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2,3,4aβ,8aβ-Tetramethyl-4a,5,8,8a-tetrahydro-1-naphthoquin-4α-ol*

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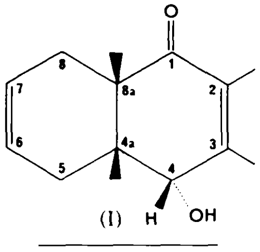
Abstract. $C_{14}H_{20}O_2$, M_r = 220·3, triclinic, $P\bar{1}$, a = 6·9600 (5), b = 7·4762 (4), c = 12·4931 (11) Å, α = 83·875 (6), β = 78·039 (6), γ = 76·866 (5)°, Z = 2, D_x = 1·18 Mg m^{-3}, $F(000)$ = 240; R = 0·041 for 1677 observed reflections. The conformation of the molecule is twisted, with the bridgehead methyl groups staggered with a torsion angle of 63·0 (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)···O(4) = 2·782 (2) Å.

Introduction. 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 2,3,4aβ,8aβ-tetramethyl-4a,5,8,8a-tetrahydro-1-naphthoquin-4α-ol (I).



(I)

Recrystallization from dioxane afforded large colourless needles from which a fragment of dimensions *ca* 0·3 × 0·3 × 0·1 mm was cut. 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 (35 < θ < 45°, graphite-monochromated Cu $K\alpha$ radiation). The intensities were collected with an ω–2θ scan, $\Delta\omega$ = (0·7 + 0·14 × tan θ)°, an aperture 4 mm high and (1·75 + 1·0 tan θ) mm wide, a final acceptance limit of 30σ at 10·06° min^{-1} (in ω), and a maximum recording time of 75 s. Of 2336 recorded intensities out to θ = 70°, 1677 (72%) had $I/\sigma(I) > 3$ with $\sigma^2(I) = S + B + (0{\cdot}05S)^2$ (S being the scan and B the time-corrected background count). 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, Germain, Declercq & Woolfson, 1978) with 398 $|E|$ values >1·2 derived from a K-curve method (Ladd, 1978). 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, and an isotropic extinction parameter g (Becker & Coppens, 1974,

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* IUPAC name: 4α-hydroxy-2,3,4aβ,8aβ-tetramethyl-4a,5,8,8a-tetrahydro-1(4H)-naphthalenone.

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1975), and gave $R = 0{\cdot}041$ ($R = \sum|\Delta F|/\sum|F_o|$) for the 1677 observed reflections. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$, giving $R_w = |\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2|^{1/2} = 0{\cdot}061$ and σ_1 (goodness of fit) = 1·83. The mean and maximum shift/error on the final cycle of least squares were 0·15 and 2·3, respectively, the only values greater than 0·35 being for the H atoms of the C(31) methyl group. The final value of g was 3·0 (6) × 10^4. Weighting analyses confirmed the suitability of the chosen weights. A difference Fourier synthesis after the final cycle showed random fluctuations of up to ±0·2 e Å^{-3}. Final atomic coordinates are presented in Table 1.*

