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The Structure of 5α,8α-Dimethyl-4aβ,5,8,8aβ-tetrahydro-1-naphthoquin-4α-ol*

BY TREVOR J. GREENHOUGH AND JAMES TROTTER

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1W5

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Abstract

$C_{12}H_{16}O_2$, monoclinic, $P2_1/n$, $a = 17\cdot2650\,(15)$, $b = 7\cdot1007\,(7)$, $c = 17\cdot9363\,(22)$ Å, $\beta = 103\cdot775\,(8)^\circ$, $Z = 8$ (two molecules per asymmetric unit), $D_x = 1\cdot20$ Mg m^{-3}; $R = 0\cdot034$ for 2024 observed reflections. The conformation of the molecule is twisted with the bridgehead H atoms staggered with a torsion angle of 62 (2)°, and the hydroxyl group pseudo-equatorial to the cyclohexenone moiety. Molecules in the crystal are linked by hydrogen bonds between symmetry-related molecules with $O(1)\cdots O(4) = 2\cdot809\,(2)$ and $2\cdot815\,(3)$ Å.

Experimental

Recrystallization from petroleum ether afforded large colourless rods from which a fragment of dimensions *ca* 0·4 × 0·3 × 0·4 mm was cut. A series of precession photographs provided an initial unit cell, the Laue symmetry $2/m$ and the space group $P2_1/n$. Accurate unit-cell parameters were determined by a least-squares analysis of the setting angles of 25 reflections automatically located and centred on an Enraf–Nonius CAD-4 diffractometer ($13^\circ < \theta < 18^\circ$, graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0\cdot71073$ Å). The intensities were collected with an ω–2θ scan, $\Delta\omega = (0\cdot7 + 0\cdot35 \tan\theta)^\circ$, an aperture 4 mm high and $(1\cdot75 + 1\cdot0 \tan\theta)$ mm wide, a prescan acceptance limit of 30σ at 10·06° min^{-1} and a maximum recording time of 45 s; two backgrounds were counted for a total of half the scan time. Of 3762 recorded intensities out to $\theta = 25^\circ$, 2025 (54%) had $I/\sigma(I) \geq 3$ with $\sigma^2(I) = S + B + (0\cdot04S)^2$ (S being the scan and B the background count; the factor 0·04 was estimated from previous experience). During the data collection three standard reflections were checked periodically and their intensities remained constant to ±1%. Lorentz and polarization corrections were applied.

All non-hydrogen atoms were located by direct methods using *MULTAN* (Main, Hull, Lessinger,

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* IUPAC name: 4α-hydroxy-5α,8α-dimethyl-4aβ,5,8,8aβ-tetrahydro-1(4*H*)-naphthalenone.

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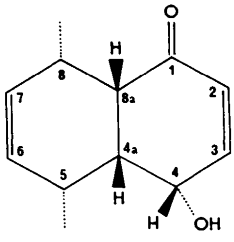
Table 1. *Final positional parameters (fractional* $\times 10^5$, *for* H $\times 10^4$) *with estimated standard deviations in parentheses*

