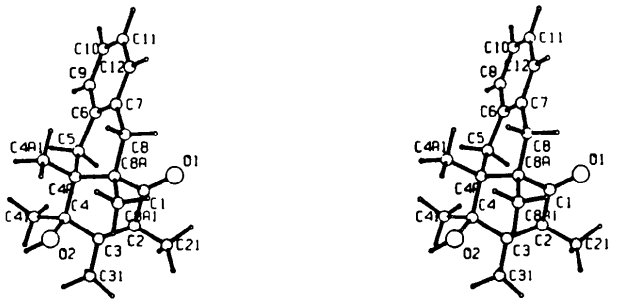

Fig. 1. Stereoscopic view of (I) with crystallographic atomic labelling.

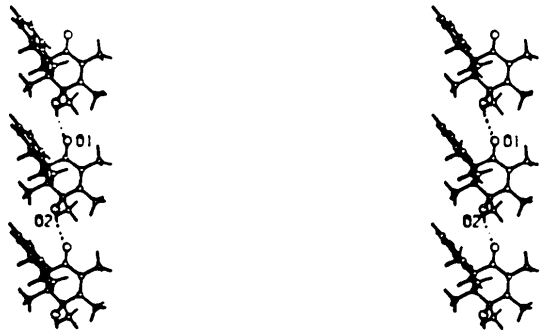

Fig. 2. Stereoscopic view of the H-bonding arrangement of (I).

Hydrogen bonding, found in all the naphthoquinols studied, is present in this structure as O(2)–H(2)···O(1) interactions linking molecules along the *b* axis (Fig. 2): O···O = 2·885 (5), H···O = 1·97 Å, O–H···O = 160°.

Acknowledgement is made to Professor J. R. Scheffer and Mr S. H. Askari for their collaborative studies on the solid-state photochemistry, the Natural Sciences and Engineering Research Council of Canada for financial support, and the University of British Columbia Computing Centre for assistance.

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

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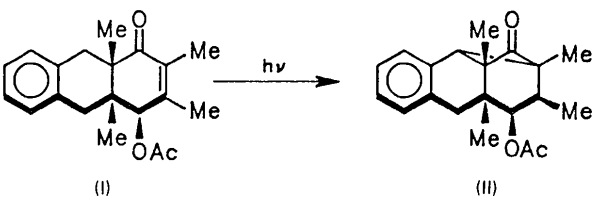
Abstract. $C_{20}H_{24}O_3$, $M_r = 312{\cdot}41$, triclinic, $P\bar{1}$, $a = 9{\cdot}4624$ (6), $b = 9{\cdot}7485$ (7), $c = 10{\cdot}6743$ (7) Å, $\alpha = 66{\cdot}641$ (5), $\beta = 79{\cdot}664$ (6), $\gamma = 70{\cdot}336$ (6)°, $V = 850{\cdot}0$ (1) Å^3, $Z = 2$, $D_x = 1{\cdot}220$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 5{\cdot}963$ cm^{-1}, $F(000) = 336$, $T = 295$ K, $R = 0{\cdot}051$ for 2391 observed reflections. The conformation of the molecule is twisted such that the bridgehead methyl groups are staggered with a torsion angle of 60·8°. Bond lengths and angles are close to normal values. The photochemical reaction in the solid state is accounted for on the basis of the molecular geometry.

* IUPAC name: 2,3,4aβ,9aβ-tetramethyl-4(1*H*)-oxo-*cis*-4a,9a,-9,10-tetrahydro-1β-anthryl acetate (note that this numbering differs from that used throughout the paper).

Introduction. Irradiation of compound (I), whether in solution or in the solid state, gives compound (II). The reaction is initiated by intramolecular allylic H-atom transfer to the β-carbon atom of the enone moiety. The crystallographic study of (I) was undertaken to establish the geometric requirements for the above reaction.



