

for the unsubstituted ring system. It is clear therefore that the energy gained by incipient nucleophilic attack of O(10) on C(3) is insufficient to distort the relatively rigid bicyclic nucleus. We have attempted to model this with empirical force-field calculations which suggest that for an O(10)–C(3) distance of 2.8 Å where an appreciable interaction might be expected to occur (BDS), there is a repulsive energy of *ca* 8.4 kJ mol⁻¹ between O(10) and C(4). Presumably, therefore, the energy of the O...C=O interaction at 2.8 Å is either positive (repulsive) or not as negative as -8.4 kJ mol⁻¹ (*i.e.* only very weakly attractive).

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

Acta Cryst. (1982). B38, 2698–2700

2,3-*endo*-Epoxybicyclo[3.2.0]heptan-6-one *p*-Nitrophenylhydrazone

BY PETER MURRAY-RUST AND ROBERT C. GLEN

Department of Chemistry, University of Stirling, Stirling FK9 4LA, Scotland

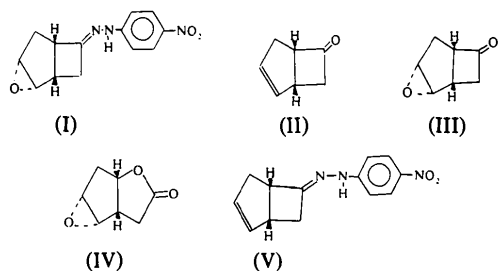
AND ROGER F. NEWTON

Glaxo Group Research Ltd, Ware, Hertfordshire SG12 0DJ, England

(Received 24 July 1980; accepted 26 October 1981)

Abstract. C₁₃H₁₃N₃O₃, *M_r* = 259.14, monoclinic, *P*2₁/*c*, *a* = 9.50 (2), *b* = 13.73 (2), *c* = 9.70 (2) Å, β = 83.19 (2)° from diffractometer measurements (Mo *K*α radiation), *V* = 1256 Å³, *Z* = 4, *D_m* = 1.37, *D_c* = 1.36 Mg m⁻³, *F*(000) = 545, μ = 0.061 mm⁻¹, approximate crystal dimensions 0.5 × 0.7 × 0.16 mm. *R* = 0.0479 for 1538 observed reflexions. The cyclopentane epoxide fragment is in the *endo* envelope conformation with the possibility of a transannular O...C=N interaction [2.990 (3) Å].

Introduction. 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).



0567-7408/82/102698-03\$01.00

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The addition of nucleophiles to (II) and the elements of HOBr to (II) proceeds with high stereo- and regio-selectivity. In contrast, the lactone (IV) gives a mixture of products when the epoxide ring is opened by nucleophiles. We are undertaking a survey of derivatives of (II), (III) and (IV) to determine the factors involved in promotion of regio- and stereo-selectivity. Here we report the crystal structure of (I), a crystalline derivative of (III) with some geometrical features which may be relevant.

Systematic absences (from precession photographs) *h0l*: *l* odd and *0k0*: *k* odd indicated space group *P*2₁/*c*. Data were collected for *h0-6l* and *0-3kl* with θ_{max} = 25° on a Stoe STADI-2 two-circle diffractometer (graphite-monochromated Mo *K*α radiation). 2164 unique data were recorded for the *b* and 832 for the *a* axis; they were merged without layer scales (*R* = 0.050) to give 2351 unique data of which 1538 with *I* > 3σ(*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 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 $R = 0.0479$ for 1538 observed reflexions ($R = \sum (|F_o| - |F_c|) / \sum |F_o|$); $R_w = 0.0459$ ($R_w = \sum (|F_o| - |F_c|) \cdot w^{1/2} / \sum (|F_o| \cdot w^{1/2})$, $w = 4.4729 / [\sigma^2(F_o) + 0.000169F_o^2]$). In the final cycle all shifts in parameters were less than their e.s.d.'s. Positional parameters are given in Table 1,

