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Structure of 6,7-Dimethyl-4a*β*,5,8,8a*β*-tetrahydronaphthoquin-1α,4α-diol,* $C_{12}H_{18}O_2$

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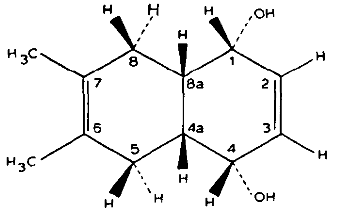
Abstract. $M_r = 194{\cdot}28$, monoclinic, $P2_1/c$, $a = 13{\cdot}870\,(2)$, $b = 18{\cdot}025\,(4)$, $c = 9{\cdot}236\,(1)$ Å, $\beta = 108{\cdot}098\,(6)°$, $V = 2194{\cdot}9\,(6)$ Å^3, $Z = 8$, $D_x = 1{\cdot}176$, D_o (flotation) = $1{\cdot}179$ g cm^{-3}, $T = 295$ K, $F(000) = 848$, μ(Mo $K\alpha$) = $0{\cdot}436$ cm^{-1}, $\lambda = 0{\cdot}71073$ Å, $R = 0{\cdot}032$ for 1461 observed data. Extensive hydrogen bonding links molecules in a three-dimensional network, with disorder of one of the hydroxyl H atoms. A structural comparison of the present compound with conformationally similar tetrahydronaphthoquinols is presented.

Introduction. Obtaining single crystals for X-ray diffraction work has in many cases been the determining factor in whether or not the solid-state structure is solved. This limitation has led to a project of investigating solid-state structures by ^{13}C NMR spectroscopy. McDowell, Naito, Scheffer & Wong (1981) have illustrated some advantages of this technique over X-ray structure analysis in their work on conformational analysis of tetrahydronaphthoquinones.

McDowell *et al.* have shown that for the tetrahydronaphthoquinones, where chemically equivalent C atoms appear as singlets in solution, doublets appear in the solid state. This is attributed to the slight environmental differences experienced by the C atoms in the solid state. It was proposed that this discriminating feature of the solid state could be exploited in identifying structurally independent molecules whose ^{13}C NMR spectra should be readily discernible.

Although the characterization of the two structurally independent molecules of unsubstituted 4a*β*,5,8,8a*β*-tetrahydro-1,4-naphthoquinone in the solid state was successful, such was not the case for the present compound (I). The multitude of peaks in the ^{13}C NMR spectrum suggested more than one independent molecule in the structure but the evidence did not unambiguously indicate the exact number.



(I)

This crystallographic analysis was undertaken in an effort (i) to establish the number of structurally independent molecules, (ii) to establish their individual conformations and if they differed from each other and (iii) to verify the isomer (with respect to the OH positions) present. Of additional interest crystallographically was how the present, fully reduced structure compared with derivatives of 4a*β*,5,8,8a*β*-tetrahydro-1-naphthoquin-4α-ol.

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* IUPAC name: 6,7-dimethyl-1,4,4a*β*,5,8,8a*β*-hexahydronaphthalene-1α,4α-diol.

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Experimental. Crystals from hexanone/*n*-hexane, 0·52 × 0·15 × 0·10 mm, CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, $\theta \leq 22{\cdot}5°$, ω–2θ scan, ω scan width $(0{\cdot}65 + 0{\cdot}35\tan\theta)°$ extended 25% on each side for background measurement, horizontal aperture $(2{\cdot}00 + \tan\theta)$ mm, vertical aperture 4 mm, Lp corrections, 2845 reflections, 1461 (51·4%) with $I \geq 3\sigma(I)$, where $\sigma^2(I) = S + 2B + [0{\cdot}04(S - B)]^2$, S = scan count, B = time-averaged background count.

The structure was solved by *MULTAN* and refined by full-matrix least squares, H atoms from a difference synthesis, H(O1) and H(O1′) each disordered over two positions with 0·50 occupancy. Final $R = 0{\cdot}032$, $R_w = 0{\cdot}035$ for 1461 data, $R = 0{\cdot}104$ for all data, $w = 1/\sigma^2(F)$, GOF = 1·62, $\pm 0{\cdot}12$ e Å^{-3} in final difference synthesis, atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). The computer programs used include locally written programs for data processing and locally modified versions of the following: *MULTAN* 80 (Main, Woolfson, Lessinger, Germain & Declercq, 1980); *ORFLS* (Busing, Martin & Levy, 1962); *ORFFE* (Busing, Martin & Levy, 1964); *FORDAP* (A. Zalkin); and *ORTEP* II (Johnson, 1976).

