

The Structure of 4 α ,5,8,8 α -Tetrahydro-1-naphthoquin-4 α -ol* and Comparison with Some of Its Derivatives

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Abstract

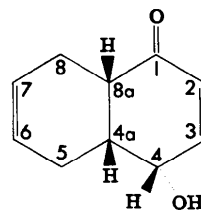
Crystals of 4 α ,5,8,8 α -tetrahydro-1-naphthoquin-4 α -ol are triclinic, space group $P1$, $a = 5.1689$ (3), $b = 7.9792$ (5), $c = 10.8212$ (7) Å, $\alpha = 81.087$ (5), $\beta = 81.059$ (5), $\gamma = 72.208$ (5)°, $Z = 2$; $R = 0.042$ for 1487 observed reflections. The molecule contains two fused six-membered rings twisted with respect to each other in the conformation which produces a pseudo-equatorial hydroxyl group. Molecules are linked *via* O...O hydrogen bonds. Irradiation of the crystals with ultraviolet light gives no photochemical conversion whereas in solution an intramolecular 2 + 2 cycloaddition is observed. The molecular structure is compared with other derivatives whose crystal structures and photochemical reaction pathways are known.

Introduction

The photochemical study of 4 α ,5,8,8 α -tetrahydro-1-naphthoquin-4 α -ol (I) and its methyl-substituted derivatives, with both 4 α -hydroxy and 4 β -hydroxy functions, has revealed photoproducts arising from intramolecular 2 + 2 cycloaddition in every substrate in solution, and either no solid-state reaction or H abstraction by the β -enone carbon (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980). A possible exception to this generalization is the 2,3,4 α ,8 α -tetramethyl 4 α -ol derivative, for which the primary photochemical reaction pathways in either solution or the solid state have not yet been fully assigned; products appear to include those arising from 2 + 2 cycloaddition and H abstraction by enone carbon in both cases (Appel, Scheffer & Walsh, 1979).

Crystals of (I) are photochemically unreactive but in solution intramolecular 2 + 2 cycloaddition occurs. The same situation occurs for the hexamethyl *syn* substrate (4 β -hydroxy *syn* to bridgehead substituents) and the 5 β ,8 β -dimethyl *anti* substrate, while the hexamethyl *anti* and tetramethyl *syn* derivatives under-

go photoconversion initiated by β -H abstraction by the β -enone carbon in the solid state (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980).



(1)

The present paper describes the analysis of the structure of (I) and comparison with its derivatives, which allows interpretation of the photochemical reactivity differences and provides structural data which might indicate the factors influencing the reaction pathways.

Experimental

Recrystallization of (I) from benzene afforded large, well formed colourless plates from which a fragment of dimensions *ca* 0.5 × 0.5 × 0.25 mm was cut. A series of precession photographs provided an initial unit cell and established the Laue symmetry $\bar{1}$ indicated by optical examination of the crystals with polarized light. Accurate unit-cell parameters were determined by a least-squares analysis of the setting angles of 25 reflections ($18^\circ < \theta < 22^\circ$; graphite-monochromated Mo $K\alpha$ radiation) automatically located and centred on an Enraf–Nonius CAD-4 diffractometer.

Crystal data

$C_{10}H_{12}O_2$, $M_r = 164.21$, triclinic, $a = 5.1689$ (3), $b = 7.9792$ (5), $c = 10.8212$ (7) Å, $\alpha = 81.087$ (5), $\beta = 81.059$ (5), $\gamma = 72.208$ (5)°, $V = 417.04$ (2) Å³, $Z = 2$, $D_x = 1.307$ Mg m⁻³, $\lambda = 0.71073$ Å, space group $P\bar{1}$.

The intensities were collected with an ω -2 θ scan, $\Delta\omega = (1.0 + 0.35 \tan \theta)^\circ$, an aperture 1 mm high and

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

($1.75 + 1.0 \tan \theta$) mm wide, a final acceptance limit of 30σ at $10.06^\circ \text{ min}^{-1}$ in ω , and a maximum recording time of 90 s. Of 1909 recorded intensities out to $\theta = 27.5^\circ$, 1487 (78%) had $I/\sigma(I) > 3$ with $\sigma^2(I) = S + B + (0.04S)^2$ (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 within $\pm 3\%$. These random fluctuations were corrected for during data processing where Lorentz and polarization corrections were applied.

