ORGANIC LETTERS

2013
Vol. 15, No. 12
2938–2941

Photochromism of a Naphthalene-Bridged Imidazole Dimer Constrained to the "*Anti*" Conformation

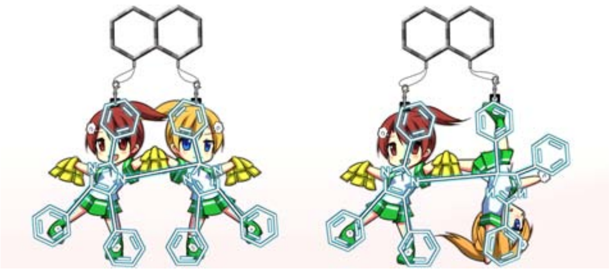
Katsuya Mutoh,[†] Kentaro Shima,[†] Tetsuo Yamaguchi,[†] Masayuki Kobayashi,[†] and Jiro Abe*[,†,‡]

Department of Chemistry, School of Science and Engineering, Aoyama Gakuin University, 5-10-1 Fuchinobe, Chuo-ku, Sagamihara, Kanagawa 252-5258, Japan, and CREST, Japan Science and Technology Agency (JST), 7 Gobancho, Chiyoda-ku, Tokyo 102-0076, Japan

jiro_abe@chem.aoyama.ac.jp

Received April 11, 2013

ABSTRACT



***Anti*-1,8-bisTPI-naphthalene in which two imidazole rings are constrained to an *anti*-conformation leading to the first-formed 1,4′-isomer of the bridged imidazole dimer has been synthesized. The color of the radicals is different from that of the previously reported bridged-imidazolyl radicals because the intramolecular interaction between the radicals becomes weak due to the *anti*-conformation. This molecular design would be a profitable strategy to control the color of the radicals of the bridged imidazole dimer for application in ophthalmic lenses.**

Photochromic molecules change their structure with the absorption spectral change by light, and the generated structural isomer reproduces the initial state photochemically or thermally. Photochromic materials have great potential for application in not only industrial uses[1] but also biological research tools.[2] Especially, the T-type photochromic molecules going back to the initial isomer thermally are expected to be applied to the opthalmic lenses. However the high optical density in the visible light region and the rapid thermal bleaching rate are generally conflicted because the faster decoloration rate of the colored species is, the lower the population of the colored species in photostationary state. Therefore, rational molecular design to solve the dilemma is required. Recently, we have developed the bridged imidazole dimers which generate the colored radicals by UV light irradiation with sufficiently high optical density to recognize the coloration and the fast back reaction to form the initial imidazole dimer.[3]

[†] Aoyama Gakuin University.

[‡] Japan Science and Technology Agency (JST).

(1) (a) Crano, J. C.; Guglielmetti, R. J. *Organic Photochromic and Thermochromic Compounds*; Plenum Press: New York, 1999. (b) Dürr, H.; Bouas-Laurent, H. *Photochromism: Molecules and Systems*; Elsevier: Amsterdam, The Netherlands, 2003.

(2) (a) Beharry, A. A.; Wong, L.; Tropepe, V.; Woolley, G. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 1325. (b) Yildiz, I.; Impellizzeri, S.; Deniz, E.; McGaughan, B.; Callan, J. F.; Raymo, F. M. *J. Am. Chem. Soc.* **2011**, *133*, 871. (c) Uda, R. M.; Hiraishi, E.; Ohnishi, R.; Nakahara, Y.; Kimura, K. *Langmuir* **2010**, *26*, 5444. (d) Yamada, M. D.; Nakajima, Y.; Maeda, H.; Maruta, S. *J. Biochem.* **2007**, *142*, 691. (e) Fujimoto, K.; Amano, M.; Horibe, Y.; Inouye, M. *Org. Lett.* **2006**, *8*, 285. (f) Woolley, G. A. *Acc. Chem. Res.* **2005**, *38*, 486.

