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# Tuning of Optical Properties and Thermal Cycloreversion Reactivity of Photochromic Diarylbenzene by Introducing Electron-Donating Substituents

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## ABSTRACT

Thermally reversible photochromic compounds having excellent physicochemical properties can be exploited for many practical applications, such as ophthalmic lenses, real-time holography, and super-resolution microscopy. In this study, we have designed and synthesized novel 1,2-diarylbenzene derivatives bearing various electron-donating substituents at *p*-position of the

phenyl ring to tune the optical and thermal properties for the practical applications. Introduction of the electron-donating groups resulted in the red-shift of the absorption spectra, increase in the absorption coefficients of the open-ring isomers, and deceleration of the thermal cycloreversion of the closed-ring isomers. Theoretical analysis based on Hammett's substituent constant and density functional theory revealed that the rate of thermal cycloreversion became lower in proportion to the electron-donating ability of the substituent. The novel 1,2-diarylbenzene derivatives synthesized here could undergo photocyclization upon irradiation with UV-A light and fast thermal cycloreversion with a half-life of a few hundred milliseconds to seconds.

## Introduction

Photochromic compounds undergoing reversible transformation between two isomers with different absorption spectra upon photoirradiation have attracted significant attention, because various physicochemical properties, such as conductivity, fluorescence, and magnetism, can be modulated without any direct physical contact.<sup>1-3</sup> Thermally reversible (T-type) photochromic molecules are promising materials for ophthalmic lenses<sup>4</sup>, photoactuators<sup>5-6</sup>, and so on. Azobenzene, spiropyran, and naphthopyran are some of the representative T-type photochromic compounds. During last two decades, several kinds of T-type photochromic compounds undergoing fast thermal bleaching with half-life ( $t_{1/2}$ ) of a few seconds or below at room temperature have been reported. Abe and co-workers developed specifically hexaarylbiimidazole derivatives, that have  $t_{1/2}$  of a few tens of milliseconds or nanoseconds for thermal bleaching, by inhibiting the diffusion of radicals by crosslinking two imidazole units.<sup>7-10</sup> They were applied to real-time holography.<sup>11-12</sup> Raymo *et al.* reported oxazine derivatives with  $t_{1/2}$  of a few tens of nanoseconds,<sup>13-14</sup> and achieved super-resolution imaging using the oxazine derivative linked to a

fluorescent dye.<sup>15-16</sup> Thus, T-type photochromic compounds undergoing fast thermal bleaching are of great interest for the various applications.

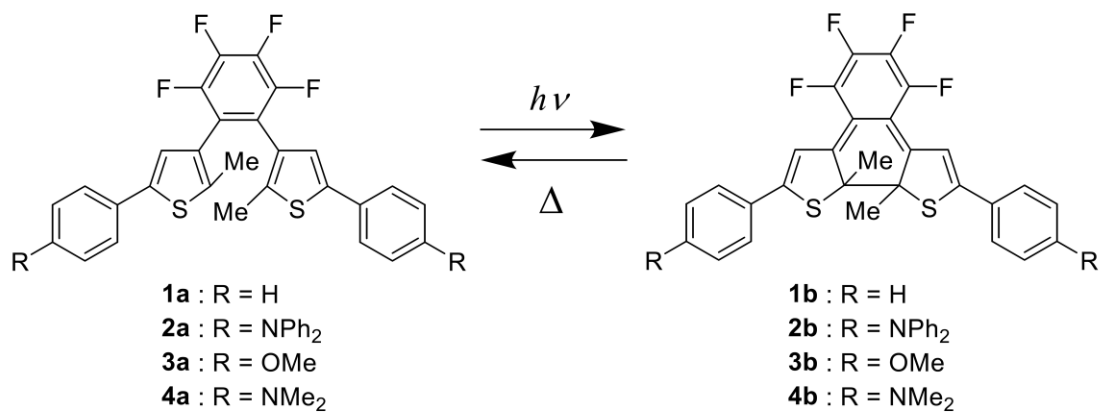
On the other hand, photochemically reversible (P-type) photochromic compounds are also gaining significant attention for optical memory media,<sup>2, 17</sup> switching devices,<sup>18</sup> display materials,<sup>19</sup> and non-linear optics.<sup>20</sup> Diarylethene (DAE) is one of the most promising P-type photochromic compounds because of their excellent properties such as high durability, high sensitivity, rapid response, and high reactivity in the solid state.<sup>21</sup> If DAE can be converted to T-type photochromic compound, a new family of T-type photochromic switch with the excellent properties mentioned above can be created. Although various approaches have been adopted to accelerate the thermal cycloreversion of DAEs,<sup>22-23</sup> there are only a few studies on DAE that undergoes thermal cycloreversion with half-life ( $t_{1/2}$ ) of the order of seconds at room temperature.<sup>24-27</sup>