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

	x	y	z	Mean U* (Å^2)
C(1)	5066 (3)	9127 (3)	2122 (2)	37
C(2)	6144 (3)	7732 (3)	1333 (2)	37
C(3)	5858 (3)	5997 (3)	1513 (2)	40
C(4)	4285 (3)	5431 (3)	2446 (2)	42
C(4a)	2773 (3)	7052 (3)	3004 (2)	37
C(5)	1290 (3)	7979 (3)	2234 (2)	43
C(6)	173 (3)	9853 (3)	2537 (2)	49
C(7)	676 (3)	10836 (3)	3219 (2)	50
C(8)	2426 (4)	10146 (3)	3766 (2)	50
C(8a)	3910 (3)	8495 (3)	3223 (2)	39
C(21)	7571 (4)	8358 (4)	366 (2)	50
C(31)	7100 (5)	4470 (4)	816 (3)	65
C(41)	1562 (4)	6314 (4)	4060 (2)	53
C(81)	5502 (4)	7708 (5)	3939 (2)	61
O(1)	5232 (2)	10721 (2)	1925 (1)	54
O(4)	3149 (3)	4361 (2)	2046 (2)	61
H(O4)	385 (7)	314 (7)	205 (3)	140
H(4)	514 (3)	444 (3)	303 (2)	60
H(51)	35 (4)	723 (4)	228 (2)	60
H(52)	199 (3)	804 (3)	148 (2)	50
H(6)	−101 (4)	1045 (4)	218 (2)	70
H(7)	−18 (4)	1211 (4)	339 (2)	60
H(81)	320 (4)	1116 (4)	372 (2)	70
H(82)	204 (4)	976 (4)	458 (2)	60
H(211)	751 (5)	781 (5)	−28 (3)	100
H(212)	886 (6)	821 (5)	43 (3)	100
H(213)	719 (6)	955 (6)	15 (3)	120
H(311)	851 (8)	436 (6)	81 (4)	140
H(312)	741 (6)	480 (6)	9 (3)	120
H(313)	670 (8)	335 (8)	81 (4)	190
H(411)	103 (5)	528 (5)	386 (3)	90
H(412)	48 (5)	717 (4)	438 (2)	80
H(413)	237 (5)	584 (5)	456 (2)	90
H(811)	663 (4)	658 (4)	361 (2)	70
H(812)	488 (4)	727 (4)	458 (2)	80
H(813)	625 (6)	866 (5)	397 (3)	110

* $10^3 (U_{11} + U_{22} + U_{33})/3$; $\sigma = 1$ for non-hydrogen atoms, 10 for H atoms.

Discussion. Molecules of (I) (Fig. 1) adopt the ring-flipped conformation with the hydroxyl group pseudo-equatorial to the cyclohexenone moiety, with 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*,*c*), the twist conformation 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 H(52) to the enone carbon atoms C(2) and C(3), a close approach of H(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 C(41)—C(4a)—C(8a)—C(81) and C(5)—C(4a)—C(8a)—C(1), which are 63·0 (2) and −60·6 (2)°, respectively, similar to those 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 these angles are 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° less here than in the 5α,8α-dimethyl 4α-ol which has H bridgehead substituents (Greenhough & Trotter, 1980*c*). This bridgehead-substituent effect is the same as found for various substituted 4a,5,8,8a-tetrahydro-1,4-naphthoquinones (Phillips & Trotter, 1977).

While (I) is photochemically reactive in the solid state, the products have not been completely characterized; it is not clear whether abstraction of H by enone carbon (as observed for the 4β-ol analogue and the hexamethyl 4α-ol substrate), or intramolecular 2 + 2 cycloaddition (not observed in any other member of the series in the solid state), or both are primary reaction pathways (Appel, Scheffer & Walsh, 1979). The intramolecular geometrical parameters relevant to abstraction of H(52) by enone carbon are

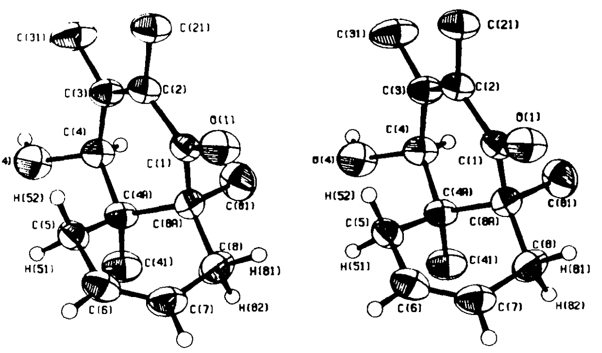

Fig. 1. Stereodiagram of 2,3,4aβ,8aβ-tetramethyl-4a,5,8,8a-tetrahydro-1-naphthoquin-4α-ol. Thermal ellipsoids are at the 50% probability level and methyl H atoms are omitted for clarity.

