Studies on Lactams. VII.[1] Conformation of D-Glucono-1,5-lactam

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Synopsis. The structure of D-glucono-lactam (5-amino-5-deoxy-D-glucono-lactam) has been established by means of X-ray crystal structure analysis. The stereochemistry of D-glucono-lactam in crystal was determined to be a half-chair conformation.

In earlier papers,[2] we reported on the lactam rule in relation to the sign of the n-π^* carbonyl Cotton effect for the stereochemistry of the lactam ring. There are, however, difficulties to decide the ring conformation of six-membered lactams from the sign of the n-π^* Cotton effect, because the ring chiralities of δ-lactams are known to take both half-chair and half-boat conformations.[3,4] In this paper, we report the conformation of D-glucono-lactam in crystal determined by X-ray analysis.

Experimental

The crystals are colorless prisms. A specimen of D-glucono-lactam with the dimensions of 0.30×0.25×0.25 mm was used for the intensity measurements. The density was measured by the flotation method in a mixture of petroleum ether and carbon tetrachloride. The cell constants were determined by the least-squares procedure from the 2θ values of 24 reflections measured on a diffractometer using monochromated Cu $K\alpha$ radiation. Three dimensional intensity data were collected on a Rigaku automatic four-circle diffractometer with graphite monochromated Cu $K\alpha$ radiation. Background was counted for 10s at both sides of each peaks. Three standard reflections were measured every 50 reflections during the course of collection. A total of 1120 of independent reflections were collected. Reflections having an intensity exceeding the corresponding standard deviations by a factor of five were treated as observed. 912 reflections with $2\theta<140°$ were retained and corrected for Lorentz and polarization factors but not for absorption factor.

Crystal Data. $C_6H_{11}O_5N$, MW 177.16, mp 207 (dec), $[\alpha]_D$ −42° (c=1, water), crystal system orthorhombic, space group $P2_12_12_1$ a=11.721(1) Å, b=13.471(2), c=4.926(1), V=777.8(1) Å^3, Z=4, $F(000)$=376, D_c=1.514 g·cm^{-3}, D_o=1.51.

Determination and Refinement of the Structure. The crystal structure was solved by the multi-solution method (MULTAN),[5] using 108 normalized structure factors with $E\geqq1.3$. Origin and enantiomorph fixings were carried out automatically by the program. Two of the eight possible solutions gave high combined figures of merit and the E map from one of these showed sensible positions and bond relations for all the non-hydrogen atoms. Refinement of the positional parameters of the twenty atoms was carried out by the block-diagonal matrix least-squares method, in which the other non-hydrogen atoms were assumed to be carbon atoms, the quantity minimized being $\sum w(|F_o|-|F_c|)^2$ with w=1.0 for all the reflections used. Five cycles of calculation gave an R-value of 0.17. The oxygen and nitrogen atoms were deduced from chemical considerations, the bond lengths and the unusually low values of the parameters due to assuming those atoms as carbon. Further refinement carried out with anisotropic thermal parameters gave an R-value of 0.07.

All the hydrogen atoms of the molecule were found from difference maps, and they were refined with isotropic thermal parameters. Five cycles of the refinement by the block-diagonal least-squares method gave the final R value of 0.043 for 912 reflections. The final atomic parameters and the atomic scattering factors for C, O, N were given by Cromer and Mann.[6] The final atomic parameters are given in Table 1. Anisotropic thermal parameters of non-hydrogen atoms and complete F_o-F_c data are deposited as Document No.8430 at the Office of the Editor of the Bull. Chem. Soc. Jpn.

