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The Crystal Structure of 5-Phenyl-2-oxazolyl Isocyanate Dimer

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The molecular structure of 5-phenyl-2-oxazolyl isocyanate dimer (II), the thermal decomposition product of benzyl 5-phenyl-2-oxazolecarbamate (I), was determined as 2-phenyl-6-(5-phenyl-2-oxazolyl)oxazolo[3,2-*a*][1,3,5]triazine-5,7-dione (IV) by X-ray analysis.

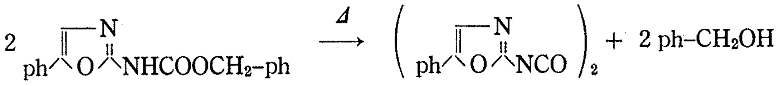
The crystal is triclinic, space group $P\bar{1}$ with the following unit cell dimensions: $a=8.472(3)$, $b=13.498(3)$, $c=7.808(2)$ Å, $\alpha=97.53(2)°$, $\beta=104.07(3)°$, $\gamma=80.58(2)°$ and $Z=2$. The structure was solved by a direct method and refined by the least-squares method to $R=0.057$.

No hydrogen bonding was observed in the crystal. The molecules were held together by the normal van der Waals contacts especially by the prominent stacking interaction between the oxazolotriazine moiety and neighboring benzene rings.

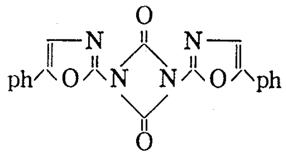
Keywords——5-phenyl-2-oxazolyl isocyanate dimer; oxazolo[3,2-*a*][1,3,5]triazine ring; X-ray analysis; stacking interaction; thermal decomposition

Introduction

The thermal decomposition of benzyl 5-phenyl-2-oxazole-carbamate (I) was shown to give 5-phenyl-2-oxazolyl isocyanate dimer (II) and benzyl alcohol.



I II



III

The structure of the dimer (II) was tentatively suggested to be III having an intramolecular centro-symmetry based on its IR and mass spectra and related data.[1]

The nuclear magnetic resonance (NMR) measurement of II, however, showed two single peaks corresponding to the C-4 proton of the oxazole ring at 7.61 and 8.69 ppm, which suggests that the molecular structureof II is not III.

In order to elucidate the molecular structure and the dimerization mechanism of II, we have determined its crystal structure by X-ray diffraction analysis.

Experimental

Crystals of II were obtained by the thermal decomposition of benzyl 5-phenyl-2-oxazolecarbamate (I). The transparent platelet crystals were recrystallized from acetonitrile.

Preliminary oscillation and Weissenberg photographs showed the crystal system to be triclinic. The space group was finally determined as $P\bar{1}$ from the statistical distribution of normalized structure factors (E). The density was measured by the flotation method in a benzene–carbon tetrachloride mixture. The unit-cell dimensions were refined on a Rigaku automatic four-circle diffractometer using graphite-monochromated Cu-$K\alpha$ radiation. The crystal data are given in Table I.

The intensity data were collected, from a single crystal with dimensions of 0.5×0.4×0.3 mm by the $\omega-2\theta$ scan technique ($\sin\theta/\lambda\leqq0.580$ Å^{-1}). Scan speed was 4°/min, and the background was measured for 5 s. The intensities of four standard reflections, measured every 100 reflections, showed that no structural deterioration was caused by X-ray radiation during the measurement of all reflections. A total of 2890 reflections ($F_0\geqq3\sigma(F_0)$) was used for the structure determination.

