

Structure of (6,7)-Benzo-2,3,4a β ,8a β -tetramethyl-4a β ,5,8,8a β -tetrahydro-1-naphthoquin-4 α -ol*

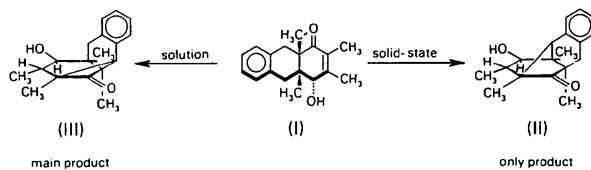
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Abstract. C₁₈H₂₂O₂, $M_r = 270.37$, monoclinic, $P2_1/n$, $a = 10.6726$ (11), $b = 18.0218$ (22), $c = 7.6798$ (5) Å, $\beta = 91.821$ (7)°, $V = 1476.4$ (3) Å³, $Z = 4$, $D_x = 1.216$ g cm⁻³, $F(000) = 584$, $T = 295$ K, Cu $K\alpha_1$, $\lambda = 1.54056$ Å, $\mu = 5.65$ cm⁻¹, $R = 0.074$ for 2301 observed reflections. The conformation of the molecule is twisted such that the bridgehead methyl groups are staggered with a torsion angle of 61.2°, and the hydroxyl group is pseudo-equatorial to the cyclohexenone moiety. Bond lengths and angles are close to normal values. Molecules in the crystal are linked by hydrogen bonds with $O(1)\cdots O(2) = 2.791$ Å. The photochemical reaction in the solid state is accounted for on the basis of the molecular geometry.

Introduction. Solid-state/solution photoreactivity differences have been observed in various substituted tetrahydronaphthoquinols (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980). In the case of the present compound (I), photolysis of its crystals gives compound (II) as the only product, while photolysis in solution gives 90% of compound (III) and only 10% of compound (II). The crystal structure of (I) was determined in order to explain the behaviour in the solid state.



Experimental. Crystal size 0.2 × 0.5 × 0.5 mm, m.p. 416–417 K, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Cu $K\alpha$ radiation, lattice parameters from setting of 25 reflections with $35 \leq \theta \leq 49^\circ$, 3368 reflections measured with $\theta \leq 75^\circ$, 2763 unique reflections ($R_{int} = 0.045$), $h = -13 \rightarrow 13$, $k = 0 \rightarrow 22$, $l = 0 \rightarrow 9$; ω -2 θ scan, ω scan width (0.90 + 0.14 tan θ)°, extended 25% on each side for background measurement, horizontal aperture (2.0 + tan θ) mm,

* IUPAC name: 4 α -hydroxy-2,3,4a β ,9a β -tetramethyl-4a β ,9,9a β -10-tetrahydro-1(4H)-anthracenone.

vertical aperture 4 mm, Lp and analytical absorption corrections (transmission factors from 0.675 to 0.892). Three standard reflections ($\bar{4}61$, 191, 004) were monitored every hour of exposure time for random intensity fluctuations ($\pm 1\%$), and were recentred every 150 reflections for orientation control. Nine intense low-order reflections omitted from final refinement because of extinction. Structure was solved by direct methods with *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$ using *SHELX76* (Sheldrick, 1976). Methyl hydrogens on the ethylenic group were put in calculated positions and then refined as rigid groups possessing a local C_3 symmetry; their temperature factors were refined isotropically. All other hydrogens were located in a difference synthesis and were refined isotropically. 257 parameters consisting of 114 positional parameters, 120 anisotropic temperature factors, 22 isotropic temperature factors, and a scale factor. Convergence at $R = 0.074$, $wR = 0.081$ for 2301 observed 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. $R = 0.089$, $wR = 0.084$ for all data, $w = 1/\sigma^2(F)$, $(\Delta/\sigma)_{max} = 0.3$, highest $\Delta\rho$ peak in final difference synthesis (0.37 e Å⁻³) is located near C(31), whose thermal motion amplitude is twice the molecular average. Atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). The high final value of R might be a result of the difficulty in treating the large thermal motion of C(31).

