  Bull. Chem. Soc. Jpn., 59, 2085—2088 (1986)

Crystal Structures of 8-Oxa-6-azabicyclo[3.2.1]octan-7-one and the 4(*e*)-Bromo-substituted Derivative

Yuanxin Gu,†† Takashi Yamane,* Tamaichi Ashida, Kazuhiko Hashimoto,† and Hiroshi Sumitomo†

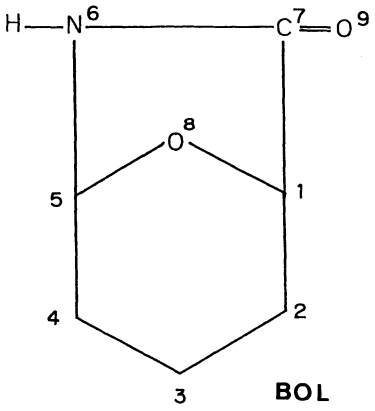
Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464

†Faculty of Agriculture, Nagoya University, Chikusa-ku, Nagoya 464

(Received February 13, 1986)

The crystal structures of the bicyclic oxalactam, 8-oxa-6-azabicyclo[3.2.1]octan-7-one(BOL) and the 4(*e*)-bromo-substituted derivative(Br-BOL) were determined by the X-ray diffraction method. Crystal data: (BOL) $P2_12_12_1$, a=10.926(3), b=9.115(2), c=6.280(2) Å, Z=4; (Br-BOL) $P2_12_12_1$, a=10.708(3), b=11.053(3), c=6.208(2) Å, Z=4. Refinements were carried out by the full-matrix least-squares method. R values are; (BOL) 0.050 for 601 reflections, (Br-BOL) 0.028 for 866 reflections. Both structures are quite similar to each other. The packing scheme of BOL is essentially the same as that of Br-BOL. Molecules are linked by N-H···O hydrogen bonds around a two-fold screw axis, giving rise to infinite chains extended along the c axis.

A bicyclic oxalactam, 8-oxa-6-azabicyclo[3.2.1]octan-7-one(abbreviated as BOL), is an interesting starting material for new functional polymers with permselectivity. The anionic solution polymerization of BOL leads to a high molecular weight polyamide (poly(BOL)) and the resulting poly(BOL) is easily cast to a hygroscopic membrane which has an excellent permeability for water and permselectivity for solutes of different sizes in an aqueous solution.[1-3] It may also be used as a component for graft and block copolymers.[4-6]



BOL

Anionic polymerization of BOL is known to proceed through the N^6–C^7 scission of the amide group.[1,2] The mechanism is the same as that in common lactams. On the other hand the cationic oligomerization of BOL was recently confirmed by the X-ray and NMR analyses of the resulting dimer [abbreviated as $(BOL)_2$],[7,8] to proceed through the C^5–N^6 scission of the amide group in the monomer unit.

The reactivity of such a novel bicyclic oxalactam should be closely related to the molecular structure. Therefore the 4-bromo-substituted derivative, 4(*e*)-bromo-8-oxa-6-azabicyclo[3.2.1]octan-7-one(abbreviated as Br-BOL), was synthesized in order to obtain an information on the structural and electronic effects upon their reactivity.[9] In this paper the structures of BOL and Br-BOL determined by the X-ray diffraction method were described.

Experimental

The BOL crystals obtained from a hexane solution were colorless plates and Br-BOL crystals grown from an ethyl acetate solution were colorless needles. The X-ray intensity data were collected on a Rigaku four-circle diffractometer, using graphite monochromated radiation; Cu $K\alpha$(λ=1.5405 Å) for BOL and Mo $K\alpha$(λ=0.70926 Å) for Br-BOL. Unit cell dimensions were obtained by the least-squares fit using 11 reflections with $40°<2\theta<56°$ for BOL and 14 reflections with $27°<2\theta<38°$ for Br-BOL. Crystal data and experimental conditions are shown in Table 1.

