N-(6-*endo*-Methoxy-3-oxo-2-oxabicyclo[3.2.1]oct-8-yl)-*N*-methyl-*p*-toluenesulphonamide

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Abstract. $C_{16}H_{21}NO_5S$, $M_r = 339.4$, monoclinic, $P2_1/c$, $a = 6.46$ (2), $b = 11.77$ (1), $c = 22.62$ (1) Å, $\beta = 101.97$ (1)° from diffractometer measurements (Mo $K\alpha$ radiation), $V = 1683$ Å^3, $Z = 4$, $D_m = 1.35$, $D_c = 1.34$ Mg m^{-3}, $F(000) = 720$, $\mu = 0.172$ mm^{-1}, approximate crystal dimensions $0.6 \times 0.2 \times 0.6$ mm. $R = 0.057$ for 1655 observed reflexions. The conformation about the C(6)–C(7) bond is almost eclipsed and steric hindrance appears to prevent any interaction between the methoxy and lactone groups.

Introduction. We are currently surveying 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.

The hydroxylactone (II) rearranges remarkably easily to the *γ*-lactone (III) (Crossland, Roberts, Newton & Webb, 1978). This reaction seems to be promoted by the steric properties of the molecule and in particular by the possibility of a transannular intramolecular reaction between the hydroxy and the lactone group (see scheme). In favourable cases it may be possible to observe incipient reactions of this type frozen-in in the crystalline state (Bürgi, Dunitz & Shefter, 1974, hereafter BDS). Accordingly, we have studied the model compound (I), in which we hoped to observe a transannular interaction similar to that in related molecules (Brown, Glen, Murray-Rust, Murray-Rust & Newton, 1980).
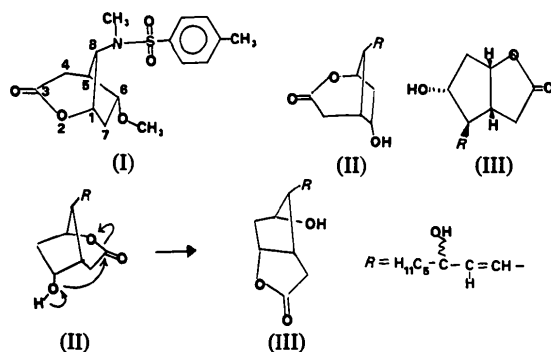
Systematic absences (from precession photographs) *h*0*l*: *l* odd and 0*k*0: *k* odd indicated space group $P2_1/c$. Data were collected for 0–6*kl* with $\theta_{max} = 25°$ on a Stoe STADI-2 two-circle diffractometer (graphite-monochromated Mo $K\alpha$ radiation). This gave 3253 data of which 1655 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 were 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 $R = 0.057$ for 1655 observed reflexions $(R = \sum ||F_o| - |F_c||/\sum |F_o|)$; $R_w = 0.0407$ $\{R_w = \sum (||F_o| - |F_c|| . w^{1/2})/\sum (|F_o| . w^{1/2})$, $w = 3.76/[\sigma^2(F_o) + 0.000022F_o^2]\}$. The H atoms attached to C(23) were disordered and were refined as two methyl groups with occupancies summing to unity. In the final cycle, all shifts in parameters were less then their e.s.d.'s. Positional parameters are given in Table 1,
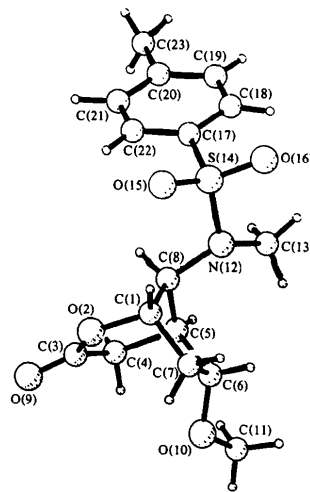

Fig. 1. The structure and conformation of (I). The methyl group at C(23) is disordered and only the most important conformation is shown.