TABLE I. Crystal Data

Chemical formula	$C_{20}H_{12}N_4O_4$
Molecular weight	372.34
Crystal system	Triclinic
Space group	$P\bar{1}$
Cell constant	
a (Å)	8.472(3)
b (Å)	13.498(3)
c (Å)	7.808(2)
α (°)	97.53(2)
β (°)	104.07(3)
γ (°)	80.58(2)
Volume (Å^3)	848.9(3)
Z	2
D_m (g cm^{-3})	1.452(4)
D_x (g cm^{-3})	1.457

TABLE II-a. Atomic Coordinates of Non-hydrogen ($\times 10^4$) and Hydrogen Atoms ($\times 10^3$) with Their Standard Deviations in Parentheses

Atom	x	y	z
O (1)	795(2)	1041(2)	786(2)
C (2)	958(2)	1019(2)	764(2)
C (3)	975(2)	930(2)	664(3)
N (4)	820(2)	897(2)	620(2)
C (5)	772(2)	808(2)	522(2)
O (6)	861(2)	744(2)	456(2)
N (7)	606(2)	804(2)	512(2)
C (8)	498(3)	881(2)	592(3)
O (9)	356(2)	868(2)	569(2)
N (10)	561(2)	964(2)	688(2)
C (11)	751(2)	965(2)	697(2)
C (12)	1066(2)	1093(2)	852(2)
C (13)	1007(3)	1183(3)	938(3)
C (14)	1111(3)	1253(3)	1024(4)
C (15)	1276(3)	1233(3)	1024(3)
C (16)	1336(3)	1143(3)	937(3)
C (17)	1233(3)	1073(3)	853(3)
O (18)	464(2)	722(2)	247(2)
C (19)	538(2)	718(2)	420(2)
N (20)	535(3)	637(2)	483(2)
C (21)	448(3)	579(3)	338(3)
C (22)	405(2)	630(2)	195(3)
C (23)	320(2)	608(2)	11(3)
C (24)	312(3)	672(3)	−116(3)
C (25)	233(3)	650(3)	−291(3)
C (26)	164(4)	561(4)	−343(3)
C (27)	170(4)	496(3)	−218(4)
C (28)	248(3)	520(3)	−41(3)
H (3)	106(2)	89(3)	62(3)
H (13)	89(3)	120(3)	95(4)
H (14)	106(3)	132(4)	109(4)
H (15)	135(3)	128(3)	108(3)
H (16)	145(3)	113(3)	94(3)
H (17)	127(3)	101(3)	79(3)
H (21)	43(4)	51(3)	34(3)
H (24)	36(3)	73(3)	−8(3)
H (25)	23(4)	70(4)	−39(3)
H (26)	12(4)	54(4)	−47(3)
H (27)	13(4)	44(3)	−25(4)
H (28)	25(5)	48(4)	5(4)

TABLE II-b. Anisotropic Thermal Parameters ($\times 10^4$) of Non-hydrogen Atoms with Their Standard Deviations in Parentheses

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O (1)	103(2)	42(1)	166(3)	−28(2)	66 (4)	−24(3)
C (2)	97(3)	44(1)	149(4)	−21(3)	63 (6)	16(4)
C (3)	108(4)	42(1)	166(5)	−37(3)	57 (7)	−6(4)
N (4)	101(3)	39(1)	151(4)	−24(3)	51 (5)	−11(3)
C (5)	120(4)	39(1)	133(4)	−25(3)	33 (6)	7(4)
O (6)	140(3)	46(1)	226(4)	−25(3)	94 (6)	−90(3)
N (7)	113(3)	40(1)	142(4)	−36(3)	38 (5)	−12(3)
C (8)	114(4)	46(1)	151(4)	−28(4)	56 (6)	1(4)
O (9)	111(3)	64(1)	244(4)	−59(3)	87 (5)	−43(4)
N (10)	108(3)	46(1)	172(4)	−31(3)	72 (6)	−20(3)
C (11)	111(4)	38(1)	134(4)	−20(3)	46 (6)	0(4)
C (12)	117(4)	41(1)	145(4)	−36(3)	48 (6)	14(4)
C (13)	128(4)	49(2)	257(7)	−38(4)	118 (8)	−35(5)
C (14)	184(5)	51(2)	281(7)	−60(5)	132(10)	−61(6)
C (15)	158(5)	52(2)	241(6)	−78(5)	80 (9)	−14(5)
C (16)	120(4)	57(2)	222(6)	−50(4)	81 (8)	20(5)
C (17)	126(4)	45(1)	191(5)	−29(4)	95 (7)	−1(4)
O (18)	127(3)	38(1)	137(3)	−48(2)	15 (4)	4(3)
C (19)	115(4)	43(1)	144(4)	−33(4)	28 (6)	5(4)
N (20)	194(4)	46(1)	167(4)	−67(4)	20 (7)	27(4)
C (21)	192(5)	45(2)	192(5)	−72(5)	25 (8)	20(5)
C (22)	118(4)	36(1)	167(5)	−32(3)	49 (7)	1(4)
C (23)	104(4)	44(1)	163(5)	−23(4)	33 (6)	−12(4)
C (24)	115(4)	56(2)	175(5)	−38(4)	52 (7)	−13(5)
C (25)	150(5)	82(2)	179(5)	−40(5)	27 (8)	5(5)
C (26)	189(6)	96(3)	193(6)	−76(6)	−22 (9)	−39(6)
C (27)	201(6)	65(2)	280(8)	−87(6)	−39(11)	−59(6)
C (28)	172(5)	50(2)	224(6)	−57(5)	25 (9)	−14(5)

