

Table 1. Final least-squares parameters for C, N and O in the diammonium salt of tetranitrobiimidazole ( $\times 10^4$ ) and equivalent isotropic  $U$  values ( $\times 10^2$ )

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	$x$	$y$	$z$	$U_{eq}$ ( $\text{\AA}^2$ )
C(1)	5115 (6)	5547 (2)	4709 (1)	2.4 (2)
C(2)	6067 (6)	6516 (3)	3677 (1)	2.7 (2)
C(3)	4840 (6)	7560 (3)	4145 (1)	2.8 (2)
N(1)	6248 (5)	5220 (2)	4035 (1)	2.8 (2)
N(2)	4242 (5)	6951 (2)	4811 (1)	2.8 (2)
N(3)	6996 (6)	6608 (2)	2916 (1)	3.5 (2)
N(4)	4322 (7)	9105 (2)	4043 (1)	4.1 (3)
O(1)	9050 (5)	5723 (2)	2709 (1)	5.4 (2)
O(2)	5675 (6)	7564 (2)	2507 (1)	5.3 (2)
O(3)	5912 (6)	9742 (2)	3579 (1)	6.3 (3)
O(4)	2352 (7)	9708 (2)	4440 (1)	7.2 (3)
Ammonium ion				
N(5)	10054 (8)	2558 (3)	3829 (2)	3.9 (3)

C<sub>6</sub>N<sub>8</sub>O<sub>8</sub><sup>2-</sup> anion and one NH<sub>4</sub><sup>+</sup> cation. The rings are planar within 0.03 Å. The nitro groups are twisted out of the ring plane by 18.9 (1) and 21.6 (1)°. The ammonium ion is hydrogen bonded to four different molecules. Two H atoms make hydrogen bonds to ring N atoms and two to O atoms. This rigid structure is compatible with the relatively high decomposition temperature (without melting) of 523–533 K. Bond distances are very similar to those found in biimidazole (Cromer, Ryan & Storm, 1987) and in tetranitrobiimidazole dihydrate (Cromer & Storm, 1990).

**Related literature.** References to structures of other small high-energy molecules are given by Cromer, Hall, Lee & Ryan (1988).

Table 2. Bond lengths (Å) and angles (°) in the diammonium salt of tetranitrobiimidazole

C(1)—C(1)	1.451 (1)	C(3)—N(2)	1.347 (3)	
C(1)—N(1)	1.346 (3)	C(3)—N(4)	1.438 (3)	
C(1)—N(2)	1.345 (3)	N(3)—O(1)	1.221 (3)	
C(2)—N(1)	1.346 (3)	N(3)—O(2)	1.229 (3)	
C(2)—N(3)	1.434 (3)	N(4)—O(3)	1.223 (3)	
C(2)—C(3)	1.379 (3)	N(4)—O(4)	1.220 (3)	
Hydrogen bonds				
		Symmetry		
X—H...Y	operation on Y	$d(X—Y)$	$d(H...Y)$	$\angle X—H...Y$
N(5)—H(1)...N(1)	$x, y, z$	2.898 (3)	2.00 (4)	173 (3)
N(5)—H(3)...N(2)	$2-x, 1-y, 1-z$	3.091 (3)	2.36 (6)	160 (5)
N(5)—H(2)...O(2)	$2-x, -\frac{1}{2}+y, \frac{1}{2}-z$	3.017 (3)	2.04 (6)	177 (6)
N(5)—H(4)...O(3)	$x, -1+y, z$	3.065 (4)	2.35 (5)	168 (6)

#### Hydrogen bonds

#### References

- CROMER, D. T., HALL, J. H., LEE, K.-Y. & RYAN, R. R. (1988). *Acta Cryst.* **C44**, 1144–1147.
- CROMER, D. T., RYAN, R. R. & STORM, C. B. (1987). *Acta Cryst.* **C43**, 1435–1437.
- CROMER, D. T. & STORM, C. B. (1990). *Acta Cryst.* **C46**, 1957–1958.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

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## Structure of *tert*-Butyl 4-Aminomethyl-3-carboxymethyl-2,3,4-trideoxy-5-hydroxymethyl- $\alpha$ -D-lyxopyranoside- $\delta$ -lactam

