

Fig. 5. Valeur moyenne des angles pour les trois iodures.

angulaires peuvent influencer sur les déplacements chimiques des carbones porteurs des groupes en *syn* et en *anti* de l'ammonium, on peut admettre que l'effet en est identique dans les trois hydrazoniums puisqu'elles sont les mêmes. Par conséquent la comparaison des résultats obtenus en RMN pour les trois cations apparaît raisonnable.

Concernant l'hydrazonium (3*E*), si le blindage du carbone méthylé *syn* C(2) semble résulter de l'encombrement stérique du groupe ammonium, il est vraisemblable au vu de la structure (Fig. 4) qu'il existe aussi une interaction γ entre le groupe isopropyle et ce carbone C(2); la position des méthyles de ce groupe à 'l'intérieur' de l'angle C(2)—C(1)—C(3) et la position de l'hydrogène H(1) la rendent possible sinon probable. Ainsi le blindage de C(2) résulterait de deux effets stériques simultanés. Par ailleurs on peut remarquer que le carbone méthinique C(3) est libre de toute interaction stérique dans le système des atomes N(2), C(1), C(3) ce qui contribuerait à la valeur importante de son déplacement chimique.

Pour l'hydrazonium (1*E*), par analogie avec (3*E*) et compte tenu que le déplacement chimique de l'atome C(2) a presque la même valeur, on peut tout aussi vraisemblablement interpréter le blindage par deux interactions stériques, l'une avec le groupement ammonium et l'autre avec le groupement phényle.

Enfin pour le cation (2) la suggestion que chacun des carbones méthiniques C(2) et C(3) subisse un effet de blindage semble devoir être confirmée. En effet pour l'atome C(2) il s'agirait du blindage par interaction stérique avec l'ammonium constaté aussi dans les cations (1*E*) et (3*E*). Pour l'atome C(3) le blindage proviendrait d'une interaction γ avec le groupe isopropyle *syn*, étant donné la position de l'hydrogène H(2) et celles des méthyles de l'isopropyle *syn* à 'l'intérieur' de l'angle C(2)—C(1)—C(3) (Fig. 3). Autrement dit il s'agirait d'un effet d'engrenage induit par effet stérique de l'ammonium, responsable des conformations privilégiées observées pour les deux groupes isopropyle. Cet effet d'engrenage n'existant ni dans la diméthyl-2,4 pentanone-3 ni dans l'hydrazonium (3*E*), les atomes de carbone méthinique de ces deux composés doivent donc être déblindés par rapport à ceux de (2): c'est effectivement ce que nous avons observé.

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Structure of 2,3,4 α ,4 $\alpha\beta$,6,7,8 $\alpha\beta$ -Heptamethyl-4 $\alpha\beta$,5,8,8 $\alpha\beta$ -tetrahydro-1-naphthoquin-4 β -ol* and a Comparison with Four Other Derivatives

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Abstract

Crystals of C₁₇H₂₆O₂, *M_r* = 262.4, are monoclinic, *P*2₁/*c*, *a* = 7.497 (2), *b* = 16.792 (3), *c* =

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

12.687 (3) Å, β = 105.30 (1)°, *Z* = 4, *D_c* = 1.141, *D_o* = 1.140 g cm⁻³. The structure was solved by direct methods and the subsequent structural refinement yielded a final *R* value of 0.041 for 1934 reflections. Despite the *syn* hydroxyl group, the bulkier methyl causes the molecules to adopt a conformation typical of

OH-*anti* derivatives. The photochemical reaction in the solid state is accounted for on the basis of the molecular geometry, and a comparison is made with four other tetrahydronaphthoquinol derivatives.

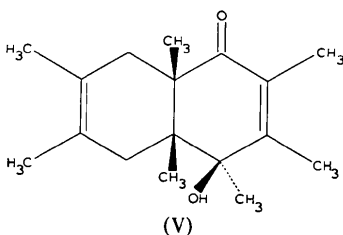
Introduction

Solid-state/solution photoreactivity differences have been observed in various substituted tetrahydronaphthoquinols (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980*a,b*; Appel, Herbert, Jiang, Scheffer & Walsh, 1982). The divergence in reactivity patterns has been rationalized mainly by considering the fundamental distinction between the two phases, namely rigidity in the lattice *versus* mobility in solution. Reactions in solution, where molecular conformational equilibration is facile, are governed chiefly by kinetics, whereas the solid-state reactions are topochemically controlled. This lattice control can be exploited by designing a molecule so that its lowest-energy conformation (in which it is most likely to crystallize) is one which predisposes the molecule to a specific reaction.

In an effort to test this conformational argument the title compound was synthesized. This structural study was undertaken to verify the predicted conformation and to elucidate the geometric parameters involved in the observed photochemical reaction. A comparison of this compound and four other tetrahydronaphthoquinol derivatives (I)–(IV) is made in an attempt to ascertain substituent effects on the various structures and their reactivities.

