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Topochemical Studies. XVI.[1] Direct Observation of the Solid-State Photoreaction of α-(Acetylamino)cinnamic Acid Dihydrate by Single Crystal X-Ray Diffraction

Tetsuyuki Iwamoto† and Setsuo Kashino*
Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700

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The crystal structure at an intermediate stage in the solid-state photodimerization of α-(acetylamino)-cinnamic acid dihydrate has been analyzed at the conversion rate of 12%: $C_{11}H_{11}NO_3\cdot 2H_2O$, $M_r=241.24$, monoclinic, $P2_1/a$, $a=18.346(5)$, $b=6.072(2)$, $c=11.310(4)$ Å, $\beta=105.90(2)°$, $V=1211.8(6)$ Å^3, $Z=4$, $D_x=1.323$ Mg m^{-3}, Cu $K\alpha$ ($\lambda=1.5418$ Å), $\mu=0.89$ mm^{-1}, $F(000)=512$, $T=295$ K, $R=0.108$ for 1678 unique reflections with $|F_o|$ larger than $\sigma(F_o)$. The present study revealed the structures of the monomer and photodimer components at the intermediate stage. The results made possible the discussion on the role of intermolecular hydrogen bonds and on the feature of the atomic movements accompanied by the reaction.

α-(Acetylamino)cinnamic acid has been found to be photodimerizable in the crystal of its dihydrate (AC2) to form a tetrahydrate of the photodimer (ACD4) without a loss of the water molecules during the reaction.[2] The crystal structure of ACD4 was closely related to that of AC2, and the space group and the mode of the hydrogen bonds of ACD4 were the same as those in AC2.[2]

In the present work, we have determined the crystal structure at an intermediate stage of the single-crystal to single-crystal transformation in order to establish the manner of the atomic movements including the water molecules, and to analyze a possible mode of coexistence of the molecules of the reactant and the product in the crystal.

On the solid-state (2+2) photoaddition the dynamic single-crystal X-ray diffraction studies have been reported on the reaction of 2-benzyl-5-benzylidenecyclopentanone and its *p*-bromo derivatives,[3] and on psoralen-thymine cycloaddition.[4] Changes in crystal structure during polymerization and oligomerization of 2,5-distyrylpyrazine have been investigated by X-ray crystallographic method.[5] Kinetic features of the topochemical process have been reviewed.[6]

Experimental

The crystals of the monomer, α-(acetylamino)cinnamic acid dihydrate (AC2) were grown from an ethanol solution by slow evaporation.[2] Photodimerization of the crystal was observed on exposure to room daylight. The crystals of an intermediate stage of the photoreaction (ACDR12) were obtained after three months exposure at room temperature. A transparent crystal was chosen for intensity measurement. The crystal used was a colorless prism elongated along the *b* axis with dimensions 0.05×0.45×0.12 mm. Intensity date were measured by using Rigaku AFC-5 four-circle diffractometer equipped with rotating anode (40 kV, 200 mA, Ni-filtered Cu $K\alpha$). The lattice parameters were determined with 20 reflections within $20\leqq 2\theta\leqq 42°$. Intensity data were collected within $2\theta_{\max}=125°$ ($-20\leqq h\leqq 20$, $0\leqq k\leqq 6$, $0\leqq l\leqq 13$) 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 57 reflections. The fluctuation was within 2% in $|F_o|$. Lorentz and polarization corrections were applied, but no absorption correction was made. A total of 1922 unique reflections were measured, $R_{\text{int}}=0.154$ for 107 $hk0$ reflections. The value was rather high, probably because some inhomogeneity was induced in the specimen by the reaction. The equivalent reflections were averaged and used for the structure analysis. Systematic absences for $P2_1/a$ were held. In structure analysis and refinement 1678 reflections with $|F_o|$ larger than $\sigma(F_o)$ were used.