Structure solution and refinement

All non-hydrogen atoms were located by direct methods by the use of *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) with 397 $|E|$ values > 1.2 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. There were two peaks corresponding to reasonable positions for the hydroxyl H atom; the proximity of each to its symmetry-related neighbour (1.1 and 1.5 Å) led to the

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

	<i>x</i>	<i>y</i>	<i>z</i>	Mean <i>U</i> (Å ²)*
C(1)	7198 (3)	8324 (2)	1119 (1)	40
C(2)	6762 (3)	10050 (2)	1556 (1)	45
C(3)	4936 (3)	10582 (2)	2522 (2)	47
C(4)	3172 (3)	9500 (2)	3251 (1)	42
C(4a)	4375 (2)	7538 (2)	3093 (1)	35
C(5)	6798 (3)	6627 (2)	3843 (1)	40
C(6)	8393 (3)	4857 (2)	3431 (2)	50
C(7)	8101 (4)	4304 (2)	2390 (2)	56
C(8)	6191 (4)	5371 (2)	1469 (2)	53
C(8a)	5166 (3)	7311 (2)	1687 (1)	39
O(1)	9078 (3)	7776 (2)	321 (1)	69
O(4)	2684 (3)	9834 (2)	4536 (1)	63
H(2)	778 (4)	1073 (2)	110 (2)	55
H(3)	469 (4)	1171 (3)	282 (2)	69
H(4)	133 (4)	996 (2)	289 (2)	58
H(4a)	299 (3)	696 (2)	339 (1)	42
H(51)	616 (4)	647 (2)	473 (2)	64
H(52)	802 (4)	741 (2)	376 (2)	53
H(6)	969 (5)	412 (3)	399 (2)	77
H(7)	912 (4)	315 (3)	215 (2)	75
H(81)	713 (4)	523 (2)	65 (2)	73
H(82)	466 (4)	488 (2)	152 (2)	64
H(8a)	351 (4)	792 (2)	124 (2)	55
H(O4)	116 (8)	983 (6)	500 (5)	76
H(O4')	392 (10)	969 (6)	478 (5)	76

* $10^3(U_{11} + U_{22} + U_{33})/3$; $\sigma = 1$ for non-hydrogen atoms, 6 for H atoms.

introduction of two half-weight H atoms, and the successful refinement of both confirmed the disorder. 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 gave $R = 0.042$ ($R = \sum | \Delta F | / \sum | F_o |$) for the 1487 observed reflections. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$, giving $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.063$ and σ_1 (goodness of fit) = 1.65. The mean and maximum shift/error on the final cycle of least squares were 0.007 and 0.102 respectively. Weighting analyses confirmed the suitability of the chosen weights. A difference Fourier synthesis after the final cycle showed random fluctuations of up to $\pm 0.1 \text{ e } \text{Å}^{-3}$. Final atomic coordinates are given in Table 1.*

Results and discussion

The structure of (I)

The molecular structure of (I) is illustrated in Fig. 1, showing the molecule adopting the conformation with the hydroxyl group pseudo-equatorial to the cyclohexenone moiety, with the two fused six-membered rings twisted with respect to each other about C(4a)–C(8a). Both these structural features are common to all the tetrahydronaphthoquinols so far studied in this series (Table 2), while the conformer observed for (I) is common to the other *anti* substrates (II), (V), and (VI). The staggering of the bridgehead H substituents by a torsion angle of $63 (1)^\circ$ is similar to that

* Lists of structure factors, thermal parameters, bond distances involving H atoms, and a packing diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35550 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

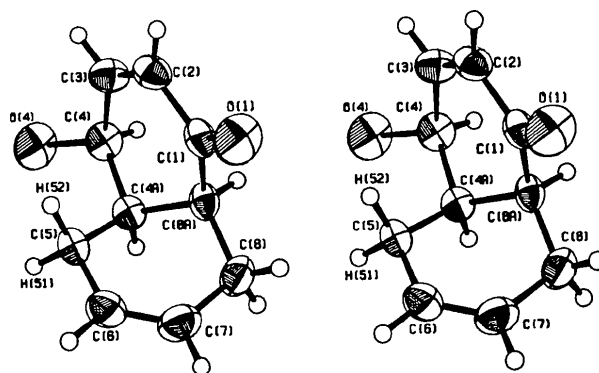


Fig. 1. Stereodiamagram of 4a β ,5,8,8a β -tetrahydro-1-naphthoquin-4a-ol. Thermal ellipsoids are drawn at the 50% probability level. [H atoms on C(8) are: upper = H(81), lower = H(82).]

in substrates (II)–(VI) and in various substituted tetrahydronaphthoquinones (Phillips & Trotter, 1977).

The consequences of the ring-flipped twisted conformation for (I) are an approach of H(52) towards the enone carbons 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. The C_β–H [C(3)···H(52)] intramolecular distance of 2.81 (2) Å is within the suggested limit of 2.90 Å (Scheffer & Dzakpasu, 1978) for H abstraction by enone carbon, and is similar to that in substrate (IV) where this is the primary photochemical reaction in the solid state (Table 2). The O(1)···H(81) distance is 2.49 (2) Å and the geometry again seems favourable for abstraction (Scheffer & Dzakpasu, 1978) although this reaction has not been observed in this series of tetrahydronaphthoquinols (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980).

