

Fig. 1. The conformation and numbering of (I) with the intramolecular O(8)···C(6) interaction shown as a broken line.

The overall molecular structure of (I) is similar to that of (V) (Brown, Murray-Rust, Murray-Rust & Newton, 1979) from which it differs by only one O atom. (V) was found to crystallize as two independent molecules (*a*) and (*b*). Inspection of the torsion angles of (I), (*Va*) and (*Vb*) (Table 4) indicates that the conformation of the cyclopentane ring in (I) is similar to that in (*Va*) whilst the cyclobutane ring in (I) is found to be similar to that in (*Vb*). In (I), torsional strain is thus not completely transmitted from the cyclopentane ring to the cyclobutane ring since C(4)–C(5)–C(1)–C(2) is nearly 7° larger than C(6)–C(5)–C(1)–C(7). In contrast, both molecules in (V) are almost free from this distortion about C(1)–C(5). Since (I) and (V) are similar in so many

features it is possible that the distortion is in part related to the transannular interaction. This could be explained if the C(6)···O(8) interaction is weakly repulsive at this distance with C(6) pushed away from O(8) and consequently flattening the cyclobutane ring. However, the degree of flexibility of the bicyclo[3.2.0] system could be considerable [as shown by (V)], and more structural data are required.

We thank Glaxo Group Research (Ware) Ltd and the SRC for a CASE studentship (to RCG).

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Acta Cryst. (1982). **B38**, 2700–2702

(2*S*,3*S*)-2-*exo*-Bromo-3-*endo*-hydroxybicyclo[3.2.0]heptan-6-one

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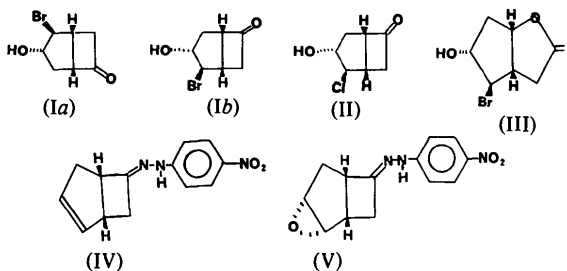
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(Received 24 July 1980; accepted 26 October 1981)

Abstract. C₇H₉BrO₂, *M_r* = 204.9, trigonal, *P*3₁ (from structure determination), *a* = 10.13 (2), *c* = 6.66 (1) Å from diffractometer measurements (Mo *K*α radiation), *V* = 592 Å³, *Z* = 3, *D_m* = 1.72, *D_c* = 1.73 Mg m⁻³, *F*(000) = 306, *μ* = 5.22 mm⁻¹, crystal dimensions 0.3 × 0.3 × 0.5 mm. *R* = 0.0416 for 563 observed reflexions. The absolute chirality has been determined. The hydroxy group is pseudo axial and there is evidence for a weak O···C=O interaction.

Introduction. We are currently surveying the geometries of intermediates in a new prostaglandin synthesis (Newton, Howard, Reynolds, Wadsworth,

Crossland & Roberts, 1978) to determine the factors involved in observed stereo- and regio-selectivity. Here we report the crystal structure of (I), a preliminary report of which has already been published (Brown,



Glen, Murray-Rust, Murray-Rust & Newton, 1980) including confirmation of the proposed absolute chirality.

Systematic absences (from Weissenberg and precession photographs) $000l:l = 3n$ indicated space group $P3_1$ or $P3_2$. Data were collected for $hki0-6$ with $\theta_{\max} = 25^\circ$ on a Stoe STADI-2 two-circle diffractometer (graphite-monochromated Mo $K\alpha$ radiation). This gave 752 data of which 563 unique reflexions (including 52 Friedel pairs of the form $hki0$) with $I > 3\sigma(I)$ were used in subsequent calculations. Lorentz and polarization corrections (but none for extinction or absorption) were applied and the data scaled by a Wilson plot. The structure was solved by the heavy-atom method with *SHELX 76* (Sheldrick, 1976) which was also used for refinement. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The absolute configuration of the molecule (Fig. 1) was determined from the anomalous-dispersion effect of the Br atoms. Weighted full-matrix least-squares refinement (including isotropic H atoms) converged at $R = 0.0416$ in $P3_1$ for 563 observed reflexions ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$); $R_w = 0.0287$ [$R_w = \sum (|F_o| - |F_c|) \cdot w^{1/2} / \sum (|F_o| \cdot w^{1/2})$, $w = 3.0286 / [\sigma^2(F_o) + 0.000036F_o^2]$]. $R = 0.045$ for the enantiomeric structure in $P3_2$. The R -factor ratio (Hamilton, 1965) was 1.082. Since $\mathcal{R}_{1,466,0.005} = 1.0079$ we may reject the structure in $P3_2$ at lower than the 0.005 level. This result was subsequently confirmed by examination of 41 Bijvoet pairs. In the final cycle all shifts in parameters were less

