Photochromism of Diarylethenes Having Isopropyl Groups at the Reactive Carbons. Thermal Cycloreversion of the Closed-Ring Isomers

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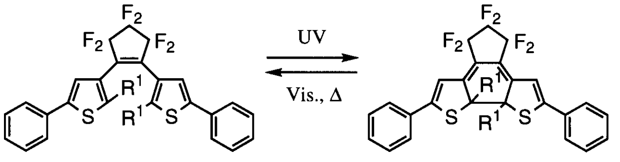
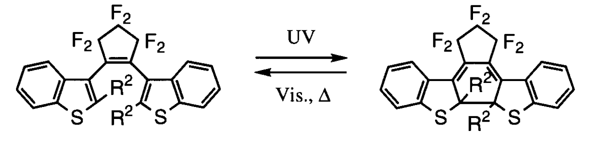
Diarylperfluorocyclopentenes having 2-isopropyl-5-phenylthiophene and 2-isopropyl-1-benzothiophene aryl groups underwent thermally reversible photochromism in solution. The photogenerated colored closed-ring isomers returned to the initial colorless open-ring isomers above 60 °C. The activation energies of the thermal cycloreversion were estimated to be 118 and 132 kJ/mol for the thiophene and benzothiophene derivatives, respectively.

Photochromism is referred as a reversible photoisomerization between two isomers having different absorption spectra.[1,2] Among a number of photochromic compounds, diarylethenes with heterocyclic aryl groups, such as thiophene or benzothiophene aryl groups, are the most promising compounds for applications to optical memories and switches because they undergo thermally irreversible and fatigue resistant photochromic reactions.[3] The thermal stability of the colored closed-ring isomers of diarylethenes is known to depend on the aryl groups.[4] When the aryl groups are phenyl or pyrrole derivatives with high aromatic stabilization energy, the closed-ring isomers become thermally unstable. The closed-ring isomer of 1,2-bis(2-cyano-1,5-dimethyl-4-pyrrolyl)perfluorocyclopentene returns to the open-ring isomer with a half-life time of 37 s in ethyl acetate at room temperature.[5] Here, we examined the effect of bulky substituents at the reactive carbons on the thermal stability of the closed-ring isomers. The cycloreversion rates of **1b** and **2b** were measured and compared with the rates of **3b** and **4b**. 1,2-Bis(2-isopropyl-5-phenylthien-3-yl)perfluorocyclopentene (**1a**), 1,2-bis(2-isopropyl-1-benzothiophen-3-yl)perfluorocyclopentene (**2a**), and their 2-methyl substituted derivatives (**3a** and **4a**) were synthesized by similar methods according to the literature.[6–8]



1a: $R^1 = CH(CH_3)_2$
3a: $R^1 = CH_3$

1b: $R^1 = CH(CH_3)_2$
3b: $R^1 = CH_3$



2a: $R^2 = CH(CH_3)_2$
4a: $R^2 = CH_3$

2b: $R^2 = CH(CH_3)_2$
4b: $R^2 = CH_3$

Figure 1a shows the absorption spectral change of **1a** by irradiation with 290 nm light. **1a** has the absorption maximum at 290 nm in hexane. Upon irradiation with 290 nm light, the colorless solution of **1a** turned blue, in which the visible absorption maximum was observed at 600 nm. The colored product was isolated by HPLC (silica gel; hexane as the eluent), and the structure was analyzed by mass spectrum, ^{1}H NMR spectrum, and elemental analysis.[9] All data agreed well with the closed-ring isomer **1b**. The absorption spectrum of **1b** is also shown in Figure 1a. The spectrum is almost similar to that of the photostationary state, indicating high conversion from **1a** to **1b**. The conversion from **1a** to **1b** in the photostationary state under irradiation with 290 nm light was 91%. The blue color disappeared by irradiation with visible light (λ > 500 nm), and the absorption spectrum returned to that of **1a**.

Figure 1b shows the absorption spectral change of **2a** by irradiation with 313 nm light. Upon irradiation with 313 nm light, the colorless solution of **2a** turned red, in which the visible absorption maximum was observed at 535 nm. The conversion from **2a** to **2b** in the photostationary state under irradiation with 313 nm light was 55%. The red color disappeared by irradiation with visible light (λ > 450 nm), and the absorption spectrum returned to that of **2a**.

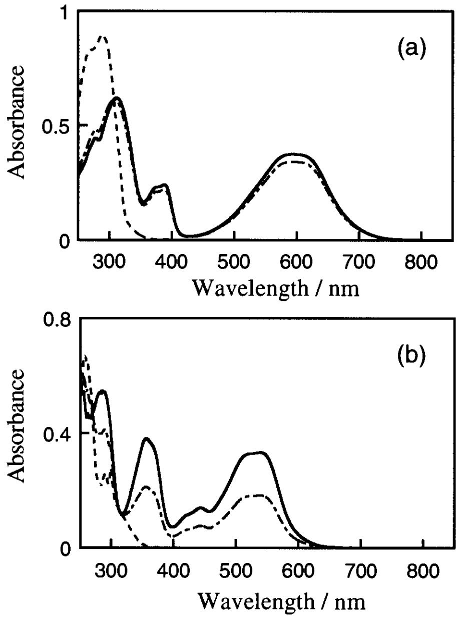


Figure 1. Absorption spectral changes of **1** (2.3×10^{-5} mol/L) (a) and **2** (3.7×10^{-5} mol/L) (b) in hexane at 25 °C: open-ring isomer (- - -), closed-ring isomer (——), the photostationary solution under irradiation with UV light (– – –).

