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Crystal Chemistry of Photodimers of 2-Benzyl-5-benzylidenecyclopentanone

Kazumasa Honda

Institute for Materials and Chemical Process,
National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565

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The crystal structure of the photodimer of 2-benzyl-5-benzylidenecyclopentanone was determined using a recrystallized crystal. It was identical to that of an as-photoirradiated dimer crystal obtained by a single-crystal-to-single-crystal photoreaction of the monomer. This suggests that the starting material already possesses the most favored crystal phase for the products.

Single crystals of 2-benzyl-5-benzylidenecyclopentanone (BBCP) undergo a single-crystal-to-single-crystal (SCSC) reaction when irradiated with UV light, yielding a photodimer (Chart 1).[1] This reaction obeys a very precise and constant pseudo-first order kinetics until the conversion is fully achieved.[2–4] The packing motif of the dimerized BBCP crystal is quite similar to that of the starting monomer crystal,[1] suggesting that the dimer is formed and packed under topochemical control of the monomer lattice. It is of interest to investigate why the dimer molecules are stably packed under the crystal phase. It is not certain that the monomer lattice will be the phase most favorable to the dimer molecule itself. We therefore prepared crystals of the dimer by recrystallization from organic solvents, which should allow the molecules to pack in the most stable manner. The structure of the recrystallized dimer crystal was compared with that of the as-photoirradiated dimer crystal.

Figure 1 illustrates an ORTEP[5] drawing of the photodimer in the recrystallized crystal. Selected bond distances and angles are listed in Table 1. The molecule has its center of mass on the crystallographic inversion center (0, 0.5, 0), on which two monomer molecules were related to each other before the photodimerization reaction. C(5) and C(13) atoms form a cyclobutane ring accompanied by the symmetry-related C(5)* and C(13)* atoms ($-x$, $1-y$, $-z$). One of the phenyl rings (C(7), C(8), C(9), C(10), C(11), and C(12)) seems to be disordered. The equivalent isotropic temperature factors for C(9), C(10), and C(11) atoms (8.83(9), 9.9(1), and 9.5(1) e Å^{-3}, respectively) are considerably larger than those of C(7), C(8), and C(12) atoms (5.16(4), 6.33(6), and 7.09(7) e Å^{-3}, respectively). Another attempt to analyze the structure of the crystal obtained from another batch of recrystallizations gave quite similar results. A high thermal motion and disorder of the phenyl ring were also suggested for the as-photodimerized molecule.[1]

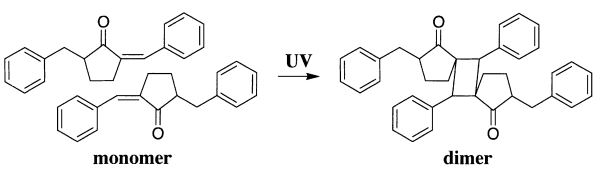

Chart 1.

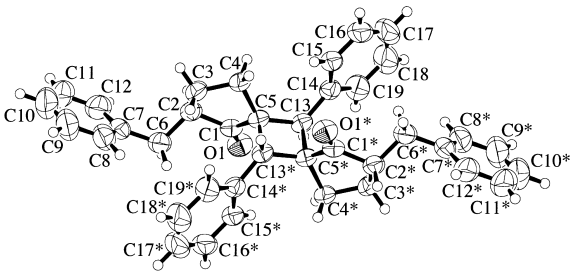

Fig. 1. Molecular structure of the BBCP photodimer. Thermal ellipsoids are drawn at 50% probability level. Symmetry code; (*) $-x$, $1-y$, $-z$.

Table 1. Selected Geometric Parameters (Å, °) for the BBCP Photodimer

Bond distances			
O(1)–C(1)	1.208(2)	C(1)–C(2)	1.525(2)
C(1)–C(5)	1.520(2)	C(2)–C(3)	1.534(3)
C(2)–C(6)	1.529(3)	C(3)–C(4)	1.532(3)
C(4)–C(5)	1.532(2)	C(5)–C(13)	1.550(2)
C(5)–C(13)^{i}	1.586(2)	C(6)–C(7)	1.495(3)
C(13)–C(14)	1.502(2)		
Bond angles			
O(1)–C(1)–C(2)	124.6(2)	O(1)–C(1)–C(5)	125.8(2)
C(2)–C(1)–C(5)	109.6(1)	C(1)–C(2)–C(3)	103.5(1)
C(1)–C(2)–C(6)	111.4(1)	C(3)–C(2)–C(6)	117.2(2)
C(2)–C(3)–C(4)	104.5(2)	C(3)–C(4)–C(5)	102.8(1)
C(1)–C(5)–C(4)	101.2(1)	C(1)–C(5)–C(13)	113.3(1)
C(1)–C(5)–C(13)^{i}	114.2(1)	C(4)–C(5)–C(13)	125.3(1)
C(4)–C(5)–C(13)^{i}	113.5(1)	C(13)–C(5)–C(13)^{i}	89.9(1)
C(2)–C(6)–C(7)	114.3(2)	C(5)–C(13)–C(5)^{i}	90.1(1)
C(5)–C(13)–C(14)	122.9(1)	C(5)^{i}–C(13)–C(14)	120.4(1)