Experimental

The title compound was prepared by methyl lithium treatment of the ene-dione, 2,3,4*αβ*,6,7,8*αβ*-hexamethyl-1,4-naphthoquinone. The two epimers formed were separated by fractional crystallization from cyclohexane/ethyl acetate which yielded acicular crystals of (V).



Data were collected on an Enraf–Nonius CAD-4 diffractometer with a crystal of dimensions 0.1 × 0.2 × 0.4 mm and graphite-monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$, $\mu = 0.675 \text{ cm}^{-1}$). 3516 reflections were collected in the θ range 0.0–27.5° with an ω – θ scan type. The ω scan width was calculated from the expression $(0.80 + 0.35 \tan \theta)^\circ$ and extended 25% on

each side of the peak for background measurement. The vertical aperture was constant at 4 mm and the horizontal width was varied with θ according to the relationship $(2.00 + 1.00 \tan \theta) \text{ mm}$. In an attempt to improve the accuracy of the data, a non-equal test, whereby two final scans are performed in opposite directions, was applied to each reflection. The odd and even increments in the 96-step intensity profile were compared on a statistical basis and a difference between corresponding values in the two scans of more than one standard deviation was the criterion for a repeat of measurement; failure a second time caused that reflection to be tagged making it readily identifiable after data processing.

Processing the data, which included Lorentz and polarization corrections applied in the usual manner, indicated that no reflection failed the non-equal test twice. Of the 3516 reflections collected, 1934 (55.0%) had $I \geq 3\sigma(I)$ where $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$, S being the scan count and B the time-averaged background.

Solution and refinement

The positions of the 19 non-hydrogen atoms were located by *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Isotropic refinement, followed by two anisotropic cycles and a subsequent difference-Fourier synthesis yielded the coordinates for the 26 H atoms. Refinement continued until convergence at $R = 0.041$ and $R_w = 0.056$, where $R = \sum ||F_o| - k|F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - k|F_c|)^2 / \sum w|F_o|^2]^{1/2}$. The quantity $\sum w(|F_o| - k|F_c|)^2$ was minimized throughout the least-squares refinement. Towards the end of refinement the weighting scheme was changed from unit weights to $w = 1/\sigma^2(F)$ where $\sigma^2(F)$ is calculated from the $\sigma^2(I)$ defined above. A weighting analysis confirmed the suitability of the chosen weights. Following convergence a final difference synthesis was calculated. The resulting map indicated residual density of 0.2 e \AA^{-3} in the region of O(4). This residue is possibly due to one of the O lone pairs. The mean parameter shift on the final cycle of refinement was 0.198 σ . The maximum shift of 1.290 σ corresponded to the oscillating temperature factor of the methyl H atom H1(21). The standard deviation in an observation of unit weight was 1.77. Scattering factors for the non-hydrogen atoms were taken from Cromer & Mann (1968) while those for the H atoms were from Stewart, Davidson & Simpson (1965). Final atomic coordinates are given in Table 1.*

* Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving hydrogen atoms, torsion angles and a packing diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36799 (39 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 $\times 10^5$, H $\times 10^3$) and isotropic thermal parameters ($U \times 10^3 \text{ \AA}^2$)

U_{eq} is one third the trace of the diagonalized anisotropic temperature factor matrix. $\sigma(U_{\text{eq}}) \approx 1 \times 10^3 \text{ \AA}^2$.