The structure of the monomer component (the monomer

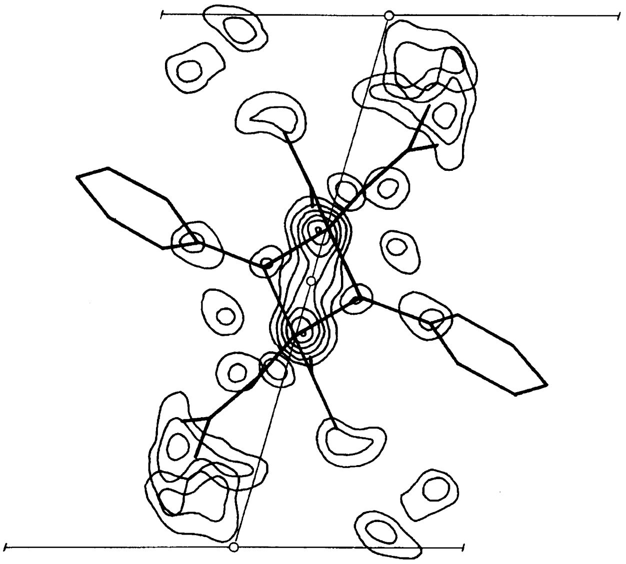

Fig. 1. Difference Fourier map viewed down the *b* axis at the stage of $R=0.129$ for ACDR12. Contours are drawn from 0.10 Å^{-3} with intervals of 0.10 e Å^{-3}. The molecular skeleton shows the structure of the photodimer based on the atomic coordinates of ACD4. The *a* axis points from left to right, the *b* axis onto the plane of the paper and the *c* axis downwards.

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†On leave from Kobe Women's University Seto Junior College, Seto, Akaiwa, Okayama 709-08.

Table 1. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters

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

Atom	x	y	z	B_{eq}/Å^2
Monomer component				
O(1M)	0.5894(2)	0.7249(6)	0.8097(3)	3.8(2)
O(2M)	0.5350(2)	0.9841(6)	0.6737(3)	3.8(2)
O(3M)	0.4268(2)	0.5896(6)	0.8541(3)	4.5(2)
O(4WM)	0.6897(2)	0.9875(7)	0.9200(5)	6.3(2)
O(5WM)	0.6562(2)	0.3968(6)	0.9850(3)	4.4(2)
N(1M)	0.4789(2)	0.4277(6)	0.7207(4)	3.1(2)
C(1M)	0.3700(3)	0.5438(9)	0.4651(5)	3.3(3)
C(2M)	0.3471(3)	0.3317(9)	0.4912(5)	3.9(2)
C(3M)	0.2839(4)	0.237(1)	0.4129(6)	5.3(3)
C(4M)	0.2425(3)	0.345(1)	0.3094(7)	5.1(4)
C(5M)	0.2646(3)	0.551(1)	0.2789(6)	5.0(3)
C(6M)	0.3279(3)	0.6457(9)	0.3567(5)	3.9(3)
C(7M)	0.4333(3)	0.6700(8)	0.5433(4)	2.4(2)
C(8M)	0.4793(3)	0.6261(7)	0.6526(4)	2.3(2)
C(9M)	0.5367(3)	0.7950(9)	0.7120(5)	3.1(3)
C(10M)	0.4521(3)	0.4215(9)	0.8180(5)	3.1(2)
C(11M)	0.4549(3)	0.194(1)	0.8818(7)	5.4(3)
Photodimer component				
O(1D)	0.5848(8)	0.678(3)	0.793(1)	2.3(3)
O(2D)	0.535(1)	0.926(3)	0.665(2)	3.4(4)
O(3D)	0.426(1)	0.584(3)	0.816(2)	6.1(6)
O(4WD)	0.682(1)	0.941(4)	0.929(2)	5.3(5)
O(5WD)	0.655(1)	0.354(4)	1.001(2)	4.9(5)
N(1D)	0.4852(9)	0.370(3)	0.694(2)	2.0(4)
C(1D)	0.366(1)	0.537(3)	0.436(2)	2.6(5)
C(2D)	0.341(1)	0.329(3)	0.460(2)	2.8(5)
C(3D)	0.268(1)	0.276(5)	0.397(2)	3.8(6)
C(4D)	0.221(2)	0.403(5)	0.306(3)	5.8(8)
C(5D)	0.248(2)	0.612(5)	0.293(3)	5.0(7)
C(6D)	0.319(2)	0.685(5)	0.356(2)	5.0(7)
C(7D)	0.448(3)	0.619(8)	0.485(5)	9(1)
C(8D)	0.504(2)	0.539(5)	0.610(3)	4.3(7)
C(9D)	0.531(1)	0.735(3)	0.694(2)	2.6(5)
C(10D)	0.449(1)	0.412(3)	0.780(2)	4.2(7)
C(11D)	0.452(1)	0.231(3)	0.872(2)	1.3(4)