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

	x	y	z	U_{eq}/U (\AA^2)
C(1)	963 (3)	5748 (2)	1285 (2)	555 (15)
C(2)	1018 (3)	6364 (2)	9 (2)	561 (16)
C(3)	2213 (3)	6095 (2)	-977 (2)	630 (18)
C(4)	3028 (4)	5274 (2)	-429 (2)	693 (16)
C(5)	2375 (3)	5151 (2)	1071 (2)	556 (16)
C(6)	2867 (2)	5744 (2)	2230 (2)	474 (14)
C(7)	1460 (3)	6260 (2)	2575 (3)	577 (18)
C(11)	5335 (2)	6426 (2)	4463 (2)	476 (13)
C(12)	6465 (3)	5789 (2)	4132 (2)	502 (15)
C(13)	7660 (3)	5856 (2)	4804 (2)	525 (15)
C(14)	7721 (2)	6560 (2)	5813 (2)	510 (15)
C(15)	6609 (3)	7185 (2)	6169 (3)	628 (18)
C(16)	5417 (3)	7123 (2)	5499 (3)	629 (18)
O(8)	2259 (2)	6975 (1)	-172 (2)	648 (11)
O(18)	9975 (2)	6073 (2)	6197 (2)	838 (14)
O(19)	8972 (2)	7216 (2)	7485 (2)	877 (15)
N(9)	4060 (2)	5754 (1)	2710 (2)	525 (15)
N(10)	4144 (2)	6391 (2)	3798 (2)	561 (14)
N(17)	8974 (2)	6624 (2)	6536 (2)	613 (15)
H(1A)	87 (26)	5358 (17)	1477 (23)	74 (8)
H(2A)	252 (27)	6710 (17)	-263 (24)	71 (8)
H(3A)	2209 (24)	6162 (16)	-1968 (27)	73 (7)
H(4A)	4024 (37)	5436 (21)	-521 (31)	111 (12)
H(4B)	2848 (29)	4653 (21)	-956 (29)	95 (9)
H(5A)	2309 (24)	4488 (18)	1294 (23)	66 (7)
H(7A)	986 (28)	6026 (18)	3449 (30)	87 (9)
H(7B)	1493 (25)	6983 (18)	2483 (23)	71 (8)
H(10A)	3471 (23)	6755 (15)	4051 (20)	41 (7)
H(12A)	6370 (24)	5302 (15)	3461 (24)	60 (7)
H(13A)	8440 (23)	5398 (15)	4551 (20)	52 (6)
H(15A)	6652 (26)	7665 (17)	6868 (25)	76 (8)
H(16A)	4660 (26)	7549 (18)	5745 (24)	74 (8)

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 (\AA) with e.s.d.'s in parentheses

C(1)–C(2)	1.496 (3)	C(11)–C(12)	1.393 (3)
C(1)–C(5)	1.565 (3)	C(11)–C(16)	1.396 (3)
C(1)–C(7)	1.557 (3)	C(11)–N(10)	1.369 (3)
C(2)–C(3)	1.444 (4)	C(12)–C(13)	1.378 (3)
C(2)–O(8)	1.441 (3)	C(13)–C(14)	1.382 (3)
C(3)–C(4)	1.500 (4)	C(14)–C(15)	1.373 (3)
C(3)–O(8)	1.442 (3)	C(14)–N(17)	1.454 (3)
C(4)–C(5)	1.522 (3)	C(15)–C(16)	1.375 (3)
C(5)–C(6)	1.507 (3)	O(18)–N(17)	1.230 (3)
C(6)–C(7)	1.515 (3)	O(19)–N(17)	1.228 (3)
C(6)–N(9)	1.275 (3)	N(9)–N(10)	1.380 (2)