(I) (II)

0108-2701/87/061103-03$01.50

Experimental. Crystal size 0·2 × 0·2 × 0·3 mm, m.p. 405–406 K, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Cu $K\alpha$ radiation, lattice parameters from setting of 25 reflections with $33 \le \theta \le 47°$, 3030 unique reflections with $\theta \le 75°$, $h = -11 \rightarrow 11$, $k = -12 \rightarrow 12$, $l = 0 \rightarrow 13$; ω–2θ scan, ω scan width $(0{\cdot}80+0{\cdot}14\tan\theta)°$, extended 25% on each side for background measurement, horizontal aperture $(1{\cdot}0+\tan\theta)$ mm, vertical aperture 4 mm, Lp corrections, three standard reflections. Structure was solved by direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$ using *SHELX*76 (Sheldrick, 1976). All H atoms were located in a difference synthesis and were refined isotropically. 304 parameters consisting of 141 positional parameters, 138 anisotropic temperature factors, 24 isotropic temperature factors and a scale factor. Convergence at $R = 0{\cdot}051$, $wR = 0{\cdot}047$ for 2391 observed reflections for which $F \ge 3\sigma(F)$, where $\sigma^2(I) = S + 2B + [0{\cdot}04(S-B)]^2$, S = scan count, B = time-averaged background count. $R = 0{\cdot}072$, $wR = 0{\cdot}052$ for all data, $w = 1/\sigma^2(F)$, $(\Delta/\sigma)_{max} = 0{\cdot}2$, $\pm 0{\cdot}20$ e Å^{-3} in final difference synthesis, atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). No corrections for absorption or secondary extinction.

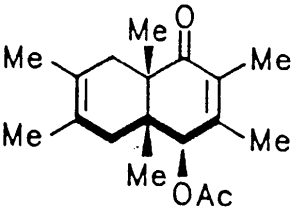
Table 1. *Atom coordinates* (C, O ×10⁴; H ×10³) *and temperature factors* (Å² ×10³)

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}/U_{iso}
O(1)	9017 (2)	2743 (2)	9202 (2)	65
O(2)	8044 (1)	3202 (1)	4318 (1)	42
O(3)	8427 (2)	1124 (2)	3749 (2)	83
C(1)	8938 (2)	2419 (2)	8227 (2)	42
C(2)	10093 (2)	2592 (2)	7095 (2)	42
C(21)	11487 (3)	2836 (4)	7344 (3)	64
C(3)	9871 (2)	2516 (2)	5911 (2)	38
C(31)	11021 (3)	2645 (3)	4734 (2)	56
C(4)	8478 (2)	2224 (2)	5715 (2)	34
C(41)	8127 (2)	2500 (2)	3435 (2)	47
C(42)	7823 (3)	3674 (3)	2018 (2)	63
C(4*A*)	7127 (2)	2593 (2)	6695 (2)	35
C(4*A*1)	6477 (2)	4371 (2)	6317 (2)	46
C(5)	5917 (2)	1922 (2)	6593 (2)	44
C(6)	6279 (2)	164 (2)	7238 (2)	43
C(7)	7411 (2)	−728 (2)	8160 (2)	43
C(8)	8396 (2)	8 (2)	8494 (2)	44
C(8*A*)	7690 (2)	1789 (2)	8168 (2)	39
C(8*A*1)	6437 (3)	2044 (3)	9250 (2)	59
C(9)	5442 (2)	−589 (3)	6932 (2)	55
C(10)	5720 (3)	−2192 (3)	7532 (3)	64
C(11)	6838 (3)	−3070 (3)	8440 (3)	66
C(12)	7673 (3)	−2349 (2)	8755 (2)	54
H(211)	1225 (5)	187 (5)	775 (5)	146 (15)
H(212)	1189 (4)	359 (5)	661 (4)	120 (11)
H(213)	1133 (4)	331 (5)	802 (4)	134 (13)
H(311)	1206 (3)	241 (3)	495 (3)	78 (8)
H(312)	1113 (3)	189 (4)	436 (3)	98 (10)
H(313)	1072 (3)	369 (4)	400 (3)	97 (9)
H(4)	870 (2)	110 (2)	583 (2)	36 (4)
H(421)	863 (4)	413 (4)	171 (4)	114 (11)
H(422)	700 (4)	466 (4)	208 (4)	111 (10)
H(423)	779 (4)	313 (5)	146 (4)	129 (12)
H(4*A*1)	558 (3)	462 (3)	689 (3)	74 (7)
H(4*A*2)	620 (3)	496 (3)	529 (3)	80 (8)
H(4*A*3)	721 (3)	488 (3)	647 (2)	65 (7)
H(51)	500 (2)	241 (2)	698 (2)	48 (5)
H(52)	572 (3)	223 (3)	559 (3)	70 (7)
H(81)	938 (2)	−23 (2)	802 (2)	40 (5)
H(82)	862 (2)	−54 (3)	955 (3)	62 (6)
H(8*A*1)	693 (3)	151 (3)	1014 (3)	78 (8)
H(8*A*2)	599 (3)	323 (4)	907 (3)	95 (9)
H(8*A*3)	570 (3)	154 (3)	923 (3)	74 (7)
H(9)	458 (3)	7 (3)	630 (3)	83 (8)
H(10)	510 (3)	−264 (3)	723 (2)	62 (6)
H(11)	703 (3)	−418 (3)	889 (3)	87 (8)
H(12)	842 (3)	−295 (3)	949 (3)	61 (6)

