

# Kinetic and Mechanistic Study on Single-Crystal-to-Single-Crystal Photodimerization of 2-Benzyl-5-benzylidenecyclopentanone Utilizing X-ray Diffraction

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Received April 27, 1999. Revised Manuscript Received June 30, 1999

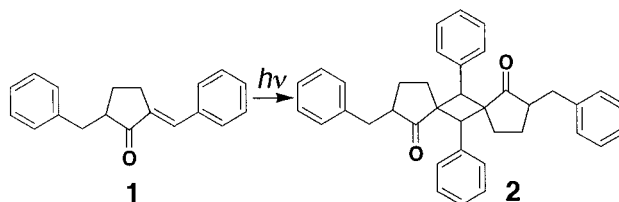
**Abstract:** The single-crystal-to-single-crystal photodimerization reaction of 2-benzyl-5-benzylidenecyclopentanone was studied in situ using X-ray diffraction. It was found that the degree of monomer conversion could be precisely measured from the change in X-ray diffraction intensities, leading to the determination of a rate constant. The rate constant was found to increase linearly as the temperature increased to  $\sim 200$  K, yielding an activation of  $\sim 13$  kJ mol<sup>-1</sup>. Above this threshold temperature, the rate constant was found to decrease. Structure analyses of the monomer crystal at various temperatures revealed that below 200 K the intermolecular distance of two reactive olefin groups in adjacent molecules remained at a constant 4.15 Å, yet this distance expanded above 200 K. The thermal parameters of the olefin carbon atoms increased linearly over the temperature range 132–324 K. These results suggest that the reaction is dominated by thermal vibration of the lattice below the threshold temperature while above it the reaction is likely to be dependent on the expanding intermolecular carbon–carbon distance. This is the first quantitative study of such a solid-state reaction.

## Introduction

Solid-state chemical reactions have attracted much attention as “clean” solvent-free reaction systems.<sup>1</sup> The high potential for molecular engineering applications has also been of great interest.<sup>2</sup> A special category of such reactions are the so-called single-crystal-to-single-crystal (SCSC) systems, where single-crystal integrity is maintained throughout the reaction. Such model reaction systems are rare, yet nonetheless extremely important in understanding the underlying mechanism of general solid-state reactions. Their very nature presents the closest analogy to solution chemistry in that the progress of the reaction is not diminished by the breakdown of the crystals lattice, observed in all other solid-state reactions. This fact presents the possibility of a thorough kinetic study of the progress of a solid-state reaction and the extraction of important mechanistic information.

Single crystals of 2-benzyl-5-benzylidenecyclopentanone (BBCP, **1**) undergo such a SCSC reaction when irradiated with UV light, yielding the dimer **2**<sup>3</sup> (Scheme 1). In a previous communication, we demonstrated that diffracted X-ray intensities from a BBCP crystal during its SCSC photoreaction could provide the precise monomer/dimer composition at any time during the reaction,<sup>4</sup> allowing the reaction kinetics to be analyzed. The reaction obeys first-order kinetics over a wide temperature range and is proportional to the incident UV photon flux, indicating the photoreaction to be a one-photon process.

## Scheme 1



The rate constant showed an Arrhenius type decrease at temperatures under  $\sim 173$  K and the activation energy estimated by an Arrhenius-type plot was 13.2 kJ mol<sup>-1</sup>. In this study, the diffraction technique was extended to include X-ray structure analysis of a BBCP monomer crystal at temperatures ranging from 132 to 324 K. This served to clarify the temperature dependence of the reaction rate as regards the bulk crystal structure. In addition, chromatographic analysis was used as an independent check to confirm the accuracy of the monomer/dimer composition as determined by X-ray diffraction.

