Synchrotron Radiation Structure Analyses of the Light-induced Radical Pair of a Hexaarylbiimidazolyl Derivative. Origin of the Spin-Multiplicity Change

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In situ synchrotron radiation structure analyses of a light-induced radical pair from *o*-Cl-HABI were performed by using an X-ray vacuum camera at 23–70 K at the BL02B1 station of SPring-8. The combined results of X-ray analysis with theoretical calculation, IR, and UV-vis spectroscopy reveal that a slight conformational change of the radical pair causes the drastic spin-multiplicity change during 2–140 K.

Open-shell organic compounds have been paid considerable attention in that they provide implication for materials science and basic study on the spin alignment.[1] Spin-multiplicity change is an intriguing subject regarding to molecular bistability.[2] Crystallographic information is important to clarify the spin dynamics in the molecular bistability. Although a number of radicals have been investigated by spectroscopic methods, a crystallographic approach is rare for unstable radicals,[3] particularly for radical pairs. Recently, we succeeded in the in situ crystal structure analysis of a photo-induced unstable radical pair (RP I) in a crystal of 2,2′-di(orthochlorophenyl)-4,4′,5,5′-tetraphenylbiimidazole (*o*-Cl-HABI) at 103 K.[4] In addition, Abe et al. found that ultraviolet irradiation of a crystal of *o*-Cl-HABI at 2 K produced a triplet-state radical pair (RP II) having a different D value.[5] Interestingly, the triplet ESR signal of RP II disappeared at 30–40 K, though a triplet ESR signal of RP I appeared above 40 K. The ground state of RP I is singlet and the thermally excited triplet state is populated at the maximum at 70 K as reported in Ref. 5. We investigated the origin of the spin-multiplicity change of these radical pairs by X-ray crystallography and spectroscopic methods.

X-ray diffraction photographs of *o*-Cl-HABI were taken at low temperatures (23–70 K) using a synchrotron radiation (12.03 keV) and the low-temperature vacuum X-ray camera with an IP area detector at BL02B1 station. The intensity data were collected with a ϕ-oscillation method. Several sets of intensity data were measured at ca. 30 K before and after photo-irradiation, and 40 and 70 K after irradiation. A crystal with dimensions of $0.25 \times 0.20 \times 0.15\,\text{mm}^3$ (batch I) or $0.30 \times 0.15 \times 0.12\,\text{mm}^3$ (batch II) cooled at ca. 30 K was irradiated with a high pressure Hg lamp with a thermal cut filter and a focussed lens for 60 min. The crystallographic data are summarized in Table 1.[6] The initial structure before irradiation is substantially the same as the earlier result.[4] Figure 1 shows a disordered structure after irradiation at 30 K, which includes the initial molecule and the photo-induced radical pair.[7] Figure 2 shows a superimposed structure of the radical pairs at 23 and 70 K.[8] Although frost formation (solid N_2) around a crystal specimen in the intensity measurements hampered accurate analyses, we could obtain the following important knowledge about the photo-induced radical pair:

1. Although, judging from EPR, we expected conformational

Table 1. Summary of Crystallographic Data

Data set	A1	A2	B1	B2	B3	B4
Crystal batch	I	I	II	II	II	II
	Before irradiation	After irradiation	Before irradiation	After irradiation	After irradiation	After irradiation
T/K	24(1)	23(1)	33(1)	30(1)	40(1)	70(1)
Space group	*Pbca*	*Pbca*	*Pbca*	*Pbca*	*Pbca*	*Pbca*
a/Å	16.6350(1)	16.613(2)	16.6330(1)	16.6080(3)	16.6170(3)	16.6370(2)
b/Å	17.2740(1)	17.293(3)	17.2660(1)	17.3010(4)	17.3020(4)	17.3100(2)
c/Å	45.8350(3)	45.811(7)	45.8090(3)	45.7880(7)	45.8080(8)	45.8240(5)
V/Å^3	13170.8(1)	13161.0(3)	13155.7(1)	13156.5(4)	13170.1(4)	13196.7(3)
Z	16	16	16	16	16	16
D_{calcd}, Mg/m^3	1.331	1.332	1.332	1.332	1.331	1.328
λ/Å	1.032	1.032	1.032	1.032	1.032	1.032
θ_{max}/deg	45	45	45	45	45	45
No. unique refln	13939	13884	13800	12090	14496	13545
No. obsd refln	11634	11160	11993	9568	12531	11875
$R_1(F)$, % ($I > 2\sigma$)	4.18	7.21	3.79	8.54	9.34	5.99
Residual density Max, min, e/Å^3	0.43,–0.42	0.66,–0.65	0.36,–0.42	0.68,–0.98	0.84,–0.96	0.48,–0.75
Population of radical pair, %	0	15.1(3)	0	24.4(3)	21.7(3)	14.3(2)

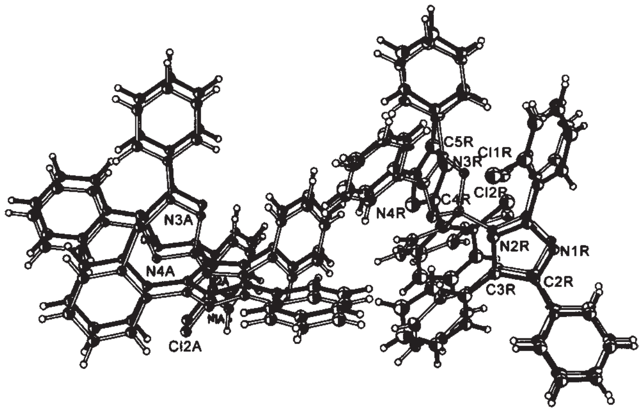

Figure 1. Thermal ellipsoid (probability level 50%) plot of *o*-Cl-HABI (open line: left 85.4(6)%, right 75.6(3)% and left solid line: 14.6(7)%; percentage indicates occupancy) and a photo-induced radical pair (right solid line: 24.4(3)%) after UV-irradiation at 30 K.

