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).

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

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

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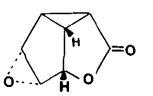
Abstract. $C_7H_6O_3$, $M_r = 138·1$, monoclinic, $P2_1/c$, $a = 6·36$ (1), $b = 9·58$ (2), $c = 9·71$ (1) Å, $\beta = 75·13$ (2)° from diffractometer measurements (Mo $K\bar{\alpha}$ radiation), $V = 572$ Å^3, $Z = 4$, $D_m = 1·60$, $D_c = 1·60$ Mg m^{-3}, $F(000) = 288$, $\mu = 0·08$ mm^{-1}, crystal 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.



(I)

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 $\theta_{max} = 25°$ on a Stoe STADI-2 two-circle diffractometer (graphite-monochromated Mo $K\bar{\alpha}$ 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

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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 $R = 0{\cdot}041$ for 1124 observed reflexions ($R = \sum ||F_o| - |F_c||/\sum |F_o|$); $R_2 = 0{\cdot}045$ $\{R_w = \sum (||F_o| - |F_c||.w^{1/2})/\sum (|F_o|.w^{1/2})$, $w = 3{\cdot}1037/[\sigma^2(F_o) + 0{\cdot}000368F_o^2]\}$. 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.*

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 (Å^2)
C(1)	3457 (2)	1263 (2)	4286 (2)	342 (9)
C(3)	5460 (2)	1127 (2)	1996 (2)	285 (8)
C(4)	3561 (2)	193 (2)	2103 (2)	296 (9)
C(5)	2533 (3)	10 (2)	3655 (2)	347 (9)
C(6)	1213 (2)	650 (2)	2750 (2)	331 (9)
C(7)	686 (2)	2124 (2)	3224 (2)	325 (9)
C(8)	1972 (2)	2503 (2)	4199 (2)	343 (9)
O(2)	5551 (2)	1542 (1)	3315 (1)	353 (7)
O(9)	6901 (2)	1404 (1)	970 (1)	466 (8)
O(10)	2469 (2)	3098 (1)	2782 (1)	336 (7)
H(1*A*)	3747 (31)	1094 (21)	5217 (22)	48 (5)
H(4*A*)	3739 (31)	−580 (19)	1463 (19)	40 (5)
H(5*A*)	2239 (32)	−878 (22)	4115 (21)	51 (6)
H(6*A*)	164 (34)	150 (21)	2464 (21)	47 (5)
H(7*A*)	−710 (34)	2502 (22)	3257 (19)	51 (6)
H(8*A*)	1498 (34)	3143 (23)	5009 (23)	56 (6)

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, $T = \exp(-8\pi^2 U \times \sin^2\theta/\lambda^2)$.

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

C(1)–C(5)	1·533 (2)	C(4)–C(6)	1·529 (2)
C(1)–C(8)	1·534 (2)	C(5)–C(6)	1·494 (2)
C(1)–O(2)	1·446 (2)	C(6)–C(7)	1·496 (2)
C(3)–C(4)	1·486 (2)	C(7)–C(8)	1·448 (2)
C(3)–O(2)	1·357 (2)	C(7)–O(10)	1·446 (2)
C(3)–O(9)	1·198 (2)	C(8)–O(10)	1·448 (2)
C(4)–C(5)	1·492 (2)		