3a and **4a** showed thermally irreversible photochromism.[7,10] Absorbance of the closed-ring isomers, **3b** and **4b**, remained constant in toluene solutions even at 100 °C, as shown in Figure 2. This is one of the main advantageous characters of diarylethene photochromic compounds. However, the colored toluene solutions of **1b** and **2b** were faded at 100 °C, as shown in Figure 2. ^{1}H NMR analysis of the bleached products indicated that **1b** and **2b** thermally returned to **1a** and **2a**, respectively.

Figure 2 shows the decay curves of absorbance of the closed-ring isomers at several temperatures. The decay curves followed the first-order kinetics. Absorbance of **1b** and **2b** decreased slowly at 60 °C, and the half-life time was estimated to be 35 and 106 h for **1b** and **2b**, respectively. At higher temperatures, the decay was accelerated. The half-life time was 3.3 and 7.0 h at 80 °C for **1b** and **2b**, respectivey.

The temperature dependences of the rates (k) are plotted in Figure 3. The activation energy (E_a) and frequency factor (A) of the cycloreversion were determined from the linear relation. The values are summarized in Table 1. Extrapolation of the temperature dependence indicates that the half-life time of the closed-ring isomer **1b** is 91 days at 30 °C and that of the closed-ring isomer **2b** is 580 days at 30 °C. The half-life time of the closed-ring isomer **3b** was estimated to be 1900 years at 30 °C.[7] This indicates that introduction of bulky substituents such as isopropyl substituents at the 2- and 2'-positions of the thiophene or benzothiophene aryl groups can control the thermal cycloreversion reaction.

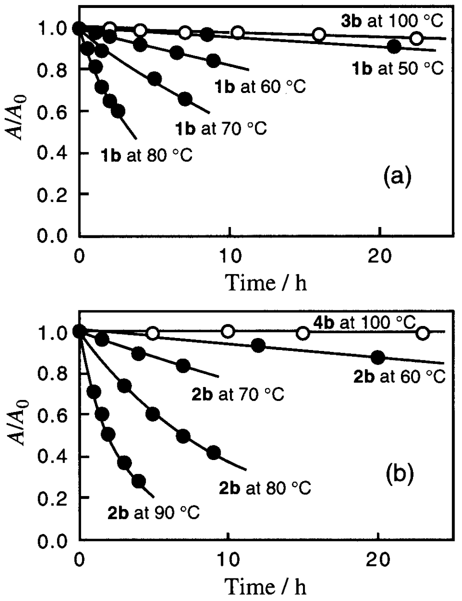


Figure 2. Decay curves of the thermal cycloreversion of **1b** (●) and **3b** (○) (a) and **2b** (●) and **4b** (○) (b).

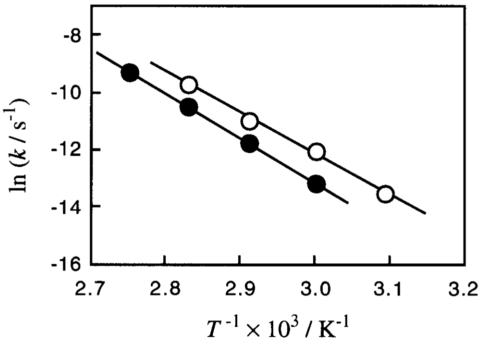


Figure 3. Temperature dependence of the thermal cycloreversion rates of **1b** (○) and **2b** (●).

Table 1. Arrhenius parameters of thermal cycloreversion reactions

	Activation energy / kJ mol^{-1}	Frequency factor / s^{-1}
1b → **1a**	118	1.9×10^{13}
2b → **2a**	132	7.7×10^{14}

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References and Notes

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8 **1a**: colorless crystals: mp 178–179 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.96 (d, J = 6.8 Hz, 12H), 2.80 (sept, J = 6.8 Hz, 2H), 7.20 (s, 2H), 7.2–7.6 (m, 10H); MS m/z (M^+) 576. Anal. Calcd for $C_{31}H_{26}F_6S_2$: C, 64.57; H, 4.54%. Found: C, 64.73; H, 4.63%.
9 **1b**: dark blue colored crystals: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.22 (d, J = 6.4 Hz, 12H), 3.30 (sept, J = 6.4 Hz, 2H), 6.70 (s, 2H), 7.3–7.7 (m, 10H); MS m/z (M^+) 576. Anal. Calcd for $C_{31}H_{26}F_6S_2$: C, 64.57; H, 4.54%. Found: C, 64.96; H, 4.73%.
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