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Crystal Structures of *N*-Benzoyl Derivatives of 8-Oxa-6-azabicyclo[3.2.1]octan-7-one, ε-Caprolactam and 2-Pyrrolidone

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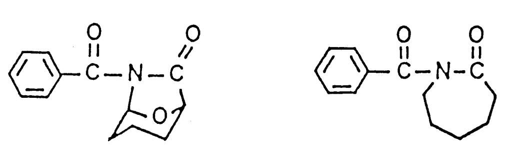
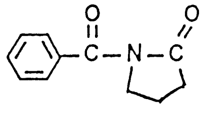
The crystal structures of *N*-benzoyl-8-oxa-6-azabicyclo[3.2.1]octan-7-one (Bz-BOL), *N*-benzoyl-ε-caprolactam (Bz-CLA), and *N*-benzoyl-2-pyrrolidone (Bz-PYR) have been determined in order to clarify the relation between their structures and reactivities by *N*-benzoyl substitution. Bz-BOL belongs to monoclinic, $P2_1/n$, $a=10.372(1)$, $b=23.155(5)$, $c=9.737(4)$ Å, $\beta=100.92(2)^\circ$, $Z=8$. Bz-CLA is monoclinic, $P2_1/c$, $a=9.234(2)$, $b=8.532(3)$, $c=15.097(3)$ Å, $\beta=92.42(2)^\circ$, $Z=4$. Bz-PYR is monoclinic, $P2_1/n$, $a=10.801(3)$, $b=6.020(1)$, $c=15.082(3)$ Å, $\beta=97.95(2)^\circ$, $Z=4$. The final R-values are 0.049 for 2867 reflections of Bz-BOL, 0.069 for 1634 reflections of Bz-CLA, and 0.053 for 1175 reflections of Bz-PYR. In these compounds the orientaion of the benzoyl moiety against the lactam moiety is essentially the same, and the phenyl group is nearly perpendicular to the lactam–amide plane. The C–N bond distance of the lactam moieties in benzoyl derivatives is significantly prolonged, as compared with that in the original lactams, though the C–N distance is apparently equal to that of acyl moieties in these benzoyl derivatives. This suggests that the C–N bond of the lactam moieties in the benzoyl derivatives is weakened by acylation and is easily broken by a nucleophilic attack, as compared with that of the original lactams.

A bicyclo compound, 8-oxa-6-azabicyclo[3.2.1]octan-7-one (abbreviated as BOL), is an interesting starting material to prepare new functional polyamides with high water permeability and permselectivity for solutes of different size.[1–4] The ring-opening polymerization reaction of lactams is accelerated by adding their *N*-acyl derivative as an initiator.[5,6] The acceleration of the ring-opening reactivity of BOL is also observed by an acylation of the N^6 atom in the BOL skeleton.[7] This shows that the acylation of BOL induces an increment of the ring-opening reactivity, as compared with that of BOL. This may be attributed to the difference of the steric strain stored in the amide moiety in both BOL skeletons. In order to study the relation between the structure and reactivity of *N*-acyl-BOL, therefore, the crystal structure of the *N*-benzoyl derivative of BOL, *N*-benzoyl-8-oxa-6-azabicyclo[3.2.1]octan-7-one (abbreviated as Bz-BOL), has been determined and compared with that of the BOL previously reported.[8] Considering the effect of the fused skeleton of BOL in which both the seven-membered lactam and five-membered oxazolidinone are included, the crystal structures of *N*-benzoyl-ε-caprolactam (abbreviated as Bz-CLA) and *N*-benzoyl-2-pyrrolidone (abbreviated as Bz-PYR) have also been studied.



Bz-BOL Bz-CLA



Bz-PYR

Scheme 1.

Experimental

The crystals of Bz-BOL recrystallized from a hexane solution were colorless pillars. Both crystals of Bz-CLA and Bz-PYR obtained from a hexane solution were colorless plates. The X-ray intensity data were collected on a Rigaku four-circle diffractometer, using graphite monochromated Cu $K\alpha$ radiation($\lambda=1.5418$ Å). Unit-cell dimensions were obtained by the least-squares fits using 16 reflections with $41^\circ < 2\theta < 51^\circ$ for Bz-BOL, 15 reflections with $36^\circ < 2\theta < 61^\circ$ for Bz-CLA, and 13 reflections with $38^\circ < 2\theta < 53^\circ$ for Bz-PYR. Although the intensity data were corrected for Lorentz and polarization effects, no absorption correction was applied. Crystal data and experimental conditions are given in Table 1.

