A stereoscopic view of the crystal structure is shown in Fig. 2. The Cl atom of the reference molecule is situated at a distance of 3·565 (4) Å from the plane of the fused ring of the molecule $(1-z, -y, 1-z)$.

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Structure of 1,3,4,5,6,9-Hexamethyl-8-*exo*-methylenetricyclo[4.4.0.0^{3,9}]dec-4-en-2-one, $C_{17}H_{24}O$

BY ANTHONY S. SECCO AND JAMES TROTTER

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Y6

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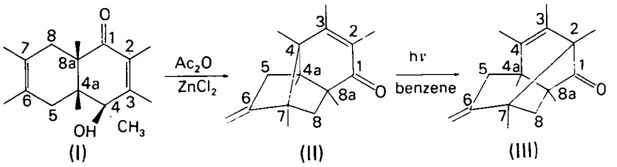
Abstract. $M_r = 244{\cdot}36$, monoclinic, $P2_1/a$, $a = 12{\cdot}374\ (2)$, $b = 8{\cdot}771\ (1)$, $c = 13{\cdot}743\ (2)$ Å, $\beta = 104{\cdot}027\ (6)°$, $V = 1447{\cdot}1\ (3)$ Å^3, $Z = 4$, $D_c = 1{\cdot}222$ g cm^{-3}, λ (Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}626$ cm^{-1}, $T = 295$ K. Final $R = 0{\cdot}037$ for 1369 observed reflections. The structural analysis showed that a deconjugative 1,3-shift occurred on photolysis of the isomeric precursor in solution.

Introduction. Although efforts to relate structure with the solid-state photoreactivity of tetrahydronaphthoquinols have met with much success (Greenhough & Trotter, 1981; Appel, Jiang, Scheffer & Walsh, 1982; Secco & Trotter, 1982), one aspect of the study, that of hydrogen-bonding effects on reactivity, has been more difficult to ascertain. The present compound arose from attempts to acetylate the heptamethyl-4β-ol derivative (I) in the hope that by replacing OH with OAc, the reactivity in the absence of hydrogen bonding could have then been studied. Instead, however, the *exo*-methylene ketone (II) was formed as the major product, from which the title compound (III) was subsequently produced. The following crystal analysis shows that a deconjugative 1,3-shift resulted from the photolysis of (II) in solution leading to the isometric *exo*-methylene ketone (III).



Experimental. Generated from 2,3,4α,4aβ,6,7,8aβ-heptamethyl-4aβ,5,8,8aβ-tetrahydronaphthoquin-4β-ol (I) *via* intermediate 1,3,6,7,8,9-hexamethyl-4-*exo*-methylenetricyclo[4.4.0.0^{3,7}]dec-7-en-10-one (II) (Jiang, Scheffer, Secco, Trotter & Wong, 1982); recrystallization of methylene ketone (III) from a hexane/acetone solution yielded translucent crystals whose faces appeared related by a twofold rotation axis parallel to the long axis of the crystals; 0·3 × 0·2 × 0·3 mm, CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$, ω–(5/3)θ scan, $\theta \leq 27{\cdot}5°$, ω-scan width $(0{\cdot}65 + 0{\cdot}35\tan\theta)°$ extended 25% on each side for background measurement, horizontal aperture $(2{\cdot}00 + \tan\theta)$ mm, vertical aperture 4 mm, scan speeds 0·91–10·06 deg min^{-1}, maximum scan time 75 s, cell parameters from least-squares fit of $\sin\theta$ values for 22 reflections with $11 < \theta < 18°$, Lp corrections, 3297 reflections, 1369 (41·5%) with $I \geq 3\sigma(I)$ where $\sigma^2(I) = S + 2B + [0{\cdot}04(S - B)]^2$, S = scan count, B = time-averaged background count; structure

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solved by *MULTAN* 80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), refined by full-matrix least squares, H atoms from a difference synthesis, isotropic type (I) (domain misorientation) extinction correction, final $g = 5{\cdot}44 \times 10^4$ (Coppens & Hamilton, 1970), final $R = 0{\cdot}037$, $R_w = 0{\cdot}039$ for 260 variables, 1369 data, $R = 0{\cdot}132$, $R_w = 0{\cdot}075$ for all data, $w = 1/\sigma^2(F)$, g.o.f. = 0·74, $\pm 0{\cdot}15$ e Å^{-3} in final difference synthesis, $F(000) = 536$, atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965), local adaptations of standard computer programs *ORFLS* (Busing, Martin & Levy, 1962), *ORFFE* (Busing, Martin & Levy, 1964), *FORDAP* (A. Zalkin) and *ORTEP* II (Johnson, 1976).