	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$
C(1)	85627 (25)	11022 (13)	72597 (15)	41
C(2)	77531 (27)	3371 (13)	68018 (15)	43
C(21)	89061 (42)	-1482 (23)	62201 (27)	70
C(3)	60946 (28)	1079 (12)	68910 (16)	42
C(31)	52062 (46)	-6420 (20)	63359 (33)	72
C(4)	49635 (25)	5859 (12)	75154 (15)	40
C(41)	41960 (40)	191 (19)	82425 (24)	62
C(4a)	60761 (24)	12836 (12)	81957 (15)	36
C(4a1)	47429 (35)	18757 (16)	85213 (23)	54
C(5)	74006 (29)	9490 (13)	92495 (16)	41
C(6)	89347 (27)	14904 (13)	98534 (16)	44
C(61)	98744 (50)	11991 (23)	109961 (21)	69
C(7)	93887 (28)	21435 (13)	94122 (17)	47
C(71)	108809 (50)	27135 (23)	99922 (30)	78
C(8)	84279 (33)	23770 (14)	82623 (19)	49
C(8a)	72905 (25)	17195 (12)	75529 (15)	37
C(8a1)	62208 (36)	20932 (18)	64595 (20)	54
O(1)	101829 (19)	12595 (10)	73321 (14)	64
O(4)	34349 (19)	8803 (10)	66657 (12)	51
H1(21)	818 (6)	-26 (2)	549 (4)	145 (14)
H2(21)	903 (6)	-68 (3)	646 (4)	150 (18)
H3(21)	989 (8)	13 (3)	612 (4)	182 (20)
H1(31)	384 (5)	-65 (2)	623 (2)	93 (10)
H2(31)	552 (6)	-108 (2)	680 (3)	127 (15)
H3(31)	545 (5)	-71 (2)	562 (3)	110 (12)
H1(41)	353 (3)	33 (1)	871 (2)	64 (7)
H2(41)	327 (4)	-35 (2)	777 (2)	79 (9)
H3(41)	523 (4)	-32 (2)	873 (2)	73 (8)
H1(O4)	246 (4)	95 (2)	690 (2)	86 (9)
H1(4a1)	380 (4)	157 (2)	884 (2)	74 (7)
H2(4a1)	539 (4)	228 (2)	900 (2)	66 (8)
H3(4a1)	398 (4)	215 (2)	788 (2)	75 (8)
H1(5)	795 (3)	44 (1)	908 (2)	43 (5)
H2(5)	668 (3)	79 (1)	975 (2)	61 (7)
H1(61)	1008 (5)	61 (2)	1103 (3)	123 (13)
H2(61)	1096 (6)	137 (2)	1122 (4)	136 (17)
H3(61)	918 (7)	135 (3)	1160 (4)	161 (18)
H1(71)	1179 (6)	277 (2)	960 (4)	128 (16)
H2(71)	1036 (6)	329 (3)	977 (4)	166 (19)
H3(71)	1139 (6)	259 (2)	1074 (4)	137 (15)
H1(8)	931 (4)	254 (1)	790 (2)	63 (7)
H2(8)	752 (3)	284 (1)	822 (2)	66 (7)
H1(8a1)	561 (4)	171 (2)	599 (2)	69 (9)
H2(8a1)	712 (4)	233 (2)	610 (3)	99 (10)
H3(8a1)	533 (4)	251 (1)	655 (2)	71 (8)

Discussion

Molecules of (V) crystallize with the conformation common to all naphthoquinols studied in this series in which the bulkier substituent on C(4) assumes the pseudo-equatorial position. Although the 4-OH is *syn** to the bridgehead methyl groups, the conformation

* *cis* (or *trans*) is used here to specify the configuration of ring junction, and *syn* (or *anti*) to specify relation between the ring junction and the rest of the molecule.

adopted (Fig. 1) is characteristic of the naphthoquinols which have the hydroxyl group *anti* to the bridgehead substituents, *i.e.* a half-chair cyclohexene ring *cis*-fused to a half-chair cyclohexenone moiety, with the bulkier 4-methyl substituent pseudo-equatorial. The degree of twist in the conformation is described by the C(1)–C(8a)–C(4a)–C(5) torsion angle of $62.2(2)^\circ$. The spatial consequence of this arrangement is the proximity of the β -enone carbon, C(3), to H1(5) [2.81(2) Å]. Furthermore, the angle between the C(3)···H1(5) vector and its projection on the plane of the C(3)=C(2) double bond [C(1), C(2), C(3), C(4)], τ_c , and the angle between the C(3)···H1(5) and the C(3)=C(2) vectors, Δ_c , are 50 and $78.3(4)^\circ$ (Table 2), respectively. This geometry is highly favorable for H abstraction by the β -enone C and it is therefore not surprising that this is the dominant reaction observed in the solid-state photolysis (Jiang, Scheffer, Secco & Trotter, 1981). Irradiation in solution affords only the intramolecular 2 + 2 cycloaddition photoproduct, probably due to the presence of a high-energy conformer not available in the crystal lattice.

It is interesting to note that O abstraction of a β -H from C(8) does not occur despite molecular fulfillment of the geometric requirements. The β -H deviates only 1° from the plane of the carbonyl at a distance of 2.41(2) Å from O(1). The C=O··· β -H angle of $82.7(6)^\circ$ completes the almost perfect alignment of the β -H with the non-bonding orbital of O(1). However, 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 from which the C abstraction of H1(5) is considered to originate. The lack of β -H abstraction by O in this system lends support to the above argument but does little to clarify the role(s) of the C(2) and C(3) substituents.