Both structures were solved by the direct method (*MULTAN* 80).[10] The refinement was carried out by the full-matrix least-squares method(*FMLS*).[11] The function minimized was $\sum w(|F_o|-|F_c|)^2$. After the anisotropic refinements of non-hydrogen atoms, all the hydrogen atoms were picked up on the difference-Fourier maps, and were included in the refinement with the isotropic temperature factors. The final R values were 0.050(R_w=0.069) for BOL, and 0.028(R_w=0.035) for Br-BOL, respectively. The weighting scheme adapted was $w=(\sigma^2(F_o)+a|F_o|^2)^{-1}$ for the observed reflections with a=0.0 for BOL and 0.002 for Br-BOL. All the scattering factors were taken from the International Tables for X-Ray Crystallography, Vol. IV.[12] The atomic parameters of the non-hydrogen atoms with equivalent temperature factors(B_{eq})[13] are given in Table 2.* All the calculations were carried out on a

†† On leave from Institute of Physics, Chinese Academy of Science, Beijing, China.

* The anisotropic thermal parameters of non-hydrogen atoms, the parameters of hydrogen atoms, the equations of best-planes, and the tables of the observed and the calculated structure factors were kept at the Chemical Society of Japan(as Doc. No. 8637).

Table 1. Crystal Data and Experimental Conditions

	BOL	Br-BOL
Chemical formula	$C_6H_9NO_2$	$C_6H_8NO_2Br$
Mr	127.14	206.04
Space group	$P2_12_12_1$	$P2_12_12_1$
a/Å	10.926(3)	10.708(3)
b/Å	9.115(2)	11.053(3)
c/Å	6.280(2)	6.208(2)
V/Å^3	625.5(3)	734.7(4)
Z	4	4
d_{calcd}/(g cm^{-3})	1.350	1.862
μ/cm^{-1}	8.59(Cu $K\alpha$)	58.55(Mo $K\alpha$)
Crystal size/mm	0.2×0.2×0.5	0.2×0.2×0.4
Scan method	ω—2θ	ω—2θ
$\Delta\omega$/°	2.0+0.15 tan θ	1.0+0.35 tan θ
ω scan rate/(°min^{-1})	6—1*1	3—1*1
Background counting time/s	5—30*2	5—15*2
$2\theta_{max}$/°	125	55
No. of reflections measured	613	1004
No. of reflections observed($\|F_o\| \geq 3\sigma(F_o)$)	601	866

*1 The scan rate was varied as a function of 2θ angle.
*2 The background counting time is changed correlated with the scan rate.

Table 2. Final Fractional Coordinates(×10^4) and Equivalent Isotropic Temperature Factors, with Their Estimated Standard Deviations in Parentheses

(a) 8-Oxa-6-azabicyclo[3.2.1]octan-7-one

Atom	x	y	z	B_{eq}/Å^2
C (1)	6462(2)	3455(2)	45(4)	3.3(1)
C (2)	5100(2)	3619(4)	409(5)	3.8(1)
C (3)	4725(2)	2920(4)	2510(5)	4.4(2)
C (4)	5666(3)	3205(3)	4291(4)	4.4(1)
C (5)	6953(2)	3090(3)	3445(4)	3.9(1)
N (6)	7158(2)	1711(2)	2304(4)	3.9(1)
C (7)	6830(2)	1853(3)	277(4)	3.3(1)
O (8)	7100(2)	4135(2)	1771(3)	4.2(1)
O (9)	6783(2)	914(2)	−1118(3)	4.6(1)

b) 4-Bromo-8-oxa-6-azabicyclo[3.2.1]octan-7-one

Atom	x	y	z	B_{eq}/Å^2
Br	4295(1)	207(1)	2202(1)	4.31(2)
C (1)	6165(4)	2804(3)	−2550(7)	2.9(2)
C (2)	4776(4)	2625(4)	−3068(8)	3.5(2)
C (3)	4251(4)	1582(4)	−1750(7)	3.5(2)
C (4)	4685(4)	1671(4)	564(7)	2.9(2)
C (5)	6086(4)	1913(3)	676(7)	2.9(2)
N (6)	6797(3)	1125(3)	−718(6)	3.0(2)
C (7)	6843(3)	1591(3)	−2712(7)	2.6(2)
O (8)	6263(3)	3069(2)	−272(5)	3.3(1)
O (9)	7288(3)	1158(2)	−4351(5)	3.6(1)

