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## The Structure of 2,3,6,7-Tetramethyl-4 $\alpha\beta$ ,5,8,8 $\alpha\beta$ -tetrahydro-1-naphthoquin-4 $\alpha$ -ol\*

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(Received 19 June 1981; accepted 22 October 1981)

### Abstract

Crystals of the title compound,  $C_{14}H_{20}O_2$ ,  $M_r = 220.31$ , are monoclinic,  $C2/c$ , with  $a = 13.898$  (3),  $b = 5.228$  (1),  $c = 17.316$  (3) Å,  $\beta = 97.442$  (7)°,  $V = 1247.7$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.1728$ ,  $D_o = 1.174$  g cm<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 0.714$  cm<sup>-1</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å. Data were collected on a CAD-4 single-crystal X-ray diffractometer using Mo  $K\alpha$  radiation. The structure was determined by direct methods and refined to  $R = 0.058$  for 888 independent observed reflections. The structure contains molecules lying on twofold axes as a result of disorder within the lattice. Two types of hydrogen bonding, O(4)···O(1) and O(4)···O(4), join molecules into a network within slabs parallel to (001). Molecules adopt a conformation where the hydroxyl group occupies a position pseudo-equatorial to the cyclohexenone ring. On the basis of the molecular conformation and the relatively short C(3)···H(5) distance, the photochemical reaction involving hydrogen abstraction is rationalized.

### Introduction

Several structural analyses on tetrahydronaphthoquinols have been reported (Greenhough & Trotter, 1980*a,b,c*) in conjunction with photochemical studies on their solid-state reactions. As part of these continuing studies, a structural determination of the present compound was undertaken to verify the molecular conformation in the solid state and to elucidate the geometric parameters in the photoreaction involving hydrogen abstraction by the  $\beta$ -enone carbon.

\* IUPAC name: 4 $\alpha$ -hydroxy-2,3,6,7-tetramethyl-4 $\alpha\beta$ ,5,8,8 $\alpha\beta$ -tetrahydro-1(4*H*)-naphthalenone.

### Experimental

The title compound was synthesized *via* sodium borohydride reduction of the 2,3-dimethyl-*p*-benzoquinone/2,3-dimethyl-1,3-butadiene Diels–Alder adduct (Fig. 1) and was subsequently recrystallized from an ethanol/petroleum ether solution. The crystal used for photographs and data collection measured approximately 0.3 × 0.6 × 0.4 mm, having seven well defined faces.

Preliminary precession and Weissenberg photographs revealed the following absence conditions:  $h0l$ ,  $l = 2n + 1$ , and  $hkl$ ,  $h + k = 2n + 1$ , characteristic of the space groups  $Cc$  and  $C2/c$ .

The crystal was mounted in a general orientation on an Enraf–Nonius CAD-4 diffractometer. Cell constants and an orientation matrix were determined from a least-squares refinement of the setting angles for 25

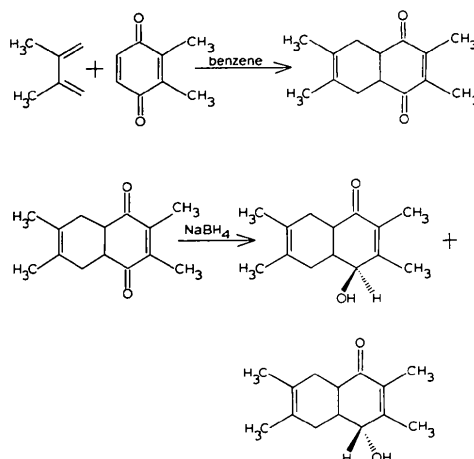


Fig. 1. Preparative reaction scheme leading to 2,3,6,7-tetramethyl-4 $\alpha\beta$ ,5,8,8 $\alpha\beta$ -tetrahydro-1-naphthoquin-4 $\alpha$ -ol.

centered reflections. A Delaunay reduction program provided the transformation matrix required to convert the primitive cell found by the CAD-4 to the corresponding *C*-centered cell indicated on the photographs.

Data were collected in the  $\theta$  range 0.0–27.5° using graphite-monochromatized Mo radiation with  $\omega$  scan speeds of 2.01–10.06 deg min<sup>-1</sup>. From an analysis of various peak profiles, the best scan type was determined to be an  $\omega-2(\frac{1}{2})\theta$  scan with an  $\omega$ -scan angle of  $(1.30 + 0.35 \tan \theta)^\circ$  (each scan being extended by 25% on both sides for background measurement). A variable horizontal-aperture width of  $(2.00 + 1.00 \tan \theta)$  mm was employed and the vertical aperture was fixed at 4 mm.