Bond distances and angles (Tables 3–5) generally do not deviate significantly from accepted values with the

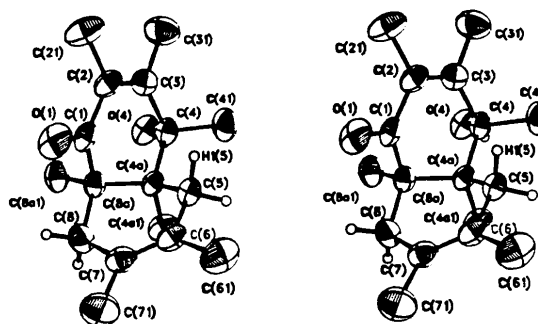
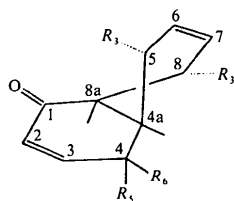
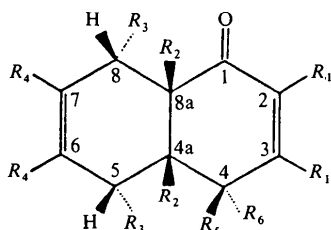


Fig. 1. Stereodiagram of 2,3,4 α ,4a β ,6,7,8a β -heptamethyl-4a β ,5,8,8a β -tetrahydro-1-naphthoquin-4 β -ol. Thermal ellipsoids are at 50% probability. H1(8) is the upper H on C(8).

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



The conformation common to all *anti* derivatives [the bulkier group on C(4) is *anti* to bridgehead substituents]

Compounds	(I)	(II)	(III)	(IV)	(V)
Reference*	(a)	(b)	(b)	(c)	(d)
R_1	H	Me	H	Me	Me
R_2	H	H	H	H	Me
R_3	H	H	H	H	H
R_4	H	H	Me	Me	Me
R_5	H	H	H	H	OH
R_6	OH	OH	OH	OH	Me

	(I)	(II)	(III)	(IV)	(V)
Intramolecular geometries†					
C(2)···H1(5)	2.94 (2)	2.92 (4)	2.92 (3)	2.91 (5)	2.86 (2)
$\tau_{C(2)}$	52.1	52.0	53.8	51.7	48.9
$\Delta_{C(2)}$	71.3 (3)	73.2 (7)	72.5 (7)	73 (1)	74.5 (4)
C(3)···H1(5)	2.81 (2)	2.84 (4)	2.82 (3)	2.84 (5)	2.81 (2)
$\tau_{C(3)}$	55.7	54.1	56.7	53.5	50.0
$\Delta_{C(3)}$	82.2 (4)	79.7 (8)	80.9 (7)	79 (1)	78.3 (4)
O···H1(8)	2.49 (2)	2.49 (4)	2.49 (4)	2.58	2.41 (2)
τ_O	0.6	1	4	3	1
Δ_O	81.8 (5)	83 (1)	81 (1)	89	82.7 (6)
C(3)···C(6)	4.381 (2)	4.442 (5)	4.397 (6)	4.457 (3)	4.453 (3)
C(2)···C(7)	4.392 (2)	4.427 (5)	4.427 (6)	4.457 (3)	4.419 (3)
d_1	4.35	4.40	4.37	4.42	4.40
C(1)···C(6)	3.404 (2)	3.379 (5)	3.414 (5)	3.415 (3)	3.293 (3)
O(1)···C(7)	3.395 (2)	3.332 (4)	3.419 (5)	3.487 (5)	3.217 (3)
θ	89	88	90	87	98
d_2	3.35	3.30	3.36	3.38	3.19
Hydrogen bonding					
O(1)···O(4)	—	—	—	2.652 (5)	2.855 (2)
O(4)···O(4)	2.747 (3)	2.830 (2)	2.783 (2)	2.804 (2)	—
	2.833 (3)				
Primary photochemical reaction‡					
Solution	(1)	(1)	(1)	(1)	(1)
Solid state	(2,3)	(2)	(2,3)	(2)	(2)

* References: (a) Greenhough & Trotter (1981); (b) Secco & Trotter (1982b); (c) Secco & Trotter (1982a); (d) this work.

† For the C···H interactions Δ_C 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 the C=C center-to-center distance, d_2 is the C=O, C(6)=C(7) center-to-center distance. θ is the angle between the normals to the carbonyl and the C(5)–C(6)=C(7)–C(8) mean planes.

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

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

	(I)	(II)	(III)	(IV)	(V)
C(1)–C(2)	1.467 (2)	1.471 (5)	1.463 (6)	1.484 (3)	1.473 (3)
C(2)–C(3)	1.326 (2)	1.351 (5)	1.321 (5)	1.339 (3)	1.335 (3)
C(3)–C(4)	1.499 (2)	1.514 (5)	1.487 (6)	1.505 (3)	1.531 (3)
C(4)–C(4a)	1.524 (2)	1.518 (5)	1.519 (6)	1.514 (3)	1.560 (3)
C(4a)–C(5)	1.527 (2)	1.530 (5)	1.521 (6)	1.515 (3)	1.545 (3)
C(5)–C(6)	1.497 (2)	1.497 (5)	1.520 (6)	1.484 (3)	1.507 (3)
C(6)–C(7)	1.317 (2)	1.310 (5)	1.327 (5)	1.339 (3)	1.316 (3)
C(7)–C(8)	1.490 (2)	1.489 (6)	1.501 (6)	1.505 (3)	1.499 (3)
C(8)–C(8a)	1.518 (2)	1.525 (6)	1.514 (5)	1.514 (3)	1.533 (3)
C(8a)–C(1)	1.516 (2)	1.512 (5)	1.514 (6)	1.515 (3)	1.520 (3)
C(8a)–C(4a)	1.537 (2)	1.533 (5)	1.525 (5)	1.533 (4)	1.556 (2)
C(1)–O(1)	1.216 (2)	1.221 (4)	1.219 (4)	1.199 (4)	1.223 (2)
C(4)–O(4)	1.426 (2)	1.438 (4)	1.437 (5)	1.356 (4)	1.438 (2)