## Results and Discussion

**Selection of Wavelength.** The He–Cd laser emits two major lines at 325 and 442 nm. In this study, the 325-nm UV line was used. The other 442-nm line gave a slight conversion of  $\sim 10\%$  after 3 h of irradiation. It has been suggested that irradiation at a low absorption tail far from the absorption maximum induces SCSC photoreaction homogeneously throughout the entire volume of the crystal.<sup>5</sup> Although 325-nm light is not at the “absorption-tail” in reference to the absorption

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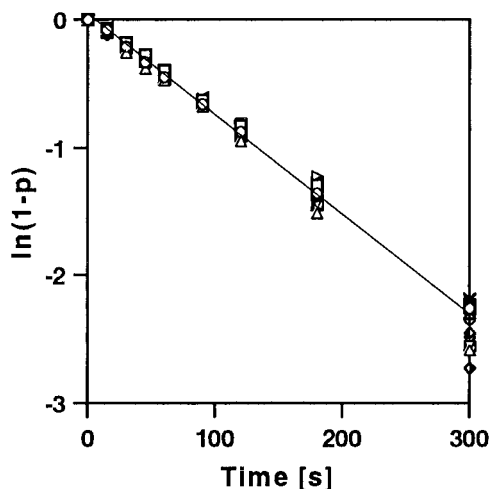
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**Figure 1.** Semilog plot of the  $1 - p(t)$ , mole fraction of the monomer molecules, against total UV irradiation time for 16 reflections. The solid line indicates the linear calibration curve for the weighted average  $[\ln(w(1 - p))]$  for the sixteen  $\ln(1 - p(t))$  values.

spectrum of the BBCP in solid state,<sup>6</sup> the reaction occurs quickly and very smoothly. The fully dimerized crystal, with the mosaicity increased, is stable over 15 months when kept in a dark environment.

**Estimation of Mole Fraction of the Dimer from Diffraction Intensities.** As previously reported,<sup>4</sup> the intensity of any reflection  $I(t)$  after irradiation time  $t$  can be expressed by

$$I(t) = (1 - p(t))I_m + p(t)I_d \quad (1)$$

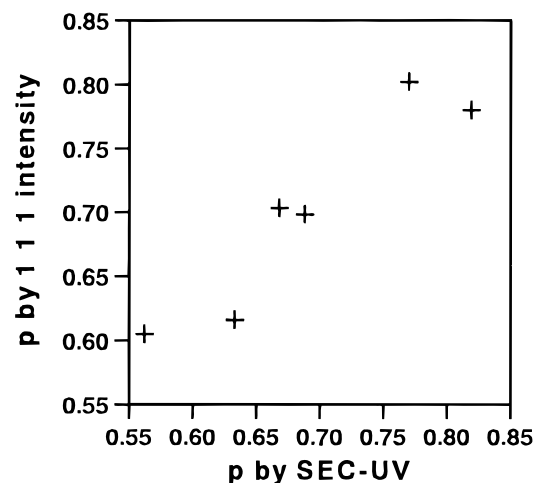
where  $I_d$  and  $I_m$  are the intensity of that reflection in the pure dimer and pure monomer crystal, respectively. Often these intensities are quite different, yet since the variation in the unit cell parameters between a pure BBCP monomer crystal and a pure dimer crystal is very small (much less than 1%<sup>3,4</sup>) the Bragg angle remains almost constant. For the X-ray diffraction experiment, the crystal can be modeled as a mixed crystal with monomer and dimer components;  $I(t)$  changes as the mole fraction of dimer,  $p(t)$ , increases.

This scheme should be general and applicable to other SCSC reactions. The composition of the dimer in the crystal at any time during the reaction is then given by

$$p(t) = \frac{I(t) - I_m}{I_d - I_m} \quad (2)$$

Experimentally,  $I_m$  is substituted by the intensity before the UV irradiation ( $t = 0$ ) and  $I_d$  by the intensity after the reaction is completed.

To determine kinetic parameters, a mean for  $(1 - p(t))$  at regular irradiation time intervals was calculated from the change in intensities of 16 selected reflections, which showed large intensity differences between  $I_m$  and  $I_d$ . The mean value was weighted by the standard deviations of the diffraction intensities of these reflections. Figure 1 represents a semilog plot of the  $(1 - p(t))$  value for the 16 reflections against the irradiation time. The solid line indicates the linear calibration curve for their weighted average. The plot of each of the 16 reflections was linear, thus demonstrating that the reaction obeys first-order kinetics. Furthermore, the rate constant,  $k$ , is given by the slope. It is found that certain reflections tend to show slow decay and



