Crystal Structure of 6-[6(e)-Carbamoyltetrahydro-2(e)-pyranyl]-8-oxa-6-azabicyclo[3.2.1]octan-7-one

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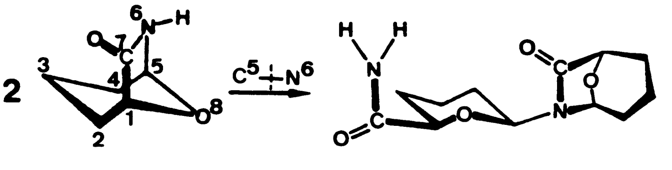
The structure of the dimerization product of bicyclic oxalactam, 8-oxa-6-azabicyclo[3.2.1] octan-7-one, was determined by the X-ray diffraction method. The final R value was 0.062 for 2009 reflections. The structure suggests that the cationic oligomerization of the bicyclic oxalactam proceeds through the C^5-N^6 scission, differing from the cases of other common lactams.

Cationic oligomerization of optically active bicyclic oxalactam, 8-oxa-6-azabicyclo[3.2.1]octan-7-one (abbreviated as BOL), produces the oligomer mixture.[1] The GPC analysis showed that the main product is the dimer, $(BOL)_2$. On the basis of IR and NMR data, an equatorial orientation of the BOL moiety with respect to the tetrahydropyran ring has been expected.[1] Therefore, the anticipated structure of $(BOL)_2$ and the dimerization mechanism are deduced as Eq. 1. It shows that the reaction proceeds through the C^5-N^6 scission of the oxaamide unit in BOL, though the N^6-C^7 scission is generally observed in the cases of other common lactams. In order to confirm the molecular structure and to elucidate the oligomerization mechanism, the crystal structure of $(BOL)_2$ has been studied by the X-ray diffraction method.



(+)-BOL

$(BOL)_2$

Eq. 1.

Results and Discussion

Crystal Data. $C_{12}H_{18}N_2O_4$, M.W.=254.29, $P2_1$, a=10.814(1), b=9.964(1), c=11.975(2) Å, β=101.44(1)°, U=1264.6(3) Å^3, Z=4, D_m=1.33, D_x=1.333 gcm^{-3}, μ(Cu $K\alpha$)=8.6 cm^{-1}. Intensity data with $2\theta \leq 120°$ were collected on a Rigaku four-circle diffractometer using graphite-monochromated Cu $K\alpha$ radiation (λ=1.5405 Å). The structure was solved by the use of *MULTAN 78*.[2] The refinement was carried out by the block-diagonal least-squares method.[3] The function minimized was $\sum w(|F_o|-|F_c|)^2$, and the weighting scheme at the final stage of the refinement was $w=[\sigma^2(F_o)-1.566|F_o|+0.079|F_o|^2]^{-1}$ for $|F_o|>0$, and w=1.016 for $|F_o|=0$. The final R value is 0.062 for 2009 independent reflections. All the scattering factors were taken from the International Tables for X-Ray Crystallography, Vol. IV.[4] The final atomic parameters with equivalent temperature factors are listed in Table 1.* The bond distances and angles are given in Fig. 1,

Table 1. Final fractional coordinates(×10^4) and equivalent isotropic temperature factors, with their estimated standard deviations in parentheses

