

Formation of hexaarylbiimidazole heterodimers *via* the cross recombination of two lophyl radicals†

Atsushi Kimoto, Shimpei Niitsu, Fumiyasu Iwahori and Jiro Abe*

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The formation of hexaarylbiimidazole heterodimers has been investigated in detail by X-ray crystallography and ¹H NMR spectroscopy.

Hexaarylbiimidazole (HABI) derivatives are well-known as photo/thermochromic compounds, and photoinitiators for polymerization in imaging materials and holographic photopolymers.¹ HABIs are readily cleaved, both thermally and photochemically, into a pair of 2,4,5-triarylimidazolyl radicals, which thermally recombine to reproduce a dimer.^{2,3} The photochromic behavior of HABI derivatives can be attributed to the photoinduced homolytic reversible cleavage of the C–N bond between the imidazole rings.^{4–8} Among them, Dylux[®], developed by the DuPont Company, also includes HABI derivatives, and the optimization of their chemical structures to improve their light absorption range has been widely investigated. From the 1960s to the 1970s, various HABI homodimers (homo-HABI), including *o*-Cl-HABI (**1-1**), were prepared and their photochemical response to yield imidazolyl radicals was investigated for improved photosensitivity. In the 1980s, for the best spectral sensitivity, “HABI heterodimer” (hetero-HABI) was prepared by the co-oxidation of two different triarylimidazoles, without any isolation processes, consisting of an admixture of homo- and hetero-HABIs.^{9,10} Despite their large contributions to industry, however, no investigations have been undertaken to reveal the formation and recombination processes of hetero- and homo-HABIs *via* co-oxidation. There has also been no attempt to study the photoreaction of hetero-HABIs in detail, which can be reconstructed into homodimers by homolytic cleavage and cross recombination. This is very important, not only for their industrial properties, such as stability, durability, reproducibility and so on, but also for the basic chemistry, such as the structural aspects of their cleavage/recombination behavior. Here, we report for the first time the photochemical cleavage and dimerization behavior of hetero-HABIs using X-ray crystallography and ¹H NMR spectroscopy.

In order to reveal the photoreactions of hetero-HABIs, we first attempted to find an appropriate combination of two

triphenylimidazole derivatives. In order to isolate the possible four hetero/homodimers derived from the radical coupling reactions of two triphenylimidazoles, a large difference in R_f values between the two homodimers is required. We therefore checked the R_f value of many accessible HABI derivatives (ESI, Fig. S1†). We chose *o*-Cl-HABI (**1-1**) and 2,3,5-triCl-HABI (**2-2**) because they showed the greatest difference in R_f value in chloroform. Upon reacting these two triphenylimidazole derivatives, **1** and **2**, the R_f values of heterodimers **1-2** and **2-1** would be between those of homodimers **1-1** and **2-2**, resulting in the successful isolation of four hetero/homo-HABIs.