All of the structures were solved by the direct method (MULTAN 78).[9] A refinement was carried out by a full-matrix least-squares metod (FMLS).[10] The function minimized was $\Sigma w\,(|F_o|-|F_c|)^2$. The weighting scheme adopted in the function was $w=(\sigma^2(F_o)+a|F_o|^2)^{-1}$ for the observed reflections ($|F_o|\geq 3\sigma(F_o)$), where $\sigma(F_o)$ is the standard deviation based on counting statistics. The hydrogen atoms were picked up on difference Fourier maps, and were included in the refinement with the isotropic temperature factors fixed to the equivalent temperature factors (B_{eq})[11] of the atoms to which they are bound. The final R values were 0.049 ($R_w=0.051$ where $a=0.0$) for Bz-BOL, 0.069 ($R_w=0.082$ where $a=0.011$) for Bz-CLA, and 0.053 ($R_w=0.058$ where $a=0.0$) for Bz-PYR, respectively. All of 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.[13] All of the calculations were carried

Table 1. Crystal Data and Experimental Conditions

	Bz-BOL	Bz-CLA	Bz-PYR
Formula	$C_{13}H_{13}NO_3$	$C_{13}H_{15}NO_2$	$C_{11}H_{11}NO_2$
MW	231.25	217.27	189.22
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a/Å	10.372(1)	9.234(2)	10.801(3)
b/Å	23.155(5)	8.532(3)	6.020(1)
c/Å	9.737(4)	15.097(3)	15.082(3)
β/°	100.92(2)	92.42(2)	97.95(2)
V/Å^3	2296(1)	1188.3(6)	971.3(3)
D_x/g cm^{-3}	1.338	1.214	1.294
Z	8	4	4
μ(Cu $K\alpha$)/cm^{-1}	8.03	6.74	7.43
Crystal size/mm	0.3×0.3×0.25	0.4×0.4×0.4	0.4×0.3×0.2
$2\theta_{max}$/°	120	120	120
Scan method	ω	ω–2θ	ω–2θ
Scan range(ω)/°	2.4	1.4+0.14tanθ	1.4+0.14tanθ
Scan speed(ω)/°min^{-1} a)	6—1.5	8—3	8—3
Background/s a)	6—24	2—5.33	2—5.33
No. of reflections			
measured	3513	1767	1439
observed ($\lvert F_o\rvert \geqslant 3\sigma(F_o)$)	2867	1634	1175

a) The scan speed and the background counting time at both ends of a scan were stepwisely changed, according to the 2θ angle of a reflection.

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

(a) Bz-BOL

Atom	x	y	z	B_{eq}/Å^2
C^1**A**	2065(2)	214(1)	6481(2)	50(1)
C^2**A**	3277(3)	475(1)	6037(3)	60(2)
C^3**A**	3518(3)	1085(1)	6642(3)	63(2)
C^4**A**	3341(2)	1116(1)	8167(3)	54(1)
C^5**A**	2122(2)	785(1)	8355(2)	44(1)
N^6**A**	946(1)	956(1)	7316(1)	38(1)
C^7**A**	928(2)	629(1)	6105(2)	40(1)
O^8**A**	2267(1)	196(1)	7987(1)	51(1)
O^9**A**	223(1)	688(1)	4977(1)	46(1)
C^{10}**A**	285(2)	1466(1)	7505(2)	41(1)
C^{11}**A**	−1038(2)	1566(1)	6648(2)	41(1)
C^{12}**A**	−1417(3)	2136(1)	6346(2)	52(1)
C^{13}**A**	−2671(3)	2258(1)	5624(3)	61(1)
C^{14}**A**	−3540(3)	1813(1)	5218(3)	63(2)
C^{15}**A**	−3180(2)	1249(1)	5514(3)	56(1)
C^{16}**A**	−1923(2)	1122(1)	6233(2)	46(1)
O^{17}**A**	796(1)	1806(1)	8391(2)	57(1)
C^1**B**	2447(2)	3836(1)	5653(2)	49(1)
C^2**B**	2069(3)	3292(1)	4806(3)	64(2)
C^3**B**	2985(3)	2796(1)	5389(3)	64(2)
C^4**B**	3207(3)	2778(1)	6999(3)	56(1)
C^5**B**	3428(2)	3381(1)	7602(2)	43(1)
N^6**B**	4478(1)	3690(1)	7055(1)	36(1)
C^7**B**	3911(2)	3948(1)	5787(2)	40(1)
O^8**B**	2320(1)	3733(1)	7082(1)	51(1)
O^9**B**	4449(1)	4179(1)	4934(1)	47(1)
C^{10}**B**	5777(2)	3584(1)	7657(2)	40(1)
C^{11}**B**	6836(2)	3956(1)	7316(2)	38(1)
C^{12}**B**	6680(2)	4544(1)	7020(2)	42(1)
C^{13}**B**	7746(3)	4864(1)	6787(2)	53(1)
C^{14}**B**	8952(3)	4603(1)	6818(3)	60(1)
C^{15}**B**	9115(2)	4023(1)	7138(3)	60(1)
C^{16}**B**	8058(2)	3700(1)	7394(2)	50(1)
O^{17}**B**	6015(1)	3189(1)	8497(2)	59(1)

