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Photochromism of diarylethene derivatives having an indene unit

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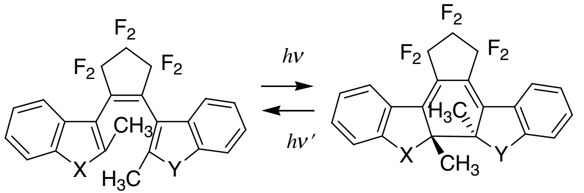
Abstract—Photochromic indene derivatives, 1-(2-methyl-1-inden-3-yl)-2-(2-methyl-1-benzothien-3-yl)perfluorocyclopentene and 1-(2-methyl-1-inden-3-yl)-2-(2-methyl-1-benzofuran-3-yl)perfluorocyclopentene, were synthesized and their photochromic performance was examined.

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 resistant and thermally irreversible properties.[2,3] Diarylethene derivatives so far synthesized have hetero-aryl moieties such as thiophene,[4] benzothiophene,[5] thiazole,[6] crysothiophene,[7] and indole rings.[8] Their photochromic performance is strongly dependent on the aryl moieties. When the aryl groups have low aromatic stabilization energy, the derivatives undergo thermally irreversible photochromic reactions. When benzothiophene rings are used as heterocyclic groups, it showed fatigue resistant performance (coloration/decoloration cycles >10,000).[3] Indene is an attractive aryl unit because of its low aromatic stabilization energy and the structure is similar to benzothiophene. Photochromic indene derivatives have not yet been synthesized in the past. In this letter, diarylethene derivatives having an indene group were synthesized and the photochromic performance was compared with a derivative having benzothiophene aryl groups.

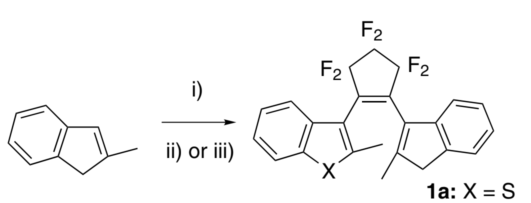


1a: X = S, Y=CH$_2$
2a: X = O, Y=CH$_2$
3a: X = S, Y= S

1b: X = S, Y=CH$_2$
2b: X = O, Y=CH$_2$
3b: X = S, Y= S

Diarylethenes **1a** and **2a** were synthesized according to Scheme 1. The coupling reaction of 2-methyl-1-indene with 1-(2-methyl-1-benzothien-3-yl)heptafluorocyclopentene gave diarylethene **1a**[9,10] in 24% yield. The synthetic route of **2a** was the same as that for **1a**. The coupling reaction of 2-methylindene with 1-(2-methyl-1-benzofuran-3-yl)heptafluorocyclopentene **4**[11] gave diarylethene **2a**[12] in 13% yield. Bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene **3a** was also synthesized as a reference compound.[5]

Figure 1 shows the absorption spectral change of **1a** by photoirradiation in hexane. At the photostationary state under irradiation with 313 nm light, 52% of the open-ring isomer **1a**, which has the maxima at 255 nm



1a: X = S
1a, 2a **2a**: X = O

Scheme 1. Synthesis of indene derivatives **1** and **2**. Reagents and conditions: (i) *n*-BuLi (1.1 equiv), THF at −78 °C and (ii) 1-(2-methyl-1-benzothiophen-3-yl)heptafluorocyclopentene (24%) or (iii) 1-(2-methyl-1-benzofuran-3-yl)heptafluorocyclopentene (13%).

Keywords: Photochromism; Diarylethene; Indene.

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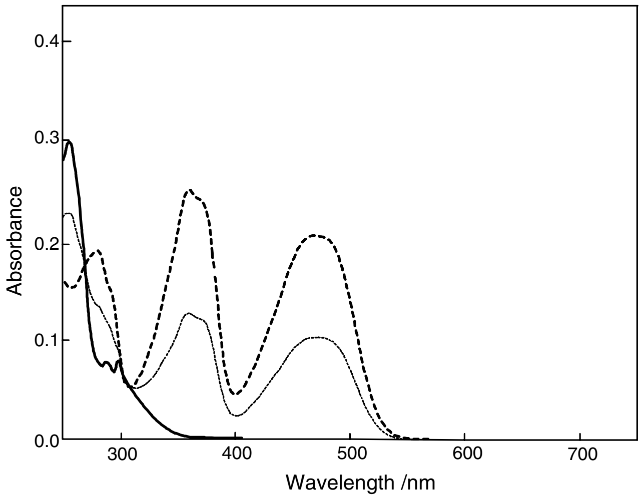

Figure 1. Absorption spectra of **1a** (solid line), **1b** (broken line) and at the photostationary state (dotted line) under irradiation with 313 nm light in hexane (1.72×10^{-5} mol/L).