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**Abstract.** C<sub>13</sub>H<sub>23</sub>NO<sub>4</sub>·H<sub>2</sub>O,  $M_r = 275.34$ , monoclinic, C2,  $a = 15.725$  (6),  $b = 6.871$  (2),  $c = 14.100$  (7) Å,  $\beta = 93.70$  (3)°,  $V = 1520.3$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.203$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $\mu(\text{Cu } K\alpha) = 0.721$  mm<sup>-1</sup>,  $F(000) = 600$ ,  $T = 293$  K,  $R = 0.047$ ,

$wR = 0.046$  for 1511 observed reflections. The title compound contains a bicyclic  $\alpha$ -D-pyranoside system that has a *cis* ring junction with the  $\delta$ -lactam ring. The molecules are held in the crystal by hydrogen bonds of the O—H...O type or N—H...O type. The O...O distances range from 2.707 (3) to 2.875 (4) Å, while the N...O distance is 2.876 (4) Å.

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**Experimental.** As part of a general strategy towards the synthesis of indole alkaloids such as ajmalicine (1), and some of its natural stereoisomers, intermediate (2) was obtained. Although the structure of the olefinic precursor (3a), derived in nine steps from D-glucose, had already been confirmed by X-ray analysis (Léger, Bélanger-Gariépy, Hanessian & Brisse, 1984), further transformations to (2) necessitated stereochemical assignment by X-ray crystallography. In this paper, we report the crystal structure of (2) (m.p. 434–436 K, ether–chloroform) by X-ray analysis.

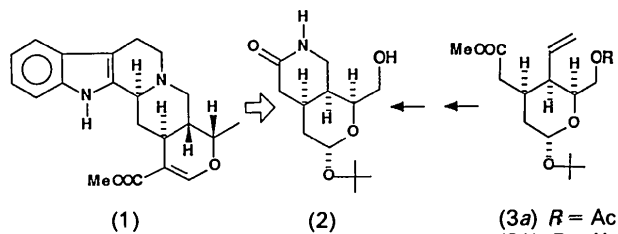


Plate-shape crystal of  $C_{13}H_{23}NO_4 \cdot H_2O$  bounded by {001}, {101}, {111}; dimensions 0.11 × 0.14 × 0.47 mm. Unit cell from 25 well centered reflections in the range  $20 \leq \theta \leq 23^\circ$ . Nonius CAD-4 diffractometer, graphite-monochromatized  $Cu K\alpha$  radiation,  $\omega$  scan technique,  $\Delta\omega = (1.00 + 0.14 \tan \theta)^\circ$ ,  $2\theta_{max} = 140.0^\circ$  ( $-19 \leq h \leq 19$ ,  $0 \leq k \leq 8$ ,  $-17 \leq l \leq 17$ ). Orientation monitored every 200 measurements, intensity checked every hour using seven standard reflections, largest intensity fluctuation 1.0%. 3145 measured reflections, 1698 reflections ( $hkl$ ,  $\bar{h}k\bar{l}$ ) retained after averaging of equivalent reflections to Laue 2 symmetry ( $R_{int}$  0.043) of which 1515 where  $I \geq 1.96\sigma(I)$  retained for structure determination and refinement. Lp correction, no absorption correction.

The structure was solved by direct methods (MULTAN80)\* and difference Fourier calculations (SHELX). Full-matrix least-squares refinement based on  $F$ , all non-H atoms anisotropic. All H atoms found on difference Fourier synthesis. Function minimized:  $\sum w(|F_o| - |F_c|)^2$ . In the last refinement cycles, four reflections (020,  $\bar{1}31$ ,  $\bar{1}32$  and  $\bar{2}03$ ) with high residuals were given zero weight because of suspected errors in intensity measurements. Final  $R = 0.047$ ,  $wR = 0.046$  {weights derived from the counting statistics  $w = 1/[\sigma^2(F) + 0.0001F^2]}$  and  $S = 2.145$  for 271 parameters. Maximum ( $\Delta/\sigma$ ) = 0.35, average ( $\Delta/\sigma$ ) = 0.03, residual electron den-

\* The programs used here are modified versions of NRC-2, data reduction, NRC-10 bond distances and angles and NRC-22, mean planes (Ahmed, Hall, Pippy & Huber, 1973); MULTAN80, multi-solution program (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); SHELX, program for structure determination (Sheldrick, 1976) and ORTEP, stereodrawings (Johnson, 1965).