Discussion. Positional and isotropic thermal parameters are given in Table 1.*

Table 1. *Final positional (fractional* × 10^4, H × 10^3) *and isotropic thermal parameters* (U × 10^3 Å^2), *with estimated standard deviations in parentheses*

Unprimed atoms correspond to molecule *A*; primed atoms correspond to molecule *B*.

U_{eq} is equal to one third the trace of the diagonalized anisotropic temperature-factor matrix.

	x	y	z	U_{eq}/U_{iso}
C(1)	2331 (3)	1126 (2)	3501 (3)	49
C(2)	1501 (3)	952 (2)	2067 (4)	55
C(3)	647 (3)	1320 (2)	1581 (4)	49
C(4)	407 (2)	1964 (2)	2409 (3)	41
C(4a)	972 (2)	1922 (2)	4103 (3)	35
C(5)	585 (3)	1330 (2)	4946 (3)	43
C(6)	1287 (3)	1165 (2)	6529 (3)	46
C(61)	789 (5)	715 (3)	7482 (5)	74
C(7)	2242 (3)	1393 (2)	7001 (3)	48
C(71)	2973 (4)	1236 (3)	8559 (5)	78
C(8)	2706 (3)	1837 (2)	6001 (4)	53
C(8a)	2099 (2)	1816 (2)	4315 (3)	41
O(1)	2539 (3)	489 (1)	4464 (3)	70
O(4)	−676 (2)	1997 (1)	2042 (2)	51
C(1′)	−4175 (2)	801 (2)	−2861 (3)	42
C(2′)	−3370 (3)	668 (2)	−1378 (4)	51
C(3′)	−2615 (3)	1128 (2)	−783 (4)	49
C(4′)	−2493 (2)	1851 (2)	−1491 (3)	39
C(4a′)	−3013 (2)	1848 (2)	−3194 (3)	35
C(5′)	−2470 (2)	1398 (2)	−4087 (3)	38
C(6′)	−3095 (2)	1254 (2)	−5716 (3)	42
C(61′)	−2490 (4)	954 (3)	−6685 (5)	63
C(7′)	−4084 (3)	1376 (2)	−6224 (3)	45
C(71′)	−4730 (4)	1264 (3)	−7862 (5)	78
C(8′)	−4673 (3)	1637 (2)	−5200 (4)	51
C(8a′)	−4107 (2)	1574 (2)	−3508 (3)	40
O(1′)	−4148 (3)	199 (1)	−3851 (3)	49
O(4′)	−1440 (2)	2046 (1)	−1162 (3)	51
H(1)	299 (2)	122 (1)	326 (3)	49 (8)
H(2)	160 (2)	53 (2)	154 (4)	67 (10)
H(3)	12 (2)	121 (2)	68 (3)	56 (9)
H(4)	62 (2)	242 (1)	209 (3)	35 (8)
H(4a)	91 (2)	239 (1)	454 (3)	32 (7)
H1(5)	−9 (2)	145 (2)	503 (3)	63 (10)
H2(5)	44 (2)	85 (1)	438 (3)	36 (7)
H1(61)	27 (4)	98 (3)	770 (6)	167 (24)
H2(61)	133 (4)	61 (2)	834 (6)	135 (21)
H3(61)	52 (4)	26 (3)	702 (6)	151 (23)
H1(71)	337 (3)	84 (2)	850 (4)	95 (15)
H2(71)	271 (3)	115 (2)	937 (4)	87 (14)
H3(71)	343 (3)	169 (3)	889 (5)	127 (19)
H1(8)	278 (2)	235 (2)	634 (3)	72 (11)
H2(8)	337 (2)	165 (2)	611 (3)	73 (11)
H(8a)	230 (2)	220 (1)	381 (3)	38 (8)
H(O1)	306 (6)	17 (4)	443 (6)	70 (18)
H(O1)*	247 (9)	49 (6)	501 (13)	163 (61)
H(O4)	−85 (2)	235 (2)	260 (4)	76 (12)
H(1′)	−484 (2)	74 (1)	−275 (3)	38 (8)
H(2′)	−342 (2)	19 (2)	−90 (3)	69 (11)
H(3′)	−208 (3)	99 (2)	12 (4)	73 (11)
H(4′)	−283 (2)	226 (1)	−110 (3)	44 (8)
H(4a′)	−306 (2)	238 (1)	−356 (3)	32 (7)
H1(5′)	−189 (2)	165 (2)	−412 (3)	49 (9)
H2(5′)	−222 (2)	90 (1)	−360 (3)	26 (7)
H1(61′)	−286 (3)	68 (2)	−750 (4)	96 (14)
H2(61′)	−200 (3)	60 (2)	−609 (5)	112 (18)
H3(61′)	−212 (3)	130 (2)	−695 (5)	118 (17)
H1(71′)	−437 (3)	119 (2)	−855 (5)	117 (18)
H2(71′)	−514 (4)	162 (3)	−823 (6)	145 (27)
H3(71′)	−520 (4)	85 (3)	−794 (5)	146 (19)
H1(8′)	−493 (2)	217 (2)	−546 (3)	59 (9)
H2(8′)	−532 (3)	133 (2)	−547 (3)	73 (10)
H(8a′)	−443 (2)	193 (2)	−292 (3)	56 (8)
H(O1′)	−374 (8)	13 (6)	−400 (12)	50 (53)
H(O1′)*	−464 (8)	7 (7)	−464 (14)	140 (53)
H(O4′)	−115 (3)	203 (2)	−10 (5)	107 (15)

