

Table 11. The C(sp<sup>3</sup>)—C(sp<sup>3</sup>) distances and C—C—C bond angle at C(5) in the non-planar thiazine rings with the indication of maximum puckering at C(5)

Some information concerning the data collection and refinement is also presented.

Compound	C(4)—C(5)	C(5)—C(6)	C(4)—C(5)—C(6)	ΔC(5)	Diffractometer	Radiation	R	Number of reflections/parameter
(Ia)	1.48 (1) Å	1.46 (1) Å	113 (1)°	0.87	Syntex P2 <sub>1</sub>	Mo Kα	0.04	6
(Ib)	1.38 (1)	1.34 (1)	128 (1)	0.40				
(IIa)	1.52 (1)	1.49 (1)	111 (1)	0.81	Philips	Cu Kα	0.05	7
(IIb)	1.46 (1)	1.40 (1)	120 (1)	0.54				
(IIIa)	1.44 (1)	1.44 (1)	114 (1)	0.68	Philips	Mo Kα	0.05	10
(IIIb)	1.49 (1)	1.46 (1)	113 (1)	0.58				
(IV)	1.41 (1)	1.43 (1)	123 (1)	0.28	Philips	Mo Kα	0.06	9
(V)	1.46 (1)	1.46 (1)	114 (1)	0.68	Syntex P1	Mo Kα	0.09	10
(VIa)	1.49 (1)	1.50 (1)	114 (1)	0.64	Syntex P2 <sub>1</sub>	Mo Kα	0.05	7
(VIb)	1.45 (1)	1.41 (1)	118 (1)	0.57				
(VII)	1.48 (1)	1.50 (1)	113 (1)	0.67	Stoe two-circle	Cu Kα	0.07	8

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## The Structure of 2,3,4aβ,6,7β,8aβ-Hexamethyl-4a,7,8,8a-tetrahydro-1,4-naphthoquinone

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### Abstract

Crystals of 2,3,4aβ,6,7β,8aβ-hexamethyl-4a,7,8,8a-tetrahydro-1,4-naphthoquinone are monoclinic,  $a = 6.865$  (1),  $b = 16.043$  (2),  $c = 13.166$  (2) Å,  $\beta = 99.57$  (1)°, space group  $P2_1/c$ ,  $Z = 4$ . The structure

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was refined to  $R = 0.047$  for 1862 independent observed reflections. The crystal structure consists of well separated molecules with the two fused six-membered rings in distorted half-chair conformations and twisted with respect to each other. A comparison with *cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone and

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its derivatives reveals conformational differences in the ring with the carbonyl functions and in the degree of twist. Completely different products are obtained when this  $\beta,\gamma$ -unsaturated ketone is photolysed in solution and the solid state, providing the first example of complete unimolecular solid-state/solution reactivity differences.

### Introduction

The photochemical study of *cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone derivatives in solution (Scheffer, Jennings & Louwerens, 1976) and the solid state (Dzakpasu, Phillips, Scheffer & Trotter, 1976), in conjunction with crystallographic studies of several derivatives and their photoproducts (Phillips & Trotter, 1977*b*), has revealed unusual reaction pathways and provided ranges of interatomic distances and angles which allow photochemical conversions to proceed *via* initial mechanisms such as  $\beta$ - or  $\gamma$ -H abstraction by carbonyl O, H abstraction by enone C, or intermolecular dimerization. While crystal-lattice control of bimolecular organic photochemical reactions has been observed (Scheffer & Dzakpasu, 1978), the starting diketone 2,3,4a $\beta$ ,6,7 $\beta$ ,8a $\beta$ -hexamethyl-4a,7,8,8a-tetrahydro-1,4-naphthoquinone (I, Fig. 1) provides the first example of complete unimolecular solid-state/solution reactivity differences (Appel, Greenhough, Scheffer & Trotter, 1979). In order that reaction pathways might be postulated for the two photochemical conversions, the crystal structure of (I) was determined.

