

6,7-endo-Epoxy-2-oxabicyclo[3.3.0]octan-3-one

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Abstract. $C_7H_8O_3$, $M_r = 140.13$, monoclinic, $P2_1/c$, $a = 4.98$ (5), $b = 10.42$ (1), $c = 12.36$ (1) Å, $\beta = 85.80$ (2)° from diffractometer measurements (Mo $K\alpha$ radiation), $V = 640$ Å³, $Z = 4$, $F(000) = 296$, $\mu = 0.071$ mm⁻¹, approximate crystal dimensions $0.5 \times 0.4 \times 0.3$ mm. The cyclopentane epoxide fragment is in the envelope conformation and the lactone ring is twisted, possibly due to an O=C...O transannular interaction.

Introduction. Systematic absences (from precession photographs) $h0l$: l odd and $0k0$: k odd indicated space group $P2_1/c$. Data were collected for $h0-5l$ with $\theta_{\max} = 25^\circ$ on a Stoe STADI-2 two-circle diffractometer (graphite-monochromated Mo $K\alpha$ radiation). This gave 1071 data of which 879 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 phasing methods with *SHELX 76* (Sheldrick, 1976), which was

used for all calculations. 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 $R = 0.0361$ for 879 observed reflexions [$R = \sum (|F_o| - |F_c|) / \sum |F_o|$]; $R_w = 0.0444$ [$R_w = (\sum |F_o| - |F_c| w^{1/2}) / (\sum |F_o| w^{1/2})$, $w = 5.88 / [\sigma^2(F_o) + 0.0001F_o^2]$]. In the final cycle all shifts in parameters

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

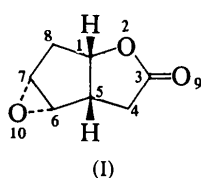
	x	y	z
C(1)	9195 (3)	8129 (1)	2252 (1)
C(3)	5803 (3)	8568 (2)	3584 (1)
C(4)	7286 (4)	9810 (2)	3399 (2)
C(5)	8948 (3)	9600 (1)	2334 (1)
C(6)	7547 (3)	9961 (2)	1347 (1)
C(7)	7430 (3)	8874 (2)	621 (1)
C(8)	8821 (4)	7752 (2)	1084 (1)
O(2)	6997 (2)	7623 (1)	2977 (1)
O(9)	3859 (3)	8352 (1)	4184 (1)
O(10)	5046 (2)	9260 (1)	1277 (1)
H(1A)	1085 (3)	783 (2)	254 (1)
H(4A)	595 (4)	1055 (2)	345 (1)
H(4B)	829 (4)	994 (2)	402 (1)
H(5A)	1061 (3)	997 (2)	236 (1)
H(6A)	741 (4)	1082 (2)	116 (1)
H(7A)	735 (3)	896 (2)	-19 (1)
H(8A)	770 (4)	694 (2)	109 (1)
H(8B)	1058 (4)	765 (2)	67 (1)

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

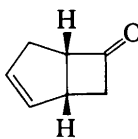
C(1)–C(5)	1.539 (3)	C(1)–H(1A)	0.98 (2)
C(1)–C(8)	1.522 (3)	C(4)–H(4A)	1.02 (3)
C(1)–O(2)	1.462 (2)	C(4)–H(4B)	0.96 (3)
C(3)–C(4)	1.499 (3)	C(5)–H(5A)	0.91 (2)
C(3)–O(2)	1.349 (3)	C(6)–H(6A)	0.92 (3)
C(3)–O(9)	1.197 (3)	C(7)–H(7A)	1.01 (2)
C(4)–C(5)	1.518 (3)	C(8)–H(8A)	1.01 (3)
C(5)–C(6)	1.498 (3)	C(8)–H(8B)	0.99 (3)
C(6)–C(7)	1.449 (3)		
C(6)–O(10)	1.453 (3)		
C(7)–C(8)	1.494 (3)		
C(7)–O(10)	1.446 (3)		
C(8)–C(1)–C(5)	107.8 (2)	H(1A)–C(1)–C(5)	111 (1)
O(2)–C(1)–C(5)	105.4 (2)	H(1A)–C(1)–C(8)	116 (1)
O(2)–C(1)–C(8)	110.5 (2)	H(1A)–C(1)–O(2)	106 (1)
O(2)–C(3)–C(4)	110.6 (2)	H(4A)–C(4)–C(3)	109 (2)
O(9)–C(3)–C(4)	128.6 (2)	H(4A)–C(4)–C(5)	119 (2)
O(9)–C(3)–O(2)	120.8 (2)	H(4B)–C(4)–C(3)	106 (2)
C(5)–C(4)–C(3)	103.9 (2)	H(4B)–C(4)–C(5)	116 (2)
C(4)–C(5)–C(1)	103.7 (2)	H(4B)–C(4)–H(4A)	103 (2)
C(6)–C(5)–C(1)	103.7 (2)	H(5A)–C(5)–C(1)	110 (1)
C(6)–C(5)–C(4)	114.4 (2)	H(5A)–C(5)–C(4)	111 (1)
C(7)–C(6)–C(5)	110.5 (2)	H(5A)–C(5)–C(6)	113 (1)
O(10)–C(6)–C(5)	112.0 (2)	H(6A)–C(6)–C(5)	119 (2)
O(10)–C(6)–C(7)	59.8 (1)	H(6A)–C(6)–C(7)	126 (2)
C(8)–C(7)–C(6)	109.5 (2)	H(6A)–C(6)–O(10)	113 (2)
O(10)–C(7)–C(6)	60.2 (1)	H(7A)–C(7)–C(6)	124 (1)
O(10)–C(7)–C(8)	112.8 (2)	H(7A)–C(7)–C(8)	120 (1)
C(7)–C(8)–C(1)	104.7 (2)	H(7A)–C(7)–O(10)	116 (1)
C(3)–O(2)–C(1)	111.0 (2)	H(8A)–C(8)–C(1)	108 (1)
C(7)–O(10)–C(6)	60.0 (1)	H(8A)–C(8)–C(7)	113 (1)
		H(8B)–C(8)–C(1)	111 (1)
		H(8B)–C(8)–C(7)	108 (1)
		H(8B)–C(8)–H(8A)	113 (2)