The anisotropic temperature factors are expressed in the form; $\exp\{-B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl\}$.

The structure was solved by a direct method (MULTAN program.[2]) An E-map computed using 212 reflections with $|E| \geqq 1.78$ gave reasonable positions of all the nonhydrogen atoms. The atomic coordinates were refined by a block-diagonal least-squares method with anisotropic temperature factors.

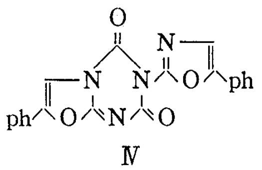
The positional parameters of all hydrogen atoms could be determined from a difference Fourier map. The refinement was then continued including these parameters with isotropic temperature factors until the R-value decreased to 0.057. The final positional and thermal parameters are given in Table II.

Numerical calculations were carried out on an ACOS-700 computer of the Computation Center of Osaka University using programs of the UNICS system.[3] Atomic scattering factors in "International Tables for X-ray Crystallography"[4] were used.

Results and Discussion

Molecular Structure

Fig. 1 shows the bond lengths and angles of nonhydrogen atoms, along with the atomic numbering used in this work. As is obvious from the figure, the molecular structure of II was shown to be 2-phenyl-6-(5-phenyl-2-oxazolyl)-oxazolo[3,2-a][1,3,5]triazine-5,7-dione(IV), in which the isocyanate groups cyclize to a triazine ring and condense with an oxazole ring. A similar cyclic condensation was also reported in a 2-(2-thiazolyl)thiazolo-[3,2-a][1,3,5]triazine-1,3-dione compound.[5]



