Nicolet Instrument Corporation (1986). *SHELXTL* for Desktop 30 (Microeclipse), PN 269–1040340, April.
SASADA, Y. & NITTA, I. (1956). *Acta Cryst.* **9**, 205–214.
SHIMANOUCHI, H. & SASADA, Y. (1973). *Acta Cryst.* **B29**, 81–90.
SHIONO, R. (1961). *Acta Cryst.* **14**, 42–47.

VÖGTLE, F., MÜLLER, W. M. & WATSON, W. H. (1984). *Top. Curr. Chem.* **125**, 131–166.
WATSON, W. H., GALLOY, J., GROSSIE, D. A., VÖGTLE, F. & MÜLLER, W. M. (1984). *J. Org. Chem.* **49**, 347–353.
WEILER, L. (1972). *Can. J. Chem.* **50**, 1975–1977.

Structure and Absolute Configuration of (Z)-(+)-2-Bromo-2-cycloundecenyl Camphanate

BY SATORU ITO* AND HERMAN ZIFFER

Laboratory of Chemical Physics, NIDDK, National Institutes of Health, Bethesda, MD 20892, USA

AND J. V. SILVERTON†

Laboratory of Chemistry, NHLBI, National Institutes of Health, Bethesda, MD 20892, USA

Abstract. $C_{21}H_{31}BrO_4$, $M_r = 427 \cdot 38$, monoclinic, $P2_1$, $a = 8 \cdot 050$ (1), $b = 12 \cdot 703$ (3), $c = 10 \cdot 658$ (1) Å, $\beta = 102 \cdot 56$ (2)°, $V = 1063 \cdot 80$ Å^3, $Z = 2$, $D_x = 1 \cdot 334$ g cm^{-3}, $\lambda(Cu\,K\alpha) = 1 \cdot 5418$ Å, $\mu = 28 \cdot 09$ cm^{-1}, experimental temperature 296 K. $F(000) = 448$, $R = 0 \cdot 045$ for 2015 unique reflections with $I \geq \sigma(I)$. The conformation of the 11-membered ring in this compound and its absolute configuration ($1R$) have been determined.

Introduction. As part of a study of the chiroptical properties of medium-ring 2-cycloalkenyl *p*-bromobenzoates, several *E*- and *Z*- 2-substituted 2-cycloalkenyl esters were required (Ito, Kasai & Ziffer, 1987, 1988). In order to simplify the chemistry necessary to assign the absolute stereochemistry of some of these compounds we prepared several 2-bromo derivatives, using a procedure employing silver salt solvolyses of the appropriate dibromobicyclo[*n*.1.0]alkane (Ito, Ziffer & Bax, 1986). While our reaction conditions yielded the expected 2-bromo-2-cycloalkenyl acetates, we were surprised to find that the geometry about the double bond differed in some cases from that anticipated for a concerted reaction. In those cases where it was not possible to determine the geometry about the double bond by comparing the physical properties of the compound with data in the literature, it became necessary to make the assignment from data on $^3J(C-H)$ coupling constants (Ito, Ziffer & Bax, 1986) rather than invoking arguments concerning the mechanism of the solvolysis. There were few model compounds in which the geometry about such trisubstituted double bonds had been established rigorously. We converted one critical compound that had been prepared by this reaction sequence, 2-bromo-2-cycloundecenyl acetate, to the corresponding camphanate ester (1) which had been employed for resolving the allylic alcohol. The crystals were well formed and were chosen for an X-ray structure determination to establish the geometry about the double bond, the absolute configuration about the carbinol C atom and the conformation of the 11-membered ring, since to our knowledge there has been no previous crystallographic work on such compounds. Camphanate derivatives have been used several times to determine absolute configuration, *e.g.* Cane, Nachbar, Clardy & Finer (1977); Parker (1983); Dung, Armstrong, Anderson & Williams (1983); Parker, Taylor, Ferguson & Tonge (1986).