Table 1. Final atomic coordinates and their e.s.d.'s ( $\times 10^4$ ) and  $U_{eq}$  values ( $\text{\AA}^2 \times 10^3$ ) for  $C_{13}H_{23}NO_4 \cdot H_2O$

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_j$$

	x	y	z	$U_{eq}$
O(1)	7237 (1)	4103 (4)	6623 (1)	54
O(5)	7886 (1)	7146 (4)	6910 (1)	52
O(6)	7546 (1)	9586 (4)	9132 (2)	66
O(8)	10886 (1)	3520 (4)	9062 (2)	59
OW	8775 (2)	9437 (4)	10675 (2)	73
N(8)	10142 (2)	6247 (4)	8708 (2)	48
C(1)	7961 (2)	5247 (5)	6517 (2)	52
C(2)	8709 (2)	4184 (5)	6999 (2)	50
C(3)	8653 (2)	4134 (4)	8075 (2)	41
C(4)	8561 (2)	6208 (4)	8461 (2)	39
C(5)	7800 (2)	7167 (5)	7925 (2)	44
C(6)	7678 (2)	9307 (5)	8157 (3)	56
C(7)	9416 (2)	3102 (5)	8575 (2)	46
C(8)	10202 (2)	4326 (5)	8789 (2)	44
C(9)	9380 (2)	7364 (5)	8395 (2)	48
C(10)	6436 (2)	4561 (6)	6088 (2)	61
C(11)	6558 (3)	5100 (7)	5083 (3)	88
C(12)	5951 (3)	5992 (8)	6622 (4)	118
C(13)	5966 (3)	2552 (7)	6103 (3)	100

Table 2. Interatomic distances ( $\text{\AA}$ ), bond angles ( $^\circ$ ) and torsion angles ( $^\circ$ ) with their e.s.d.'s for  $C_{13}H_{23}NO_4 \cdot H_2O$