### Experimental

Recrystallization of (I) from *n*-hexane/petroleum ether afforded colourless prisms which were poorly formed.

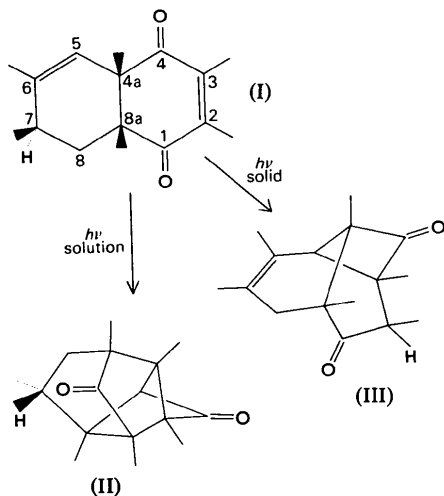


Fig. 1. The starting diketone 2,3,4a $\beta$ ,6,7 $\beta$ ,8a $\beta$ -hexamethyl-4a,7,8,8a-tetrahydro-1,4-naphthoquinone (I), with the solution photoproduct (II) and the solid-state photoproduct (III).

The unit cell and space group were determined initially by photographic methods. A crystal of dimensions *ca* 0.4 × 0.4 × 0.2 mm, cut from a larger crystal, was mounted in a Nonius CAD-4F diffractometer and a least-squares analysis of the setting angles of 25 reflections ( $20^\circ < \theta < 35^\circ$ , Ni-filtered Cu  $K\alpha$  radiation) provided accurate unit-cell parameters.

### Crystal data

$C_{16}H_{22}O_2$ ,  $M_r = 246.35$ , monoclinic,  $a = 6.865$  (1),  $b = 16.043$  (2),  $c = 13.166$  (2) Å,  $\beta = 99.57$  (1)°,  $V = 1429.9$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.144$  Mg m<sup>-3</sup>,  $\mu(\text{Cu } K\alpha) = 0.54$  mm<sup>-1</sup>,  $\lambda = 1.54178$  Å, space group  $P2_1/c$  ( $h0l$ ,  $l = 2n$ ;  $0k0$ ,  $k = 2n$ ).

Data were collected at room temperature with the Nonius CAD-4F procedures described fully elsewhere (Greenhough, Scheffer, Trotter & Walsh, 1979); details pertinent to this collection are:  $1^\circ < \theta < 75^\circ$ ,  $\omega$ - $2\theta$  scan,  $\omega$  scan angle  $\Delta\omega = (1.1 + 0.15 \tan \theta)^\circ$ , SIGPRE = 0.5, SIGMA = 0.05, NPIPRE = 2 (10.06° min<sup>-1</sup>), ITMAX = 180 s, 2952 observations, 1862 observed [ $3\sigma(I)$ ] reflections with  $\sigma^2(I) = S + B + (0.06S)^2$  ( $S$  = scan count,  $B$  = background). A periodic measurement of three check reflections revealed a decrease in intensity of 12% during data collection; this was accounted for during data processing where Lorentz and polarization corrections were applied in the normal manner.

### Structure solution and refinement

The structure was solved by direct methods using 410  $|E|$  values  $> 1.5$  derived by the Wilson-plot method. The  $|E|$  statistics all agreed well with a centrosymmetric distribution. An outstanding solution with 206 positive and 204 negative  $E$  values and a 78% consistency index was obtained by a symbolic addition procedure (Long, 1965), and a subsequent  $E$  map provided the positions of the 16 non-hydrogen atoms. Two cycles of isotropic followed by two of anisotropic full-matrix least-squares refinement of C and O gave  $R = 0.098$  for the observed reflections, with unit weights and minimization of  $\sum w(|F_o| - |F_c|)^2$ . The atomic scattering factors were taken from Cromer & Mann (1968). A difference-Fourier synthesis revealed the 22 H atoms and further least-squares refinement including isotropic H atoms reduced  $R$  to 0.050. The scattering factors for H were taken from Stewart, Davidson & Simpson (1965). The final refinements included an isotropic extinction parameter  $g$  (Becker & Coppens, 1974, 1975; Coppens & Hamilton, 1970) and weights  $1/\sigma^2(F)$ , and gave the final  $R$  value of 0.047. The final value of  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$  was 0.074 for the 1862 observed reflections, with  $g = 2.9 \pm 7 \times 10^3$  and  $\sigma_1$  (GOF) = 1.32. Mean and maximum

