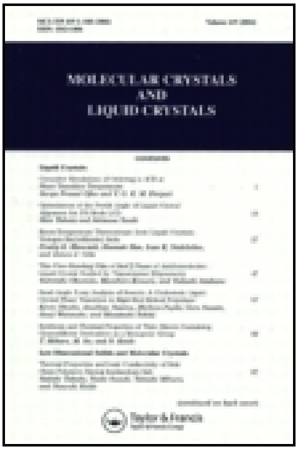

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Photochromism of 1,2-Bis(3-n-alkyl-1-benzothiophen-2-yl)perfluorocyclopentene Derivatives

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Diarylethene derivatives having 1,2-bis(3-n-alkyl-1-benzothiophen-2-yl)perfluorocyclopentene have been synthesized to examine their photochromic properties in solution. All the derivatives underwent photochromism in hexane. The introduction of long-chain substituents to the 3-positions of a 1-benzothiophene unit leads to longer wavelengths of the absorption band of the closed-ring isomer. However, the cyclization quantum yields of these compounds showed no increase with alkyl chain length.

Keywords: benzothiophene; diarylethene; photochromism

INTRODUCTION

Photochromism has attracted considerable attention because of its potential application to molecular devices, such as optical memories and switches [1]. Among various thermally irreversible photochromic compounds, diarylethene derivatives are the most promising compounds because of their fatigue resistance and thermally irreversible properties [2–10]. It has been reported that the absorption maxima of dithienylethenes are dependent on the position connecting thienyl groups to the ethene moiety [11,12]. For a full-color display, it is

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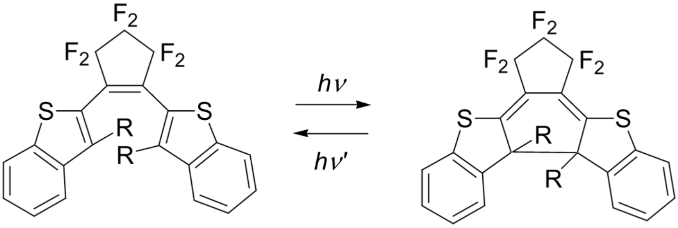
desired to develop yellow photochromic compounds that have low photocycloreversion quantum yields and thermal stability at room temperature [13]. When the thienyl ring is connected at the 2-position, the absorption maximum of the closed-ring form shifts to a shorter wavelength connected at the 3-position.

We found that the absorption maxima of the colored isomers 1,2-bis(2-*n*-alkyl-1-benzothiophen-3-yl)perfluorocyclopentene [14] and 1,2-bis(2-*n*-alkyl-1-benzofuran-3-yl)perfluorocyclopentenes [15,16] shift to longer wavelengths with increasing alkyl chain length. The cyclization quantum yields of these derivatives increase with increasing alkyl chain length. This is related to the ratio of the parallel (photo-inactive) conformation to the antiparallel (photo-active) conformation, as determined by ^{1}H NMR measurement at low temperature [14,16]. The cyclization quantum yield of 3-*n*-alkyl-1-benzothiophen-2-yl derivatives has not been examined so far.

In this article, we report on the photochromic properties of 1,2-bis(3-*n*-alkyl-1-benzothiophen-2-yl)perfluorocyclopentene derivatives (**1a**–**4a**) and examine *n*-alkyl substituent effects.

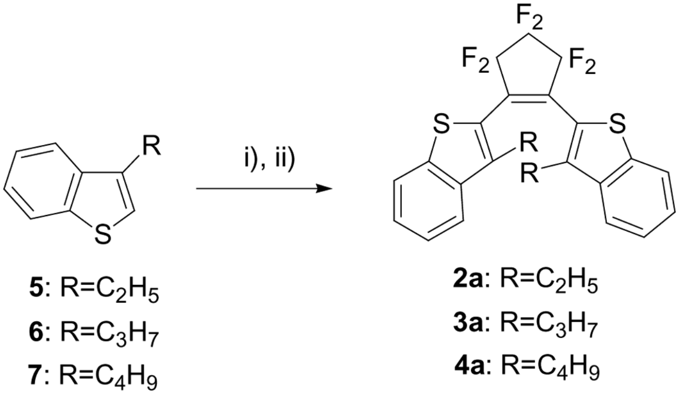


1a: R=CH_3
2a: R=C_2H_5
3a: R=C_3H_7
4a: R=C_4H_9

1b: R=CH_3
2b: R=C_2H_5
3b: R=C_3H_7
4b: R=C_4H_9

EXPERIMENTAL

The solvents used were of spectrograde and were purified by distillation before use. Absorption spectra were measured with a spectrophotometer (Shimadzu, UV-2100). A mercury lamp (Ushio, 500 W) was used as the light source. Light of appropriate wavelength was isolated by passing light through a monochromator (Ritsu MC-10N). Quantum yield was determined by comparing the reaction rates of the diarylethene derivatives in hexane with those of furylfulgide in