Very recently, we have succeeded in developing a T-type photochromic compound, 1,2-diarylbenzene (DAB) by only introducing a tetrafluorobenzene ring to the ethene bridge of a representative DAE, 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**Scheme 1**).<sup>28</sup> DAB (**1a**) undergoes photocyclization upon irradiation with ultraviolet (UV) light and fast thermal cycloreversion with a  $t_{1/2}$  of 130 ms at 298 K. However, **1a** has several limitations in practical applications such as photochromic ophthalmic lenses. Specifically, **1a** has almost no absorption in the UV-A region (315-400 nm), and the absorbance at visible region of the closed-ring isomer **1b** upon irradiation with UV (313 nm) light is very small because of the extremely rapid thermal cycloreversion. Several approaches to overcome this drawback can be proposed based on the studies on DAEs.<sup>29-30</sup> The absorption spectrum of DAE open-ring isomer can be red-shifted by extending the  $\pi$ -conjugation.<sup>29</sup> Besides, changing the aryl moiety from the thiophene ring to an aromatic ring with lower aromatic stabilization energy could decelerate the thermal cycloreversion

of DAE closed-ring isomer.<sup>30</sup> However, a combination of the multiple molecular modifications may make the prediction of physicochemical properties difficult, because it may simultaneously affect many properties. Hence, a rational designing of the molecules is highly sought after.

Irie and coworkers reported that the introduction of electron-donating substituents at *p*-position of the phenyl rings of a DAE derivative, 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene, leads to a red-shift in the absorption spectrum of the open-ring isomer and increases of the absorption coefficient while maintaining the photocyclization quantum yield.<sup>31</sup> Moreover, the thermal cycloreversion of DAE closed-ring isomers becomes slow when electron-donating groups are introduced in the aryl groups.<sup>32</sup> If the introduction of electron-donating groups confers the same properties to DAB, as those conferred to DAE, an effective method for improving the physicochemical properties of DAB can be established. Considering this, here, we have introduced electron-donating groups at the *p*-position of the phenyl rings of **1a**, with the aim of addressing the problems arising because of multiple molecular modifications.

In this work, we have designed and synthesized novel DABs **2a–4a** having *N,N*-diphenylamino, methoxy, or *N,N*-dimethylamino groups as the electron-donating substituents at the *p*-position of the phenyl rings (Scheme 1). The photochromic and thermal properties in solution were investigated, and the synthesized compounds exhibited the desired optical properties and thermal cycloreversion reaction.



**Scheme 1.** 1,2-Diarylbene derivatives used in this work.

## Experimental Section

### Materials

Chemicals used for the syntheses were commercially available and used without further purification. Compound **1a** was prepared by a method described previously.<sup>28</sup> The protocol for the synthesis of DABs **2a–4a** are given in the Supporting Information.

### Spectroscopic measurements

All the solvents used were of spectroscopic grade and purified by distillation before use. <sup>1</sup>H NMR (300 MHz) spectra were recorded on a Bruker AV-300N spectrometer using tetramethylsilane as the internal standard. High-resolution mass spectra were obtained on a Bruker FT-ICR/solariX mass spectrometer. Matrix-assisted laser desorption/ionization was used for ionization, and *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile was used as the matrix. UV-Vis absorption spectra were acquired on a JASCO V-560 absorption spectrometer. The light power was measured using a Neark PM-335A power meter. Fluorescence spectra were acquired on a JASCO FP-8300 fluorescence spectrophotometer, and the fluorescence quantum yield was with the aid of a JASCO ILF-835 integrating sphere. The sample solutions for fluorescence spectroscopic measurements were deaerated by bubbling with argon gas for 10 min before the measurements.

### Photochromic Reaction

Transient absorption spectra were measured using a Nikon ECLIPSE E600 optical microscope equipped with Ocean Optics USB4000 fiber multichannel analyzer as the photodetector. Samples



were irradiated using a 200 W mercury–xenon lamp (MORITEX MSU-6) as the light source. Monochromatic light was obtained by passing the light through a band-pass filter.

### **Thermal Cycloreversion Reaction**

The thermal cycloreversion of DAB closed-ring isomers was carried out in *n*-hexane. The open-ring isomers were put in an optical quartz cuvette. The solution in the cuvette was irradiated at 313 nm using a 300W xenon lamp (Asahi Spectra MAX-301) to give the closed-ring isomers at the temperature of measurement. Monochromatic light was obtained by passing the light through a band-pass filter. The cuvette was placed in a cryostat for spectroscopic measurements (UNISOKU CoolSpek UV/CD) during the thermal cycloreversion reaction.

### **Theoretical studies**

Geometry optimizations and harmonic frequency calculations of open-ring isomers, closed-ring isomers, and transition states were performed using Gaussian 09 Rev.C.01 program package. The transition-state search was performed with Opt = TS keyword, using Berny algorithm to optimize to a transition state rather than a local minimum. Each stationary point was characterized by the number of imaginary frequencies ( $N_{\text{Imag}} = 1$  for transition state and  $N_{\text{Imag}} = 0$  for the local minimum) and by zero-point vibrational energies. To follow unrestricted Kohn–Sham solution, the broken-symmetry (BS) guess was generated and followed using keyword Guess (mix, always) for transition state.<sup>33</sup> The B3LYP level of density functional theory (DFT) was used in combination with a 6-31G(d) basis set. Time dependent (TD)-DFT calculation was performed at the CAM-B3LYP/6-31G(d) level using the optimized molecular structures.