shift/error figures in the last cycle were 0.047 and 0.464 respectively, a difference-Fourier synthesis showing random fluctuations of up to  $\pm 0.2 e \text{ \AA}^{-3}$ . Final positional parameters are given in Table 1.\*

### Results and discussion

The crystal structure consists of well separated molecules having the 'twist conformation' observed for several derivatives of 1,4-naphthoquinone (Phillips &

\* Lists of structure factors, thermal parameters and some additional torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34860 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

	x	y	z
C(1)	9446 (3)	1193 (1)	1871 (2)
C(2)	8077 (3)	1874 (1)	1471 (1)
C(3)	6476 (3)	2030 (1)	1894 (2)
C(4)	6069 (3)	1528 (1)	2782 (2)
C(4a)	6905 (3)	651 (1)	2912 (1)
C(5)	5792 (3)	118 (1)	2052 (2)
C(6)	6577 (3)	-462 (1)	1538 (2)
C(7)	8763 (4)	-643 (1)	1714 (2)
C(8)	9840 (3)	-210 (1)	2670 (2)
C(8a)	9125 (3)	675 (1)	2806 (1)
C(9)	8645 (5)	2384 (2)	604 (2)
C(10)	5034 (6)	2721 (2)	1551 (3)
C(11)	6534 (4)	300 (2)	3943 (2)
C(12)	5300 (6)	-962 (2)	707 (3)
C(13)	9205 (6)	-1588 (2)	1766 (3)
C(14)	10384 (4)	1097 (2)	3747 (2)
O(1)	10899 (3)	1071 (1)	1474 (2)
O(4)	5060 (2)	1824 (1)	3368 (1)
H(5)	439 (4)	22 (2)	183 (2)
H(7)	935 (4)	-42 (2)	105 (2)
H(81)	961 (3)	-55 (1)	329 (2)
H(82)	1127 (4)	-21 (2)	273 (2)
H(91)	765 (6)	258 (2)	16 (3)
H(92)	907 (7)	194 (3)	23 (4)
H(93)	994 (7)	266 (3)	82 (3)
H(101)	516 (7)	302 (3)	87 (4)
H(102)	367 (9)	252 (4)	153 (4)
H(103)	547 (6)	318 (3)	189 (3)
H(111)	713 (3)	-28 (2)	400 (2)
H(112)	703 (4)	68 (2)	454 (2)
H(113)	502 (5)	29 (2)	385 (2)
H(121)	533 (5)	-152 (2)	88 (3)
H(122)	571 (5)	-89 (2)	1 (3)
H(123)	392 (6)	-71 (2)	47 (3)
H(131)	874 (4)	-183 (2)	242 (2)
H(132)	1054 (6)	-166 (2)	194 (3)
H(133)	861 (5)	-195 (2)	115 (3)
H(141)	980 (4)	166 (2)	390 (2)
H(142)	1169 (5)	117 (2)	364 (2)
H(143)	1031 (4)	77 (2)	438 (2)