**Figure 2.** Correlation of the dimer mole fraction estimated by the SEC/UV analysis and the  $p$  value calculated from eq 3.

certain reflections showed fast decay in each crystal, although the deviation of the rate constants was small. For example, the rate constant obtained from the  $p(t)$  values of the 1 5 2 reflection was always slightly large and that from the 0 2 1 reflection was always slightly small. We think that this may represent a property of the photoreaction. In other words, the photodimerization has anisotropy. The crystal perturbation along the [1 5 2] direction proceeds earlier and that along the [0 2 1] direction follows later. Among the 16 reflections it was found that the 1 1 1 reflection intensity showed the typical  $p(t)$  values for all the examined crystals and therefore the rate constant obtained by the  $p(t)$  value of the 1 1 1 reflection, abbreviated to  $p(111)$  hereafter, is used for further discussion.

**Chromatographic Determination of Mole Fraction of the Dimer in a BBCP Crystal.** It is important to confirm that the dimerization factor  $p(t)$  estimated by the present diffraction method agrees with that obtained by other established analyses. During the photodimerization experiments of BBCP crystals, we found that the ratio of the monomer intensity  $I_m$  to the dimer intensity  $I_d$  was almost constant for every crystal. Thus eq 2 can be transformed to:

$$p(t) = [I(t) - I_m/I_d]/[1 - I_m/I_d]$$

and then

$$p(t) = [I(t) - C]/[1 - C] \quad (3)$$

where

$$C = I_m/I_d \approx \text{constant} \quad (4)$$

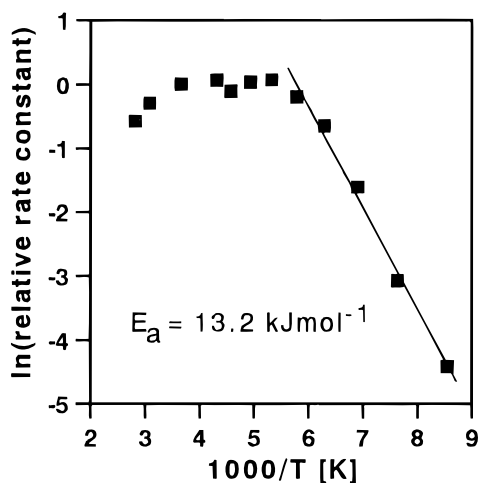
For example, the  $C$  for the 1 1 1 reflection is 8.8. Hence, from eq 3, we can estimate the  $p(t)$  values of partially dimerized BBCP crystals without obtaining the  $I_d$  values. Six partially dimerized crystals were prepared and their  $p(111)$  values determined in this way. The dimer mole fraction of these crystals was then estimated by a size exclusion chromatography (SEC) analysis. As seen in Figure 2, good agreement between the two techniques was found. Hence the  $p(t)$  value obtained by the diffraction intensity can be confidently treated as a measure of the dimer molecule composition in the photoirradiated BBCP crystal.

**Reaction Rate Dependence on Temperature.** Figure 3 shows a plot of  $\ln(k)$  vs  $1/T$ . Some data points from our previous report have been reexamined. The results are similar, but our

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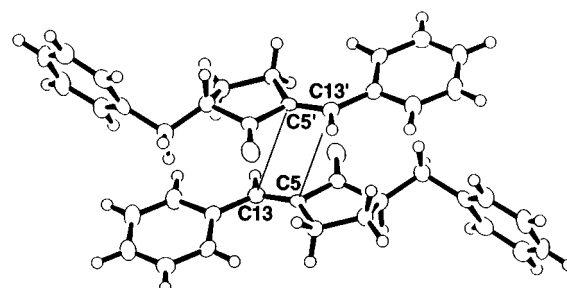
**Table 1.** Crystal and Experimental Data