Crystal-orientation checks were performed on three reference reflections after every 100 reflections collected. The intensities of three check reflections which were monitored hourly throughout data collection were found to decay by not more than 0.3%. Lorentz and polarization corrections were applied in the usual manner to the 1435 reflections collected of which 61.9% (888) had  $I \geq 3\sigma(I)$  {where  $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$ ,  $S$  = scan count and  $B$  = background}.

### Solution and refinement

Although the *E* statistics did not indicate unequivocally an acentric distribution, a non-centrosymmetric solution was sought on the basis of the molecule being asymmetric and the unit cell containing only four such molecules.

Full-matrix least-squares refinement of the non-centrosymmetric solution from *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) led to an *R* value of 0.17 after six cycles with 14 C and two O atoms (and anisotropic thermal parameters). The large degree of correlation between parameters of the cyclohexenone moiety and those of the cyclohexene part of the molecule suggested that the asymmetric unit consisted of less than one molecule. A difference-Fourier map indicated excess density peaks of 2–3 e Å<sup>-3</sup> within bonding distances of C(5) and C(8). Combined with the large magnitude of the temperature factors of the two O atoms, these excess density peaks suggested a disordered structure whereby the molecule appears as two fused cyclohexenone moieties. Refinement proceeded in the centrosymmetric space group *C2/c* with the molecule lying on the twofold rotation axis. O atoms were included initially with isotropic thermal parameters and at 50% occupancy, thus allowing for the rotational disorder.

Ten H atoms were located from a difference-Fourier map while those on C(8) and O(4) were not found due to the nature of the disorder. In the latter stages, all non-hydrogen atoms were refined anisotropically

whereas the H atoms were included with isotropic thermal parameters. The O atoms and the two H atoms attached to C(5) were held at 50% occupancy. The structure converged at  $R = \sum |F_o| - k|F_c| / \sum |F_o| = 0.058$ ,  $R_w = [\sum w(|F_o| - k|F_c|)^2 / \sum |F_o|^2]^{1/2} = 0.078$  for the 888 reflections with  $I \geq 3\sigma(I)$ .\* For the complete data set  $R = 0.088$  and  $R_w = 0.078$ . The final difference synthesis revealed two peaks (0.208, 0.231, 0.245) and (0.179, 0.131, 0.271) of magnitudes 0.479 and 0.508 e Å<sup>-3</sup> respectively in the region of O(4). However, these cannot be directly attributable to the missing hydrogen, H(O4), in view of the poor bonding geometry they require at O(4) and the spatial proximity to that atom. The largest peak on the difference map has coordinates (0.030, 0.248, 0.539) and a magnitude of 0.516 e Å<sup>-3</sup>. The mean and maximum parameter shifts on the final cycle were 0.037 and 0.203  $\sigma$ , respectively. The standard deviation of an observation of unit weight is 1.0017.

The function minimized throughout refinement was  $\sum w(F_o - kF_c)^2$ . Reflections for which  $I < 3\sigma(I)$  were classified as unobserved and not used in the refinement. Observed reflections were assigned weights calculated from the polynomial,  $w = (A + BF_o + CF_o^2 + DF_o^3)^{-1}$ , where  $A = 0.3385$ ,  $B = 0.02351$ ,  $C = 0.002002$  and  $D = 0.000097$ . This gave uniform

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36488 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

Primed (') atoms are at positions of 50% occupancy.

	<i>x</i>	<i>y</i>	<i>z</i>	* $U_{eq}/U_{iso}$
C(1)	-465 (2)	-156 (4)	3237 (1)	52 (1)
C(2)	467 (2)	-740 (4)	3727 (1)	52 (1)
C(21)	395 (3)	-2626 (6)	4375 (2)	73 (2)
C(3)	1290 (2)	399 (4)	3589 (1)	57 (1)
C(31)	2248 (3)	-95 (10)	4084 (2)	96 (2)
C(4)	1340 (2)	2235 (5)	2926 (1)	58 (1)
C(8a)	-466 (1)	2114 (4)	2693 (1)	48 (1)
O(1')	-1157 (3)	-1380 (11)	3362 (3)	93 (3)
O(4')	2172 (2)	2032 (6)	2599 (2)	64 (2)
H1(21)	56 (3)	-196 (7)	482 (2)	103 (11)
H2(21)	1 (3)	-402 (8)	421 (3)	138 (15)
H3(21)	98 (4)	-362 (9)	449 (3)	160 (18)
H1(31)	218 (3)	-15 (9)	458 (3)	129 (14)
H2(31)	262 (4)	-176 (11)	409 (3)	181 (22)
H3(31)	266 (4)	110 (10)	399 (3)	163 (20)
H(4)	142 (2)	392 (6)	314 (2)	88 (9)
H1(5')	68 (4)	-182 (9)	211 (3)	58 (12)
H2(5')	99 (4)	5 (11)	148 (3)	59 (16)
H(8a)	-45 (2)	363 (5)	302 (1)	56 (6)

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

averages of  $w(F_o - kF_c)^2$  over ranges of  $|F_o|$ . Scattering factors for non-hydrogen atoms were taken from Cromer & Mann (1968) while those for H atoms were from Stewart, Davidson & Simpson (1965). Final positional and thermal parameters are presented in Table 1. All computer programs used in solving and refining this structure are local adaptations of standard crystallographic programs.