Discussion. Final atomic coordinates are in Table 1, bond distances, bond angles, and selected torsion angles in Table 2.†

The molecular conformation of the title compound (Fig. 1) is twisted about the C(4a)–C(8a) bond, so that

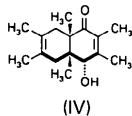
† Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond distances and angles involving hydrogen atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43640 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atom coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
O(1)	4713 (2)	1468 (1)	7870 (2)	60
O(2)	4555 (2)	2144 (1)	14592 (3)	55
C(1)	4898 (2)	1557 (1)	9434 (3)	38
C(2)	4238 (2)	1081 (1)	10663 (3)	38
C(21)	3429 (3)	478 (2)	9861 (5)	55
C(3)	4389 (2)	1188 (1)	12399 (3)	38
C(31)	3803 (4)	673 (2)	13704 (5)	110
C(4)	5178 (3)	1804 (2)	13167 (3)	39
C(4a)	5465 (2)	2428 (1)	11880 (3)	36
C(4a1)	6478 (3)	2939 (2)	12701 (5)	57
C(5)	4262 (3)	2888 (1)	11500 (4)	41
C(6)	4383 (2)	3442 (1)	10056 (3)	38
C(7)	5251 (2)	3348 (1)	8766 (3)	38
C(8)	6159 (3)	2706 (2)	8805 (4)	43
C(8a)	5895 (2)	2090 (1)	10137 (3)	35
C(8a1)	7085 (3)	1604 (2)	10352 (5)	49
C(9)	3614 (3)	4074 (2)	10007 (4)	48
C(10)	3696 (3)	4592 (2)	8705 (4)	56
C(11)	4550 (3)	4500 (2)	7422 (5)	58
C(12)	5316 (3)	3875 (2)	7439 (4)	50

the bridgehead methyl groups are staggered, as in the related compound 2,3,4a β ,6,7,8a β -hexamethyl-4a β ,5,8,8a β -tetrahydro-1-naphthoquin-4a-ol (IV) (Greenhough & Trotter, 1980). The degree of 'twist' is shown by the torsion angles C(5)–C(4a)–C(8a)–C(1), $-63.5 (3)^\circ$, and C(4a1)–C(4a)–C(8a)–C(8a1), $61.2 (3)^\circ$. In (IV) the corresponding values for the two angles are $-63.2 (1)$ and $59.9 (1)^\circ$ respectively. Bond lengths and bond angles are not significantly different from those in (IV), except for the increase in C(6)–C(7), $1.388 (4)$ vs $1.333 (2)$ Å, resulting from the lower bond order. The C(sp³)–C(sp³) bond distances (Table 2) are in the range $1.534 (4)$ – $1.553 (4)$ Å, mean 1.544 Å; the longest is C(4a)–C(8a), $1.553 (4)$ Å, probably because of steric effects due to the methyl groups on C(4a) and C(8a).



Molecules of (I) crystallize with the conformation common to all naphthoquinols studied, in which the bulkier substituent on C(4) assumes the pseudo-equatorial position (Secco & Trotter, 1982a). The spatial consequence of this arrangement is the proximity of the β -enone carbon, C(3), to H(52) [$2.75 (4)$ Å]. Furthermore, the angle between the C(3)–H(52) vector and its projection on the plane of the C(3)=C(2) double bond [C(1), C(2), C(3), C(4)], τ , and the angle between the C(3)–H(52) and the C(3)=C(2) vectors, Δ , are 54.4 and 77.1° , respectively. This geometry is highly favourable for H-abstraction by the β -enone C, which is observed in the solid-

state photolysis. The corresponding values for the C(3)–H(52) distance, τ and Δ for compound (IV) are $2.72 (2)$ Å, 53.2 and 78.5° respectively, allowing the corresponding H-abstraction by the β -enone C photolysis to occur in the solid state (Jiang, Scheffer, Secco & Trotter, 1981).