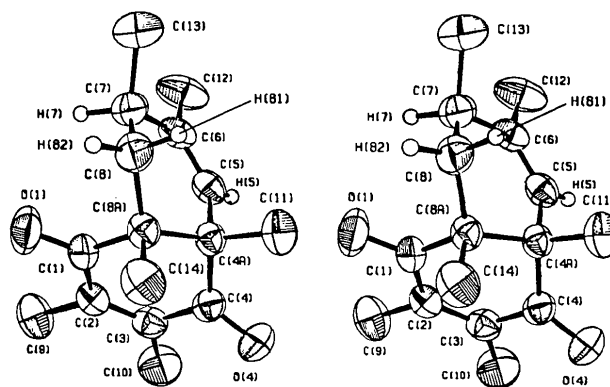


Fig. 2. Stereodiagram of 2,3,4a $\beta$ ,6,7 $\beta$ ,8a $\beta$ -hexamethyl-4a,7,8,8a-tetrahydro-1,4-naphthoquinone showing the numbering scheme. Thermal ellipsoids are at the 50% probability level, and methyl H atoms are omitted.

Table 2. Bond distances ( $\text{\AA}$ ) with e.s.d.'s in parentheses

C(1)—C(2)	1.480 (3)	C(5)—H(5)	0.97 (3)
C(2)—C(3)	1.336 (3)	C(7)—H(7)	1.08 (3)
C(3)—C(4)	1.484 (3)	C(8)—H(81)	1.02 (2)
C(4)—C(4a)	1.520 (3)	C(8)—H(82)	0.97 (3)
C(4a)—C(5)	1.520 (3)	C(9)—H(91)	0.87 (4)
C(5)—C(6)	1.317 (3)	C(9)—H(92)	0.94 (5)
C(6)—C(7)	1.508 (3)	C(9)—H(93)	1.00 (5)
C(7)—C(8)	1.518 (3)	C(10)—H(101)	1.04 (6)
C(8)—C(8a)	1.524 (3)	C(10)—H(102)	0.99 (6)
C(8a)—C(1)	1.530 (3)	C(10)—H(103)	0.88 (4)
C(4a)—C(8a)	1.553 (2)	C(11)—H(111)	1.01 (2)
C(1)—O(1)	1.217 (2)	C(11)—H(112)	1.00 (3)
C(2)—C(9)	1.507 (3)	C(11)—H(113)	1.02 (3)
C(3)—C(10)	1.505 (3)	C(12)—H(121)	0.93 (4)
C(4)—O(4)	1.215 (2)	C(12)—H(122)	1.01 (3)
C(4a)—C(11)	1.531 (3)	C(12)—H(123)	1.03 (4)
C(6)—C(12)	1.513 (3)	C(13)—H(131)	1.04 (3)
C(7)—C(13)	1.546 (3)	C(13)—H(132)	0.91 (4)
C(8a)—C(14)	1.544 (3)	C(13)—H(133)	1.02 (4)
		C(14)—H(141)	1.03 (3)
		C(14)—H(142)	0.94 (3)
		C(14)—H(143)	0.99 (3)

Trotter, 1977b). The molecular structure is shown in Fig. 2. Bond lengths and angles are given in Tables 2 and 3 and selected torsion angles in Table 4. The six-membered strained ring containing the carbonyl groups is in a distorted half-chair conformation with C(4a) displaced by 0.56  $\text{\AA}$  from the C(1) to C(4), C(8a) plane, with O(1) in plane and O(4) displaced by -0.43  $\text{\AA}$ . The conformation of this ring differs from that in other 1,4-naphthoquinone derivatives in that here C(4a) deviates from the essentially planar remainder of the ring, while the comparable cases show conformations ranging from a planar C(1) to C(4a) fragment with C(8a) displaced in the opposite sense to C(4a) here, to a planar C(1) to C(4) fragment with C(4a) and C(8a) displaced by similar amounts on either side of the plane