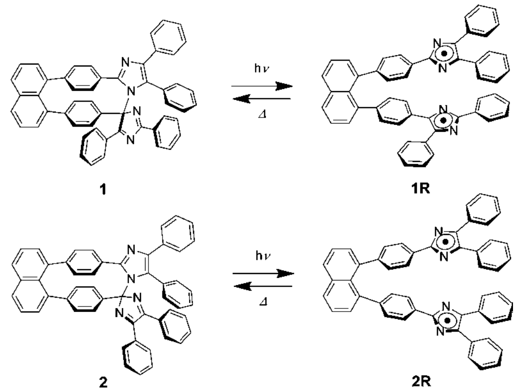
(3) (a) Hatano, S.; Horino, T.; Tokita, A.; Oshima, T.; Abe, J. *J. Am. Chem. Soc.* **2013**, *135*, 3164. (b) Mutoh, K.; Abe, J. *J. Phys. Chem. C* **2013**, *117*, 4808. (c) Ishii, N.; Kato, T.; Abe, J. *Sci. Rep.* **2012**, *2*, 819. (d) Mutoh, K.; Abe, J. *Chem. Commun.* **2011**, *47*, 8868. (e) Kishimoto, Y.; Abe, J. *J. Am. Chem. Soc.* **2009**, *131*, 4227. (f) Fujita, K.; Hatano, S.; Kato, D.; Abe, J. *Org. Lett.* **2008**, *10*, 3105. (g) Iwahori, F.; Hatano, S.; Abe, J. *J. Phys. Org. Chem.* **2007**, *20*, 857.

(4) (a) Yamashita, H.; Abe, J. *J. Phys. Chem. A* **2011**, *115*, 13332. (b) Mutoh, K.; Abe, J. *J. Phys. Chem. A* **2011**, *115*, 4650. (c) Mutoh, K.; Hatano, S.; Abe, J. *J. Photopolym. Sci. Technol.* **2010**, *23*, 301.

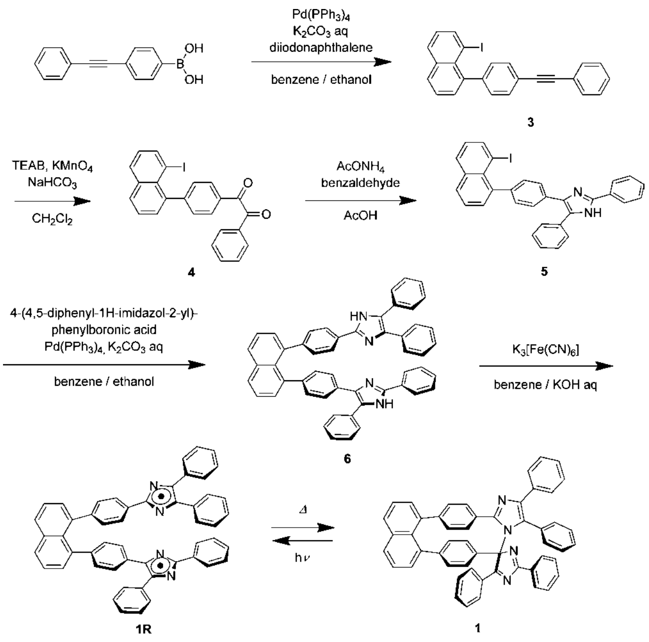
(5) (a) Kawai, S.; Yamaguchi, T.; Kato, T.; Hatano, S.; Abe, J. *Dyes Pigm.* **2012**, *92*, 872. (b) Harada, Y.; Hatano, S.; Kimoto, A.; Abe, J. *J. Phys. Chem. Lett.* **2010**, *1*, 1112.

10.1021/ol401012u

Scheme 1. Photochromism of **1** and **2**



Scheme 2. Synthesis of **1**



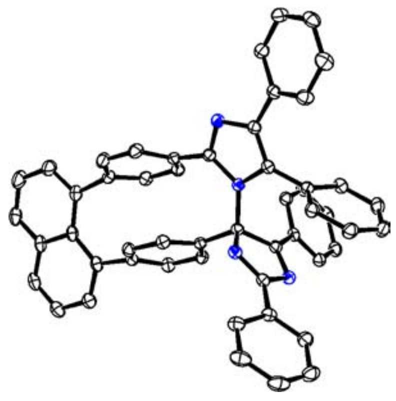


Figure 1. ORTEP representation of the molecular structure of **1** with thermal ellipsoids (50% probability), where nitrogen atoms are highlighted in blue. The hydrogen atoms, and the solvent molecule (benzene) are omitted for clarity.

Moreover, we have succeeded in establishing efficient strategies for molecular design to control photosensitivity[4] and the thermal back reaction rate[5] of the bridged imidazole dimers. However, the strategy for controlling the color of the radicals has not been developed because of the broad absorption bands of the radicals ranging from 500 to 1000 nm. The absorption band from 700 to 1000 nm inevitably appears because the bridged imidazole dimer generates the radical pair which can easily interact with each other.

In this study, we have designed a novel naphthalene-bridged imidazole dimer, *anti*-1,8-bisTPI-naphthalene (**1**), which constrained the two imidazole rings to the *anti*-conformation (Scheme 1). All of the bridged imidazole dimers that we previously reported have the *syn*-arranged structure, and the two imidazole rings are connected with the C−N bond between N1 and C2′ of each of the imidazole rings. Therefore, this is the first report of the *anti*-constrained bridged imidazole dimer. We revealed that it has a unique structure and photochromic properties.