	temp/K							
	132	175	190	204	219	250	273	324
crystal data								
chemical formula	C <sub>19</sub> H <sub>18</sub> O							
formula wt	262.35							
crystal system	orthorhombic							
space group	<i>Pbca</i>							
crystal description	colorless transparent plate							
<i>a</i> /Å	31.235(4)	31.263(4)	31.276(3)	31.284(2)	31.292(2)	31.317(2)	31.333(2)	31.378(2)
<i>b</i> /Å	10.637(1)	10.668(1)	10.687(1)	10.702(1)	10.714(1)	10.747(1)	10.771(1)	10.839(1)
<i>c</i> /Å	8.579(3)	8.604(4)	8.620(3)	8.629(2)	8.637(2)	8.660(2)	8.677(2)	8.714(2)
<i>V</i> /Å <sup>3</sup>	2850(1)	2870(1)	2881(1)	2889.1(7)	2896.0(7)	2914.7(7)	2928.6(7)	2963.5(7)
<i>Z</i>	8							
refinement								
no. of reflns used	1543	1445	1412	1344	1399	1335	1522	1375
<i>R</i> ( <i>F</i> )	0.063	0.067	0.075	0.081	0.068	0.078	0.061	0.061
<i>S</i>	1.16	1.06	1.22	1.31	1.22	1.22	1.41	1.38

**Figure 3.** Reaction rate dependence on temperature.

interpretation has been modified to some extent. Rate constants were estimated in the range of 354–117 K, with the value at 273 K set to 1. It can be clearly seen that  $\ln(k)$  exhibits the maximum value at  $\sim 200$  K and a marked decrease over the 173–117 K range. The activation energy estimated from the slope of the plot over this temperature range was  $13.2 \text{ kJ mol}^{-1}$ , as previously reported.<sup>4</sup> Similar values of 10.0,  $\sim 13$ , and  $15.2 \text{ kJ mol}^{-1}$  were reported for the photodimerization of acenaphthylene,<sup>7</sup> photopolymerization of *trans,trans*-2,5-distyrylpyrazine,<sup>8</sup> and photodimerization of a styrylpyrylium salt,<sup>9</sup> respectively.

The behavior of  $\ln(k)$  above 200 K is extremely interesting. It actually *decreases* over the 200–324 K temperature range. The photopolymerization of *p*-phenylenediacetic acid diethyl ester (PDAEt)<sup>10</sup> and photodimerization of cinnamic acid<sup>11</sup> have been reported to have the maximum reaction rate at ca. 253 and 293 K, respectively. For PDAEt, a threshold temperature in the activation energy has also been reported;<sup>12</sup> the activation energy is nearly zero between 4.2 and 90 K, whereas it is  $7 \text{ kJ mol}^{-1}$  between 100 and 170 K. Such transition in the temper-

**Figure 4.** An ORTEP<sup>20</sup> drawing of the molecular configuration of the BBCP monomers in the crystal at 132 K. Displacement ellipsoids are drawn at the 50% probability level.

ature dependence of the reactions kinetics is attributed to the change in the crystal lattice rigidity,<sup>11</sup> although no quantitative explanation has been examined in connection with a crystal structure analysis.

In this study, the cell parameters *a*, *b*, *c*, and *V* of the BBCP crystals shrink linearly without any inflection point as the temperature decreases from 354 to 117 K. No superlattice was detected. The orthorhombic *Pbca* space group was maintained under the threshold temperature. In the investigated temperature region, differential scanning calorimetric (DSC) measurement showed neither heat absorption nor loss. Thus, crystal-phase transitions were not expected. This has been indicated by a Raman study as well.<sup>6</sup>

**X-ray Structure Analysis of a BBCP Crystal at Different Temperatures.** To elucidate the kinetic behavior as regards the crystal structure, a series of structure analyses of the monomer crystal at different temperatures were performed. The same crystal was used throughout the measurements. Table 1 summarizes the crystal and experimental data. The crystal structures were all isostructural and also identical with the reported structure at ambient temperature.<sup>3</sup> It was again confirmed that no phase transition occurred. Figure 4 depicts the molecular configurations of the two BBCP monomers related by the crystallographic inversion center. These two molecules dimerize by photoreaction. They face each other, thus forming a dimeric structure and the pair stacks along the *c* axis. The thin solid lines which connect the C5 $\cdots$ C13( $-x, 1-y, -z$ ) and C13 $\cdots$ C5( $-x, 1-y, -z$ ) atoms indicate that new covalent bonds are formed by the reaction. They are crystallographically equivalent and the two intermolecular distances are the same. As the reaction rate should depend on the overlap of the molecular orbitals at the two C5–C13 olefin bonds, the C5 $\cdots$ C13( $-x, 1-y, -z$ ) intermolecular distance and the temperature factors