## Results and Discussion

### Molecular Design using Theoretical Calculation

First, we attempted to predict the influence of the electron-donating groups in the *p*-position of the phenyl ring on the spectral properties of DAB. Figure 1 shows the calculated absorption spectra and the oscillator strength ( $f$ ) of DAB open-ring isomers calculated by TD-DFT at the CAM-B3LYP/6-31G(d)//B3LYP/6-31G(d) level. The calculated  $f$  values are listed in Table S1. The maximum value of  $f$  for **1a** was observed at 270.6 nm, which is close to the absorption maximum of **1a** ( $\lambda_{\text{max}} = 285$  nm). On the other hand, the maximum values of  $f$  for **2a–4a** were observed at 319.6, 276.6, and 294.7 nm, respectively. It is evident that the absorption spectra of **2a–4a** are red-shifted with respect to that of **1a**. The maximum  $f$  values of **2a–4a** were calculated to be 1.743, 1.120, and 1.391, respectively, which were higher than that of **1a** ( $f = 0.928$ ). Therefore, theoretical calculations predicted that the introduction of electron-donating groups to **1a** results in the red-shift of the absorption spectra and increases in the absorption coefficient in the open-ring isomers. The  $f$  values predict that **2a** and **4a** are likely to have higher absorbance in the UV-A region.

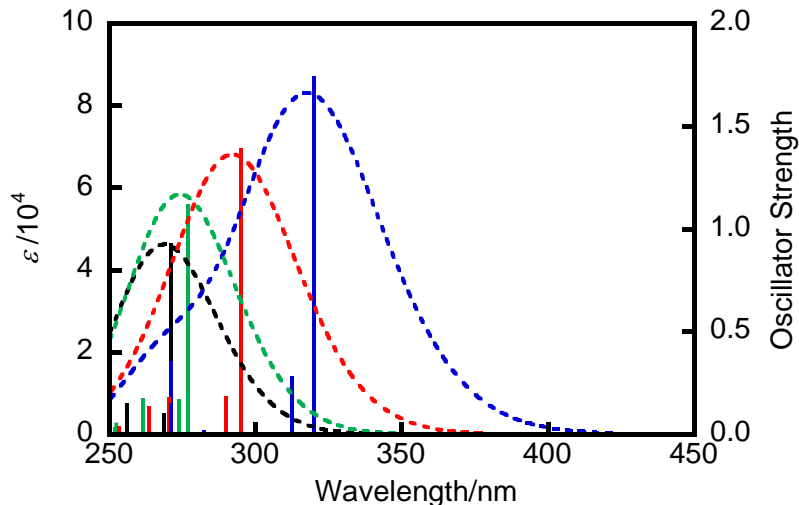


Figure 1. Calculated absorption spectra of **1a** (black line), **2a** (blue line), **3a** (green line), and **4a** (red line) by TD-DFT (CAM-B3LYP/6-31G(d)//B3LYP/6-31G(d) level of the theory), modeled with a HWHM of  $2690\text{ cm}^{-1}$ .

Next, we estimated the influence of the electron-donating substituents on the thermal cycloreversion. To predict the reactivity of **2b–4b** in the thermal cycloreversion, the activation energies ( $E_a$ ) required for the transformation from the closed-ring isomer to the open-ring isomer were estimated by DFT calculation (Table S2). The  $E_a$  values of **2–4** (61.27, 62.02, and 66.45  $\text{kJ mol}^{-1}$  for **2**, **3**, and **4**, respectively) are higher than that of **1** (57.45  $\text{kJ mol}^{-1}$ ). Therefore, the thermal cycloreversion of **2b–4b** is expected to be slower than that of **1b**. Thus, the introduction of the electron-donating groups at the *p*-position of the phenyl rings of **1a** led to the deceleration of the thermal cycloreversion. Therefore, the electron-donating groups play an important role in determining not only the spectral properties but also the thermal cycloreversion reactivity of DABs used in this work.