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

The molecular conformation of the title compound (Fig. 1) is twisted about the C(4*A*)–C(8*A*) bond, so that the bridgehead methyl groups are staggered, as in the related compound 2,3,4aβ,6,7,8aβ-hexamethyl-4a,5,8,8a-tetrahydro-1-naphthoquin-4β-yl acetate (III) (Ariel & Trotter, 1985). The degree of 'twist' is shown by the torsion angle C(4)–C(4*A*)–C(8*A*)–C(8), −57·5 (2)°, and C(4*A*1)–C(4*A*)–C(8*A*)–C(8*A*1), 60·8 (2)°. In (III) the corresponding values for the two angles are −58·9 (2) and 59·6 (2)°, respectively. Bond lengths and bond angles are not significantly different from those in (III), except for the increase in C(6)–C(7), 1·395 (3) *vs.* 1·326 (3) Å, resulting from the lower bond order. The C(sp^3)–C(sp^3) bond distances (Table 2) are in the range 1·529 (3)–1·554 (3) Å, mean 1·541 Å.



(III)

Molecules of (I) crystallize with the conformation where the bulkier acetate substituent occupies the more sterically favoured pseudo-equatorial position, just like compound (III) (Ariel & Trotter, 1985). The consequence of this arrangement is the proximity of the β-enone carbon, C(3), to H(81) (2·85 Å). Furthermore, the angle between the C(3)···H(81) vector and its projection on the plane of C(3)=C(2) double bond [C(1),C(2),C(3),C(4)], τ, and the angle between the C(3)···H(81) and the C(3)=C(2) vectors, Δ, are 49 and 74°, respectively. This geometry is highly favourable for H-abstraction by the β-enone C, which is observed

* Lists of structure factors, anisotropic thermal parameters, and bond distances and angles involving hydrogen atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43702 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°)

C(1)–O(1)	1·222 (3)	C(5)–C(6)	1·511 (3)
C(1)–C(2)	1·473 (3)	C(6)–C(7)	1·395 (3)
C(2)–C(3)	1·352 (3)	C(7)–C(8)	1·510 (4)
C(2) C(21)	1·501 (4)	C(8)–C(8A)	1·552 (3)
C(3)–C(4)	1·503 (3)	C(1)–C(8A)	1·523 (3)
C(3)–C(31)	1·502 (3)	C(4A)–C(8A)	1·554 (3)
C(4)–C(4A)	1·538 (2)	C(8A)–C(8A1)	1·529 (3)
C(4)–O(2)	1·460 (2)	C(6)–C(9)	1·396 (4)
C(41)–O(2)	1·346 (3)	C(9)–C(10)	1·383 (3)
C(41)–O(3)	1·189 (3)	C(10)–C(11)	1·376 (4)
C(41)–C(42)	1·497 (3)	C(11)–C(12)	1·375 (5)
C(4A)–C(5)	1·535 (3)	C(7)–C(12)	1·400 (3)
C(4A)–C(4A1)	1·537 (2)		

