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Crystal Structures of the Configurationally Isomeric Dimers of 4(*e*)-Bromo-8-oxa-6-azabicyclo[3.2.1]octan-7-one

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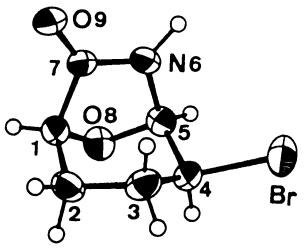
The crystal structures of the major(Major) and minor(Minor) components of the dimer obtained from the anionic reaction of the racemates of 4(*e*)-bromo-8-oxa-6-azabicyclo[3.2.1]octan-7-one (Br-BOL) have been determined by X-ray method. Crystal data are: (Major) $P2_1/c$, a=10.852(3), b=5.207(3), c=22.146(5) Å, β=92.75(2)°, Z=4, R=0.083 for 1744 reflections; (Minor) $P2_1/c$, a=16.825(5), b=7.844(3), c=11.483(3) Å, β=121.40(2)°, Z=4, R=0.038 for 2026 reflections. The structure of each dimer is constructed of an original Br-BOL skeleton at a terminus and an rearranged bicyclic skeleton at another terminus. The configuration of the chiral C atom contained in the rearranged skeleton of Major is different from that of Minor, when the chirarity of a terminal Br-BOL skeleton in Major is coincided with that in Minor.

A bicyclic epoxy lactam, 8-oxa-6-azabicyclo[3.2.1]-octan-7-one (abbreviated as BOL), is an interesting starting material for new functional polymers with water permeability and ion selectivity.[1-4] The anionic polymerization of BOL in solution leads to a high-molecular-weight polyamide (poly(BOL)) through the N^6–C^7 scission of the amide group.[1,3] The conformation of the optically active poly(BOL) was revealed to be a double-stranded 10_3 helix by the X-ray diffraction method.[5] While the oligomers are obtained in the cationic reaction of BOL, suggesting that the reaction mechanism differs from that of the anionic polymerization.[6] In order to make the reaction mechanism clear the X-ray analysis of the resulting dimer (abbreviated as $(BOL)_2$) was carried out, and supports the mechanism that the cationic oligomerization proceeds through the C^5–N^6 scission of BOL.[7] In $(BOL)_2$ the BOL skeleton is conserved at a terminus and the tetrahydropyran ring occurs by the ring-opening in the second residue.[7]



Br-BOL

Recently 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 upon the reactivity of the BOL skeleton.[8] The equatorial location of the Br atom with respect to the 6-membered ring was confirmed by the X-ray analysis of Br-BOL.[9] The anionic reaction of the racemates of Br-BOL forms an oligomer mixture containing mainly the dimer and the trimer.[8] By the IR and NMR studies of the oligomers the original Br-BOL skeleton was assigned at a terminus, though the remaining structure could not be confirmed. Furthermore the dimer was separated into two components, the major and minor component respectively, during the purification. The yielding ratio of the two components is about 6:1. The structural difference between the major and the minor components was conjectured to be a configurational difference of the chiral atom in each component. Therefore in order to determine the molecular structures of the dimers and to elucidate the oligomerization mechanism of Br-BOL, the crystal structure analyses of the dimers were undertaken.

Experimental

The crystals of the major component (abbr. as Major) obtained from an ethyl acetate–chloroform solution were colorless needles, and the crystals of the minor component (abbr. as Minor) grown from an ethyl acetate solution were colorless plates. The density of each component was measured by the flotation method in a 1,2-dibromoethane–CCl_4 solution. The X-ray intensity data were collected on a Rigaku four-circle diffractometer, using graphite monochromated radiation; Cu $K\alpha$(λ=1.5418 Å) for Major and Mo $K\alpha$(λ=0.71073 Å) for Minor. The intensity data were corrected for Lorentz and polarization effects, but the absorption correction was not carried out. Unit cell dimensions were obtained by the least-squares fit using 11 reflections with $55°<2\theta<70°$ for Major and 15 reflections with $20°<2\theta<32°$ for Minor. Crystal data and experimental conditions are shown in Table 1.