(b) Bz-CLA

Atom	x	y	z	B_{eq}/Å^2
C^1	11859(3)	3118(4)	3207(2)	64(1)
C^2	12677(3)	3603(4)	4072(2)	77(2)
C^3	12347(4)	2620(4)	4872(2)	78(2)
C^4	10769(4)	2554(3)	5089(2)	70(2)
C^5	9793(3)	1860(3)	4357(1)	58(1)
N^6	9334(2)	2994(2)	3658(1)	45(1)
C^7	10348(2)	3757(2)	3152(1)	50(1)
O^9	10013(2)	4907(2)	2720(1)	68(1)
C^{10}	7871(2)	3450(2)	3638(1)	46(1)
C^{11}	7136(2)	3889(2)	2780(1)	39(1)
C^{12}	7420(2)	3113(2)	2004(1)	47(1)
C^{13}	6536(3)	3397(3)	1253(1)	61(1)
C^{14}	5420(3)	4454(4)	1280(1)	65(1)
C^{15}	5156(3)	5239(3)	2047(2)	63(1)
C^{16}	5999(2)	4944(3)	2797(1)	52(1)
O^{17}	7170(2)	3360(3)	4296(1)	75(1)

(c) Bz-PYR

Atom	x	y	z	B_{eq}/Å^2
C^1	8620(3)	7810(5)	4747(2)	56(1)
C^5	7394(2)	4738(6)	4097(2)	54(1)
N^6	8588(1)	4858(3)	3732(1)	42(1)
C^7	9358(2)	6555(4)	4135(1)	44(1)
C^8	7338(3)	6889(9)	4590(3)	82(2)
O^9	10434(1)	6870(3)	4032(1)	56(1)
C^{10}	8893(2)	3175(4)	3172(1)	42(1)
C^{11}	9892(2)	3538(4)	2597(1)	40(1)
C^{12}	9917(2)	5479(5)	2107(1)	52(1)
C^{13}	10730(3)	5647(6)	1475(2)	63(2)
C^{14}	11546(3)	3947(6)	1363(2)	61(2)
C^{15}	11545(3)	2046(5)	1868(2)	59(2)
C^{16}	10698(2)	1813(4)	2477(2)	50(1)
O^{17}	8292(1)	1458(3)	3117(1)	59(1)

out on a FACOM M680 at the Nagoya University Computation Center.