* H atoms bonded to O(1) and O(1′) are in positions of 50% occupancy; asterisks denote additional H positions arising from the disorder.

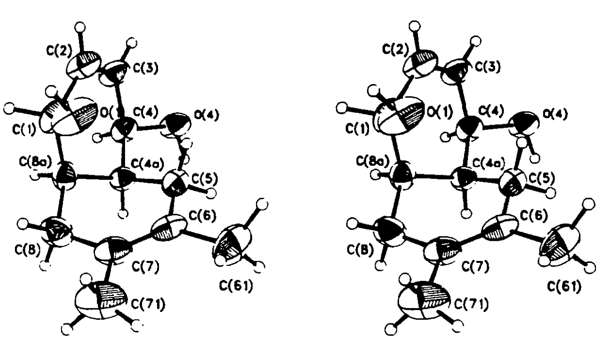

Fig. 1. Stereodiagram of a type *A* molecule of 6,7-dimethyl-4aβ,5,8,8aβ-tetrahydronaphthoquin-1α,4α-diol. Thermal ellipsoids are at 50% probability.

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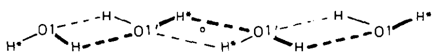
* Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving hydrogen atoms, torsion angles and a packing diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38151 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The structure consists of two crystallographically independent molecules, *A* (Fig. 1) and *B*, per asymmetric unit, hydrogen bonded to each other through O(4′)—H···O(4) interactions. The molecules are related by a pseudo twofold rotation axis approximately parallel to **b** and passing through the mid-point of O(4) and O(4′). Additional hydrogen bonds, linking neighboring asymmetric units, result in a three-dimensional bonding network thus increasing the packing energy and rigidity of the structure. Each asymmetric unit experiences six hydrogen bonds.

The half-occupied positions of the H atoms bonded to O(1) and O(1′) are of course not well defined, but do correspond to a reasonable hydrogen-bonding arrangement with discrete units of four molecules about a (statistical) center of symmetry:



These units are linked by infinite chains of O(4)···O(4′) hydrogen bonds (Table 2).

The conformation adopted by each molecule consists of a half-chair cyclohexene ring *cis*-fused to a half-chair cyclohexenediol moiety. 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 4·2° are observed in corresponding (heavy-atom) angles involving O atoms in *A* and *B*, and may be attributed to the effects of hydrogen bonding. Bond lengths and other bond angles do not differ significantly between molecules. Examination of the torsion angles indicates further minor conformational differences.

