)	26 (5)	8012 (9)	-827 (23)	858 (8)	31 (5)	
H(5)	1796 (9)	3505 (25)	1600 (9)	36 (5)	8964 (9)	-227 (22)	316 (9)	32 (5)	
H(52)	2340 (12)	2692 (27)	1193 (10)	51 (7)	9286 (10)	665 (24)	897 (9)	36 (6)	
H(6)	2160 (12)	636 (29)	1934 (10)	56 (8)	9653 (11)	-2366 (25)	730 (10)	50 (6)	
H(7)	1274 (11)	-1001 (29)	1784 (10)	59 (7)	9265 (11)	-3586 (29)	1612 (10)	54 (7)	
H(8)	766 (11)	-362 (28)	788 (11)	61 (7)	8645 (10)	-2069 (25)	2359 (10)	44 (6)	
H(82)	340 (12)	168 (28)	1376 (11)	64 (8)	8120 (10)	-2725 (24)	1881 (8)	29 (5)	
H(8a)	545 (9)	2152 (22)	488 (9)	30 (5)	7849 (11)	-56 (25)	1872 (9)	44 (6)	

\*  $U_{\text{eq}}$  is one third the trace of the diagonalized anisotropic temperature-factor matrix.

Table 2. Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

	Molecule A	Molecule B		Molecule A	Molecule B
C(1)—O(1)	1.440 (3)	1.441 (3)	C(2)—C(1)—O(1)	106.7 (2)	106.4 (2)
C(4)—O(4)	1.438 (3)	1.433 (3)	C(1)—C(2)—C(3)	123.7 (2)	124.1 (2)
C(1)—C(2)	1.495 (3)	1.503 (3)	C(2)—C(3)—C(4)	123.2 (2)	123.6 (2)
C(2)—C(3)	1.312 (4)	1.308 (3)	C(3)—C(4)—O(4)	111.1 (2)	109.5 (2)
C(3)—C(4)	1.497 (3)	1.490 (3)	C(3)—C(4)—C(4a)	110.6 (2)	110.7 (2)
C(4)—C(4a)	1.513 (3)	1.519 (3)	C(4a)—C(4)—O(4)	110.1 (2)	112.6 (2)
C(4a)—C(5)	1.521 (3)	1.516 (3)	C(4)—C(4a)—C(5)	114.1 (2)	114.7 (2)
C(5)—C(6)	1.505 (3)	1.497 (3)	C(4a)—C(5)—C(6)	110.9 (2)	111.0 (2)
C(6)—C(7)	1.301 (4)	1.318 (4)	C(5)—C(6)—C(7)	123.1 (2)	122.6 (2)
C(7)—C(8)	1.492 (4)	1.490 (4)	C(6)—C(7)—C(8)	124.5 (2)	124.7 (2)
C(8)—C(8a)	1.533 (3)	1.531 (3)	C(7)—C(8)—C(8a)	113.4 (2)	113.1 (2)
C(4a)—C(8a)	1.523 (3)	1.533 (3)	C(1)—C(8a)—C(8)	113.6 (2)	113.4 (2)
C(1)—C(8a)	1.546 (3)	1.534 (3)	C(4)—C(4a)—C(8a)	108.9 (2)	108.9 (2)
			C(5)—C(4a)—C(8a)	111.7 (2)	111.0 (2)
			C(1)—C(8a)—C(4a)	114.0 (2)	112.6 (2)
			C(4a)—C(8a)—C(8)	110.4 (2)	110.4 (2)
			C(8a)—C(1)—O(1)	114.6 (2)	114.5 (2)
			C(8a)—C(1)—C(2)	112.9 (2)	112.2 (2)

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

	O...O	O—H	H...O	O—H...O
[O(1)—H] $_A(x, y, z) \cdots$ O(1) $_B(x, y, z)$	2.909 (3)	0.88 (3)	2.03 (3)	177 (3)
[O(4)—H] $_A(x, y, z) \cdots$ O(4) $_B(-x, -y, -z)$	2.732 (3)	0.79 (3)	1.96 (3)	169 (3)
[O(1)—H] $_B(x, y, z) \cdots$ O(1) $_A(-x, \frac{1}{2} + y, \frac{1}{2} - z)$	2.890 (3)	0.90 (3)	1.99 (3)	180 (3)
[O(4)—H] $_B(\frac{1}{2} + x, \frac{1}{2} - y, -z) \cdots$ O(4) $_A(x, y, z)$	2.729 (3)	0.90 (3)	1.86 (3)	173 (3)