SCHEME 1 Synthesis of diarylethenes **2a–4a**: i) *n*-BuLi (1.1 eq.), THF at −78°C, ii) octafluorocyclopentene (0.5 eq.).

toluene. ^{1}H NMR was recorded on a Gemini 200 (200-MHz) spectrometer with $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. For low-temperature analysis, ^{1}H NMR was recorded on a Jeol ECA400 (400 MHz) instrument at −90°C with CD_3OD as a solvent and tetramethylsilane as an internal standard. X-ray crystallography was carried out using a Bruker SMART CCD X-ray diffractometer.

MATERIALS

The diarylethenes **2a–4a** were synthesized according to Scheme 1. The starting materials **5–7** were synthesized by the method in Ref. [17]. The coupling reactions of **5–7** with octafluorocyclopentene gave the diarylethenes **2a**, **3a**, and **4a** in 42, 39, and 33% yields, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectral change of **2a** induced by photoirradiation in hexane. In the photostationary state under irradiation with 313 nm light, 57% of the open-ring isomer **2a**, which has an absorption maximum at 318 nm (ε: $1.14 \times 10^4\,M^{-1}\,cm^{-1}$), converted to the closed-ring isomer **2b**, which has an absorption maximum at 455 nm (ε: $0.58 \times 10^4\,M^{-1}\,cm^{-1}$). The colorless solution changed to yellow. By changing substituents from methyl to ethyl, the absorption maximum of the closed-ring isomer shifts to a longer wavelength by as much as 17 nm (Table 1). Upon irradiation with light of wavelength

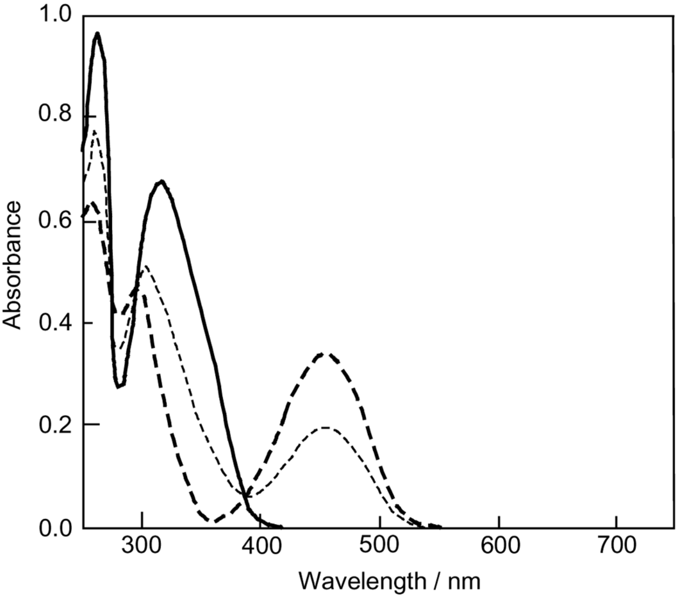


FIGURE 1 Absorption spectra of **2a** (solid line) and **2b** (dashed line) and of **2** in the photostationary state (dotted line) under irradiation with 313 nm light in hexane (5.7×10^{-5} mol/L).

longer than 440 nm, the closed-ring isomer returned to its original **2a**. Both isomers were stable at 80°C in decaline for more than 1 day.

As in the case of **2a**, **3a** underwent photochromism upon irradiation with UV and visible light in hexane (Fig. 2). Compound **3a** showed an

TABLE 1 Absorption Characteristics and Photoreactivities of Diarylethene Derivatives **1–4** in Hexane

	$\varepsilon/10^4\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$		Quantum yield		Conversion (313 nm)
Compound	**a**	**b**	Cyclization	Cycloreversion	
1	1.37 (325 nm)	0.65 (438 nm)	0.46 (313 nm)	0.47 (436 nm)	63%
2	1.14 (318 nm)	0.58 (455 nm)	0.32 (313 nm)	0.50 (436 nm)	57%
3	1.13 (319 nm)	0.55 (454 nm)	0.41 (313 nm)	0.48 (436 nm)	64%
4	1.10 (319 nm)	0.52 (455 nm)	0.42 (313 nm)	0.52 (436 nm)	64%

