Crystal Structure of *N*-Cinnamoyl-8-oxa-6-azabicyclo[3.2.1]octan-7-one

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Synopsis. The crystal structure of the title compound has been determined in order to study the structure-reactivity relationship of a bicyclo compound. $C_{15}H_{15}NO_3$, M 257.29, monoclinic, space group $P2_1/a$, a=24.122(6), b=6.990(2), c=7.800(2) Å, β=94.27(2)°, V=1311.5(6) Å^3, Z=4, D_x=1.304 g cm^{-3}, μ=7.56 cm^{-1} for Cu $K\alpha$. The final R-value is 0.062 for 1948 reflections. The molecular structure is essentially the same as that of the *N*-benzoyl derivative of the bicyclo compound. An elongation of the C–N bond distance in the lactam-amide moiety, which had been found in the *N*-benzoyl derivative, was observed and compared with that in the unmodified bicyclo compound. There seems to be little extension of the conjugation of the olefinic group to the carbonyl or phenyl groups in a cinnamoyl moiety, according to the C=C and C^{sp2}–C^{sp2} distances.

A bicyclo compound, 8-oxa-6-azabicyclo[3.2.1]octan-7-one (abbreviated as BOL), is a starting material used to prepare functional polyamides with a tetrahydropyran ring, which is a basic skeleton of cellulose.[1–4] BOL reacted with both anionic and cationic reagents through the scission of different bonds in the ring.[5,6] Another ring-opening characteristic was made clear by a crystal-structure analysis of the dimer of 4(*e*)-bromo-BOL.[7] The aminolysis of *N*-acyllactams with butylamine was investigated in order to understand the high acceleration effect of *N*-acyllactams upon the base-catalyzed ring-opening polymerization of lactams.[8] Crystal structure analyses of *N*-benzoyl-BOL and two *N*-benzoyllactams provided a plausible explanation for the increment of the ring-opening reactivity of lactams by *N*-acylation.[9] In order to study the substitution effect of BOL, the *N*-cinnamoyl derivative of BOL (abbreviated as Cin-BOL) was synthesized and a crystal-structure analysis was carried out.

Experimental

Crystals of Cin-BOL grown from a hexane solution were colorless pillars. The X-ray intensity data with $2\theta<125°$ were collected on a Rigaku four-circle diffractometer using graphite monochromated Cu $K\alpha$ radiation (λ=1.5418 Å). A crystal with dimensions of 0.5×0.4×0.3 mm was mounted, and a total of 2065 reflections were measured by the ω–2θ scan technique; the scan width was $\Delta\omega=(1.4+0.14\tan\theta)°$. The scan rate and the background counting time at both ends of the scan were stepwisely changed from 8 to 2° min^{-1}, and from 2.5 to 10 s, respectively, according to the 2θ angles of the reflections. Although intensity data were corrected for Lorentz and polarization effects, the absorption effect was not corrected [μ(for Cu $K\alpha$)=7.56 cm^{-1}].

The structure was solved by a direct method (MULTAN 78).[10] The refinement was carried out by a full-matrix least-squares method (FMLS)[11] using 1948 observed ($|F_o|>3\sigma(F_o)$) reflections; $\sigma(F_o)$ is the standard deviation obtained from the counting statistics. The minimized function was $\Sigma w(|F_o|-|F_c|)^2$, and the weighting scheme was $w=1/\sigma^2(F_o)$.

Table 1. Fractional Coordinates (×10^4) and Equivalent Isotropic Temperature Factors (B_{eq}, ×100), with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}
C1	545(1)	6879(3)	9863(2)	355(8)
C2	886(1)	8666(3)	10272(2)	414(9)
C3	1018(1)	9659(3)	8592(3)	432(10)
C4	509(1)	9705(3)	7290(3)	411(9)
C5	212(1)	7807(3)	7254(2)	352(8)
N6	602(1)	6207(2)	6992(2)	326(6)
C7	836(1)	5646(2)	8603(2)	311(7)
O8	35(1)	7379(2)	8907(1)	393(6)
O9	1207(1)	4534(2)	8923(1)	427(6)
C10	736(1)	5705(3)	5337(2)	356(8)
C11	1112(1)	4072(3)	5174(2)	357(8)
C12	1321(1)	3693(3)	3686(2)	393(9)
C13	1700(1)	2124(3)	3342(2)	366(8)
C14	2013(1)	2234(4)	1915(3)	506(11)
C15	2389(1)	809(5)	1588(3)	621(14)
C16	2454(1)	−731(4)	2642(3)	568(13)
C17	2138(1)	−912(4)	4040(3)	513(11)
C18	1772(1)	535(3)	4401(3)	425(9)
O19	525(1)	6605(2)	4129(2)	538(8)

