

STRUCTURE OF 2,3,4,5-TETRA-O-ACETYL-6-AMINO-6-DEOXY-D-ALLONOLACTAM

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The crystal structure of 2,3,4,5-tetra-O-acetyl-6-amino-6-deoxy-D-allonolactam was solved by direct methods and refined anisotropically to $R = 0.085$ for 1 345 unique observed reflections. The title compound crystallizes in $A2$ space group with the lattice parameters $a = 11.756(4)$, $b = 8.139(3)$, $c = 23.713(11)$ Å, $\beta = 116.71(4)^\circ$, $V = 2 027(2)$ Å³, $Z = 4$. The ring of 2,3,4,5-tetra-O-acetyl-6-amino-6-deoxy-D-allonolactam adopts the ⁴C_{1,N}(D) conformation with the planar arrangement of the C(6)–NH–C(1)O–C(2) atoms. In the crystal structure the adjacent molecules of this lactam are bonded by one intermolecular hydrogen bond, forming a helical chain.

X-Ray measurements of ϵ -caprolactam¹ revealed that the molecule of this compound possesses the chair conformation and the C(2)–C(1)–N–C(6) "amide" segment is nearly planar, and that the crystal structure consists of centrosymmetric pairs of molecules linked by hydrogen bonds (NH...O bond length 2.90 Å).

The chair conformation, which is nearly ideal in caprolactam, can be expected to be distorted if some substituents are bonded to the carbon chain of the lactam. This has been observed, e.g., for some seven-membered lactams bonded to other rings^{2,3}. On the other hand, the chair conformation has been inferred⁴ from ¹H NMR and CD measurements for 6-amino-6-deoxyhexonolactams and their tetra-O-acetyl derivatives in solutions. The IR spectra of the latter compounds measured in nujol mulls exhibited appreciable differences in the ν_{NH} values of the various configurational isomers⁵ ($\Delta\nu$ as

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high as 100 cm^{-1}). This could be explained in terms of differences in the strength of the above-mentioned intermolecular hydrogen bonds.

X-Ray measurements of 6-amino-6-deoxyhexanolactam derivatives appeared promising for a more precise correlation of the conformation of substituted and unsubstituted seven-membered lactam rings as well as for gaining insight into the molecular packing. The present paper gives the results of an X-ray analysis of 2,3,4,5-tetra-O-acetyl-6-amino-6-deoxy-D-allonolactam, a compound which exhibits the largest ν_{NH} band shift in the IR spectrum⁵ of a nujol mull and, as indicated by the ^1H NMR spectrum of the deuteriochloroform solution, adopts the $^4\text{C}_{1,\text{N}}(\text{D})$ conformation⁴.

EXPERIMENTAL

2,3,4,5-Tetra-O-acetyl-6-amino-6-deoxy-D-allonolactam was synthesized as described in refs^{6,7}. Crystals for X-ray structural analysis were obtained by recrystallization from a chloroform-1-propanol 2 : 1 mixture. For $\text{C}_{14}\text{H}_{19}\text{NO}_9$ (345.3) calculated: 48.70% C, 5.55% H, 4.06% N; found: 48.58% C, 5.57% H, 4.27% N.

The crystal structure was elucidated by using direct methods, and anisotropically refined by the block-diagonal least-squares procedure. The hydrogen atoms were fixed in the calculated positions with fixed U_{iso} values of 1.3 times the U_{eq} value of the attached atoms. Absorption and extinction effects were ignored.

The relevant experimental and calculation data are given in Table I.

RESULTS AND DISCUSSION

The crystals of the compound studied are monoclinic, space group $A2$ (No. 5, $b c a$ non-standard setting, coordinates of equivalent positions: $x, y, z; \bar{x}, \bar{y}, \bar{z}; x, y + 1/2, z + 1/2; \bar{x}, y + 1/2, 1/2 - z$); $a = 11.756(4)$, $b = 8.139(3)$, $c = 23.713(11) \text{ \AA}$, $\beta = 116.71(4)^\circ$, $V = 2.027(2) \text{ \AA}^3$, $Z = 4$, $D_c = 1.132 \text{ g cm}^{-3}$, $\mu = 0.896 \text{ cm}^{-1}$, $F(000) = 728$.

The refined atomic coordinates⁸ and equivalent isotropic temperature factors of non-hydrogen atoms are given in Table II, the bond distances and angles are listed in Table III. The molecule studied is depicted in Fig. 1, the crystal packing, in Fig. 2.

The crystallographic data obtained indicate the following facts:

a) The 2,3,4,5-tetra-O-acetyl-6-amino-6-deoxy-D-allonolactam ring adopts the $^4\text{C}_{1,\text{N}}(\text{D})$ conformation with the planar arrangement of the C(6)-NH-C(1)O-C(2) atoms. This plane is virtually parallel (angle 172°) to that formed by the C(3)-C(4)-C(5) atoms.

b) Four bonds of each acetoxy-substituent [-O-C(=O)-C] at the carbon chain are coplanar. The two planes containing atoms of the axial acetyloxy groups on C-3 and C-5 bisect forming an angle of 90° .