## Photochromic Reaction

To study the photochromic properties of DABs, we synthesized DABs **2a–4a** (details in Supporting Information) and investigated their photochromic properties in *n*-hexane. The optical and thermal properties of **1–4** are summarized in Table 1. Figure 2a shows the absorption spectra of **1a–4a** in *n*-hexane. As predicted by TD-DFT calculations, the absorption spectra of **2a–4a** were red-shifted in comparison with that of **1a**. In addition, the absorption coefficients at  $\lambda_{\max}$  ( $\epsilon_{\max}$ ) for **2a–4a** were determined to be 55900, 35600, and 47400 M<sup>-1</sup> cm<sup>-1</sup>, respectively, which are larger than that of **1a** ( $\epsilon_{\max} = 31000$  M<sup>-1</sup> cm<sup>-1</sup>). The absorption at  $\lambda_{\max}$  was mainly assigned to HOMO–LUMO+1 transition for **1a** and HOMO–LUMO transition for **2a–4a**, respectively. The molecular orbitals related to the transitions were shown in Figure S4. The electron densities of the HOMO and LUMO+1 levels for **1a** were delocalized. On the other hand, the electron density of the HOMO level of **2a–4a** was localized around the aryl moieties, while that of the LUMO level was localized around the ethene bridges. Therefore, the transitions of **2a–4a** exhibited an intramolecular charge transfer (ICT) character, which suggests that the red-shift in the absorption spectra of **2a–4a** depends on the electron-donating ability of the substituents. In addition, the electron density of the HOMO level of **2a** presents in the diphenylamino group, suggesting that the  $\pi$ -conjugation of **2a** is longer than those of the other diarylbenzene derivatives. Therefore, **2a** exhibited the largest red-shifted absorption spectrum due to the ICT characteristics and the extending of  $\pi$ -conjugation. Moreover, a shoulder absorption band of **2a** was observed at 305 nm, which was mainly assigned to the HOMO–1–LUMO+6 transition from the aryl moieties to diphenylamino groups.

Upon irradiation with 313 nm light, new absorption bands assigned to the closed-ring isomers **2b–4b** appeared at the visible region, as shown in Figure 2b. Once the irradiation is stopped, the absorption bands rapidly disappear owing to thermal cycloreversion (Figure 2c). Thus, **2a–4a** underwent photocyclization and rapid thermal cycloreversion, similar to that observed for **1a**. The  $\lambda_{\text{max}}$  values of **2b–4b** were determined to be 770, 735, and 765 nm, respectively, all of which are red-shifted relative to that of **1b** in *n*-hexane ( $\lambda_{\text{max}} = 730$  nm). The result is consistent with the UV-vis spectra calculated by TD-DFT at the CAM-B3LYP/6-31G(d) level (Figure S5 and Table S3). The absorption bands corresponded to HOMO–LUMO transition. The red-shift in the absorption spectra of **2b–4b** was ascribed to a decrease in the HOMO–LUMO gap upon the introduction of the electron-donating groups (Table S4).

In previous report, it was confirmed that **1a** has high fatigue resistance for repeated photocyclization and thermal cycloreversion and photoreactivity in the polymer film.<sup>28</sup> To confirm their properties of **2a–4a**, we have firstly investigated repeating cycles of the photocyclization and thermal cycloreversion of **2a–4a**. Photocyclization upon irradiation with 313 nm light for 1.0 s and thermal cycloreversion at 298 K were alternately repeated for **2a–4a** in *n*-hexane (Figure S6). After 20 cycles, a significant decrease of the absorbance in their closed-ring isomers was hardly observed. Next, the absorption spectra of the polymer films containing **2a–4a**, that were prepared by casting a toluene solution containing the compounds and poly(methyl methacrylate) (PMMA) (1 : 4 w/w) on a slide glass and drying them in air, were measured. As shown in Figure S7, appearance of the absorption bands of the closed-ring isomers upon irradiation with 313 nm light and rapid disappearance by the thermal cycloreversion could be observed. Therefore, these results indicate that **2a–4a** also have the high fatigue resistance and the photoreactivity in the solid state as well as **1a**.

**Table 1.** Optical properties and Arrhenius parameters for thermal cycloreversion of 1,2-diarylbenzene derivatives in *n*-hexane.

	Open-ring isomer		Closed-ring isomer $\lambda_{\max}/\text{nm}$	$E_a/$ $\text{kJ mol}^{-1}$	$E_{a(\text{calcd.})}/$ $\text{kJ mol}^{-1a}$	$A/\text{s}^{-1}$	$k/\text{s}^{-1}$ (298 K)	$t_{1/2}/\text{ms}$ (298 K)
	$\lambda_{\max}/\text{nm}$	$\varepsilon/\text{M}^{-1}\text{cm}^{-1}$						
<b>1<sup>b</sup></b>	285	31000	730	66	57.45	$2.1 \times 10^{12}$	5.34	130
<b>2</b>	345	55900	770	69	61.27	$2.8 \times 10^{12}$	2.11	330
<b>3</b>	290	35600	735	71	62.02	$3.7 \times 10^{12}$	1.36	510
<b>4</b>	315	47400	765	77	66.45	$2.1 \times 10^{13}$	0.61	1140

<sup>a</sup>Activation energy estimated by DFT calculation. <sup>b</sup>Ref. 28.