Results and Discussion

The bond lengths and angles are given in Tables 2 and 3. No abnormal lengths and angles were found in the structure. The molecular framework with numbering of the atoms is shown in Fig. 1. From this perspective view of the molecule, the conformation of the compound clearly takes the half-chair form. As shown in Table 4, the torsional angle of C(2)-C(1)-N-C(5) is −4.8°, which means that atoms C(2), C(1), N, and C(5)

Table 1. Atomic coordinates (×10^4) and their standard deviations in parentheses and equivalent isotropic temperature factors

Atom	x	y	z	a) B_{eq}/Å^2
C (1)	9509 (3)	6911 (3)	11129 (9)	1.9
C (2)	8391 (3)	6406 (3)	10253 (9)	1.3
C (3)	7920 (3)	6817 (3)	7636 (9)	1.4
C (4)	7875 (3)	7941 (3)	7781 (9)	1.6
C (5)	9073 (3)	8369 (3)	8135 (9)	1.4
C (6)	8997 (3)	9448 (3)	8980 (11)	1.4
O (1)	10155 (2)	6484 (2)	12715 (8)	2.3
O (2)	8523 (2)	5365 (2)	10173 (7)	2.0
O (3)	6790 (2)	6475 (2)	7192 (7)	1.5
O (4)	7417 (2)	8355 (2)	5384 (7)	2.4
O (5)	10131 (2)	9850 (2)	9137 (7)	1.2
N (1)	9726 (3)	7808 (2)	10147 (8)	1.5
H (C2)	777 (4)	650 (3)	1177 (9)	1.0
H (C3)	841 (3)	662 (3)	599 (9)	1.0
H (C4)	731 (3)	811 (3)	948 (9)	0.9
H (C5)	948 (3)	832 (3)	629 (8)	0.7
H (C6)	855 (4)	978 (4)	736 (12)	1.4
H′ (C6)	865 (4)	951 (3)	1074 (10)	1.1
H (O2)	859 (4)	526 (3)	859 (11)	1.2
H (O3)	668 (4)	590 (4)	611 (11)	1.3
H (O4)	661 (5)	832 (5)	532 (16)	2.4
H (O5)	1012 (4)	1041 (3)	1031 (10)	1.1
H (N)	1041 (4)	808 (3)	1086 (10)	1.1

a) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).

Table 2. Bond lengths (l/Å) and their standard deviations in parentheses

C(1)-C(2)	1.538(6)	C(2)-H(C2)	1.04(3)
C(2)-C(3)	1.508(6)	C(3)-H(C3)	1.03(2)
C(3)-C(4)	1.517(7)	C(4)-H(C4)	1.09(4)
C(4)-C(5)	1.528(6)	C(5)-H(C5)	1.03(3)
C(5)-C(6)	1.515(6)	C(6)-H(C6)	1.05(3)
C(5)-N	1.463(8)	C(6)-H'(C6)	0.97(3)
N -C(1)	1.326(8)	O(2)-H(O2)	0.94(4)
C(1)-O(1)	1.231(7)	O(3)-H(O3)	0.95(3)
C(2)-O(2)	1.411(2)	O(4)-H(O4)	0.95(2)
C(3)-O(3)	1.419(6)	O(5)-H(O5)	0.95(3)
C(4)-O(4)	1.412(2)	N -H(N)	0.95(3)
C(6)-O(5)	1.436(5)		

Table 3. Bond angles (ϕ/°) and their standard deviations in parentheses

C(2)-C(1)-O(1)	119.7(4)	C(5)-C(4)-C(3)	110.5(3)
C(2)-C(1)-N	117.6(4)	C(5)-C(4)-O(4)	107.2(3)
O(1)-C(1)-N	122.6(4)	C(3)-C(4)-O(4)	111.6(3)
C(3)-C(2)-C(1)	112.9(3)	C(6)-C(5)-C(4)	109.8(3)
C(3)-C(2)-O(2)	112.4(3)	C(6)-C(5)-N	109.3(3)
C(1)-C(2)-O(2)	110.7(3)	C(4)-C(5)-N	111.3(3)
C(4)-C(3)-C(2)	109.8(3)	O(5)-C(6)-C(5)	108.8(4)
C(4)-C(3)-O(3)	107.4(3)	C(1)-N-C(5)	128.1(4)
C(2)-C(3)-O(3)	110.7(3)		

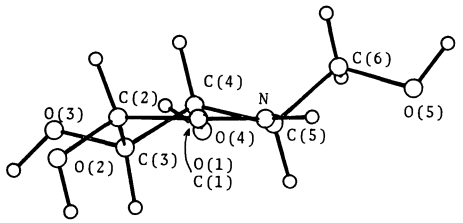

Fig. 1. A perspective view of the D-glucono-1,5-lactam molecule and the atomic numbering.

