

## In situ Observation of Molecular Swapping in a Crystal by X-ray Analysis

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X-ray diffraction analysis elucidated that a pair of hexaarylbiimidazoles was transformed to a complex composed of two lophyl radicals and a piezodimer on irradiation at low temperatures. The piezodimer, the existence of which has been assumed spectroscopically as an unstable isomer, was produced via molecular swapping of two photo-induced lophyl radicals with drastic conformational change. The black crystal reverted to the original structure on warming to 25 °C.

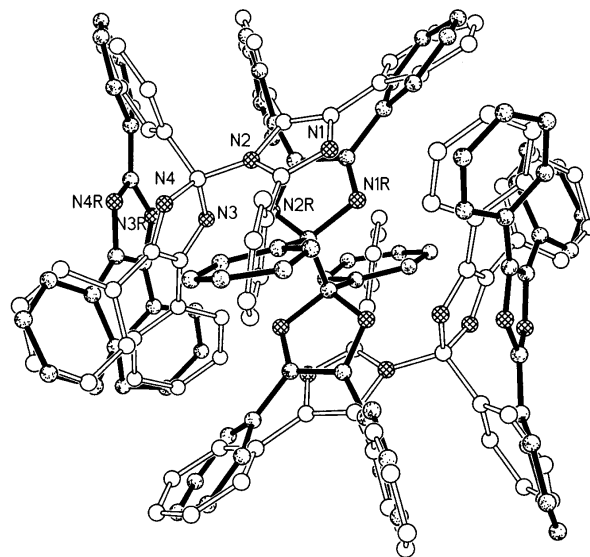
Since Schmidt and Cohen started systematic analysis of the photodimerization of cinnamic acids in crystals almost four decades ago,<sup>1</sup> the solid-state organic reactions have been extensively investigated from various aspects.<sup>2</sup> Spectroscopic methods have been playing an important role in analyzing the transient unstable species.<sup>3</sup> We have extensively studied a variety of reactions in organic and organometallic crystals with retaining single crystal form, which are called crystalline-state reactions.<sup>4</sup> The structural change in the process of crystalline-state reaction can be observed directly by X-ray analysis.

Although such in situ observations are very informative to make clear the reaction mechanism, there are many experimental difficulties when we intend to observe unstable or metastable species produced in organic crystals. In the previous paper we reported the observation of the metastable photochromic species using two-photon excitation.<sup>5</sup> If the molecular motion was somewhat large during the reaction, the cryotrapping method, which has been utilized in a variety of physicochemical measurements, was very effective to keep the crystallinity.<sup>6,7</sup> Even if the product content was less than 10% in a crystal, the product structure was successfully distinguished from the original one.<sup>8</sup>

The hexaarylbiimidazole (HABI) derivatives, which are well-known as photo/thermo/piezo-chromic materials, have been used as polymerization initiators in industry and therefore have been investigated spectroscopically<sup>9,10</sup> since Maeda and Hayashi prepared them.<sup>11</sup> It has been proposed that the photolysis of the HABI derivative in benzene instantaneously produces a pair of lophyl radicals. This lophyl radical has been proposed to be an initiator for the radical polymerization. In the previous paper the photo-produced radical pair of the *o*-Cl-HABI derivative was successfully observed by X-rays using the cryotrapping method.<sup>6</sup> When HABI was used as the mother compound, unexpected intermediates were observed. Here we report the in situ observation of photo-induced unstable intermediates derived from HABI in a crystal using the cryotrapping method.

Before irradiation the crystal structure of HABI (1,2'-dimer) was determined at 108 K by X-ray diffraction.<sup>12</sup> The bond distances and angles of HABI were identical to those of *o*-Cl-HABI within experimental errors. The C–N bond distance

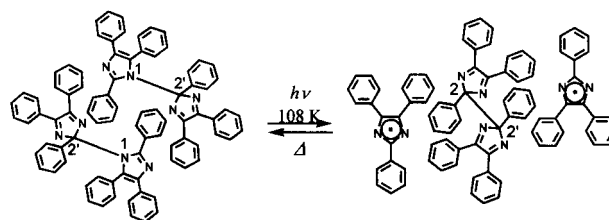
(1.482(2) Å) connecting two imidazolyl groups coincided with that of *o*-Cl-HABI.<sup>13</sup> The shortest intermolecular distance (4.32 Å) among non-hydrogen atoms was more than the sum of van der Waals radii.