and the water molecules) was refined at first by assuming the occupancy factor of 1.0. The atomic parameters of AC2[2)] were used as initial parameters and refined by block-diagonal least-squares (non-H atoms anisotropically, H-atoms isotropically). At this stage the R value was 0.129. The four largest peaks around an inversion center in a difference Fourier map suggested the formation of the cyclobutane ring in detectable extent in the crystal (Fig. 1). In a difference Fourier map calculated by assuming an occupancy factor of 0.90 for the monomer component the peaks of the monomer molecule disappeared and the peaks corresponding to all non-H atoms of the photodimer component (the dimer and the water molecules) were clearly appeared (Fig. 2).

Subsequently, the structure was refined for both monomer and photodimer components. The atomic parameters of ACD4[2)] were adopted as a starting model for the photodimer component, and the occupancy factor was set to 0.10. The structure was refined by full-matrix least-squares method. The values minimized were $\Sigma w(|F_o|-|F_c|)^2$ with

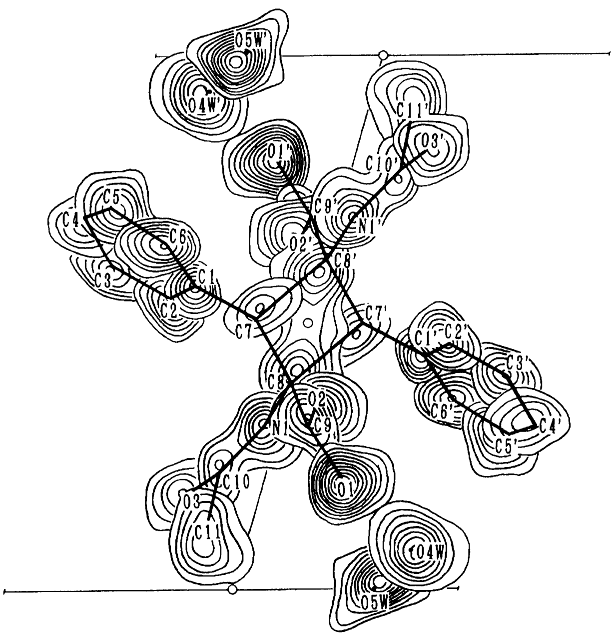

Fig. 2. Difference Fourier map calculated with an occupancy factor of 0.90 for the monomer component for ACDR12 viewed down the b axis. Contours are drawn from 0.10 e Å^{-3} with intervals of 0.10 e Å^{-3}. The molecular skeleton with atomic numbering shows the photodimer component at the final stage of R= 0.107. The a axis points from left to right, the b axis onto the plane of the paper and the c axis downwards.

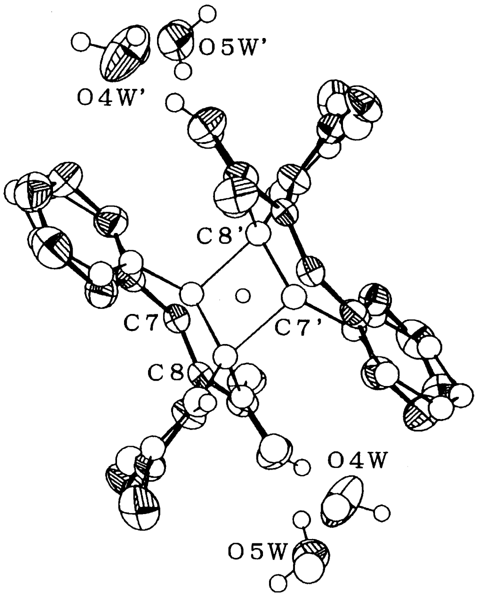

Fig. 3. The molecular structures determined for ACDR12. Ellipsoids of 50% probability are drawn for the non-H atoms of the monomer component; the H atoms are represented as spheres equivalent to B=1.0 Å^2; the non-H atoms of the photodimer component are represented as spheres equivalent to B=2.0 Å^2 for C atoms and B=3.0 Å^2 for O and N atoms.