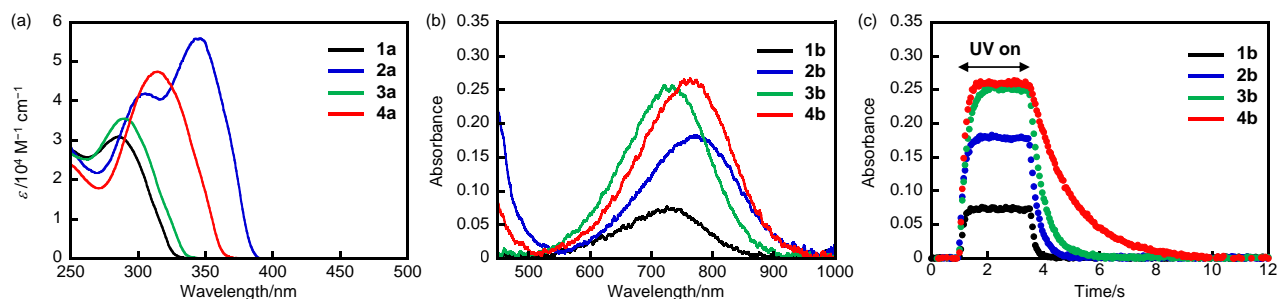


Figure 2. (a) Absorption spectra of **1a**, **2a**, **3a**, and **4a** in *n*-hexane, (b) absorption spectra of **1b**, **2b**, **3b**, and **4b** upon irradiation with 313 nm light ( $120 \text{ mW cm}^{-2}$ ) at 298 K (the absorbance at 313 nm in the solutions of open-ring isomer was set to 1.5), and (c) change in the absorbance at  $\lambda_{\max}$  upon irradiation at 313 nm.

Compounds **2a** and **4a** underwent photocyclization and fast thermal cycloreversion even upon irradiation at 365 nm owing to the red-shifted absorption spectra (Figure S8). However, no color

change of **1a** in *n*-hexane was observed upon irradiation at 365 nm (Figure S9). Unfortunately, the photochromic reaction of **2a** could not be observed with naked eyes, because **2a** exhibited bright blue fluorescence with a fluorescence maximum at 388 nm and fluorescence quantum yield of 9.3% (Figure S10). On the other hand, **4a** in *n*-hexane underwent the photochromic reaction involving a color change from colorless to green when the solution was irradiated at 365 nm (Figure 3 and Video S1). Once the irradiation was stopped, the green color rapidly disappeared. Thus, the introduction of *N,N*-dimethylamino group at the *p*-position of the phenyl ring of **1a** enabled us to design a DAB derivative that could undergo photocyclization upon irradiation with UV-A light and fast thermal cycloreversion with a half-life of a few seconds.

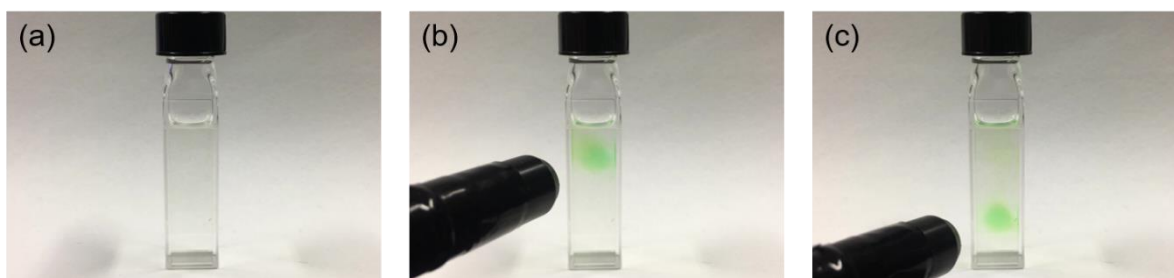


Figure 3. Photochromic reaction of **4a** in *n*-hexane ( $[\mathbf{4a}] = 9.6 \times 10^{-3}$  M): (a) before photoirradiation and upon irradiating the (b) upper part and (c) the lower part of the quartz cuvette with 365 nm light ( $60 \text{ mW cm}^{-2}$ ).

The absorbance of **1b–4b** at the stationary states increased in the order of **1b**, **2b**, **3b**, **4b** (Figure 2c), which is consistent with the order of the  $E_a$  values estimated by the theoretical calculations. It can be noted that the absorbance at the stationary state increases with increasing photocyclization

quantum yields ( $\Phi_{oc}$ ) and/or decreasing rate of thermal cycloreversion.<sup>4</sup> It is difficult to quantitatively evaluate the  $\Phi_{oc}$  of DABs due to the thermal instability of the closed-ring isomers at room temperature. However, the previous study on DAEs revealed that the introduction of the electron-donating groups to DAEs hardly affects the  $\Phi_{oc}$ .<sup>31</sup> Therefore, it is concluded that the absorbance of the closed-ring isomers at the stationary state is mostly affected by the rate of thermal cycloreversion.