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

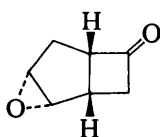
Discussion. The bicyclo[3.2.0]heptane derivatives (II) and (III) are important intermediates in a recent total synthesis of prostaglandins (Newton, Howard, Reynolds, Wadsworth, Crossland & Roberts, 1978). The addition of nucleophiles to (III) and the elements of HOBr to (II) proceeds with high regio- and stereo-selectivity. In contrast, the title compound (I) gives a mixture of products when the epoxide ring is opened by nucleophiles. We are undertaking a survey of the geometries of derivatives of (II) and (IV) to see if steric factors are involved in promoting regio- and stereo-selectivity. Here we report the crystal structure of (I), and discuss some features of its geometry which may be relevant.



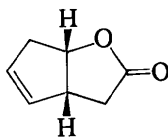
(I)



(II)

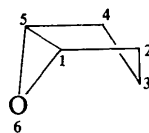


(III)

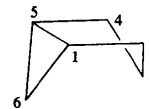


(IV)

pentane ring are somewhat shortened, especially those to C(6) and C(7). The shape of the whole molecule (Table 3) seems to be determined by the conformation of the cyclopentane epoxide fragment. This conformation is very similar to that of cyclopentane epoxide (V) itself (Hildebrandt & Wieser, 1974) and of bicyclo[3.1.0]hexane (VI) (Morris, Murray-Rust & Murray-Rust, 1977, and references therein). In (V) and (VI) the conformation of the cyclopentane ring is an envelope with the flap somewhat unexpectedly *endo* to the three-membered ring, and this was explained by consideration of the torsion angles about the 1–2 and 4–5 bonds. This approach works well for (I) as seen in Table 3(b) where most of the observed torsion angles about C(5)–C(6) and C(7)–C(8) are close to $\pm 60^\circ$. If the ring had the *exo* conformation, most of the angles would be further from the optimum. The *endo* conformation requires C(1)–C(5) to be twisted by about 19° from an eclipsed conformation, and this twist will be transmitted to the lactone ring. Rotation about O(2)–C(3) is hindered and so it might be expected that a cyclopentene-like conformation would be found, with C(5) at the flap. However, there is slight torsion about O(2)–C(3) so that a twist conformation [diad through O(2)] is the best description, corresponding to about 15° pseudorotation from the envelope.



(V)



(VI)

The molecule has the conformation shown in Fig. 1 and since there is only one intermolecular contact less than 3.5 \AA [$C(7) \cdots O(10)(1-x, 2-y, -z) = 3.35 \text{ \AA}$] packing forces are unlikely to influence the geometry to any appreciable extent. The bond lengths and angles are mainly normal, but some C–C bonds in the cyclo-

The reason for this may lie in the details of the steric forces in the lactone ring, but there is another effect

Table 3. Torsion angles ($^\circ$)

(a) Selected torsion angles (e.s.d.'s ca 0.3°)

C(5)–C(1)–O(2)–C(3)	–9.6	C(8)–C(1)–C(5)–C(6)	18.5
C(1)–O(2)–C(3)–C(4)	–5.5	C(1)–C(5)–C(6)–C(7)	–10.4
O(2)–C(3)–C(4)–C(5)	18.5	C(5)–C(6)–C(7)–C(8)	–1.6
C(3)–C(4)–C(5)–C(1)	–22.9	C(6)–C(7)–C(8)–C(1)	13.1
C(4)–C(5)–C(1)–O(2)	20.2	C(7)–C(8)–C(1)–C(5)	–19.6
C(5)–C(4)–C(3)–O(9)	–162.9		

(b) Torsion angles about C(5)–C(6) and C(7)–C(8) (e.s.d.'s ca 0.3°). Column 1 (*endo*) gives the observed values and column 2 (*exo*) those estimated for a cyclopentane ring whose flap C(1) is *exo* to the epoxide.