Compound **1** was synthesized according to Scheme 2. Initially, **3** was synthesized by a Suzuki-coupling reaction of diiodonaphthalene and 4-(phenylethynyl benzene)-boronic acid, following the oxidation of the ethynyl moiety with $KMnO_4$ to give **4**. The second Suzuki-coupling reaction of 4-(4,5-diphenyl-1*H*-imidazol-2-yl)-phenylboronic acid and **5** synthesized by imidazole condensation of **4** enabled us to obtain the desired unsymmetrical bridged biimidazole **6**. The target **1** was synthesized through the oxidation reaction of **6**. Recrystallization of **1** from a benzene/hexane solution by the liquid−liquid diffusion method gives the yellow plate crystals. The molecular structure was revealed by X-ray crystallographic analysis. As shown in Figure 1, the two imidazole rings are connected with the C−N bond between N1 and C4′ of the two imidazole rings (1,4′-isomer). The distance of the C−N bond is 1.495 Å which is identical with that of 1,8-bisTPI-naphthalene (**2**) (1.494 Å) described in Scheme 1. It should be emphasized here again that the 1,4′-isomer of the bridged imidazole dimer has never been reported to date. Hexaarylbiimidazole (HABI) has the possibility to form six structural isomers (Figure 2).[6] Although the main product is the photochromic isomer, some of the other isomers with thermochromic or piezochromic properties have been reported. Especially, the 1,4′-isomer of HABI also shows photochromism upon UV light irradiation.[6a] Thus the fast photochromic behavior of **1** was investigated in detail.

Figure 3 shows the UV−vis absorption spectra of **1** and **2** in benzene. The absorption spectrum of **1** is similar to that of **2** in the fact that both spectra have the absorption band in the UV region. The cleavage of the C−N bond

---

(6) (a) Goto, T.; Tanino, H.; Kondo, T. *Chem. Lett.* **1980**, 431. (b) Tanino, H.; Kondo, T.; Okada, K.; Goto, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1474.

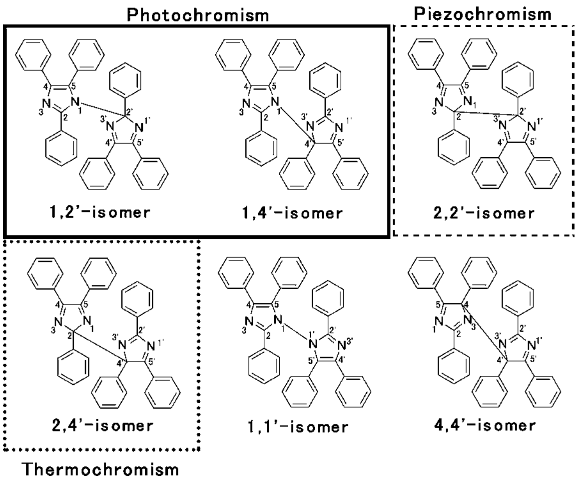


Figure 2. Possible structural isomers of HABI.

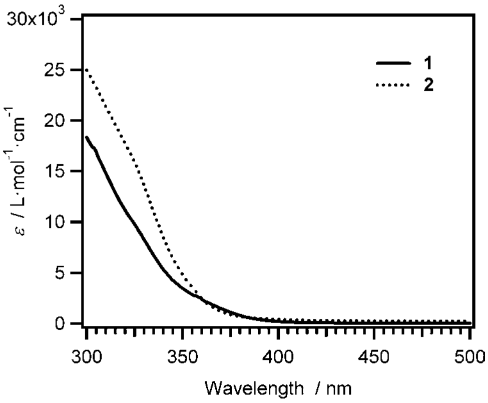


Figure 3. UV–vis absorption spectra of **1** and **2** in benzene.