### Thermal Cycloreversion Reaction

To quantitatively evaluate the reactivities of **2b–4b** in the thermal cycloreversion, we recorded the change in the absorption of **2b–4b** as a function of time at various temperatures (Figure 4). The absorption decay obeyed first-order kinetics (Figure S11). The reaction rate constants ( $k$ ) of the thermal cycloreversion of **2b–4b** at various temperatures were calculated from the slope of the linear plots (Table S5). Figure 5 shows the temperature dependence of  $k$ . The  $E_a$  values and the frequency factor ( $A$ ) of the thermal cycloreversion were determined from the slope and intercept of the linear Arrhenius plots. The results are summarized in **Table 1**. The  $E_a$  values of **2b–4b** were 69, 71, and 77 kJ mol<sup>-1</sup>, respectively. The measured  $E_a$  values are consistent with the  $E_a$  values calculated by DFT (Figure S12). Furthermore, the  $A$  values for **2b–4b** were estimated to be 2.8, 3.7, and  $21 \times 10^{12}$  s<sup>-1</sup>, respectively. Using the estimated  $E_a$  and  $A$  values,  $t_{1/2}$  of **1b–4b** at 298 K were calculated to be 130, 330, and 510, and 1140 ms, respectively. Thus,  $t_{1/2}$  also increased in the same order as the absorbance at the stationary state. This confirmed that the absorbance of the closed-ring isomers at the stationary state increased with decreasing rate of thermal cycloreversion.



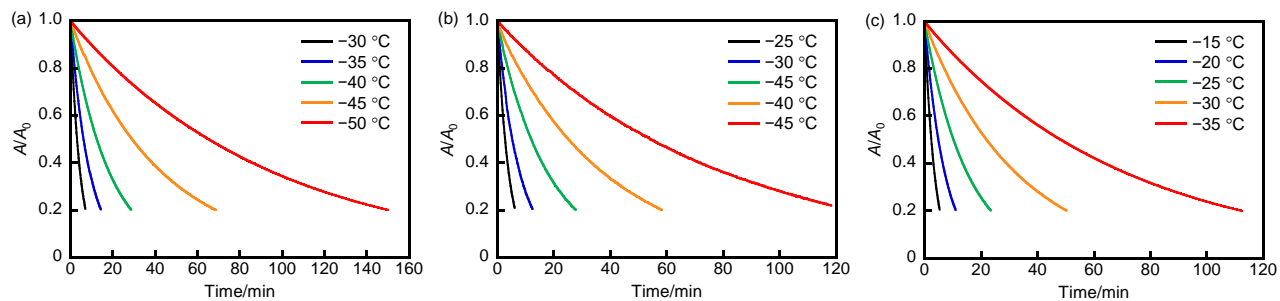


Figure 4. Absorption decay curves at  $\lambda_{\max}$  for (a) **2b**, (b) **3b**, and (c) **4b** in *n*-hexane at various temperatures.

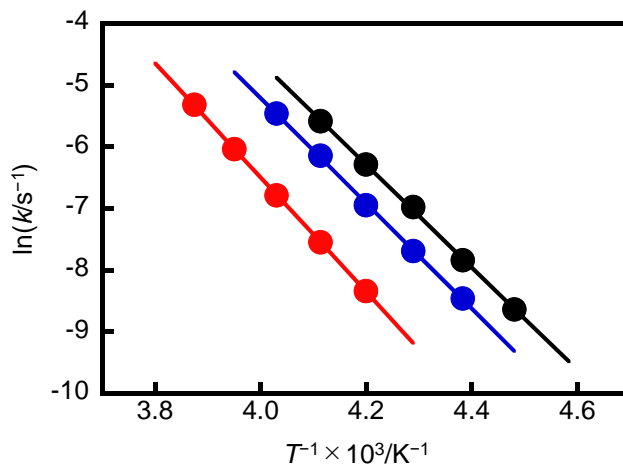


Figure 5. Temperature dependence of the rate constant ( $k$ ) for thermal cycloreversion of **2b** (black circle), **3b** (blue circle), and **4b** (red circle).

### Correlation between Electron-Donating Ability of the Substituents and Thermal Cycloreversion

To elucidate the relationship between the electron-donating ability of the substituents and the thermal cycloreversion,  $\log(k/k_H)$  at 298 K was plotted as a function of Hammett's substituent constant ( $\sigma_p$ )<sup>34</sup> (Figure 6a), where  $k_H$  is the rate constant of **1b**.  $\sigma_p$  is a typical parameter indicating the electron-donating or withdrawing ability of a substituent and useful for understanding the relationship between the rate of the reaction and the substituent effects and the reaction mechanism.<sup>35-38</sup> As can be seen in Figure 6a, it is evident that  $\log(k/k_H)$  is linearly dependent on  $\sigma_p$  ( $r^2 = 0.886$ ). The reaction constant ( $\rho$ ), as determined from the slope of the linear plot, was 1.29, which is positive. Therefore, the thermal cycloreversion is retarded in proportion to the increase in the electron-donating ability of the substituents introduced at the *p*-position of the phenyl ring of DABs. A positive  $\rho$  indicates an increase in the negative charge (or a decrease in the positive charge) at the reaction center in the transition state. Mulliken charges at the reacting carbon atoms of DABs estimated by DFT calculation (Table S6) were negative in the closed-ring isomer and the transition state. The electrostatic potentials were also negative as well as Mulliken charges (Table S7). Moreover, the values in the transition state increased in comparison with those in the closed-ring isomer, as evident from the Hammett plot. Thus, the Hammett plot revealed that the thermal cycloreversion of DABs is decelerated with increasing electron-donating ability of the substituent, owing to the negative charge of the reacting carbon atoms.