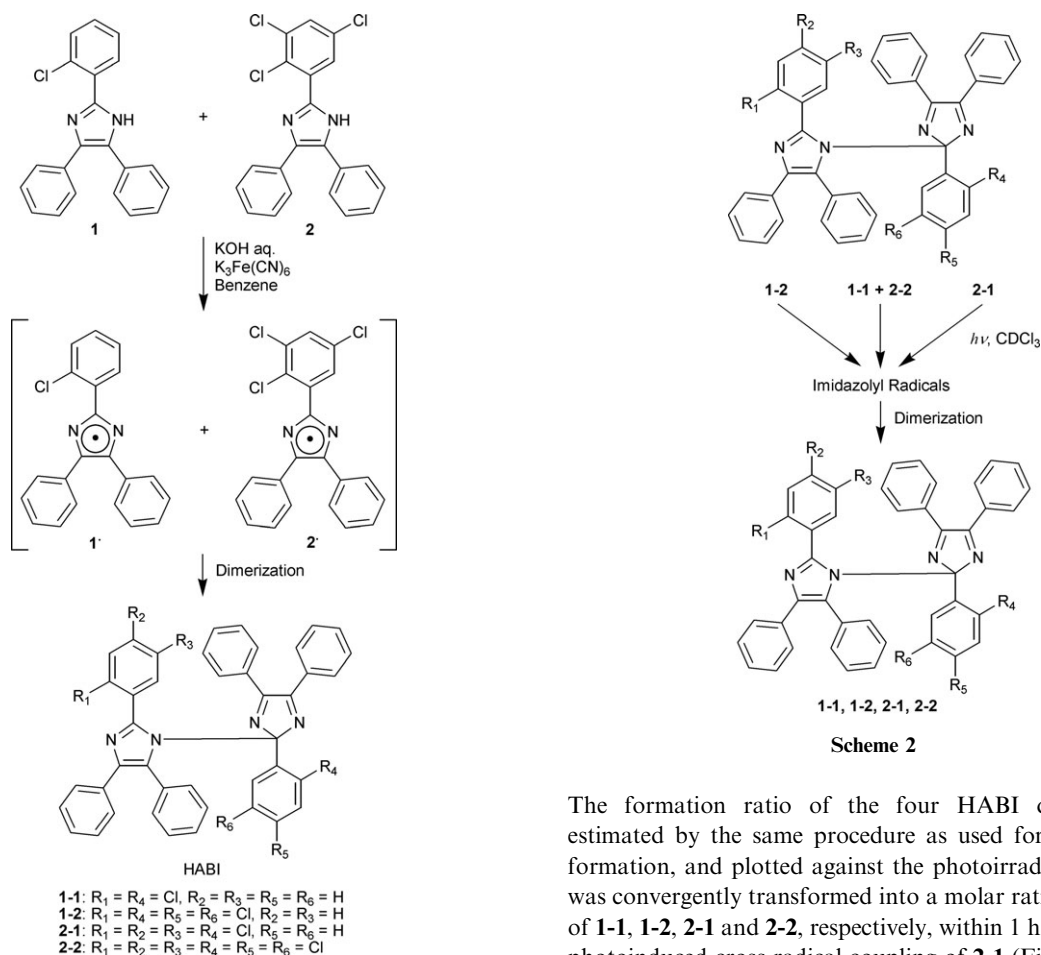
Triphenylimidazoles **1** and **2** were prepared by a literature procedure, reacting benzil with the corresponding benzaldehyde derivatives. An equimolar mixture of **1** and **2** was oxidized by $K_3Fe(CN)_6$ in benzene under basic conditions to generate two triphenylimidazolyl radicals (**1•** and **2•**) (Scheme 1). These radicals diffuse in solution and readily recombine into four cross-coupled homo- and hetero-HABI derivatives (**1-1**, **1-2**, **2-1** and **2-2**). Because of their remarkably different R_f values, we could successfully isolate the four HABI derivatives from each other by simple silica gel column chromatography. The R_f values of **1-1**, **1-2**, **2-1** and **2-2** are 0.12, 0.17, 0.38 and 0.41, respectively, using chloroform as the eluent. The chemical structures of these dimers were determined by X-ray crystallography (ESI, Fig. S2–S5†)⁸. All of the dimers, including the heterodimers, possess a C–N bond between 1- and 2'-positions of the imidazole rings. The C–N bond lengths of these four HABIs are almost identical (**1-1**: 1.484 Å, **1-2**: 1.477 Å, **2-1**: 1.475 Å and **2-2**: 1.476 Å, respectively), despite the different electronic conditions in their imidazole rings. We estimated by ¹H NMR spectroscopy in $CDCl_3$ the molar ratio of formation of these dimers after the chemical oxidation of an equimolar mixture of **1** and **2** (Fig. 1(a)). A characteristic signal attributed to **1-1** and **1-2** at δ 7.8 and 7.7 for one proton, respectively, could be observed (Fig. 1(b) and (c)). Considering that the signal at δ 6.7 is derived from **1-1** and **2-1** (Fig. 1(a) and (c)), and the one at δ 6.6 is derived from **1-2** and **2-2** (Fig. 1(b) and (d)), the ratio **1-1** : **1-2** : **2-1** : **2-2** in the crude reaction mixture was estimated to be 2 : 1 : 3 : 2.

We investigated the reaction processes for the photoinduced cross radical coupling of these HABI derivatives. **1-2** was dissolved in $CDCl_3$ and dissociated into two imidazolyl radicals, **1•** and **2•**, by irradiating it with visible light. These radicals diffused in solution during the irradiation and when the light irradiation was terminated, they recombined to form

Department of Chemistry, School of Science and Engineering, Aoyama Gakuin University, 5-10-1 Fuchinobe, Sagami-hara,

Kanagawa 229-8558, Japan. E-mail: jiro_abe@chem.aoyama.ac.jp

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imidazole dimers (HABI derivatives) (Scheme 2). Longer photoirradiation times resulted in a decreased molar ratio of **1-2**, indicating a transformation into other HABI derivatives.