(ε: 1.73×10^4 M^{-1} cm^{-1}), converted to the closed-ring isomer **1b**, which has the absorption maxima at 469 nm (ε: 1.19×10^4 M^{-1} cm^{-1}). The colorless solution changed to orange. By changing an aryl unit from a benzothiophene ring to an indene ring, the absorption maximum of the closed-ring isomer is shifted to shorter wavelength as much as 48 nm. Upon irradiation with light of wavelength longer than 400 nm light, the closed-ring isomer returned to original **1a**. Both isomers were stable at 80 °C in decaline for more than 1 day.

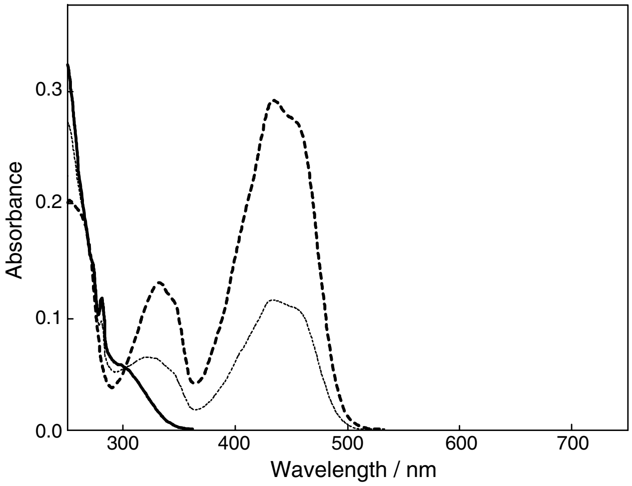

Figure 2. Absorption spectra of **2a** (solid line), **2b** (broken line) and at the photostationary state (dotted line) under irradiation with 313 nm light in hexane (1.72×10^{-5} mol/L).

Just as for **1a**, compound **2a** underwent photochromism upon irradiation with UV and visible light in hexane (Fig. 2). Compound **2a** showed the absorption maximum at 281 nm (ε: 0.68×10^4 M^{-1} cm^{-1}). Upon irradiation with 313 nm light, the diarylethene transformed into closed-ring isomer **2b** (ε: 1.68×10^4 M^{-1} cm^{-1}) at 435 nm. The absorption maximum showed a hypsochromic shift as much as 34 nm in comparison with **1b**. At the photostationary state, the conversion ratio from the open- to the closed-ring isomer was 43%. Upon irradiation with light of wavelength longer than 400 nm light, the closed-ring isomers returned to the original **2a**. Both isomers were stable at 80 °C in decaline for more than 1 day. The coloration/decoloration cycles of the hexane solution of **1** or **2** could be repeated more than 100 times without destruction.

The cyclization and cycloreversion quantum yields were measured for compounds **1** and **2** (Table 1). The data for diarylethene **3** are also shown in Table 1. Compounds **1** and **2** gave the same cyclization and cycloreversion quantum yields. These values are slightly smaller than the values of **3**.[13]

The molar absorption coefficients for the closed-ring isomers **1** and **2** (**1**: 1.19×10^4 M^{-1} cm^{-1}, **2**: 1.68×10^4 M^{-1} cm^{-1}) are larger than that of compound **3** (0.91×10^4 M^{-1} cm^{-1}). The compounds which absorb at 400–500 nm range show, in general, low molar absorption coefficient ($\varepsilon < 1.0 \times 10^4$ M^{-1} cm^{-1}).[14–17] The closed-ring isomers **1** and **2** have the highest class of the molar absorption coefficient so far reported.

Theoretical calculation for the absorption bands of the closed-ring isomer **1b**, **2b**, and **3b** was carried out with Gaussian 03.[18] The calculated wavelengths of **1b**, **2b**, and **3b** were 482.71 nm (f = 0.2236), 453.90 nm (f = 0.4124) and 533.13 nm (f = 0.1918), respectively. The absorption wavelengths correlate well with those of experimental ones.