	x	*y*	*z*
Molecule *A*			
C(1)	95395 (12)	10016 (29)	30258 (13)
C(2)	98076 (13)	14973 (32)	38346 (13)
C(3)	99188 (14)	32624 (33)	40679 (15)
C(4)	98122 (15)	49034 (30)	35274 (13)
C(4a)	93248 (12)	44163 (28)	27303 (12)
C(5)	84105 (13)	44456 (32)	26194 (12)
C(6)	80146 (17)	35047 (37)	18785 (14)
C(7)	83746 (18)	25066 (38)	14506 (15)
C(8)	92541 (18)	22085 (36)	16187 (14)
C(8a)	96237 (14)	25377 (30)	24694 (13)
C(51)	80719 (17)	36500 (43)	32665 (16)
C(81)	94972 (35)	3737 (54)	12903 (23)
O(1)	92793 (10)	−5664 (21)	28265 (9)
O(4)	95138 (12)	64345 (24)	38778 (10)
H(2)	9872 (12)	491 (32)	4205 (12)
H(3)	10051 (13)	3592 (32)	4596 (14)
H(4)	10355 (14)	5186 (34)	3480 (13)
H(O4)	9411 (17)	7366 (44)	3574 (16)
H(4a)	9453 (10)	5344 (28)	2381 (11)
H(51)	8266 (11)	5784 (31)	2574 (11)
H(511)	8172 (13)	2301 (36)	3333 (12)
H(512)	8322 (13)	4277 (33)	3773 (14)
H(513)	7515 (16)	3863 (34)	3150 (13)
H(6)	7450 (16)	3642 (35)	1739 (14)
H(7)	8064 (15)	1920 (37)	994 (16)
H(81)	9491 (12)	3204 (32)	1357 (13)
H(811)	9267 (16)	−643 (44)	1500 (16)
H(812)	9301 (17)	360 (43)	738 (19)
H(813)	10102 (24)	353 (59)	1438 (22)
H(8a)	10187 (13)	2665 (30)	2538 (12)
Molecule *B*			
C(1′)	73838 (12)	−10025 (30)	54971 (12)
C(2′)	80643 (14)	−5059 (36)	51833 (13)
C(3′)	82497 (15)	12611 (35)	50800 (14)
C(4′)	77653 (14)	28967 (30)	52230 (15)
C(4a′)	72337 (13)	24023 (29)	57579 (12)
C(5′)	76433 (15)	23765 (35)	66137 (13)
C(6′)	70924 (20)	15741 (39)	70575 (16)
C(7′)	64414 (19)	6239 (41)	67538 (16)
C(8′)	61291 (14)	2470 (36)	59110 (14)
C(8a′)	67906 (12)	5532 (29)	54861 (12)
C(51′)	84619 (18)	14154 (46)	68629 (19)
C(81′)	56766 (21)	−16050 (51)	57476 (25)
O(1′)	73101 (10)	−25950 (22)	57322 (10)
O(4′)	82899 (11)	44173 (26)	54825 (12)
H(2′)	8381 (14)	−1531 (34)	5091 (14)
H(3′)	8719 (14)	1581 (33)	4895 (13)
H(4′)	7405 (12)	3269 (29)	4702 (12)
H(O4′)	8008 (20)	5328 (51)	5597 (20)
H(4a′)	6805 (11)	3321 (28)	5681 (10)
H(51′)	7739 (14)	3734 (35)	6748 (13)
H(511′)	8417 (13)	74 (37)	6780 (12)
H(512′)	8629 (16)	1567 (38)	7416 (19)
H(513′)	8867 (19)	1969 (48)	6563 (19)
H(6′)	7230 (16)	1782 (38)	7591 (17)
H(7′)	6116 (13)	102 (33)	7067 (13)
H(81′)	5738 (12)	1250 (31)	5702 (12)
H(811′)	5203 (20)	−1542 (44)	5928 (17)
H(812′)	6025 (16)	−2741 (42)	5960 (15)
H(813′)	5505 (19)	−1903 (46)	5183 (21)
H(8a′)	6531 (12)	704 (28)	4960 (12)