Symmetry code; (*i*) $-x$, $1-y$, $-z$

The crystal structure of the recrystallized dimer is almost identical to that of the previously reported as-photodimerized crystal.[1] The lattice constants of the former (a = 31.404(3), b = 10.760(2), c = 8.654(1) Å; U = 2924.4(6) Å^3) are slightly different from those of the latter (a = 31.332(2), b = 10.785(1), c = 8.6329(7) Å; U = 2917.1(4) Å^3) but the two sets can be regarded as almost isomorphous. The space group *Pbca* is the same and the packing motifs are similar to each other. Differences of the atomic positions of the recrystallized dimer from the as-photoirradiated dimer are almost negligible in consideration of the disorder of the phenyl ring (maximum

0.12 Å for C(8)). These results mean that the as-photodimerized crystal, having a crystal structure similar to that of the recrystallized one, adopts the most stable crystal phase for the dimer molecules. As mentioned above, the as-photodimerized crystal is yielded under a topochemical control of the monomer lattice. In other words, the crystal structure of the starting material already possesses the most favored packing mode for the product molecules. Therefore the BBCP photoreaction proceeds quantitatively with very slight loss of the crystal integrity, yielding a stable dimer crystal.[3] This 'smooth' reaction feature is quite unique compared with other SCSC photodimerization reactions.

On the SCSC photodimerization reaction of a styrylpyrilium salt,[6] the as-photoirradiated dimer crystal and the recrystallized one adopt completely different crystal forms. The former is a meta-stable form. A dimensional mismatch between the reactant monomer and product dimer lattices is significant. The single-crystalline nature is destroyed during the photoreaction when the crystal is irradiated with wavelengths in the range of the absorption maximum of the reactant molecule; the reaction takes place only at the incident surface, producing a large strain to the crystal. This is similar to a photodimerization reaction of cinnamic acid crystal,[7] although no recrystallized form of its photodimer has yet been investigated.

In previous work, we observed by a spectroscopic study that the BBCP monomers form a dimeric conjugate in a solution when the concentration is high.[8] It is speculated that, on crystallization, the BBCP monomers form a dimer-like pair and thus adopt a similar packing arrangement to that of the dimer molecules.

Experimental

Synthesis of the BBCP dimer was already reported precisely.[8] Isostructural crystals were obtained by slow evaporation from chloroform-methanol and ethyl acetate solutions. The single crystal with dimensions of $0.45 \times 0.20 \times 0.08$ mm^3 from the former solution was used for the structure analysis. Cell parameters were determined on a Bruker-Nonius CAD4 diffractometer with a monochromated Mo $K\alpha_1$ radiation (λ =0.70930 Å). This diffractometer gives a good $K\alpha_1$-$K\alpha_2$ resolution and has been used for determining the cell parameters for the monomer[3] and as-photodimerized crystals. Diffraction intensities were collected on a Rigaku AFC7R diffractometer with a monochromated Mo $K\alpha$ radiation (λ = 0.7107 Å) from a rotating anode source. $C_{38}H_{36}O_2$, MW = 524.70, T = 298 K; orthorhombic space group *Pbca*, a = 31.404(3), b = 10.760(2), c = 8.654(1) Å, U = 2924.4(6) Å^3, Z = 4, D_c = 1.192 g cm^{-3}, μ = 0.072 mm^{-1}, $F(000)$ = 1120. Of the 3729 reflections, 3359 were unique (R_{int} = 0.012). Reflection data were corrected for Lorenz and polarization effects and an empirical absorption correction using ψ-scan was applied (transmission factors raging from 0.924 to 0.994). The structure was solved by a direct method (SIR92[9]). Final $R1$ = 0.0434 for 1830 reflections with $F^2 > 2\sigma(F^2)$ and $wR2$ = 0.0907 for all reflections (253 parameters). All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located in difference Fourier maps and refined isotropically. Refinements were carried out by a full-matrix least squares method based on F^2. All the calculations were performed using teXsan crystallographic software package.[10] Crystallographic data are deposited as Document No. 75047 at the Office of the Editor of Bull. Chem. Soc. Jpn. They have also been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 191153.

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