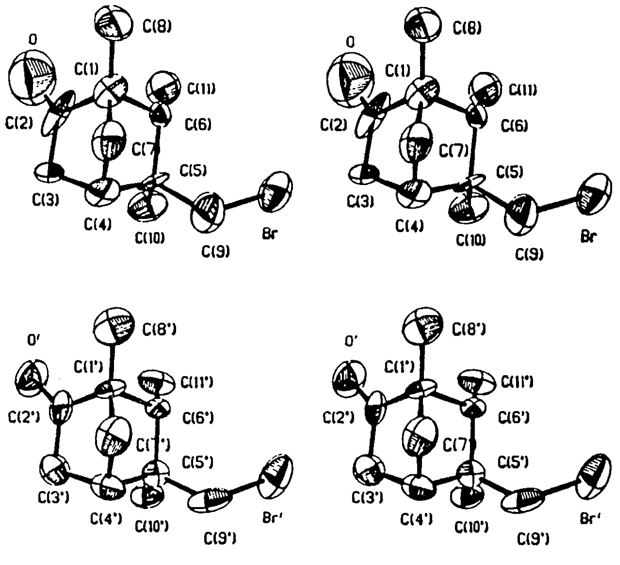

Fig. 1. Stereoviews of the two independent 8-bromo-6-*endo*-methylisofenchone molecules. [Crystallographic numbering for the peripheral methyl groups is in the order of the numbers of the skeletal carbon atoms to which they are bonded; in the usual chemical numbering, C(8), C(9), C(10) are numbered 10, 8, 9, respectively. With respect to the camphor precursor, the methyl groups are scrambled as a result of methyl shifts (Money, 1985).]

derivatives (Rettig & Trotter, 1986). The C(1)—C(7)—C(4) angle is 96·5 (10)°, and C—Br is 1·99 (2) Å. Intermolecular distances correspond to van der Waals interactions.

We thank Dr T. Money for the crystals, 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 (1*R*,5*R*,6*R*)-1,5-Dimethyl-9-methylene-3-oxabicyclo[4.3.0]nonan-4-one

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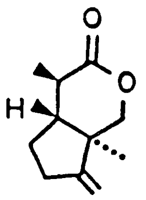
Abstract. $C_{11}H_{16}O_2$, $M_r = 180·248$, monoclinic, $P2_1$, $a = 10·0945$ (3), $b = 6·5393$ (2), $c = 7·7191$ (2) Å, $\beta = 90·528$ (2)°, $V = 509·52$ (3) Å^3, $Z = 2$, $D_x = 1·174$ (1) g cm^{-3}, Cu $K\alpha$, $\lambda\alpha_1 = 1·54056$ Å, $\mu = 6·0$ cm^{-1}, $F(000) = 196$, $T = 295$ K, $R = 0·046$ for 1020 reflections. The molecule contains *trans*-fused five- and six-membered rings, with envelope and distorted half-chair conformations, respectively; bond lengths and angles are normal.

Introduction. In the development of a synthetic route from camphor to optically active terpenoids and steroids (Hutchinson, Money & Piper, 1984, 1986; Hutchinson & Money, 1985), a lactone intermediate was isolated; the present analysis was designed to establish the relative (and, tentatively, the absolute) configurations of the chiral centres of this lactone.



Experimental. Colourless crystals, dimensions 0·35 × 0·35 × 0·35 mm, {100}, {001}, {10$\bar{1}$} developed with additional small irregular faces, Enraf–Nonius CAD-4*F* diffractometer, lattice parameters from 25 reflections with $\theta = 40$–47°. Intensities for $\theta \le 75°$, *hkl*: −12 to 12, 0 to 8, 0 to 9, ω–2θ scan, ω-scan width $(0·85 + 0·14\tan\theta)°$ at 1·3–10° min^{-1}, extended 25% on each side for background measurement, three standard reflections (no decay), Lp corrections, no