The well separated non-parallel double bonds show that the observed intramolecular 2 + 2 cycloaddition in solution is probably facilitated by the presence of conformers which better fulfil the requirements for such a reaction (Schmidt, 1971; Scheffer & Dzakpasu, 1978; Appel, Greenhough, Scheffer, Trotter & Walsh, 1980).

Both six-membered rings are in distorted half-chair conformations with C(4a), C(8a) deviating by –0.504 (1), 0.223 (1) Å from the C(1) to C(4) plane and by 0.366 (1), –0.377 (1) Å from the C(5) to C(8) plane. The carbonyl group is only slightly non-planar with C(1) 0.008 (1) Å out of the mean plane of the group.

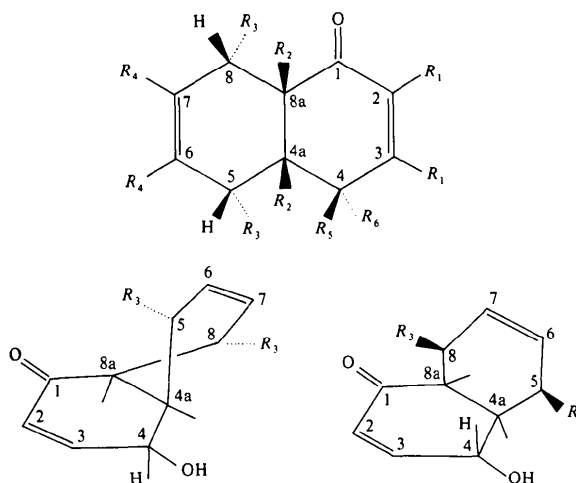
Molecules in the crystal are linked by hydrogen bonds to form chains running in the *a* direction. The hydrogen bonding is *via* disordered hydroxyl H atoms to give O(4)(*x,y,z*)···O(4)(1 – *x*, 2 – *y*, 1 – *z*) = 2.833 (3) Å and O(4)(*x,y,z*)···O(4)(–*x*, 2 – *y*, 1 – *z*) = 2.747 (3) Å. The O(4)···H and O(4)···H–O(4) parameters are 1.92 (4) Å, 161 (5)° and 2.16 (4) Å, 160 (4)°, although the half-weight H(O4) atoms are not well defined. The carbonyl oxygen O(1) is not involved in the hydrogen bonding as it is in substrates (II)–(VI), and it is perhaps noteworthy that each carbonyl-group plane in (I) is parallel to its two immediate centrosymmetrically related neighbours, with the C=O bonds in head-to-tail fashion and midpoint separations of 4.07 Å (*x,y,z* to 1 – *x*, 2 – *y*, –*z*) and 4.13 Å (*x,y,z* to 2 – *x*, 2 – *y*, –*z*). The crystal-packing diagram has been deposited.

Structures (I)–(VI)

Molecular-conformation parameters, bond lengths, bond angles, and torsion angles for the common part of structures (I) to (VI) are given in Tables 2, 3, 4, and 5, allowing substitution effects for this series of 4aβ-, 5,8,8aβ-tetrahydronaphthoquinols to be recognized.

The C(6)=C(7) distance shows a trend related to substitution, as do the bond angles at C(6) and C(7). With H at these positions the mean C(6)=C(7) distance is 0.023 Å less than with Me substituents, and the internal angles also show a decrease with Me at these positions. These effects are as found for various substituted tetrahydronaphthoquinones (Phillips & Trotter, 1977), although the concomitant increase in the C(5)–C(6) and C(7)–C(8) distances there is not convincingly reproduced here. These effects are more consistent with Me···Me steric interactions than with hybridization effects, since C(5)–C(6) and C(7)–C(8) seem relatively unaffected, although the external angles at C(6) and C(7) (not shown in Table 4) show mean

Table 2. Derivatives whose structures have been determined, with molecular conformations, parameters relevant to photochemical activity, and hydrogen-bond distances (distances in Å, angles in degrees)



The ring-flipped conformation common to all the *anti* substrates (OH *anti* to bridgehead substituents)

The ring-flipped conformation common to all the *syn* substrates (OH *syn* to bridgehead substituents)

Substrate	(I)	(II)	(III)	(IV)	(V) <i>A</i>	(V) <i>B</i>	(VI)
	This work	(<i>a</i>)	(<i>a</i>)	(<i>b</i>)	(<i>c</i>)	(<i>c</i>)	(<i>d</i>)
Reference*							
R ₁	H	Me	Me	Me	H	H	Me
R ₂	H	Me	Me	Me	H	H	Me
R ₃	H	H	H	H	Me	Me	H
R ₄	H	Me	Me	H	H	H	H
R ₅	H	H	OH	OH	H	H	H
R ₆	OH	OH	H	H	OH	OH	OH

The two independent molecules of (V) are denoted *A* and *B*. Hydrogen atoms in the table are all R₃, except for (V) where the H is a methyl (R₃) hydrogen. In the *anti* substrates H is at C(5) for C···H and at C(8) for O···H. In the *syn* substrates H is at C(8) for C···H.