Atom	x	y	z	$B_{eq}$$^{5)}$/Å^2
C(1)**A**	3616(3)	1888(4)	4375(3)	4.2(1)
C(2)**A**	3924(4)	2661(4)	3403(4)	5.1(2)
C(3)**A**	3450(5)	1921(6)	2264(4)	7.2(3)
C(4)**A**	2142(5)	1336(5)	2222(5)	7.9(3)
C(5)**A**	2056(3)	710(4)	3356(4)	5.2(2)
C(7)**A**	4071(3)	441(4)	4358(3)	3.7(1)
C(62)**A**	1796(3)	−3500(3)	4091(3)	3.4(1)
C(63)**A**	1593(3)	−4051(4)	2886(3)	4.2(1)
C(64)**A**	2671(4)	−3643(3)	2323(4)	5.0(2)
C(65)**A**	2839(3)	−2119(4)	2376(3)	4.5(2)
C(66)**A**	3007(3)	−1664(3)	3605(3)	3.5(1)
C(67)**A**	677(3)	−3789(3)	4644(3)	3.5(1)
N(6)**A**	3082(2)	−229(3)	3760(3)	3.6(1)
N(69)**A**	−22(3)	−2776(3)	4835(3)	4.2(1)
O(8)**A**	2295(2)	1717(3)	4211(3)	5.6(1)
O(71)**A**	5113(3)	13(3)	4754(2)	5.9(1)
O(61)**A**	1983(2)	−2076(2)	4104(2)	3.5(1)
O(68)**A**	443(2)	−4951(3)	4854(2)	5.1(1)
C(1)**B**	3370(4)	−59(5)	9318(3)	5.8(2)
C(2)**B**	3861(4)	748(4)	8431(4)	5.2(2)
C(3)**B**	3655(5)	26(5)	7350(4)	6.7(2)
C(4)**B**	2365(5)	−601(5)	7039(4)	7.6(2)
C(5)**B**	2000(3)	−1271(5)	8074(5)	6.6(2)
C(7)**B**	3855(4)	−1481(4)	9392(3)	5.2(2)
C(62)**B**	1861(3)	−5499(4)	9096(3)	4.0(1)
C(63)**B**	1642(3)	−6076(4)	7894(3)	4.6(2)
C(64)**B**	2686(4)	−5634(3)	7293(4)	5.0(2)
C(65)**B**	2784(3)	−4114(4)	7330(3)	4.4(2)
C(66)**B**	3002(3)	−3633(4)	8556(3)	4.0(1)
C(67)**B**	804(3)	−5870(4)	9681(3)	4.5(2)
N(6)**B**	3018(3)	−2187(3)	8660(3)	4.2(1)
N(69)**B**	162(3)	−4858(4)	10021(3)	4.6(1)
O(8)**B**	2062(3)	−268(4)	8950(4)	8.5(2)
O(71)**B**	4839(4)	−1888(4)	9963(4)	9.3(2)
O(61)**B**	1988(2)	−4078(3)	9097(2)	4.0(1)
O(68)**B**	564(3)	−7042(3)	9818(3)	7.2(2)

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*The anisotropic thermal parameters, the parameters of H atom and the tables of the observed and the calculated structure factors are kept as Document No. 8537 at the Office of the Chemical Society of Japan.

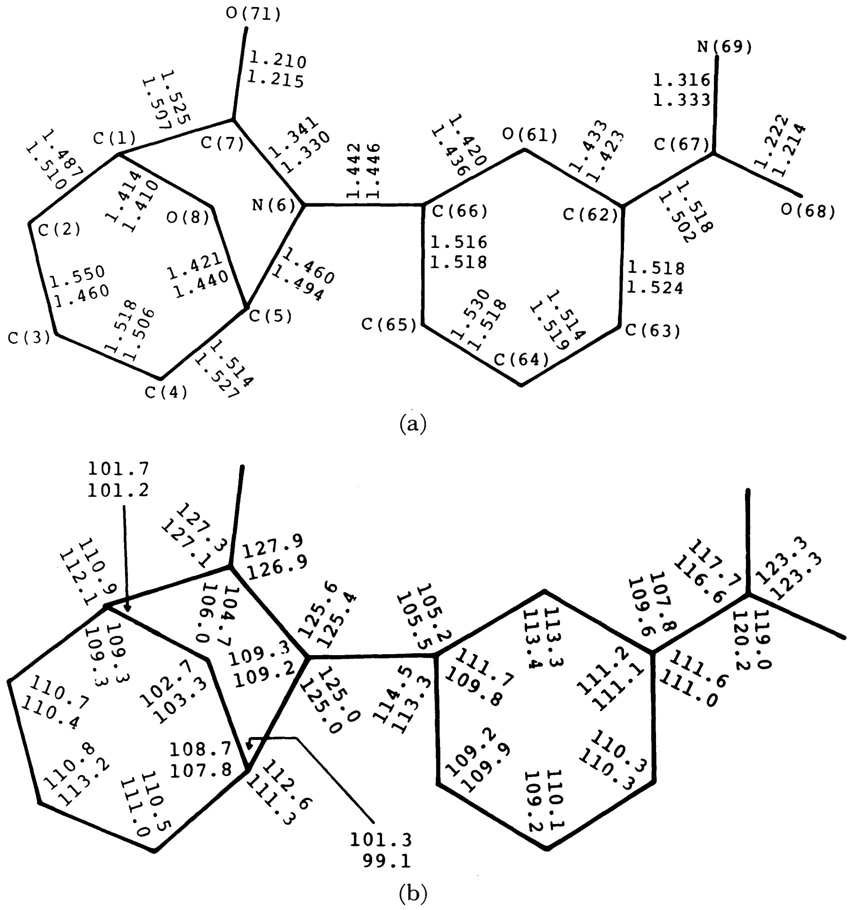

Fig. 1. (a) Bond distances (l/Å), (b) bond angles (ϕ/°) for molecule **A** (upper) and molecule **B** (lower). The estimated standard deviations are 0.005—0.007 Å for bond distances and 0.3—0.4° for bond angles.