Table 3. *Bond angles* (°) *with e.s.d.'s in parentheses*

C(8)–C(1)–C(5)	106·2 (1)	C(5)–C(6)–C(4)	59·1 (1)
O(2)–C(1)–C(5)	105·5 (1)	C(7)–C(6)–C(4)	121·0 (1)
O(2)–C(1)–C(8)	107·3 (1)	C(7)–C(6)–C(5)	108·8 (1)
O(2)–C(3)–C(4)	110·0 (1)	C(8)–C(7)–C(6)	108·5 (1)
O(9)–C(3)–C(4)	128·8 (1)	O(10)–C(7)–C(6)	114·9 (1)
O(9)–C(3)–O(2)	120·8 (1)	O(10)–C(7)–C(8)	60·0 (1)
C(5)–C(4)–C(3)	106·2 (1)	C(7)–C(8)–C(1)	107·6 (1)
C(6)–C(4)–C(3)	123·2 (1)	O(10)–C(8)–C(1)	111·7 (1)
C(6)–C(4)–C(5)	59·3 (1)	O(10)–C(8)–C(7)	59·9 (1)
C(4)–C(5)–C(1)	101·4 (1)	C(3)–O(2)–C(1)	107·9 (1)
C(6)–C(5)–C(1)	104·2 (1)	C(8)–O(10)–C(7)	60·0 (1)
C(6)–C(5)–C(4)	61·6 (1)		

Table 4. *Torsion angles* (°) (*e.s.d.'s ca* 0·2°)

C(8)–C(1)–C(5)–C(4)	84·7	C(6)–C(4)–C(5)–C(1)	−100·0
C(8)–C(1)–C(5)–C(6)	21·4	C(3)–C(4)–C(6)–C(5)	−89·9
O(2)–C(1)–C(5)–C(4)	−28·9	C(3)–C(4)–C(6)–C(7)	4·4
O(2)–C(1)–C(5)–C(6)	−92·2	C(5)–C(4)–C(6)–C(7)	94·5
C(5)–C(1)–C(8)–C(7)	−15·5	C(1)–C(5)–C(6)–C(4)	95·5
C(5)–C(1)–C(8)–O(10)	−79·4	C(4)–C(5)–C(6)–C(7)	−115·4
O(2)–C(1)–C(8)–C(7)	96·9	C(4)–C(6)–C(7)–C(8)	−53·8
O(2)–C(1)–C(8)–O(10)	33·0	C(5)–C(6)–C(7)–O(10)	10·9
C(5)–C(1)–O(2)–C(3)	28·8	C(5)–C(6)–C(7)–C(8)	10·8
O(2)–C(3)–C(4)–C(5)	−2·9	C(5)–C(6)–C(7)–O(10)	75·6
O(2)–C(3)–C(4)–C(6)	60·6	C(6)–C(7)–C(8)–C(1)	3·2
O(9)–C(3)–C(4)–C(5)	169·2	O(10)–C(7)–C(8)–C(1)	−105·3
O(9)–C(3)–C(4)–C(6)	−127·1	C(6)–C(7)–O(10)–C(8)	−97·8
C(4)–C(3)–O(2)–C(1)	−16·3	C(1)–C(8)–O(10)–C(7)	98·3
O(9)–C(3)–O(2)–C(1)	170·7	C(8)–C(1)–O(2)–C(3)	−84·1
C(3)–C(4)–C(5)–C(1)	19·3	C(6)–C(7)–C(8)–O(10)	108·6
C(3)–C(4)–C(5)–C(6)	119·3		

Discussion. The crystal structure consists of discrete molecules (Fig. 1) with no unusually short intermolecular contacts. The ring fusions probably govern the configurations of the five-membered rings; the cyclopentane ring is in an envelope conformation [mirror plane bisecting C(7)—C(8)] with the flap *exo* to the epoxide and the lactone ring is also an envelope [mirror plane bisecting C(3)—C(4)]. The O(10)···C(3) distance is 2·651 (2) Å, which is unusually small for a non-bonded contact of this type and is in part due to geometrical constraints imposed on the two five-membered rings by the C(4)–C(6) bond. Incipient nucleophilic attack by the lone pair of O(10) on the carbonyl C(3) of the type described by Bürgi, Dunitz & Shefter (1974, hereafter BDS) is observed; in confirmation of this, C(3) is displaced from the plane

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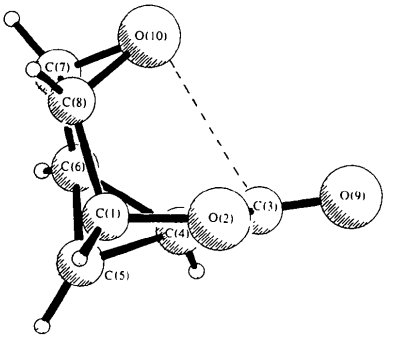
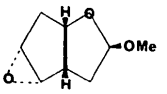


Fig. 1. The conformation and numbering of (I) with the intramolecular O(10)···C(3) interaction shown as a broken line.