The formation ratio of the four HABI derivatives was estimated by the same procedure as used for their chemical formation, and plotted against the photoirradiation time. **1-2** was convergently transformed into a molar ratio of 2 : 1 : 5 : 2 of **1-1**, **1-2**, **2-1** and **2-2**, respectively, within 1 h (Fig. 2(a)). The photoinduced cross radical coupling of **2-1** (Fig. 2(b)), and an equimolar mixture of **1-1** and **2-2** (Fig. 2(c)), were also investigated. Both of these reactions reached a photostationary state within 1 h. The ratio of **1-1** : **1-2** : **2-1** : **2-2** at their photostationary states was also 2 : 1 : 5 : 2 for each cross radical coupling. For these three reactions, two imidazolyl radicals,

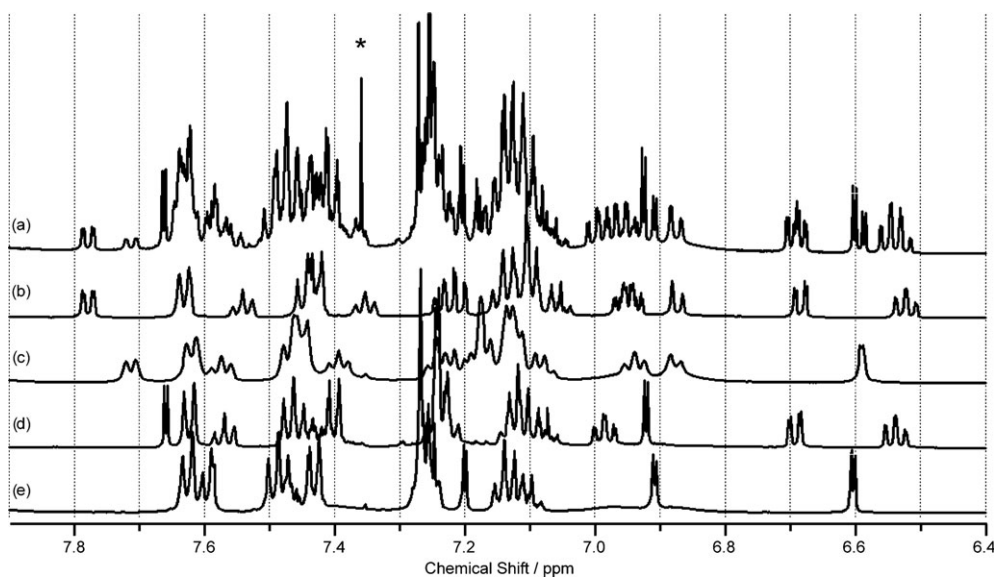


Fig. 1 ^1H NMR spectra of (a) the reaction mixture after the cross radical coupling *via* chemical oxidation, (b) **1-1**, (c) **1-2**, (d) **2-1** and (e) **2-2** in CDCl_3 (the peak with an asterisk is due to residual benzene solvent).

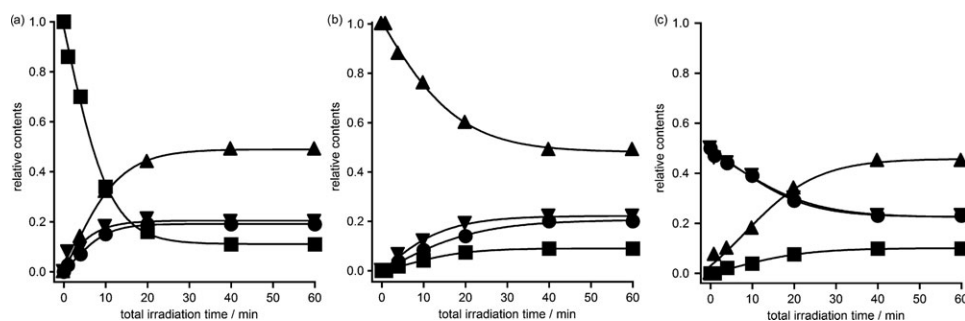


Fig. 2 ^1H NMR analysis of the photoinduced cross radical coupling of the HABI derivatives in CDCl_3 : (a) **1-2**, (b) **2-1** and (c) an equimolar mixture of **1-1** and **2-2**. ●: **1-1**, ■: **1-2**, ▲: **2-1** and ▼: **2-2**.