Table 3. *Interbond angles (°) with e.s.d.'s in parentheses*

C(2)—C(1)—C(8a)	121.3 (2)	C(5)—C(4a)—C(11)	108.5 (2)
C(2)—C(1)—O(1)	118.9 (2)	C(8a)—C(4a)—C(11)	113.5 (2)
C(8a)—C(1)—O(1)	119.7 (2)	C(4a)—C(5)—C(6)	125.6 (2)
C(1)—C(2)—C(3)	120.5 (2)	C(5)—C(6)—C(7)	122.6 (2)
C(1)—C(2)—C(9)	116.2 (2)	C(5)—C(6)—C(12)	120.6 (2)
C(3)—C(2)—C(9)	123.3 (2)	C(7)—C(6)—C(12)	116.8 (2)
C(2)—C(3)—C(4)	120.2 (2)	C(6)—C(7)—C(8)	112.0 (2)
C(2)—C(3)—C(10)	124.0 (2)	C(6)—C(7)—C(13)	112.3 (2)
C(4)—C(3)—C(10)	115.8 (2)	C(8)—C(7)—C(13)	110.3 (2)
C(3)—C(4)—C(4a)	118.3 (2)	C(7)—C(8)—C(8a)	113.7 (2)
C(3)—C(4)—O(4)	119.4 (2)	C(1)—C(8a)—C(4a)	111.1 (1)
C(4a)—C(4)—O(4)	122.3 (2)	C(1)—C(8a)—C(8)	108.6 (2)
C(4)—C(4a)—C(5)	107.7 (1)	C(1)—C(8a)—C(14)	105.7 (2)
C(4)—C(4a)—C(8a)	108.9 (1)	C(4a)—C(8a)—C(8)	109.1 (2)
C(4)—C(4a)—C(11)	109.0 (2)	C(4a)—C(8a)—C(14)	111.5 (2)
C(5)—C(4a)—C(8a)	109.1 (2)	C(8)—C(8a)—C(14)	110.8 (2)

Table 4. *Selected torsion angles (°) with e.s.d.'s in parentheses*

C(1)—C(2)—C(3)—C(4)	0.9 (2)
C(2)—C(3)—C(4)—C(4a)	-25.5 (2)
C(3)—C(4)—C(4a)—C(8a)	48.3 (2)
C(4)—C(4a)—C(8a)—C(1)	-46.5 (2)
C(4a)—C(8a)—C(1)—C(2)	26.9 (2)
C(8a)—C(1)—C(2)—C(3)	-2.7 (2)
C(4a)—C(5)—C(6)—C(7)	-3.1 (2)
C(5)—C(6)—C(7)—C(8)	11.2 (2)
C(6)—C(7)—C(8)—C(8a)	-40.7 (2)
C(7)—C(8)—C(8a)—C(4a)	61.1 (2)
C(8)—C(8a)—C(4a)—C(5)	-48.9 (2)
C(8a)—C(4a)—C(5)—C(6)	22.6 (2)
C(1)—C(8a)—C(4a)—C(5)	70.8 (2)
C(4)—C(4a)—C(8a)—C(8)	-166.2 (2)
C(4)—C(4a)—C(5)—C(6)	140.7 (2)
C(1)—C(8a)—C(8)—C(7)	-60.2 (2)
C(8)—C(8a)—C(1)—C(2)	146.9 (2)
C(5)—C(4a)—C(4)—C(3)	-69.9 (2)
C(11)—C(4a)—C(8a)—C(14)	-50.4 (2)
C(8a)—C(8)—C(7)—C(13)	-166.5 (2)

(Phillips & Trotter, 1977*b*). Thus in the derivatives with CN bridgehead substituents (Phillips & Trotter, 1976*a,b*) and in 5 $\alpha$ ,8 $\alpha$ -dimethyl-4 $\alpha\beta$ ,5,8,8 $\alpha\beta$ -tetrahydro-1,4-naphthoquinone (Phillips & Trotter, 1977*a*) the C(2)=C(3) and C(3)—C(4) skeletal torsion angles are near zero, giving an essentially planar C(1) to C(4a) fragment with O(4) in plane, and in the derivatives with Me bridgehead substituents (Phillips & Trotter, 1976*c,d*) the bridgehead C atoms deviate from the C(1) to C(4) plane by similar but opposite amounts, as do O(1) and O(4). The 'twist' torsion angle Me(11)—C(4a)—C(8a)—Me(14) is -50.4 (2)°, *ca* 10° less than that in various 1,4-naphthoquinone derivatives with C(2)=C(3) and C(6)=C(7) (Phillips & Trotter, 1977*b*), where the corresponding angle is rela-

