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Topochemical Studies. XV.[1] Structure of Triclinic Form of the Photodimer of Cinnamamide

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New polymorph of the photodimer of cinnamamide has been found: 2,4-Diphenyl-1,3-cyclobutanedicarboxamide, $C_{18}H_{18}N_2O_2$, $M_r=294.16$, mp=553—555 K, triclinic, $P\bar{1}$, $a=8.756(1)$, $b=16.969(1)$, $c=5.2499(3)$ Å, $\alpha=93.104(6)$, $\beta=106.514(7)$, $\gamma=97.035(8)°$, $V=738.9(1)$ Å^3, $Z=2$, $D_m=1.32(1)$, $D_x=1.323$ Mg m^{-3}, Cu $K\alpha$ ($\lambda=1.54178$ Å), $\mu=0.71$ mm^{-1}, $F(000)=312$, $T=295$ K, $R=0.045$ for 2138 unique reflections with $|F_o|$ larger than $\sigma(F_o)$. The crystal structure has close relationship with that of cinnamamide. The structure is also discussed in comparison with that of the monoclinic form of the photodimer.

The photochemical behavior of the crystals of cinnamamide is of interest in view of the mechanism of the solid state photoreaction, since the reproducibility of the photodimerization is poor,[2,3] and the formation of different modifications of the crystals of the photodimer is suggested.[4] The crystal structures of a monohydrate of the photodimer and a monoclinic form of the photodimer have been reported recently.[3,5] In the present work, we have determined the crystal structure of a triclinic form of the photodimer in order to compare the modes of the hydrogen bonding and the molecular arrangement with those in the monomer (cinnamamide) crystals and the monoclinic form of the photodimer.

Experimental

Careful microscopic observation revealed that the single crystals of triclinic form of the photodimer were formed as a mixture with the monoclinic form from an ethanol solution of the irradiated sample[3] by slow evaporation. D_m was determined by flotation in aqueous KI. The crystal used for intensity measurement was a colorless prism elongated along c with dimensions 0.12×0.15×0.10 mm. Intensity data were collected by using Rigaku AFC-5 four-circle diffractometer equipped with rotating anode (40 kV, 200 mA, Ni-filtered Cu $K\alpha$). 20 reflections within $33 \leqq 2\theta \leqq 41°$ were used to determine the lattice parameters. Intensity data were collected within $2\theta_{max}=125°$ ($-10 \leqq h \leqq 9$, $-19 \leqq k \leqq 19$, $0 \leqq l \leqq 6$) by ω–2θ scan method [scan speed 4° min^{-1} in ω, scan range $(1.2+0.15 \tan\theta)°$ in ω]. Background was measured for 4 s on either side of the peak. Three standard reflections were recorded every 97 reflections. The fluctuation was within 1% in $|F_o|$. Lorentz and polarization corrections were applied, but no absorption correction was made. In total 2341 unique reflections were measured, $R_{int}=0.012$ for 293 $hk0$ reflections. In structure analysis and refinement 2138 reflections with $|F_o|$ larger than $\sigma(F_o)$ were used. The structure was solved by MULTAN78 and refined by block-diagonal least-squares (non-H atoms anisotropically). H atoms were determined from a difference Fourier map and refined isotropically; $\sum w(|F_o|-|F_c|)^2$ was minimized with $w=1.0/[\sigma(F_o)^2-0.0204\times|F_o|+0.0020|F_o|^2]$. Final $R=0.045$ for 2138 reflections, $wR=0.047$, $S=1.688$ and $(\Delta/\sigma)_{max}=0.5$. The residual electron density in the final difference map was −0.19 to 0.15 eÅ^{-3}.

Atomic scattering factors were taken from International Tables for X-ray Crystallography.[6] Programs used were MULTAN78,[7] HBLS-V and DAPH,[8] MOLCON,[9] and ORTEP.[10] Computations were carried out at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University, and at the Okayama University Computer Center.

Results and Discussion

The final atomic parameters are listed in Table 1.[11] Thermal ellipsoids with the atomic numbering are shown in Fig. 1. Bond lengths and angles, and geometry of the hydrogen bonds are listed in Table 2. Stereoscopic view of the crystal structure is shown in Fig. 2.