C(41)–O(2)–C(4)	118·5 (1)	C(42)–C(41)–O(3)	125·1 (2)
C(2)–C(1)–O(1)	119·9 (2)	O(3)–C(41)–O(2)	123·8 (2)
C(8A)–C(1)–O(1)	121·4 (2)	C(4A)–C(5)–C(6)	115·1 (2)
C(8A)–C(1)–C(2)	118·7 (2)	C(7)–C(6)–C(5)	121·6 (2)
C(21)–C(2)–C(1)	116·7 (2)	C(9)–C(6)–C(5)	119·5 (2)
C(3)–C(2)–C(1)	119·9 (2)	C(9)–C(6)–C(7)	118·9 (2)
C(3)–C(2)–C(21)	123·4 (2)	C(8)–C(7)–C(6)	121·5 (2)
C(31)–C(3)–C(2)	122·4 (2)	C(12)–C(7)–C(6)	119·2 (2)
C(4)–C(3)–C(2)	121·8 (2)	C(12)–C(7)–C(8)	119·2 (2)
C(4)–C(3)–C(31)	115·7 (2)	C(8A)–C(8)–C(7)	113·4 (2)
C(4A)–C(4)–C(3)	115·1 (1)	C(4A)–C(8A)–C(1)	108·4 (1)
C(4A)–C(4)–O(2)	108·3 (1)	C(8)–C(8A)–C(4A)	109·5 (2)
C(3)–C(4)–O(2)	107·4 (1)	C(8A1)–C(8A)–C(4A)	112·8 (2)
C(4A1)–C(4A)–C(4)	109·9 (2)	C(8)–C(8A)–C(1)	106·9 (2)
C(8A)–C(4A)–C(5)	109·4 (2)	C(8A1)–C(8A)–C(1)	110·2 (2)
C(5)–C(4A)–C(4A1)	109·6 (2)	C(8A1)–C(8A)–C(8)	108·9 (2)
C(8A)–C(4A)–C(4A1)	110·9 (2)	C(10)–C(9)–C(6)	120·9 (2)
C(5)–C(4A)–C(4)	109·3 (2)	C(11)–C(10)–C(9)	120·1 (3)
C(8A)–C(4A)–C(4)	107·6 (1)	C(12)–C(11)–C(10)	119·8 (2)
C(42)–C(41)–O(2)	111·1 (2)	C(11)–C(12)–C(7)	121·1 (2)