* Hydrogen atom coordinates are deposited with the authors and can be obtained on request.

c) The absolute values of the endocyclic torsion angles in the structure investigated approach closely those in caprolactam (Table IV).

d) In contrast to the pairing of molecules of caprolactam in its crystal structure¹, adjacent molecules of the lactam under study are bonded by a hydrogen bond forming a helical chain. The distance between the donor and acceptor atoms in the hydrogen bond in this arrangement, however, is nearly the same (2.86 Å) as in the caprolactam "dimer" (2.90 Å, ref.¹).

TABLE I
Data collection and structure refinement parameters

Crystal dimensions, mm	0.38 × 0.15 × 0.12
Diffractometer and radiation used	Enraf-Nonius CAD4, λ(MoKα) = 0.71073 Å
Scan technique	ω/2θ
Number and θ range of reflections for lattice parameter refinement	20; 12 → 16°
Range of <i>h</i> , <i>k</i> and <i>l</i>	-11 → 11, 0 → 8, -26 → 26
Standard reflections	1 0 5, - 1 1 4
Interval of standard reflection monitoring; intensity fluctuation	120 min; -2.5 %
Total number of reflections measured, 2θ range	7 547
Number of unique observed reflections	1 345
Criterion for observed reflections	$I \geq 1.96 \sigma(I)$
Value of R_{int}	0.054
Function minimized	$\sum w (F_o - F_c)^2$
Weighting scheme	$w = [\sigma^2(F_o) + 0.0009 F_o^2]^{-1}$
Parameters refined	217
Value of <i>R</i> , <i>wR</i> and <i>S</i>	0.085, 0.089, 1.468
Ratio of max. LS shift to e.s.d. (Δ/σ)	0.001
Max. and min. heights in final Δρ map	0.32; -0.38 eÅ ⁻³
Source of atomic scattering factors	ref. ⁹
Programs used	SPD (ref. ⁸), SHELX 76 (ref. ⁹), SHELXS 86 (ref. ¹⁰), PARST (ref. ¹¹)
Computer used	DEC PDP 11/73, PC AT 286

TABLE II

Final coordinates ($\cdot 10^4$) for non-hydrogen atoms and their equivalent isotropic thermal parameters ($\cdot 10^3$) as $U_{eq} = [U_{22} + 1 / \sin^2\beta (U_{11} + U_{33} + 2U_{13} \cos \beta)]/3$

Atom	x	y	z	$U_{eq}, \text{\AA}^2$
O1	-524(5)	-224(9)	2350(3)	61(2)
O2	-931(5)	-237(9)	1453(3)	62(2)
O3	-2891(6)	-1318(12)	1078(4)	92(3)
O4	1724(5)	-1426(9)	2032(2)	57(2)
O5	2140(7)	-3965(11)	1803(3)	81(3)
O6	2411(5)	-275(10)	1083(2)	67(2)
O7	1757(7)	832(16)	142(3)	103(4)
O8	2474(5)	1984(9)	2009(2)	57(2)
O9	3805(6)	3032(12)	1665(3)	79(3)
N	-19(6)	1865(10)	1896(3)	51(3)
C1	-338(7)	338(11)	1923(3)	47(3)
C2	-463(7)	-797(12)	1377(4)	56(3)
C3	797(7)	-1100(12)	1374(3)	51(3)
C4	1234(7)	248(13)	1094(3)	51(3)
C5	1426(7)	1971(13)	1381(3)	54(3)
C6	243(8)	2630(13)	1405(4)	53(3)
C7	-2189(8)	-2459(16)	1314(4)	73(4)
C8	-2521(11)	-4082(19)	1464(5)	94(5)
C9	2259(8)	-2928(13)	2166(4)	62(4)
C10	3066(8)	-3088(17)	2886(4)	77(4)
C11	2592(8)	90(20)	593(4)	90(5)
C12	3795(10)	-335(31)	649(5)	120(7)
C13	3604(8)	2576(14)	2079(4)	64(4)
C14	4534(9)	2534(21)	2755(5)	96(5)

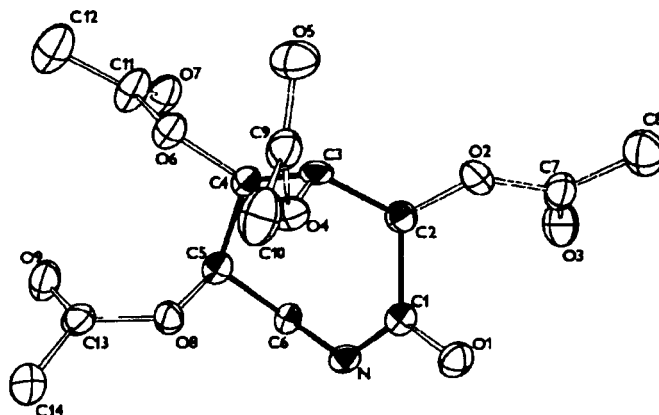


FIG. 1

The ORTEP plot of the studied molecule with atom numbering. Thermal ellipsoids are drawn at the 50% probability