* References are Greenhough & Trotter (1980*x*) where *x* is *a*, *b*, *c*, *d*.

Table 2 (cont.)

OH configuration	4 α <i>anti</i>	4 α <i>anti</i>	4 β <i>syn</i>	4 β <i>syn</i>	4 α <i>anti</i>	4 α <i>anti</i>	4 α <i>anti</i>
Intramolecular geometries*							
C α ...H	2.94 (2)	2.78 (2)	2.88 (2)	2.74 (4)	2.81 (2)	2.81 (2)	2.82 (2)
$\tau_{c\alpha}$	52.1	51.6	50.1	53.4	70.4	68.8	51.0
$\Delta_{c\alpha}$	71.3 (3)	73.3 (3)	77.9 (5)	80.7 (8)	88.2 (5)	90.2 (5)	74.7 (5)
C β ...H	2.81 (2)	2.72 (2)	2.92 (2)	2.85 (4)	2.78 (2)	2.67 (3)	2.78 (2)
$\tau_{c\beta}$	55.7	53.2	49.3	50.6	74.8	77.4	51.9
$\Delta_{c\beta}$	82.2 (4)	78.5 (3)	75.2 (5)	71.6 (8)	97.1 (5)	95.3 (8)	77.5 (5)
O...H	2.49 (2)	2.45 (2)	—	—	2.38 (3)	2.35 (3)	2.41 (3)
τ_o	0.6	4.8	—	—	12.7	8.7	1.3
Δ_o	81.8 (5)	82.7 (4)	—	—	103.2 (8)	106.3 (8)	84.3 (7)
C(3)...C(6)	4.381 (2)	4.400 (2)	4.471 (3)	4.369 (7)	4.486 (4)	4.471 (4)	4.371 (3)
C(2)...C(7)	4.392 (2)	4.417 (2)	4.490 (3)	4.393 (7)	4.460 (4)	4.493 (4)	4.343 (3)
d_1	4.35	4.37	4.44	4.35	4.44	4.45	4.32
C(1)...C(6)	3.404 (2)	3.396 (2)	—	—	3.428 (3)	3.479 (3)	3.263 (3)
O(1)...C(7)	3.395 (2)	3.430 (2)	—	—	3.385 (3)	3.484 (3)	3.233 (3)
θ	89	88	—	—	87	88	97
d_2	3.35	3.37	—	—	3.34	3.42	3.19
Hydrogen bonding							
O(1)...O(4)	—	2.802 (1)	2.846 (2)	2.770 (4)	2.809 (2)	2.815 (3)	2.782 (2)
O(4)...O(4)†	2.747 (3) 2.833 (3)	—	—	—	—	—	—
Primary photochemical reaction‡							
Solution	(1)	(1)	(1)	(1)	(1)	(1)	(1,2)?
Solid state	None	(2)	None	(2)	None	None	(1,2)?

* For the C...H interactions Δ_o is the C=C...H angle and τ_c is the angle between the C...H vector and the enone plane defined by $R_1-C_2=C_3-R_1$. For the O...H interactions Δ_o is the C=O...H angle and τ_o is the angle between the O...H vector and the carbonyl mean plane. d_1 is C=C centre-to-centre distance, d_2 is C=O, C(6)=C(7) centre-to-centre distance. θ is the angle between the normals to the carbonyl and C(5)—C(6)=C(7)—C(8) mean planes.

† For substrate (1) the hydrogen bonding is between hydroxyl groups *via* the disordered hydroxyl H atom.

‡ (1) Intramolecular 2 + 2 cycloaddition. (2) H abstraction by the β -enone carbon C(3).

Table 3. Bond distances (Å) with e.s.d.'s in parentheses for derivatives (I)–(VI)

	(I)	(II)	(III)	(IV)	(V)A	(V)B	(VI)
C(1)—C(2)	1.467 (2)	1.479 (2)	1.464 (3)	1.462 (6)	1.457 (3)	1.462 (3)	1.476 (3)
C(2)—C(3)	1.326 (2)	1.339 (2)	1.347 (3)	1.343 (6)	1.321 (3)	1.319 (3)	1.345 (3)
C(3)—C(4)	1.499 (2)	1.516 (2)	1.517 (3)	1.500 (6)	1.499 (3)	1.489 (3)	1.521 (3)
C(4)—C(4a)	1.524 (2)	1.535 (2)	1.532 (3)	1.509 (5)	1.517 (3)	1.518 (3)	1.536 (3)
C(4a)—C(5)	1.527 (2)	1.538 (2)	1.537 (3)	1.543 (6)	1.544 (3)	1.530 (3)	1.553 (3)
C(5)—C(6)	1.497 (2)	1.502 (2)	1.501 (3)	1.506 (8)	1.499 (3)	1.491 (4)	1.486 (3)
C(6)—C(7)	1.317 (2)	1.333 (2)	1.330 (3)	1.280 (8)	1.306 (4)	1.313 (4)	1.328 (4)
C(7)—C(8)	1.490 (2)	1.502 (2)	1.503 (3)	1.491 (7)	1.491 (4)	1.503 (4)	1.483 (3)
C(8)—C(8a)	1.518 (2)	1.536 (2)	1.542 (3)	1.549 (6)	1.525 (3)	1.532 (3)	1.536 (3)
C(8a)—C(1)	1.516 (2)	1.527 (2)	1.522 (3)	1.504 (6)	1.509 (3)	1.503 (3)	1.529 (3)
C(8a)—C(4a)	1.537 (2)	1.549 (2)	1.547 (3)	1.563 (5)	1.543 (3)	1.539 (3)	1.551 (3)
C(1)—O(1)	1.216 (2)	1.217 (2)	1.229 (2)	1.228 (4)	1.222 (2)	1.224 (2)	1.217 (2)
C(4)—O(4)	1.426 (2)	1.427 (2)	1.421 (3)	1.433 (5)	1.413 (3)	1.415 (3)	1.432 (3)