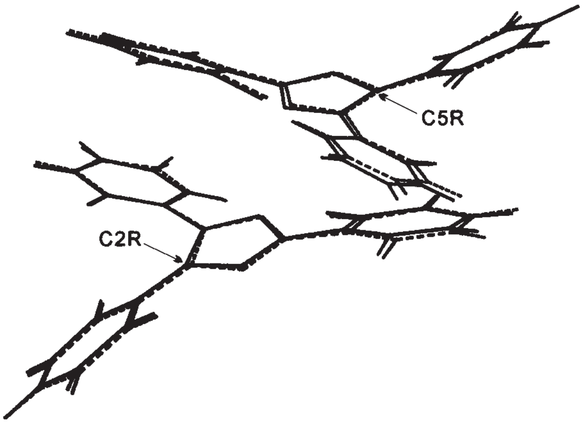

Figure 2. Superimposed view of the structures of photoproducts at 23 K (solid lines) and 70 K (broken lines). Unreacted *o*-Cl-HABI molecules are omitted for clarity.

change of radical pair, the structure obtained at 23 K was surprisingly similar to that at 70 K. The conformation of the radical pair slightly changed after thermal activation.

2. Below 30 K, ultraviolet irradiation could produce radical pairs in yields as high as 24% without any crystal deterioration.

3. Comparing the structures of radical pairs, the observed change (0.05 Å) of an interatomic distance between the atoms (C2R···C5R), for which the highest spin densities are estimated by density-functional theory calculation, is in good agreement with the estimated change (0.06 Å) of the distance between unpaired electrons by EPR.[9]

Figure 3 shows the IR spectra of *o*-Cl-HABI in a KBr matrix before and after ultraviolet irradiation at 5 K.[10] The difference spectrum between before and after irradiation (scale factor = 0.8) is in excellent agreement with the simulated one of a lophyl radical by UB3LYP/6-31G* level of theory. Temperature-dependent IR measurements show that photo-induced radical pairs survive with no spectral change in the range of 1700–600 cm^{-1} at 5–40 K.[11] In addition, the UV-vis spectra of the photo-induced radical pair in a KBr matrix at 7–300 K indicate the existence of radical pairs.[12] These facts suggest that a diamagnetic π-dimer rather than a σ-dimer formed with retaining the molecular structure of the lophyl radical during the ESR silent period.

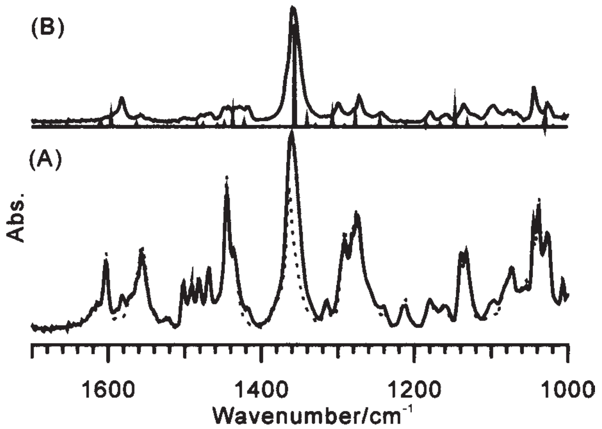

Figure 3. IR spectra before and after UV-irradiation at 5 K. (A) solid line: after irradiation, dot line: before irradiation. (B) difference spectrum between before and after irradiation (scale factor = 0.8). Bar: simulated spectrum by UB3LYP/6-31G* level of theory (scale factor = 0.975).

The combined evidence of X-ray analysis, IR, and UV-vis spectroscopy suggests that a slight conformational change of a radical pair should cause the spin-multiplicity change. This fact implicates that a slight modification of molecular packing could control the spin multiplicity and the magnetic property.

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References and Notes

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6 Crystallographic details and complete listings have been deposited at the Cambridge Crystallographic Data Center (Deposition No. CCDC 193898-193902).

7 The disordered *o*-Cl-HABI structure, slightly shifted from the original position, showed up, probably because of the large yield. Prior to this work, no disordered part was observed.

8 The crystal structure refinements of the 30 and 40 K structures resulted in high residual density (0.68 to $-0.98\,\mathrm{e\AA^{-3}}$ and 0.84 to $-0.94\,\mathrm{e\AA^{-3}}$, respectively), which may be due partly to the coexistence of intermediate structures. Structure modeling of the intermediates was unsuccessful.

9 Interatomic distances between the atoms (C2R···C5R): 6.28(4) Å at 23 K, 6.23(3) Å at 70 K. Distances between unpaired electrons estimated by EPR: 6.32 Å at 23 K, 6.26 Å at 70 K.

10 A single crystal ($0.5 \times 0.5 \times 0.06\,\mathrm{mm}^3$) IR spectra were also measured at 5–300 K before and after irradiation. The tendency of spectral change is the same as one in a KBr matrix.

11 Spectral change at 30–40 K might be expected in the far-infrared region. Above 50 K, the intensity at 1357 cm^{-1} characteristic of lophyl radical decreased gradually. The intensity at 70 K decreased by ca. 8% (on a basis of the peak area calculated in the region of 1394–1320 cm^{-1}) compared with that at 40 K.

12 The spectra are the same as a solution spectrum in benzene, indicating no absorption attributed to intermolecular interaction.