1 $^{\bullet}$ and **2 $^{\bullet}$** , were produced by the photodissociation of the hetero-HABI derivative or an equimolar mixture of two homo-HABI derivatives. The photochemical formation ratio of the four dimers was slightly different from the ratio derived after chemical oxidation. We should note that this difference is based on the reaction conditions for the formation/recombination of the imidazolyl radicals, such as solvent, concentration and so on. The favored molar ratio of this cross radical coupling is based on the electronic and structural properties of the triphenylimidazole derivatives and radicals. If the recombination takes place at random, the relative proportions of dimers **1-1**, **1-2**, **2-1** and **2-2** should be 1 : 2 : 2 : 1. From the experimental results, the actual proportions are 2 : 1 : 3 : 2 (in benzene by chemical oxidation) and 2 : 1 : 5 : 2 (in CDCl_3 by photochemical dissociation and recombination). The proportions of homodimers **1-1** and **2-2** are the same, with no solvent or polarity effects, and the steric interactions due to chlorine at the *ortho* position of the 2-phenyl ring are the same for both lophyl radicals **1 $^{\bullet}$** and **2 $^{\bullet}$** , since the chlorines at the *meta* and *para* positions in **2 $^{\bullet}$** should have no steric effect upon dimer formation, as supported by the equal proportion of dimers **1-1** and **2-2**. For the formation of **1-2** and **2-1**, there are some effects of solvent polarity. These results reflect the influence of the activation energy and transition state on the formation of the heterodimers.

In conclusion, we have isolated two hetero-HABI compounds and revealed their chemical structures by X-ray crystallography. We then quantitatively determined the molar ratio of four HABI derivatives derived from the radical cross coupling of two imidazolyl radicals by chemical oxidation. We also revealed the photoinduced radical cross coupling of hetero-HABI derivatives and estimated the favored molar ratio of HABI derivatives derived from the transformation of hetero-HABIs by photodissociation. At this stage, it is not our goal to control the molar ratio of the HABI derivatives obtained from the recombination of imidazolyl radical pairs, chemically or photochemically. The important point is to demonstrate the first isolation of two hetero-HABIs and to obtain structural information and information about their dissociation/recombination behavior. The photodissociation of a hetero-HABI caused the formation of hetero- and cross-coupled homo-HABIs. These results reveal the process of photoinduced cross radical coupling of HABI derivatives for the first time. Irradiating with light converted them into two dissociated imidazolyl free radicals, which, after diffusion,

recombined into HABI derivatives to form both hetero- and homo-imidazole dimers. We believe these results give a new insight into the chemistry of hetero-HABI systems for the progress of both industrial and scientific interests.

Experimental

General

^1H NMR spectra were obtained at 500 MHz using a JMN-ECP500A (JEOL) spectrometer. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane.

Materials

All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Wakogel C-300 45–75 μm). All reagents except benzene were purchased from TCI and Wako Co. Ltd., and were used without further purification. Benzene was distilled over appropriate drying agents prior to use.

Synthesis

All manipulations were carried out with the exclusion of light. Under nitrogen, to a solution of **1** (125.0 mg, 0.38 mmol) and **2** (151.0 mg, 0.38 mmol) in benzene (190 mL) was added 15% aqueous KOH (95 mL), and the solution was stirred at room temperature for 30 min. Potassium ferricyanide (2.30 g, 7.60 mmol) was then added and the solution was vigorously stirred overnight. The organic layer was separated, exhaustively washed with water and concentrated *in vacuo*. From the residue, **1-1** (79.6 mg, 0.121 mmol, yield: 32%; $R_f = 0.12$), **1-2** (33.6 mg, 0.0463 mmol, yield: 12%; $R_f = 0.17$), **2-1** (34.4 mg, 0.0474 mmol, yield: 12%; $R_f = 0.38$) and **2-2** (53.7 mg, 0.0676 mmol, yield: 18%; $R_f = 0.41$) were isolated by silica gel column chromatography using CHCl_3 as the eluent.