Table 4. Some torsional angles (ϕ/°)

C(2)-C(1)-N-C(5)	−4.8
C(1)-C(2)-C(3)-C(4)	−50.0
C(4)-C(5)-N-C(1)	16.2
C(3)-C(2)-C(1)-N	21.7
C(3)-C(4)-C(5)-C(6)	−166.1
C(3)-C(4)-C(5)-N	−43.8
C(2)-C(1)-N-H(N)	177.1
O(1)-C(1)-N-H(N)	−1.9

are placed on the same plane. Torsional angles C(1)-N-C(5)-C(4) and N-C(1)-C(2)-C(3) are 16.2° and 21.7° respectively. Vertical distances of C(3) and C(4) from the plane (C(2)-C(1)-N-C(5)) are 0.44 and 0.30 Å respectively. The vicinal coupling constant between the hydrogen atoms attached to C(2) and C(3), C(3), and C(4), C(4), and C(5) should be all *ca.* 10 Hz, because the dihedral angles H(2)-C(2)-C(3)-H(3), H(3)-C(3)-C(4)-H(4), and H(4)-C(4)-C(5)-H(5) are 169.0°, 176.9°, and 166.9° respectively. The observed coupling constants (in $CDCl_3$) $J_{2,3}$, $J_{3,4}$, and $J_{4,5}$ of the compound are all 9.5 Hz, which indicate that the conformation of D-glucono-lactam has the same half-chair conformation both in crystal and in solution. The crystal structure of the compound projected along the c axis is shown in Fig. 2. Hydrogen bonds are shown by broken lines. The hydrogen bonding distances and angles are listed in Table 5.

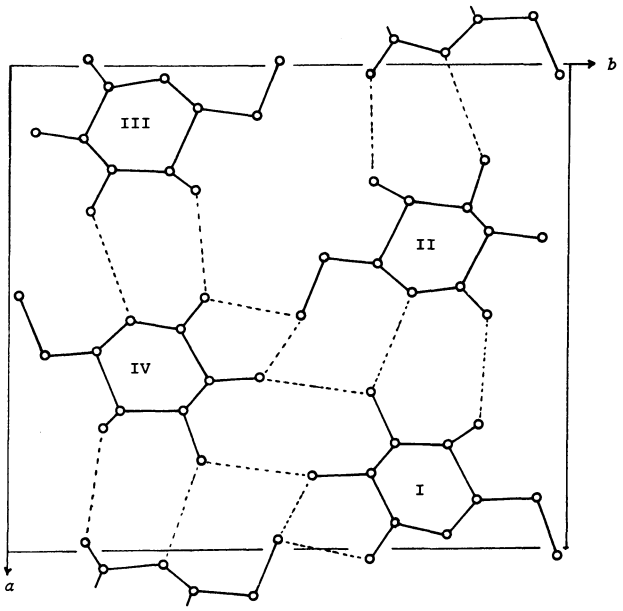

Fig. 2. Projection of the Crystal Structure along c Axis.

Table 5. Bond lengths and bond angles of intermolecular hydrogen bond

	Length(l/Å)	Angle(ϕ/°)
N-H···O(3)	2.92	178
O(1)···H-O(4)	2.82	165
O(2)-H···O(5)	2.73	171
O(5)-H···O(1)	2.71	171
O(3)-H···O(2)	2.70	160

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