

Definitive Evidence for the Contribution of Biradical Character in a Closed-Shell Molecule, Derivative of 1,4-Bis-(4,5-diphenylimidazol-2-ylidene)cyclohexa-2,5-diene

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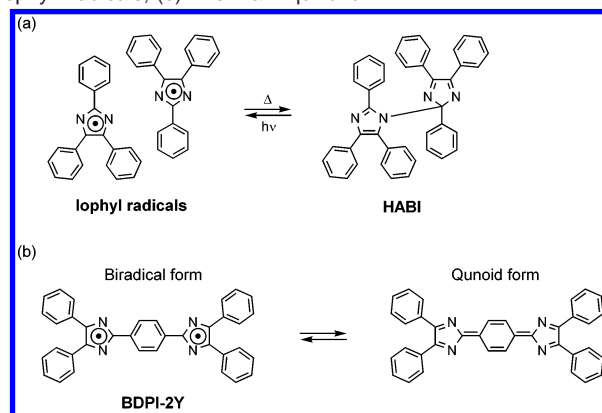
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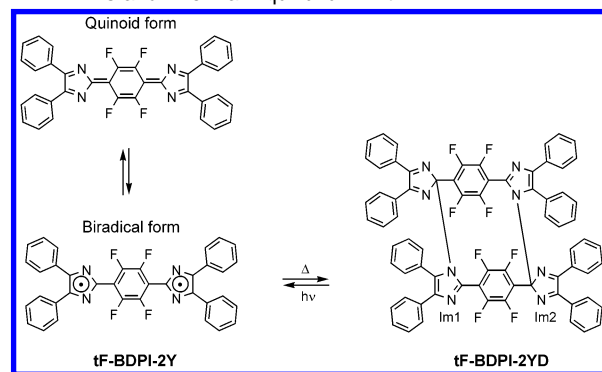
Radical pairs (RPs) are important intermediates for bond formation and bond dissociation in many chemical reactions. We have previously reported the in situ direct observation of a light-induced RP in a crystal of *o*-Cl-HABI by X-ray diffraction.¹ HABI's are readily cleaved, both thermally and photochemically, into a pair of colored triarylimidazolyl radicals called lophyl radicals that can recombine to form the lophine dimer (Scheme 1a).² However, the bisimidazole derivative, 1,4-bis-(4,5-diphenylimidazol-2-ylidene)-cyclohexa-2,5-diene (BDPI-2Y), would not dimerize to form an imidazole dimer. BDPI-2Y was prepared for the first time by Zimmermann et al. in 1966 and was obtained as deep greenish-blue fine prisms with metallic luster.³ The combined studies with UV, ESR measurements for BDPI-2Y showed that about 0.1% of the molecules in a solution are paramagnetic at room temperature, and this fraction increases with increasing temperature.^{3d} These facts suggested that there is the equilibrium between a diamagnetic-quinoid ground state and a paramagnetic-biradical thermally excited state in both solids and solutions (Scheme 1b). However, the lack of direct evidence for the existence of the biradical state has been making it the subject of considerable study. There are so far very few definitive demonstrations of biradical contribution to the ground state of closed-shell molecules.⁴ Despite the fact that the electronic structure of Chichibabin's hydrocarbon has been the subject of considerable study, an important question remains unanswered. Early experimental studies on Chichibabin's hydrocarbon led to speculation as to whether it exists as a singlet, a triplet, or a mixture of the two spin states.⁵ We have considered that the biradical character of BDPI-2Y could be conclusively proved by the detection of imidazole dimer, and the dimerization of BDPI-2Y could be realized by increasing the population of the biradical species by the chemical modification with a suitable substituent. Herein, we wish to describe the syntheses and the X-ray and the electronic structures of a novel photochromic BDPI-2Y derivative, tF-BDPI-2Y, where four hydrogen atoms at the central phenylene ring are substituted with four fluorine atoms of BDPI-2Y.

We have carried out theoretical investigations for the closed-shell quinoid state and the open-shell triplet-biradical state of BDPI-2Y and tF-BDPI-2Y prior to the experiments. The optimized geometries by the DFT-B3LYP/6-31G(d) method have shown that the total energies of the quinoid state are lower than those of the triplet-biradical state for both BDPI-2Y and tF-BDPI-2Y. The energy gap of tF-BDPI-2Y was calculated to be 4.35 kcal/mol, which is much smaller than the corresponding value of 7.54 kcal/mol for BDPI-2Y. These results suggest that the four substituted fluorine atoms at the central phenylene ring of tF-BDPI-2Y would destabilize the quinoid state and stabilize the biradical state. Therefore, the biradical state of tF-BDPI-2Y should be densely populated in the equilibrium at room temperature. Due to the fact that the dimerization of radical species follows second-order

Scheme 1. (a) Reversible Photodissociation of HABI into Two Lophyl Radicals; (b) Thermal Equilibrium in BDPI-2Y



Scheme 2. Reversible Photodissociation of tF-BDPI-2YD into Two tF-BDPI-2Y's and Thermal Equilibrium in tF-BDPI-2Y



kinetics, the increase in the population of radical species would lead to the formation of the imidazole dimer in a nonlinear manner.

tF-BDPI-2Y was prepared by oxidation of the corresponding lophine derivative, tF-BDPI-2Y-lophine, according to the known procedure.^{1,2} tF-BDPI-2Y-lophine was suspended into a benzene-aqueous potassium hydroxide heterogeneous solution, and the oxidation was initiated by an aqueous potassium ferricyanide at room temperature. During the oxidation, the color of the benzene layer readily turns from pale yellow to blue-purple. From the blue-purple benzene layer, tF-BDPI-2Y was obtained as a greenish-blue powder. Recrystallization from hot benzene gave colorless plate single crystals of tF-BDPI-2YD (Scheme 2).