exception of bonds C(3)–C(4) and C(4)–C(4a) whose lengths of 1.531 (3) and 1.560 (3) Å, respectively, are anomalously large compared to the same bonds in the closely related hexamethyl 4a-ol derivative (Greenhough & Trotter, 1980). At present, we offer no explanation for these seemingly long bonds except to note the obvious difference between these two derivatives being the additional methyl group on C(4) in this structure. It is not expected that steric effects alone, due to the introduction of the C(41) methyl group, would account for the increase in the length of the above bonds.

Hydrogen bonding, found in all the naphthoquinols studied in this series, is present in this structure as O(4)–H···O(1) interactions linking molecules along the *a* axis: O···O = 2.855 (2), H···O = 1.99 (3) Å, O–H···O = 173 (3)°.

Comparison of compounds (I)–(IV)

Comparisons of bond lengths and angles and torsion angles in analogous tetrahydronaphthoquinones (Phillips & Trotter, 1977) and more recently in tetrahydronaphthoquinols (Greenhough & Trotter, 1981) have revealed the gross effects of substituents on the parent ring system. Many of the trends noted previously are corroborated in the present comparison of an additional four tetrahydronaphthoquinol derivatives (Secco & Trotter, 1982a,b). The appropriate information regarding the parent, unsubstituted compound (Greenhough & Trotter, 1981) has been reproduced (Tables 2–4, 6) to facilitate comparisons.

All six-membered rings adopt the half-chair conformation, close to those predicted by Bucourt & Hainaut (1965) as the most energetically stable conformation for both unsubstituted and substituted cyclohexenes. Although the tetrahydronaphthoquinols studied thus far include examples of OH-*anti* and OH-*syn* conformations, only the former are represented here for comparison with compound (V) in which, despite the pseudo axial *syn*-position of the hydroxy group, the conformation is similar to the OH-*anti* compounds.

Table 4. Bond angles (°) with *e.s.d.*'s in parentheses for compounds (I)–(V)

	(I)	(II)	(III)	(IV)	(V)
C(2)–C(1)–C(8a)	116.7 (1)	117.5 (3)	116.7 (4)	116.6 (2)	118.1 (2)
C(2)–C(1)–O(1)	120.5 (1)	121.2 (3)	120.6 (4)	116.6 (3)	121.0 (2)
C(8a)–C(1)–O(1)	122.8 (1)	121.3 (3)	122.6 (4)	126.5 (3)	120.6 (2)
C(1)–C(2)–C(3)	121.5 (1)	120.8 (3)	121.4 (5)	120.6 (2)	120.9 (2)
C(2)–C(3)–C(4)	123.6 (1)	121.8 (3)	123.5 (4)	123.0 (2)	123.2 (2)
C(3)–C(4)–C(4a)	112.0 (1)	113.9 (3)	111.9 (4)	113.7 (2)	113.1 (1)
C(3)–C(4)–O(4)	109.4 (1)	111.3 (3)	108.1 (4)	113.3 (2)	103.5 (1)
C(4a)–C(4)–O(4)	112.9 (1)	111.7 (3)	112.5 (3)	110.5 (2)	111.1 (2)
C(4)–C(4a)–C(5)	113.0 (1)	113.6 (3)	113.6 (4)	114.2 (2)	109.5 (1)
C(4)–C(4a)–C(8a)	109.6 (1)	109.2 (3)	109.6 (4)	109.7 (2)	111.4 (1)
C(8a)–C(4a)–C(5)	111.1 (1)	110.5 (3)	109.7 (4)	109.8 (1)	107.0 (1)
C(4a)–C(5)–C(6)	112.2 (1)	112.2 (3)	114.1 (4)	116.6 (2)	116.8 (2)
C(5)–C(6)–C(7)	123.8 (1)	124.1 (3)	122.0 (4)	120.6 (2)	122.3 (2)
C(6)–C(7)–C(8)	124.3 (1)	123.9 (4)	123.0 (4)	123.0 (2)	121.3 (2)
C(7)–C(8)–C(8a)	111.8 (1)	111.8 (4)	113.2 (4)	113.7 (2)	115.7 (2)
C(8)–C(8a)–C(1)	112.7 (1)	113.4 (3)	113.5 (4)	114.2 (2)	110.3 (2)
C(8)–C(8a)–C(4a)	111.7 (1)	111.2 (3)	111.6 (4)	109.7 (2)	110.0 (2)
C(4a)–C(8a)–C(1)	110.1 (1)	109.5 (3)	110.0 (3)	109.8 (1)	107.4 (2)
C(1)–C(2)–C(21)	–	115.9 (4)	–	115.0 (2)	115.6 (2)
C(21)–C(2)–C(3)	–	123.3 (4)	–	124.4 (2)	123.4 (2)
C(2)–C(3)–C(31)	–	122.7 (4)	–	122.3 (2)	120.5 (2)
C(31)–C(3)–C(4)	–	115.5 (4)	–	114.7 (2)	116.2 (2)
C(5)–C(6)–C(61)	–	–	113.8 (5)	115.0 (2)	113.0 (2)
C(61)–C(6)–C(7)	–	–	124.1 (5)	124.4 (2)	124.6 (2)
C(6)–C(7)–C(71)	–	–	123.1 (5)	122.3 (2)	124.3 (2)
C(71)–C(7)–C(8)	–	–	113.9 (5)	114.7 (2)	114.4 (2)