Germain, Declercq & Woolfson, 1978) using 500 $|E|$ values $>1{\cdot}4$ derived from a K-curve method (Ladd, 1978). An automatic solution was obtained with four general reflections in the starting set. The $|E|$ statistics were consistent with the centrosymmetric space group. Following anisotropic refinement of C and O, the H atoms were located from a difference map and were assigned isotropic thermal parameters. Scattering factors for H were taken from Stewart, Davidson & Simpson (1965) and all others from Cromer & Mann (1968). The final refinements included all atomic parameters, the 509 reflection being deleted with $|F_o| = 5{\cdot}1$ and $|F_c| = 0{\cdot}2$ at the penultimate stage, and gave $R = 0{\cdot}034$ ($R = \sum|\Delta F|/\sum|F_o|$) for the 2024 observed reflections. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$, giving $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0{\cdot}041$ and σ_1 (GOF) $= [\sum w(F_o - F_c)^2]/(m - n) = 1{\cdot}31$. The mean and maximum shift/error on the final cycle of least-squares were 0·07 and 0·55, respectively. Weighting analyses (examination of $\sum w\Delta F^2$ *vs* F_o, $\sin\theta$, Miller indices) confirmed the suitability of the chosen weights. A difference Fourier synthesis after the final cycle showed random fluctuations of up to $\pm 0{\cdot}2$ e Å^{-3}. Locally adapted versions of *ORFLS*, *FORDAP*, and *ORTEP* programs were used. Final atomic coordinates are presented in Table 1.*

Discussion

The photochemical study of various substituted 4aβ,5,8,8aβ-tetrahydro-1-naphthoquin-4-ol systems has revealed reactivity differences with either no solid-state reaction or the formation of different products in solution and the solid state (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980). The present paper continues these investigations, and describes the structure of 5α,8α-dimethyl-4aβ,5,8,8aβ-tetrahydro-1-naphthoquin-4α-ol (I).



(I)

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* Lists of structure factors, thermal parameters, bond distances involving H atoms, torsion angles, and a packing diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35255 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The molecular structure of one of the independent molecules is shown in Fig. 1. The two molecules have almost identical bond lengths and angles (Table 2); C(4a)–C(5) and C(4a′)–C(5′) differ by 3·3σ, and all other differences between corresponding dimensions are $<3\sigma$. The torsion angles show only minor conformational differences. Molecules of (I) adopt the ring-flipped conformation with the hydroxyl group pseudo-equatorial to the cyclohexenone moiety, and the two fused rings twisted with respect to each other about the C(4a)–C(8a) bond. Both these structural features are common to all the tetrahydronaphthoquinols so far studied in this series (Greenhough & Trotter, 1980*a*,*b*), the twist conformation also being similar to that found in various substituted tetrahydro-1,4-naphthoquinones (Phillips & Trotter, 1977). The consequences of this conformation are that there is a close approach of the methyl group Me(51) to the enone carbon atoms C(2) and C(3), a close approach of Me(81) to the carbonyl oxygen O(1), and well separated, non-parallel C=C bonds within the molecule. The degree of twist is described by the bridgehead torsion angles H(4a)–C(4a)–C(8a)–H(8a) and C(5)–C(4a)–C(8a)–C(1) which are 62 (2) and −70·8 (2)° in molecule *A*, and 61 (2) and −70·0 (2)° in molecule *B*. The former angle is similar to that in the 2,3,4aβ,6,7,8aβ-hexamethyl 4α-ol derivative and the 4β-ol analogues with 2,3,4aβ,6,7,8aβ-hexamethyl and 2,3,4aβ,8aβ-tetramethyl substituents (Greenhough & Trotter, 1980*a*,*b*) where this angle is constant at *ca* 60°. The internal twist angle C(5)–C(4a)–C(8a)–C(1) [described by C(4)–C(4a)–C(8a)–C(8) in the 4β-ols which have the other ring-flipped conformation to that in the 4α-ols] is *ca* 10° greater here than in the other three compounds, all of which have methyl bridgehead substituents and this angle constant at *ca* 60° (Greenhough & Trotter, 1980*a*,*b*). This bridgehead-substituent effect is the same as found for various substituted 4a,5,8,8a-tetrahydro-1,4-naphthoquinones (Phillips & Trotter, 1977). While the hexamethyl 4α-ol substrate is photochemically reactive in the solid state with abstraction of a hydrogen at C(5) by the β carbon C(3), substrate (I) is unreactive, with the abstractable H replaced by the methyl group Me(51) (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980). The geometrical parameters in (I) for abstraction of a methyl hydrogen by the β carbon C(3) seem favour-