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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 35484 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

C(2)···H(52) = 2·82 (2), C(3)···H(52) = 2·78 (2) Å, ΔC_2 |C(3)–C(2)···H(52)| = 74·7 (5), ΔC_3 |C(2)–C(3)···H(52)| = 77·5 (5)°, and τc_n = 51·0 (n = 2) and 51·9° (n = 3). [τc_n = angle between the C(n)···H(52) vector and the enone plane defined by C(21)–C(2)=C(3)–C(31).] The τ and Δ values are similar to those in the other substrates which react photochemically by this mechanism (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980), while the C···H separations also seem favourable (Scheffer & Dzakpasu, 1978), being less than 2·90 Å and similar to C(3)···H(52) = 2·72 (2) Å in the hexamethyl 4α-ol substrate and C(3)···H(82) = 2·85 (4) Å in the 4β-ol analogue of (I) (Greenhough & Trotter, 1980*a*,*b*), both of which react photochemically in the solid state *via* H abstraction by C(3) (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980).

The C=C bonds in (I) are well separated and non-parallel, with C(2)···C(7) and C(3)···C(6) = 4·343 (3) and 4·371 (3) Å, respectively. These distances are greater than the suggested limit of 4·1 Å required for successful 2 + 2 cycloaddition (Schmidt, 1971; Scheffer & Dzakpasu, 1978) and similar to the distances in other substrates, which fall in the range 4·369 (7)–4·493 (4) Å.

It is of interest that the relationship between the C(6)=C(7) and C(1)–O(1) bonds, with a midpoint separation m = 3·19 Å, C(6)···C(1) = 3·263 (3), O(1)···C(7) = 3·233 (3) Å, and θ [angle between carbonyl and C(5)–C(6)=C(7)–C(8) mean planes] = 97°, is remarkably similar to that in the 5α,8α-dimethylnaphthoquinone analogue with CN bridgehead substituents [m = 3·20 Å, C(6)···C(1) = 3·37, O(1)···C(7) = 3·20 Å, θ = 99·2°] (Scheffer & Dzakpasu, 1978), which undergoes oxetane formation in the solid state by C(1) to C(6) and O(1) to C(7) bonding (Scheffer, Jennings & Louwerens, 1976).

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

C(1)–C(2)	1·476 (3)	C(1)–C(8a)	1·529 (3)
C(2)–C(3)	1·345 (3)	C(4a)–C(8a)	1·551 (3)
C(3)–C(4)	1·521 (3)	C(1)–O(1)	1·217 (2)
C(4)–C(4a)	1·536 (3)	C(2)–C(21)	1·502 (3)
C(4a)–C(5)	1·553 (3)	C(3)–C(31)	1·503 (3)
C(5)–C(6)	1·486 (3)	C(4)–O(4)	1·432 (3)
C(6)–C(7)	1·328 (4)	C(4a)–C(41)	1·533 (3)
C(7)–C(8)	1·483 (3)	C(8a)–C(81)	1·541 (3)
C(8)–C(8a)	1·536 (3)		

C(8a)–C(1)–C(2)	118·7 (2)	C(4)–C(4a)–C(8a)	109·5 (2)
C(8a)–C(1)–O(1)	121·1 (2)	C(41)–C(4a)–C(5)	108·2 (2)
C(2)–C(1)–O(1)	120·0 (2)	C(41)–C(4a)–C(8a)	112·3 (2)
C(1)–C(2)–C(3)	120·1 (2)	C(5)–C(4a)–C(8a)	108·6 (2)
C(1)–C(2)–C(21)	116·4 (2)	C(4a)–C(5)–C(6)	113·4 (2)
C(3)–C(2)–C(21)	123·5 (2)	C(5)–C(6)–C(7)	124·2 (2)
C(2)–C(3)–C(4)	122·5 (2)	C(6)–C(7)–C(8)	122·6 (2)
C(2)–C(3)–C(31)	122·2 (2)	C(7)–C(8)–C(8a)	113·1 (2)
C(4)–C(3)–C(31)	115·2 (2)	C(8)–C(8a)–C(1)	110·1 (2)
C(3)–C(4)–C(4a)	114·2 (2)	C(8)–C(8a)–C(4a)	110·5 (2)
C(3)–C(4)–O(4)	109·9 (2)	C(4a)–C(8a)–C(81)	113·4 (2)
C(4a)–C(4)–O(4)	107·0 (2)	C(81)–C(8a)–C(8)	109·1 (2)
C(4)–C(4a)–C(5)	109·4 (2)	C(81)–C(8a)–C(1)	105·8 (2)
C(4)–C(4a)–C(41)	108·8 (2)	C(4a)–C(8a)–C(1)	107·9 (2)

The geometrical parameters in (I) for abstraction of H by O(1) seem favourable (Scheffer & Dzakpasu, 1978) with H(81)···O(1) = 2·41 (3) Å. 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 one case *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 available structural data on this series of naphthoquinols indicate that the most probable primary reaction pathway is abstraction of H(52) by the β-enone carbon C(3). Intramolecular 2 + 2 cycloaddition seems an unlikely solid-state mechanism in view of the structural precedents; such a reaction may be occurring at defect sites and/or regions of local melting (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980).