TABLE III
Bond distances (in Å) and angles (in °), symmetry code: (i) $-x, 1/2 + y, 1/2 - z$

Atoms	Distances	Atoms	Distances
O1-C1	1.217(12)	O9-C13	1.169(14)
O2-C2	1.437(12)	N-C1	1.308(12)
O2-C7	1.365(11)	N-C6	1.470(14)
O3-C7	1.201(14)	C1-C2	1.543(13)
O4-C3	1.471(7)	C2-C3	1.505(13)
O4-C9	1.346(12)	C3-C4	1.488(14)
O5-C9	1.168(13)	C4-C5	1.531(14)
O6-C4	1.459(11)	C5-C6	1.515(14)
O6-C11	1.306(13)	C7-C8	1.466(20)
O7-C11	1.236(13)	C9-C10	1.541(11)
O8-C5	1.444(7)	C11-C12	1.403(17)
O8-C13	1.351(12)	C13-C14	1.480(12)
Atoms	Angles	Atoms	Angles
C2-O2-C7	116.8(8)	O8-C5-C4	110.6(6)
C3-O4-C9	117.3(6)	C4-C5-C6	112.7(8)
C4-O6-C11	119.0(7)	O8-C5-C6	109.3(6)
C5-O8-C13	117.7(6)	N-C6-C5	113.7(7)
C1-N-C6	127.5(7)	N-C6-H1C6	108.6(11)
O1-C1-N	124.1(7)	O2-C7-O3	121.0(10)
N-C1-C2	116.7(7)	O3-C7-C8	127.4(1)
O1-C1-C2	119.2(8)	O2-C7-C8	111.5(9)
O2-C2-C1	109.0(7)	O4-C9-O5	126.4(8)
C1-C2-C3	112.3(7)	O5-C9-C10	124.4(10)
O2-C2-C3	106.7(8)	O4-C9-C10	109.1(8)
O2-C2-HC2	112.5(10)	O6-C11-O7	120.0(10)
O4-C3-C2	106.6(6)	O7-C11-C12	125.2(10)
C2-C3-C4	114.8(8)	O6-C11-C12	115.0(9)
O4-C3-C4	111.5(6)	O8-C13-O9	124.7(9)
O6-C4-C3	108.3(7)	O9-C13-C14	126.0(10)
C3-C4-C5	119.2(6)	O8-C13-C14	109.4(8)
O6-C4-C5	108.9(7)	O8-C13-C14	109.4(8)
Hydrogen bond contact			
N...O1 ⁱ	2.862(11)		
N-HN...O1 ⁱ	146.6(8)		

TABLE IV
Endocyclic torsion angles (in °) of 2,3,4,5-tetra-O-acetyl-6-amino-6-deoxy-D-allonolactam in comparison with those of ϵ -caprolactam¹

Bonds	Torsion angle	
	present compound	ϵ -caprolactam
C6-N-C1-C2	-0.36	-4.2
N-C1-C2-C3	67.27	-63.1
C1-C2-C3-C4	-79.86	81.9
C2-C3-C4-C5	58.98	-63.5
C3-C4-C5-C6	-55.88	60.7
C4-C5-C6-N	73.98	-77.0
C5-C6-N-C1	-66.40	67.8
C6-N-C1-O	178.86	176.6
HN-N-C1-O	-1.17	3.0
HN-N-C1-C2	179.60	-178.0

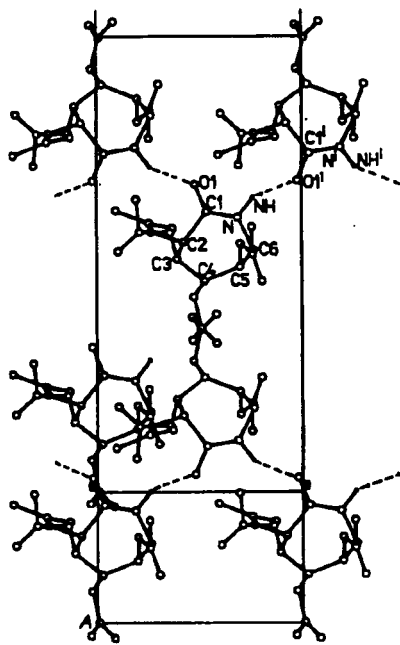


FIG. 2
Crystal packing. Dashed lines indicate the hydrogen bonding

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