C(7)=C(6)— R_4 and C(6)=C(7)— R_4 greater than mean C(5)—C(6)— R_4 and C(8)—C(7)— R_4 by 9.5° with R_4 = Me [(II) and (III)], and by 6.1° with R_4 = H [(I), (IV), (V), and (VI)], although the four angles in (VI) do not differ significantly. Accompanying the geometrical changes at C(6) and C(7) are increases in the mean C(6)—C(5)—C(4a) and C(7)—C(8)—C(8a) angles by

3.9° when H at C(6) and C(7) is replaced by Me. The trend noted for the analogous tetrahydronaphthoquinone series (Phillips & Trotter, 1977) for C(4a)—C(5) to be consistently longer than C(8a)—C(8) is not noted here except in (V)A and (VI), although a lengthening of C(8)—C(8a) is generally noted when H at the C(4a), C(8a) bridgeheads is replaced by Me.

Table 4. Bond angles (°) with e.s.d.'s in parentheses for derivatives (I)–(VI)

	(I)	(II)	(III)	(IV)	(V) <i>A</i>	(V) <i>B</i>	(VI)
C(2)–C(1)–C(8a)	116.7 (1)	118.8 (1)	119.4 (2)	119.4 (3)	115.2 (2)	115.2 (2)	118.7 (2)
C(2)–C(1)–O(1)	120.5 (1)	119.7 (1)	121.0 (2)	119.6 (4)	121.3 (2)	121.0 (2)	120.0 (2)
C(8a)–C(1)–O(1)	122.8 (1)	121.3 (1)	119.4 (2)	120.9 (4)	123.5 (2)	123.9 (2)	121.1 (2)
C(1)–C(2)–C(3)	121.5 (1)	120.6 (1)	120.3 (2)	119.8 (4)	122.2 (2)	121.9 (2)	120.1 (2)
C(2)–C(3)–C(4)	123.6 (1)	122.5 (1)	122.0 (2)	121.8 (4)	123.1 (2)	123.6 (2)	122.5 (2)
C(3)–C(4)–C(4a)	112.0 (1)	114.0 (1)	114.2 (2)	114.6 (3)	112.8 (2)	112.2 (2)	114.2 (2)
C(3)–C(4)–O(4)	109.4 (1)	110.9 (1)	106.8 (2)	109.3 (4)	108.2 (2)	108.1 (2)	109.9 (2)
C(4a)–C(4)–O(4)	112.9 (1)	106.9 (1)	111.7 (2)	109.4 (3)	114.6 (2)	113.9 (2)	107.0 (2)
C(4)–C(4a)–C(5)	113.0 (1)	109.4 (1)	109.1 (2)	108.8 (4)	116.1 (2)	115.6 (2)	109.4 (2)
C(4)–C(4a)–C(8a)	109.6 (1)	109.7 (1)	108.6 (2)	108.7 (3)	109.4 (2)	109.1 (2)	109.5 (2)
C(8a)–C(4a)–C(5)	111.1 (1)	108.7 (1)	108.5 (2)	109.0 (4)	112.2 (2)	112.6 (2)	108.6 (2)
C(4a)–C(5)–C(6)	112.2 (1)	115.1 (1)	116.1 (2)	112.2 (2)	110.2 (2)	109.8 (2)	113.4 (2)
C(5)–C(6)–C(7)	123.8 (1)	122.3 (1)	122.3 (2)	125.3 (5)	125.6 (3)	124.5 (3)	124.2 (2)
C(6)–C(7)–C(8)	124.3 (1)	121.8 (1)	121.7 (2)	123.6 (6)	124.2 (3)	125.1 (3)	122.6 (2)
C(7)–C(8)–C(8a)	111.8 (1)	115.7 (1)	114.7 (2)	112.2 (5)	110.1 (2)	110.1 (2)	113.1 (2)
C(8)–C(8a)–C(1)	112.7 (1)	110.6 (1)	106.2 (2)	107.7 (4)	117.9 (2)	118.4 (2)	110.1 (2)
C(8)–C(8a)–C(4a)	111.7 (1)	109.8 (1)	109.6 (2)	109.8 (3)	110.2 (2)	109.7 (2)	110.5 (2)
C(4a)–C(8a)–C(1)	110.1 (1)	109.3 (1)	109.8 (2)	107.3 (3)	109.4 (2)	109.7 (2)	107.9 (2)