C(41)–O(2)–C(4)–C(3)	113·5 (2)
C(41)–O(2)–C(4)–C(4A)	−121·6 (2)
C(4)–O(2)–C(41)–O(3)	5·9 (3)
C(4)–O(2)–C(41)–C(42)	−173·1 (2)
O(1)–C(1)–C(2)–C(21)	12·6 (3)
O(1)–C(1)–C(2)–C(3)	−167·9 (2)
C(8A)–C(1)–C(2)–C(21)	−165·6 (2)
C(8A)–C(1)–C(2)–C(3)	14·0 (3)
O(1)–C(1)–C(8A)–C(4A)	138·3 (2)
O(1)–C(1)–C(8A)–C(8)	−103·7 (2)
O(1)–C(1)–C(8A)–C(8A1)	14·5 (3)
C(2) C(1) C(8A) C(4A)	43·5 (2)
C(2)–C(1)–C(8A)–C(8)	74·5 (2)
C(2)–C(1)–C(8A)–C(8A1)	−167·4 (2)
C(1)–C(2)–C(3)–C(4)	−1·3 (3)
C(2)–C(3)–C(4)–O(2)	141·3 (2)
C(2)–C(3)–C(4)–C(4A)	20·6 (3)
C(31)–C(3)–C(4)–O(2)	−41·3 (2)
C(31)–C(3)–C(4)–C(4A)	−161·9 (2)
O(2)–C(4)–C(4A)–C(4A1)	−48·5 (2)
O(2)–C(4)–C(4A)–C(5)	71·9 (2)
O(2)–C(4)–C(4A)–C(8A)	−169·4 (1)
C(3)–C(4)–C(4A)–C(4A1)	71·6 (2)
C(3)–C(4)–C(4A)–C(5)	−168·0 (2)
C(3)–C(4)–C(4A)–C(8A)	−49·3 (2)
C(4)–C(4A)–C(5)–C(6)	72·8 (2)
C(4A1)–C(4A)–C(5)–C(6)	−166·7 (2)
C(8A)–C(4A)–C(5)–C(6)	−44·8 (2)
C(4)–C(4A)–C(8A)–C(1)	58·8 (2)
C(4)–C(4A)–C(8A)–C(8)	−57·5 (2)
C(4)–C(4A)–C(8A)–C(8A1)	−178·9 (2)
C(4A1)–C(4A)–C(8A)–C(1)	−61·5 (2)
C(4A1)–C(4A)–C(8A)–C(8)	−177·8 (2)
C(4A1)–C(4A)–C(8A)–C(8A1)	60·8 (2)
C(5)–C(4A)–C(8A)–C(1)	177·5 (2)
C(5)–C(4A)–C(8A)–C(8)	61·2 (2)
C(5)–C(4A)–C(8A)–C(8A1)	−60·2 (2)
C(4A)–C(5)–C(6)–C(7)	16·4 (3)
C(4A)–C(5)–C(6)–C(9)	−165·1 (2)
C(6)–C(7)–C(8)–C(8A)	20·9 (3)
C(12)–C(7)–C(8)–C(8A)	−161·2 (2)
C(7)–C(8)–C(8A)–C(1)	−166·6 (2)
C(7)–C(8)–C(8A)–C(4A)	−49·3 (2)
C(7)–C(8)–C(8A)–C(8A1)	74·4 (2)

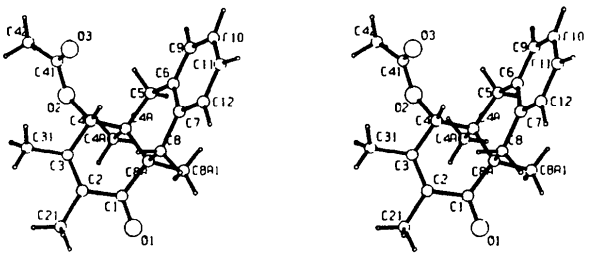


Fig. 1. Stereoscopic view of (I) with crystallographic atomic labelling.

in the solid state and solution photolysis, followed by C(2)–C(8) bonding, C(2)···C(8) = 3·168 (3) Å, to generate compound (II). The corresponding values for the C(3)···H(81) distance, τ, and Δ for compound (III), are 2·84 Å, 50, and 74°, respectively, allowing the H-abstraction by the β-enone C photolysis to occur in the solid state (Ariel & Trotter, 1985).

The distance between the carbonyl oxygen, O(1), and the β-hydrogen, H(82), is 3·21 Å, larger than the 2·7 Å van der Waals O···H contact; thus, the photochemical reaction pathway for β-hydrogen abstraction from C(8) by O(1) is not feasible. O(1) is 2·50 Å away from another β-hydrogen, H(8A1), and the other relevant geometric parameters for this β-hydrogen abstraction by O(1), described by τ [the degree by which H(β) lies outside the plane of the carbonyl group], and Δ [the angle C(1)–O(1)···H(β)], are $\tau = 8°$, $\Delta = 81°$. Thus there is an almost perfect alignment of the β-H with the non-bonding orbital of O(1). However, no such product has been observed.

Intermolecular distances correspond to normal van der Waals interactions.

Acknowledgement is made to Professor J. R. Scheffer and Mr S. H. Askari for their collaborative studies on the solid-state photochemistry, the Natural Sciences and Engineering Research Council of Canada for financial support, and the University of British Columbia Computing Centre for assistance.

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