1-1 was recrystallized from acetonitrile to give yellow needles. ^1H NMR (500 MHz, CDCl_3): $\delta = 7.78$ (dd, $J = 7.6$ and 1.8 Hz, 1H), 7.63 (d, $J = 7.6$ Hz, 2H), 7.54 (t, $J = 7.6$ Hz, 1H), 7.54–7.42 (m, 4H), 7.35 (t, $J = 7.6$ Hz, 1H), 7.25–7.20 (m, 2H), 7.16–7.05 (m, 12H), 6.97–6.93 (m, 2H), 6.87 (d, $J = 8.0$ Hz, 1H), 6.68 (dd, $J = 8.0$ and 1.8 Hz, 1H) and 6.52 (t, $J = 8.0$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): $\delta = 168.44, 165.69, 144.06, 138.40, 134.05, 134.83, 134.62, 134.57, 134.40, 132.66, 132.02, 131.78, 131.20, 131.07, 130.83, 130.55, 129.89, 129.77, 129.71,$

129.56, 128.72, 128.68, 128.32, 128.11, 127.77, 127.75, 127.67, 127.55, 127.01, 126.06, 125.77 and 110.77.

1-2 was recrystallized from dichloromethane/ethanol to give yellow needles. ^1H NMR (500 MHz, CDCl_3): δ = 7.71 (d, J = 7.6 Hz, 1H), 7.63–7.56 (m, 3H), 7.41–7.35 (m, 3H), 7.26–7.06 (m, 12H), 6.95–6.87 (m, 3H) and 6.59 (d, J = 2.4 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 168.98, 166.89, 144.11, 138.44, 137.95, 134.82, 134.55, 134.50, 134.25, 132.55, 131.66, 131.57, 131.52, 131.41, 131.34, 130.27, 130.18, 129.86, 129.67, 129.59, 128.90, 128.84, 128.47, 128.41, 127.84, 127.78, 127.02, 127.00, 126.29, 126.11 and 110.05.

2-1 was recrystallized from dichloromethane/acetonitrile to give yellow blocks. ^1H NMR (500 MHz, CDCl_3): δ = 7.66 (d, J = 2.4 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.48–7.39 (m, 6H), 7.26–7.21 (m, 6H), 7.14–7.06 (m, 6H), 7.00–6.97 (m, 1H), 6.92 (d, J = 2.4 Hz, 1H), 6.69 (dd, J = 8.0 and 1.6 Hz, 1H) and 6.55–6.52 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 168.38, 166.15, 142.12, 137.72, 134.21, 134.12, 132.89, 131.95, 131.84, 131.68, 131.30, 131.28, 130.91, 130.87, 130.11, 130.03, 129.94, 129.56, 129.43, 128.80, 128.47, 128.40, 128.03, 127.89, 127.87, 127.70, 126.92, 126.31, 125.87 and 110.52.

2-2 was recrystallized from dichloromethane/acetonitrile to give yellow blocks. ^1H NMR (500 MHz, CDCl_3): δ = 7.63–7.59 (m, 5H), 7.50–7.42 (m, 7H), 7.27–7.24 (m, 6H), 7.20 (d, J = 2.4 Hz, 1H), 7.15–7.10 (m, 3H), 6.91 (d, J = 2.4 Hz, 1H) and 6.60 (d, J = 2.4 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 168.92, 167.34, 142.12, 138.67, 137.35, 137.22, 134.88, 133.90, 133.06, 132.07, 132.05, 131.76, 131.64, 131.60, 131.33, 130.83, 130.72, 130.48, 129.81, 129.67, 129.64, 129.56, 128.97, 128.70, 128.54, 128.00, 127.95, 127.89, 127.28, 126.92, 126.54 and 109.80.

Photoinduced cross radical coupling was monitored by ^1H NMR spectroscopy of an equimolar mixture of **1-1** and **2-2**, **1-2** or **2-1** as the starting material (6.7 mM in CDCl_3). The solution was de-gassed by a freeze–pump–thaw cycle, allowed to dissociate into two imidazolyl radicals by irradiating it with visible light (400–700 nm, 16.6 mW cm^{-2}) and recombined into HABIs. After terminating the photoirradiation, the reaction solution was cooled for 10 min at room temperature and its ^1H NMR spectrum measured. This protocol was repeated until a photostationary state was reached.

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