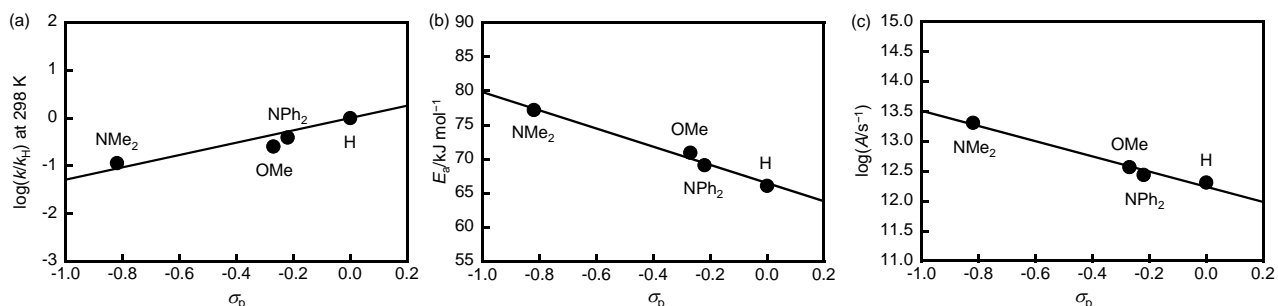


Figure 6. Hammett plots of the (a) rate constant at 298 K ( $r^2 = 0.886$ ), (b) activation energy ( $r^2 = 0.984$ ), and (c) frequency factor ( $r^2 = 0.978$ ) for the thermal cycloreversion.

Since the rate of thermal cycloreversion depends on  $E_a$  and  $A$ , it is expected that  $E_a$  and/or  $A$  will be linearly dependent on  $\sigma_p$ . Figure 6b shows the relationship between  $E_a$  and  $\sigma_p$ .  $E_a$  exhibited a good correlation with  $\sigma_p$  ( $r^2 = 0.984$ ), indicating that the activation energy for the transformation from the closed-ring isomer to the open-ring isomer increases with increasing electron-donating ability of the substituent. Moreover,  $\log(A)$  and  $\sigma_p$  were linearly dependent, with  $r^2 = 0.978$  (Figure 6c). Thus, the electron-donating groups affect not only the activation energy but also the frequency factor of the thermal cycloreversion of DABs. Increasing the electron-donating ability increases  $E_a$  and  $\log(A)$  and decreases  $\log(k)$ . This indicates that the change in  $E_a$  by the electron-donating substituents primarily affects the rate of thermal cycloreversion; the influence on the frequency factor is rather small.

The reactivity in thermal cycloreversion, i.e.  $E_a$ , relates to the energy difference ( $\Delta E$ ) between the closed-ring isomer and open-ring isomer in the ground state. Smaller  $\Delta E$  leads to higher  $E_a$  and thus, a decrease in the reactivity in the thermal cycloreversion. This is known as the Bell–Evans–Polanyi (BEP) principle.<sup>39</sup> The  $\Delta E$  values of **1–4** were determined to be 112.23, 103.62, 106.36, and 98.58 kJ mol<sup>-1</sup>, respectively, by DFT calculation (Table S2).  $E_a$  exhibited a linear relationship with  $\Delta E$  (Figure S13), suggesting that the thermal cycloreversion of DABs could be interpreted based on the BEP principle. When the closed-ring isomer is relatively stabilized with respect to the open-ring isomer, the reaction coordinates in the transition state shift toward the open-ring isomer, as shown in Figure 7. Thus, the geometry of DABs in the transition state should be closer

to that of the open-ring isomer, with relative stabilization of the closed-ring isomer. This is known as Hammond's postulate.<sup>39</sup> To evaluate the geometry in the transition state, the distance between the reacting carbon atoms and torsion angle of the methyl group on the reacting carbon atom relative to the thiophene ring were calculated (Table S6).<sup>40</sup> Figure 8 shows the relationship of these parameters relative to  $E_a$ ; the average value of two torsion angles was used. As can be seen, both the parameters increased with increasing  $E_a$ . This indicates that the geometry of the transition state of the more thermally stable DAB is closer to the open-ring isomer. Moreover, these parameters for the open- and closed-ring isomers were nearly constant (Figure S14), suggesting that the potential energy surface of the closed-ring isomer is relatively stabilized without a change in the reaction coordinate of both the open- and closed-ring isomers (Figure 7). It is thus concluded that since the reacting carbon atoms have negative charge in the transition state, the potential energy surface of the closed-ring isomer is relatively stabilized with respect to the open-ring isomer upon the introduction of the electron-donating substituents at the *p*-position of the phenyl ring, thereby resulting in an increase in  $E_a$ , a decrease in  $\Delta E$ , and a shift in the reaction coordinate of the transition state toward to the open-ring isomer. As a result, the rate of thermal cycloreversion is lowered, and the extent of decrease is proportional to the electron-donating ability of the substituents.

