

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).

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

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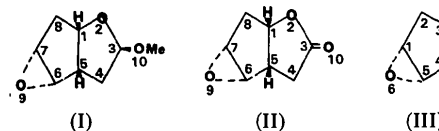
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Abstract. C₈H₁₂O₃, $M_r = 156.18$, monoclinic, $C2/c$, $a = 17.15$ (2), $b = 6.15$ (2), $c = 14.99$ (2) Å, $\beta = 82.47$ (3)° from diffractometer measurements (Mo $K\alpha$ radiation), $V = 1567$ Å³, $Z = 8$, $D_c = 1.32$ Mg m⁻³, $F(000) = 672$, $\mu = 0.061$ 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.



Systematic absences (from Weissenberg and precession photographs) $hkl: h + k = 2n; h0l: l = 2n; 0k0: k = 2n$ indicated space group $C2/c$. Data were collected for $h0-7l$ with $\theta_{\max} = 25^\circ$ on a Stoe STADI-2 two-circle diffractometer (graphite-monochromated Mo $K\alpha$ radiation). This gave 1698 data of which 905 unique reflexions 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 direct methods 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). Weighted full-matrix least-squares refinement (including isotropic H atoms) converged at $R = 0.0483$ for 905 observed reflexions ($R = \sum |F_o| - |F_c| / \sum |F_o|$); $R_w = 0.0510$ ($R_w = \sum (|F_o| - |F_c|) \cdot w^{1/2} / \sum (|F_o| \cdot w^{1/2})$, $w = 3.16 / [\sigma^2(F_o) + 0.001F_o^2]$). In the final cycle all shifts in parameters were less 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 36518 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

	x	y	z	U_{eq}/U (\AA^2)
C(1)	950 (2)	1096 (5)	9078 (2)	430 (16)
C(3)	1429 (2)	1907 (6)	10393 (2)	451 (17)
C(4)	1645 (2)	-439 (6)	10234 (2)	488 (19)
C(5)	1253 (2)	-1068 (5)	9410 (2)	433 (16)
C(6)	1796 (2)	-1953 (7)	8627 (2)	539 (21)
C(7)	1772 (2)	-568 (6)	7842 (2)	530 (20)
C(8)	1197 (2)	1230 (7)	8055 (2)	548 (21)
C(11)	497 (3)	4183 (8)	11242 (3)	752 (29)
O(2)	1328 (1)	2776 (3)	9541 (1)	493 (12)
O(9)	2436 (1)	-454 (4)	8341 (1)	626 (14)
O(10)	725 (1)	2006 (4)	10999 (1)	545 (13)
H(1A)	374 (16)	1169 (52)	9252 (17)	52 (8)
H(3A)	1850 (16)	2817 (51)	10640 (16)	45 (7)
H(4A)	2252 (16)	-550 (50)	10069 (17)	49 (7)
H(4B)	1467 (19)	-1331 (64)	10729 (22)	75 (11)
H(5A)	824 (17)	-2086 (56)	9549 (16)	49 (8)
H(6A)	1932 (16)	-3457 (60)	8618 (18)	50 (9)
H(7A)	1903 (18)	-1097 (59)	7239 (21)	70 (9)
H(8A)	1413 (19)	2645 (61)	7873 (19)	62 (10)
H(8B)	716 (20)	991 (57)	7769 (20)	66 (9)
H(11A)	-17 (28)	4053 (93)	11674 (32)	122 (15)
H(11B)	347 (25)	5167 (95)	10727 (35)	133 (18)
H(11C)	884 (25)	4870 (84)	11551 (28)	105 (15)

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

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

C(1)–C(5)	1.535 (4)	C(5)–C(6)	1.502 (4)
C(1)–C(8)	1.540 (4)	C(6)–C(7)	1.457 (5)
C(1)–O(2)	1.444 (3)	C(6)–O(9)	1.454 (4)
C(3)–C(4)	1.501 (5)	C(7)–C(8)	1.488 (5)
C(3)–O(2)	1.418 (3)	C(7)–O(9)	1.444 (3)
C(3)–O(10)	1.414 (3)	C(11)–O(10)	1.429 (5)
C(4)–C(5)	1.533 (4)		

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

C(8)–C(1)–C(5)	108.0 (2)	C(7)–C(6)–C(5)	109.8 (3)
O(2)–C(1)–C(5)	105.8 (2)	O(9)–C(6)–C(5)	111.6 (3)
O(2)–C(1)–C(8)	111.0 (2)	O(9)–C(6)–C(7)	59.5 (2)
O(2)–C(3)–C(4)	106.0 (2)	C(8)–C(7)–C(6)	110.5 (3)
O(10)–C(3)–C(4)	108.4 (2)	O(9)–C(7)–C(6)	60.1 (2)
O(10)–C(3)–O(2)	111.5 (2)	O(9)–C(7)–C(8)	113.5 (3)
C(5)–C(4)–C(3)	104.2 (2)	C(7)–C(8)–C(1)	105.2 (2)
C(4)–C(5)–C(1)	104.2 (2)	C(3)–O(2)–C(1)	106.2 (2)
C(6)–C(5)–C(1)	105.2 (2)	C(7)–O(9)–C(6)	60.4 (2)
C(6)–C(5)–C(4)	115.4 (2)	C(11)–O(10)–C(3)	112.7 (3)

Table 4. Torsion angles ($^\circ$) (e.s.d.'s ca 0.4 $^\circ$)