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors ($\times 10^4$; $\times 10^3$ for H) with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U (\AA^2)
C(1)	10760 (14)	3842 (13)	4044 (20)	456 (55)
C(2)	9339 (10)	2926 (10)	5226 (18)	327 (43)
C(3)	8022 (12)	2229 (12)	3701 (16)	341 (47)
C(4)	8694 (13)	1882 (16)	1866 (19)	364 (58)
C(5)	10330 (17)	3203 (14)	1885 (21)	425 (64)
C(6)	10665 (12)	4773 (13)	1168 (21)	499 (66)
C(7)	11095 (17)	5405 (15)	3276 (22)	439 (64)
O(3)	7614 (11)	3348 (10)	3194 (15)	441 (39)
O(6)	10575 (13)	5273 (10)	-402 (15)	913 (58)
Br(1)	-1253 (1)	-1891 (1)	0 (1)	460 (4)
H(1 <i>A</i>)	1152 (13)	372 (12)	407 (17)	3 (40)
H(2 <i>A</i>)	908 (7)	367 (8)	647 (12)	12 (22)
H(3 <i>A</i>)	704 (8)	119 (8)	427 (12)	17 (21)
H(3 <i>O</i>)	700 (12)	307 (14)	276 (20)	34 (56)
H(4 <i>A</i>)	837 (8)	197 (8)	59 (14)	0 (23)
H(4 <i>B</i>)	835 (9)	66 (11)	232 (14)	58 (25)
H(5 <i>A</i>)	1085 (9)	292 (9)	134 (13)	2 (26)
H(7 <i>A</i>)	1195 (12)	613 (11)	342 (15)	27 (33)
H(7 <i>B</i>)	1061 (12)	589 (11)	387 (16)	42 (41)

For non-H atoms, $U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{12}\cos\gamma + 2U_{13}\cos\beta + 2U_{23}\cos\alpha)$. For H atoms, $T = \exp(-8\pi^2 U \times \sin^2\theta/\lambda^2)$.

than their *e.s.d.*'s. Positional parameters are given in Table 1, bond distances in Table 2, bond angles in Table 3, and torsion angles in Table 4.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36517 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (\AA) with *e.s.d.*'s in parentheses

C(1)–C(2)	1.489 (14)	C(4)–C(5)	1.524 (19)
C(1)–C(5)	1.547 (16)	C(5)–C(6)	1.528 (15)
C(1)–C(7)	1.532 (16)	C(6)–C(7)	1.513 (18)
C(2)–C(3)	1.539 (12)	C(6)–O(6)	1.185 (13)
C(3)–C(4)	1.523 (13)	Br(1)–C(2)	1.955 (10)
C(3)–O(3)	1.428 (12)		

Table 3. Bond angles ($^\circ$) with *e.s.d.*'s in parentheses

C(5)–C(1)–C(2)	104.4 (10)	C(6)–C(5)–C(1)	89.2 (10)
C(7)–C(1)–C(2)	117.8 (11)	C(6)–C(5)–C(4)	119.3 (11)
C(7)–C(1)–C(5)	89.6 (9)	C(7)–C(6)–C(5)	91.0 (10)
C(3)–C(2)–C(1)	106.4 (10)	O(6)–C(6)–C(5)	134.1 (12)
C(4)–C(3)–C(2)	104.5 (8)	O(6)–C(6)–C(7)	134.8 (11)
O(3)–C(3)–C(2)	108.7 (8)	C(6)–C(7)–C(1)	90.3 (10)
O(3)–C(3)–C(4)	109.5 (9)	Br(1)–C(2)–C(1)	111.9 (10)
C(5)–C(4)–C(3)	101.9 (10)	Br(1)–C(2)–C(3)	108.0 (10)
C(4)–C(5)–C(1)	109.3 (11)		

Table 4. Torsion angles ($^\circ$) (*e.s.d.*'s ca 0.8°)