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Table 1. *Final positional (fractional* $\times 10^4$, H $\times 10^3$) *and isotropic thermal parameters* ($U \times 10^3$ Å^2) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}*/U_{iso}
O(1)	3365 (2)	7101	10590 (3)	76
O(2)	5493 (3)	6616 (7)	10547 (4)	92
C(1)	1991 (3)	6943 (7)	7968 (3)	58
C(2)	2122 (4)	7723 (9)	9802 (4)	72
C(3)	4491 (3)	6816 (8)	9712 (5)	69
C(4)	4462 (3)	6649 (8)	7747 (4)	64
C(5)	3232 (3)	7684 (7)	7020 (3)	56
C(6)	2831 (5)	7475 (9)	5103 (4)	76
C(7)	1433 (6)	8296 (11)	5082 (6)	92
C(8)	880 (3)	7904 (8)	6888 (4)	71
C(9)	1816 (4)	4619 (7)	7947 (5)	72
C(10)	5745 (5)	7455 (10)	6963 (10)	95
C(11)	−325 (4)	8244 (11)	7439 (7)	99
H(2*a*)	217 (5)	935 (12)	966 (6)	103 (15)
H(2*b*)	138 (3)	740 (5)	1060 (4)	45 (7)
H(4)	436 (3)	504 (6)	755 (4)	55 (8)
H(5)	328 (3)	944 (7)	731 (4)	62 (9)
H(6*a*)	281 (4)	599 (10)	478 (6)	84 (13)
H(6*b*)	348 (4)	838 (8)	439 (6)	85 (12)
H(7*a*)	137 (9)	949 (20)	484 (13)	198 (42)
H(7*b*)	83 (4)	738 (9)	423 (6)	88 (13)
H(9*a*)	251 (4)	385 (8)	872 (5)	71 (10)
H(9*b*)	176 (4)	415 (10)	682 (6)	92 (14)
H(9*c*)	90 (4)	444 (9)	833 (5)	87 (12)
H(10*a*)	574 (6)	725 (13)	580 (7)	127 (21)
H(10*b*)	592 (8)	901 (21)	716 (11)	177 (30)
H(10*c*)	641 (6)	702 (12)	767 (7)	116 (19)
H(11*a*)	−106 (5)	884 (11)	680 (7)	106 (15)
H(11*b*)	−46 (6)	795 (13)	882 (8)	134 (21)

* $U_{eq} = \frac{1}{3}$ trace of diagonalized $\mathbf{U}$ tensor.

absorption correction, 1146 independent reflections measured, 1020 with $I \geq 3\sigma(I)$, where $\sigma^2(I) = S + 4(B_1 + B_2) + (0{\cdot}02S)^2$, S = scan, B_1 and B_2 = background counts. Structure by direct methods, refined by full-matrix least squares on F, H atoms from a difference map, refined (isotropic), $w = 1/\sigma^2(F)$, scattering factors from *International Tables for X-ray Crystallography* (1974), locally written, or locally modified versions of standard computer programs,* final $R = 0{\cdot}046$, $wR = 0{\cdot}064$ for 1020 reflections [the wR-ratio for the refined enantiomorph structure was 1·0010, so that the absolute configuration is established, but only at the 75% significance level; the configuration determined is in agreement with that deduced from chemical considerations], $S = 2{\cdot}409$, 182 parameters [including extinction correction, $g = 1{\cdot}08\,(16) \times 10^{-4}$], $R = 0{\cdot}054$ for all 1146 reflections, $\Delta/\sigma = 0{\cdot}06$ (mean), 0·39 (maximum), maximum final difference density 0·16 e Å^{-3}. Thermal parameters interpretable in terms of rigid-body motion, bond lengths corrected for libration.

Discussion. Final positional parameters are in Table 1, and other data have been deposited.* The molecule (Fig. 1) contains *trans*-fused five- and six-membered rings. The five-membered ring is a C(5)-envelope (crystallographic numbering system), and the six-membered ring has a distorted half-chair conformation, with C(1) below and C(5) above the roughly planar C(2)—O(1)—C(3)—C(4) fragment [torsion angle −14·4 (6)°]. Bond lengths and angles (Table 2) are close to normal values: C=C 1·313 (5), C—C 1·517–1·546 (4–7), C=O 1·205 (4), C—O 1·350 (4) [C(3)—O(1)], 1·455 (4) [C(2)—O(1)] Å, C—O—C

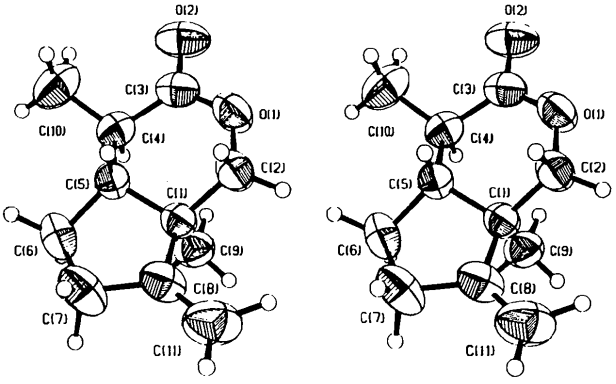

Fig. 1. Stereoview of the 3-oxabicyclononane derivative (crystallographic numbering scheme).

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

	Uncorr.	Corr.		Uncorr.	Corr.
O(1)—C(2)	1·448 (4)	1·455	C(3)—C(4)	1·521 (5)	1·531
O(1)—C(3)	1·341 (4)	1·350	C(4)—C(5)	1·518 (4)	1·526
O(2)—C(3)	1·202 (4)	1·205	C(4)—C(10)	1·528 (5)	1·535
C(1)—C(2)	1·509 (4)	1·519	C(5)—C(6)	1·537 (4)	1·544
C(1) C(5)	1·535 (4)	1·546	C(6) C(7)	1·510 (7)	1·517
C(1)—C(8)	1·527 (4)	1·534	C(7)—C(8)	1·529 (7)	1·539
C(1)—C(9)	1·530 (5)	1·539	C(8)—C(11)	1·311 (5)	1·313