Both structures were solved by the heavy atom method. The refinement was carried out by the block-diagonal least-squares method (*HBLS* VI).[10] The function minimized was $\sum w(|F_o|-|F_c|)^2$. The weighting scheme adapted was $w=(\sigma^2(F_o)+a|F_o|^2)^{-1}$ for the observed reflections, where $\sigma(F)$ is the standard deviation based on counting statistics. The isotropic temperature factors of the H atoms are fixed to the equivalent temperature factors(B_{eq})[11] of the corresponding atoms to which they are bound. At final stages of the

Table 1. Crystal Data and Experimental Conditions

	Major	Minor
Chemical formula	$C_{12}H_{15}N_2O_4Br$	$C_{12}H_{15}N_2O_4Br$
Mr	331.17	331.17
Space group	$P2_1/c$	$P2_1/c$
a/Å	10.852(3)	16.825(5)
b/Å	5.207(3)	7.844(3)
c/Å	22.146(5)	11.483(3)
β/°	92.75(2)	121.40(2)
V/Å^3	1249.9(8)	1293.4(8)
Z	4	4
d_{calcd}/g cm^{-3}	1.766	1.701
d_{obsd}/g cm^{-3}	1.71	1.69
μ/cm^{-1}	51.0(Cu $K\alpha$)	33.9(Mo $K\alpha$)
Crystal size/mm	0.5×0.05×0.05	0.5×0.5×0.2
Scan method	ω—2θ	ω—2θ
$\Delta\omega$/°	1.5+0.15 tan θ	2.0+0.35 tan θ
ω scan rate/(°min^{-1})	6—2[a]	3—1.5[a]
Background counting time/s	3—9[b]	4—8[b]
$2\theta_{max}$/°	125	55
No. of reflections		
measured	1983	2984
observed ($\|F_o\| > 3\sigma(F_o)$)	1744	2026

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

refinement, for Major a=0.017 and for Minor a=0.001 were applied. The final R values were 0.083 (R_w=0.111) for Major, and 0.038 (R_w=0.048) for Minor, respectively. 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 B_{eq}'s are given in Table 2.[††] All the calculations were carried out on a FACOM M382 at Nagoya University Computation Center.

Results and Discussion

The bond distances and angles of Major and Minor are given in Fig. 1, together with the numbering of atoms. The corresponding bond distances and angles between the two components are in good agreements with each other, except for the N16–C22–C21 angle. The ∠N16–C22–C21 of Minor, 116.2(6)° is significantly larger than that of Major, 109.8(3)°. The fairly short contact of the Br···O28, 3.210(5) Å is observed in Minor. Therefore the widening of the ∠N16–C22–C21 of Minor may be to reduce the steric repulsion between the Br and O28 atoms. The bond distances and angles of the BOL skeleton within the two components are also quite normal when they are compared with those of BOL,[9] Br-BOL,[9] and $(BOL)_2$,[7] with the exception of the N16–C17 distance. The N16–C17 distances of 1.365(5) Å(Major) and 1.36(1) Å(Minor) are slightly longer than those of 1.329(4) Å(BOL[9]), 1.342(6) Å(Br-BOL[9]), and 1.341(5) and 1.330(5) Å($(BOL)_2$[7] in which two molecules are included in an asymmetric unit).

Stereoscopic views of Major and Minor drawn by *ORTEP* II[13] are shown in Fig. 2. At a terminus the original Br-BOL skeleton is conserved in both the

Table 2. Fractional Coordinates (×10^4) and Equivalent Isotropic Temperature Parameters (B_{eq}, ×10), with Their Estimated Standard Deviations in Parentheses

(a) Major

Atom	x	y	z	B_{eq}/Å^2
Br	−82(1)	1383(1)	1582(1)	39(1)
C11	3621(3)	5248(9)	1986(2)	34(2)
C12	3080(4)	4232(9)	2555(2)	35(2)
C13	1966(3)	2531(9)	2387(2)	29(2)
C14	1172(3)	3819(7)	1887(2)	25(1)
C15	1939(3)	4793(7)	1376(2)	23(1)
N16	2819(2)	2887(6)	1175(1)	21(1)
C17	3868(3)	3069(8)	1537(2)	28(2)
O18	2703(3)	6735(5)	1652(1)	34(1)
O19	4798(2)	1803(8)	1504(1)	43(1)
C21	3656(3)	3135(7)	167(2)	23(1)
C22	2829(3)	1632(7)	581(1)	20(1)
N23	1594(2)	1507(6)	302(1)	22(1)
C24	1200(3)	2942(7)	−170(2)	22(1)
C25	2135(3)	4787(7)	−416(2)	26(1)
C26	2890(4)	3341(9)	−870(2)	35(2)
C27	3804(4)	1879(8)	−449(2)	31(2)
O28	3034(2)	5531(5)	44(1)	24(9)
O29	180(2)	2676(5)	−428(1)	28(1)