C(5)–C(1)–C(2)–C(3)	-19.2	Br(1)–C(2)–C(3)–O(3)	158.5
C(5)–C(1)–C(2)–Br(1)	97.9	C(2)–C(3)–C(4)–C(5)	-34.4
C(7)–C(1)–C(2)–C(3)	78.0	O(3)–C(3)–C(4)–C(5)	83.6
C(7)–C(1)–C(2)–Br(1)	-164.7	C(3)–C(4)–C(5)–C(1)	22.7
C(2)–C(1)–C(5)–C(4)	-2.6	C(3)–C(4)–C(5)–C(6)	-76.9
C(2)–C(1)–C(5)–C(6)	116.9	C(1)–C(5)–C(6)–C(7)	0.0
C(7)–C(1)–C(5)–C(4)	-119.8	C(4)–C(5)–C(6)–C(7)	111.7
C(2)–C(1)–C(7)–C(6)	-106.5	C(4)–C(5)–C(6)–O(6)	-66.3
C(5)–C(1)–C(7)–C(6)	0.0	C(5)–C(6)–C(7)–C(1)	0.0
C(1)–C(2)–C(3)–C(4)	34.1	O(6)–C(6)–C(7)–C(1)	177.9
C(1)–C(2)–C(3)–O(3)	-82.7	C(7)–C(1)–C(5)–C(6)	0.0
Br(1)–C(2)–C(3)–C(4)	-84.4	C(1)–C(5)–C(6)–O(6)	-177.9

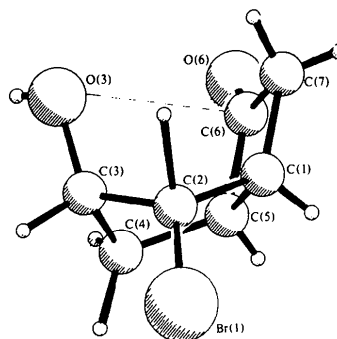


Fig. 1. The conformation and absolute chirality of (I) with the transannular $O \cdots C=O$ interaction shown as a dotted line.

Discussion. The structure of (I) consists of molecules hydrogen bonded along the 3_1 axis [$O(3) \cdots O(3)(1 - y, x - y, \frac{1}{3} + z) = 2.766$ (15) Å]. The molecule (Fig. 1) adopts a conformation with the cyclopentane ring in the *endo* arrangement [approximate mirror plane through C(3) and the mid-point of C(1)–C(5)]. This envelope conformation, which has also been observed in (II) and (III), is probably inherent in the steric properties of bicyclo[3.2.0]heptane (Brown *et al.*, 1980). As in (II) and (III) the ring substituents are pseudo axial in an approximate *trans* arrangement [Br(1)–C(2)–C(3)–O(3) = 158° (1)]. Since the C(1)–C(5) bond is almost eclipsed ($\tau = -2.7^\circ$) in the cyclopentane ring, this provides a driving force for the cyclobutane ring to be completely flat [C(1)–C(5)–C(6)–C(7) = 0(1)°]. This is in contrast to other structures such as (IV) (Murray-Rust, Murray-Rust & Brown, 1979) and (V) (Murray-Rust, Glen & Newton, 1982) where the different constraints in the five-membered ring cause noticeable puckering in the four-membered ring ($|\tau| = 5-11^\circ$). An additional feature is the C(6)···O(3) distance of 2.990 (15) Å which may indicate weak incipient nucleophilic attack by O(3) on C(6) of the type proposed by Bürgi, Dunitz & Shefter (1974). In keeping with this C(6) is displaced from the plane C(7), C(5), O(6) by 0.013 Å towards

O(3). However, although of the expected magnitude, this displacement is of the same order as the e.s.d. (0.015 Å) and the interaction can only be inferred by comparison with other molecules, for example (V).

We thank Glaxo Group Research (Ware) Ltd and the SRC for a CASE studentship (to RCG).

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Acta Cryst. (1982). B38, 2702–2704

3-*exo*-Methoxy-6,7-*endo*-epoxy-2-oxabicyclo[3.3.0]octane

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(Received 24 July 1980; accepted 26 October 1981)

Abstract. C₈H₁₂O₃, $M_r = 156.18$, monoclinic, $C2/c$, $a = 17.15$ (2), $b = 6.15$ (2), $c = 14.99$ (2) Å, $\beta = 82.47$ (3)° from diffractometer measurements (Mo $K\alpha$ radiation), $V = 1567$ Å³, $Z = 8$, $D_c = 1.32$ Mg m⁻³, $F(000) = 672$, $\mu = 0.061$ mm⁻¹, crystal dimensions 0.5 × 0.3 × 0.2 mm. $R = 0.0483$ for 905 observed reflexions. The conformation of the bicyclic system is determined by the epoxy and methoxy substituents.

Introduction. We are undertaking a survey of the geometries of intermediates in a recent prostaglandin synthesis (Newton, Howard, Reynolds, Wadsworth,

Crossland & Roberts, 1978) to determine the factors involved in observed stereo- and regio-selectivity. As part of this investigation we require information about the geometrical constraints imposed by epoxide groups on cyclopentane rings. Here the crystal structure of (I) is reported which consists of discrete molecules with no unusually short intermolecular contacts.