The OH configurations in each molecule are both *anti* with respect to the bridgehead H atoms. This confirms the expected major isomer formed by the reduction of the 1,4-dione by NaBH$_4$, the method by which the present compound was prepared.

Despite the favorable geometry for a H-abstraction reaction involving the upper H on C(5) (Fig. 1) and the C(3) atom, such a reaction does not proceed photochemically (at ≥350 nm) due to the lack of a suitable chromophore. Bonds joining atoms C(1), C(2), C(3), C(4), C(4a) and C(5), and similarly C(1′), C(2′), C(3′), C(4′), C(4a′) and C(5′), are all shorter than accepted values (Sutton, 1965). This may be due to slight hybridization deviations from the formal sp^3 and sp^2 states. The larger than normal endocyclic bond angles at these centers are consistent with this rationale.

Table 2. *Bond distances* (Å), *bond angles* (°) *and hydrogen-bonding geometry*

	Molecule *A*	Molecule *B*
C(1)–C(2)	1·493 (4)	1·493 (4)
C(1)–C(8a)	1·539 (4)	1·529 (4)
C(1)–O(1)	1·426 (4)	1·428 (4)
C(2)–C(3)	1·309 (4)	1·316 (4)
C(3)–C(4)	1·485 (4)	1·491 (4)
C(4)–C(4a)	1·519 (4)	1·513 (4)
C(4)–O(4)	1·435 (3)	1·439 (3)
C(4a)–C(5)	1·514 (4)	1·515 (4)
C(4a)–C(8a)	1·525 (4)	1·536 (4)
C(5)–C(6)	1·513 (4)	1·507 (4)
C(6)–C(61)	1·513 (5)	1·504 (4)
C(6)–C(7)	1·324 (4)	1·323 (4)
C(7)–C(71)	1·508 (5)	1·513 (5)
C(7)–C(8)	1·508 (4)	1·504 (4)
C(8)–C(8a)	1·523 (4)	1·520 (4)
C(2)–C(1)–C(8a)	112·4 (3)	112·7 (3)
C(2)–C(1)–O(1)	109·6 (3)	107·7 (3)
C(8a)–C(1)–O(1)	112·3 (3)	115·1 (2)
C(1)–C(2)–C(3)	124·3 (4)	123·6 (3)
C(2)–C(3)–C(4)	122·9 (3)	123·5 (3)
C(3)–C(4)–C(4a)	111·4 (3)	111·8 (3)
C(3)–C(4)–O(4)	107·3 (3)	111·5 (3)
C(4a)–C(4)–O(4)	114·4 (2)	110·2 (2)
C(4)–C(4a)–C(5)	114·4 (3)	114·2 (3)
C(4)–C(4a)–C(8a)	108·6 (2)	108·8 (2)
C(5)–C(4a)–C(8a)	111·0 (2)	110·7 (2)
C(4a)–C(5)–C(6)	114·2 (3)	114·0 (3)
C(5)–C(6)–C(61)	113·2 (4)	113·7 (3)
C(5)–C(6)–C(7)	122·4 (3)	122·5 (3)
C(61)–C(6)–C(7)	124·5 (4)	123·8 (3)
C(6)–C(7)–C(71)	124·3 (4)	124·0 (4)
C(6)–C(7)–C(8)	122·4 (3)	122·3 (3)
C(71)–C(7)–C(8)	113·3 (4)	113·6 (4)
C(7)–C(8)–C(8a)	114·0 (3)	114·5 (3)
C(1)–C(8a)–C(4a)	113·6 (3)	113·4 (2)
C(1)–C(8a)–C(8)	112·7 (3)	113·3 (3)
C(4a)–C(8a)–C(8)	110·3 (3)	109·5 (3)

Hydrogen-bonding geometry (distances in Å, angles in deg)