The hydrogen atoms were picked up on a difference Fourier map, and included in a refinement with the isotropic temperature factors fixed to the equivalent temperature factors (B_{eq})[12] of the non-hydrogen atoms to which they attached. The final R-value was 0.062; R_w was 0.077. The atomic scattering factors used were taken from International Tables for X-Ray Crystallography.[13] All of the calculations were carried out on a FACOM M680 at the Nagoya University Computation Center. The atomic parameters of the non-hydrogen atoms with B_{eq}'s are given in Table 1.[14]

Results and Discussion

Selected bond distances and angles are given in Table 2. The corresponding bond distances and angles

Table 2. Selected Bond Distances (l) and Angles (φ)

Distance	l/Å		l/Å
C^1–C^7	1.517(3)	C^1–O^8	1.434(3)
C^5–N^6	1.484(3)	C^5–O^8	1.420(3)
N^6–C^7	1.395(3)	N^6–C^{10}	1.398(3)
C^7–O^9	1.199(3)	C^{10}–O^{19}	1.212(3)
Angle	**φ/°**		**φ/°**
C^7–C^1–O^8	102.8(2)	N^6–C^5–O^8	101.7(2)
C^5–N^6–C^7	107.8(2)	C^5–N^6–C^{10}	120.6(2)
C^1–C^7–N^6	104.4(2)	C^1–C^7–O^9	127.4(2)
C^7–N^6–C^{10}	130.9(2)	N^6–C^7–O^9	128.0(2)
N^6–C^{10}–C^{11}	117.5(2)	N^6–C^{10}–O^{19}	118.3(2)
C^{11}–C^{10}–O^{19}	124.2(2)	C^{10}–C^{11}–C^{12}	120.6(2)
C^{11}–C^{12}–C^{13}	126.4(2)		

between Cin-BOL and the *N*-benzoyl derivative of BOL[9] (abbreviated Bz-BOL), in which two molecules are contained in an asymmetric unit, are in good agreement with each other. The N^6–C^7 bond distance (1.395(3) Å) is the same as that of Bz-BOL (1.398(3) and 1.398(3) Å) and is longer by about 0.05 Å than that of BOL and 4(*e*)-bromo-BOL (abbreviated Br-BOL)[15] (1.329(4) and 1.342(6) Å, respectively). However, the C^7=O^9 bond distance, Cin-BOL (1.199(3) Å) and Bz-BOL (1.207(3) and 1.208(3) Å) reversely comes to be a little bit shorter than that of BOL and Br-BOL (1.227(4) and 1.221(6) Å) by acylations. The N^6–C^7 bond distance found in the BOL dimer (two molecules in an asymmetric unit),[6] of which the N^6 atom was substituted by a tetrahydropyranyl moiety (1.341(5) and 1.330(5) Å) are very close to the values found in the original BOL skeleton. This shows that an elongation of the N^6–C^7 bond distance and an increment of the double-bond character of the C^7=O^9 bond in the lactam-amide moiety are induced by acylation: That is, an attachment of the cinnamoyl or benzoyl moieties to the N^6 atom. The C^7–N^6–C^{10} angle is wider than the C^5–N^6–C^{10} angle by about 10°. The same tendency is observed in Bz-BOL; the C^7–N^6–C^{10} angle (129.9(2) and 131.5(2)°) and the C^5–N^6–C^{10} angle (119.8(2) and 118.9(2)°). This may reduce the steric repulsion between the lactam-carbonyl group and the C^{11} atom (Cin-BOL) or phenyl moiety (Bz-BOL).

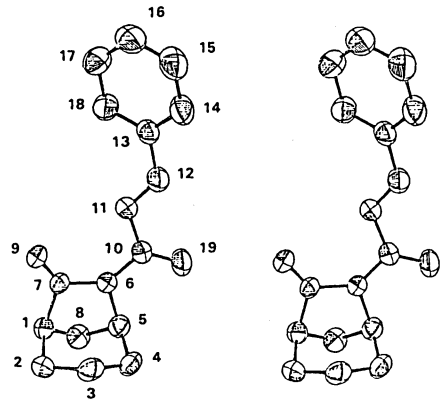

Fig. 1. Stereoscopic view drawn by ORTEP II,[16] with thermal ellipsoids at the 50% probability level. The atom numbering is indicated by numerals.