IV

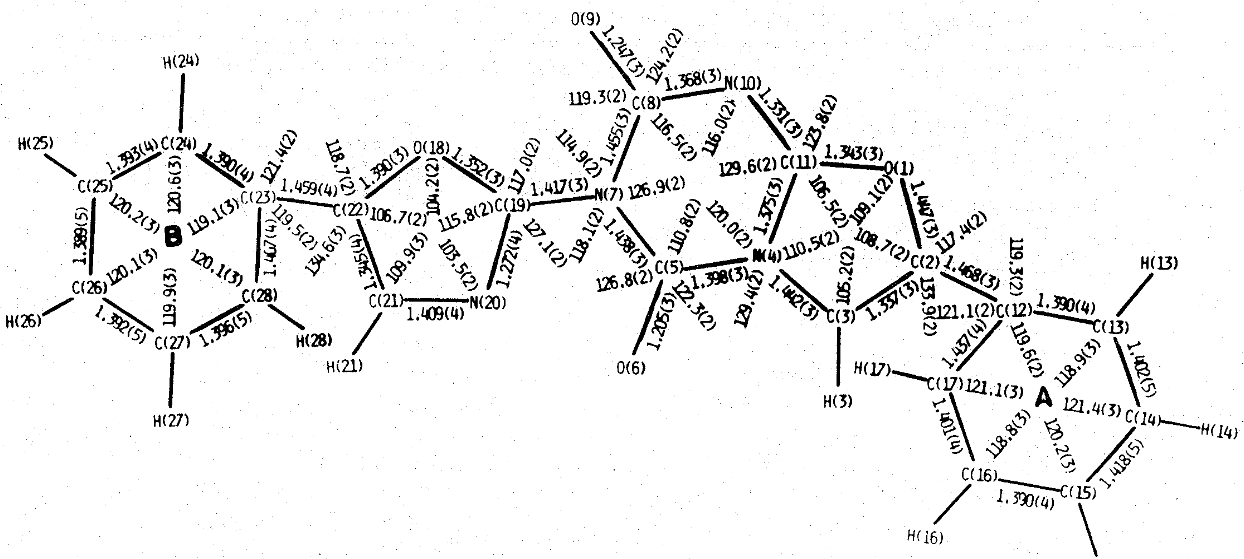
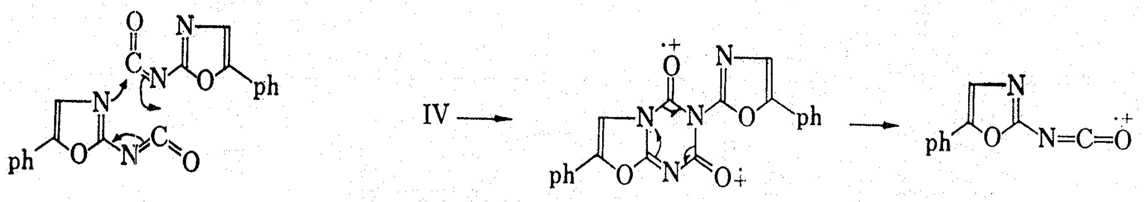


Fig. 1. Bond Lengths (Å) and Angles (°)

The mechanism of the dimerization of 5-phenyl-2-oxazolyl isocyanate can be considered to involve attack of the ring nitrogen atom on the isocyanate carbonyl carbon atom of another molecule as follows to give IV.

The mass spectrum of IV showed a peak corresponding to half of the total molecular weight (m/e=186). This is presumably due to the ionization and splitting of the oxazolotriazine ring as follows.



The bonding parameters for the triazine ring and oxazole ring are in agreement with those of related compounds; 2-phenylimino-3-phenyl-4-thioxothiazolo[3,2-*a*]tetrahydro[1,3,5]triazine[6] and bis(dihydro-1*H*,3*H*,5*H*-oxazolo[3,2-*c*]oxazole-7*a*-carboxylato)copper.[7]

The planarities of the oxazolotriazine, oxazole and benzene rings are shown in Table III. The oxazolotriazine ring is nearly planar, and the dihedral angle between the oxazole and triazine rings is 0.9°. The dihedral angle between this oxazolotriazine ring and the benzene ring A is 5.4°, showing that the two aromatic rings are almost coplanar. In the 5-phenyl-2-oxazolyl moiety of IV, the dihedral angle between the oxazole ring and the benzene ring B is 7.4°, and both rings are also in an almost coplanar arrangement. The C(2)–C(12) and C(22)–C(23) distances (1.468(3) and 1.459 (4) Å, respectively) are somewhat shorter than the standard C–C single bond distance (1.541 (3)Å),[8] and are in the range of C–C partial double bond distances (1.460(3)Å).[8] These results suggest that the benzene rings A and B are resonating with the oxazolotriazine and oxazole rings, respectively.

On the other hand, the oxazolotriazine ring is almost at right angles to the oxazole ring (dihedral angle=88.4°), probably due to the steric hindrances between O(6) and N(20) atoms and between O(9) and O(18) atoms.

Crystal Structure

The molecular packing viewed along the *c*-axis is shown in Fig. 2, and short contacts (less than 3.5 Å) are listed in Table IV.

Table III. Deviations of Atoms from the Least-squares Planes

Equations of the best planes with $m_1x+m_2y+m_3z=d$ in an orthogonal space.