Table 5. Torsion angles (°) with e.s.d.'s in parentheses for derivatives (I)–(VI)

	(I)	(II)	(III)	(IV)	(V) <i>A</i>	(V) <i>B</i>	(VI)
C(1)–C(2)–C(3)–C(4)	0.1 (2)	4.9 (1)	4.3 (2)	–2.6 (5)	–2.5 (3)	–3.9 (3)	6.6 (2)
C(2)–C(3)–C(4)–C(4a)	20.8 (2)	16.3 (1)	18.9 (2)	21.2 (5)	18.2 (3)	20.9 (3)	12.4 (2)
C(3)–C(4)–C(4a)–C(8a)	–49.1 (1)	–46.9 (1)	–48.9 (2)	–49.2 (4)	–46.0 (2)	–48.0 (2)	–45.5 (2)
C(4)–C(4a)–C(8a)–C(1)	58.1 (1)	56.3 (1)	56.4 (2)	58.5 (4)	59.6 (2)	60.1 (2)	58.8 (2)
C(4a)–C(8a)–C(1)–C(2)	–38.6 (1)	–37.9 (1)	–36.6 (2)	–43.5 (4)	–45.1 (2)	–44.1 (2)	–42.8 (2)
C(8a)–C(1)–C(2)–C(3)	9.4 (2)	7.0 (1)	5.4 (2)	15.6 (5)	16.8 (2)	16.3 (2)	10.0 (2)
C(4a)–C(5)–C(6)–C(7)	12.9 (2)	16.9 (1)	13.9 (2)	15.2 (6)	11.4 (2)	15.2 (3)	14.8 (2)
C(5)–C(6)–C(7)–C(8)	1.2 (2)	0.9 (2)	–0.1 (2)	–0.9 (7)	–2.7 (3)	–2.3 (3)	–0.5 (3)
C(6)–C(7)–C(8)–C(8a)	14.6 (2)	13.0 (2)	17.5 (2)	17.3 (6)	21.9 (3)	18.1 (3)	16.9 (3)
C(7)–C(8)–C(8a)–C(4a)	–43.6 (1)	–42.9 (1)	–47.1 (2)	–46.5 (4)	–49.0 (2)	–45.6 (2)	–46.7 (2)
C(8)–C(8a)–C(4a)–C(5)	58.4 (1)	58.2 (1)	58.5 (2)	60.2 (4)	60.4 (2)	62.0 (2)	59.7 (2)
C(8a)–C(4a)–C(5)–C(6)	–41.6 (1)	–46.2 (1)	–43.0 (2)	–43.8 (5)	–39.6 (2)	–44.6 (2)	–43.4 (2)
<i>R</i> ₂ –C(4a)–C(8a)– <i>R</i> ₂ *	63 (1)	59.9 (1)	58.6 (2)	58.1 (5)	62 (2)	61 (2)	63.0 (2)
C(4)–C(4a)–C(8a)–C(8)	–176.0 (1)	177.8 (1)	–60.0 (2)	–58.3 (4)	–169.2 (2)	–168.3 (2)	179.1 (2)
C(1)–C(8a)–C(4a)–C(5)	–67.5 (1)	–63.2 (1)	174.8 (2)	177.0 (4)	–70.8 (2)	–70.0 (2)	–60.6 (2)
C(3)–C(4)–C(4a)–C(5)	75.4 (1)	72.3 (1)	–167.0 (2)	–167.8 (4)	82.2 (2)	80.1 (2)	73.4 (2)
C(8)–C(8a)–C(1)–C(2)	–164.0 (1)	–158.9 (1)	81.8 (2)	74.6 (4)	–172.0 (2)	–171.0 (2)	–163.4 (2)
O(1)–C(1)–C(8a)–C(4a)	143.0 (1)	147.6 (1)	147.1 (2)	139.2 (4)	136.1 (2)	137.4 (2)	142.8 (2)
O(1)–C(1)–C(8a)–C(8)	17.6 (2)	26.7 (2)	–94.4 (2)	–102.7 (4)	9.2 (3)	10.6 (2)	22.2 (2)
O(1)–C(1)–C(2)–C(3)	–172.1 (1)	–178.5 (1)	–178.3 (2)	–167.0 (4)	–164.3 (2)	–165.3 (2)	–175.5 (2)
O(4)–C(4)–C(3)–C(2)	146.7 (2)	137.0 (1)	142.8 (2)	144.4 (4)	146.0 (2)	147.2 (2)	132.6 (2)
O(4)–C(4)–C(4a)–C(5)	–48.6 (1)	–50.6 (1)	71.8 (2)	69.1 (4)	–42.2 (2)	–43.1 (2)	–48.5 (2)
O(4)–C(4)–C(4a)–C(8a)	–173.1 (1)	–169.8 (1)	–170.2 (2)	–172.3 (3)	–170.4 (2)	–171.1 (2)	–167.4 (2)

* Bridgehead twist torsion angle. See Table 2.