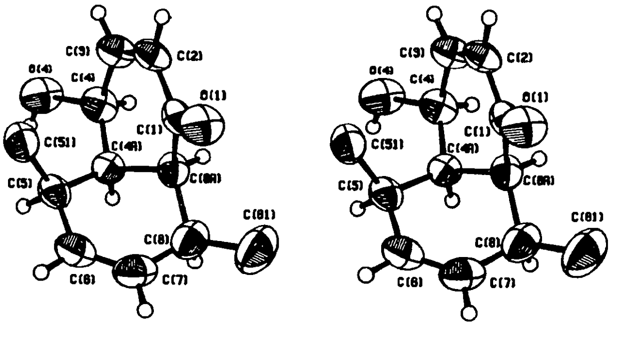

Fig. 1. Stereodiagram of molecule *A* of 5α,8α-dimethyl-4a,5,8,8a-tetrahydro-1-naphthoquin-4α-ol. Thermal ellipsoids are at the 50% probability level with methyl H atoms omitted for clarity.

Table 2. *Bond distances* (Å) *and angles* (°)

	Molecule *A*	Molecule *B**
C(1)–C(2)	1·457 (3)	1·462 (3)
C(2)–C(3)	1·321 (3)	1·319 (3)
C(3)–C(4)	1·499 (3)	1·489 (3)
C(4)–C(4a)	1·517 (3)	1·518 (3)
C(4a)–C(5)	1·544 (3)	1·530 (3)
C(5)–C(6)	1·499 (3)	1·491 (4)
C(6)–C(7)	1·306 (4)	1·313 (4)
C(7)–C(8)	1·491 (4)	1·503 (4)
C(8)–C(8a)	1·525 (3)	1·532 (3)
C(1)–C(8a)	1·509 (3)	1·503 (3)
C(4a)–C(8a)	1·543 (3)	1·539 (3)
C(1)–O(1)	1·222 (2)	1·224 (2)
C(5)–C(51)	1·527 (3)	1·537 (4)
C(8)–C(81)	1·529 (4)	1·522 (4)
C(4)–O(4)	1·413 (3)	1·415 (3)
C(8a)–C(1)–C(2)	115·2 (2)	115·2 (2)
C(8a)–C(1)–O(1)	123·5 (2)	123·9 (2)
C(2)–C(1)–O(1)	121·3 (2)	121·0 (2)
C(1)–C(2)–C(3)	122·2 (2)	121·9 (2)
C(2)–C(3)–C(4)	123·1 (2)	123·6 (2)
C(3)–C(4)–C(4a)	112·8 (2)	112·2 (2)
C(3)–C(4)–O(4)	108·2 (2)	108·1 (2)
C(4a)–C(4)–O(4)	114·6 (2)	113·9 (2)
C(4)–C(4a)–C(5)	116·1 (2)	115·6 (2)
C(4)–C(4a)–C(8a)	109·4 (2)	109·1 (2)
C(5)–C(4a)–C(8a)	112·2 (2)	112·6 (2)
C(4a)–C(5)–C(6)	110·2 (2)	109·8 (2)
C(4a)–C(5)–C(51)	117·5 (2)	118·1 (2)
C(6)–C(5)–C(51)	109·4 (2)	109·5 (2)
C(5)–C(6)–C(7)	125·6 (3)	124·5 (3)
C(6)–C(7)–C(8)	124·2 (3)	125·1 (3)
C(7)–C(8)–C(8a)	110·1 (2)	110·1 (2)
C(7)–C(8)–C(81)	113·7 (3)	113·1 (3)
C(8a)–C(8)–C(81)	115·3 (3)	115·9 (2)
C(4a)–C(8a)–C(1)	109·4 (2)	109·7 (2)
C(4a)–C(8a)–C(8)	110·2 (2)	109·7 (2)
C(8)–C(8a)–C(1)	117·9 (2)	118·4 (2)

* Primed atoms.