C(1)—O(1)	1.399 (4)	O(1)—C(1)—O(5)	112.6 (3)
C(1)—O(5)	1.426 (5)	O(1)—C(1)—C(2)	107.2 (3)
C(1)—C(2)	1.509 (4)	O(5)—C(1)—C(2)	110.5 (3)
C(2)—C(3)	1.526 (4)	C(1)—C(2)—C(3)	111.4 (3)
C(3)—C(4)	1.536 (4)	C(2)—C(3)—C(4)	110.1 (2)
C(3)—C(7)	1.527 (4)	C(2)—C(3)—C(7)	112.1 (2)
C(4)—C(5)	1.523 (4)	C(4)—C(3)—C(7)	110.9 (2)
C(4)—C(9)	1.521 (4)	C(3)—C(4)—C(5)	108.3 (2)
C(5)—O(5)	1.446 (4)	C(3)—C(4)—C(9)	111.3 (2)
C(5)—C(6)	1.521 (5)	C(5)—C(4)—C(9)	112.6 (2)
C(6)—O(6)	1.417 (4)	O(5)—C(5)—C(4)	111.5 (2)
C(7)—C(8)	1.509 (4)	O(5)—C(5)—C(6)	104.1 (2)
C(8)—O(8)	1.248 (4)	C(4)—C(5)—C(6)	114.7 (3)
C(8)—N(8)	1.328 (5)	C(5)—C(6)—O(6)	111.6 (3)
C(9)—N(8)	1.467 (4)	C(3)—C(7)—C(8)	116.3 (3)
C(10)—O(1)	1.460 (4)	O(8)—C(8)—N(8)	121.5 (3)
C(10)—C(11)	1.489 (5)	O(8)—C(8)—C(7)	119.5 (3)
C(10)—C(12)	1.480 (6)	N(8)—C(8)—C(7)	119.0 (3)
C(10)—C(13)	1.567 (6)	C(4)—C(9)—N(8)	112.8 (3)
		O(1)—C(10)—C(11)	112.7 (3)
		O(1)—C(10)—C(12)	109.6 (3)
		O(1)—C(10)—C(13)	101.3 (3)
		C(11)—C(10)—C(12)	114.9 (3)
		C(11)—C(10)—C(13)	108.8 (3)
		C(12)—C(10)—C(13)	108.6 (3)
		C(1)—O(1)—C(10)	120.3 (2)
		C(1)—O(5)—C(5)	114.2 (2)
		C(8)—N(8)—C(9)	126.7 (3)
<b>Ring A</b>		<b>Ring B</b>	
C(1)—C(2)—C(3)—C(4)	-54.8 (3)	C(3)—C(7)—C(8)—N(8)	12.8 (4)
C(2)—C(3)—C(4)—C(5)	54.5 (3)	C(7)—C(8)—N(8)—C(9)	-2.1 (5)
C(3)—C(4)—C(5)—O(5)	-56.2 (3)	C(8)—N(8)—C(9)—C(4)	18.7 (4)
C(4)—C(5)—O(5)—C(1)	59.2 (3)	N(8)—C(9)—C(4)—C(3)	-44.4 (3)
C(5)—O(5)—C(1)—C(2)	-57.1 (3)	C(9)—C(4)—C(3)—C(7)	54.8 (3)
O(5)—C(1)—C(2)—C(3)	54.6 (3)	C(4)—C(3)—C(7)—C(8)	-39.0 (3)
<b>Inter-ring</b>			
C(1)—C(2)—C(3)—C(7)	-178.7 (3)	C(5)—C(4)—C(3)—C(7)	179.1 (2)
O(5)—C(5)—C(4)—C(9)	67.4 (3)	C(8)—C(7)—C(3)—C(2)	84.5 (3)
C(2)—C(3)—C(4)—C(9)	-69.9 (3)	N(8)—C(9)—C(4)—C(5)	-166.4 (2)
<b>Substituents</b>			
O(1)—C(1)—C(2)—C(3)	-68.5 (3)	C(6)—C(5)—O(5)—C(1)	-176.7 (2)
O(1)—C(1)—O(5)—C(5)	62.7 (3)	C(6)—C(5)—C(4)—C(3)	-174.1 (2)
C(10)—O(1)—C(1)—C(2)	-168.9 (2)	C(6)—C(5)—C(4)—C(9)	-50.5 (3)
C(10)—O(1)—C(1)—O(5)	69.4 (3)	O(6)—C(6)—C(5)—O(5)	177.5 (2)
C(1)—O(1)—C(10)—C(11)	42.1 (4)	O(6)—C(6)—C(5)—C(4)	-60.4 (3)
C(1)—O(1)—C(10)—C(12)	-87.3 (4)	O(8)—C(8)—C(7)—C(3)	-169.1 (3)
C(1)—O(1)—C(10)—C(13)	158.1 (3)	O(8)—C(8)—N(8)—C(9)	179.9 (3)

Table 3. Bond distances (Å) and angles (°) involving hydrogen bonds for C<sub>13</sub>H<sub>23</sub>NO<sub>4</sub>·H<sub>2</sub>O

A—H...B	A—B	A—H	H—B	A—H—B
O(6)—HO(6)...O(8 <sup>ii</sup> )	2.707 (3)	0.90 (2)	1.82 (2)	169.9 (13)
N(8)—HN(8)...OH <sup>iii</sup>	2.876 (4)	0.90 (2)	2.07 (1)	147.9 (12)
OW—HOH(1)...O(6)	2.817 (3)	1.14 (2)	1.69 (2)	171.5 (11)
OW—HOH(2)...O(8 <sup>iii</sup> )	2.875 (4)	0.69 (1)	2.20 (1)	168.5 (15)
O(6)...OH...O(8 <sup>ii</sup> )	100.16 (11)	HOH(1)—OW—HOH(2)	103.0 (14)	
O(6)...OH...N(8 <sup>ii</sup> )	128.66 (12)	HOH(1)—OW...HN(8 <sup>ii</sup> )	121.8 (8)	
O(8 <sup>ii</sup> )...OH...N(8 <sup>ii</sup> )	127.12 (12)	HOH(2)—OW...HN(8 <sup>ii</sup> )	132.1 (12)	
OW...O(6)—C(6)	127.5 (2)	HOH(1)...O(6)—C(6)	130.5 (5)	
OW...O(8 <sup>iii</sup> )—C(8 <sup>iii</sup> )	128.4 (2)	HOH(2)...O(8 <sup>iii</sup> )—C(8 <sup>iii</sup> )	126.7 (4)	
OW...N(8 <sup>ii</sup> )—C(8 <sup>ii</sup> )	134.0 (2)	HN(8)—N(8)—C(8)	113.2 (9)	
OW...N(8 <sup>ii</sup> )—C(9 <sup>ii</sup> )	98.5 (2)	HN(8)—N(8)—C(9)	120.0 (9)	