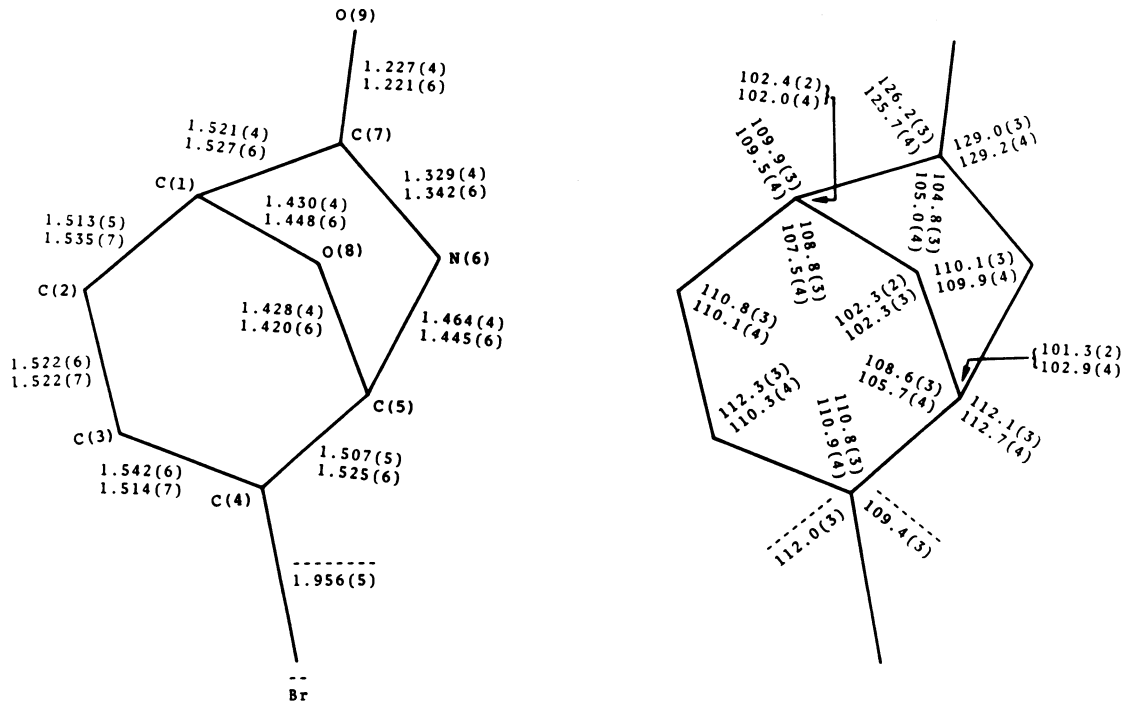


Fig. 1. (a) Bond distances (l/Å) and (b) bond angles (ϕ/°) for BOL (upper) and Br-BOL (lower). Estimated standard deviations are in parentheses.

FACOM M382 at Nagoya University Computation Center.

Results and Discussion

The bond distances and angles of BOL and Br-BOL are given in Fig. 1, with the numbering of atoms. The corresponding bond distances and angles between BOL and Br-BOL are in good agreements with each other, except for the C(3)-C(4) distance and the C(4)-C(5)-O(8) angle. The C(3)-C(4) distance of BOL seems slightly longer than that of Br-BOL. The C(4)-C(5)-O(8) angle, 108.6(3)°, of BOL is larger than that of Br-BOL, 105.7(4)°. The C(4)-C(5)-O(8) angle of BOL is similar to the corresponding ones in $(BOL)_2$,[7] 108.7(3) and 107.8(4)°, in which two molecules are included in the asymmetric unit, and the BOL skeleton is conserved at a terminus. The C(1)-C(7)-O(9) angle is smaller than the N(6)-C(7)-O(9) angle in both BOL and Br-BOL. These angles are, however, almost equal in the BOL moieties of $(BOL)_2$; that is, 127.3(4) and 127.1(4)° for ∠C(1)-C(7)-O(9), and 127.9(4) and 126.9(4)° for ∠N(6)-C(7)-O(9).