Table 3. *Geometrical parameters of intramolecular* C···H *and* O···H *contacts*

τ_X = angle between the $X\cdots$H vector and either the carbonyl plane (X = O) or the enone plane (X = C) defined by H–C=C–H.

Δ_X = C=$X\cdots$H angle (Scheffer & Dzakpasu, 1978).

X	H	$X\cdots$H	τ_X	Δ_X
C(2)	H(511)	2·81 (2) Å	70·4°	88·2°
C(3)	H(512)	2·78 (2)	74·8	97·1
O(1)	H(811)	2·38 (3)	12·7	103·2
C(2′)	H(511′)	2·81 (2)	68·8	90·2
C(3′)	H(513′)	2·67 (3)	77·4	95·3
O(1′)	H(812′)	2·35 (3)	8·7	106·3

able (Scheffer & Dzakpasu, 1978) as do those for H abstraction from Me(81) by the oxygen O(1) (Table 3). However, while several substituted 4a,5,8,8a-tetrahydro-1,4-naphthoquinones react photochemically in both solution and the solid state *via* reaction pathways initiated by β-H abstraction by O (Scheffer, Jennings & Louwerens, 1976; Dzakpasu, Phillips, Scheffer & Trotter, 1976), and in the case of the naphthoquinone analogue of (I) *via* γ-H abstraction by O in solution (Scheffer, Jennings & Louwerens, 1976), this reaction pathway has not been observed in the naphthoquinols in this study (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980) despite seemingly favourable geometries (Scheffer & Dzakpasu, 1978) in the 4α-ol substrates.

The photochemical conversion in solution proceeds *via* intramolecular 2 + 2 cycloaddition (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980); the non-parallel C=C bonds, with C(2)···C(7) and C(3)···C(6) separations of 4·486 (4) and 4·460 (4) Å in molecule *A* and 4·471 (4) and 4·493 (4) Å in molecule *B*, suggest that the conversion in solution is facilitated by the presence of molecular conformers which better fulfil the geometric requirements for the observed reaction (Schmidt, 1971; Scheffer & Dzakpasu, 1978).

The bond lengths and angles generally show normal values, with C(8)—C(8a)—C(1) 8° larger than the tetrahedral value, reflecting the steric interaction between O(1) and Me(81). All six-membered rings are in distorted half-chair conformations, with C(4a), C(8a) deviating ($\sigma \sim 0{\cdot}002$ Å) from the C(1) to C(4) mean plane by −0·39, 0·35 Å in molecule *A* and −0·43, 0·32 Å in molecule *B*, and from the C(5) to C(8) mean plane by 0·24, −0·49 Å and 0·34, −0·41 Å in molecules *A* and *B*, respectively. Atom C(1) deviates from the carbonyl mean plane by only 0·006 Å (3σ) in molecule *A* and 0·008 Å (4σ) in molecule *B*.

Molecules in the crystal are linked by hydrogen bonds between O(1) and O(4) of symmetry-related molecules to form chains running in the **b** direction in each case. For *A* molecules O(1)···O(4) = 2·809 (2), O(1)···H(O4) = 1·96 (3) Å, and O(1)···H(O4)—O(4) = 173°, and for *B* molecules O(1′)···O(4′) = 2·815 (3), O(1′)···H(O4′) = 1·96 (4) Å, and O(1′)···H(O4′)—O(4) = 173°. The molecular-packing diagram is available (see deposition footnote). The molecules given in Table 1 are related by the relationship $A(x,y,z) \sim B(0{\cdot}43 + z, 0{\cdot}2 + y, 1{\cdot}5 - x)$, corresponding to a pseudo-screw type axis parallel to **b** at $x = 1{\cdot}0$, $z = 0{\cdot}56$.

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