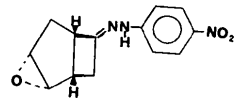
O(2)—C(4)—O(9) by 0·052 (1) Å towards O(10). This agrees well with the relationship that BDS derived between the out-of-plane displacement of the C atom (Δ) and the nucleophile ···C=O distance.

The angle between the plane of the epoxide [C(7),C(8),O(10)] and the plane of C(6),C(7),C(8) and C(1) (planar to within 0·018 Å) is 107·0 (2)°, which is significantly larger than in less hindered cyclopentene epoxides. Thus, in cyclopentene epoxide itself (II) gas-phase electron diffraction gives an interplanar angle of 104·7 (1)° (Hilderbrandt & Wieser, 1974) and in three other structures we have studied with the cyclopentene epoxide ring system [(III) (Murray-Rust, Glen & Newton, 1982*a*), (IV) (Murray-Rust, Glen & Newton, 1982*b*) and (V) (Brown *et al.*, 1980)] this angle is in the range 104·9 (3) to 104·7 (3)°. To obtain more data on the cyclopentene epoxide geometry, we searched the Cambridge Crystallographic Database file (Allen *et al.*, 1979) for molecules containing the fragment (II). Two structures with $R < 0{\cdot}06$ were found: (VI) (De Lacy & Kennard, 1972) and (VII) (Van Meerssche, Germain, Declercq, Bodart-Gilmont, Viehe & Francotte, 1977).

(II)



(III)



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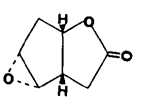
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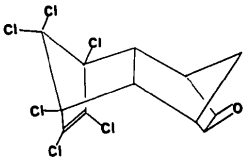
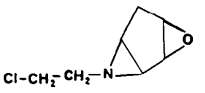
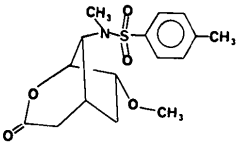

(VI)



(VII)

The relationship between the close approach of another atom or group (X) to the epoxide (O) and the effect on the cyclopentene epoxide geometry is given in Table 5. When another atom or group is constrained to a distance from the epoxide O atom of less than the sum of their van der Waals radii, the angle θ is seen to increase as expected, primarily due to steric repulsion. In (I) this effect does not appear to be moderated by the BDS interaction; therefore at this distance the O···C=O interaction is repulsive or very weakly attractive. This is in keeping with our structural results on other similar molecules [(IV) (Murray-Rust *et al.*, 1982*b*) and (VIII) (Murray-Rust *et al.*, 1982*c*)] in both of which there is evidence that the O···C=O interaction does not play an important role in determining the conformation of the molecule.

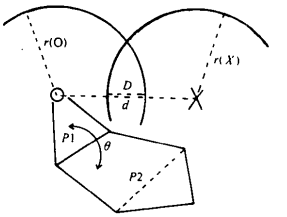

(VIII)

Although, therefore, the O···C=O intramolecular interaction is quite frequently seen [defined by the criterion of d(O···C) less than *ca* 3 Å, a related non-planarity of the carbonyl group and O···C=O angles of about 110°] it would seem to be a *consequence* of constraints rather than an important constraint in itself.