	O–H	H···O	O–H···O
O(4′)(*x,y,z*)–H···O(4)(*x,y,z*)	0·94 (4)	1·88 (4)	176 (3)
O(4)(*x,y,z*)–H···O(4′)($x,\frac{1}{2}-y,\frac{1}{2}+z$)	0·90 (3)	1·93 (3)	169 (3)
O(1)(*x,y,z*)–H···O(1′)(−*x*,−*y*,−*z*)	0·93 (9)	1·87 (9)	158 (5)
O(1′)(*x,y,z*)–H···O(1)(−*x*,−*y*,−*z*)	0·63 (11)	2·16 (12)	159 (12)
O(1′)(*x,y,z*)–H*···O(1′)(−*x*−1,−*y*,−*z*−1)	0·86 (10)	1·89 (10)	170 (12)

*Comparison with tetrahydronaphthoquin-*4α*-ols*. The present molecular conformations are similar to the least-energy conformations predicted by Bucourt & Hainaut (1965) and found in previously studied naphthoquinols (Greenhough & Trotter, 1981; Secco & Trotter, 1982). Many of the structural trends noted in these past studies are also observed in the current diol compound. Like the other naphthoquinols, the *cis*-fused rings in the diol molecules form three approximate planes – two planes defined by each of the double bonds [C(1), C(2), C(3), C(4); and C(5), C(6), C(7), C(8)] are almost perpendicular to each other (with a dihedral angle of 96°) and each of these planes subtends an angle of approximately 141° with respect to the third plane containing atoms C(4)–C(4a)–C(8a)–C(8) [and similarly C(4′)–C(4a′)–C(8a′)–C(8′) in the other molecule].

Since the molecules in the asymmetric unit are very similar, structural features and values for *B* molecules will be recorded in square brackets following the corresponding quantities for the *A* molecules.

Ring twist, which is strictly defined as the H(4a)—C(4a)—C(8a)—H(8a) torsion angle {−60 (3)° [−58 (2)°]}, is also described to a good approximation by the more accurately determined C(1)—C(8a)—C(4a)—C(5) torsion angle of 69·4 (3)° [68·5 (3)°]. The latter torsion angles are slightly larger in the present structures than in any other 4α-naphthoquinol studied in the series, probably as a result of crowding of the pseudo-axial O(1) substituent.

The C(6)=C(7) bond length of 1·324 (4) Å [1·323 (4) Å] is not significantly longer than that in similarly substituted tetrahydro-1-naphthoquin-4α-ol derivatives (Greenhough & Trotter, 1981; Secco & Trotter, 1982); the increased endocyclic angles around C(6) and C(7) in the present structure follow the previously noted trend of internal-angle enlargement accompanying increased substitution at these centers. The C(5)—C(6) and C(7)—C(8) bonds are longer in the diol than in the unsubstituted tetrahydronaphthoquinol, as expected on the basis of previous trends observed in the naphthoquinols with methyl substituents at C(6) and C(7).

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Structures of Free Radical Salts and Complexes.
XV.* 1,2,4-Trimethylpyridinium 7,7,8,8-Tetracyano-*p*-quinodimethanide (1:2), $C_8H_{12}N^+.2C_{12}H_4N_4^{\frac{1}{2}-}$

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Abstract. MDMP$^+$ $(TCNQ)_2^-$, $M_r = 530·55$, monoclinic, $P2_1/c$, $a = 13·796$ (1), $b = 12·889$ (1), $c = 7·846$ (2) Å, $\beta = 92·18$ (1)°, $U = 1394·1$ (5) Å^3, $Z = 2$, $D_m = 1·26$ (1), $D_c = 1·264$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1·5418$ Å, $\mu = 0·656$ mm^{-1}, $F(000) = 550$. $R = 0·0613$ for 1110 significant reflections [$I > 3\sigma(I)$]. The TCNQ's are stacked plane-to-plane, in groups of two, with no direct overlap between adjacent pairs. Within the pairs, there is a favourable exocyclic-double-bond–quinonoid-ring overlap of adjacent molecules, with short mean perpendicular distances of 3·20 (2) Å. The cation appears to occupy at random two slightly separated centrosymmetrically related positions.

Introduction. The title substance shows an interesting anomaly in the temperature dependence of the microwave conductivity, which is not shown in the d.c. conductivity measurements (Swietlik, Przybylski & Graja, 1981). As a possible aid to the explanation of this phenomenon, the room-temperature crystal structure has been determined.

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* Part XIV: Ashwell & Wallwork (1979).

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