C(2)—O(1)—C(3)	124·2 (3)	C(3)—C(4)—C(5)	110·2 (3)
C(2)—C(1)—C(5)	106·0 (3)	C(3)—C(4)—C(10)	111·2 (4)
C(2)—C(1)—C(8)	115·5 (3)	C(5)—C(4)—C(10)	113·2 (4)
C(2)—C(1)—C(9)	110·8 (3)	C(1)—C(5)—C(4)	110·6 (2)
C(5)—C(1)—C(8)	102·0 (3)	C(1)—C(5)—C(6)	102·8 (3)
C(5)—C(1)—C(9)	113·8 (3)	C(4)—C(5)—C(6)	121·6 (3)
C(8)—C(1)—C(9)	108·6 (3)	C(5)—C(6)—C(7)	102·5 (3)
O(1)—C(2)—C(1)	111·5 (3)	C(6)—C(7)—C(8)	106·2 (3)
O(1)—C(3)—O(2)	117·2 (3)	C(1)—C(8)—C(7)	107·1 (3)
O(1)—C(3)—C(4)	120·3 (3)	C(1)—C(8)—C(11)	124·9 (4)
O(2)—C(3)—C(4)	122·4 (3)	C(7)—C(8)—C(11)	127·9 (4)

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* *MULTAN*80, Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson (1980); *ORFLS* and *ORFFE*, Busing, Martin & Levy (1962, 1964); *FORDAP*, Zalkin (unpublished); *ORTEP*II, Johnson (1976).

* Lists of anisotropic thermal parameters, bond lengths and angles involving hydrogen atoms, torsion angles, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43191 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

124·2 (3), C—C—C 102·0–107·1 (3) (5-ring), 117·2–127·9 (3–4) (other sp^2), 106·0–113·8 (3–4)° (other sp^3). Intermolecular distances correspond to van der Waals interactions; the shortest are O(1)···O(2) 3·291 (4), O(2)···C(3) 3·145 (5) Å.

We thank Dr T. Money for the crystals, 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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Acta Cryst. (1986). C**42**, 1804–1807

Structure of 2,3,6,7-Dibenzo-4a*β*,8a*β*-dimethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone*

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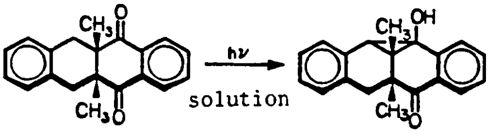
(*Received* 1 *March* 1986; *accepted* 22 *May* 1986)

Abstract. $C_{20}H_{18}O_2$, $M_r = 290·36$, triclinic, $P\bar{1}$, $a = 9·907\ (3)$, $b = 12·094\ (4)$, $c = 13·049\ (4)$ Å, $\alpha = 80·54\ (2)$, $\beta = 85·03\ (2)$, $\gamma = 89·73\ (2)$°, $V = 1536·3\ (8)$ Å^3, $Z = 4$ (two molecules per asymmetric unit), $D_x = 1·255$ g cm^{-3}, $\lambda(\text{Mo } K\alpha_1) = 0·70926$ Å, $\mu = 0·71$ cm^{-1}, $F(000) = 616$, $T = 295$ K, final $R = 0·046$ for 4388 observed reflections. The crystallographically independent molecules are related by roughly $P2_1/b11$ symmetry, and adopt a similar conformation, with a half-chair cyclohexene ring *cis*-fused to a half-chair cyclohexene-1,4-dione moiety; each molecule is twisted so that the bridgehead methyl groups are staggered with torsion angles of 63 and 65°. The solution and solid-state photochemistry are interpretable in terms of molecular conformation and packing.

Introduction. As part of a study of the photochemistry of various substituted 1,4-naphthoquinone systems it was found that irradiation of the title compound (I) in solution leads to cyclopropanol formation *via* β-H-atom abstraction by carbonyl O and closure of the resulting biradical (Ariel, Askari, Scheffer & Trotter, 1986); the title compound is, however, photochemically inert when irradiated in the solid state. The crystal-structure determination of compound (I) has been undertaken in an attempt to resolve the photoreactivity differences in the two media.



(I) (Ia)

Experimental. Crystal size 0·4 × 0·5 × 0·5 mm, m.p. 374–375 K, CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, lattice parameters from setting of 23 reflections with $20 \leq \theta \leq 24$°. 5817 unique reflections with $\theta \leq 27$°, h −12→12, k −15→15, l 0→16, ω–2θ scan, ω-scan width $(1·0 + 0·35\tan\theta)$°, extended 25% on each side for background measurement, horizontal aperture $(2·0 + \tan\theta)$ mm, vertical aperture 4 mm, Lp corrections, three standard reflections, no intensity variation. The structure was solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by full-matrix least squares using *SHELX*76

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* IUPAC name: 5a*β*,11a*β*-dimethyl-5a,6,11,11a-tetrahydronaphthacene-5,12-dione.

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