Table 1. Activation Parameters of the Themal Back Reaction of **1R** and **2R**

	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J mol^{-1} K^{-1}	$\Delta G^{\ddagger}$/ kJ mol^{-1}
1R	42.3	−105.5	73.7
2R	44.8	−94.5	73.0

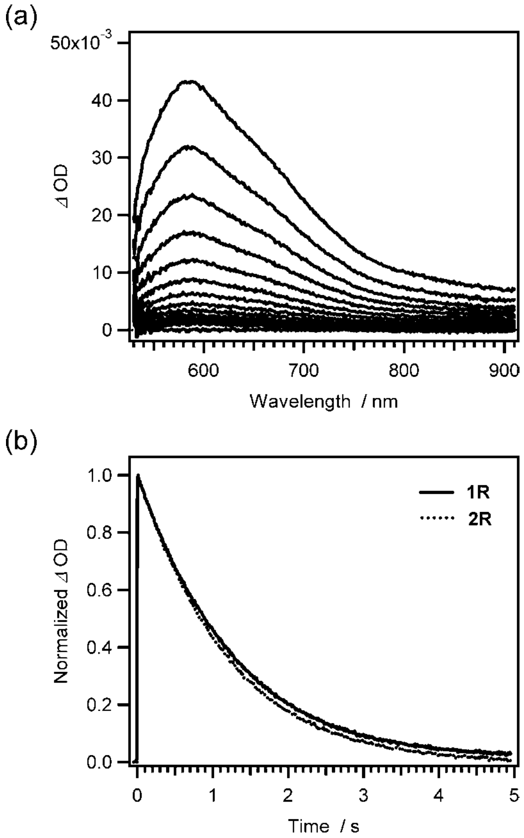


Figure 4. (a) Transient vis–NIR absorption spectra of **1R** in degassed benzene at 25 °C (5.5×10^{-5} M, light path length: 10 mm). Each of the spectra was recorded at 400 ms intervals after excitation with a nanosecond laser pulse (excitation wavelength, 355 nm; pulse width, 5 ns; power 3 mJ/pulse). (b) Decay profiles of the colored species **1R** and **2R** monitored at 400 nm in degassed benzene at 25 °C (**1**: 5.5×10^{-5} M; **2**: 1.1×10^{-4} M; light path length: 10 mm).

upon UV light irradiation of **1** produces the radical species (**1R**) accompanied by the color change from colorless to green. In the presence of oxygen, the imidazolyl radicals react with oxygen, resulting in the formation of the O_2 adduct.[7] Compound **1** also reacts with oxygen under continuous UV light irradiation and generates an O_2 adduct.

Figure 4a shows the transient vis–NIR absorption spectra of **1R** in degassed benzene at 25 °C measured by the laser flash photolysis with 355 nm irradiation. All of the absorption bands decay monotonically with the same time constant, indicating the presence of the single component of the radical. The thermal bleaching process of **1R** in degassed benzene is shown in Figure 4b. Compound **1R** goes back to the initial dimer monoexponentially within 5 s at 25 °C as rapidly as the thermal bleaching reaction of **2R**. The activation enthalpies and entropies ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively) for the thermal back reaction calculated from the Eyring plots (Figure S14) are estimated to be 42.3 kJ mol^{-1} and −105.5 J K^{-1} mol^{-1}, respectively. The free energy barrier of the thermal back reaction of **1R** ($\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$) is estimated to be 73.7 kJ mol^{-1} at 25 °C. The negative value of $\Delta S^{\ddagger}$ suggests that the degrees of freedom are reduced because of the intramolecular recombination reaction between the radicals. The influence of $\Delta S^{\ddagger}$ on the thermal recombination reaction of the bridged imidazole dimers was discussed in our previous paper.[5a] The thermal recombination reaction of the 3′,4′,5′-triphenyl-1,1′:2′,1″-terphenyl-substituted

---

(7) (a) Edkins, R. M.; Probert, M. R.; Fucke, K.; Robertson, C. M.; Howard, J. A. K.; Beeby, A. *Phys. Chem. Chem. Phys.* **2013**, *15*, 7848. (b) Hatano, S.; Abe, J. *Phys. Chem. Chem. Phys.* **2013**, *14*, 5855.

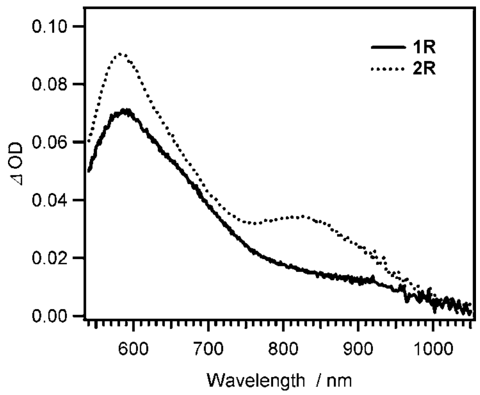


Figure 5. Transient vis–NIR absorption spectra of **1R** and **2R** just after laser excitation in degassed benzene at 25 °C (**1**: 1.0 × 10^{-4} M; **2**: 1.5 × 10^{-4} M; light path length: 10 mm).