Molecular Structure. The molecule of the photo-

Table 1. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters (B_{eq}) with esd's in Parentheses

$$B_{eq}=(4/3)\sum_i \beta_{ii}/a_i^{*2}$$

Atom	x	y	z	B_{eq}/Å^2
O(1A)	0.9793(1)	0.08981(6)	0.6934(2)	3.54(5)
O(1B)	0.9229(1)	0.39475(6)	0.3334(2)	4.11(5)
N(1A)	0.9290(2)	0.07305(7)	0.2486(3)	3.48(6)
N(1B)	0.8855(2)	0.44732(8)	0.7097(4)	5.06(8)
C(1A)	1.1726(2)	0.30672(8)	0.8022(3)	3.01(7)
C(2A)	1.2196(2)	0.3605(1)	1.0290(4)	3.90(8)
C(3A)	1.3724(2)	0.4033(1)	1.1143(4)	4.74(9)
C(4A)	1.4819(2)	0.3925(1)	0.9770(5)	4.80(9)
C(5A)	1.4378(2)	0.3391(1)	0.7539(4)	4.9(1)
C(6A)	1.2841(2)	0.2964(1)	0.6666(4)	3.93(8)
C(7A)	1.0060(2)	0.26013(8)	0.7187(3)	2.78(7)
C(8A)	0.9423(2)	0.20642(8)	0.4559(3)	2.78(7)
C(9A)	0.9519(2)	0.11802(8)	0.4756(3)	2.72(6)
C(1B)	0.6300(2)	0.18445(8)	0.4247(3)	3.03(7)
C(2B)	0.6326(2)	0.1413(1)	0.6429(4)	3.83(8)
C(3B)	0.4987(2)	0.0912(1)	0.6537(4)	4.81(9)
C(4B)	0.3574(2)	0.0844(1)	0.4493(5)	5.1(1)
C(5B)	0.3504(2)	0.1283(1)	0.2374(5)	4.9(1)
C(6B)	0.4856(2)	0.1781(1)	0.2227(4)	3.87(8)
C(7B)	0.7745(2)	0.23801(8)	0.4002(3)	2.84(7)
C(8B)	0.8541(2)	0.30493(8)	0.6327(3)	3.00(7)
C(9B)	0.8897(2)	0.38597(8)	0.5431(3)	3.20(7)

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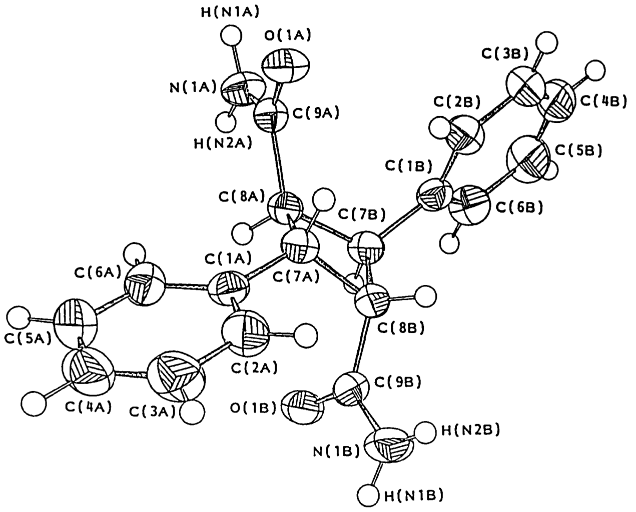

Fig. 1. The thermal ellipsoids with atomic numbering. Ellipsoids of 50% probability are drawn for the non-H atoms; the H atoms are represented as spheres equivalent to B=1.0 Å^2.

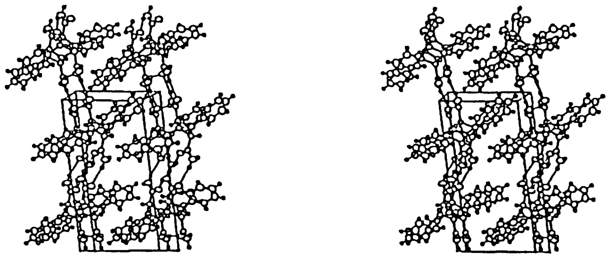

Fig. 2. Stereoscopic view of the crystal structure. The a axis points from left to right, the b axis upwards and the c axis onto the plane of the paper.

dimer has no center of symmetry as found in the crystals of the monoclinic form. As seen from the torsion angles in Table 2, the conformation of the molecule deviates largely from a pseudo-centrosymmetric conformation observed in the monohydrate.[3] The molecules in the anhydrates take more strained conformation than that in the monohydrate.