Table 2. Bond Lengths (l) and Angles (ϕ) with esd's in Parentheses

Monomer	l/Å		l/Å
O(1)–C(9)	1.323(6)	C(2)–C(3)	1.377(8)
O(2)–C(9)	1.225(6)	C(3)–C(4)	1.375(9)
O(3)–C(10)	1.236(6)	C(4)–C(5)	1.39(1)
N(1)–C(8)	1.431(6)	C(5)–C(6)	1.376(9)
N(1)–C(10)	1.323(6)	C(7)–C(8)	1.319(6)
C(1)–C(2)	1.411(8)	C(8)–C(9)	1.491(6)
C(1)–C(6)	1.401(8)	C(10)–C(11)	1.553(9)
C(1)–C(7)	1.468(7)		

	Monomer ϕ/°	Photodimer ϕ/°
O(1)–C(9)–O(2)	122.6(5)	113(3)
O(1)–C(9)–C(8)	114.8(4)	111(3)
O(2)–C(9)–C(8)	122.6(5)	128(4)
O(3)–C(10)–N(1)	120.7(5)	133(5)
O(3)–C(10)–C(11)	123.3(5)	110(4)
N(1)–C(10)–C(11)	116.1(5)	115(4)
N(1)–C(8)–C(9)	116.3(4)	103(3)
C(1)–C(2)–C(3)	119.5(5)	116(4)
C(1)–C(6)–C(5)	122.8(6)	117(4)
C(1)–C(7)–C(8)	131.0(5)	124(4)
C(1)–C)7)–C(8′)		101(4)
N(1)–C(8)–C(7′)		104(3)
C(2)–C(3)–C(4)	121.3(6)	125(4)
C(3)–C(4)–C(5)	120.7(6)	115(4)
C(4)–C(5)–C(6)	118.1(2)	124(5)
C(6)–C(1)–C(2)	117.5(5)	122(4)
C(6)–C(1)–C(7)	116.9(5)	113(4)
C(7)–C(1)–C(2)	125.6(5)	124(4)
C(7)–C(8)–C(9)	118.3(4)	110(4)
C(7)–C(8)–N(1)	125.3(4)	125(4)
C(8)–N(1)–C(10)	122.0(4)	125(3)
C(7)–C(8)–C(7′)		86(3)
C(8)–C(7)–C(8′)		94(4)
C(9)–C(8)–C(7′)		130(3)

$w=1.0/\sigma(F_o)^2$. For the photodimer component the non-H atoms were refined isotropically and the H atoms were not included in the calculation. The bond lengths except for C(7)–C(8′) in the cyclobutane ring were constrained at the values found in ACD4.[2)] When the C(7)–C(8′) length was constrained, the calculation did not converge to reasonable structure.

The difference Fourier map at the stage of R=0.111 showed positive peaks for the photodimer component. Thus, the occupancy factor was increased to 0.12. The refined values of the thermal parameters of the photodimer component became close to those found in ACD4. The final R value was 0.108 for 1678 reflections, wR 0.092, S 2.140. $(\Delta/\sigma)_{\max}$ was 0.42 for the monomer component and 0.82 for the photodimer component. $\Delta\rho_{\max}$ and $\Delta\rho_{\min}$ in final difference Fourier map were 0.32 and −0.41 e Å^{-3}, respectively. Thus, the rate of the photodimerization was estimated to be 12%.

Atomic scattering factors were taken from International Tables for X-Ray Crystallography.[7)] Programs used were HBLS-V and DAPH,[8)] modified version of CRLS,[9)] MOLCON,[10)] and ORTEP.[11)] Computations were carried out at the Okayama University Computer Center.

Results and Discussion

The crystal of ACDR12 belongs to the same space group, $P2_1/a$, as AC2 and ACD4. The length of a is longer by 0.06 Å than that of AC2 and shorter by 0.81 Å than that of ACD4. The length of c is shorter by 0.10 Å than that of AC2 and longer by 1.01 Å than that of ACD4. The values of b and β are close to the corresponding ones of AC2 and ACD4. The cell volume is smaller than that of AC2 by 8.9 Å^3. The cell volume of ACD4 is smaller than that of AC2 by 67.1 Å^3. The difference in cell volume between AC2 and ACDR12 corresponds to 13% of that between AC2 and ACD4.