tively constant at *ca* 60° whether the bridgehead substituents are H, Me, or CN. This difference is reflected in the C(4)—C(4a)—C(8a)—C(1) torsion angle which is *ca* 10° less here than in 2,3,4 $\alpha\beta$ ,5 $\beta$ ,8 $\beta$ ,8 $\alpha\beta$ - and *cis*-2,3,4 $\alpha$ ,6,7,8 $\alpha$ -hexamethyl-4 $\alpha$ ,5,8,8 $\alpha$ -tetrahydro-1,4-naphthoquinone (Phillips & Trotter, 1976*c,d*), both with methyl bridgehead substituents.

The decrease in twist for (I) may be due to the change in hybridization at C(5) and C(7), either directly or as a result of the different steric interactions produced. The second six-membered ring is in a less-distorted half-chair conformation, with C(8a) displaced 0.51 Å from the C(4a), C(5) to C(7) plane, and C(8) displaced by 0.22 Å on the other side of the plane. If the double bond in this ring is equated with that in the comparable ring in the 1,4-naphthoquinones with C(6)=C(7), the conformation is remarkably similar, with, for example, differences of only 1–2° from 5 $\alpha$ ,8 $\alpha$ -dimethyl-4 $\alpha\beta$ ,5,8,8 $\alpha\beta$ -tetrahydro-1,4-naphthoquinone (Phillips & Trotter, 1977*a*). The deviation of C(8) from the half-chair conformation relieves the H(81)···Me(11) contact, with a H(81)···H(111) distance of about 2.1 Å. This contact may be responsible in part for the small 'twist' angle which itself produces a close Me···Me bridgehead contact, the steric interactions being further evidenced by the H temperature factors, which average  $U = 7.8 \text{ \AA}^2$  for the bridgehead Me groups and 13.8 Å<sup>2</sup> for the other Me groups, with values of 5.6 (6) and 6.3 (7) Å<sup>2</sup> for H(81) and H(111), respectively. The twist between the two fused rings is further described by the C(1)—C(8a)—C(4a)—C(5) torsion angle of 70.8 (2)°, which, although not strictly comparable with the C(6)=C(7) 1,4-naphthoquinones, again shows a 10° smaller twist than in those derivatives with Me bridgehead substituents (Phillips & Trotter, 1976*c,d*), but is comparable to related molecules with H bridgehead substituents (Phillips & Trotter, 1977*b*). Despite the deviation of C(8) from the half-chair conformation there is still a staggering of the two H atoms at C(8) and the H and Me [C(13)] at C(7), with a C(8a)—C(8)—C(7)—C(13) torsion angle of -166.5 (2)°. This staggered conformation at C(7) and C(8) produces a pseudo-equatorial H(82) with an

Table 5. *Selected intramolecular non-bonded distances (Å) and e.s.d.'s*

C(1)···C(7)	2.984 (3)	O(1)···H(7)	2.64 (3)
C(2)···C(5)	3.374 (3)	O(1)···H(82)	2.62 (3)
C(3)···C(5)	3.116 (3)	C(2)···H(7)	3.83 (3)
C(4)···C(5)	2.454 (3)		
C(7)···O(1)	3.156 (3)	H(81)···H(111)	2.12 (3)
C(8)···O(1)	2.759 (3)	H(91)···H(101)	2.20 (6)
C(8)···C(11)	3.146 (4)	H(112)···H(143)	2.30 (4)
C(1)···C(6)	3.292 (3)	H(121)···H(133)	2.32 (5)
C(2)···C(6)	3.891 (3)	H(123)···H(5)	2.30 (4)
C(3)···C(6)	4.027 (3)	H(131)···H(81)	2.39 (3)
		H(132)···H(7)	2.38 (4)

O(1)···H(82) distance of 2.62 (3) Å, and a pseudo-axial H(7) with O(1)···H(7) = 2.64 (3) Å. Other interesting intramolecular non-bonded contact distances are included in Table 5.