[2.2]PC-bridged imidazole dimer is decelerated compared with that of *pseudogem*-DPI-PI[2.2]PC due to the large nuclear configuration change in the transition state, resulting in the entropically unfavorable large negative $\Delta S^{\ddagger}$ value. By comparing the $\Delta S^{\ddagger}$ values of **1R** and **2R**, we cannot confirm significant differences (Table 1) suggesting that no distinguished degrees of freedom are confirmed in the transition state of **1R** compared with that of **2R** even though the binding manner of the products after the thermal back reaction of **1R** and **2R** are the 1,4′- and 1,2′-isomers, respectively. Normally, the photochromic properties of the film cannot be consistent with those in solutions because the reaction rate of photochromism is generally influenced by the environment around the photochrome.[8] Therefore the photochromism of **1** would be also affected by the matrixes. However, we recently found that the bridged imidazole dimers can keep their photochromic properties in the polymer matrix with a plasticizer.[9] Thus, the application to the ophthalmic lenses should be achievable with a plasticizer. The fast photochromic behavior of the anticonformation bridged imidazole dimer in the polymer matrix will be investigated in future studies.

Figure 5 shows the transient absorption spectra of **1** and **2**, measured upon 355 nm excitation in benzene. These absorption bands can be ascribed to the radical species, **1R** and **2R**. The absorption bands around 600 nm in both absorption spectra of **1R** and **2R** can be assigned to the typical absorption of triphenylimidazolyl radicals (TPIRs). On the other hand, the decrease in the absorption intensity at 830 nm of **1R** is clearly confirmed, compared with that of **2R**. The absorption band around 830 nm of the radical species of the bridged imidazole dimer is attributed to the radical–radical interaction resulting from the face to face alignment of a pair of the radicals.[10] Therefore, the overlap between the π orbitals of the two imidazolyl radicals is the important factor for the color of the radicals. The radical of the TPIR moiety is delocalized in the phenyl rings connected to the imidazole ring. By restricting the TPIR moiety to the anticonformation, the spatial overlap of the phenyl rings is decreased. Thus, the decrease in the absorption band at 830 nm suggests that the overlap integral of the π orbitals between two radicals is reduced due to the *anti*-alignment of the TPIRs.

In conclusion, we have reported the new bridged imidazole dimer **1** in which triphenylimidazolyl parts are connected with naphthalene in an *anti*-alignment manner. It is noted that **1** has the C–N bond between N1 and C4′ of the two imidazole rings which is the first report of the 1,4′-isomer of the bridged imidazole dimer. The photochromism of **1** shows the rapid thermal bleaching reaction to be as fast as that of **2**. The colored species of **1** has the only absorption band which is characteristic of TPIR although the classical bridged imidazole dimer has the broad absorption bands which cover the whole visible region. Thus, the control of the color of the radicals would be facile compared to the previously reported bridged imidazole dimers. This work would present a profitable strategy to develop the bridged imidazole dimer for application in ophthalmic lenses.

Acknowledgment. This work was supported partly by the Core Research for Evolutional Science and Technology (CREST) program of the Japan Science and Technology Agency (JST) and a Grant-in-Aid for Scientific Research (A) (22245025) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

Supporting Information Available. Synthesis, ^{1}H, ^{13}C NMR spectra; HPLC chromatogram; X-ray crystallographic analysis; experimental details for the laser flash photolysis measurements; kinetics for the thermal back reaction in benzene. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

---

(8) (a) Ercole, F.; Davis, T. P.; Evans, R. A. *Macromolecules* **2009**, *42*, 1500. (b) Norikane, Y.; Davis, R.; Tamaoki, N. *New J. Chem.* **2009**, *33*, 1327. (c) Ercole, F.; Malic, N.; Davis, T. P.; Evans, R. A. *J. Mater. Chem.* **2009**, *19*, 5612. (d) Sriprom, W.; Néel, M.; Gabbutt, C. D.; Heron, B. M.; Perrier, S. *J. Mater. Chem.* **2007**, *17*, 1885. (e) Such, G. K.; Evans, R. A.; Davis, T. P. *Macromolecules* **2006**, *39*, 1391. (f) Evans, R. A.; Hanley, T. L.; Skidmore, M. A.; Davis, T. P.; Such, G. K.; Yee, L. H.; Ball, G. E.; Lewis, D. A. *Nat. Mater.* **2005**, *4*, 249.

(9) Ishii, N.; Abe, J. *Appl. Phys. Lett.* **2013**, *102*, 163301.

(10) (a) Hatano, S.; Sakai, K.; Abe, J. *Org. Lett.* **2010**, *12*, 4152. (b) Mutoh, K.; Nakano, E.; Abe, J. *J. Phys. Chem. A* **2012**, *116*, 6792.