	<i>endo</i>	<i>exo</i>
C(4)–C(5)–C(6)–O(10)	–58	–35
H(5A)–C(5)–C(6)–H(6A)	–51	–28
C(4)–C(5)–C(6)–H(6A)	77	100
H(5A)–C(5)–C(6)–C(7)	109	132
O(10)–C(7)–C(8)–H(8A)	65	42
H(7A)–C(7)–C(8)–H(8A)	–77	–100
H(7A)–C(7)–C(8)–H(8B)	47	24
C(6)–C(7)–C(8)–H(8B)	–104	–127

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34415 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

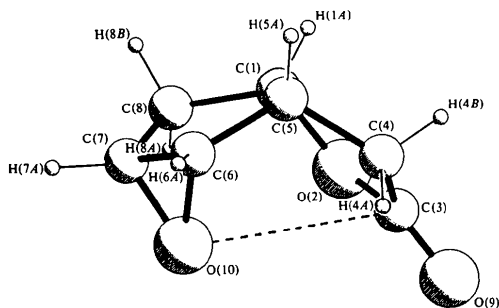


Fig. 1. The conformation and numbering of (I) with the intramolecular O(10)···C(3) interaction shown as a broken line.

which appears to be more important. The O(10)···C(3) distance is 2.992 (2) Å, which is short enough to be considered as an interaction of the type described by Bürgi, Dunitz & Shefter (1974) (BDS) as incipient nucleophilic attack by the epoxide O atom on the carbonyl of the lactone. In confirmation of this C(3) is displaced from the plane of C(4), O(2), O(9) by 0.010 (2) Å towards O(10). These parameters exactly fit the relationship of BDS and the O(10)···C(3)—O(9) angle of 118.8° is close to optimum. The strongest interactions found by BDS had an O···C distance of about 2.6 Å whereas at 3.1 Å the interaction seemed to be negligible. A model of (I) shows that the C(3)···O(10) distance is longer for the envelope configuration of the lactone ring so that the oxygen-carbonyl interaction may well influence the conformation of the lactone ring.

We have observed this transannular interaction in other derivatives of (II) and (IV) and shall review the effect synoptically elsewhere.

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Enantholactam (7-Heptanelactam) at 98 K*

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Abstract. C₇H₁₃NO, *M_r* = 127.18, monoclinic, *C*2/*c*, *Z* = 8, *a* = 21.998 (15), *b* = 7.204 (3), *c* = 9.107 (5) Å, β = 102.89 (6)°, *V* = 1406.8 Å³, *D_c* = 1.201 Mg m⁻³. Significant differences in bond lengths and angles between the protonated and unprotonated forms of enantholactam occur only for the amide moiety.

Introduction. In a previous study of the deformations of the secondary amide group caused by ring strain and protonation, the crystal structures of a number of medium-ring lactams and of their adducts with hydrochloric acid have been determined (Dunitz & Winkler, 1975). Since enantholactam could not be crystallized at that time the dimensions of the protonated amide group in the corresponding hydrochloride (Winkler & Dunitz, 1975) had to be compared to those of the standard *cis* amide group. It was thus left uncertain to what extent the observed deformations were caused by incor-

poration of the *cis* amide group in an eight-membered ring. The present analysis allows a more reliable determination of the effects of protonation because protonated and unprotonated forms of the molecule show essentially the same conformation in their respective crystals. This similarity could not be taken for granted since the infrared spectrum of enantholactam in dilute chloroform solution suggests the presence of two conformers of about equal free energy (Hallam & Jones, 1967).

Crystals of enantholactam (Fluka AG, m.p. 301 K) were obtained by sublimation of a small amount of material within an evacuated capillary of 0.5 mm diameter. Slight warming of the sample over a period of 48 h yielded a single crystal, about 0.25 mm in edge, at one end of the capillary cooled to about 273 K by a nitrogen gas stream. After further slow cooling to 98 K intensities were collected on an automated Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo *K*α radiation (λ = 0.71069 Å); 1684 independent reflections (θ ≤ 27°) were measured of which 1067 were observed [*I* ≥ 3σ(*I*)]. The structure was solved by direct methods (*MULTAN*; Germain,

* Medium-Ring Compounds. XXX. Part XXIX: Winkler, Seiler, Chesick & Dunitz (1976).

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