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

C(5)–C(1)–C(2)	104.0 (2)	C(16)–C(11)–C(12)	119.3 (2)
C(7)–C(1)–C(2)	115.2 (2)	N(10)–C(11)–C(12)	121.7 (2)
C(7)–C(1)–C(5)	90.4 (2)	N(10)–C(11)–C(16)	118.9 (2)
C(3)–C(2)–C(1)	110.5 (2)	C(13)–C(12)–C(11)	120.3 (2)
O(8)–C(2)–C(1)	112.2 (2)	C(14)–C(13)–C(12)	119.2 (2)
O(8)–C(2)–C(3)	60.0 (2)	C(15)–C(14)–C(13)	121.3 (2)
C(4)–C(3)–C(2)	110.9 (2)	N(17)–C(14)–C(13)	119.3 (2)
O(8)–C(3)–C(2)	59.9 (2)	N(17)–C(14)–C(15)	119.3 (2)
O(8)–C(3)–C(4)	112.8 (2)	C(16)–C(15)–C(14)	119.6 (2)
C(5)–C(4)–C(3)	104.7 (2)	C(15)–C(16)–C(11)	120.2 (3)
C(4)–C(5)–C(1)	108.4 (2)	C(3)–O(8)–C(2)	60.1 (2)
C(6)–C(5)–C(1)	87.4 (2)	N(10)–N(9)–C(6)	114.9 (2)
C(6)–C(5)–C(4)	121.8 (2)	N(9)–N(10)–C(11)	120.6 (2)
C(7)–C(6)–C(5)	94.2 (2)	O(18)–N(17)–C(14)	119.0 (2)
N(9)–C(6)–C(5)	130.3 (2)	O(19)–N(17)–C(14)	118.2 (2)
N(9)–C(6)–C(7)	135.5 (2)	O(19)–N(17)–O(18)	122.7 (2)
C(6)–C(7)–C(1)	87.4 (2)		

Table 4. Comparison of ring torsion angles ($^\circ$) in the title compound (I) and the cycloalkene (V) [the latter has two independent molecules (a and b) in the asymmetric unit]

Approximate e.s.d.'s are 0.3 $^\circ$ for (I) and 0.5 $^\circ$ for (V).

	(I)	(Va)	(Vb)
C(1)–C(2)–C(3)–C(4)	0.0	0.8	0
C(2)–C(3)–C(4)–C(5)	-8.2	-9.2	-6.0
C(3)–C(1)–C(5)–C(1)	12.6	13.5	8.7
C(4)–C(5)–C(1)–C(2)	-12.3	-13.0	-8.2
C(5)–C(1)–C(2)–C(3)	7.3	7.8	4.8
C(1)–C(5)–C(6)–C(7)	5.8	11.4	6.5
C(5)–C(6)–C(7)–C(1)	-5.8	-11.4	-6.5
C(6)–C(7)–C(1)–C(5)	5.6	11.0	6.2
C(7)–C(1)–C(5)–C(6)	-5.6	-11.1	-6.3

bond distances in Table 2, bond angles in Table 3 and selected torsion angles in Table 4.*

Discussion. Molecules of (I) (Fig. 1) are hydrogen bonded to form chains $N(10)(x, \frac{1}{2}-y, z - \frac{1}{2}) \cdots O(8) = 2.970(2) \text{ \AA}$. The five-membered ring has the envelope conformation with the flap *endo* to the epoxide [mirror plane bisects C(2)–C(3)]. The O(8)–C(6) distance at 2.990(3) \AA is short enough to be considered as incipient nucleophilic attack of the type specified by Bürgi, Dunitz & Shefter (1974). In confirmation of this, C(6) is displaced from the plane C(7), C(5), N(9) by 0.008(3) \AA towards O(8) and the angle of attack of O(8) on C(6) [O(8)–C(6)–N(9)] is near the optimum at 122.7 $^\circ$. Transannular interactions of this type have been observed in other derivatives of (II) and (IV) (Brown, Glen, Murray-Rust, Murray-Rust & Newton, 1980) and the effect will be reviewed synoptically elsewhere.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36516 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

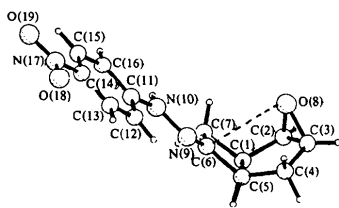


Fig. 1. The conformation and numbering of (I) with the intramolecular O(8)···C(6) interaction shown as a broken line.

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

BY PETER MURRAY-RUST AND ROBERT C. GLEN

Department of Chemistry, University of Stirling, Stirling FK9 4LA, Scotland

AND ROGER F. NEWTON

Glaxo Group Research Ltd, Ware, Hertfordshire SG12 0DJ, England

(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,