The final atomic parameters of ACDR12 are listed in Table 1.[12)] The bond lengths of the monomer component and bond angles for the monomer and photodimer components are listed in Table 2. The selected torsion angles are listed in Table 3. Atomic numbering for the photodimer component is given in Fig. 2. The atoms related by an inversion center are denoted with a prime. The corresponding numbering scheme is adopted for the monomer component. The molecular structures of the photodimer component and the thermal ellipsoids

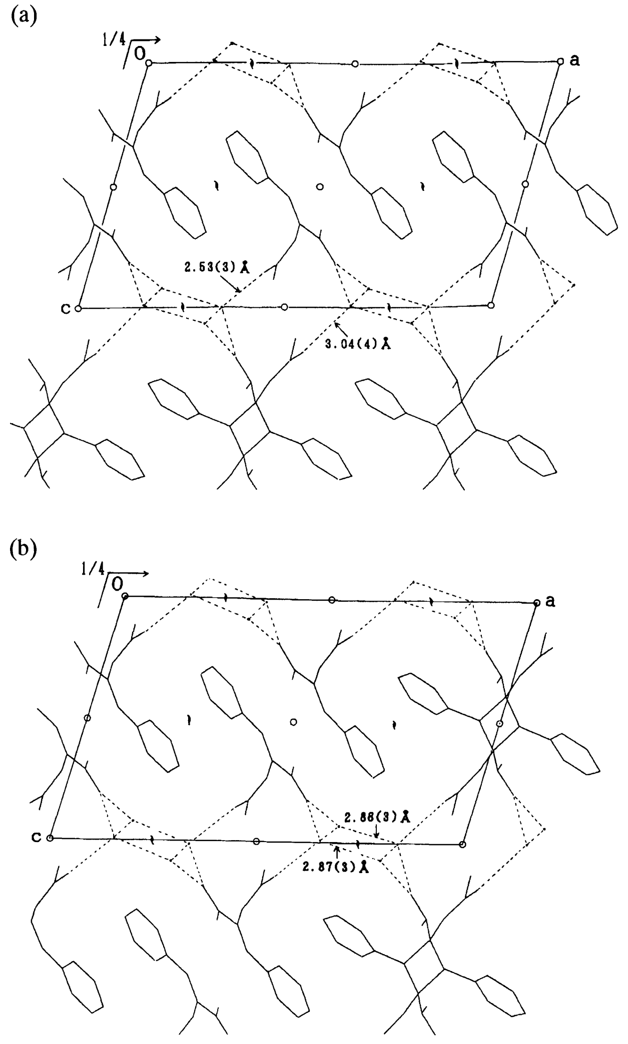

Fig. 4. The molecular arrangements in the monomer-photodimer coexistance domain in ACDR12 viewed along *b*. (a) Unfavorable arrangement. (b) Most probable arrangement.

of the monomer component are shown in Fig. 3. For the monomer component, the bond lengths, the bond angles and the torsion angles are essentially the same as those found in AC2. For the photodimer component, the cyclobutane ring has an inversion center as found in ACD4. The C(7)–C(8′) bond length is determined to be 1.84(7) Å. However, further discussion on the molecular structure is out of the limit of the precision.

Possible Mode of Hydrogen Bonds Between the Monomer and the Photodimer Components. In the crystal the existence of three parts may be assumed. The first part is composed of the monomer components, the second one is composed of the photodimer components, and the third one is composed of the monomer and photodimer components. Table 4 shows that in the first part the geometries of the hydrogen bonds are substantially the same as the corresponding ones of AC2 as expected from the similar cell