(b) Minor

Atom	x	y	z	B_{eq}/Å^2
Br	961(1)	6088(1)	4599(1)	36(1)
C11	2020(5)	569(9)	5184(7)	28(2)
C12	972(5)	691(11)	4424(9)	36(3)
C13	652(5)	2550(10)	4022(8)	31(3)
C14	1273(5)	3708(8)	5221(7)	24(2)
C15	2301(4)	3324(8)	5840(6)	20(2)
N16	2578(4)	3067(6)	4835(5)	21(2)
C17	2422(5)	1423(7)	4408(6)	22(2)
O18	2387(3)	1644(6)	6378(5)	26(2)
O19	2564(5)	762(6)	3588(6)	36(2)
C21	2870(5)	5839(8)	3993(7)	22(2)
C22	3231(4)	4116(7)	4677(6)	20(2)
N23	4080(4)	4349(6)	6011(6)	23(2)
C24	4448(4)	5887(8)	6577(7)	23(2)
C25	3912(5)	7406(8)	5723(7)	23(2)
C26	4163(5)	7750(10)	4639(8)	31(3)
C27	3452(6)	6613(10)	3457(7)	32(3)
O28	2946(3)	7011(5)	4992(5)	22(1)
O29	5174(4)	6024(6)	7672(5)	35(2)

[††] 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 Document No. 8766).

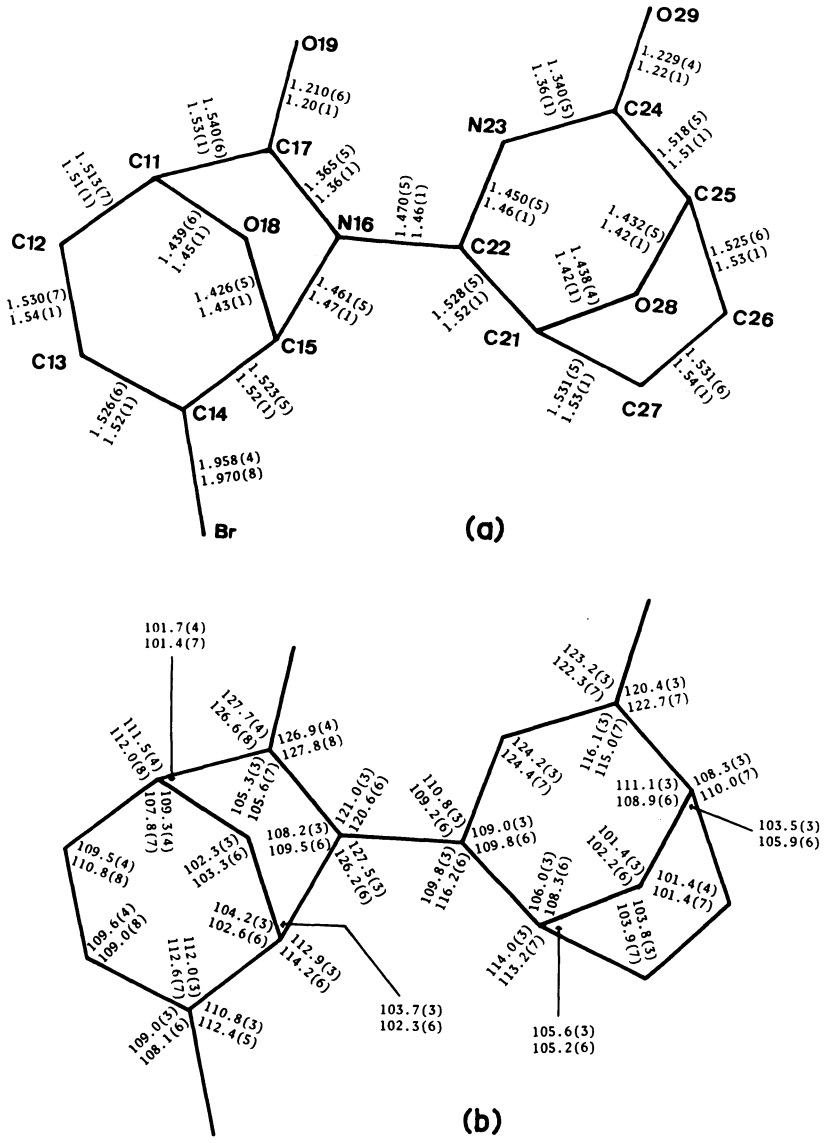


Fig. 1. (a) Bond distances(l/Å) and (b) bond angles(φ/°) for Major(upper) and Minor(lower).