A single crystal **1a** was obtained by recrystallization from hexane and X-ray crystallographic analysis of the crystal was carried out. Figure 3 shows the ORTEP drawing of **1a**. The aryl moieties are in an anti-parallel conformation. As expected C24a carbon has sp3 structure. Although the aryl groups are in an anti-parallel conformation, the distance between the reactive carbons is 0.451 nm. The distance is too far for the molecule to undergo the photochromic reaction in the

Table 1. Absorption characteristics and photoreactivity of diarylethene derivatives **1**–**3** in hexane

Compound	ε/10^4 dm^3 mol^{-1} cm^{-1}		Quantum yield	
	a	**b**	Cyclization	Cycloreversion
1	1.73 (255 nm)	1.19 (469 nm)	0.32 (313 nm)	0.25 (469 nm)
2	0.68 (281 nm)	1.68 (435 nm)	0.32 (313 nm)	0.25 (435 nm)
3	1.40 (254 nm)	0.91 (517 nm)	0.35 (313 nm)	0.35 (517 nm)

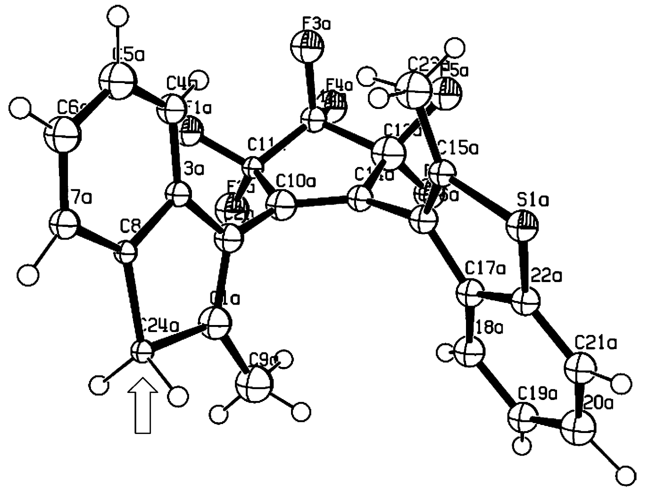

Figure 3. The ORTEP drawings of **1a**. The ellipsoids represent 50% displacement of atoms. The arrow indicates a C24a carbon atom.

crystal.[19] Any photocoloration was not observed in the crystal.

In conclusion, a new type of photochromic compounds having an indene unit was synthesized and their photochromic reactivity was examined in hexane.

Acknowledgments

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9. Compound **1a**: colorless crystals; mp 139–140 °C; ^{1}H NMR (200 MHz) δ 1.57 (s, 4H), 2.02 (s, 2H), 3.33 (s, 0.67H), 3.51 (s, 1.33H), 6.99–7.22 (m, 6H), 7.38–7.47 (m, 2H). Ms (EI) *m*/*z* 450 (M^+); Anal. Calcd for $C_{24}H_{16}F_6S$: C, 63.99; H, 3.58%. Found: C, 64.01; H, 3.54%.
10. Crystal data for **1a**: $C_{24}H_{16}F_6S$, MW = 450.43, monoclinic, space group $P2_1/n$, $a = 8.0890(17)$ Å, $b = 18.886(4)$ Å, $c = 13.144(3)$ Å, $\alpha = 90°$, $\beta = 90.882(3)°$, $\gamma = 90°$, $V = 2007.8(8)$ Å^3, $Z = 4$, $D_c = 1.490$ g cm^{-3}, $R_1 = 0.0536$ for 2460 observed reflections with $I > 2\sigma(I)$ from 2881 unique reflections. CCDC deposition number: 291105.
11. Compound **4**: colorless liquid; ^{1}H NMR (200 MHz) δ 2.50 (s, 3H), 7.13–7.37 (m, 2H), 7.43–7.56 (m, 2H). Ms (EI) *m*/*z* 320 (M^+).
12. Compound **2a**: Colorless crystals; mp 105–106 °C; ^{1}H NMR (200 MHz) δ 1.87 (s, 3H), 2.15 (s, 3H), 3.13 (s, 1H), 3.37 (s, 1H), 2.47 (s, 4.2H), 7.07–7.34 (m, 6H), 7.37–7.52 (m, 2H). Ms (EI) *m*/*z* 434 (M^+); Anal. Calcd for $C_{24}H_{16}F_6O$: C, 66.36; H, 3.71%. Found: C, 66.49; H, 3.90%.
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