Results and Discussion

The bond distances and angles of Bz-BOL, together with the numbering of atoms, are given in Fig. 1. For Bz-BOL crystals two independent molecules, **A** and **B**, are included in an asymmetric unit. The overall structure of the two molecules is almost the same. The corresponding bond distances and angles between molecules **A** and **B** are in good agreement with each other. The bond distances and angles of the BOL skeleton found in Bz-BOL are very similar to those of both BOL and 4(*e*)-bromo-BOL (abbreviated as Br-BOL),[8] except for the N^6–C^7 distance. The bond distances and angles of the lactam moieties in Bz-CLA and Bz-PYR show good agreements to those of ε-caprolactam (abbreviated as CLA)[14] and 2-pyrrolidone (abbreviated as PYR),[15] respectively, except for the C^1–X^8 and C^5–X^8 distances (X=O for Bz-BOL, and X=C for Bz-PYR) which reflect an exchange of the X^8 atom between Bz-BOL and Bz-PYR. The elongation of the N^6–C^7 distance and narrowing of the C^5–N^6–C^7 angle in Bz-BOL are observed, compared with those in BOL's; the same tendency is found between those in Bz-CLA and CLA. The bond angles concerning the seven-membered ring of Bz-BOL are significantly smaller than those of Bz-CLA. The C^5–N^6–C^7 and C^1–C^7–N^6 angles, 108.0(1) and 104.8(2)° for molecule **A** and 108.1(2) and 104.3(2)° for molecule **B**, are especially smaller than those of Bz-CLA, 121.1(2) and 116.5(3)° respectively, by about 13°. On the contrary, the C^7–N^6–C^{10} and N^6–C^7–O^9 angles, 129.9(3) and 128.0(2)° for molecule **A** and 131.5(2) and 128.6(2)° for molecule **B** respectively, come to be wide by about 8°, compared with those of Bz-CLA, 121.7(2) and 120.7(2)°, respectively. A comparison of the angles concerning the five-membered ring of Bz-PYR with those of Bz-BOL does not give such marked differences. Though slight enlargements of the C^5–N^6–C^7 and C^1–C^7–N^6 angles of Bz-PYR, by about 3°, are observed, compared with those of Bz-BOL, this may show that the strain due to the formation of a fused ring in the BOL skeleton is localized mainly in the seven-membered ring.

The conformations of molecules **A** and **B** of Bz-BOL are almost the same as each other. A stereoscopic view of molecule **B** drawn by ORTEP II[16] is shown in Fig. 2.

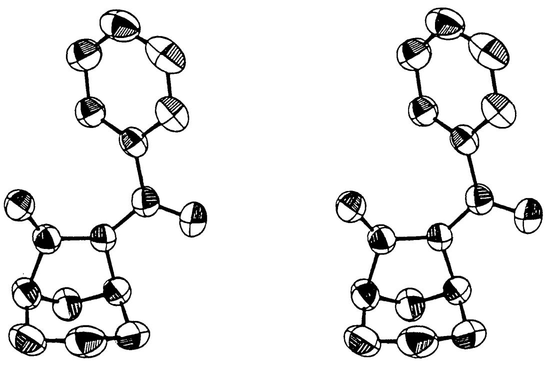


Fig. 2. Stereoview of the molecule **B** of Bz-BOL.

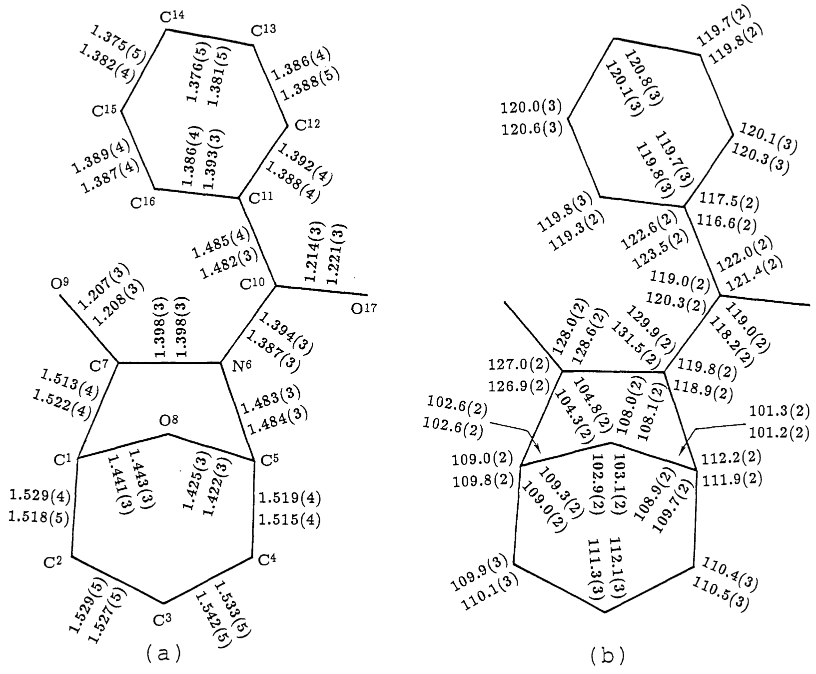
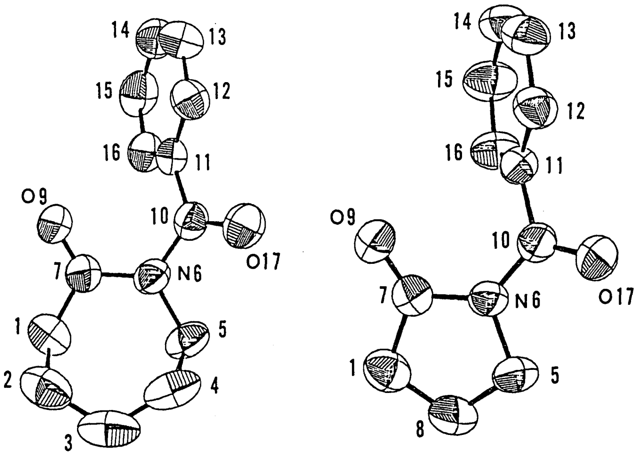