Bond lengths and angles compare well with accepted values (Sutton, 1965; Bastiansen & Trætteberg, 1962) and those in related molecules (Phillips & Trotter, 1977*b*), with mean values (and r.m.s. deviations from means): C(sp<sup>3</sup>)—C(sp<sup>3</sup>) 1.536 (14), C(sp<sup>2</sup>)—C(sp<sup>2</sup>) 1.482 (3), C(sp<sup>2</sup>)=C(sp<sup>2</sup>) 1.327 (13), C(sp<sup>2</sup>)—C(sp<sup>3</sup>) 1.515 (9), C=O 1.216 (1), and C—H 0.99 (6) Å. The mean angle at C(4a) and C(8a) is 109.5 (2.0)°, with maximum deviations shown by C(8a)—C(4a)—C(11) [113.5 (2)°] and C(1)—C(8a)—C(14) [105.7 (2)°]; both distortions are consistent with reducing the bridge-head Me···Me and the Me(11)···H(81) steric interactions.

Both carbonyl groups are slightly but significantly non-planar with deviations of up to 8σ [C(1)] in one group and 4σ [C(4)] in the other. The C=C torsion angles are 0.9 (2)° [C(2)=C(3)] and -3.1 (2)° [C(5)=C(6)].

Intermolecular contacts correspond to van der Waals distances with no C···O or C···C contacts less than 3.5 Å, no C···H or O···H other than O(4)···H(142) = 2.62 (3) Å and O(1)···H(5) = 2.73 (3) Å less than 2.85 Å, and only H(93)···H(131) = 2.48 (6) and H(133)···H(141) = 2.49 (4) Å with H···H less than 2.55 Å. The molecular packing is illustrated in Fig. 3.

The elucidation of the crystal structure of (I) allows a rationalization of the photochemical reactions in solution and the solid state (Appel, Greenhough, Scheffer & Trotter, 1979), which give product (III) (Fig. 1) in the solid state (Scheffer, Bhandari, Gayler & Wostradowski, 1975) and product (II) (Fig. 1) in solution (Greenhough & Trotter, 1979). While geometric factors appear to favour H(82) abstraction by

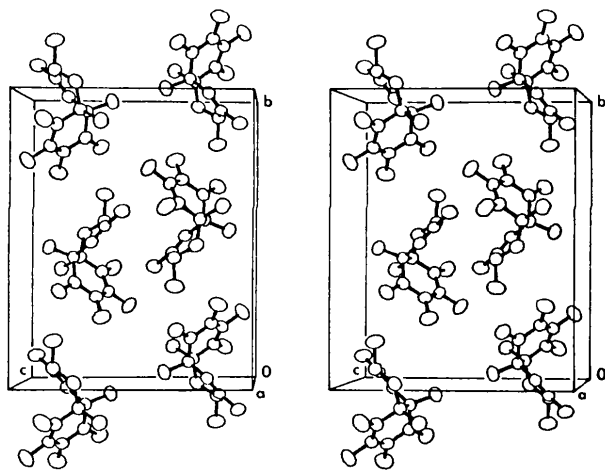


Fig. 3. Stereodiagram of the molecular packing viewed approximately down *a*.

