Efficient Photocycloreversion Reaction of Diarylethenes by Introduction of Cyano Subsutituents to the Reactive Carbons

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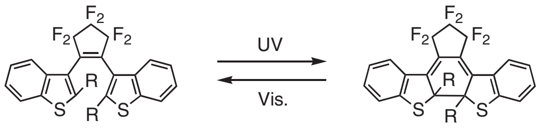
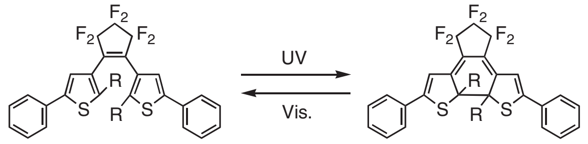
Highly efficient photocycloreversion reaction was observed for diarylethene derivatives with cyano groups at the reactive carbons of the thiophene rings. The cycloreversion quantum yield of 1,2-bis(2-cyano-5-phenyl-3-thienyl)perfluorocyclopentene was found to be ca. 30 times larger than that of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene.

Photochromism is defined as a reversible isomerization between two isomers having different absorption spectra by photoirradiation.[1] Various types of photochromic compounds have been so far developed in an attempt to apply the compounds to optoelectronic devices, such as memories and switches. Among these compounds, diarylethenes are the most promising candidates for the application because of their thermal irreversibility and fatigue-resistance.[2,3] Recently, we have found that dithienylethenes having alkoxy groups at the reactive carbons of the thiophene rings remarkably decrease the cycloreversion quantum yield.[4,5] The cycloreversion quantum yields are lower than 10^{-3}. A strategy to increase the cycloreversion quantum yield of diarylethenes, however, has not been found out yet. Here, we report that cyano groups at the reactive carbons of diarylethenes increase the cycloreversion quantum yield considerably and the theoretical calculation supports the effect.

1,2-Bis(2-cyano-1-benzothien-3-yl)perfluorocyclopentene (**1a**)[6] was synthesized by reacting 1,2-bis(2-formyl-5-phenyl-3-thienyl)perfluorocyclopentene with hydroxylammonium chloride in the presence of sodium hydrogencarbonate in ethanol at room temperature and by dehydration. The formyl diarylethene derivative was obtained by coupling 3-bromo-2-(2,5-dioxolanyl)benzothiophene and octafluorocyclopentene followed by deprotection. 1,2-Bis(2-cyano-5-phenyl-3-thienyl)perfluorocyclopentene (**4a**)[7] was also prepared according to a procedure similar to that used for **1a**. 1,2-Bis(2-methoxy-1-benzothien-3-yl)perfluorocyclopentene (**3a**)[8] was prepared from 2-methoxybenzothiophene and octafluorocyclopentene.



1a: R=CN, **2a**: R=Me, **3a**: R=OMe **1b**: R=CN, **2b**: R=Me, **3b**: R=OMe



4a: R=CN, **5a**: R=Me, **6a**: R=OMe **4b**: R=CN, **5b**: R=Me, **6b**: R=OMe

Figure 1 shows the absorption spectra of **1a** and **1b** in hexane. **1a** has the absorption maxima at 273, 315, and 327 nm in hexane. Upon irradiation with 313-nm light, the colorless solution of **1a** turned to orange which is due to the formation of the closed-ring isomer **1b**.[9] The visible absorption maximum of **1b** was observed at 496 nm, which is 21 nm shorter than that of methyl derivative **2b**. The orange color of **1b** in hexane immediately disappeared upon irradiation with visible light ($\lambda > 500$ nm) and the absorption spectrum returned to that of **1a**. The conversion from **1a** to **1b** in the photostationary state upon irradiation with 313-nm light was 58%. The bisphenylthienylethene **4** having cyano groups at the reactive carbons also showed similar photochromic behavior to **1**. The colorless **4a** has the absorption maximum at 284 nm, and changed to purple colored isomer **4b**[10] upon irradiation with 313-nm light in hexane. **4b** returned to **4a** immediately upon irradiation with visible light. Thermal decoloration of **1b** and **4b** was not observed even after a day at room temperature. The absorption maxima of **1b**–**6b** are summarized in Table 1. The methoxy derivatives **3b** and **6b** shifted the visible absorption maxima 30 and 50 nm longer than those of methyl derivatives **2b** and **5b**, respectively. On the other hand, the cyano derivatives **1b** and **4b** shifted the maxima 21 and 30 nm shorter than those of methyl derivatives **2b** and **5b**, respectively.

To examine the substituent effect on photochromic reactivity we measured cyclization and cycloreversion quantum yields of the diarylethenes in hexane. Table 1 summarizes the quantum yields of **1**–**6**. The cyano groups at the reactive carbons did not affect the cyclization quantum yields of **1** and **4**, and the values are similar to those of the methyl substituted derivatives **2** and

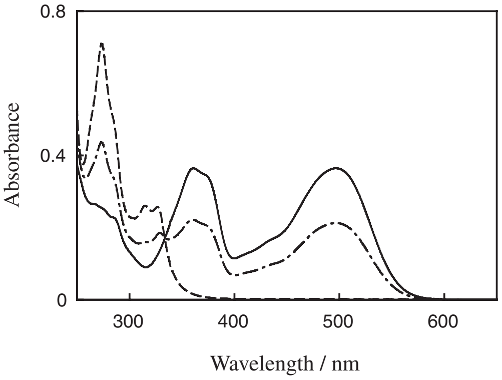


Figure 1. Absorption spectral change of **1** in hexane (3.0×10^{-5} mol dm^{-3}) by photoirradiation: **1a** (- - - -), **1** in the photostationary state under irradiation with 313-nm light (– - –), and **1b** (—).