Fig. 1. (a) Bond distances (*l*/Å) and (b) bond angles (*ϕ*/°) for molecules **A** (upper) and **B** (lower) of Bz-BOL. Estimated standard deviations are in parentheses.

ORTEP drawings of Bz-CLA and Bz-PYR are given in Fig. 3, together with the numbering of the atoms. The orientation of the benzoyl moiety to the lactam in Bz-BOL is essentially similar to that of Bz-CLA as well as that of Bz-PYR, in spite of the presence of a fused or single-ring skeleton and differences in the packing schemes. This conformation of the benzoyl moiety therefore seems to be a most stable one among the structures of *N*-benzoyl lactams.

The atoms contained in the resonance-system form three planes in the *N*-benzoyl derivatives; lactam–amide plane I (C^1, C^7, N^6, O^9), acyl–amide plane II (C^{11}, C^{10}, N^6, O^{17}), phenyl plane III for Bz-BOL (C^{10}, C^{11}, C^{12}, C^{13}, C^{14}, C^{15}, C^{16}) and III′ for Bz-CLA and Bz-PYR (C^{11}, C^{12}, C^{13}, C^{14}, C^{15}, C^{16}). The selected dihedral angles and torsion angles are given in Tables 3 and 4. The C^{10} atoms of Bz-CLA and Bz-PYR deviate significantly from plane III′, i.e. by 0.216(7) Å for Bz-CLA and 0.190(9) Å for Bz-PYR, respectively. On the other hand the C^{10} atom in Bz-BOL is coplanar on the aromatic group, and was therefore contained in the calculation of the best plane. Planes I and II, thus the lactam carbonyl group and acyl carbonyl group, are not coplanar in all of the derivatives. Furthermore, planes II and III (or III′) are not coplanar. This is shown by the deviations of the torsion angles around the N^6–C^{10} and C^{10}–C^{11} bonds from the trans conformation. Both torsion angles of C^7–N^6–C^{10}–O^{17} and N^6–C^{10}–C^{11}–C^{12} are about −150° in the derivatives, though the torsion angle of the C^1 and C^{10} atoms are roughly trans around the C^7–N^6 bond. The deviations of the C^{10} atom from plane I are 0.233(7) and 0.165(8) Å for molecules **A** and **B** in Bz-BOL, 0.06(1) Å for Bz-CLA, and 0.10(1) Å for Bz-PYR. The planarity around the N^6 atom is not good in all of the benzoyl derivatives. The dihedral angles between planes I and III (or III′) are 123.4(1) and 128.8(1)° for Bz-BOL, 111.3(1)° for Bz-CLA, and 114.5(1)° for Bz-PYR. The phenyl group is therefore nearly perpendicular to the lactam-amide plane in Bz-CLA and Bz-PYR, and both are roughly perpendicular to each other in Bz-BOL.



