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

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The title crystal structure was solved by direct methods and refined anisotropically to $R = 0.082$ for 1 612 unique observed reflections. The compound crystallizes in $P\,2_12_12_1$ space group with the lattice parameters $a = 8.317(1)$, $b = 8.412(1)$, $c = 24.091(3)$ Å, $V = 1\,685.5(3)$ Å^3, $Z = 4$.

The geometry of the seven-membered lactam ring is known from the X-ray structure studies of ε-caprolactam[1] and other lactams[2,12]. The chair conformation of caprolactam molecule with practically planar "amide" segment C(2)–C(1)–N–C(6), and the crystal packing consisting from centrosymmetric pairs of molecules linked by hydrogen bonds (N–H ... O = 2.90 Å), resulted from that measuring[1].

It is possible to assume some deformation of the nearly ideal chair conformation described for caprolactam, when some substituents are bound on the carbon chain of lactam molecule. This assumption was confirmed, for example, for some seven-membered lactams bound to another rings[2,3]. On the other hand, the chair conformation of 6-amino-6-deoxyhexonolactams and their tetra-O-acetylderivatives were found in solution by ^{1}H NMR and CD techniques[4]. IR spectra of the latter compounds measured in Nujol showed significant differences (up to $\Delta\nu$ 100 cm^{-1}) in the ν_{N-H} values for various configurational isomers[5], which could be explained by differences in strength of the above mentioned intermolecular hydrogen bonds.

For more precise correlation of the conformation of substituted and unsubstituted seven-membered lactam rings as well as for obtaining information about molecular packing, the X-ray study of 6-amino-6-deoxyhexonolactam derivative is necessary. In this paper the results of X-ray analysis of 2,3,4,5-tetra-O-acetyl-6-amino-6-deoxy-D-galactonolactam are described. This compound is characterized by the two N–H bands[5]

in the Nujol IR spectra and adopts the $^4C_{1,N}$ (D) conformation[4] according to ^1H NMR spectrum in solution of deuteriochloroform.

EXPERIMENTAL

Preparation of 2,3,4,5-tetra-O-acetyl-6-amino-6-deoxy-D-galactonolactam is described in refs[6,7]. Crystals for X-ray structural analysis were obtained by recrystallization from a mixture of chloroform–1-propanol (2 : 1). For $C_{14}H_{19}NO_9$ (345.3) calculated: 48.70% C, 5.55% H, 4.06% N; found: 48.58% C, 5.57% H, 4.27% N.

Crystal Structure Determination

Orthorhombic, space group $P\,2_12_12_1$ (No. 19), a = 8.317(1), b = 8.412(1), c = 24.091(3) Å, V = 1 685.5(3) Å^3, Z = 4, D_c = 1.361 g cm^{-3}, D_m = 1.37 g cm^{-3}, μ = 1.077 cm^{-1}, $F(000)$ = 728.

The structure was solved by direct methods and anisotropically refined by full-matrix least-squares procedure. The C-bonded hydrogen atoms were fixed in calculated positions with fixed U_{iso} values equivalent to the U_{eq} value of the attached atoms. Absorption and extinction effects were ignored.

Parameters describing the data collection and structure refinement are listed in Table I.

TABLE I
Data collection and structure refinement parameters

Crystal dimensions, mm	0.1 × 0.15 × 0.45
Diffractometer and radiation used	Enraf–Nonius CAD4 equipped with a graphite monochromator, MoKα, λ = 0.71073 Å
Scan technique	ω/2θ
Number and θ range of reflections for lattice parameters refinement	22, 13 – 16°
Interval of standard reflection monitoring, intensity fluctuation	120 min, –0.4%
Total number of reflections measured, 2θ range	2 817, 50°
Range of h, k, l	–9, 9; 0, 10; 0, 28
Number of unique observed reflections	1 612
Criterion for observed reflections	$I > 3\sigma(I)$
Value of R_{int}	0.044
Function minimized	$\sum w (\lvert F_o \rvert - \lvert F_c \rvert)^2$
Weighting scheme	$w = 1$
Parameters refined	219
Value of R, R_w, S	0.082, 0.071, 0.64
Ratio of max. LS shift to e.s.d. (Δ/σ)	0.1
Max. and min. heights in finals $\Delta\rho$ map	0.31, –0.27 e Å^{-3}
Programms used	SHELXS-86 (ref.[8]), CRYSTALS (ref.[9]), SDP (ref.[10])
Computer used	PC 386

RESULTS AND DISCUSSION

The final atomic coordinates and equivalent isotropic temperature factors of non-H atoms are given in Table II. Bond distances and angles are listed in Table III. The studied molecule and crystal packing are shown in Fig. 1.