Table 5. Supplementary distances (Å) and angles (°) for substrate (V), with *e.s.d.*'s in parentheses

C(2)–C(21)	1.514 (3)	C(3)–C(4)–C(41)	109.4 (2)
C(3)–C(31)	1.509 (3)	C(41)–C(4)–C(4a)	111.3 (2)
C(4)–C(41)	1.539 (3)	C(41)–C(4)–O(4)	108.2 (2)
C(4a)–C(4a1)	1.541 (3)	C(4)–C(4a)–C(4a1)	110.1 (2)
C(6)–C(61)	1.516 (3)	C(4a1)–C(4a)–C(5)	108.5 (2)
C(7)–C(71)	1.508 (3)	C(4a1)–C(4a)–C(8a)	110.3 (2)
C(8a)–C(8a1)	1.541 (3)	C(1)–C(8a)–C(8a1)	105.6 (2)
		C(4a)–C(8a)–C(8a1)	115.2 (2)
		C(8)–C(8a)–C(8a1)	108.2 (2)

Compounds (I)–(V) consist of two *cis*-fused cyclohexene rings, the C skeleton of which may be described by three approximate planes. Two planes containing atoms C(1) to C(4) and C(5) to C(8) make an angle of approximately 85° and subtend angles of close to 140° with respect to the third plane defined by atoms C(4), C(4a), C(8a) and C(8). The C(4)–C(4a)–C(8a)–C(8) torsion angles (Table 6), averaging 175.7 (5)°, indicate the extent to which these atoms approximate a plane. Torsion angles for the other planes range from –3.4 (3) to 2.3 (5)°.

Substituents on C(4a) and C(8a) appear to have little effect on the bridgehead torsion angle R_2 –C(4a)–C(8a)– R_2 (Table 2) which remains fairly constant, averaging –63° for compounds (I)–(V). However, the internal twist angle C(1)–C(8a)–C(4a)–C(5) decreases by *ca* 5° upon methyl substitution at the

bridgehead C atoms [compound (V)]; similar results were observed in several naphthoquinone derivatives (Phillips & Trotter, 1977) and in other naphthoquinols (Greenhough & Trotter, 1981). Whether this internal torsional decrease without a concomitant external increase is due to hybridization or steric effects is still not clear.

Generally, increased substitution in the naphthoquinols results in an enlarged ring size. This is evident in the increases in several bond lengths and angles (Tables 3 and 4). The C(2)=C(3) bond in compounds (II) and (IV) has a mean value of 1.345 Å which is 0.019 Å longer than the same but unsubstituted bond in the parent compound, (I). The C(2)=C(3) bond in (V) also appears to be lengthened, although the difference from (I) is not definitely significant in this case (2.5σ). Substituents at positions C(2) and C(3) affect the C(2)–C(1)–C(8a) and C(3)–C(4)–C(4a) angles by enlarging them marginally (<1.4°) with concomitant decreases in the internal C(2)=C(3) double-bond angles. Similar substituent-associated effects are apparent at the C(6)=C(7) end of the ring. With methyl substituents at positions C(6) and C(7), the C(6)=C(7) double bond is lengthened by an average of 0.016 Å compared to the same bond in (I) where H atoms are the substituents. Compound (V), whose C(6)=C(7) bond length is essentially the same as that in (I), does not seem to follow this trend. The angles C(4a)–C(5)–C(6) and C(7)–C(8)–C(8a) show an increase of 1.4–4.6° for $R_4 = \text{Me}$, whereas the