Table 3. Selected Torsion Angles ($\tau/°$) and esd's in Parentheses

ACDR12	(Monomer)	(Photodimer)	ACD4[a)]
	$\tau/°$	$\tau/°$	$\tau/°$
C(10)–N(1)–C(8)–C(7)	−106.0(6)	−84(6)	−85.2(1)
C(10)–N(1)–C(8)–C(7′)		180(4)	171.8(1)
C(10)–N(1)–C(8)–C(9)	73.8(6)	42(5)	47.7(1)
C(2)–C(1)–C(7)–C(8)	−3.6(9)	−29(7)	−38.8(2)
C(2)–C(1)–C(7)–C(8′)		73(5)	73.1(2)
C(6)–C(1)–C(7)–C(8)	174.9(5)	156(5)	148.3(1)
C(6)–C(1)–C(7)–C(8′)		−102(4)	−99.8(1)
C(1)–C(7)–C(8)–N(1)	2.7(8)	2(8)	10.0(1)
C(1)–C(7)–C(8)–C(7′)		106(5)	124.2(1)
C(1)–C(7)–C(8)–C(9)	−177.0(5)	−122(5)	−122.1(1)
C(8′)–C(7)–C(8)–N(1)		−105(4)	−114.3(1)
C(8′)–C(7)–C(8)–C(7′)		0	0.0
C(8′)–C(7)–C(8)–C(9)		132(3)	113.7(1)
C(1)–C(7)–C(8′)–N(1′)		110(4)	105.3(1)
C(1)–C(7)–C(8′)–C(7′)		−126(4)	−131.3(1)
C(1)–C(7)–C(8′)–C(9′)		−12(6)	−17.7(1)
C(8)–C(7)–C(8′)–N(1′)		−125(3)	−123.5(1)
C(8)–C(7)–C(8′)–C(7′)		0	0.0
C(8)–C(7)–C(8′)–C(9′)		113(5)	113.6(1)
N(1)–C(8)–C(9)–O(1)	12.1(6)	52(4)	43.0(1)
N(1)–C(8)–C(9)–O(2)	−167.6(4)	−160(4)	−142.2(1)
C(7)–C(8)–C(9)–O(1)	−168.1(4)	−172(4)	−179.5(1)
C(7)–C(8)–C(9)–O(2)	12.2(7)	−25(6)	−4.7(1)
C(7′)–C(8)–C(9)–O(1)		−70(5)	−80.4(1)
C(7′)–C(8)–C(9)–O(2)		77(6)	94.4(1)

a) Ref. 2.

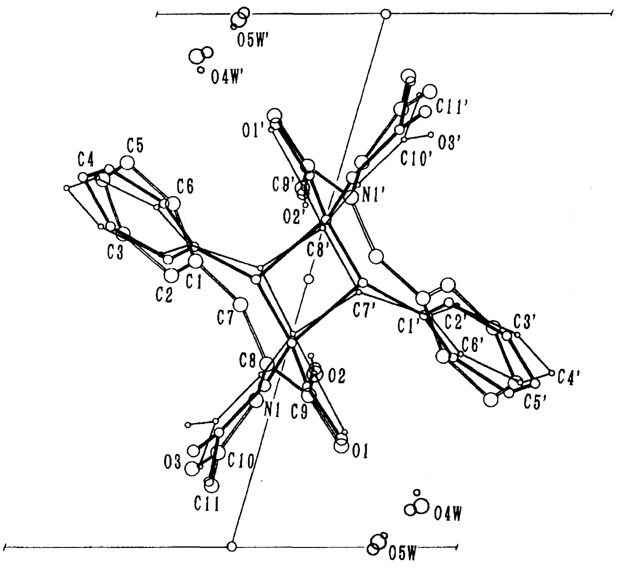

Fig. 5. The composite diagram around an inversion center at (1/2, 1/2, 1/2) of the photodimer component in ACDR12, and the molecules in AC2 and ACD4. The monomer component in ACDR12 is omitted, whose position is essentially the same as that of the monomer in AC2. Open bonds and large circles for AC2, bold bonds and medium circles for the photodimer component of ACDR12, and thin bonds and small circles for ACD4. The *a* axis points from left to right, the *b* axis onto the plane of the paper and the *c* axis downwards.

Table 4. Geometry of Hydrogen Bonds of ACDR12 in Comparison with Those of AC2 and ACD4