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 (Å²)
C(1)	385 (7)	7221 (4)	−298 (2)	555 (28)
C(3)	−89 (10)	9141 (5)	−619 (2)	693 (35)
C(4)	2229 (11)	9190 (4)	−628 (2)	626 (33)
C(5)	3449 (8)	8064 (3)	−472 (2)	400 (23)
C(6)	2788 (8)	7192 (3)	−981 (2)	448 (24)
C(7)	709 (9)	6712 (5)	−875 (2)	607 (31)
C(8)	2581 (7)	7564 (3)	48 (2)	386 (22)
C(11)	4447 (12)	7747 (6)	−1760 (3)	754 (40)
C(13)	5955 (8)	6414 (5)	298 (2)	506 (29)
C(17)	4842 (7)	7162 (3)	1515 (1)	383 (21)
C(18)	6892 (9)	6886 (4)	1767 (2)	379 (28)
C(19)	8214 (10)	7677 (4)	2105 (2)	628 (33)
C(20)	7486 (10)	8751 (4)	2202 (2)	587 (29)
C(21)	5413 (10)	9001 (4)	1960 (2)	589 (29)
C(22)	4074 (10)	8220 (4)	1622 (2)	489 (26)
C(23)	8981 (14)	9631 (7)	2550 (4)	918 (51)
O(2)	−919 (6)	8229 (3)	−420 (1)	768 (22)
O(9)	−1238 (7)	9942 (3)	−789 (1)	1143 (27)
O(10)	2543 (5)	7648 (2)	−1576 (1)	620 (19)
O(15)	1103 (5)	6452 (2)	1000 (1)	552 (17)
O(16)	4076 (5)	5091 (2)	1147 (1)	571 (16)
S(14)	3271 (2)	6220 (1)	1010 (4)	437 (6)
N(12)	3705 (5)	6534 (2)	334 (1)	360 (17)
H(1A)	−306 (73)	6758 (31)	−61 (17)	71 (15)
H(4A)	2568 (69)	9437 (29)	−1017 (17)	65 (13)
H(4B)	2897 (79)	9714 (35)	−378 (18)	79 (16)
H(5A)	4896 (59)	8250 (24)	−376 (13)	28 (10)
H(6A)	2505 (54)	8094 (25)	349 (12)	36 (10)
H(7A)	3811 (60)	6601 (27)	−952 (13)	43 (11)
H(8A)	827 (69)	5951 (34)	−846 (16)	67 (15)
H(8B)	−309 (82)	6967 (35)	−1215 (18)	89 (17)
H(11A)	4208 (77)	7990 (34)	−2151 (20)	84 (16)
H(11B)	5298 (85)	7043 (40)	−1733 (18)	97 (18)
H(11C)	5321 (112)	8403 (47)	−1489 (24)	134 (25)
H(13A)	6488 (63)	5735 (28)	526 (15)	53 (11)
H(13B)	6806 (68)	7073 (31)	485 (15)	62 (14)
H(13C)	6083 (59)	6302 (25)	−116 (15)	46 (11)
H(18A)	7482 (65)	6194 (31)	1667 (15)	63 (12)
H(19A)	9530 (67)	7496 (29)	2265 (14)	43 (13)
H(21A)	4655 (88)	9716 (35)	2030 (16)	72 (14)
H(22A)	2764 (60)	8390 (25)	1446 (13)	31 (12)
H(23A)*	9249 (96)	10243 (55)	2303 (25)	88 (12)
H(23B)*	10115 (116)	9373 (51)	2784 (31)	88 (12)
H(23C)*	8736 (149)	9784 (87)	2895 (38)	88 (12)
H(23D)†	9391 (313)	9373 (134)	2200 (72)	88 (12)
H(23E)†	7603 (321)	10390 (150)	2576 (115)	88 (12)
H(23F)†	10620 (249)	9431 (100)	2259 (60)	88 (12)

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

* Occupancy 0·81 (4).
† Occupancy 0·19 (4).

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

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36515 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

C(1)−C(7)	1·491 (6)	C(13)−N(12)	1·480 (5)
C(1)−C(8)	1·526 (5)	C(17)−C(18)	1·368 (6)
C(1)−O(2)	1·449 (5)	C(17)−C(22)	1·380 (5)
C(3)−C(4)	1·503 (8)	C(17)−S(14)	1·757 (4)
C(3)−O(2)	1·320 (6)	C(18)−C(19)	1·382 (6)
C(3)−O(9)	1·212 (5)	C(19)−C(20)	1·381 (6)
C(4)−C(5)	1·546 (6)	C(20)−C(21)	1·370 (6)
C(5)−C(6)	1·535 (5)	C(20)−C(23)	1·521 (9)
C(5)−C(8)	1·523 (5)	C(21)−C(22)	1·380 (6)
C(6)−C(7)	1·521 (6)	O(15)−S(14)	1·423 (3)
C(6)−O(10)	1·428 (4)	O(16)−S(14)	1·437 (2)
C(8)−N(12)	1·491 (4)	S(14)−N(12)	1·651 (3)
C(11)−O(10)	1·382 (6)		