(a) (b)

Fig. 3. ORTEP drawings of (a) Bz-CLA, and (b) Bz-PYR.

The bond distances of the amide group in the benzoyl derivatives are summarized in Table 5, together with those of the original lactams and $(BOL)_2$,[17] that is, the

Table 3. Selected Dihedral Angles (ϕ)

	I/II[a] (ϕ/°)	II/III (or III′) (ϕ/°)	I/III (or III′) (ϕ/°)	Deviation of C^{10} from Plane III′ (l/Å)
Bz-BOL(**A**)	152.8(1)	147.6(1)	123.4(1)	
(**B**)	157.4(1)	149.2(1)	128.8(1)	
Bz-CLA	143.4(3)	141.7(2)	111.3(1)	0.216(7)
Bz-PYR	155.3(1)	134.4(1)	114.5(1)	0.190(9)

a) The definition of best planes are;
plane I: C^1, N^6, C^7, O^9,
plane II: N^6, C^{10}, C^{11}, O^{17},
plane III: C^{10}, C^{11}, C^{12}, C^{13}, C^{14}, C^{15}, C^{16}, for Bz-BOL,
plane III′: C^{11}, C^{12}, C^{13}, C^{14}, C^{15}, C^{16}, for Bz-CLA and Bz-PYR.

Table 4. Selected Torsion Angles (ϕ)

	Bz-BOL		Bz-CLA (ϕ/°)	Bz-PYR (ϕ/°)
	Mol. **A** (ϕ/°)	Mol. **B** (ϕ/°)		
C^1–C^7–N^6–C^{10}	167.1(2)	170.6(2)	−177.7(2)	174.6(2)
C^7–N^6–C^{10}–O^{17}	−148.9(2)	−154.8(2)	−145.9(2)	−155.6(3)
C^7–N^6–C^{10}–C^{11}	33.1(4)	27.3(4)	40.6(3)	28.5(4)
N^6–C^{10}–C^{11}–C^{12}	−150.7(2)	−151.4(2)	−152.0(2)	−141.4(3)
N^6–C^{10}–C^{11}–C^{16}	33.9(4)	32.9(4)	37.4(3)	46.3(4)

Table 5. Selected Bond Distances (l) in Lactam and Acyl Moieties

	Bz-BOL (l/Å)	BOL a) (l/Å)	$(BOL)_2$ b) (l/Å)	Bz-CLA (l/Å)	CLA c) (l/Å)	Bz-PYR (l/Å)	PYR d) (l/Å)
C^7-O^9	1.207(3) 1.208(3)	1.227(4) 1.221(6)	1.210(4) 1.215(4)	1.212(3)	1.242(3)	1.209(3)	1.26(1)
C^7-N^6	1.389(3) 1.389(3)	1.329(4) 1.341(6)	1.341(4) 1.330(4)	1.394(3)	1.327(3)	1.402(3)	1.39(1)
C^{10}-O^{17}	1.214(3) 1.221(3)			1.212(4)		1.217(3)	
C^{10}-N^6	1.394(3) 1.387(3)			1.405(3)		1.388(3)	

a) Two crystals of BOL and Br-BOL. See Ref. 8. b) Two molecules in an asymmetric unit. See Ref. 17. c) Quoted from Ref. 14. d) Quoted from Ref. 15.