Stereoscopic views of BOL and Br-BOL drawn by *ORTEP* II[14] are shown in Fig. 2. The overall structures of both molecules are quite similar with each other, and they are also almost the same as the structures of the BOL moieties in $(BOL)_2$. The six-membered ring including C(1), C(2), C(3), C(4), C(5), and O(8) takes a chair conformation in each

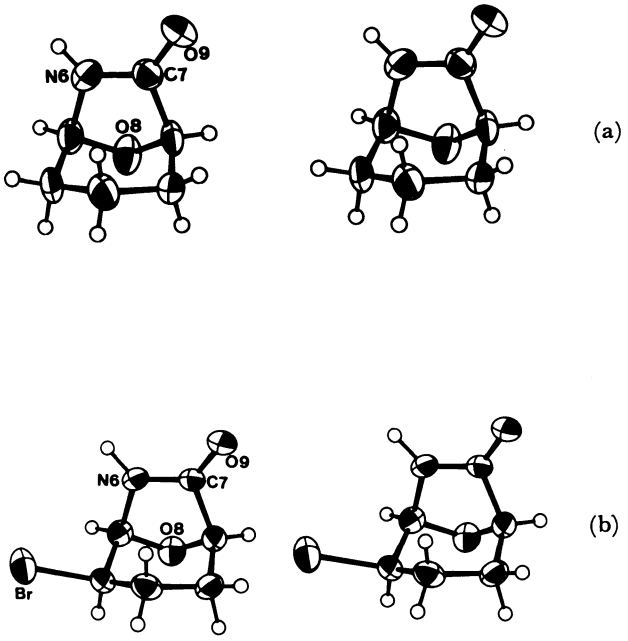


Fig. 2. Stereodrawings of (a) BOL and (b) Br-BOL. Atoms are drawn with 50% probability thermal ellipsoids.

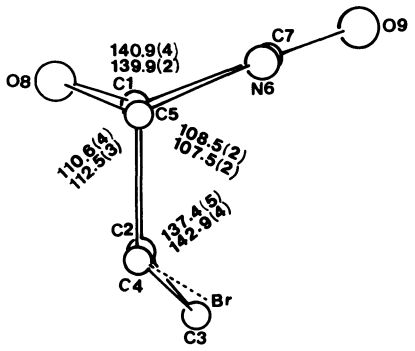


Fig. 3. Selected dihedral angles among the best-planes. Definitions are: plane I C(1), C(7), N(6), C(5), and O(9); plane II C(1), O(8) and C(5); plane III C(1), C(2), C(4) and C(5); plane IV C(2), C(3) and C(4). BOL upper, and Br-BOL lower.

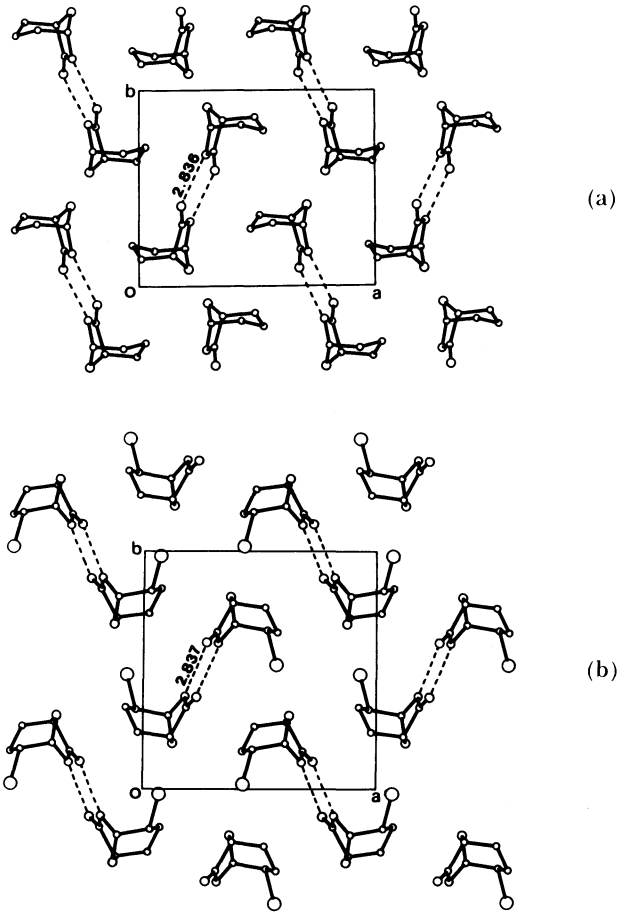


Fig. 4. Crystal structures of (a) BOL and (b) Br-BOL, projected along the c axis. Broken lines show the hydrogen bonds.