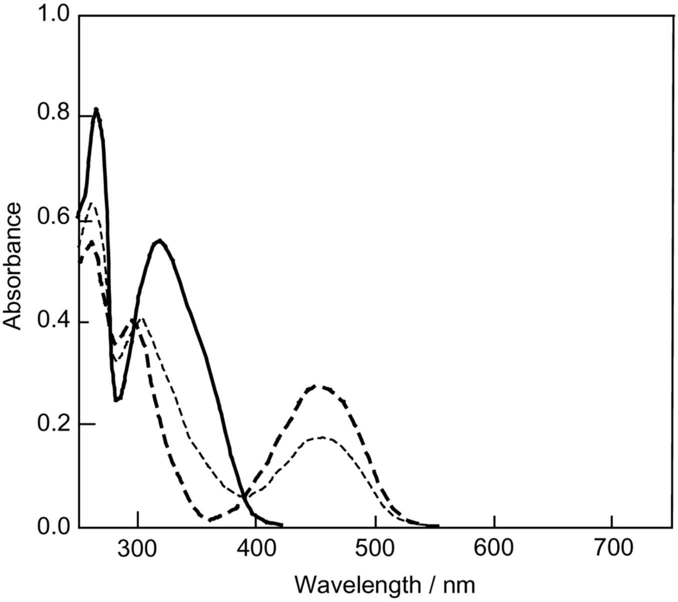


FIGURE 2 Absorption spectra of **3a** (solid line) and **3b** (dashed line) and of **3** in the photostationary state (dotted line) under irradiation with 313 nm light in hexane (5.1×10^{-5} mol/L).

absorption maximum at 319 nm (ε_{max}: $1.13 \times 10^4\,M^{-1}\,cm^{-1}$). Upon irradiation with 313 nm light, the diarylethene transformed into the closed-ring isomer **3b** at 454 nm (ε_{max}: $0.55 \times 10^4\,M^{-1}\,cm^{-1}$). In the photostationary state, the conversion ratio from the open-ring isomer to the closed-ring isomer was 64%. Upon irradiation with light of wavelength longer than 440 nm light, the closed-ring isomer returned to the original **3a**. The absorption characteristics of **4a** and **4b** were similar to those of **3a** and **3b**, respectively.

Cyclization and cycloreversion quantum yields were measured for the compounds **1–4** (Table 1). The absorption maximum of the colored isomers of 1,2-bis(3-*n*-alkyl-1-benzothiophen-2-yl)perfluorocyclopentene shifted to longer wavelengths with increasing the alkyl chain length, as in the case of 1,2-bis(2-n-alkyl-1-benzothiophen-3-yl)perfluorocyclopentene derivatives [14]. Compound **1** has the highest cyclization quantum yield (0.46). The cyclization quantum yields of **3** and **4** are almost the same, whereas **2** is slightly lower. The cyclization quantum yields are related to the ratio of the parallel conformation to the antiparallel conformation. The population ratio of the parallel conformation to antiparallel conformation of **2a** is 1:9 at −90°C in CD_3OD.

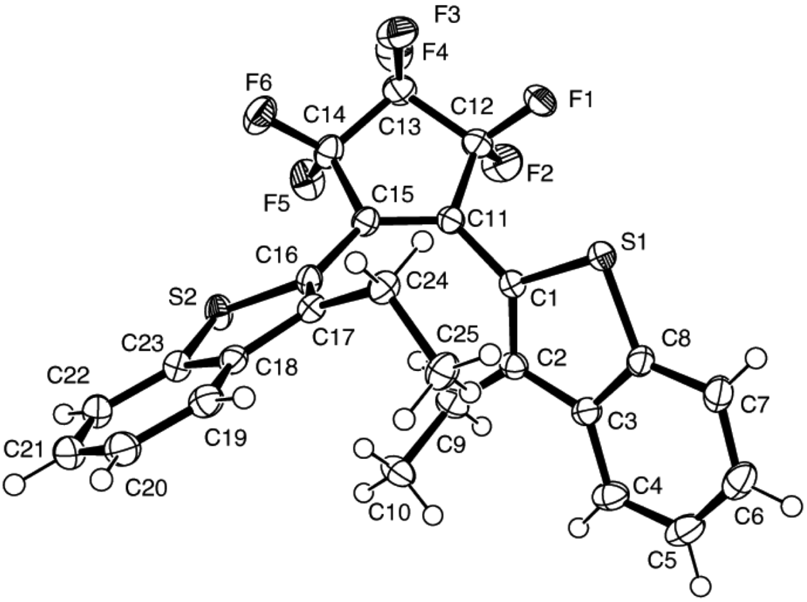


FIGURE 3 ORTEP drawing of **2a**. The ellipsoids represent 50% displacement of atoms.

The other compounds **1a**, **3a**, and **4a** showed only an antiparallel conformation in the low-temperature measurement.

For 1,2-bis(2-*n*-alkyl-1-benzothiophen-3-yl)perfluorocyclopentene derivatives, cyclization quantum yield decreased with increasing alkyl chain length. The cycloreversion quantum yields of **1–4** were almost the same (0.47–0.52). Cycloreversion quantum yields had no effect on alkyl chain length.