As shown in Figure 1, the dimer structure of tF-BDPI-2YD was determined by X-ray diffraction. tF-BDPI-2YD has two kinds of imidazolyl rings, Im1 and Im2 (see Scheme 2). Im1 is a resonant planar structure with the characteristic bond distances for a 6 π -electron system. Im2 has two localized C=N double bonds (1.281(3) Å, 1.294(3) Å) and one sp³ carbon connecting Im1 to be

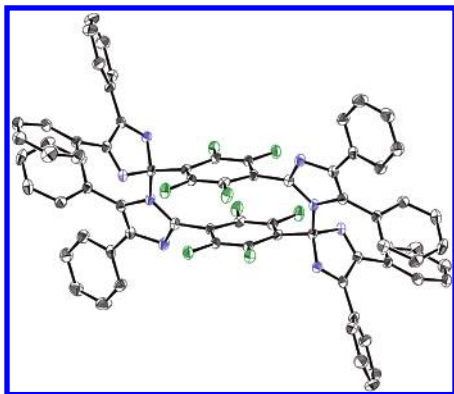


Figure 1. Perspective view of tF-BDPI-2YD with thermal ellipsoids (30% probability). The hydrogen atoms and the solvents are omitted.

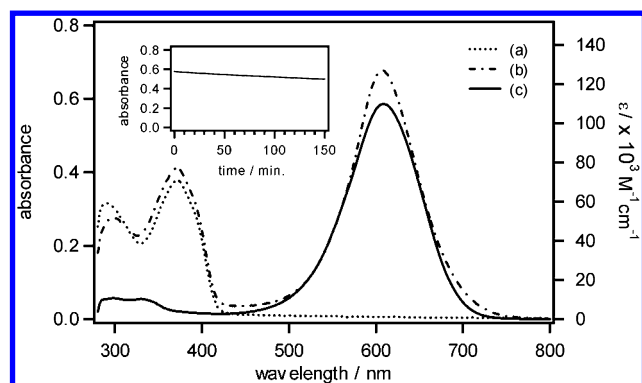


Figure 2. Absorption spectra of tF-BDPI-2YD in benzene (6.25×10^{-6} M) (a) before irradiation and (b) immediately after irradiation with 360 nm light at room temperature, and (c) BDPI-2Y in benzene (1.25×10^{-5} M) (right axis). Inset: Plot of absorbance at 610 nm of tF-BDPI-2YD kept in the dark at 293 K after irradiation (1 min at 360 nm). All of the measurements were carried out by using a 10 mm cell.

consistent with a 4π -electron system. The C–N bonds (1.499(3) Å) connecting Im1 and Im2 are shorter than those reported for HABI.¹ The central phenylene rings exist in a bending manner because of the steric repulsion between the fluorine atoms. The closest contact between two best-fit planes containing the central phenylene rings was about 2.89 Å which is much shorter than the ordinary π – π stacking interaction of the phenylene rings. These results suggest that Im1 and Im2 of tF-BDPI-2YD maintain their structure similar to those of HABI other than the out-of-plane deformation of the central phenylene rings.

Figure 2 shows the photochromic color changes for tF-BDPI-2YD in benzene. On irradiation with 360 nm light, the colorless benzene solution quickly turned to blue-purple and gave rise to a broad absorption band centered at 609 nm. The absorption spectrum of tF-BDPI-2YD after the photoirradiation (Figure 2b) has a close resemblance to that of BDPI-2Y (Figure 2c), revealing the similarity in the electronic structures of the chemical species involved in these two solutions. On standing in the dark, the blue-purple color gradually faded with a decrease in the absorbance in the visible light region. The thermal recombination reaction to form tF-BDPI-2YD was observed over a period of 2 days at 293 K in the dark, indicating that the light-induced paramagnetic species are very stable in solution at room temperature. Moreover, the increase in the

population of biradical species of tF-BDPI-2Y (0.4%) as compared with BDPI-2Y (0.1%) in solution could be confirmed by the observation of the enhanced ESR signal intensity for the light-irradiated solution of tF-BDPI-2YD (see Supporting Information).

In conclusion, this study provides conclusive proof that the thermally excited open-shell state with biradical character is contributing to the ground state of tF-BDPI-2Y. Of course, the electronic structure of tF-BDPI-2Y is somewhat different from that of BDPI-2Y in which no dimerization reaction could be found. However, a small increase in the population of the biradical species of tF-BDPI-2Y should be considered to result in the formation of the dimer form. Controlling the equilibrium between a closed-shell quinoid state and an open-shell biradical state will also provide significant progress in the field of biradical chemistry, and especially in the field of π -conjugated delocalized biradical chemistry. Moreover, the effects of the intermolecular interactions of the delocalized biradicals on the electronic wave functions for the cumulated systems have never been investigated in detail. The study of their properties will allow for a better understanding of the factors for spin interactions in π -conjugated delocalized biradicals and will lead to the rational development of new molecular organic materials.

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Supporting Information Available: Details of DFT calculations, experimental preparations for tF-BDPI-2YD and crystallographic data (CIF), and ESR studies of tF-BDPI-2YD. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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