**Figure 1.** Disordered structures of 1,2'-dimers and photo-products after irradiation. Open lines indicate two 1,2'-dimers of HABI. Solid lines indicate photoproducts of planar lophyl radicals and a 2,2'-dimer.

A pale yellow crystal of HABI was irradiated at low temperatures under 108 K with a high-pressure mercury lamp for 30 min. The disordered molecular structures of 1,2'-dimers (open line) and photoproducts (solid line) are depicted in Figure 1.<sup>14</sup> The space group ( $P\bar{1}$ ) was retained after irradiation. The structure of the photoproduct clearly indicated the progress of reaction (Scheme 1). Two C–N bonds connecting two imida-

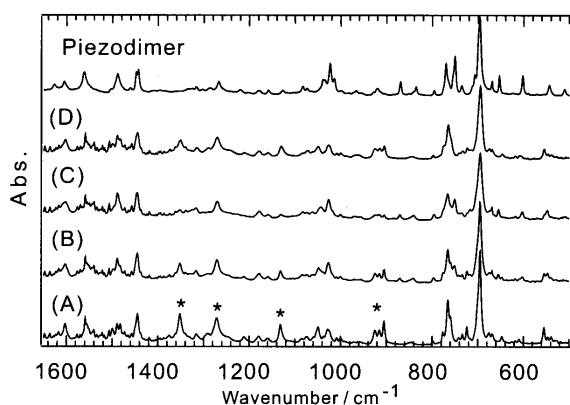
### Scheme 1.



zolyl groups in two inversion-center-related 1,2'-dimers were cleaved on irradiation to produce two planar lophyl radicals and a 2,2'-dimer in 13.9(2)% yields in a unit cell. Two imidazolyl rings with a 6 $\pi$ -electron system in two 1,2'-dimers moved inward (by max 1.69 Å) to form a bridging C–C bond of 2,2'-

dimer. This was accompanied with drastic conformational changes of one of phenyl rings (the central one in Figure 1 was rotated by 60°). The intermolecular distance between the bridging carbon atoms before irradiation was 4.87 Å. Two other imidazolyl rings with a 4 $\pi$ -electron system moved outward (by max 1.86 Å) to form two planar lophyl radicals sandwiching the 2,2'-dimer. On warming to 25 °C, the black crystal returned to the initial pale-yellow HABI crystal. The black crystal was considerably stable at room temperature in contrast with the irradiated crystal of *o*-Cl-HABI containing lophyl radical pairs only.

ESR spectra of a single crystal of HABI irradiated at 77 K for 30 min showed a broad doublet signal corresponding to free lophyl radicals at  $g = 2.003$ . Reflective visible spectra of an irradiated KBr pellet of HABI also indicated the presence of lophyl radicals ( $\lambda_{\text{max}} = 566 \text{ nm}$ ). In addition, its infrared spectra consisted of bands assigned to an unreacted 1,2'-dimer, a piezodimer of HABI<sup>15</sup> and lophyl radicals. Figure 2 shows the



**Figure 2.** IR spectra of HABI before/after irradiation and a piezodimer (independently prepared) in KBr matrix at 25 °C: (A) 1,2'-dimer before irradiation. (B) After 2 min irradiation. (C) After 37 min irradiation. (D) After thermal deactivation.

IR spectra of 1,2'-dimer (A–D) and piezodimer independently prepared according to Reference 15. The bands with asterisks of 1,2'-dimer in (A) showed salient changes on irradiation. The spectrum of C indicates the appearance of piezodimers and the decrease of 1,2'-dimer. The IR spectra of A–D show that this photochemical process is reversible. These facts support that the piezodimer and lophyl radicals were formed from HABI. Although the formation of a piezodimer from HABI has been assumed without knowledge of its structural formula, its structure has never been determined because of the difficulty in obtaining single crystals. The recrystallization of the independently prepared piezodimers led to the formation of stable 1,2'-dimers owing to the thermodynamical instability; a 2,2'-dimer (a 4 $\pi$ –4 $\pi$  electron system) is less stable than a 1,2'-dimer (a 4 $\pi$ –6 $\pi$  electron system) because of lack of resonance effects in the imidazolyl rings. In this study HF/6-31G calculations predicted that a 1,2'-dimer is more stable by 5.9 kcal mol<sup>-1</sup> than a 2,2'-dimer.