**Experimental.** Crystals from *n*-hexane/acetone, 0.28 × 0.20 × 0.49 mm, CAD-4 diffractometer, graphite-monochromatized Mo *K* $\alpha$ , lattice parameters from setting of 25 reflections with  $15 \leq \theta \leq 20^\circ$ ; 3544 unique reflections with  $\theta \leq 25^\circ$ ,  $\omega - (2/3)\theta$  scan,  $\omega$  scan width  $(1.1 + 0.3 \tan \theta)^\circ$ , extended 25% on each side for background measurement, horizontal aperture  $(1.0 + \tan \theta)$  mm, vertical aperture 4 mm, *h* 0–24, *k* 0–9, *l* 0–25, *L*<sub>p</sub> corrections, three standard reflections stable; structure solved by direct methods using *SHELX* (Sheldrick, 1976), refined by full-matrix least squares minimizing  $\sum w(|F_o| - |F_c|)^2$ , 329 parameters consisting of 156 positional parameters, 144 anisotropic temperature factors, 28 isotropic temperature factors and a scale factor; H atoms from a difference synthesis;  $R = 0.048$ ,  $R_w = 0.040$  for 1953 reflections for which  $F \geq 3\sigma(F)$ , where  $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$ ,  $S$  = scan count,  $B$  = time-averaged background count;  $R = 0.079$ ,  $R_w = 0.048$  for all data;  $w = 1/\sigma^2(F)$ ,  $\Delta\rho$  excursions  $\pm 0.18 \text{ e } \text{\AA}^{-3}$  in final difference synthesis, atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). Final atomic coordinates are in Table 1.\*

**Discussion.** The structure consists of two crystallographically independent molecules, *A* (Fig. 1) and *B*, per asymmetric unit, related to each other by a pseudo  $4_1$  axis parallel to **b**. Molecules *A* and *B* are hydrogen bonded to each other through  $[\text{O}(1) - \text{H}]_A \cdots \text{O}(1)_B$  and  $[\text{O}(1) - \text{H}]_B \cdots \text{O}(1)_A$  of 2.9 Å forming a hydrogen-bonded column of type 1, and  $[\text{O}(4) - \text{H}]_A \cdots \text{O}(4)_B$  and  $[\text{O}(4) - \text{H}]_B \cdots \text{O}(4)_A$  of 2.7 Å forming a hydrogen-bonded column of type 2 (Fig. 2). More geometrical details about the hydrogen-bonding arrangement are in Table 2.

The conformation adopted by each molecule consists of a half-chair cyclohexene ring *cis*-fused to a half-chair cyclohexenediol moiety. The OH configurations in each molecule are both *anti* with respect to the bridgehead H atoms. One OH is pseudo-equatorial, the other is pseudo-axial. This confirms the expected major isomer formed by the reduction of the 1,4-dione by NaBH<sub>4</sub>, the method by which the present compound was prepared.

Although the gross molecular conformations are the same for both molecules in the asymmetric unit, detailed differences are noticeable. Bond lengths and angles are given in Table 2. Deviations of up to 2.5 (3)° are observed in corresponding (heavy-atom) angles involving O atoms in molecules *A* and *B*, and may be attributed to the effects of hydrogen bonding. Bond

lengths and other bond angles do not differ significantly between the two molecules. Examination of the torsion angles indicates again that molecules *A* and *B* are of very similar conformation [the maximum difference being 8 (1)° between torsion angles involving O(1)].

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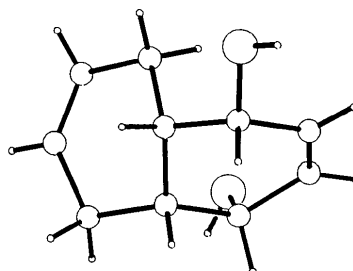


Fig. 1. Diagram of a type *A* molecule of (I).

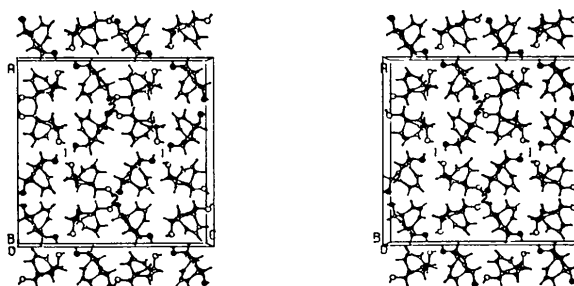


Fig. 2. Stereoscopic view of the packing arrangement of (I). The two different motifs of the hydrogen bonding are specified by 1 and 2. Molecule *A* oxygen atoms are filled circles, molecule *B* oxygens are open circles.

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\* Lists of structure factors, anisotropic thermal parameters and bond distances and angles involving hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38834 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.