molecule. The C(1), C(7), N(6), C(5), O(8) five-membered ring shows an envelope conformation, with the O(8) out of plane[deviation: −0.604(5) Å for BOL and −0.59(1) Å for Br-BOL]. The Br atom is in equatorial with respect to the six-membered ring in Br-BOL. The molecule consists of four planes: plane I defined with C(1), C(7), N(6), C(5), and O(9); plane II C(1), O(8), and C(5); plane III C(1), C(2), C(4), and C(5); plane IV C(2), C(3), and C(4). The selected dihedral angles among the planes in the present two compounds are given in Fig. 3. A significant difference is found in the dihedral angles between the plane III and IV. The corresponding ones in $(BOL)_2$ are 139.7(5) and 140.6(5)°, which are intermediate between the present two compounds. Therefore marked changes on the molecular geometry of BOL skeleton are not observed by the substitution of Br at C(4), though the substitution may have significant effects on the intermolecular interactions due to the bulkiness and the strong electronegativity of the Br atom.

The packing of molecules in BOL and Br-BOL are drawn in Figs. 4(a) and (b), respectively. The packing schemes of both crystals are essentially the same, thus the present two compounds are isostructural. The elongation of the period of the b axis of Br-BOL, as compared with that of BOL, appears to be occured by the substitution of the bulky Br atoms, with the direction of C(4)-Br roughly parallel to the b axis. The hydrogen bonds occur between N(6)···O(9^{i}) 2.836(4) Å in BOL and N(6)···O(9^{ii}) 2.837(5) Å in Br-BOL. [Symmetry code: (i) $1.5-x$, $1-y$, $0.5+z$; (ii) $1.5-x$, $-y$, $0.5+z$] The H···O and ∠N-H···O are 1.99(5) Å and 167(5)° for BOL and 1.84(6) Å and 143(4)° for Br-BOL. Molecules are linked by hydrogen bonds around a two-fold screw axis, giving rise to infinite helical chains extended along the c axis.

One of the authors(Gu) thanks the Japan Society for the Promotion of Science for this research at Nagoya University.

References

1) H. Sumitomo and K. Hashimoto, *Macromolecules*, **10**, 1327 (1977).
2) K. Hashimoto and H. Sumitomo, *Macromolecules*, **13**, 786 (1980).
3) H. Sumitomo, K. Hahimoto, and T. Ohyama, *Polym. Bull.*, **1**, 133 (1978).
4) K. Hashimoto, H. Sumitomo, and M. Kawasumi, *Polym. Bull.*, **11**, 121 (1984).
5) K. Hashimoto, H. Sumitomo, and H. Yamamori, *Polym. J.*, **17**, 679 (1985).
6) K. Hashimoto, H. Sumitomo, and M. Kawasumi, *Polym. J.*, **17**, 1045 (1985).
7) T. Yamane, H. Nanayama, T. Ashida, K. Hashimoto, and H. Sumitomo, *Bull. Chem. Soc. Jpn.*, **58**, 2304 (1985).
8) K. Hashimoto and H. Sumitomo, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 1733 (1984).
9) K. Hashimoto, H. Sumitomo, and M. Suzuki, *Chem. Lett.*, **1986**, 767.
10) P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Deqlercq, and M. M. Woolfson, "*MULTAN* 80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data," Univs. of York, England, and Louvain, Belgium (1980).
11) T. Ashida, "*UNICS-NAGOYA*," Nagoya University, Nagoya, Japan p. 73 (1981).
12) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, p. 71.
13) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).
14) C. K. Johnson, "*ORTEP* II," *Report ORNL*-5138, Oak Ridge National Laboratory, Tennessee, USA (1976).