(1)
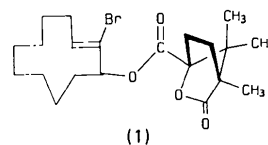
Experimental. Preparation of (1): Cyclodecene (10 g), prepared by dehydrating cyclodecanol with phosphoric acid, was treated with bromoform (17 g) and potassium *tert*-butoxide (8·4 g) in 15 ml of hexane at 273 K as described by Skattebol & Solomon (1973). The resulting dibromobicyclo[10.1.0]undecane was rearranged to 2-bromo-2-cycloundecenyl acetate by treating 2·03 g of the compound in 5 ml of acetonitrile with silver acetate (1·33 g) and acetic acid (2 ml). The mixture was refluxed for 1 h and cooled to room temperature. The solution was filtered and the filtrate

* Present address: Fujurebio Inc. Research Laboratory, 51 Komiya-cho, Hachioji, Tokyo 192, Japan.
† Author to whom correspondence should be addressed at: NIH, 10/7N-309, Bethesda, MD 20892, USA.

was diluted with ether. The ether extract was washed with aq. $NaHCO_3$ and aq. NaCl and concentrated. The crude acetate was purified by chromatography on silica gel to yield 1·32 g of 2-bromo-2-cycloundecenyl acetate. Hydrolysis of the acetate with KOH in aqueous methanol yielded 2-bromo-2-cycloundecenol. The alcohol (888 mg) was reacted with (−)-camphanoyl chloride in pyridine (5 ml) containing N,N-dimethyl-4-aminopyridine at 273 K overnight. The product was purified by chromatography on silica gel to give 1·12 g of the ester (1).

Crystallization of (1) from hexane–ethyl acetate yielded colorless needles, m.p. 422–423·5 K (uncorrected), $[\alpha]_D + 27\cdot6°$ ($c = 0\cdot5$, $CHCl_3$). Anal. calcd for $C_{21}H_{31}BrO_4$: C, 59·02; H, 7·26; Br, 18·73, found: C, 59·25; H, 7·40; Br, 18·45%. The crystal used for all X-ray investigations was a needle cut to 0·23 × 0·38 × 0·15 mm and lattice parameters were obtained by least-squares refinement using Bragg angles of 17 reflections with $20 < \theta < 30°$ measured with Cu $K\alpha$ X-radiation at $\pm\theta$. The Friedel group was $2/m$ and the sole systematic absence was $0k0$ for $k \neq 2n$. The only space group obeying the reflection conditions and suitable for an optically active compound is $P2_1$ with the polar axis b. The intensity data were measured with an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Cu $K\alpha$ radiation and no significant changes were observed in the intensities of three standard reflections (105, 25$\bar{1}$, 33$\bar{3}$) measured every 3 h. 2249 unique reflections were measured [maximum θ angle: 74°, $(\sin\theta)/\lambda$(max.): 0·623 Å^{-1}, extrema of h, k and l: 0,10; 0,15 and 12,−13 respectively]. 234 reflections with $I < \sigma(I)$ were considered unobserved. The phase problem was solved by direct methods (Gilmore, 1983). The presence of a single heavy atom in the asymmetric unit caused the E map to have pseudosymmetry but the structure was gradually elucidated, once the camphanate moiety was recognized, using weighted Fourier maps, and then refined by the programs of the XRAY72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The function minimized was $\Sigma[w(|F_o| − |F_c|)]^2$ with $w = 1/\sigma$ and σ calculated following Peterson & Levy (1957).

All heavier atoms were successfully identified from bond lengths and thermal parameters and indications were found for all expected H atoms. The configuration of the camphanate corresponded to the absolute configuration of (−)-camphanic acid as unambiguously determined by its synthesis from (+)-camphor (Gerlach, 1968). Refinement was continued with anisotropic thermal parameters of the form $\exp(−2\pi^2\Sigma_i\Sigma_j U_{ij}h_ih_ja_i^*a_j^*)$, anomalous-dispersion corrections (*International Tables for X-ray Crystallography*, 1974) for all the heavier atoms and isotropic parameters (unrefined) for the H atoms to a final R factor at convergence of 0·045. For completeness, the

Table 1. *Final coordinates for the heavier atoms*

All parameters are multiplied by 10^4 except for the values for Br where an extra factor of 10 has been applied. The equivalent U values are the geometric means of the diagonal terms of the vibration tensors. The origin was specified by fixing the Br y value.