Discussion. Positional and isotropic thermal parameters are given in Table 1.*

The structure consists of molecules composed of a twisted half-chair cyclohexenone ring *cis*-fused to a twisted boat cyclohexane moiety. In addition to the bridging bond C(4a)—C(8a)†, the two six-membered rings are joined *via* atoms C(2) and C(7) forming a five-membered ring with atoms C(1), C(8a) and C(8) (Fig. 1). The molecule is highly strained, as evidenced by marked deviations from the expected values of angles associated with atoms of given hybridizations (Table 2). The endocyclic angles of the five-membered ring, which includes a formally sp^2-hybridized C atom, range from 94 to 105°; the experimental value for the angles of unsubstituted cyclopentane is 111·7(2)° (Adams, Geise & Bartell, 1970) and for planar aromatic cyclopentadienyl is 108°. Further angular strain is noticeable in those angles containing methyl groups. Each methyl substituent is eclipsed with at least one other methyl group on an adjacent C atom. Except for C(31)—C(3)—C(2)—C(21) [11·5 (3)°] and C(41)—C(4)—C(4a)—C(4a1) [−24·4 (4)°], H_3C—C—C—CH_3 torsion angles range from −1·2 (3) to −2·9 (4)°. The steric repulsion of the eclipsed substituents results in a widening of the H_3C—C—C angles by as much as 7·4° in the case of C(8a1)—C(8a)—C(4a); the combined effect at the bridgeheads is a net increase of 8·5°.

The overall stress in the molecule is alleviated somewhat by the lengthening of the bridging bonds C(4a)—C(8a) and C(2)—C(7) to distances of 1·604 (4) and 1·602 (4) Å, respectively (Table 2). This increase in length of approximately 0·07 Å over accepted values (Sutton, 1965) for $C(sp^3)$—$C(sp^3)$ bonds is not enough to eliminate the repulsive effect of the eclipsed methyl groups (see above).