A single crystal was obtained by recrystallization from hexane. An X-ray crystallography of the crystal was carried out. Figure 3 shows the ORTEP drawing of **2a**. The aryl groups are in an antiparallel conformation, and the distance between the reactive carbons is 0.393 nm. This distance is small enough for the reaction to take place in the crystalline phase [18]. However, no photochromism was observed in the single crystal.

DATA

1a: ^{1}H NMR (400 MHz, MeOD, −90°C) δ 1.74 (s, 6H), 7.44–7.50 (m, 4H), 7.71–7.73 (m, 2H), 7.99–8.01 (m, 2H).

2a: Yellow crystals; mp. 106–107°C; ^{1}H NMR (200 MHz, $CDCl_3$, 25°C) δ 0.92 (t, $J = 3.8$ Hz, 6H), 2.65 (t, $J = 3.8$ Hz, 4H), 7.34–7.37 (m, 4H), 7.67–7.69 (m, 2H), 7.79–7.81 (m, 2H). ^{1}H NMR (400 MHz, MeOD, −90°C) δ 0.56 (brs, 5.4H), 1.22 (brs, 0.6H), 2.59–2.61 (m, 3.6H), 2.79–2.81 (m, 0.4H), 7.40–7.49 (m, 4H), 7.80–7.83 (m, 2H), 7.98–8.00 (m, 2H). Ms (EI) m/z 496 (M^+); anal. calcd. for $C_{25}H_{18}F_6S_2$: C, 60.47; H, 3.65%. Found: C, 60.53; H, 3.69%.

3a: Colorless liquid; ^{1}H NMR (200 MHz, $CDCl_3$, 25°C) δ 0.85 (t, $J = 3.8$ Hz, 6H), 1.26–1.39 (m, 4H), 2.49–2.54 (m, 4H), 7.32–7.41 (m, 4H), 7.63–7.66 (m, 2H), 7.80–7.83 (m, 2H). ^{1}H NMR (400 MHz, MeOD, −90°C) δ 0.76–0.78 (m, 6H), 0.98–1.05 (m, 4H), 2.41–2.47 (m, 4H), 7.40–7.50 (m, 4H), 7.76–7.78 (m, 2H), 7.98–8.00 (m, 2H). Ms (EI) m/z 524 (M^+); anal. calcd. for $C_{27}H_{22}F_6S_2$: C, 61.82; H, 4.23%. Found: C, 61.71; H, 4.22%.

4a: Colorless liquid; ^{1}H NMR (200 MHz, $CDCl_3$, 25°C) δ 0.74 (t, $J = 3.6$ Hz, 6H), 1.17–1.29 (m, 8H), 2.51–2.55 (m, 4H), 7.35–7.42 (m, 4H), 7.64–7.66 (m, 2H), 7.81–7.83 (m, 2H). ^{1}H NMR (400 MHz, MeOD, −90°C) δ 0.72 (t, $J = 3.6$ Hz, 6H), 1.12–1.24 (m, 8H), 2.50–2.54 (m, 4H), 7.39–7.46 (m, 4H), 7.71–7.73 (m, 2H), 7.91–7.93 (m, 2H). Ms (EI) m/z 552 (M^+); anal. calcd. for $C_{29}H_{26}F_6S_2$: C, 63.03; H, 4.74%. Found: C, 63.03; H, 4.74%.

Crystal data for **2a**: $C_{25}H_{18}F_6S_2$, MW = 450.43, monoclinic, space group $P2_1/n$, $a = 13.4907(5)$ Å, $b = 9.3852(3)$ Å, $c = 18.4729(7)$ Å, $\alpha = 90°$, $\beta = 110.139(2)°$, $\gamma = 90°$, $V = 2195.91(14)$ Å^3, $Z = 4$, $D_c = 1.502$ g cm^{-3}, $R_1 = 0.0567$ for 7575 observed reflections with $I > 2\sigma(I)$ $\sigma(I)$ from 10854 unique reflections. CCDC deposition number 639921.

CONCLUSION

Diarylethene derivatives having 1,2-bis(3-*n*-alkyl-1-benzothiophen-2-yl)perfluorocyclopentene have been synthesized, and their photochromic reactivity in hexane has been examined. By changing the substituents from methyl to ethyl, the absorption maximum of the closed-ring isomer shifts to longer wavelengths by as much as 17 nm in hexane. The cyclization quantum yields of **1**, **3**, and **4** are almost constant except that of the ethyl derivative **2**. The cycloreversion quantum yields of **1–4** are almost the same (0.47–0.52).

ACNOWLEDGMENT

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