The photochemical conversion in solution apparently proceeds mainly *via* intramolecular 2 + 2 cycloaddition (Appel, Scheffer & Walsh, 1979), as observed for all the other substrates studied, suggesting 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 (Table 2) in the tetramethyl 4α-ol (I) compare well with those in the 4β-ol analogue (Greenhough & Trotter, 1980*b*) and in the 4β-ol and 4α-ol hexamethyl substrates (Greenhough & Trotter, 1980*a*). Differences in torsion angles between (I) and the 4β-ol analogue occur where C(2) is involved, *e.g.* C(1)–C(2)–C(3)–C(4) = 6·6 (2) and –2·6 (5)°, C(2)–C(3)–C(4)–C(4a) = 12·4 (2) and 21·2 (5)° for (I) and the 4β-ol analogue, respectively. These torsional changes are consistent with the C(2)···H(52) and C(3)···H(52) distances here [2·82 (2) and 2·78 (2) Å] being more similar than the C···H(82) distances in the 4β-ol analogue [2·74 (4) and 2·85 (4) Å].

Both six-membered rings have distorted half-chair conformations; C(4a) and C(8a) deviate by –0·426 (2) and 0·347 (2) Å from the mean plane of C(1) to C(4), and by 0·355 (2) and –0·402 (2) Å from the mean plane of C(5) to C(8). In the carbonyl group C(1) is displaced by 0·039 (2) Å from the plane of C(2), C(8a), and O(1).

Molecules in the crystal are linked by hydrogen bonds, O(4)–H(O4) = 0·93 (5), O(1)···O(4) = 2·782 (2) Å, O(1)···H(O4)–O(4) = 175 (4)°, to form chains along **a**. Other intermolecular contacts correspond to normal van der Waals distances. The molecular-packing diagram has been deposited.

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2,2′,4,4′,6,6′-Hexa-*tert*-butylazobenzene*†

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Abstract. $C_{36}H_{58}N_2$, orthorhombic, *Pbca*, $a = 16{\cdot}537$ (2), $b = 17{\cdot}314$ (2), $c = 23{\cdot}074$ (3) Å at 115 K, $Z = 8$, $D_{\rm calc} = 1{\cdot}04$ Mg m^{-3}, $R_F = 6{\cdot}3\%$, $wR_F = 3{\cdot}9\%$. At room temperature the space group is the same and the cell parameters are $a = 16{\cdot}832$ (3), $b = 17{\cdot}343$ (2), $c = 23{\cdot}334$ (4) Å. The crystals are red-orange rectangular parallelepipeds limited by the forms {100}, {010} and {001}. Considerable distortions in the central part of the molecule are due to stresses provoked by the interaction of terminal methyl groups.

Introduction. Several azobenzene derivatives have been prepared (Holm, 1979). The structures of some of these are determined in this series in order to study the effects of crowding on the geometry of the central part of the molecule. This series is merely a presentation of the structural results while the preparation and the chemical properties of the hindered azobenzenes will be reported separately. The diffraction intensities of a roughly equidimensional sample of approximate diameter 0·18 mm of the title compound were measured. Graphite-monochromatized Cu $K\alpha$ radiation generated at 40 kV and 16 mA was used in a $\theta/2\theta$ scan with line-profile analysis (Grant & Gabe, 1978). One unique set was collected at 115 K up to 100° (2θ) giving 3391 unique measurements leading to 1743 observed $[I_{\rm net} > 2\sigma(I_{\rm net})]$ and 1648 unobserved reflections while only 2 out of the 428 measurements of the systematic absences satisfied the observation criterion.

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* Structures of Hindered Azobenzenes. I.

† NRC No. 18592.

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