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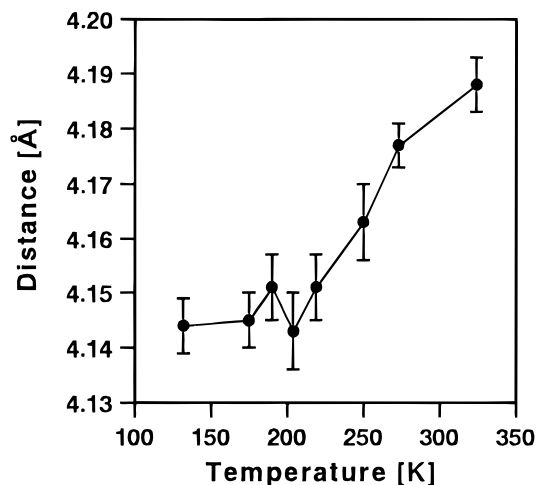


Figure 5. Change in the intermolecular  $C5 \cdots C13(-x, 1-y, -z)$  distance with temperature.

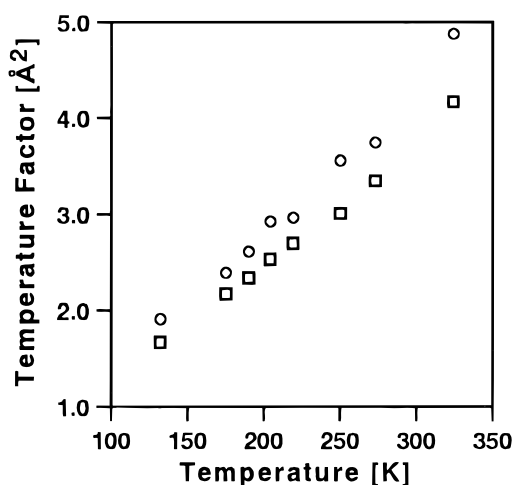


Figure 6. Change in C5 (square) and C13 (circle) equivalent isotropic temperature factors with temperature.

of those atoms must be essential parameters in the determination of the reaction rate. Figures 5 and 6 compare the  $C5 \cdots C13(-x, 1-y, -z)$  intermolecular distance and the equivalent isotropic thermal parameters of the C5 and C13 atoms in all the temperature analyses. As shown in Figure 5, the  $C5 \cdots C13(-x, 1-y, -z)$  intermolecular distance is almost constant (4.15 Å) within experimental error under 204 K and increases at higher temperatures. It should be mentioned that the change in the  $C5 \cdots C13(-x, 1-y, -z)$  intermolecular distance also has the threshold temperature of  $\sim 200$  K, similar to that observed in the reaction rate dependence on temperature. Figure 6 shows that the C5 and C13 temperature factors simply increase linearly as temperature increases. This was also the case for the lattice parameters. This suggests that the lattice thermal vibration is purely temperature dependent.

To correlate these structural observations to the reaction rate dependence on temperature, we hypothesize as follows. Below the threshold temperature of  $\sim 200$  K, the C5 and C13 atoms in the BBCP molecules locate at the most potentially stable position. Therefore, the intermolecular distances are unchanged. In this region, the reaction probability is purely proportional to the thermal vibration of the C5 and C13 atoms. Hasegawa<sup>13</sup> proposed a reaction model to explain such kinetic behavior of the topochemical reaction in olefin bonds. In general, it is

thought that the thermal vibration of organic molecules in the crystal is mainly derived from lattice vibration. Thus, the entire reaction is dependent on the lattice vibration. This conclusion is consistent with observations made by Swiatkiewicz et al.,<sup>6</sup> who reported that BBCP monomer crystal showed a strong temperature-dependent reaction rate at extremely low temperatures and also exhibited a possible electron-phonon coupling Raman spectra at 4.2 K, indicating that the photodimerization would be a phonon-assisted reaction. As a phonon can be interpreted by the lattice vibration mode, the "phonon-assisted" reaction can be said to be a reaction regulated by thermal vibration of the crystal lattice. Above the threshold temperature of  $\sim 200$  K, the thermal motions of the C5 and C13 atoms become large, such that their averaged position diverges from the potential minimum. The intermolecular distances are thus gradually expanded, resulting in a decrease in the overlap of the molecular orbitals. This could be the reason for the slight decrease of the reaction rate in the higher temperature region.