C(8)–C(1)–C(5)–C(4)	132.3	C(3)–C(4)–C(5)–C(1)	8.5
C(8)–C(1)–C(5)–C(6)	10.5	C(3)–C(4)–C(5)–C(6)	123.3
O(2)–C(1)–C(5)–C(4)	13.5	C(1)–C(5)–C(6)–C(7)	-5.3
O(2)–C(1)–C(5)–C(6)	-108.3	C(1)–C(5)–C(6)–O(9)	58.6
C(5)–C(1)–C(8)–C(7)	-11.7	C(4)–C(5)–C(6)–C(7)	-119.6
O(2)–C(1)–C(8)–C(7)	103.7	C(4)–C(5)–C(6)–O(9)	-55.6
C(5)–C(1)–O(2)–C(3)	-32.1	C(5)–C(6)–C(7)–C(8)	-2.0
C(8)–C(1)–O(2)–C(3)	-148.9	C(5)–C(6)–C(7)–O(9)	103.9
O(2)–C(3)–C(4)–C(5)	-28.4	O(9)–C(6)–C(7)–C(8)	-106.0
O(10)–C(3)–C(4)–C(5)	91.4	C(5)–C(6)–O(9)–C(7)	-100.9
C(4)–C(3)–O(2)–C(1)	38.2	C(6)–C(7)–C(8)–C(1)	8.5
O(10)–C(3)–O(2)–C(1)	-79.5	O(9)–C(7)–C(8)–C(1)	-56.8
C(4)–C(3)–O(10)–C(11)	176.0	C(8)–C(7)–O(9)–C(6)	101.0
O(2)–C(3)–O(10)–C(11)	-67.6		

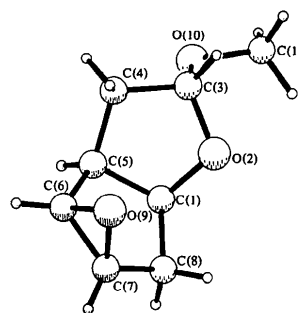


Fig. 1. The conformation and numbering of (I).

Discussion. The cyclopentane ring of molecule (I) (Fig. 1) adopts a shallow envelope conformation with the flap *endo* to the epoxide [C(6)–C(5)–C(1)–C(8) = 10.5 $^\circ$]. An approximate mirror plane passes through C(1) and O(9). A similar molecule (II) (Murray-Rust, Murray-Rust & Newton, 1979), differing only in the replacement of the acetal by the more rigid lactone group, has a much more puckered carbocyclic ring [C(6)–C(5)–C(1)–C(8) = 18.5 $^\circ$]. This suggests that an

important factor in the conformation of (I) is the effect of the pseudo axial methoxy group on the conformation of the tetrahydrofuran ring which is forced to take up a twist arrangement [diad through C(5)]. The torsional strain about O(2)—C(3) is thus much reduced [C(1)—O(2)—C(3)—O(10) = -79.5°], but only at the cost of transmitting some strain to the carbocyclic ring. In confirmation of this, the unsubstituted cyclopentane oxide (III) (Hilderbrandt & Wieser, 1974) is considerably more puckered than either (I) or (II) [C(2)—C(3)—C(4)—C(5) in (III) is 27.9°]. Relief of torsional strain about O(2)—C(3) might also have been possible if the methoxy group had taken up a pseudo equatorial position, but models suggest that a rather short O(9)···C(3) distance would then be found. The geometry of the epoxide group is reviewed elsewhere (Murray-Rust, Glen, Newton & Ali, 1982).

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7,8-*endo*-Epoxy-2-oxatricyclo[3.3.0.0^{4,6}]octan-3-one

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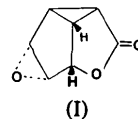
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Abstract. C₇H₆O₃, $M_r = 138.1$, monoclinic, $P2_1/c$, $a = 6.36$ (1), $b = 9.58$ (2), $c = 9.71$ (1) Å, $\beta = 75.13$ (2)° from diffractometer measurements (Mo $K\alpha$ radiation), $V = 572$ Å³, $Z = 4$, $D_m = 1.60$, $D_c = 1.60$ Mg m⁻³, $F(000) = 288$, $\mu = 0.08$ mm⁻¹, crystal dimensions 0.5 × 0.2 × 0.1 mm. $R = 0.041$ for 1124 observed reflexions. This highly strained tricyclic molecule has an unusually short transannular O···C=O interaction [2.651 (2) Å] and a significant [0.052 (1) Å] displacement of C(3) from the plane of the carbonyl group.

Introduction. We are undertaking a survey of the geometries of intermediates in a recent synthesis of prostaglandins (Newton, Howard, Reynolds, Wadsworth, Crossland & Roberts, 1978) to determine the factors involved in observed stereo- and regioselectivity (Murray-Rust, Murray-Rust & Newton, 1979). We have already noted the possibility of a transannular O···C=O interaction (Brown, Glen,

Murray-Rust, Murray-Rust & Newton, 1980). To gain more information about this effect, we have (Ali, Chapleo, Roberts, Wooley & Newton, 1980) synthesized (I) in which the tricyclic system constrains the epoxide to a close approach on the lactone group. Here its crystal structure is reported.



Systematic absences (from precession photographs) $h0l:l$ odd and $0k0:k$ odd indicated space group $P2_1/c$. Data were collected for $h0-10l$ with $\theta_{\max} = 25^\circ$ on a Stoe STADI-2 two-circle diffractometer (graphite-monochromated Mo $K\alpha$ radiation). This gave 1481 data of which 1124 unique reflexions with $I > 3\sigma(I)$ were used in subsequent calculations. Lorentz and polarization corrections (but none for extinction or