	x	y	z	$U_{eq}(\text{Å}^2)$
O1	7670 (5)	1041 (3)	2115 (3)	55 (1)
C1	8581 (6)	1923 (4)	1707 (4)	49 (1)
C2	8199 (5)	2909 (5)	2354 (4)	49 (1)
C3	7811 (6)	3818 (5)	1785 (7)	60 (2)
C4	7538 (10)	4873 (6)	2334 (11)	85 (3)
C5	8858 (14)	5665 (8)	2289 (16)	133 (5)
C6	10654 (12)	5416 (10)	2631 (12)	120 (4)
C7	11487 (11)	4919 (7)	1647 (8)	88 (3)
C8	12989 (9)	4180 (7)	2214 (7)	81 (2)
C9	12426 (9)	3136 (6)	2635 (7)	77 (2)
C10	11572 (7)	2423 (5)	1537 (6)	66 (2)
C11	10428 (7)	1603 (5)	1966 (6)	63 (2)
C1′	5347 (5)	−7 (4)	2190 (4)	44 (1)
C2′	5085 (9)	307 (5)	3519 (6)	69 (2)
C3′	4607 (11)	−767 (6)	4031 (6)	77 (2)
C4′	4747 (7)	−1559 (5)	2937 (5)	57 (2)
C5′	3273 (7)	−1227 (5)	1885 (5)	63 (2)
O5′	1934 (5)	−1655 (5)	1457 (5)	91 (2)
O6′	3661 (4)	−269 (3)	1437 (3)	55 (1)
C7′	6231 (6)	−1084 (4)	2408 (4)	45 (1)
C8′	6421 (9)	−1591 (5)	1150 (6)	65 (2)
C9′	7938 (9)	−1113 (6)	3354 (6)	67 (2)
C10′	4760 (13)	−2721 (6)	3289 (8)	84 (3)
O11′	5422 (5)	1213 (4)	486 (4)	76 (1)
C11′	6098 (6)	829 (4)	1467 (4)	47 (1)
Br	84318 (8)	27607	41704 (5)	824 (3)

opposite enantiomorph was also refined and convergence was attained at $R = 0\cdot048$. The weighted R factors were 0·050 and 0·053 respectively. The ratio of R factors (1·06) is higher than the value of 1·002 required for the Hamilton (1965) R-factor ratio at a probability level of 0·005 and the enantiomorph with the lower R factor corresponds to the known camphanate configuration. The largest ratio of parameter shift to standard deviation was 0·12 and the goodness-of-fit parameter was 1·616 at the conclusion of the refinement of the correct enantiomorph. Atomic parameters for the heavier atoms are given in Table 1.*

Discussion. The absolute configuration shown in Fig. 1 corresponds to $R(\text{C1})$; the known configurations are $S(\text{C1}')$ and $R(\text{C4}')$ as depicted. The geometry of the olefinic bond is Z with a torsion angle of −175 (1)°. Bond lengths and some angles are shown in Fig. 1. In general, lengths and angles are as expected except near C5, which has very large thermal parameters whose size may not be caused by real thermal motion but may reflect conformational disorder at this position in the ring. Two-site refinement was attempted but proved

---

*Lists of all refinement parameters, structure factors and molecular dimensions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44376 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
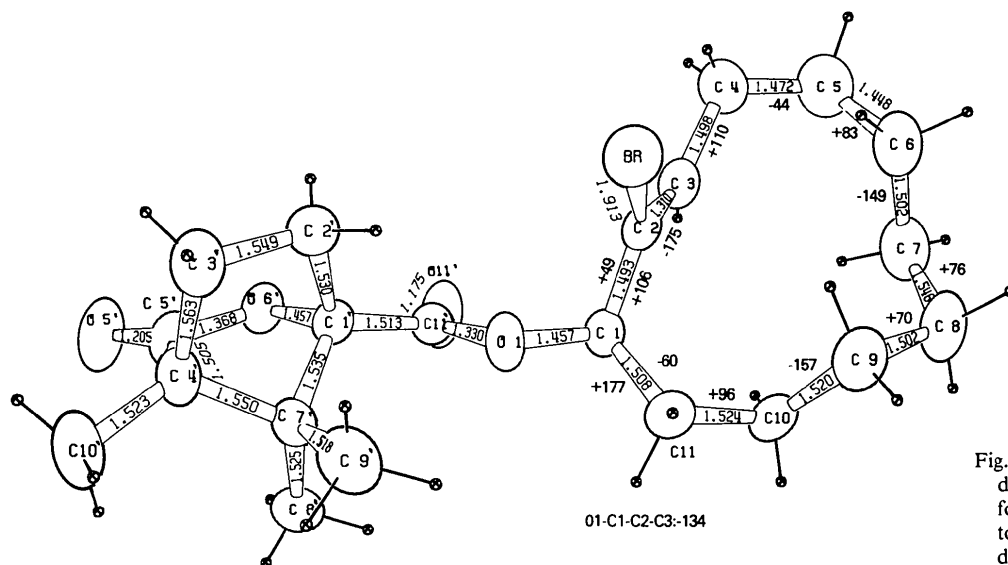
Fig. 1. *ORTEP* (Johnson, 1965) drawing showing crystal conformation, bond lengths and torsion angles in the undecene ring.
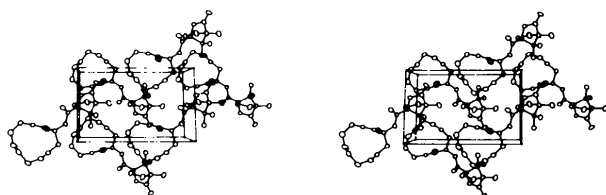
01-C1-C2-C3:-134