In summary, the reaction is regulated by both the lattice thermal vibration and the intermolecular distance of the olefin bonds; the dominating factor switches at the threshold temperature of  $\sim 200$  K. It should be noted that the kinetic behavior of topochemical reactions is elucidated quantitatively for the first time by means of crystal structure analysis. The lattice vibration mode is dominant at low temperatures, that is, those at which the distance of the reactants stays at the minimum value. At high temperatures, the reaction is mainly affected by the thermally expanding intermolecular distance. Such reasoning could be applied to other organic solid-state reactions. A decrease in the reaction rate in the high-temperature region in PDAEt<sup>10</sup> and cinnamic acid<sup>11</sup> crystals would occur in the region where the displacement of the reactants is dominant.

Our argument has focused on the structure analysis of molecules in the ground state. It has been suggested that the driving force of solid-state photoreactions is molecular rearrangement in the excited state.<sup>14</sup> Thus the reaction rate should, in some part, be a function of the efficiency of the excitation and relaxation processes, which in turn may show some temperature dependence. To probe this relationship we plan to make transient absorption spectra measurements with the use of a femtosecond laser pulse.<sup>15</sup>

## Conclusions

The reaction rate constant of BBCP photodimerization exhibited a maximum value at  $\sim 200$  K and an Arrhenius-type decrease under this threshold temperature. Contrary to expectations based on general knowledge of chemical reactions, the rate constant was slightly reduced at higher temperatures. The intermolecular distance of two reacting carbon atoms, C5 and C13( $-x, 1-y, -z$ ), was found to be constant under the threshold temperature of  $\sim 200$  K. Above  $\sim 200$  K, the intermolecular distance expanded as the temperature increased. No apparent crystal phase transition was observed around the threshold temperature. We suggest that this "weak" structural change in the monomer crystal is strongly related to the unique temperature dependence on the reaction rate. In a further study, we will investigate the origin of the structural dependence on temperature. The two reacting monomers face each other,

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forming a dimeric structure, as seen in Figure 4. Close C $\cdots$ H intermolecular contacts are observed between the aromatic carbon atoms C14, C15, C16, C17, C18, and C19 and the aliphatic hydrogen atom H7(-x, 1 - y, -z) (3.03(4), 3.15(4), 3.31(4), 3.36(4), 3.23(4), and 3.08(4) Å, respectively at 132 K). This suggests that the two molecules are weakly bound by CH/ $\pi$  interactions.<sup>16</sup> Another weak intermolecular interaction, the  $\pi$ - $\pi$  interaction, could be considered as existing between the C5-C13 olefin bonds. The contribution of these weak intermolecular interactions to the crystal structure is now under quantitative evaluation by computational methods.

## Experimental Section

**Preparation.** BBCP was synthesized according to the method suggested in the literature<sup>17</sup> and the single crystals were prepared by slow evaporation from a methanol/chloroform solution.

**Photodimerization and Monitoring Diffraction.** The detailed protocol of the photodimerization experiment was reported in a previous paper.<sup>4</sup> A 325-nm UV line emitted from a helium-cadmium laser was introduced with an optical fiber to irradiate a BBCP crystal mounted on a Nonius CAD4 four-circle diffractometer. The crystal was rotated about the diffractometer phi axis during UV irradiation. At regular time intervals, UV irradiation was halted to allow the measurement of selected diffracted X-ray intensities. These measurements were made by an  $\omega$ -scan method. The orientation matrix was redetermined by centering 15 strong high  $2\theta$  reflections after UV irradiation, when the scanned peak intensities showed unequal left and right backgrounds. The other intensity measurements were then performed. The temperature of the system was kept at a stable value to guard against potential heat dissipation from the photoreaction and the laser irradiation. During the experiments, the crystal was mounted under a nitrogen gas stream of constant temperature, from a Nonius FR558S liquid nitrogen gas-stream cryostat.