5, respectively. On the contrary, the cycloreversion quantum yields are strongly affected by the substituents at the reactive carbons. As shown in Table 1, the cycloreversion quantum yields of **1** and **4** are 0.59 and 0.41, which are 1.7 and 30 times larger than those of **2** and **5**, respectively. The cyano groups increase the cycloreversion quantum yields. The cycloreversion quantum yield of **1** is larger than the cyclization quantum yield of **1**. Consequently, we can control the cycloreversion reactivity of the diarylethenes as much as 24000 times for **4** and **6**.

The theoretical calculations in excited states of a model system of the diarylethenes (scheme in Figure 2) were carried out with Gaussian 98[13] and GAMESS[14] program packages in order to confirm the substituent effect.[15] As shown in Figure 2, upon excitation to the allowed 1B state which is so close in energy to the 2A state, very fast internal conversion to the 2A state is assumed. The excited state potential energy surface possesses two minima (2Ac and 2Ao) in the proximity of the closed-ring isomer at the transition state. Consequently, an energy barrier exists on the pathway from closed- to open-ring isomers in excited state. When the 2Ac point is populated, the cycloreversion quantum yield depends on the ability of the system to overcome the energy barrier between 2Ac and 2Ao. The barrier is related to the energy difference, ΔE ($= E(\text{2Ao}) - E(\text{2Ac})$). When the energy difference is small, the barrier is expected to become small. The calculated energy differences were 1.1,[16] 5.9, and 13.9 kcal mol^{-1} for the cyano, methyl, and methoxy derivatives, respectively.[15] The order of ΔE, which depended on the substituents, is well correlated with that of the cycloreversion quantum yields obtained experimentally.

Table 1. Absorption maxima of closed-ring isomers and quantum yields in hexane

	$\lambda_{\max}/\text{nm}^a$	$\Phi_{o\to c}{}^b$	$\Phi_{c\to o}{}^c$
1	496	0.28	0.59
2[11]	517	0.35	0.35
3	547	0.34	0.030
4	545	0.42	0.41
5[12]	575	0.59	0.013
6[4]	625	0.44	1.7×10^{-5}

[a] Absorption maxima of the closed-ring isomers in the visible region; [b] Photocyclization quantum yields; [c] Photocycloreversion quantum yields.

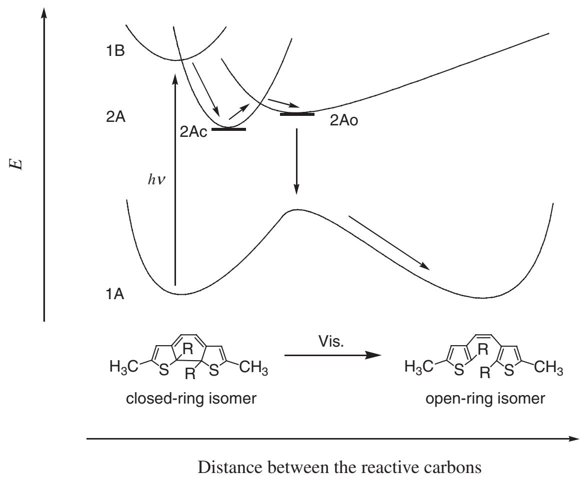


Figure 2. Schematic representation of the potential energy profile of the model system (R=CN, Me, OMe).

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5 K. Morimitsu, K. Shibata, S. Kobatake, and M. Irie, *J. Org. Chem.*, **67**, 4574 (2002).
6 **1a**: colorless crystals: mp 232.5–233.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.5–8.2 (m, 8H); MS m/z (M^+) 490. Anal. Calcd. for $C_{23}H_8F_6N_2S_2$: C, 56.33; H, 1.64; N, 5.71%. Found: C, 56.30; H, 1.60; N, 5.69%.
7 **4a**: pale yellow colored crystals: mp 165.5–166.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.4–7.7 (m, 12H); MS m/z (M^+) 542. Anal. Calcd. for $C_{27}H_{12}F_6N_2S_2$: C, 59.77; H, 2.23; N, 5.16%. Found: C, 59.91; H, 2.31; N, 5.22%.
8 **3a**: colorless crystals: mp 171.9–172.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.6 (s, 6H), 7.1–7.6 (m, 8H); MS m/z (M^+) 500. Anal. Calcd. for $C_{23}H_{14}F_6O_2S_2$: C, 55.20; H, 2.82%. Found: C, 55.17; H, 2.81%.
9 **1b** was isolated by HPLC (silica gel; hexane/ethyl acetate = 91/9 as the eluent), **1a** and **1b** were eluted at 52 and 68 min, respectively.
10 **4b** was isolated by HPLC (silica gel; hexane/ethyl acetate = 97/3 as the eluent), **4a** and **4b** were eluted at 18 and 28 min, respectively.
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16 The value was determined for 1,2-bis(2-cyano-5-phenyl-3-thienyl)ethene in this work.

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