The distance between the carbonyl oxygen, O(1), and the β -hydrogen, H(82), is $2.46 (3)$ Å, compared with $2.45 (2)$ Å in (IV). Since the van der Waals O–H contact is about 2.7 Å, the photochemical reaction pathway for β -hydrogen abstraction from C(8) by O(1) is feasible for both (I) and (IV). The other relevant geometric parameters for β -hydrogen abstraction by O(1), described by τ [the degree by which H(β) lies outside the plane of the carbonyl group], and Δ [the

Table 2. Bond lengths (Å), bond angles ($^\circ$) and selected torsion angles ($^\circ$)

C(1)–O(1)	1.222 (3)	C(6)–C(7)	1.388 (4)
C(1)–C(2)	1.471 (4)	C(7)–C(8)	1.509 (4)
C(2)–C(3)	1.351 (4)	C(8)–C(8a)	1.542 (4)
C(2)–C(21)	1.508 (4)	C(1)–C(8a)	1.520 (4)
C(3)–C(4)	1.503 (4)	C(4a)–C(8a)	1.553 (4)
C(3)–C(31)	1.516 (5)	C(8a)–C(8a1)	1.547 (4)
C(4)–C(4a)	1.534 (4)	C(6)–C(9)	1.403 (4)
C(4)–O(2)	1.436 (4)	C(9)–C(10)	1.373 (5)
C(4a)–C(4a1)	1.540 (5)	C(10)–C(11)	1.373 (5)
C(4a)–C(5)	1.548 (4)	C(11)–C(12)	1.391 (5)
C(5)–C(6)	1.502 (4)	C(7)–C(12)	1.397 (4)
C(2)–C(1)–O(1)	119.3 (3)	C(6)–C(5)–C(4a)	113.9 (2)
C(8a)–C(1)–O(1)	121.4 (2)	C(7)–C(6)–C(5)	121.3 (2)
C(8a)–C(1)–C(2)	119.0 (2)	C(9)–C(6)–C(5)	119.7 (2)
C(3)–C(2)–C(1)	120.4 (2)	C(9)–C(6)–C(7)	118.9 (2)
C(21)–C(2)–C(1)	115.9 (2)	C(8)–C(7)–C(6)	121.5 (2)
C(3)–C(2)–C(21)	123.6 (3)	C(12)–C(7)–C(6)	119.1 (3)
C(31)–C(2)–C(21)	121.8 (3)	C(12)–C(7)–C(8)	119.3 (2)
C(4)–C(3)–C(2)	122.6 (2)	C(8a)–C(8)–C(7)	115.8 (2)
C(4)–C(3)–C(31)	115.5 (2)	C(8)–C(8a)–C(1)	111.1 (2)
C(3)–C(4)–O(2)	110.3 (2)	C(8a1)–C(8a)–C(1)	104.1 (2)
C(4a)–C(4)–O(2)	106.6 (2)	C(8a1)–C(8a)–C(8)	108.2 (2)
C(4a)–C(4)–C(3)	114.2 (2)	C(8a1)–C(8a)–C(4a)	113.2 (2)