Table 6. *Torsion angles (°) with e.s.d.'s in parentheses for compounds (I)–(V)*

	(I)*	(II)	(III)	(IV)	(V)
C(1)–C(2)–C(3)–C(4)	–0.1 (2)	–0.5 (4)	2.3 (5)	–2.3 (3)	–3.4 (3)
C(2)–C(3)–C(4)–C(4a)	–20.8 (2)	–18.8 (4)	–23.1 (5)	–16.3 (3)	–9.8 (3)
C(3)–C(4)–C(4a)–C(8a)	49.1 (1)	48.2 (3)	50.4 (4)	46.5 (2)	40.9 (2)
C(4)–C(4a)–C(8a)–C(1)	–58.1 (1)	–59.0 (3)	–58.0 (4)	–58.9 (2)	–57.4 (2)
C(4a)–C(8a)–C(1)–C(2)	38.6 (1)	42.0 (4)	38.5 (4)	42.0 (3)	46.3 (2)
C(8a)–C(1)–C(2)–C(3)	–9.4 (2)	–12.0 (4)	–10.4 (5)	–11.5 (3)	–16.5 (3)
C(4a)–C(5)–C(6)–C(7)	–12.9 (2)	–13.7 (4)	–12.9 (5)	–11.5 (3)	–13.9 (3)
C(5)–C(6)–C(7)–C(8)	–1.2 (2)	–0.3 (5)	–2.7 (5)	–2.3 (3)	–1.6 (3)
C(6)–C(7)–C(8)–C(8a)	–14.6 (2)	–15.7 (5)	–13.6 (5)	–16.3 (3)	–15.6 (3)
C(7)–C(8)–C(8a)–C(4a)	43.6 (1)	45.0 (4)	44.7 (4)	46.5 (2)	46.4 (2)
C(8)–C(8a)–C(4a)–C(5)	–58.4 (1)	–59.5 (3)	–59.5 (4)	–58.9 (2)	–57.9 (2)
C(8a)–C(4a)–C(5)–C(6)	41.6 (1)	42.6 (3)	43.0 (4)	42.0 (3)	43.1 (2)
R ₁ –C(4a)–C(8a)–R ₂	–63 (1)	–62 (3)	–65 (3)	–63 (3)	–62.7 (2)
C(4)–C(4a)–C(8a)–C(8)	176.0 (1)	174.8 (3)	175.1 (3)	174.9 (2)	–177.5 (2)
C(1)–C(8a)–C(4a)–C(5)	67.5 (1)	66.6 (3)	67.3 (4)	67.3 (3)	62.2 (2)
C(3)–C(4)–C(4a)–C(5)	–75.4 (1)	–75.6 (3)	–72.7 (4)	–77.1 (2)	–77.3 (2)
C(8)–C(8a)–C(1)–C(2)	164.0 (1)	166.9 (3)	164.2 (4)	165.6 (2)	166.2 (2)
O(1)–C(1)–C(8a)–C(4a)	–143.0 (1)	–139.8 (3)	–143.2 (4)	–145.2 (5)	–138.7 (2)
O(1)–C(1)–C(8a)–C(8)	–17.6 (2)	–15.0 (4)	–17.4 (5)	–21.6 (5)	–18.8 (3)
O(1)–C(1)–C(2)–C(3)	172.1 (1)	169.8 (4)	171.2 (4)	175.0 (4)	168.5 (2)
O(4)–C(4)–C(3)–C(2)	–146.7 (2)	–146.2 (3)	–147.6 (4)	–143.5 (3)	110.6 (2)
O(4)–C(4)–C(4a)–C(5)	48.6 (1)	51.6 (3)	49.3 (4)	51.5 (3)	166.8 (1)
O(4)–C(4)–C(4a)–C(8a)	173.1 (1)	175.4 (3)	172.4 (3)	175.2 (2)	–75.0 (2)
C(1)–C(8a)–C(8)–C(7)	–80.9 (1)	–78.9 (4)	–80.2 (4)	–77.1 (2)	–72.0 (2)

* Torsion angles for (I) refer to the enantiomer of the parent compound in Greenhough & Trotter (1981).

internal angles C(5)–C(6)=C(7) and C(6)=C(7)–C(8) generally decrease by 0.9–3.2° for the same substitution. It is apparent from the above comparison that the increase in the internal angles involving the O-bearing C atoms as vertices is due mainly to substitution at the double-bonded C atoms and not to the bridgehead substituents (Greenhough & Trotter, 1981). It is not clear, however, why the double-bond distances in (V) do not follow the trend observed for the substituted double bonds of other naphthoquinol derivatives (*cf.* Greenhough & Trotter, 1981).