Table 1. *Final positional* ($\times 10^5$, H $\times 10^3$) *and isotropic thermal parameters* ($\times 10^3$ Å^2) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}*/U_{iso}
C(1)	55042 (23)	13913 (33)	65380 (19)	45
C(2)	60655 (21)	−160 (32)	70552 (19)	42
C(21)	53993 (39)	−14597 (49)	66836 (35)	71
C(3)	60690 (21)	4181 (33)	81383 (19)	45
C(31)	56373 (40)	−7121 (57)	87757 (31)	76
C(4)	64132 (22)	18184 (35)	84397 (20)	46
C(41)	64072 (42)	24161 (63)	94693 (28)	78
C(4a)	69955 (23)	27705 (32)	77830 (20)	51
C(4a1)	70615 (53)	44767 (46)	80587 (38)	88
C(5)	81862 (25)	21046 (40)	80195 (26)	59
C(6)	81535 (21)	4419 (36)	77570 (20)	49
C(61)	88274 (32)	−5574 (61)	83079 (31)	79
C(7)	72670 (21)	625 (32)	68131 (19)	44
C(71)	75583 (38)	−13489 (49)	62815 (31)	73
C(8)	71454 (27)	14881 (37)	61453 (23)	51
C(8a)	64186 (24)	25406 (33)	66145 (20)	48
C(8a1)	60276 (53)	39753 (49)	60040 (36)	85
O	45341 (16)	15105 (25)	60954 (15)	70
H1(21)	534 (3)	−157 (3)	598 (3)	84 (12)
H2(21)	576 (3)	−241 (5)	706 (3)	101 (14)
H3(21)	465 (3)	−131 (4)	675 (3)	97 (14)
H1(31)	584 (3)	−40 (5)	948 (3)	118 (14)
H2(31)	485 (4)	−83 (4)	856 (3)	115 (15)
H3(31)	599 (4)	−176 (6)	873 (4)	162 (22)
H1(41)	598 (4)	181 (5)	983 (3)	143 (20)
H2(41)	711 (3)	250 (4)	984 (3)	96 (14)
H3(41)	614 (4)	352 (6)	939 (4)	161 (22)
H1(4a1)	750 (3)	496 (5)	765 (3)	118 (17)
H2(4a1)	625 (4)	503 (5)	800 (3)	124 (16)
H3(4a1)	747 (3)	461 (4)	875 (3)	88 (11)
H1(5)	853 (2)	229 (3)	876 (2)	58 (8)
H2(5)	863 (2)	267 (3)	762 (2)	71 (9)
H1(61)	936 (3)	−24 (3)	893 (2)	79 (10)
H2(61)	876 (3)	−160 (4)	812 (2)	77 (12)
H1(71)	828 (3)	−112 (4)	615 (3)	108 (15)
H2(71)	700 (3)	−151 (3)	560 (3)	84 (11)
H3(71)	759 (3)	−235 (4)	669 (3)	100 (13)
H1(8)	673 (2)	122 (3)	542 (2)	57 (8)
H2(8)	786 (3)	193 (3)	610 (2)	76 (10)
H1(8a1)	562 (3)	368 (4)	533 (3)	98 (13)
H2(8a1)	668 (3)	462 (5)	598 (3)	114 (17)
H3(8a1)	550 (3)	452 (4)	633 (3)	92 (14)

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

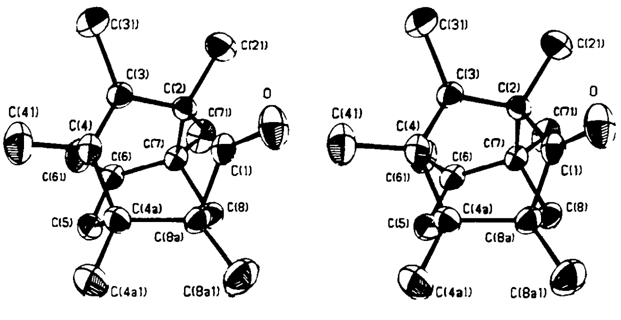

Fig. 1. Stereodiagram of 1,3,4,5,6,9-hexamethyl-8-*exo*-methylenetricyclo[4.4.0.0^{3,9}]dec-4-en-2-one with 50% probability thermal ellipsoids.

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* Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving H atoms, torsion angles and a packing diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38146 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Note, atom labels refer to the same system used in naming the naphthoquinol progenitor (I).

Table 2. *Bond angles* (°) *and lengths* (Å) *with e.s.d.'s in parentheses*

Accepted values are enclosed in brackets.