**Chromatographic Determination of the Mole Fraction of Dimer in a BBCP Crystal.** The partially dimerized crystals were dissolved in tetrahydrofuran and applied to a SEC analysis with the use of two Tosoh TSK-gel G3000XL columns (7.8 mm i.d.  $\times$  300 mm) and tetrahydrofuran as an eluent. The separated and eluted dimer and monomer molecules were detected by a Shimadzu SPD-2A spectrophotometer with the detection wavelength set to 265 nm. The mole fraction of the dimer was estimated from the ratio of the dimer peak area to the monomer peak area with the use of a calibration curve, obtained by plotting the peak ratio of several mixtures of authentic monomer and dimer solutions.

**DSC Analysis.** DSC measurement was performed with a Seiko DSC 220C system. In an aluminum pan, 10 mg of the BBCP powder was heated under a nitrogen gas stream in the range of 130-370 K at an increasing rate of 5 deg min<sup>-1</sup>.

**Reaction Rate Dependence on Temperature.** To overcome the nonuniformity of the reaction rate between two individual crystals, experiments were performed at different temperatures for the *same* crystal. For the first crystal, the reaction rate was determined at a constant temperature,  $T_1$ , until the reaction was estimated to be  $\sim$ 30% complete. The temperature was then cooled to  $T_2$  and the reaction rate

was determined over the  $\sim$ 30-60% conversion range. The temperature was cooled again to  $T_3$ , and the reaction rate was determined over the final  $\sim$ 60-100% conversion range. The same experiment was then performed for the next crystal but the starting temperature was set at  $T_3$  and cooling temperatures at  $T_4$  and  $T_5$ . The ratio between the two values of the rate at  $T_3$  was then used to determine the rates at  $T_4$  and  $T_5$  relative to  $T_1$ . This procedure was repeated for a total of 10 crystals over a temperature range of 354-117 K at 15-30 deg decrements. The relative rate at 117 K to 273 K estimated by this procedure matched well with the value obtained by directly taking the ratio of the rates at 117 K to 273 K in another crystal. The temperature of the crystal was estimated by placing a very fine copper-constantan thermocouple at the crystal position.

**X-ray Structure Analysis of a BBCP Crystal at Different Temperatures.** The crystal data and experimental data are summarized in Table 1. All the measurements were carried out with a Nonius CAD4 diffractometer with a Nonius FR558S liquid nitrogen gas-stream cryostat. The same BBCP crystal with a dimension of 0.50  $\times$  0.37  $\times$  0.32 mm<sup>3</sup> was used throughout the analysis. The crystal was fixed on the tip of a broken glass capillary with silicon oil for the measurements at 132, 175, 140, 204, 219, and 250 K. The intensities were corrected for absorption using the  $\psi$ -scan method. The crystal was then mounted on a glass fiber for 273 and 324 K measurements. No absorption correction was made for the data. The Lorentz and polarization correction were applied to all of the data. Three standard reflections measured at a constant interval showed slight decay of 2.5 and 3.1% for 132 and 324 K data, respectively. Linear decay corrections were then applied. The other measurements showed no significant decrease in the standard reflections. The structures were solved by a direct method (SHELXS86)<sup>18</sup> and refined by a full-matrix least-squares method on  $F$  using the program TEXSAN.<sup>19</sup> All the hydrogen atoms were located from difference Fourier maps and refined isotropically. Anisotropic thermal parameters were assumed for all of the non-hydrogen atoms. Atomic scattering factors were taken from the *International Tables for X-ray Crystallography*, 1992, Vol. C.

**Acknowledgment.** The authors thank Dr. W. Jones and Prof. K. Tokumaru for many helpful comments. They are also grateful to Drs. K. Kato, S. Kinugasa and M. Shibakami for technical advice and help in the laser, SEC, and DSC measurements, respectively. Funding from the Royal Society, New Energy and Industrial Technology Development Organization, and Agency of Industrial Science and Technology is appreciated.

**Supporting Information Available:** Tables of crystal data and experimental details as well as fractional atomic coordinates and equivalent isotropic displacement parameters (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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