It is observed in compounds (II)–(V) that methyl substitution at the double bond tends to increase the single-bond lengths between the substituted double-bond C atoms and the adjacent ring C atoms. These bonds average 0.014 Å greater than the related bonds in the parent compound. The C(5)–C(6) distance of 1.484 (3) Å in (IV) seems anomalous with respect to the above trend; however, this may be a result of imperfections in the model owing to the disorder in that structure. Methyl substitution at C(2) and C(3) affects the external angles C(2)–C(1)–O(1) and C(3)–C(4)–O(4), generally by widening them 0.5–0.7° and 1.9–3.9°, respectively. This is attributed to steric effects between the O atoms and the bulky methyl groups. The tendency for the methyl groups to bend away from each other is limited by the opposing O atoms which lie nearly in the same plane.

Molecules within crystals of each of the compounds (I)–(V) are linked by hydrogen bonding. Molecules of (II) and (III) are joined *via* O(4)···O(4) whereas (V) is

linked by O(4)–H···O(1) interactions. Due to the disorder in (IV), it is difficult to discern the actual type of hydrogen bonding, but it has been suggested (Secco & Trotter, 1982a) that the two types O(4)···O(4) and O(4)···O(1) are operative. The parent compound (I) exhibits O(4)···O(4) intermolecular hydrogen bonding through disordered hydroxyl H atoms (Greenhough & Trotter, 1981).

The photochemistry of these compounds in solution and the solid state has been discussed elsewhere (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980a,b; Jiang, Scheffer, Secco & Trotter, 1981; Appel, Herbert, Jiang, Scheffer & Walsh, 1982). Compounds (I)–(V) all react in the solid state. The pertinent geometrical parameters are given in Table 2.

It has been suggested (Scheffer & Dzakpasu, 1978) that the intramolecular H abstraction by C or O can occur over distances as great as the sum of the van der Waals radii of the two atoms involved. For C abstraction of H the suggested upper limit is 2.90 Å [$\bar{r}_w(\text{C}) = 1.70 \text{ Å}$, $\bar{r}_w(\text{H}) = 1.20 \text{ Å}$], whereas for abstraction by O the limit suggested is 2.72 Å [$\bar{r}_w(\text{O}) = 1.52 \text{ Å}$, $\bar{r}_w(\text{H}) = 1.20 \text{ Å}$]. Table 2 shows C(2)···H distances all greater than the 2.90 Å limit while the C(3)···H distances range from 2.81 to 2.84 Å. Implicit in the above suggested limits is the requirement of otherwise favorable reacting geometry. This is indicated by the orientation of the orbital involved in the abstraction process relative to the position of the abstractable H. Although the exact orientation of the abstracting orbital with respect to the

H atom to be abstracted is not directly observable, it can be inferred from the two angles τ and Δ . In the abstraction-by-C process τ_C is the angle between the C_{abs}···H_{abs} vector and the plane of the C(2)=C(3) double bond, and Δ_C is the angle between the C_{abs}···H_{abs} and the C(2)=C(3) vectors. Angles of 90° for both τ_C and Δ_C imply the most favorable abstracting geometry with the abstracting C 2p orbital collinear with the vulnerable H. All compounds (I)–(V) react *via* H(5) abstraction by the β -enone C atom, C(3), although the τ_C values in Table 2 appear much less than favorable. However, it is not unreasonable to expect 30–40° rotation around the C(2)=C(3) double bond upon (π, π^*) excitation (Marsh, Kearns & Schaffner, 1971; Devaquet, 1972). Rotation in a favorable sense yields a τ_C value of close to 90° for the molecule in the excited state.

The secondary solid-state reaction observed in (I) and (III) results in a dihydroxy 1,6-bonded product analogous to naphthoquinone products resulting from β -H abstraction reactions (Scheffer & Dzakpasu, 1978). Inspection of Table 2 reveals the favorable geometry of all compounds for the occurrence of carbonyl O abstraction of β -H with O···H separations of less than 2.58 Å, and τ_O and Δ_O angles of 0° and 90°, respectively; τ_O being the angle subtended by the O_{abs}···H_{abs} vector and the plane of the carbonyl, and Δ_O being the angle between the O_{abs}···H_{abs} and the O=C vectors. The ideal geometry is based on the alignment of the abstractable H on C(8) and the *n* orbital on the O which lies in the plane of the carbonyl group and perpendicular to the double bond. However, only (I) and (III) were observed to undergo this type of reaction. It was suggested in an earlier paper (Secco & Trotter, 1982*b*) that substituents on the enone double bond and their effects on the excited state of the molecule may be the critical feature in determining the probability of the above reaction.

No intramolecular 2 + 2 cycloaddition products are observed in the solid state while, in solution, where conformational equilibration is facile, all compounds undergo this reaction. The absence of cycloaddition products in the solid state is rationalized on the basis of the remoteness of the double bonds and their askew orientations. For the above compounds the angle between the vectors C(6)–C(7) and C(3)–C(2) is *ca* 50° and their double-bond center-to-center separations

are >4.3 Å. Similarly, unfavorable intramolecular cycloaddition geometries exist for the C=O and C(6)=C(7) double bonds (Table 2).

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