components, as indicated by the spectral data.[8] A ring-opened skeleton was expected at the other terminus as similar to the structure of $(BOL)_2$.[7] The bicyclic skeleton (rearranged skeleton), however, is also kept at the other terminus in Major and Minor, though the skeletal rearrangement occurs via a transfer reaction. This may be a main reason why the structure of the oligomer could not be confirmed by the spectral data. A conformational difference around the N16–C22 bond is clearly observed between Major and Minor. For the molecules having the Br-BOL skeleton of the same configuration in Fig. 2, the torsion angles of C15–N16–C22–C21 and C15–N16–C22–N23 are 93.1(4) and −27.4(5)° for Major, and −75.5(9) and 49.4(9)° for Minor. BOL contains two asymmetric C atoms, C1 and C5, respectively. Each structure of the Br-BOL skeleton drawn in Fig. 2 is an enantiomer with C1 S and C5 R. The two components are, furthermore, essentially different in the configuration of the C25 atom contained in the rearranged skeleton, where the C25 atom corresponds to C1 in BOL. The configurations of the C11 (correspond to C1) and C25 atoms are the same in Major, and those are different in Minor. Thus it is shown that the oligomerization of Br-BOL prefers between the molecules with the same configuration of the BOL skeleton to between the molecules with the different configuration, taking the yielding ratio of the major and minor components into consideration. Therefore the configuration of the C1 and the corresponding C atoms in the trimer of Br-BOL was expected to be the same, and the expectation was confirmed by the structure analysis of the trimer.[14] A following mechanism for the oligomeric reaction is

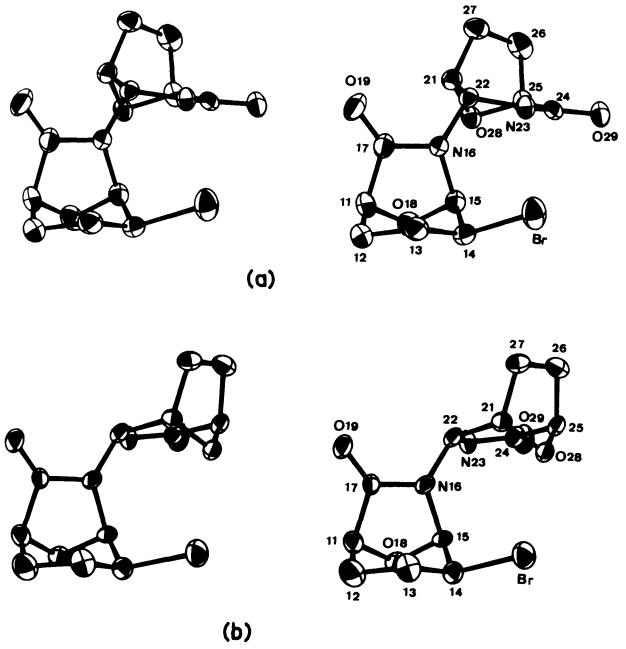


Fig. 2. Stereodrawings of (a) Major and (b) Minor. Atoms are drawn with 50% probability thermal ellipsoids. Both Br-BOL skeletons have the same configuration.

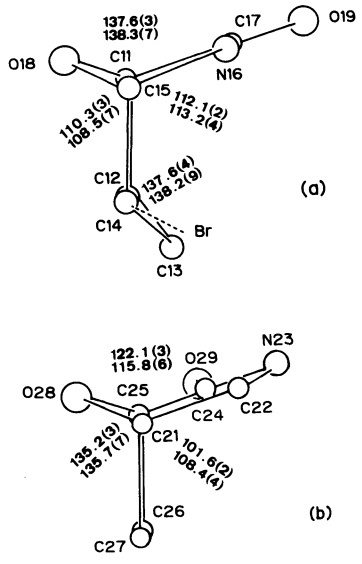


Fig. 3. Selected diheddral angles(φ/°) among the best-planes. Definitions are: (a) Br-BOL skeleton, plane I C11, C15, N16, C17, O19; plane II C11, C15 O18; plane III C11, C12, C14, C15; plane IV C12 C13, C14, (b) rearranged skeleton, plane V C22, N23, C24, C25, O29; plane VI C21, C25, O28; plane VII C21, C25, C26, C27. Major upper and Minor lower.

