

## The First in Situ Direct Observation of the Light-Induced Radical Pair from a Hexaarylbiimidazolyl Derivative by X-ray Crystallography

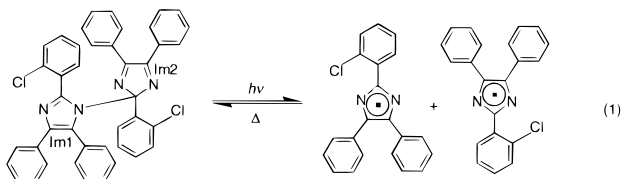
Masaki Kawano,<sup>†</sup> Tomokatsu Sano,<sup>‡</sup> Jiro Abe,<sup>‡</sup> and Yuji Ohashi<sup>\*,†,§</sup>

CREST, Japan Science and Technology Corporation, and  
Department of Chemistry  
Tokyo Institute of Technology, Tokyo 152-8551 Japan  
Department of Photo-Optical Engineering  
Tokyo Institute of Polytechnics  
Kanagawa 243-0297 Japan

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Radical species play an important role as reactive intermediates in chemical reactions and biological systems. While a number of radicals have been extensively investigated in the solid state by spectroscopic methods,<sup>1</sup> a crystallographic approach is relatively less common for unstable radicals and has been applied to stable radicals, e.g., radical ion pairs, stabilized radicals, and so on, which can be crystallized. To our knowledge, a crystallographic investigation of an energetically unstable reactive radical pair (RP) has never been reported. Here we report an unprecedented example of the in situ direct observation of a light-induced RP in a crystal of 2,2'-di(ortho-chlorophenyl)-4,4',5',5'-tetraphenylbiimidazole (*o*-Cl-HABI) by X-ray diffraction.<sup>2</sup>



HABI derivatives are well-known as photo/thermochromic compounds and polymerization photoinitiators in imaging materials and holographic photopolymers.<sup>3</sup> Despite the intriguing properties of HABI derivatives, there is no crystallographic study on this class of compounds except one recent report.<sup>4</sup> In general, it is difficult to observe a reactive intermediate generated in a single crystal of a small molecule by X-ray diffraction.<sup>5</sup> There are many technical difficulties in its in situ observation, e.g., a

small unit cell (it is difficult to retain crystallinity upon relatively large structural changes),<sup>6</sup> low populations,<sup>6</sup> reactive intermediates, short lifetime, etc.

As shown in Figure 1, the dimer structure of *o*-Cl-HABI was unambiguously determined by X-ray diffraction involving the use of a SMART CCD area detector diffractometry system.<sup>7</sup> There are two crystallographically independent *o*-Cl-HABI molecules, A and B, resulting in 16 molecules in a unit cell. One of the triarylbiimidazolyl groups of A is rotated by ca. 180° about the C–N bond compared with the corresponding one of B. The intramolecular bond distances of A and B are identical within an error of about 3σ. A and B molecules are well-separated by more than 3.5 Å (intermolecular distances of non-hydrogen atoms). *o*-Cl-HABI has two kinds of imidazolyl rings, Im1 and Im2. Im1 is a resonant planar structure having the characteristic bond distances for a 6π-electron system. Im2 has two localized C=N double bonds (1.288(2)–1.297(2) Å) and one sp<sup>3</sup> carbon connecting Im1 to be consistent with a 4π-electron system.

On irradiation the crystal turned from pale yellow to reddish-brown. A sufficient amount of the light-induced RP (Figure 2) was trapped in the crystal to allow an X-ray diffraction study.<sup>8</sup> The space group (*Pbca*) is retained after irradiation, and the cell lengths decreased by 0.03 Å (*a* axis), 0.02 Å (*b* axis), and 0.09 Å (*c* axis). The C–N bond connecting Im1 and Im2 was cleaved to yield two planar radicals closely located in a crystal cage which form RP. Although a comparison of the detailed structural parameters of RP is statistically insignificant owing to large errors, the thermal and geometrical parameters are reasonable. Moreover, the observed geometry of RP is in good agreement with that calculated by DFT Becke3LYP/6-31G\*.<sup>9</sup> The C–C (1.47(3) Å vs 1.486 (calcd) Å) and C–N (1.31(3)–1.42(3) Å vs 1.326–1.378 (calcd) Å) bond distances in the imidazolyl rings of RP indicate that an unpaired electron is delocalized over each imidazolyl ring. The short intermolecular distance within RP is