C(sp^3)—C(sp^3)—C(sp^3)	[109·5]	C(8)—C(7)—C(6)	106·1 (2)
C(21)—C(2)—C(7)	114·7 (3)	C(4a)—C(8a)—C(1)	107·4 (2)
C(4a1)—C(4a)—C(5)	108·9 (3)	C(8)—C(8a)—C(1)	94·3 (2)
C(4a1)—C(4a)—C(8a)	110·6 (3)	C(8a1)—C(8a)—C(1)	112·5 (3)
C(5)—C(4a)—C(8a)	109·5 (2)	C(sp^2)—C(sp^3)—C(sp^2)	[109·5]
C(2)—C(7)—C(71)	113·8 (3)	C(1)—C(2)—C(3)	98·4 (2)
C(2)—C(7)—C(8)	101·4 (2)	*X*(sp^2)—C(sp^2)—C(sp^3)	[120·0]
C(71)—C(7)—C(8)	112·0 (3)	O—C(1)—C(2)	126·5 (3)
C(7)—C(8)—C(8a)	102·8 (2)	O—C(1)—C(8a)	128·0 (3)
C(4a)—C(8a)—C(8)	109·4 (2)	C(4)—C(3)—C(2)	117·1 (2)
C(4a)—C(8a)—C(8a1)	116·9 (3)	C(4)—C(3)—C(31)	123·9 (3)
C(8)—C(8a)—C(8a1)	113·9 (3)	C(3)—C(4)—C(41)	122·5 (3)
C(sp^3)—C(sp^3)—C(sp^2)	[109·5]	C(3)—C(4)—C(4a)	118·7 (2)
C(21)—C(2)—C(1)	111·8 (3)	C(5)—C(6)—C(61)	122·2 (3)
C(21)—C(2)—C(3)	113·8 (3)	C(61)—C(6)—C(7)	124·8 (3)
C(7)—C(2)—C(1)	102·2 (2)	C(sp^3)—C(sp^2)—C(sp^3)	[120·0]
C(7)—C(2)—C(3)	114·0 (2)	C(2)—C(1)—C(8a)	105·3 (2)
C(4a1)—C(4a)—C(4)	112·9 (3)	C(2)—C(3)—C(31)	118·9 (3)
C(5)—C(4a)—C(4)	103·3 (2)	C(41)—C(4)—C(4a)	118·2 (3)
C(8a)—C(4a)—C(4)	111·3 (2)	C(5)—C(6)—C(7)	113·0 (2)
C(4a)—C(5)—C(6)	110·4 (2)		
C(2)—C(7)—C(6)	110·3 (2)		
C(71)—C(7)—C(6)	112·4 (3)		

C(sp^3)—C(sp^3)	[1·537 (5)]*	C(2)—C(3)	1·535 (4)
C(2)—C(21)	1·530 (4)	C(31)—C(3)	1·504 (4)
C(2)—C(7)	1·602 (4)	C(41)—C(4)	1·511 (4)
C(4a)—C(4a1)	1·541 (5)	C(4a)—C(4)	1·532 (4)
C(4a)—C(5)	1·544 (4)	C(5)—C(6)	1·500 (5)
C(4a)—C(8a)	1·604 (4)	C(7)—C(6)	1·519 (4)
C(7)—C(71)	1·524 (5)	C(sp^2)—C(sp^2)	[1·335 (5)]
C(7)—C(8)	1·537 (4)	C(3)—C(4)	1·333 (4)
C(8)—C(8a)	1·536 (6)	C(6)—C(61)	1·316 (6)
C(8a)—C(8a1)	1·525 (5)	C(sp^2)—O	[1·215 (5)]
C(sp^3)—C(sp^2)	[1·510 (5)]	C(1)—O	1·212 (3)
C(2)—C(1)	1·507 (4)		
C(8a)—C(1)	1·500 (4)		

* Accepted values from Sutton (1965).

The strain induced in the cyclohexenone ring on bonding C(2) to C(7) is compensated somewhat by the stretching of the bridge C(4a)—C(8a); in addition, bonds C(2)—C(3) and C(4a)—C(4) show increases as well, averaging 0·024 Å greater than the accepted value of 1·510 Å for C(sp^3)—C(sp^2). Other bonds within the structure (Table 2) do not deviate significantly from accepted values. Intermolecular contacts generally correspond to van der Waals distances (shortest C···C = 3·61, C···O = 3·45, O···O > 4·2 Å).

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Tricyclo[4.4.0.0^{3,8}]dec-9-ene-2,5-dione (a Twistenone), $C_{10}H_{10}O_2$

BY ANTHONY S. SECCO AND JAMES TROTTER

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Y6

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Abstract. $M_r = 162·19$, monoclinic, $P2_1/n$, $a = 6·381$ (2), $b = 19·454$ (2), $c = 6·708$ (2) Å, $\beta = 106·24$ (1)°, $V = 799·5$ (3) Å^3, $Z = 4$, $D_x = 1·347$ g cm^{-3}, μ(Mo $K\alpha$) = 0·87 cm^{-1}, $\lambda = 0·71073$ Å. Final $R = 0·037$ for 930 observed reflections. All six-membered rings of the twistane skeleton have

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