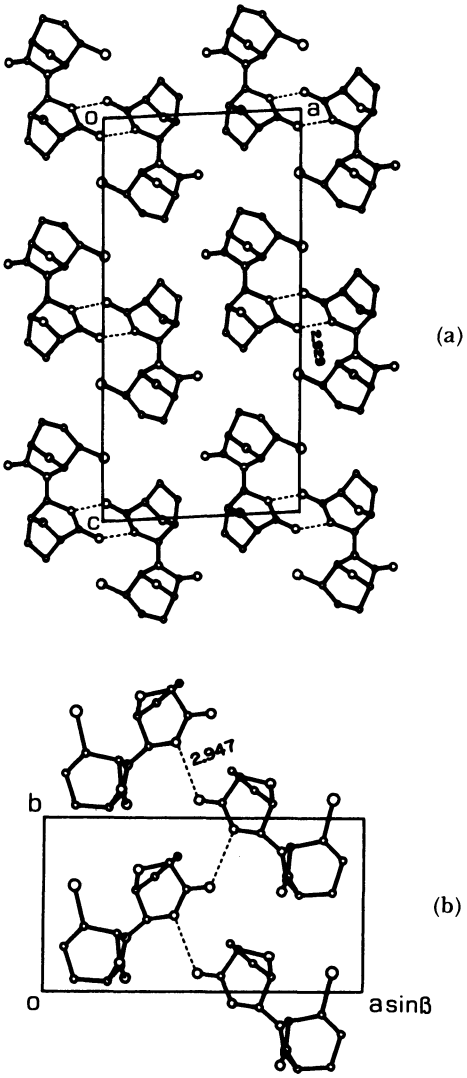


Fig. 4. Crystal Structures of (a) Major projected along the b axis, and (b) Minor projected along the c axis(Molecules on the equvalent positions (x, y, z) and ($-x$, $1/2+y$, $1/2-z$) only are drawn for clarity). Hydrogen bonds are shown with broken lines, and the distances are given in Å unit.

suggested; (i) The N6 atom of the amide group of a Br-BOL moiety at a terminus attacks at first the C5 atom of another Br-BOL molecule, (ii) the scission of the C5–O8 bond of the attacked part occurs, leading to the collapse of the bicyclic skeleton, (iii) the O8 atom approaches the C4 to which the Br bonds, and (iv) the formation of the C4–O8 bond generates the rearranged bicyclic skeleton, together with the elimination of the Br atom.

The dimer consists of seven planes: (a) BOL skeleton, plane I defined by C11, C15, N16, C17, and O19; plane II C11, C15, and O18; plane III C11, C12, C14, and C15; plane IV C12, C13, and C14, (b) rearranged skeleton, plane V C22, N23, C24, C25, and O29; plane VI C21, C25, and O28; plane VII C21, C25, C26, and C27. The C21 atom deviates by 0.38 Å in Major, and by 0.13 Å in Minor, from the plane V. The selected dihedral angles among the planes are given in Fig. 3. The dihedral angles in the BOL skeleton show good agreements with those found in the other

BOL skeleton.[7,9] The dihedral angles are, however, significantly different between the planes V and VI and between the planes V and VII, as compared with those in Major and Minor. This may reflect the configurational difference of the C25 atoms of Major and Minor.

The packing schemes of molecules in Major and Minor are shown in Figs. 4(a) and (b), respectively. The hydrogen bond of 2.929(4) Å occurs between N23 and O29$^{(i)}$ in Major, and that of 2.947(9) Å occurs between N23 and O29$^{(ii)}$ in Minor. [Symmetry code: (*i*) $(-x,-y,-z)$, (*ii*) $(1-x,-1/2+y,3/2-z)$] The H···O and ∠N-H···O are 2.29(5) Å and 160(6)° for Major, and 2.21(11) Å and 163(11)° for Minor. In Major a dimer structure is formed by hydrogen bonds related with an inversion center. On the other hand molecules are linked by hydrogen bonds around a two-fold screw axis, giving rise to infinite helical chains extended along the b axis in Minor.

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