### Discussion

The structure consists of molecules well separated along the  $c$  axis with the closest non-hydrogen approach being greater than 3.5 Å in that direction. There are two possible intermolecular O...O contact distances less than 3 Å. These contacts can occur between the hydroxyl O atom of one molecule and that of the carbonyl in the adjacent molecule, related by the centering condition, or between the same hydroxyl oxygen and the twofold-symmetry-related oxygen in the neighboring centered molecule. The O(4)-(x,y,z)...O(1)(½ + x, ½ - y, z) distance of 2.652 (5) Å suggests that hydrogen bonds link molecules in the [110] and [110] directions. However, the O(4)-(x,y,z)...O(4)(½ - x, ½ + y, ½ - z) distance of 2.804 (4) Å suggests that hydrogen bonding takes place between disordered molecules. The above intermolecular distances are consistent with the observation that the crystal cleaves easily parallel to the (001) face.

Disorder in the structure, assumed to be 50:50, results in an apparent twofold symmetry axis through the molecule. This disorder may be rationalized on the basis that there appears to be little stereochemical hindrance preventing the two molecular orientations from co-existing in the same crystal, providing alignment for hydrogen bonding is maintained.

The disorder arises from packing arrangements in which slabs parallel to (001) contain molecules of two types, *A* and *B* (where *B* is *A* rotated 180° about *b*). Two kinds of hydrogen bonding are possible within the slabs. They join molecules in the sequence *A*...*A* (or *B*...*B*) and *A*...*B* (or *B*...*A*). The bonds linking molecules of similar type are O(4)(x,y,z)-H...O(1)(½ + x, ½ - y, z) interactions whereas molecules of different types are joined by O(4)(x,y,z)-H...O(4)(½ - x, ½ + y, ½ - z) hydrogen bonds. There are several packing arrangements consistent with the dual composition and available hydrogen bonding within each slab, and since packing forces are a major influence on the crystal energy, the arrangements leading to hydrogen-bonding networks linking the maximum number of molecules within the slabs yield the most probable structure.

Fig. 2 shows the contents of the unit cell with C(4) labelled by its adjoining hydrogen. The molecules adopt a conformation which consists of a half-chair cyclo-

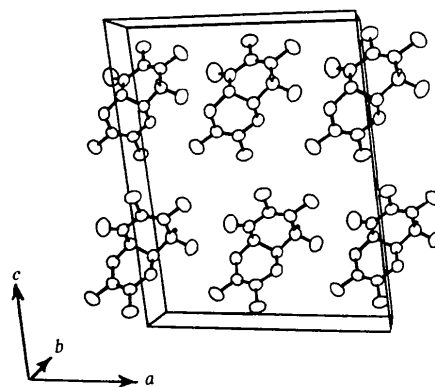


Fig. 2. The molecular packing of type-*A* molecules viewed approximately down *b*.

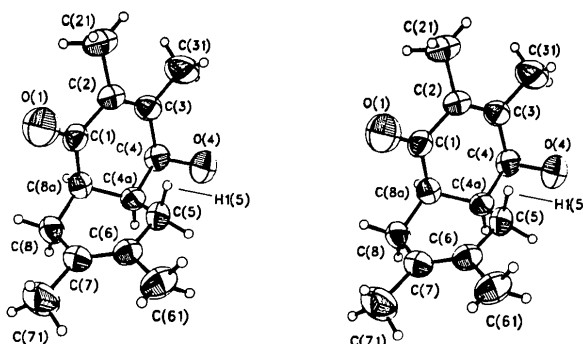


Fig. 3. Stereodiamgram of 2,3,6,7-tetramethyl-4aβ,5,8,8aβ-tetrahydro-1-naphthoquin-4a-ol. Thermal ellipsoids are at 50% probability.

hexene ring *cis*-fused to a second half-chair cyclohexenone moiety (Fig. 3) similar to previously studied naphthoquinols (Greenhough & Trotter, 1980*a,b*).