The presented crystallographic data allow to characterize the spatial arrangement of the molecule by the following features:

a) The ring of 2,3,4,5-tetra-O-acetyl-6-amino-6-deoxy-D-galactonolactam adopts conformation near to the $^4C_{1,N}$ (D) with the slightly nonplanar arrangement of the atoms C(6)–N–C(1)–C(2) (torsion angle equals 12°). The mean plane of these atoms is practically coplanar (dihedral angle is 172.55°) with the plane of the atoms C(3)–C(4)–C(5).

b) In the present structure the absolute values of the endocyclic torsion angles (Table IV) are not so close to those ones of ε-caprolactam as in crystallinic 2,3,4,5-tetra-O-acetyl-6-amino-6-deoxy-D-allonolactam[11]. The non-planar arrangement of amidic sequence C(6)–N–C(1)–C(2) causes a small twist of the chair of galactonolactam.

c) In the crystal structure the adjacent molecules of this lactam are coupled by intermolecular hydrogen bonds, forming a helical chain.

The data presented in this and also in preceding papers[11,12] confirm the premise implied on the basis of the measuring of IR spectra of the eight isomeric 2,3,4,5-tetra-O-acetyl-6-amino-6-deoxyhexonolactams in crystal form[5]: according to their $\nu_{C=O}$ values, two groups of lactams could be differentiated.

Lactams of the first group (including isomers of D-*allo*-, D-*galacto*-, L-*gulo*- and D-*talo*-configuration) have associated amidic carbonyl in the intermolecular hydrogen bond N–H ... O(1), similary to ε-caprolactam[1]. However, in contrast to them, the mole-

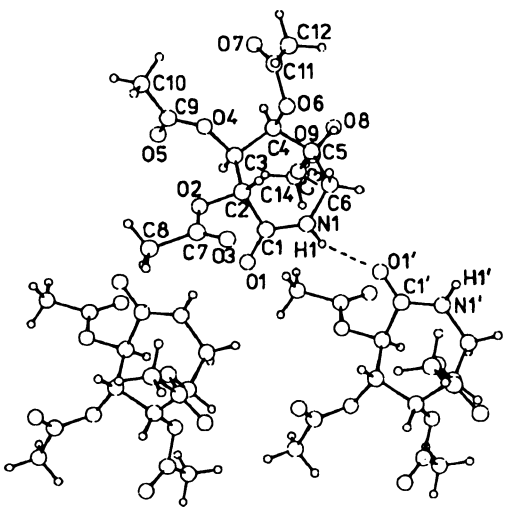
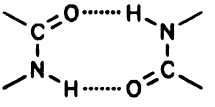
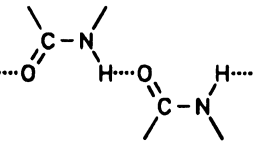


FIG. 1
Crystal packing. Dashed lines indicate the hydrogen bonding

cules of the four up named acetylated sugar lactams do not form the dimers bonded by couple of intermolecular hydrogen bonds (Formula *I*), but they form a helical chain with molecule bonded each other by one intermolecular hydrogen bond only (Formula *II*).



I



II

TABLE II

Final coordinates for non-hydrogen atoms[a] and their equivalent isotropic thermal parameters $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$

Atom	*x*	*y*	*z*	U_{eq}, Å^2
O(1)	0.7425(6)	0.2229(7)	0.0197(2)	0.0498
O(2)	0.5831(5)	0.2268(6)	0.1131(2)	0.0470
O(3)	0.6968(7)	-0.0150(7)	0.1209(3)	0.0657
O(4)	0.6068(5)	0.4646(6)	0.1807(2)	0.0441
O(5)	0.4137(7)	0.6028(9)	0.1393(3)	0.0729
O(6)	0.9194(5)	0.4926(5)	0.2002(2)	0.0382
O(7)	0.8050(8)	0.6812(6)	0.2545(2)	0.0649
O(8)	0.9389(6)	0.6440(6)	0.0599(2)	0.0463
O(9)	1.0817(8)	0.8605(7)	0.0790(2)	0.0748
N(1)	0.9725(6)	0.3190(7)	0.0540(2)	0.0400
C(1)	0.8186(8)	0.2782(8)	0.0577(3)	0.0386
C(2)	0.7390(7)	0.2969(8)	0.1160(3)	0.0349
C(3)	0.7088(7)	0.4696(8)	0.1320(2)	0.0372
C(4)	0.8578(8)	0.5647(8)	0.1508(2)	0.0394
C(5)	0.9967(8)	0.5684(8)	0.1099(2)	0.0398
C(6)	1.0650(8)	0.4056(8)	0.0949(3)	0.0420
C(7)	0.581(1)	0.066(1)	0.1132(3)	0.0527
C(8)	0.410(1)	0.012(1)	0.1040(4)	0.0683
C(9)	0.4654(8)	0.5384(9)	0.1796(3)	0.0496
C(10)	0.3833(9)	0.534(1)	0.2343(3)	0.0648
C(11)	0.8812(8)	0.5617(9)	0.2497(3)	0.0452
C(12)	0.946(1)	0.465(1)	0.2966(3)	0.0631
C(13)	0.9913(9)	0.7938(9)	0.0497(3)	0.0438
C(14)	0.912(1)	0.858(1)	-0.0011(3)	0.0686

[a] H atom coordinates are deposited at authors and may be obtained on request.