C(4a1)–C(4a)–C(4)	109.1 (2)	C(8)–C(8a)–C(4a)	110.7 (2)
C(5)–C(4a)–C(4)	109.3 (2)	C(4a)–C(8a)–C(1)	109.4 (2)
C(5)–C(4a)–C(4a1)	108.9 (2)	C(10)–C(9)–C(6)	121.3 (3)
C(8a)–C(4a)–C(4)	109.8 (2)	C(11)–C(10)–C(9)	120.0 (3)
C(8a)–C(4a)–C(5)	108.3 (2)	C(12)–C(11)–C(10)	119.6 (3)
C(8a)–C(4a)–C(4a1)	111.4 (2)	C(11)–C(12)–C(7)	121.0 (3)
O(1)–C(1)–C(2)–C(21)	3.7 (4)	C(3)–C(4)–C(4a)–C(5)	72.0 (3)
O(1)–C(1)–C(2)–C(3)	–177.3 (3)	C(3)–C(4)–C(4a)–C(8a)	–46.6 (3)
C(8a)–C(1)–C(2)–C(21)	–169.8 (2)	C(4)–C(4a)–C(5)–C(6)	–171.4 (2)
C(8a)–C(1)–C(2)–C(3)	9.1 (4)	C(4a1)–C(4a)–C(5)–C(6)	69.5 (3)
O(1)–C(1)–C(8a)–C(4a)	148.0 (3)	C(8a)–C(4a)–C(5)–C(6)	–51.8 (3)
O(1)–C(1)–C(8a)–C(8)	25.5 (4)	C(4)–C(4a)–C(8a)–C(1)	55.8 (3)
O(1)–C(1)–C(8a)–C(8a1)	–90.7 (3)	C(4)–C(4a)–C(8a)–C(8)	178.6 (2)
C(2)–C(1)–C(8a)–C(4a)	–38.6 (3)	C(4)–C(4a)–C(8a)–C(8a1)	–59.7 (3)
C(2)–C(1)–C(8a)–C(8)	–161.1 (2)	C(4a1)–C(4a)–C(8a)–C(1)	176.8 (2)
C(2)–C(1)–C(8a)–C(8a1)	82.7 (3)	C(4a1)–C(4a)–C(8a)–C(8)	–60.5 (3)
C(1)–C(2)–C(3)–C(31)	–175.3 (3)	C(4a1)–C(4a)–C(8a)–C(8a1)	61.2 (3)
C(1)–C(2)–C(3)–C(4)	2.6 (4)	C(5)–C(4a)–C(8a)–C(1)	–63.5 (3)
C(21)–C(2)–C(3)–C(31)	3.6 (4)	C(5)–C(4a)–C(8a)–C(8)	59.3 (3)
C(21)–C(2)–C(3)–C(4)	–178.6 (3)	C(5)–C(4a)–C(8a)–C(8a1)	–179.0 (2)
C(2)–C(3)–C(4)–O(2)	137.5 (3)	C(4a)–C(5)–C(6)–C(7)	24.5 (4)
C(2)–C(3)–C(4)–C(4a)	17.5 (4)	C(4a)–C(5)–C(6)–C(9)	–154.9 (3)
C(31)–C(3)–C(4)–O(2)	–44.5 (3)	C(6)–C(7)–C(8)–C(8a)	11.4 (4)
C(31)–C(3)–C(4)–C(4a)	–164.5 (2)	C(12)–C(7)–C(8)–C(8a)	–171.1 (3)
O(2)–C(4)–C(4a)–C(4a1)	68.9 (3)	C(7)–C(8)–C(8a)–C(11)	81.8 (3)
O(2)–C(4)–C(4a)–C(5)	–50.1 (3)	C(7)–C(8)–C(8a)–C(4a)	–40.0 (3)
O(2)–C(4)–C(4a)–C(8a)	–168.7 (2)	C(7)–C(8)–C(8a)–C(8a1)	–164.6 (2)
C(3)–C(4)–C(4a)–C(4a1)	–169.0 (2)		