non-acyl derivative of BOL. Among the benzoyl derivatives, the bond distances of C^7–N^6 and C^7=O^9 in the lactam-amide moieties are almost equal to those of C^{10}–N^6 and C^{10}=O^{17} in the acyl moieties. On the contrary, the C^7–N^6 distances in the lactam-amide moiety of Bz-BOL, both 1.389(3), 1.389(3) Å, and Bz-CLA, 1.394(3) Å, are significantly prolonged compared with the corresponding distances in BOL, 1.329(4) and 1.341(6) Å, and CLA, 1.327(3) Å, by about 0.05 Å. On the other hand the C^7=O^9 distances come to be a little bit shorter due to acylation, 1.207(3) and 1.208(3)Å for Bz-BOL, and 1.212(3) Å for Bz-CLA; 1.227(4) and 1,221(6) Å for BOL, and 1.242(3) Å for CLA. The same tendency is observed in Bz-PYR and PYR, though the C^7–N^6 dstance, 1.402(3) Å of Bz-PYR is slightly longer than 1.39(1) Å of PYR. It must be, however, noted that hydrogen bonds are formed between the amide and carbonyl groups in both crystal structures of CLA and PYR. It is interesting that the C^7–N^6 distances of $(BOL)_2$, which is substituted by a tetrahydropyranyl moiety, are essentially equal to those of BOL. The rather long C^7–N^6 bond distances, 1.365(5) and 1.36(1) Å, are observed in the BOL skeleton of the major and minor components of Br-BOL dimers, in which the N^6 atom is substituted by a bulky fused-ring skeleton.18) The C^7–N^6 bond in Br-BOL dimers seems to be prolonged, thus decreasing the steric repulsion between the lactam carbonyl group and the bulky substituted moiety. Therefore, the elongation of the C–N bond in the lactam-amide moiety seems to be characteristic of the acylation of lactams. This suggests that the resonance of the lactam-amide moiety decreases due to acylation of the lactams and that the double-bond character of the carbonyl group increases reversely. As a result of the acylation of lactams, the C–N bond is weakened and easily broken by a nucleophilic attack, though the C–N distance in the lactam-amide moiety is apparently equal to that in the acyl moiety. This may be one of the

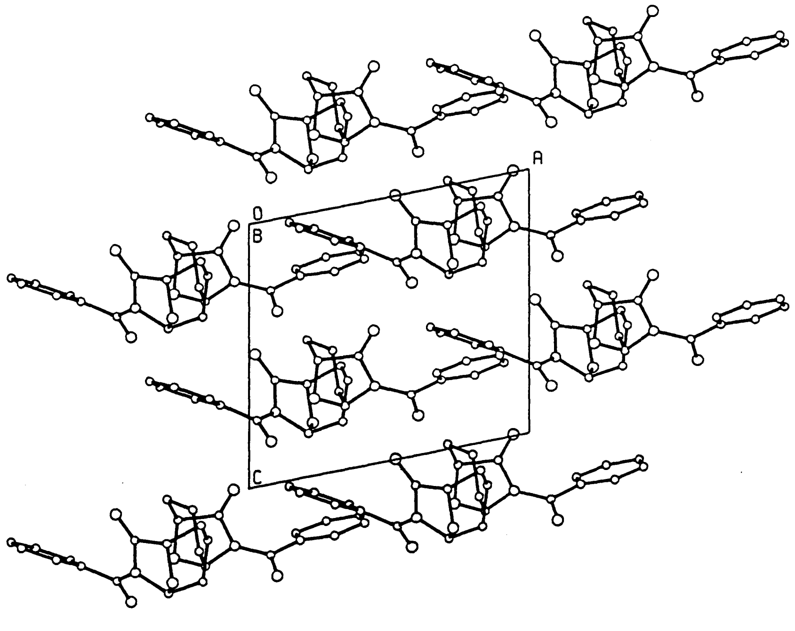


Fig. 4. Crystal structure of Bz-BOL, projected along the b-axis. Molecules on the equivalent positions (x,y,z) and ($1/2+x$, $1/2-y$, $1/2+z$) only are drawn for clarity.

reasons why *N*-acyl lactams work in the anionic polymerization of lactams as an initiator.

The packing scheme of Bz-BOL is shown in Fig. 4. Short intermolecular contacts are observed between the O^9 in the lactam carbonyl group and the acyl carbonyl moiety. The distances from O^9 of molecule **A** to N^6, C^{10}, and O^{17} of molecule **B** at $(-1/2+x,\ 1/2-y,\ -1/2+z)$ are 3.155(3), 2.960(3), and 3.262(4) Å, respectively, while the distances of O^9**B**···N^6**A**, O^9**B**···C^{10}**A**, and O^9**B**···O^{17}**A** [**A** at $(1/2+x,\ 1/2-y,\ -1/2+z)$] are 3.242(3), 3.057(3), and 3.195(3) Å, respectively. These short contacts may restrict the conformation of the acyl moiety in Bz-BOL. It is interesting that the conformation of the acyl moiety to the lactam amide moiety is essentially the same among Bz-BOL, Bz-CLA, and Bz-PYR, though these short contacts are not observed in the crystal structrues of Bz-CLA and Bz-PYR.

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