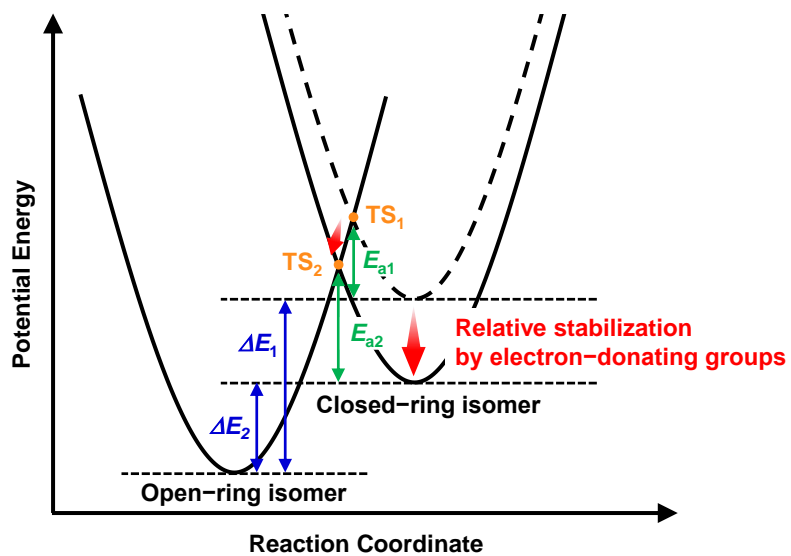


Figure 7. Correlation between the activation energy ( $E_a$ ) and energy difference ( $\Delta E$ ).

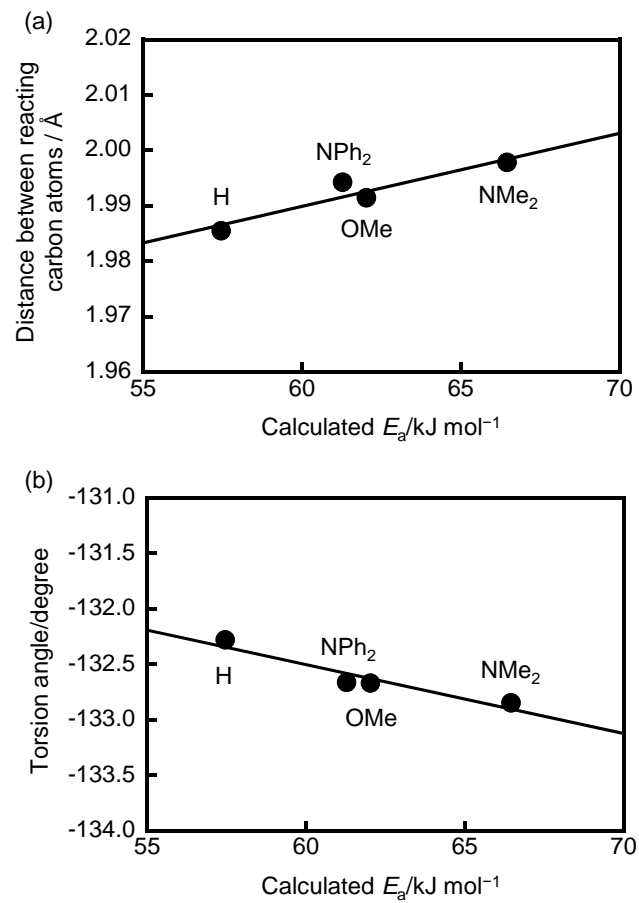


Figure 8. (a) Distance between reacting carbon atoms ( $r^2 = 0.880$ ) and (b) torsion angle of methyl group on the reacting carbon atom relative to the thiophene ring ( $r^2 = 0.910$ ) in the transition state.

## Conclusion

In summary, we synthesized 1,2-diarylbenzene (DAB) derivatives bearing various electron-donating substituents at the *p*-position of the benzene ring with the aim of tuning their optical and thermal properties. The substituted DABs exhibited red-shifted absorption spectra, higher absorption coefficients, and slower thermal cycloreversion in comparison with the unsubstituted DAB. This was also consistent with the predictions of the theoretical calculations. Moreover, the rate constants of the thermal cycloreversion were well correlated with Hammett's substituent constant, suggesting that the rate of thermal cycloreversion is lowered in proportion to the electron-donating ability of the substituent. This work would provide a guideline for designing DABs with desired optical and thermal properties.

## ASSOCIATED CONTENT

**Supporting Information.** The Supporting Information is available free of charge on the ACS Publications website at DOI: \*\*\*\*. Syntheses of 1,2-diarylbenzene derivatives, Figures S1–S14, and Tables S1–S19 (PDF)

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### Notes

The authors declare no competing financial interest.

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