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

Table 5. *Effect of non-bonded interactions on epoxide geometry*

In substituted cyclopentene epoxides, θ is the angle between the plane of the epoxide ($P1$) and the least-squares plane of the substituent atoms ($P2$). X is an atom or group forming a close non-bonded contact (d) to the epoxide O atom (O), where r(O) and $r(X)$ are their van der Waals radii (Pauling, 1960: C = 1·6, O = 1·4, N = 1·5, CH_2 = 2·0 Å) and $D = d(\mathrm{O}\cdots X) - r(\mathrm{O}) - r(X)$.



Structure	X	d (Å)	D (Å)	θ (°)
(II)	–	–	–	104·7 (1)
(IV)	O	2·99 (3)	~0	104·7 (3)
(III)	O	3·15 (4)	>0	104·9 (3)
(V)	O	2·93 (2)	>0	104·9 (3)
(I)	O	2·62 (2)	−0·18	107·0 (3)
(VII)	N	2·68 (2)	−0·22	107·9 (2)
(VI)	CH_2	2·53 (2)	−0·87	110·5 (2)

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Structure of a Thionucleoside: 5′-Deoxy-5′,6-epithio-5,6-dihydro-2′,3′-*O*-isopropylidene-3-methyluridine

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(*Received* 10 *February* 1982; *accepted* 11 *May* 1982)

Abstract. $C_{13}H_{18}N_2O_5S$, $M_r = 314{\cdot}35$, orthorhombic, $P2_12_12_1$ with $a = 39{\cdot}526\ (4)$, $b = 6{\cdot}607\ (2)$, $c = 5{\cdot}661\ (2)$ Å, $Z = 4$, $V = 1478{\cdot}36$ Å^3, $D_c = 1{\cdot}412$ Mg m^{-3}, Cu $K\alpha$ radiation. Final $R = 0{\cdot}073$ for 1154 observed counter reflections. The sulphur atom is in a pseudo-equatorial position with respect to the dihydrouracil ring. The sugar pucker is predominantly O(1′)-*exo* unlike the C(3′)-*exo*,C(4′)-*endo* observed for 2′,3′-*O*-isopropylideneuridine (ISPU). The five-membered dioxolane ring has C(7) displaced by 0·497 (7) Å from the best plane through atoms O(2′), C(2′), C(3′), O(3′), in contrast to ISPU where O(3′) shows the maximum deviation.

Introduction. We report here the structure of the thiocyclonucleoside 5′-deoxy-5′,6-epithio-5,6-dihydro-2′,3′-*O*-isopropylidene-3-methyluridine. The investigation was taken up to assess the conformational change in the molecule because of the S atom covalently linking the uracil base and the ribose moiety. We have earlier reported the structure of 2′,3′-*O*-isopropylideneuridine (ISPU) (Katti, Seshadri & Viswamitra, 1981), which does not have this linkage.

Crystals were grown by slow evaporation from solutions of the compound in 50/50 water/acetone mixtures. No suitable liquid was available for the experimental determination of the density.

The unit-cell parameters were determined from the 2θ values of 25 high-angle reflections on a CAD-4 diffractometer. 1213 unique reflections were collected with Cu $K\alpha$ radiation in the ω–2θ scan mode (θ range 0–60°). Of these, 1154 having $F \geq 3\sigma(F)$ were considered observed.

The structure was solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). The entire nucleoside molecule could be identified unambiguously from an E map using the set of phases with the best combined figure of merit (2·0). Block-diagonal isotropic least-squares refinement reduced R to 14%. The reliability index with anisotropic thermal parameters was 9·0%. At this stage the H atoms, except for those of the methyl groups, were fixed from their expected geometry. Further refinement with the Cruickshank (1961) weighting scheme converged at $R = 0{\cdot}073$. The function minimized is of the form $w(F_o - F_c)^2$ with $w = 1/(a + bF_o + cF_o^2)$, where $a = 4{\cdot}35$, $b = -0{\cdot}684$ and $c = 3{\cdot}34$.

The positional parameters of the atoms are given in Table 1,* bond distances and angles in Table 2. The

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36936 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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