(6) From this point of view, photoactive proteins having a large unit cell and high conversion rates are suitable for structural change study by X-ray diffraction. The light-induced structural changes of the carbon monoxide complex of myoglobin<sup>a</sup> and photoactive yellow protein<sup>b,c,d</sup> have been determined by time-resolved and conventional X-ray crystallography. (a) Srajer, V.; Teng, T.; Ursby, T.; Pradervand, C.; Ren, Z.; Adachi, S.; Schildkamp, W.; Bourgeois, D.; Wulff, M.; Moffat, K. *Science* **1996**, *274*, 1726–1729. (b) Genick, U. K.; Soltis, S. M.; Kuhn, P.; Canestrelli, I. L.; Getzoff, E. D. *Nature* **1998**, *392*, 206–209. (c) Perman, B.; Srajer, V.; Ren, Z.; Teng, T.; Pradervand, C.; Ursby, T.; Bourgeois, D.; Schotte, F.; Wulff, M.; Kort, R.; Hellingwerf, K.; Moffat, K. *Science* **1998**, *279*, 1946–1950. (d) Genick, U.; Borgstahl, G. E. O.; Ng, K.; Ren, Z.; Pradervand, C.; Burke, P. M.; Srajer, V.; Teng, T.; Schildkamp, W.; McRee, D. E.; Moffat, K.; Getzoff, E. D. *Science* **1997**, *275*, 1471–1475.

(7) *o*-Cl-HABI was prepared according to the ref 2b. The diffraction data of *o*-Cl-HABI was measured before irradiation and after warming a RP-contained crystal to room temperature to confirm the reversible structural changes. The following data set was measured using a thermally regenerated initial-state crystal. With irradiation and several temperature changes, the X-ray data showed no significant crystal decay. C<sub>42</sub>H<sub>28</sub>Cl<sub>2</sub>N<sub>4</sub>, MW = 659.58, orthorhombic, space group *Pbca*, λ(Mo Kα) = 0.71073 Å, T = 103(2) K, a = 16.7314(2) Å, b = 17.3877(3) Å, c = 46.0307(6) Å, V = 13391.3(3) Å<sup>3</sup>, Z = 16, d<sub>calcd</sub> = 1.309 Mg/m<sup>3</sup>. Anisotropic least-squares refinement (865 parameters) on 19426 independent merged reflections (R<sub>int</sub> = 0.0413) converged at wR<sub>2</sub>(F<sup>2</sup>) = 0.1010 for all data; R<sub>1</sub>(F) = 0.0409 for 14796 observed data (I > 2σ(I)), GOF = 1.005.

(8) A thin plate single crystal (320 × 300 × 80 μm) of *o*-Cl-HABI was gradually cooled below 103 K and irradiated with a high-pressure mercury lamp for 20 min. C<sub>42</sub>H<sub>28</sub>Cl<sub>2</sub>N<sub>4</sub>, MW = 659.58, orthorhombic, space group *Pbca*, λ(Mo Kα) = 0.71073 Å, T = 103(2) K, a = 16.6975(3) Å, b = 17.3715(3) Å, c = 45.9434(3) Å, V = 13326.4(3) Å<sup>3</sup>, Z = 16, d<sub>calcd</sub> = 1.315 Mg/m<sup>3</sup>. During the X-ray diffraction measurement below 103 K, no decay was observed. Isotropic and anisotropic least-squares refinement (632 parameters/90 restraints) on 19111 independent merged reflections (R<sub>int</sub> = 0.0588) converged at wR<sub>2</sub>(F<sup>2</sup>) = 0.1210 for all data; R<sub>1</sub>(F) = 0.0535 for 14328 observed data (I > 2σ(I)), GOF = 1.080. Since the phenyl groups of RP with relatively low populations are severely overlapped with those of the dimer, they are restrained, and the thermal parameters of B are fixed by using the dimer's structural parameters presented in ref 7.

(9) The observed geometry of *o*-Cl-HABI is also in excellent agreement with that calculated in the same way.

\* To whom correspondence should be addressed.

<sup>†</sup> CREST (JST).

<sup>‡</sup> Tokyo Institute of Polytechnics.

<sup>§</sup> Tokyo Institute of Technology.