with the numbering scheme of the atoms. Two independent molecules, **A** and **B**, are included in the asymmetric unit. The overall structure of the two molecules are almost the same. However, the thermal motion of molecule **B** is slightly larger than that of molecule **A**, as a whole. The bond distances and angles between the two molecules are in good agreement with each other, except for the C(2)–C(3) distance. An *ORTEP II*[6] drawing of molecule **A** is shown in Fig. 2. This shows that the tetrahydopyran ring takes a chair conformation, and ascertains that both the amide and the BOL moiety are equatorial with respect to the tetrahydropyran ring. This structure confirms the anticipated structure, and supports the presumed reaction mechanism of Eq. 1 that the cationic oligomerization of BOL proceeds through the C^5–N^6 scission of the oxaamide unit.

The most interesting conformational feature of the molecule is the anticlinal conformation (ac^+) around the N(6)–C(66) bond. From the spectral data, the C(7)–N(6) bond was speculated to take g^- conformation to the C(66)–O(61) bond, leading to the formation of the intramolecular hydrogen bond between N(69) and O(71). However, the torsion angle of C(7)–N(6)–C(66)–O(61) is 118.4(3)° for **A** and 104.8(4)° for **B**, and the intramolecular hydrogen bond is not made. In this structure the C(5) is g^- to the O(61) and g^+ to the C(65) around the N(6)–C(66) bond. The torsion angles of the main skeleton which is of interest in consider-

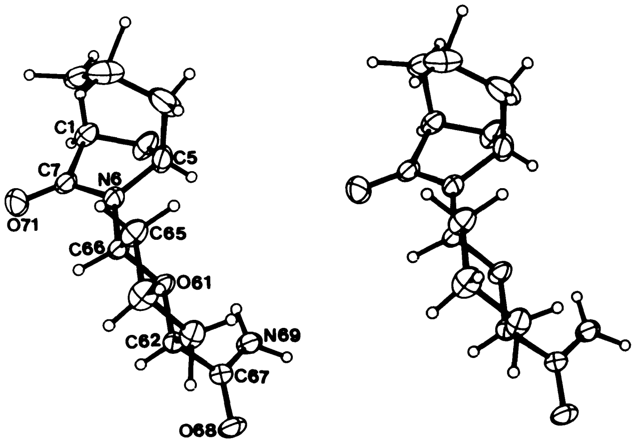

Fig. 2. Stereodrawing of molecule **A**. Atoms are drawn with 50% probability thermal ellipsoids.

Table 2. Hydrogen bonds(the estimated standard deviations are in parentheses)

D*	A*	D···A	<D—H···A	Symmetry code of A
N(69)**A**	O(8)**A**	2.952(5)Å	155(2)°	$-x,-0.5+y,1-z$
N(69)**A**	O(68)**A**	2.877(5)	134(2)	$-x,0.5+y,1-z$
	O(61)**A**	2.588(4)	107(2)	—
N(69)**B**	O(8)**B**	2.940(6)	165(2)	$-x,-0.5+y,2-z$
N(69)**B**	O(68)**B**	2.930(5)	121(2)	$-x,0.5+y,2-z$
	O(61)**B**	2.581(4)	115(2)	—

* D means a protan donor and A a proton acceptor.

ing the model structure of the polymer of BOL synthesized by the anion polymerization are: C(1)-C(7)-N(6)-C(66), −173.5(3)° for **A** and −171.0(3)° for **B**; N(6)-C(66)-O(61)-C(62), −176.8(2)° for **A** and −177.6 (3)° for **B**; C(66)-O(61)-C(62)-C(67), −179.8(2)° for **A** and 178.6(3)° for **B**; O(61)-C(62)-C(67)-N(69), 11.5 (4)° for **A** and 2.8 (5)° for **B**. Therefore the conformation around the N(6)-C(66), C(66)-O(61) and O(61)-C(62) bonds can be described as an ac^{+}-t-t conformation.

Hydrogen bonds are listed in Table 2. The fairly distorted bifurcated hydrogen bonds are observed between N(69) and O(61), and between N(69) and O(68). The former is intramolecular and the latter is intermolecular. One of the reasons for the distorsions is considered to be the formation of the five-membered ring by the N(69)···O(61) hydrogen bond.

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