Symmetry code: (i)  $-\frac{1}{2} + x, \frac{1}{2} + y, z$ ; (ii)  $2 - x, y, 2 - z$ ; (iii)  $2 - x, 1 + y, 2 - z$ .

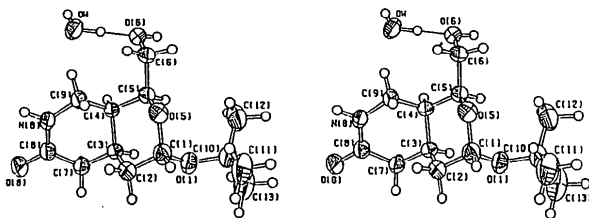


Fig. 1. Stereopair showing the molecular conformation and the atomic numbering of C<sub>13</sub>H<sub>23</sub>NO<sub>4</sub>·H<sub>2</sub>O. The ellipsoids correspond to 50% probability, except for the H atoms which are shown as spheres of arbitrary sizes.

sity fluctuation on the final difference Fourier synthesis +0.16 and -0.11 e Å<sup>-3</sup>.

The scattering curves for the non-H atoms were taken from Cromer & Mann (1968) and those for the H atoms from Stewart, Davidson & Simpson (1965).

The final coordinates for the non-H atoms are given in Table 1, selected bond distances and angles

in Table 2,\* and bond distances and angles involving hydrogen bonds in Table 3. Fig. 1 shows a thermal-ellipsoid plot with the atom numbering.

**Related literature.** For the synthesis of the compound (3a), see Hanessian, Faucher & Léger (1990).

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\* Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving H atoms, and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52891 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

### References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1973). *J. Appl. Cryst.* **6**, 309–346. Accession Nos. 133–147.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- HANESSIAN, S., FAUCHER, A.-M. & LÉGER, S. (1990). *Tetrahedron*, **46**, 231–243.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- LÉGER, S., BÉLANGER-GARIÉPY, F., HANESSIAN, S. & BRISSE, F. (1984). *Acta Cryst.* **C40**, 1844–1846.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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## Structure Studies of Mitomycins. III. Structure of M-83

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**Abstract.** 7-N-(*p*-Hydroxyphenyl)mitomycin C\* (I), C<sub>21</sub>H<sub>22</sub>N<sub>4</sub>O<sub>6</sub>·H<sub>2</sub>O, *M<sub>r</sub>* = 444.45, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 8.056 (2), *b* = 33.832 (9), *c* = 7.469 (1) Å, *V* = 2036 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* =

1.45 g cm<sup>-3</sup>, Cu *Kα*, λ = 1.54184 Å, μ = 8.8 cm<sup>-1</sup>, *F*(000) = 936, *T* = 293 K, *R* = 0.041 for 1923 observed reflections with *F* > 3σ(*F*). Although the overall structure, except the *p*-hydroxyphenyl group, is similar to mitomycin C, the bond lengths in the quinone ring are significantly influenced by the substituent. The phenyl and quinone rings are nearly planar and the two rings form a dihedral angle of

\* Mitomycin C is [1*aR*]-6-amino-8-[[aminocarbonyloxy]methyl]-1,1*a*,2,8,8*a*,8*b*-hexahydro-8*a*-methoxy-5-methylazirino-[2',3':3,4]pyrrolo[1,2-*a*]indole-4,7-dione.