The bond lengths, the bond angles and also the torsion angles are in agreement with those found in the monoclinic form within the experimental errors. The lengths of C(7A)-C(8B) and C(8A)-C(7B) are longer than those of the corresponding bonds in the monohydrate.

Crystal Structure. In the crystals the molecules related by $\bar{1}$ at (0, 1/2, 1/2) and (0, 0, 1/2) are held together by N-H···O hydrogen bonds between the carbamoyl groups to form a chain along the b axis. Furthermore, the molecules related by a c translation are held together by N-H···O hydrogen bonds between the carbamoyl groups to form a two-dimensional hydrogen-bond network on (1 0 0). The networks are stacked along the a axis by van der Waals interactions.

Table 2. Bond Lengths (l), Angles (ϕ), Selected Torsion Angles (τ) and the Geometry of Hydrogen Bonds (l, ϕ) with esd's in Parentheses

	Portion A	Portion B
	l/Å	l/Å
O(1)-C(9)	1.235(2)	1.228(2)
N(1)-C(9)	1.331(2)	1.334(3)
C(1)-C(2)	1.390(3)	1.389(3)
C(1)-C(6)	1.384(3)	1.388(3)
C(1)-C(7)	1.504(3)	1.506(3)
C(2)-C(3)	1.380(3)	1.378(3)
C(3)-C(4)	1.376(4)	1.376(4)
C(4)-C(5)	1.373(4)	1.363(4)
C(5)-C(6)	1.386(3)	1.391(3)
C(7)-C(8)	1.532(3)	1.561(3)
C(8)-C(9)	1.520(3)	1.503(3)
C(7A)-C(8B)	1.579(3)	
C(8A)-C(7B)	1.580(3)	
	ϕ/°	ϕ/°
O(1)-C(9)-N(1)	122.0(2)	122.7(2)
O(1)-C(9)-C(8)	121.0(2)	122.1(2)
N(1)-C(9)-C(8)	117.0(2)	115.2(2)
C(1)-C(2)-C(3)	121.0(2)	121.3(2)
C(1)-C(6)-C(5)	120.8(2)	120.6(2)
C(1)-C(7)-C(8)	121.4(2)	116.2(2)
C(2)-C(3)-C(4)	120.2(2)	120.3(2)
C(2)-C(1)-C(6)	118.1(2)	117.6(2)
C(2)-C(1)-C(7)	119.3(2)	123.2(2)
C(3)-C(4)-C(5)	119.5(3)	119.5(3)
C(4)-C(5)-C(6)	120.4(2)	120.7(2)
C(6)-C(1)-C(7)	122.5(2)	119.1(2)
C(7)-C(8)-C(9)	116.2(2)	114.3(2)
C(1A)-C(7A)-C(8B)	120.1(2)	
C(7A)-C(8A)-C(7B)	90.2(2)	
C(8A)-C(7A)-C(8B)	89.6(2)	
C(9A)-C(8A)-C(7B)	120.2(2)	
C(1B)-C(7B)-C(8A)		119.8(2)
C(7B)-C(8B)-C(7A)		89.2(2)
C(8B)-C(7B)-C(8A)		88.5(1)
C(9B)-C(8B)-C(7A)		113.7(2)
	τ/°	τ/°
C(1)-C(7)-C(8)-C(9)	98.4(2)	−132.9(2)
C(2)-C(1)-C(7)-C(8)	173.8(2)	−56.0(3)
C(7)-C(8)-C(9)-O(1)	13.7(3)	−30.8(3)

Donor(D)	Acceptor(A)	D···A	H···A	D-H···A
		l/Å	l/Å	ϕ/°
N(1B^{i})	O(1B^{ii})	3.377(2)	2.56(2)	154(2)
N(1A^{i})	O(1A^{iii})	3.092(1)	2.25(2)	152(2)
N(1A^{i})	O(1A^{iv})	2.978(1)	2.07(2)	168(2)
N(1B^{i})	O(1B^{v})	3.038(2)	2.19(2)	162(2)

Symmetry code: (i) x, y, z; (ii) $x, y, 1+z$; (iii) $x, y, -1+z$; (iv) $2-x, -y, 1-z$; (v) $2-x, 1-y, 1-z$.