Table 3. Selected Torsion Angles (φ)

	Cin-BOL	Bz-BOL[a) 9)]	
	φ/°	Mol. **A** φ/°	Mol. **B** φ/°
C^5–N^6–C^7–C^1	3.6(2)	4.9(3)	5.6(3)
C^{10}–N^6–C^7–C^1	173.5(2)	167.1(2)	170.6(2)
C^5–N^6–C^{10}–C^{11}	−178.2(2)	−166.5(2)	−169.1(2)
C^7–N^6–C^{10}–C^{11}	12.9(3)	33.1(4)	27.3(4)
N^6–C^{10}–C^{11}–C^{12}	−170.0(2)	−150.7(2)	−151.4(2)
C^{10}–C^{11}–C^{12}–C^{13}	179.8(2)	−176.1(2)	−177.9(2)
C^{11}–C^{12}–C^{13}–C^{14}	−160.7(3)		

a) The C^{11}, C^{12}, and C^{13} atoms are contained in a phenyl ring in Bz-BOL.

A stereoscopic view drawn by ORTEP II[16] is shown in Fig. 1. The molecular structure of the acyl-BOL moiety in Cin-BOL is very similar to that in Bz-BOL. Corresponding torsion angles between Cin-BOL and Bz-BOL are compared in Table 3. The atoms contained in the conjugation-system form four planes: a lactam-amide plane I (C^1,C^7,N^6,O^9); an acyl-amide plane II (N^6,C^{10},C^{11},O^{19}); an olefinic plane III (C^{10},C^{11}, C^{12},C^{13}); a phenyl plane IV (C^{12},C^{13},C^{14},C^{15},C^{16},C^{17},C^{18}). On the other hand, there are three planes (I, II, and IV, structurally corresponding to the plane III of Cin-BOL) in Bz-BOL. Planes I, II, and III are roughly coplanar in Cin-BOL, since the torsion angles of C^7–N^6–C^{10}–C^{11} and N^6–C^{10}–C^{11}–C^{12} correspond to the *cis* and *trans* conformations, respectively. The coplanarity among the corresponding planes in Bz-BOL is, however, rather incorrect. As a whole, the coplanarity from the lactam-amide moiety to the cinnamoyl moiety of Cin-BOL is better than that from the lactam-amide moiety to the benzoyl moiety of Bz-BOL. This may reflect differences in the steric repulsion between the O^9 atom and the olefinic group in Cin-BOL, and between the O^9 and phenyl moiety in Bz-BOL. The torsion angle of C^{11}–C^{12}–C^{13}–C^{14}, which deviates by about 20° from 180°, shows a rather twisted geometry between planes of III and IV in Cin-BOL.

Table 4. Selected Bond Distances (*l*) in the Cinnamoyl Moieties

Compound	C^{10}–C^{11}	C^{11}–C^{12}	C^{12}–C^{13}	Reference
	(*l*/Å)	(*l*/Å)	(*l*/Å)	
Cin-BOL	1.469(3)	1.327(3)	1.465(3)	This work
N-Thiocinnamoylmorpholine	1.472(4)	1.305(4)	1.463(5)	17
6-Amino-5-cinnamoyl-1,3-dimethyluracil	1.479(8)	1.323(9)	1.456(8)	18
	1.490(8)	1.321(9)	1.472(8)	
1,4-Dicinnamoylbenzene	1.485(4)	1.313(4)	1.469(4)	19
	1.473(4)	1.319(4)	1.457(4)	
t-Cinnamoyl peroxide	1.48(3)	1.32(3)	1.50(3)	20
α-Fluoro-*t*-cinnamoyl peroxide	1.45(1)	1.32(1)	1.46(1)	21
1-(4-Dimethylamino-cinnamoyl)imidazole	1.443(3)	1.341(3)	1.440(3)	22
Average[a)]	1.471	1.321	1.464	

a) Non-weighting average using bond distances except for the value in Cin-BOL.

The C^{10}–C^{11}, C^{11}=C^{12}, and C^{12}–C^{13} bond distances in the cinnamoyl moieties are compared in Table 4. Those distances in Cin-BOL are close to their average values. Therefore, C^{11}=C^{12} is a typical double bond in a cinnamoyl moiety, while C^{11}–C^{10} and C^{12}–C^{13} is close to a C^{sp2}–C^{sp2} single-bond distance. This shows that there seems to be a slight extension of the conjugation of the olefinic bond to the carbonyl or phenyl groups, in spite of a rather good planarity between these planes in the cinnamoyl moiety.

Short intermolecular contacts between the O^9 and the acyl moiety observed in Bz-BOL do not occur in the crystal structure of Cin-BOL. A stacking of the cinnamoyl moieties is observed in 1,4-dicinnamoylbenzene,[19] of which the olefinic bond is photodimerizable. The phenyl groups are stacked upon each other in 6-amino-5-cinnamoyl-1,3-dimethyluracil,[18] and stacking of a phenyl group on an olefinic group occurs in *trans*-cinnamoyl peroxide[19] and α-fluoro-*trans*-cinnamoyl peroxide.[21] In Cin-BOL, however, such stacking is not observed, partially because the bulky substituted moiety prevents any layer-stacked packing.

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