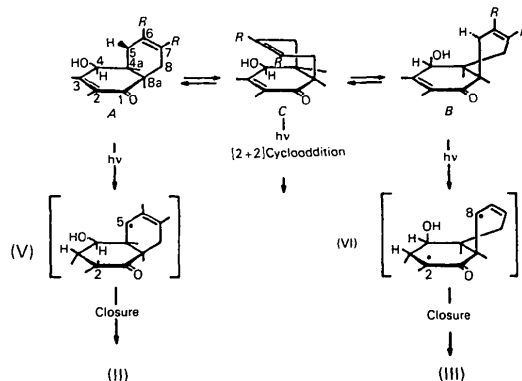
angle $C(1)-O(1)\cdots H(\beta)$, are $\tau=3.6^\circ$, $\Delta=85.3^\circ$ for (I). Although there is an almost perfect alignment of the β -H with the non-bonding orbital of O(1), no photo-products so initiated have been observed. It was argued in previous work on tetrahydronaphthoquinols (Secco & Trotter, 1982b) that substituents on the C(2) and C(3) positions of the cyclohexenone moiety play a critical role in determining the photochemical reaction pathway, possibly by lowering the energy of the (π,π^*) transition state from which the C abstraction of the γ -H is considered to originate. The lack of β -H abstraction by O in this system, as well as for compound (IV), is in accord with the above rationalization.

The result of the photochemical reactivity preference is that compound (I) when photolyzed in the solid state undergoes γ -H, H(52), abstraction by β -enone carbon, C(3). Consistent with this mechanism is the large observed thermal motion at C(31), which is indicative of more free space around this atom to accommodate the pyramidalization of C(3). The reaction is completed by C(2) \cdots C(5) bonding [C(2) \cdots C(5) distance is 3.315 (4) Å] to form keto-alcohol (II).

Hydrogen bonding, found in all the naphthoquinols studied, is present in this structure as O(2) $-H(O2)\cdots O(1)$ interactions linking molecules along the *c* axis (Fig. 2): $O\cdots O = 2.791$ (4), $H\cdots O = 2.05$ (4) Å, $O-H\cdots O = 158$ (3) $^\circ$.

In solution, tetrahydronaphthoquinol derivatives possess three distinct conformational isomers (see scheme); each one displays a unique photochemical reactivity (Appel, Jiang, Scheffer & Walsh, 1983). Two low-energy conformations (*A* and *B*) have fused six-membered rings with half-chair conformations, and are folded and twisted about the C(4a) $-C(8a)$ bond. They can be interconverted by ring 'flipping' involving single-bond rotation *via* a higher-energy conformer, *C*, which has eclipsed bridgehead substituents and parallel double bonds. For compound (I) the flipping converts

the pseudo-equatorial OH substituent at C(4) in the cyclohexenone ring of the lower-energy conformer *A* into a pseudo-axial substituent of the higher-energy conformer *B*.



Conformers *A* and *B* react differently. The suggested mechanisms are outlined in the scheme. Type *A* and type *B* H-abstractions both proceed through cyclic transition states; however, while in type *A* the allylic hydrogen being transferred is at C(5), in type *B* it is at C(8). C(2) \cdots C(8) bonding follows to generate compound (III). Type *A* photoreactivity involves a five-membered H-abstraction transition state, while type *B* involves a six-membered transition state. Thus in solution type *B* photoreactivity (*via* a six-membered transition state) is probably kinetically favoured over type *A* photoreactivity (*via* a five-membered transition state).

The photochemical conversion in solution of compound (IV) proceeds mainly *via* intramolecular (2+2) cycloaddition (type *C*, scheme), as observed for all other substrates studied (Appel *et al.*, 1983). (2+2) cycloaddition is observed exclusively because of its high relative rate even though conformers *A* and *B* are undoubtedly present in excess. Type *C* mechanism, however, is not possible for compound (I) because of

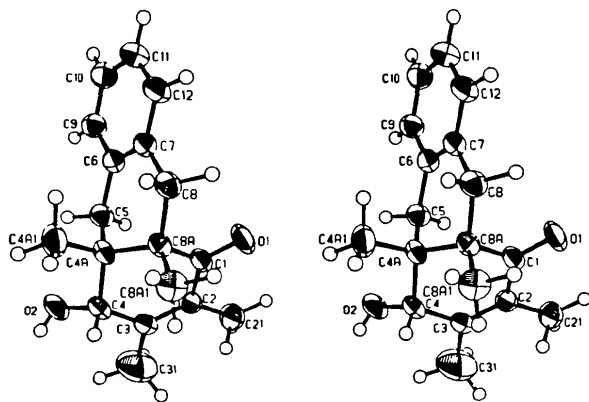


Fig. 1. Stereoscopic view of (I) with crystallographic atomic labelling.