Plane	m_1	m_2	m_3	d
Oxazolotriazine ring	0.0202	0.5741	−0.8185	2.8867
Benzene ring A	0.0993	0.5288	−0.8429	2.9133
Oxazole ring	0.8860	−0.3738	−0.2745	0.5632
Benzene ring B	0.8565	−0.4753	−0.2014	−0.3334

Deviations (in Å) from the best planes:

Oxazolotriazine ring	
O (1)*	0.0010
C (2)*	−0.0034
C (3)*	0.0031
N (4)*	−0.0029
C (5)*	0.0307
O (6)	0.0616
N (7)*	0.0220
C (8)*	−0.0119
O (9)	−0.0391
N (10)*	−0.0213
C (11)*	0.0005
H (3)	0.0031

Benzene ring A	
C (12)*	0.0079
C (13)*	0.0035
C (14)*	0.0070
C (15)*	0.0105
C (16)*	0.0002
C (17)*	0.0107
H (13)	0.0320
H (14)	0.0460
H (15)	−0.0060
H (16)	0.0491
H (17)	0.0322

Oxazole ring	
O (18)*	−0.0002
C (19)*	0.0021
N (20)*	−0.0013
C (21)*	0.0017
C (22)*	0.0003
H (21)	−0.0347

Benzene ring B	
C (23)*	0.0024
C (24)*	0.0048
C (25)*	−0.0123
C (26)*	0.0080
C (27)*	0.0025
C (28)*	−0.0046
H (24)	0.0071
H (25)	0.0134
H (26)	0.0768
H (27)	0.0389
H (28)	−0.0525

Atoms with asterisks define the plane in each case.

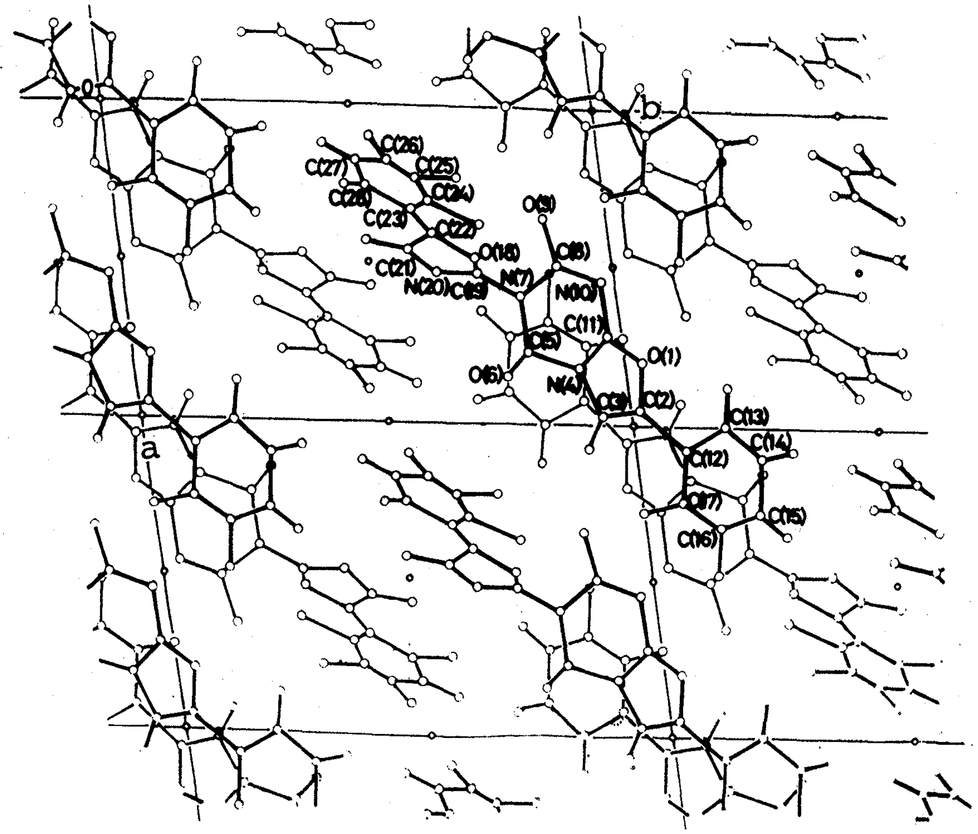


Fig. 2. Molecular Packing of IV viewed along the c-Axis

Table IV. Short Contacts (Å) of less than 3.5 Å with Their Standard Deviations in Parentheses