Donor(D)	Acceptor(A)	Part 1	Part 2	Part 3		AC2$^{a)}$	ACD4$^{a)}$
		between monomer conponents l/Å	between photodimer components l/Å	between monomer(D) and photodimer(A) l/Å	between monomer(A) and photodimer(D) l/Å	l/Å	l/Å
(1) N($1^{\rm i}$)	O($2^{\rm ii}$)	2.983(6)	2.89(4)	3.33(3)	2.55(3)	2.982(1)	2.935(1)
(2) O($1^{\rm i}$)	O($4\rm W^{i}$)	2.495(7)	2.57(4)	—	—	2.528(2)	2.549(2)
(3) O($5\rm W^{i}$)	O($1^{\rm i}$)	2.841(6)	3.07(4)	—	—	2.862(1)	2.897(1)
(4) O($4\rm W^{i}$)	O($5\rm W^{iii}$)	2.710(7)	2.72(4)	2.55(3)	2.91(3)	2.712(2)	2.780(2)
(5) O($5\rm W^{i}$)	O($3^{\rm iv}$)	2.675(6)	2.88(5)	3.13(3)	2.53(3)	2.697(1)	2.853(1)
(6) O($4\rm W^{i}$)	O($5\rm W^{v}$)	2.790(7)	2.92(4)	2.86(3)	2.87(3)	2.806(2)	2.933(1)

Symmetry code: (i) x, y, z; (ii) x, $-1+y$, z; (iii) x, $1+y$, z; (iv) $1-x$, $1-y$, $2-z$; (v) $3/2-x$, $1/2+y$, $2-z$.
a) Ref. 2.

Table 5. The Atomic Movements from the Monomer of AC2 to the Photodimer Component in ACDR12 (A) and Those of the Photodimer Component from ACDR12 to ACD4 (B) and the Net Atomic Movements from AC2 to ACD4 (C)

	(A) AC2 → Photodimer Component				(B) Photodimer Component → ACD4				(C) AC2 → ACD4
atom	$s\vert\Delta x\vert$/Å	$s\vert\Delta y\vert$/Å	$s\vert\Delta z\vert$/Å	d/Å	$s\vert\Delta x\vert$/Å	$s\vert\Delta y\vert$/Å	$s\vert\Delta z\vert$/Å	d/Å	d/Å
O(1)	−0.03	−0.32	−0.15	0.347	+0.11	−0.12	−0.19	0.270	0.541
O(2)	0.00	−0.35	−0.11	0.365	−0.07	−0.15	−0.24	0.275	0.601
O(3)	−0.01	−0.06	−0.44	0.448	+0.06	0.00	−0.46	0.449	0.893
O(4W)	−0.10	−0.32	+0.07	0.352	+0.18	−0.05	−0.45	0.531	0.554
O(5W)	+0.03	+0.29	+0.15	0.323	+0.17	+0.06	−0.36	0.445	0.447
N(1)	−0.12	+0.33	−0.28	0.470	+0.01	+0.13	−0.20	0.235	0.695
C(1)	+0.08	−0.03	+0.31	0.297	+0.08	−0.04	−0.01	0.091	0.305
C(2)	+0.09	+0.02	+0.33	0.315	+0.17	+0.02	+0.05	0.163	0.400
C(3)	+0.30	−0.27	+0.15	0.403	+0.21	+0.01	−0.06	0.229	0.788
C(4)	+0.39	−0.39	0.00	0.554	+0.24	−0.15	−0.29	0.449	0.937
C(5)	+0.31	+0.41	−0.14	0.557	+0.21	+0.14	−0.26	0.401	0.919
C(6)	+0.16	+0.23	+0.01	0.283	+0.13	0.00	−0.12	0.205	0.417
C(7)	−0.18	−0.24	−0.52	0.637	−0.03	−0.25	−0.22	0.338	0.953
C(8)	−0.40	−0.52	−0.43	0.840	−0.05	−0.15	−0.18	0.250	1.081
C(9)	−0.04	−0.36	−0.16	0.388	+0.15	−0.15	−0.24	0.342	0.667
C(10)	+0.04	+0.10	−0.40	0.427	+0.02	+0.06	−0.22	0.221	0.631
C(11)	+0.04	−0.12	−0.09	0.149	+0.11	+0.08	−0.28	0.284	0.364

dimensions of ACDR12 to those of AC2. In the second part the geometries are substantially the same as those in ACD4 in spite of the significantly shorter a axis and longer c axis of ACDR12 compared with those of ACD4. This indicates that the photodimer components can fit into the lattice of ACDR12 by some modifications of the molecular arrangements and molecular conformations from those in ACD4. In the third part the hydrogen bonds (1), (4), and (5) in Table 4 are too short or too long. Thus, the hydrogen bonds along the b axis and those around an inversion center at (1/2, 1/2, 1) are not preferable [Fig. 4(a)]. On the other hand, the length of the hydrogen bond (6) is comparable to those found in AC2 and ACD4.