TABLE III
Bond distances (in Å) and angles (in °)

Bond	Distance	Bond	Angle
O(1)–C(1)	1.206(7)	C(7)–O(2)–C(2)	115.2(6)
O(2)–C(2)	1.426(7)	C(9)–O(4)–C(3)	119.1(5)
O(2)–C(7)	1.352(9)	C(11)–O(6)–C(4)	117.6(5)
O(3)–C(7)	1.196(9)	C(13)–O(8)–C(5)	116.9(5)
O(4)–C(3)	1.449(7)	C(6)–N(1)–C(1)	126.6(6)
O(4)–C(9)	1.330(8)	H(1)–N(1)–C(1)	121.7(4)
O(5)–C(9)	1.190(8)	H(1)–N(1)–C(6)	110.2(4)
O(6)–C(4)	1.432(7)	N(1)–C(1)–O(1)	123.7(6)
O(6)–C(11)	1.363(8)	C(2)–C(1)–O(1)	120.0(6)
O(7)–C(11)	1.194(8)	C(2)–C(1)–N(1)	116.3(6)
O(8)–C(5)	1.445(7)	C(1)–C(2)–O(2)	107.4(5)
O(8)–C(13)	1.355(8)	C(3)–C(2)–O(2)	104.8(5)
O(9)–C(13)	1.175(8)	C(3)–C(2)–C(1)	113.2(5)
N(1)–C(1)	1.328(8)	C(2)–C(3)–O(4)	105.9(5)
N(1)–C(6)	1.449(8)	C(4)–C(3)–O(4)	104.4(4)
N(1)–H(1)	0.92(6)	C(4)–C(3)–C(2)	115.8(5)
C(1)–C(2)	1.560(8)	C(3)–C(4)–O(6)	108.1(5)
C(2)–C(3)	1.525(9)	C(5)–C(4)–O(6)	106.0(5)
C(3)–C94)	1.543(8)	C(5)–C(4)–C(3)	115.7(5)
C(5)–C(6)	1.526(9)	C(4)–C(5)–O(8)	107.3(5)
C(7)–C(8)	1.51(1)	C(6)–C(5)–O(8)	108.7(5)
C(9)–C(10)	1.486(9)	C(6)–C(5)–C(4)	114.7(5)
C(11)–C(12)	1.50(1)	C(5)–C(6)–N(1)	114.5(5)
C(13)–C(14)	1.49(1)	O(3)–C(7)–O(2)	123.9(7)
		C(8)–C(7)–O(2)	108.4(7)
		C(8)–C(7)–O(3)	127.6(8)
		O(5)–C(9)–O(4)	123.3(7)
		C(10)–C(9)–O(4)	112.1(6)
		C(10)–C(9)–O(5)	124.6(7)
		O(7)–C(11)–O(6)	124.6(7)
		C(12)–C(11)–O(6)	110.1(6)
		C(12)–C(11)–O(7)	125.3(7)
		O(9)–C(13)–O(8)	122.8(7)
		C(14)–C(13)–O(8)	110.2(6)
		C(14)–C(13)–O(9)	127.0(7)

C–H bond was fixed to 1.0 Å, hydrogen bond N(1)...O1′ = 2.8847 Å, N(1)–H–O1′ = 146.8° (′ = x + 1/2; $-y$ + 1/2; $-z$).

The amidic carbonyl groups in the lactams of the second group (including isomers of D-*altro*-, D-*gluco*-, L-*ido*- and D-*manno*-configuration) are not associated and the intermolecular hydrogen bonds are formed in their crystal structures by lactam's NH group of one molecule and carbonyl of some acetoxy group (in the case of D-*manno* isomer it is the acetoxy group on C(5) (ref.[12])) of vicinal molecule.

TABLE IV
Endocyclic torsion angles (in °) of 2,3,4,5-tetra-O-acetyl-6-amino-6-deoxy-D-galactonolactam in comparison with those of ε-caprolactam[1]

Bond	Torsion angle	
	present compound	ε-caprolactam
C(6)-N-C(1)-C(2)	-12.3	-4.2
N-C(1)-C(2)-C(3)	72.6	-63.1
C(1)-C(2)-C(3)-C(4)	-76.1	81.9
C(2)-C(3)-C(4)-C(5)	55.5	-63.5
C(3)-C(4)-C(5)-C(6)	-59.4	60.7
C(4)-C(5)-C(6)-N	79.8	-77.0
C(5)-C(6)-N-C(1)	-57.7	67.8
C(6)-N-C(1)-O	170.8	176.6
HN-N-C(1)-O	-6.4	3.0
HN-N-C(1)-C(2)	176.7	-178.0

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