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

C(8)−C(1)−C(7)	105·7 (4)	S(14)−C(17)−C(22)	120·2 (3)
O(2)−C(1)−C(7)	110·1 (4)	C(19)−C(18)−C(17)	120·3 (4)
O(2)−C(1)−C(8)	108·8 (3)	C(20)−C(19)−C(18)	120·8 (5)
O(2)−C(3)−C(4)	120·8 (4)	C(21)−C(20)−C(19)	118·1 (5)
O(9)−C(3)−C(4)	120·8 (6)	C(23)−C(20)−C(19)	120·4 (6)
O(9)−C(3)−O(2)	118·3 (6)	C(23)−C(20)−C(21)	121·6 (6)
C(5)−C(4)−C(3)	115·2 (4)	C(22)−C(21)−C(20)	121·8 (5)
C(6)−C(5)−C(4)	110·7 (4)	C(21)−C(22)−C(17)	119·4 (5)
C(8)−C(5)−C(4)	104·8 (4)	C(3)−O(2)−C(1)	118·0 (4)
C(8)−C(5)−C(6)	103·4 (3)	C(11)−O(10)−C(6)	112·5 (4)
C(7)−C(6)−C(5)	104·3 (4)	O(15)−S(14)−C(17)	108·8 (2)
O(10)−C(6)−C(5)	114·6 (3)	O(16)−S(14)−C(17)	108·0 (2)
O(10)−C(6)−C(7)	111·0 (4)	O(16)−S(14)−O(15)	119·5 (2)
C(6)−C(7)−C(1)	106·1 (4)	N(12)−S(14)−C(17)	105·9 (2)
C(5)−C(8)−C(1)	99·1 (3)	N(12)−S(14)−O(15)	107·4 (2)
N(12)−C(8)−C(1)	108·9 (3)	N(12)−S(14)−O(16)	106·5 (1)
N(12)−C(8)−C(5)	115·1 (3)	C(13)−N(12)−C(8)	116·7 (3)
C(22)−C(17)−C(18)	119·6 (4)	S(14)−N(12)−C(8)	115·0 (2)
S(14)−C(17)−C(18)	120·0 (3)	S(14)−N(12)−C(13)	112·8 (3)

Table 4. *Selected torsion angles* (°) (*e.s.d.'s ca* 0·5°)

C(8)−C(1)−C(7)−C(6)	−23·0	C(4)−C(5)−C(6)−C(7)	−79·9
O(2)−C(1)−C(7)−C(6)	94·3	C(4)−C(5)−C(6)−O(10)	41·6
C(7)−C(1)−C(8)−C(5)	41·9	C(8)−C(5)−C(6)−C(7)	31·8
C(7)−C(1)−C(8)−N(12)	−78·7	C(8)−C(5)−C(6)−O(10)	153·4
O(2)−C(1)−C(8)−C(5)	−76·3	C(4)−C(5)−C(8)−C(1)	71·3
O(2)−C(1)−C(8)−N(12)	−63·1	C(4)−C(5)−C(8)−N(12)	−172·7
C(7)−C(1)−O(2)−C(3)	−70·6	C(6)−C(5)−C(8)−C(1)	−44·7
C(8)−C(1)−O(2)−C(3)	44·8	C(6)−C(5)−C(8)−N(12)	71·3
O(2)−C(3)−C(4)−C(5)	7·7	C(5)−C(6)−C(7)−C(1)	−5·4
O(9)−C(3)−C(4)−C(5)	−173·0	O(10)−C(6)−C(7)−C(1)	−129·3
C(4)−C(3)−O(2)−C(1)	−9·2	C(5)−C(6)−O(10)−C(11)	82·0
O(9)−C(3)−O(2)−C(1)	171·5	C(7)−C(6)−O(10)−C(11)	−160·0
C(3)−C(4)−C(5)−C(6)	70·1	C(1)−C(8)−N(12)−C(13)	137·1
C(3)−C(4)−C(5)−C(8)	−40·8	C(5)−C(8)−N(12)−C(13)	26·9

Discussion. The crystal structure of (I) consists of discrete molecules with no unusually short inter-molecular contacts (Fig. 1). The five-membered ring has a strongly puckered envelope conformation with an approximate mirror plane through C(8). The lactone ring has a sofa conformation with C(1), O(2), C(3), C(4) and C(5) almost coplanar. The methoxy substituent is thus directed away from the ring system and the observed C(3)···O(10) distance [3·492 (6) Å] is much larger than that (3·1 Å) for the weakest interaction found by BDS. There are no structural data for the bicyclic system or analogous molecules but the geometry is essentially that which would be predicted

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$\cdots$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).

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

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Abstract. $C_{13}H_{13}N_3O_3$, M_r = 259·14, monoclinic, $P2_1/c$, a = 9·50 (2), b = 13·73 (2), c = 9·70 (2) Å, β = 83·19 (2)° from diffractometer measurements (Mo $K\bar{\alpha}$ radiation), V = 1256 Å^3, 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$\cdots$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).

(I)   (II)   (III)

(IV)   (V)

The addition of nucleophiles to (III) 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 $P2_1/c$. Data were collected for h0–6l and 0–3kl with θ_{max} = 25° on a Stoe STADI-2 two-circle diffractometer (graphite-monochromated Mo $K\bar{\alpha}$ 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 $I > 3\sigma(I)$ 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 used for all calculations. Complex neutral-atom scattering factors were taken from International