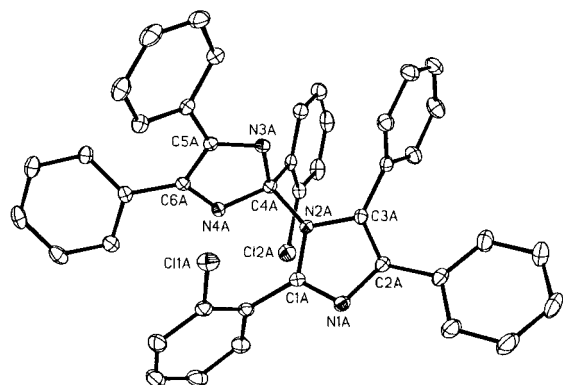
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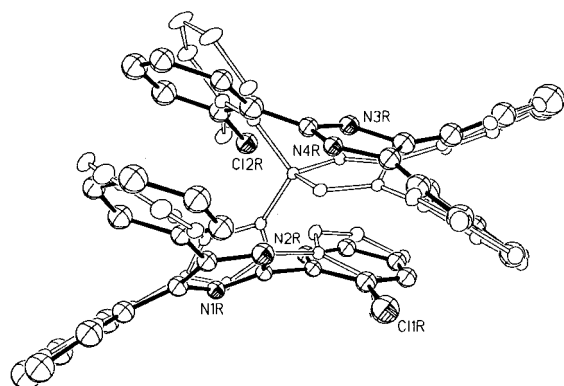
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**Figure 1.** Perspective view of molecule A. The ellipsoids are drawn at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected distances (Å): C1A–N1A, 1.3192(16); C1A–N2A, 1.3828(16); C2A–N1A, 1.3914(17); C2A–C3A, 1.3806(17); C3A–N2A, 1.4026(16); N2A–C4A, 1.4844(15); C4A–N3A, 1.4727(15); C4A–N4A, 1.4715(16); C5A–C6A, 1.5203(17); C5A–N3A, 1.2905(16); C6A–N4A, 1.2923(16).



**Figure 2.** Perspective views of *o*-Cl-HABI (open line) and its RP (solid line). The ellipsoids are drawn at the 30% probability level. Molecule A and hydrogen atoms are not shown for clarity.

in the range between 3.1 Å (N2R···C4R) and 3.5 Å. Noteworthy is that 10% of B changed into RP in a crystal, but A did not react at all. The resultant packing structure comprises a stripe-layered array. Since the C–N bond distances connecting Im1 and Im2 of both A and B are 1.4844 (15) Å and 1.4787 (16) Å, respectively, its bonding strength does not explain why only B molecules generate RP in a crystal. To estimate the steric repulsive force, we calculated the cavity size for each molecule.<sup>10</sup> The result shows that the cavity around B (381 Å<sup>3</sup>) is as large as that of RP (383 Å<sup>3</sup>), and is 26 Å<sup>3</sup> larger than that of A (355 Å<sup>3</sup>). Therefore, we propose that RP formation from A is suppressed due to steric hindrance.

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CW-ESR experiments on a powder sample and a single crystal of *o*-Cl-HABI were carried out in the temperature range from 77 K to room temperature. Irradiation of a single crystal at 77 K produced a triplet-state signal of RP and a very weak doublet one derived from a trace of a free radical. The  $\Delta m_s = 1$  region triplet-state ESR spectrum of a powder sample<sup>11</sup> is very similar to that previously reported at 77 K in chloroform/toluene (50:50, v/v).<sup>12</sup> The observation of a  $\Delta m_s = 2$  transition gives unambiguous spectral evidence of the presence of a triplet-state RP. Increasing the temperature to 183 K resulted in the disappearance of the signals originating from RP and a free radical due to the loss of the radicals by recombination. Irradiation of a single crystal at room temperature led to no observable ESR signal. In contrast, a powder sample exhibited a weak signal characteristic of a free radical.

Surprisingly the yield of RP did not depend on the thickness of a crystal, even though the absorption coefficients of *o*-Cl-HABI in solutions in the UV region are larger than  $10^4$ .<sup>13</sup> Despite the large absorption coefficient, we can obtain enough RP for a diffraction study by using a high-pressure mercury lamp. A possible reason is that *o*-Cl-HABI possesses a weak absorption in the visible region and RP does not recombine on exposure to visible light. Though a weak absorption (smaller than  $10^{-1} \text{ M}^{-1} \text{ cm}^{-1}$  in dichloromethane) in the visible region has been reported,<sup>14</sup> our UV–vis measurement in benzene and a theoretical calculation on *o*-Cl-HABI suggest no absorption in the visible region.<sup>15</sup> Another possibility is that the crystal may have large anisotropy of absorption. To elucidate the mechanism of RP formation in a crystal, more investigation is necessary.

Further physical/chemical characterization of derivatives of HABI is in progress.

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**Supporting Information Available:** Crystallographic data, figures of molecules, A, B, and RP with the atom numbering scheme, and ESR spectra of *o*-Cl-HABI (PDF) and a crystallographic file in CIF format. See any current masthead page for ordering and Internet access instructions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(11) The ESR spectra apparently depend on morphology. The detailed characterization of ESR spectra in powder and single-crystal states will be discussed elsewhere.

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(13) The size-dependence of RP's yield is as follows: size ( $\mu\text{m}$ ), yield of RP (%);  $500 \times 500 \times <10$ , 14.1(1);  $300 \times 300 \times 60$ , 13.6(1);  $320 \times 300 \times 80$ , 10.5(1). The crystal-face orientation for each crystal is unified.

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(15) The molecular structure has been fully optimized at the DFT/Becke3LYP level with the 6-31G basis set. The transition energies were calculated based on the semiempirical CNDO/S Hamiltonian with configuration interaction wave functions.