In comparison with accepted values (Sutton, 1965), the mean bond lengths are found to be slightly shorter with distances of 1.524 Å for C(*sp*<sup>3</sup>)-C(*sp*<sup>3</sup>) and 1.504 Å for C(*sp*<sup>3</sup>)-C(*sp*<sup>2</sup>). C-H bond lengths do not

Table 2. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for non-hydrogen atoms

C(1)-C(2)	1.484 (3)	C(3)-C(31)	1.510 (4)
C(1)-C(8a)	1.515 (3)	C(3)-C(4)	1.505 (3)
C(1)-O(1)	1.199 (4)	C(4)-O(4)	1.356 (4)
C(2)-C(21)	1.506 (3)	C(4a)-C(8a)	1.533 (4)
C(2)-C(3)	1.339 (3)	C(4a)-C(4)	1.514 (3)
C(2)-C(1)-C(8a)	116.6 (2)	C(31)-C(3)-C(4)	114.7 (2)
C(2)-C(1)-O(1)	116.6 (3)	C(3)-C(4)-O(4)	113.3 (2)
C(8a)-C(1)-O(1)	126.5 (3)	C(3)-C(4)-C(4a)	113.7 (2)
C(1)-C(2)-C(21)	115.0 (2)	O(4)-C(4)-C(4a)	110.5 (2)
C(1)-C(2)-C(3)	120.6 (2)	C(1)-C(8a)-C(8)	114.2 (2)
C(21)-C(2)-C(3)	124.4 (2)	C(1)-C(8a)-C(4a)	109.8 (1)
C(2)-C(3)-C(31)	122.3 (2)	C(8)-C(8a)-C(4a)	109.7 (2)
C(2)-C(3)-C(4)	123.0 (2)		

Table 3. Selected torsion angles ( $^{\circ}$ ) with estimated standard deviations in parentheses

C(8a)—[C(1)—C(2)]—C(21)	167.6 (2)
C(8a)—[C(1)—C(2)]—C(3)	-11.5 (2)
O(1)—[C(1)—C(2)]—C(21)	-5.9 (3)
O(1)—[C(1)—C(2)]—C(3)	175.0 (3)
C(1)—[C(2)—C(3)]—C(31)	178.6 (2)
C(1)—[C(2)—C(3)]—C(4)	-2.3 (2)
C(21)—[C(2)—C(3)]—C(31)	-0.4 (3)
C(21)—[C(2)—C(3)]—C(4)	178.7 (2)
C(2)—[C(3)—C(4)]—O(4)	-143.5 (2)
C(31)—[C(3)—C(4)]—O(4)	35.7 (3)

deviate significantly from the accepted values. Bond angles are normal and are given in Table 2 along with bond lengths. Some ring strain, indicated by a C(4)—C(3)—C(2)—C(1) torsion angle of  $-2.3^{\circ}$  (Table 3) and compounded by an O(1)—C(1)—C(2)—C(3) torsion angle of  $175.0^{\circ}$ , results in the carbonyl oxygen lying  $0.1 \text{ \AA}$  above the mean plane through the former four atoms and C(1) lying  $0.005 \text{ \AA}$  below the same mean plane.

The molecule, exhibiting the same ring-flipped conformation as other naphthoquinol derivatives in the series (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980), is geometrically suited to H1(5) abstraction by the  $\beta$ -enone carbon, C(3), upon photochemical excitation. The C(3) $\cdots$ H1(5) distance of  $2.84(5) \text{ \AA}$  is less than the van der Waals contact distance of  $2.90 \text{ \AA}$  and appears more favorable in leading to abstraction than does the C(2) $\cdots$ H1(5) distance of  $2.91(5) \text{ \AA}$ . Other pertinent geometric factors considered in the abstraction process include the angle C(2)—C(3) $\cdots$ H1(5),  $\Delta_c$ , and the angle subtended by the C(3) to H1(5) vector and its projection on the plane of the C=C double bond,  $\tau_c$ ; these angles were found to be  $79.5$  and  $53.5^{\circ}$ , respectively. These values are comparable to those found in similar substituted naphthoquinols that were shown to undergo H abstraction by the  $\beta$ -enone carbon (Appel *et al.*, 1980; Greenhough & Trotter, 1980c).

Photochemical results of the present compound, although not fully characterized, do indicate clearly that H1(5) abstraction by C(3) is the major process taking place. Whereas the molecular geometry is also favorable to H(8) abstraction by O(1) as in naphthoquinone derivatives (Dzakpasu & Scheffer, 1977; Appel, Greenhough, Scheffer & Trotter, 1979) this reaction has yet to be observed in the current naphthoquinol series.

Acknowledgement is made to the Natural Sciences and Engineering Research Council Canada for financial support. We thank the University of British Columbia Computing Centre for assistance, and J. R. Scheffer and L. Walsh for crystals and photochemical results.

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