From[a]	To	Distance (Å)	From[a]	To	Distance (Å)
O (1)	O (9)[b]	3.109(3)	C (21)	C (21)[d]	3.405(6)
N (10)	C (8)[b]	3.148(3)	O (9)	C (17)[e]	3.476(6)
N (10)	N (10)[b]	3.111(4)	N (10)	C (17)[e]	3.451(3)
C (11)	C (8)[b]	3.309(3)	O (18)	C (16)[f]	3.387(3)
C (11)	O (9)[b]	3.177(3)	O (1)	C (12)[g]	3.440(3)
N (20)	C (25)[c]	3.484(4)	O (1)	C (17)[g]	3.482(3)
N (20)	C (21)[d]	3.377(4)	C (16)	N (10)[g]	3.319(4)

a) x, y, z.
b) $1-x, 2-y, 1-z$.
c) $x, y, 1+z$.
d) $1-x, 1-y, 1-z$.
e) $-1-x, y, z$.
f) $2-x, 2-y, 1-z$.
g) $2-x, 2-y, 2-z$.

No hydrogen bonding was observed in this crystal. The molecules were held together by the van der Waals contacts with neighboring molecules. A prominent stacking interaction was observed between the oxazolotriazine ring and the nearest neighboring benzene ring A. The mode of overlapping of oxazolotriazine and benzene rings is presented in Fig. 3, in which the original and two nearest centrosymmetrically translated molecules are shown.

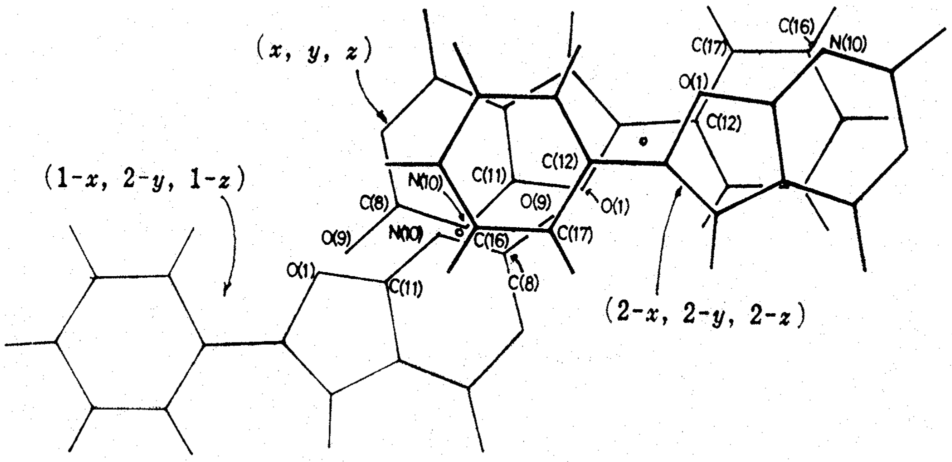


Fig. 3. Stacking Pattern viewed Perpendicular to the Original Oxazolotriazine Ring (x, y, z)

Open circles represent the centers of symmetry.

In the pair I (x, y, z: $2-x, 2-y, 2-z$), the benzene and oxazolotriazine rings are prominently stacked with a mean distance of 3.316 (3) Å and are almost parallel to each other (dihedral angle=2.3°), suggesting the existence of a weak charge-transfer interaction between these two rings.

On the other hand, some short contacts were observed between the two oxazolotriazine rings in the pair II (x, y, z: $1-x, 2-y, 1-z$), although the area of overlap between them is small. These parallel oxazolotriazine rings might exhibit dipole-dipole interaction (average vertical= 2.899(4)Å).

As is clear from Table IV, many short contacts are also observed between neighboring 5-phenyl-2-oxazolyl moieties related by a center of symmetry. These short contacts probably play an important role in the stabilization of the molecular packing along the a-direction (see Fig. 2).

References and Notes

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