This study shows the successful application of a cryotrapping method to capture light-induced unstable intermediates in a crystal and to characterize their structures by in situ X-ray crystallography.

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- HABI was prepared according to ref 11. A thin plate crystal (220 × 140 × 20  $\mu\text{m}$ ) of HABI was cooled below 108 K. The 1,2'-dimer structure of HABI was determined by X-ray diffraction involving the use of a SMART CCD area detector diffractometry system. With irradiation, the X-ray data showed no significant crystal decay.  $\text{C}_{42}\text{H}_{30}\text{N}_4$ , MW = 590.70, triclinic, space group  $P\bar{1}$ ,  $T = 108(2) \text{ K}$ ,  $a = 11.3298(4) \text{ \AA}$ ,  $b = 12.8275(4) \text{ \AA}$ ,  $c = 13.0737(4) \text{ \AA}$ ,  $\alpha = 60.634(1)^\circ$ ,  $\beta = 80.389(1)^\circ$ ,  $\gamma = 67.071(1)^\circ$ ,  $V = 1524.37(9) \text{ \AA}^3$ ,  $Z = 2$ ,  $d_{\text{calcd}} = 1.287 \text{ Mg/m}^3$ . Structural solution by direct methods and anisotropic least-squares refinement (based on  $F^2$ ) were performed with SHELXTL (version 5.0). Anisotropic least-squares refinement (416 parameters) on 8853 independent merged reflections ( $R_{\text{int}} = 0.0439$ ) converged at  $R_1(F) = 0.0462$  for 6009 observed data ( $I > 2\sigma(I)$ ),  $\text{GOF} = 1.014$ .
- o*-Cl-HABI indicates 2,2'-di(*o*-chlorophenyl)-4,4',5,5'-tetraphenyl biimidazole. Photolysis of a crystal of *o*-Cl-HABI produced radical pairs in 10% yields as reported in ref 6.
- A thin plate crystal (300 × 160 × 20  $\mu\text{m}$ ) of HABI was cooled below 108 K and irradiated with a high-pressure mercury lamp for 30 min.  $\text{C}_{42}\text{H}_{30}\text{N}_4$ , MW = 590.70, triclinic, space group  $P\bar{1}$ ,  $T = 108(2) \text{ K}$ ,  $a = 11.3660(7) \text{ \AA}$ ,  $b = 12.8563(9) \text{ \AA}$ ,  $c = 13.085(1) \text{ \AA}$ ,  $\alpha = 60.638(1)^\circ$ ,  $\beta = 80.208(1)^\circ$ ,  $\gamma = 66.501(1)^\circ$ ,  $V = 1527.5(2) \text{ \AA}^3$ ,  $Z = 2$ ,  $d_{\text{calcd}} = 1.287 \text{ Mg/m}^3$ . During the data collection below 108 K, no decay was observed. Isotropic and anisotropic least-squares refinement (378 parameters/291 restraints) on 8857 independent merged reflections ( $R_{\text{int}} = 0.0783$ ) converged at  $R_1(F) = 0.0741$  for 4643 observed data ( $I > 2\sigma(I)$ ),  $\text{GOF} = 1.031$ . Refinement: Photolysis of HABI produced three new molecular groups except the unreacted 1,2'-dimer (63.8(8)%); that is, lophyl radicals (13.9(2)%), 2,2'-dimer (13.9(2)%), and another unreacted 1,2'-dimer (22.3(5)%). The minor unreacted 1,2'-dimer was located close to the parent unreacted 1,2'-dimer. The parent 1,2'-dimer was treated as a rigid group that was modeled from the structural parameters in ref 12. The temperature parameters of the parent 1,2'-dimer were fixed. The phenyl groups of lophyl radicals and 2,2'-dimer were restrained due to severe overlaps with those of the parent 1,2'-dimer. The crystal structure of the minor 1,2'-dimer is omitted in Figure 1 for clarity.
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