Replacing H by Me as the bridgehead *R*₂ substituent affects the angles involving C(4a) and C(8a), with changes in mean values of –3.3 and –2.7° for C(8a)–C(4a)–C(5) and O(1)–C(1)–C(8a), +3.4° for C(2)–C(1)–C(8a), +1.9° for C(3)–C(4)–C(4a), –5.7° for C(4)–C(4a)–C(5), and –7.7° for C(1)–C(8a)–C(8), although the latter two angles mainly reflect *R*₃···Me steric interactions in (V).

The bridgehead torsion angle *R*₂–C(4a)–C(8a)–*R*₂ seems unaffected by substitution changes at the bridgeheads, remaining constant at ca 60°. The internal

twist angle, represented by C(1)–C(8a)–C(4a)–C(5) in the *anti* substrates and C(8)–C(8a)–C(4a)–C(4) in the *syn*, is in the range –67.5 (1) to –70.8 (2)° for *R*₂ = H and –58.3 (4) to –63.2 (1)° for *R*₂ = Me, following the trend observed in several analogous naphthoquinone derivatives (Phillips & Trotter, 1977). The C(2)=C(3) bond of the hydroxycyclohexenone ring is affected by Me substitution at C(2) and C(3) in a similar manner to C(6)=C(7), with the mean value 0.022 Å less for *R*₁ = H [1.319 (3)–1.326 (2) Å] than for *R*₁ = Me [1.339 (2)–1.347 (3) Å]. The internal C(2) and C(3)

angles are less affected than those at C(6) and C(7), with a decrease in mean value of only 1.5° when H is replaced by Me at those positions.

All six-membered rings are in half-chair conformations (Bucourt & Hainaut, 1965) with C(1) to C(4) and C(5) to C(8) forming approximate planes, with the sum of the deviations of C(4a) and C(8a) from these planes in the range $0.72\text{--}0.78$ Å for all the substrates. The C(4a) deviation from the C(1) to C(4) plane ranges from -0.392 (2) Å in (V)A to -0.529 (2) Å in (III), greater in each case than the C(8a) deviation from this plane which is in the range 0.205 (2) to 0.354 (3) Å. Apart from substrate (II), the C(4a) and C(8a) deviations from the C(5) to C(8) mean plane are in the ranges 0.241 (2) to 0.356 (4) and -0.377 (1) to -0.488 (2) Å respectively. In substrate (II) the amount of deviation is reversed with C(4a) 0.420 (1) Å out of plane and C(8a) -0.329 (1) Å; the reasons for this are not clear since the two $\text{H}(4)\cdots R_3$ intramolecular contacts which might be expected to produce this torsional change are present only in the *syn* substrates (III) and (IV) [e.g. $\text{H}(4)\cdots\text{H}(82) = 2.27$ (3) in (III) and 2.25 (5) Å in (IV)]. Apart from the intramolecular contacts and torsion angles which characterize the *syn* and *anti* conformations, none of the parameters in Tables 2–5 show discernible or convincing trends which can be related to the conformation adopted.

In all of the substrates except (I) the crystal packing is dominated by hydrogen bonding between O(1) of one molecule and O(4) of a molecule one cell translation away to form chains of molecules running in the *a* direction for (II), (III), and (IV) and in the *b* direction for (VI) and the two chains (*A*...*A*...*A*... and *B*...*B*...*B*...) in (V). The O...O distances range from 2.770 (4) to 2.846 (2) Å. The exception to this general observation, substrate (I), exhibits intermolecular hydrogen bonds between neighbouring hydroxyl groups through disordered hydroxyl H atoms, with the carbonyl not involved in the hydrogen bonding. In none of the substrates studied are there close intermolecular approaches (<4.3 Å) of roughly parallel C=C bonds, in approximately parallel enone planes, such that the bonds superpose when viewed perpendicular to one enone plane. A similar lack of correlation exists in the C=O to C=O and C=O to C=C intermolecular relationships. Even in (I) where the carbonyl planes are parallel with midpoint C=O separations of *ca* 4.1 Å, with parallel C=O bonds, the C=O midpoints for the two cases are well separated (1.8 and 4.1 Å) when the two groups are viewed in projection perpendicular to the carbonyl planes.

The photochemistry of the substrates in solution and the solid state has been discussed elsewhere (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980). The relevant geometrical details and primary photochemical reactions are given in Table 2.