Fig. 2. *ORTEP* (Johnson, 1965) drawing showing crystal packing. The projection is down **b** and the *c* axis is horizontal.

unsuccessful. A difference map calculated after convergence indicated two pairs of negative and positive peaks, $+0\cdot43$ and $-0\cdot64$, $+0\cdot42$ and $-0\cdot52$ e $Å^{-3}$, but neither these nor any of the next ten peaks and holes had any obvious association with atoms in the structure. As may best be seen from the packing diagram, Fig. 2, the observed conformation is an extended, fairly flat ring with an approximate twofold axis through C8 and the center of the C2—C3 bond (the approximate symmetry is also indicated by the rough equality of corresponding torsion angles shown in Fig. 1). A least-squares plane through the ring C atoms has maximum deviations of $+0\cdot61$ and $-0\cdot62$ Å at C9 and C7, respectively. An alternative description of the ring is that it is composed of three planar or nearly planar sets of atoms; C9, C8, C7, C3, C2 (all within $0\cdot03$ Å of their plane), C1, C10, C11 and C4, C5, C6. The two triangles have dihedral angles of 10° with the pentagon and, by analogy with previous names for ring conformations, one might coin the term 'triplanar'.

The C3—C6, C2—C9, C7—C10 and C5—C9 contacts, $3\cdot05$, $3\cdot09$, $3\cdot17$ and $3\cdot23$ Å respectively, are fairly short. All other second-neighbor C—C contacts are about $3\cdot4$ Å or greater [the van der Waals contact

distance of Bondi (1964) is $3\cdot5$ Å]. The H—H contacts are generally no smaller than $2\cdot2$ Å, which is not much less than a van der Waals contact of $2\cdot4$ Å, although there are two significantly short contacts between the H atoms of C11:C10 and C7:C6 at $2\cdot0$ and $2\cdot1$ Å, respectively. The intermolecular packing appears fairly efficient.

References

BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.

CANE, D. E., NACHBAR, R. B., CLARDY, J. & FINER, J. (1977). *Tetrahedron Lett.* pp. 4277–4280.

DUNG, J. S., ARMSTRONG, R. W., ANDERSON, O. P. & WILLIAMS, R. M. (1983). *J. Org. Chem.* **48**, 3592–3594.

GERLACH, H. (1968). *Helv. Chim. Acta,* **51**, 1587–1589, and references cited therein.

GILMORE, C. J. (1983). *MITHRIL.* Computer program for the automatic solution of crystal structures from X-ray data. Univ. of Glasgow, Scotland.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 501–510.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

ITO, S., KASAI, M. & ZIFFER, H. (1987). *Can. J. Chem.* **65**, 574–582.

ITO, S., KASAI, M. & ZIFFER, H. (1988). In preparation.

ITO, S., ZIFFER, H. & BAX, A. (1986). *J. Org. Chem.* **51**, 1130–1133.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

PARKER, D. (1983). *J. Chem. Soc. Perkin Trans.* 2, pp. 83–88.

PARKER, D., TAYLOR, R. J., FERGUSON, G. & TONGE, A. (1986). *Tetrahedron,* **42**, 617–622.

PETERSON, S. W. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 70–76.

SKATTEBOL, L. & SOLOMON, S. (1973). *Organic Syntheses,* Vol. V, p. 306. New York: John Wiley.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. W. & HALL, S. R. (1972). *XRAY72.* Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.