Comparison of the Crystal Structures. (a) With the Monoclinic Form of the Photodimer. The values of a, c and β of the triclinic form correspond to the values of c, a and β, respectively, of the monoclinic form[5] [$P2_1/a$, Z=4, a=5.256(1), b=33.741(5), c=8.706(1) Å, β=106.32(2)°]. The molecular arrangements viewed along the b axes of both forms are very similar to each other. The hydrogen bonds between the molecules related by the $\bar{1}$ at (0, 1/2, 1/2) and by the c translation in the triclinic form are also found in the monoclinic form. However, in the monoclinic form the hydrogen bond

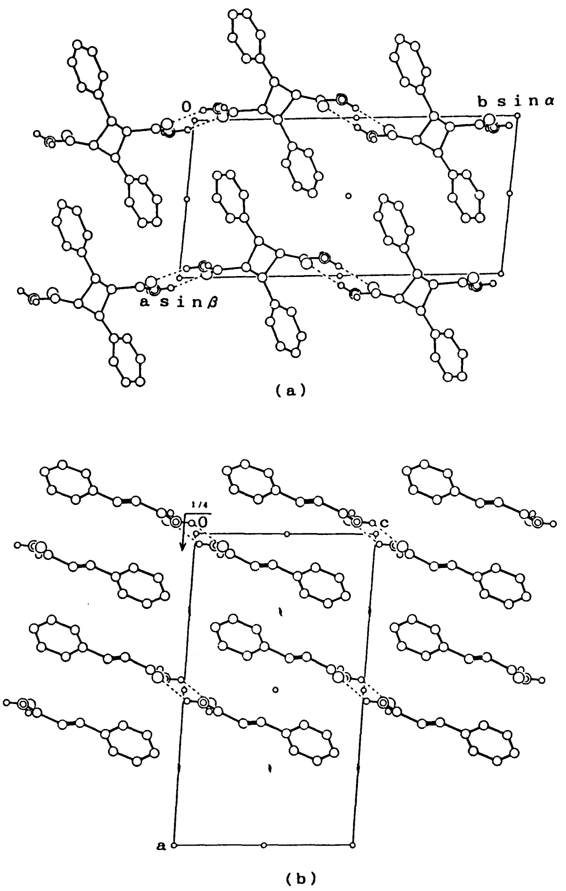

Fig. 3. Comparison of the crystal structures of the photodimer and the monomer. (a) Molecular arrangement in (001) of the triclinic form of the photodimer. (b) Molecular arrangement in (010) of the monomer crystal. The C=C double bonds are shown by thick lines.

between the molecules related by the $\bar{1}$ at (0, 0, 1/2) found in the triclinic form is replaced by a hydrogen bond between the molecules related by an *a* glide, which causes the doubling of the dimension of *b* of the monoclinic form. This glide type of hydrogen bond is not found in the monomer crystals.

(b) With the Monomer Crystal. Crystal structures of the photodimer and the monomer[2)] are compared in Fig. 3. The modes of the hydrogen bonds in both crystals are the same. The periods of *a*, *b*, and *c* of the dimer crystals correspond to *a*/2, 2*c*, and *b*, respectively, of the monomer crystals. This can be explained by the following facts. (1) The molecule of the photodimer has no center of symmetry by which the monomer molecules to be dimerized are related (doubling of *b* compared with *c* of the monomer crystals). (2) The neighboring networks in the dimer crystals are related by a translation, but the neighboring sheets in the monomer crystals are related by a 2_1 (halving of *a* compared with *a* of the monomer crystals). (3) Formation of N–H···O hydrogen bond between the carbamoyl groups related by a translation in both crystals (similar period of *c* to that of *b* of the monomer crystals).

From the above discussion, it can be concluded that the crystal structure of the triclinic form of the photodimer has close relationship to that of the monomer, but that of the monoclinic form has a glide-type hydrogen bond which dose not exist in the monomer crystal. Thus, the triclinic form may preferably be formed by the photoirradiation. Unfortunately, powder photographs of the irradiated sample showed diffuse diffraction patterns which were roughly simulated in the 2θ range from 10 to 40° based on the structures of either the triclinic form or the monoclinic form.

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