The Atomic Movements Accompanied by the Photodimerization. The photodimer component in ACDR12 viewed along the b axis is shown in Fig. 5 by superimposing the molecules in AC2 and ACD4. It can be seen that the movement accompanied by the dimerization is smaller for ACDR12 than ACD4.

In order to clarify the meaning of this phenomenon, (A) the atomic movements d's from AC2 to the photodimer component in ACDR12 and (B) those of the photodimer component from ACDR12 to ACD4 are compared in Table 5. The atomic movements along respective crystal axes, $\Delta x_{(\rm i)}$, $\Delta y_{(\rm i)}$, and $\Delta z_{(\rm i)}$ for (A) are estimated by $\Delta x_{(\rm i)}=(x_{(\rm i)\rm D}-0.5)a_{\rm D}-(x_{(\rm i)\rm M}-0.5)a_{\rm M}$, $\Delta y_{(\rm i)}=(y_{(\rm i)\rm D}-0.5)b_{\rm D}-(y_{(\rm i)\rm M}-0.5)b_{\rm M}$ and $\Delta z_{(\rm i)}=(z_{(\rm i)\rm D}-0.5)c_{\rm D}-(z_{(\rm i)\rm M}-0.5)c_{\rm M}$, respectively, where $x_{(\rm i)}$, $y_{(\rm i)}$, and $z_{(\rm i)}$ are the fractional atomic coordinates. The subscript D refers to the photodimer component of ACDR12 and M the monomer component of AC2. The plus sign is attached to $|\Delta x_{(\rm i)}|$, $|\Delta y_{(\rm i)}|$, and $|\Delta z_{(\rm i)}|$ to indicate a departure of the atoms from the inversion center at (1/2, 1/2, 1/2) and the minus sign to indicate an approach of the atoms to it. The resulting values are listed in columns of $s|\Delta x|$, $s|\Delta y|$, and $s|\Delta z|$ in Table 5. $\Delta x_{(\rm i)}$, $\Delta y_{(\rm i)}$, and $\Delta z_{(\rm i)}$ for (B) are estimated by the similar way. The d's from AC2 to ACD4 are also listed in Table 5.

$s|\Delta x|$ for most of the atoms in (B) take positive sign, corresponding to the lengthening of a of ACD4. The $s|\Delta y|$ of O(2) and N(1), and O(4W) and O(5W) are cancelled out with each other in both (A) and (B) to maintain the lengths of the hydrogen bonds along b. It is noted that in (A) the $s|\Delta y|$ of O(4W) and O(5W) are large but take different sign with each other, and their d's are fairly small. This means that the O(4W) approaches towards the inversion center and O(5W) departs from the inversion center by almost the same distances keeping their relative distance in nearly constant. This explain why and how the hydrogen bonds involving the water molecules can be held during the reaction of AC2 to ACDR12. The $s|\Delta z|$ for most of the atoms in (B) take minus sign, corresponding to the shortening of c of ACD4. The d's of O(4W) and O(5W) in (B), especially $s|\Delta z|$ are fairly large negative. This means that the water molecules linked by the hydrogen bond are transferred towards the same direction to keep the hydrogen bond between them in the course of the change from ACDR12 to ACD4. The d's in (B) for the other atoms still amount to 0.09—0.45 Å. This fact indicates that there is a small but significant difference in the molecular arrangements of the photodimer components in ACDR12 and ACD4, because the photodimer components in ACDR12 are arranged in the crystal with similar cell dimension to AC2 rather than to ACD4. Thus direct information on the atomic movements has been derived from the analysis of the structure of the intermediate stage of the reaction.

Based on the analysis described above, the most probable arrangements of the components in the third part can be constructed as shown in Fig. 4(b). The same components are stacked along the b axis and arranged along the c axis. The monomer and photodimer components are arranged side by side in the direction of the a axis. The hydrogen bond (6) involving the water molecules links the monomer and photodimer components around the two-fold screw axis at (x=3/4, z=1) of the original unit cell. In this way, the water molecules play a role to make the monomer and photodimer components possible to coexist in the crystal.

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