The crystallographic results show that substrates

(I)–(VI) are not in conformations which fulfil the requirements for successful $2 + 2$ cycloaddition according to the criteria for this mechanism in intermolecular cases (Schmidt, 1971; Scheffer & Dzakpasu, 1978); that (I), (III), and (V) are unreactive in the solid state indicates that similar geometrical relationships apply to intramolecular $2 + 2$ cycloaddition. Furthermore, the similarity between the C=C relationships in (I) and (VI) suggests that the unresolved solid-state photochemistry of (VI) is unlikely to reveal intramolecular $2 + 2$ cycloaddition as a primary reaction pathway. Substrates (I)–(VI) all undergo this photochemical reaction in solution, probably *via* the presence of conformers which better fulfil the requirements for such a mechanism (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980).

Of the substrates (I)–(V) only the hexamethyl *anti* (II) and tetramethyl *syn* (IV) undergo photoconversion in the solid state, both by abstraction of a hydrogen by the β -enone carbon. A preference for H abstraction by the β rather than α -enone carbon is indicated since the $C_\alpha\cdots\text{H}$ and $C_\beta\cdots\text{H}$ parameters are similar in each substrate. Inspection of the data in Table 2 shows that the solid-state-unreactive substrate (I) has a $C_\beta\cdots\text{H}$ relationship which conforms to the geometrical requirements necessary for such an abstraction (Scheffer & Dzakpasu, 1978). The $C_\beta\cdots\text{H}$ distance in the *syn* substrate (III), which has no other solid-state photoconversion mechanism available, is close to the suggested limit of 2.90 Å for successful abstraction. The reasons for the unreactivity of (I) in the solid state are not clear; possibilities include the lack of hydrogen bonding to the carbonyl, the unsubstituted enone carbons C(2) and C(3), or simply that the $C_\beta\cdots\text{H}$ distance is too long for successful abstraction in the case of these tetrahydronaphthoquinols. Should (VI) prove to be unreactive *via* this mechanism then only the last of these particular possibilities remains. For substrate (V) the H atom in the $C_\beta\cdots\text{H}$ relation is a methyl hydrogen.

The O... β -H separation and geometrical relationships in the *anti* substrates (I), (II), and (VI) seem favourable for the β -H abstraction process observed in several tetrahydronaphthoquinones (Scheffer & Dzakpasu, 1978; Phillips & Trotter, 1977) where distances ranging between 2.26 (3) and 2.58 (3) Å produced this primary photochemical reaction. For substrate (V) the H in the O...H relationship is a methyl (γ) hydrogen; successful abstraction of γ -H by O was observed in solution for the naphthoquinone analogue of (V) (Dzakpasu, Phillips, Scheffer & Trotter, 1976) with an O...H separation of 2.38 (3) Å (Phillips & Trotter, 1977). That (I) and (V), both with seemingly favourable O...H relationships, are unreactive in the solid state suggests that H abstraction by O either does not occur with the enone chromophore of substrates (I)–(VI), or does not occur as easily as with

the 2-ene-1,4-dione chromophore of their diketone analogues (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980).

The intramolecular relationship between C(1)=O(1) and C(6)=C(7) (Table 2) in the *anti* substrates is similar to that in the naphthoquinone analogues (Scheffer & Dzakupasu, 1978), of which the analogue of (V) with CN bridgehead substituents undergoes an intramolecular 2 + 2 cycloaddition between C=O and C=C in both solution and the solid state (Scheffer, Jennings & Louwerens, 1976). This relationship in substrate (VI) is remarkably similar to that observed in the reactive naphthoquinone analogue of (V) and is clearly the most favourable of those observed in these naphthoquinols.

The molecular geometries of the structures so far determined in this series provide much useful information concerning solid-state/solution photochemical reactivity differences (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980) and geometrical requirements for photoconversion in the solid state. The reason for the observed solid-state/solution reactivity differences appears to be crystal-lattice control in a molecular-conformational sense (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980), as opposed to the least-atomic-motion sense as observed for 2,3,4 $\alpha\beta$,6,7 β ,8 $\alpha\beta$ -hexamethyl-4a,7,8,8a-tetrahydro-1,4-naphthoquinone (Appel, Greenhough, Scheffer & Trotter, 1979) where the differing solid-state and solution photoreactions are assumed to proceed from the same molecular conformation. The geometrical data given in Table 2, particularly for substrate (I), suggest either that the distances required for successful photoconversion in the solid state are somewhat less in the hydroxycyclohexenones than in their diketone analogues, or that other molecular or intermolecular features play a role in determining the solid-state primary photochemical reaction pathways. The data also suggest that the most probable primary photo-reaction of (VI) in the solid state is H abstraction by C _{β} , although the relationships for both oxetane formation (C=O to C=C addition) and 2 + 2 cycloaddition are the most favourable in the structurally characterized substrates.

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