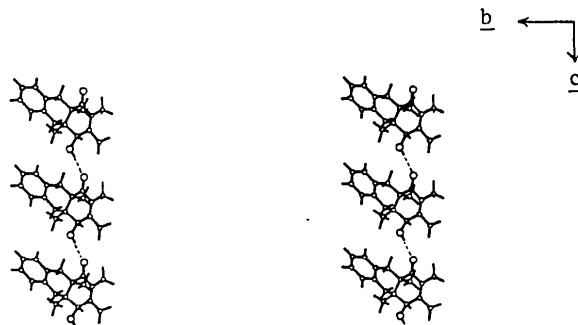


Fig. 2. Stereoscopic view of the H-bonding arrangement of (I).

the presence of the aromatic ring. It is noteworthy that this paper reports the first type *B* photochemical conversion observed in solution for substituted tetrahydronaphthoquinols.

To summarize, reactions in solution, where molecular conformational equilibrium is facile, are governed chiefly by kinetics, whereas the solid-state reactions are topochemically controlled. The lowest-energy conformation (in which it is most likely to crystallize) is one which predisposes the molecules to a specific reaction in the solid state.

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Structure of Tetramethylammonium Dihydrogenorthophosphate Monohydrate

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Abstract. N(CH₃)₄H₂PO₄·H₂O, *M_r* = 189.15, monoclinic, *P*2₁/*c*, *a* = 8.518 (1), *b* = 12.897 (2), *c* = 8.440 (2) Å, β = 99.05 (1)°, *V* = 915.6 Å³, *Z* = 4, *D_m* = 1.36 (1), *D_x* = 1.372 Mg m⁻³, λ(Mo *K*α) = 0.71073 Å, μ(Mo *K*α) = 0.2745 mm⁻¹, *F*(000) = 408, *T* = 296 (1) K, final *R* = 0.037 for 2023 unique reflections. PO₄ tetrahedra are connected to each other along the *c* axis by H bonds [O...O 2.543 (2) and 2.606 (2) Å, O—H...O 171.1 (8) and 175.6 (8)°]; other H bonds [O...O 2.809 (2) and 2.875 (2) Å, O—H...O 167.7 (8) and 167.5 (8)°] between adjacent H₂PO₄⁻ chains are formed with water molecules. Consequently a two-dimensional network of H bonds is constructed.

Introduction. In the crystal structures of alkali and ammonium dihydrogen orthophosphates, the type of hydrogen bonding between adjacent H₂PO₄⁻ groups differs with varying ionic radii of cations: *i.e.* a three-dimensionally connected framework of H₂PO₄⁻ groups for Rb or smaller cations (Haussühl, 1964;

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Tenzer, Frazer & Pepinsky, 1958; Bacon & Pease, 1953; Choudhary, Nelmes & Rouse, 1981; Catti & Ivaldi, 1977), and a two-dimensional network for Cs or Tl ions (Nelmes & Choudhary, 1978, 1981).

We report here the crystal structure of tetramethylammonium dihydrogenorthophosphate monohydrate (hereafter abbreviated as TMADP·H₂O), which contains bulky univalent tetramethylammonium ions.

Experimental. Preparation of the crystal: A solution of orthophosphoric acid was added to a solution of tetramethylammonium hydroxide and pH adjusted to 4.5. The mixed solution was concentrated to grow polycrystals of TMADP·H₂O. Single crystals were grown in a refrigerator by slow evaporation of aqueous solutions of the polycrystals. *D_m* measured by flotation in (C₂H₅)₂O/CHCl₃. Colourless ellipsoidal crystal 0.43 × 0.60 × 0.61 mm. X-ray measurements made with Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo *K*α radiation. Lattice parameters and orientation matrix by least-squares