O(1), the high C(8)—H(82) bond dissociation energy with C(8) not adjacent to the C=C bond precludes this, leaving abstraction of the pseudo-axial H(7) by O(1) as a possible initial  $\gamma$ -H-abstraction mechanism. Distances and angles relevant to this possibility are O(1)···H(7) = 2.64 (3) Å, C(1)=O(1)···H(7) = 84.7 (6)° ( $\Delta_0$ ) and  $\tau_0 = 28.5^\circ$  [ $\tau_0$  = angle subtended by the O···H vector and its projection in the O(1) carbonyl mean plane (Phillips & Trotter, 1977*b*)]. While the O(1)···H(7) distance is somewhat greater than those observed previously in solid-state intramolecular H abstraction (2.26–2.58 Å, Scheffer & Dzakpasu, 1978) it does not differ significantly from O(1)··· $\beta$ -H [at C(8)] in *cis*-2,3,4a,6,7,8a-hexamethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (Phillips & Trotter, 1976*d*) and *cis*-4a,8a-dicyano-6,7-dimethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (Phillips & Trotter, 1976*a*) where this distance is 2.47 (6) and 2.58 (3) Å, respectively. The value of  $\tau_0$  at 28.5° is considerably greater than in the near-planar abstractions previously observed (Scheffer & Dzakpasu, 1978), where  $\tau_0$  averages 5°; in 4a $\beta$ ,8a $\beta$ -dicyano-5a,8a-dimethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (Phillips & Trotter, 1976*b*)  $\tau_0$  is 24° (Me H atom) and both solid-state and solution photochemical reactions proceed *via* a 2 + 2 intramolecular cycloaddition (Scheffer & Dzakpasu, 1978; Scheffer, Jennings & Louwerens, 1976). The C(2)···H(7) distance is 3.83 (3) Å as compared to values of 2.80 (6) and 2.66 (3) Å in *cis*-2,3,4a,6,7,8a- and 2,3,4a $\beta$ ,5 $\beta$ ,8 $\beta$ ,8a $\beta$ -hexamethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (Phillips & Trotter, 1976*c,d*) respectively, where H abstraction by enone C occurs in both solution and the solid state. The angle between the normals to the planes through C(2), C(3), C(4) and C(4a), C(5), C(6) is 98° with a C(3)···C(5) separation of 3.116 (3) Å. On the basis of these structural results the solid-state photochemical conversion has been proposed as being initiated by either  $\gamma$ -H abstraction of H(7) by O(1) followed by C(3) to C(5) bonding, or initial C(3) to C(5) bonding followed by internal H transfer of H(7) to O(1) or C(2) (Appel, Greenhough, Scheffer & Trotter, 1979) to give the final photoproduct (Scheffer, Bhandari, Gayler & Wostradowski, 1975). The solution photoproduct, however (Greenhough & Trotter, 1979), suggests that the solution reaction proceeds *via* initial C(4) to C(5) [2.454 (3) Å] bridging to give a biradical which leads to the final product (Appel, Greenhough, Scheffer & Trotter, 1979). In view of the relatively large atomic and molecular motion required for the suggested photoconversion in solution, it appears that this is the favoured mechanism which is not allowed in the solid state due to crystal-lattice or topochemical control of the photorearrangement. While the mechanisms of conversion cannot be assigned with certainty, both suggested rearrangements take place *via* well precedented steps, and it is clear that the complete unimolecular

solution/solid-state reactivity difference is due to the difference between the range of allowable motions in solution and the solid state.

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## Neutron Diffraction Refinement of Partially Deuterated $\beta$ -L-Arabinopyranose and $\alpha$ -L-Xylopyranose at 123 K\*

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#### Abstract

Refinement of the hydrogen–deuterium neutron scattering parameters for partially deuterated  $\beta$ -L-arabinopyranose and  $\alpha$ -L-xylopyranose at 123 K showed no evidence of preferential substitution, despite the presence of anomeric hydroxyls and a large dif-

ference in some hydrogen-bond lengths. Comparison with the results of room-temperature studies of the undeuterated crystals showed that the marked difference in the thermal contraction in the two structures was due primarily to a weak hydrogen bond in the  $\beta$ -L-arabinopyranose structure.

#### Introduction

The experiment described herein was carried out to explore the use of partial deuterium exchange in hydroxyl groups as a probe of differences in hydrogen

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