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## Photochromism of diarylethene derivatives bearing a benzo[b]silole unit

benzo[b]silole

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was examined in solution.

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Photochromism has attracted considerable attention because of its potential application to molecular devices, such as optical memories and switches.<sup>1</sup> Among various thermally irreversible photochromic compounds, diarylethene derivatives are the most promising because of their fatigue resistance and thermally irreversible properties.<sup>2,3</sup> The diarylethene has two isomers which are called open- and closed-ring isomers. The diarylethene derivatives thus far synthesized have hetero-aryl moieties such as thiophene,4 benzothiophene,<sup>5</sup> thiazole,<sup>6</sup> oxazole,<sup>7</sup> furan,<sup>8</sup> benzofuran,<sup>9</sup> indene,<sup>10</sup> pyrrole,<sup>11</sup> indole,<sup>12</sup> imidazole,<sup>13</sup> pyrazole,<sup>14</sup> and isooxazole<sup>15</sup> rings. Benzene derivatives<sup>16</sup> also show photochromism in solution. Their photochromic properties are strongly dependent on their aryl moieties. The aryl units contain organic aromatic rings, which are carbon, hydrogen, oxygen, nitrogen, and sulfur atoms. The thermal stability of both isomers of diarylethene-type photochromic compounds can be attained by introducing heterocyclic aryl groups, which have low aromatic stabilization energy.<sup>3</sup>

Recently, interesting studies on silole and benzo[b]silole rings have been reported.<sup>17,18</sup> In this study, the novel diarylethene derivatives **1a** and **2a** having a benzo[b]silole group were synthesized and their photochromic performance was examined in solution (Scheme 1).

The diarylethenes **1a** and **2a** were synthesized according to Scheme 2. The coupling reaction of 3-bromo-1,1-dimethyl-2-phenylbenzo[*b*]silole with 1-(2-phenylbenzo[*b*]thiophene-3-yl)heptafluorocyclopentene gave diarylethene **1a** in 12% yield (Scheme 1). The synthetic route of **2a** was the same as that of **1a**. The coupling

\* Corresponding author. Tel./fax: +81 725 44 2200. E-mail address: tyamagu@hyogo-u.ac.jp (T. Yamaguchi). reaction of 3-bromo-1,1-dimethyl-2-phenylbenzo[*b*]silole with 1-(2-phenyl-1-benzofuran-3-yl)heptafluorocyclopentene gave diarylethene **2a** in 13% yield. 1,2-Bis(2-methylbenzo[*b*]thiophen-3-yl)perfluorocyclopentene (**3a**) and 1,2-bis(2-methyl-1-benzofuran-3-yl)perfluorocyclopentene (**4a**) were also synthesized as reference compounds. These structures were confirmed by <sup>1</sup>H

NMR, mass spectroscopy, and elemental analysis. The compounds

derivatives, 1-(1,1-dimethyl-2-phenylbenzo[b]silol-3-yl)-2-(2-phen-

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ylbenzo[b]thien-3-yl)perfluorocyclopentene and 1-(1,1-dimethyl-2-phenylbenzo[b]silol-3-yl)-2-(2-phe-

nyl-1-benzofuran-3-yl)perfluorocyclopentene, were synthesized and their photochromic performance

1a and 2a were also confirmed by X-ray crystallography.<sup>19,20</sup> Figure 1a shows the absorption spectral change of 1a upon photoirradiation in hexane. At the photostationary state under irradiation with 313 nm light, 16% of the open-ring isomer 1a, which has the maxima at 277 nm ( $\epsilon$ :  $1.82 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), converted to the closed-ring isomer 1b, which has the absorption maxima at 482 nm ( $\epsilon$ :  $1.31 \times 10^4 \, M^{-1} \, cm^{-1}$ ). The colorless solution became orange. Upon irradiation with light of wavelength longer than 440 nm light, the closed-ring isomer returned to the original 1a. However, the thermal stability of 1b was absent at room temperature (25 °C). When we plot the logarithmic scale of absorbance changes of **1b** at 482 nm versus the time, we get a straight line according to first order kinetics (Fig. 2). The rate constant (k) of the thermal cycloreversion reaction is 0.00283 h<sup>-1</sup>, and the lifetime of half value  $(\tau)$  from the closed isomer to the open isomer is 354 h. No degradation process occurs during the thermal stability experiment.

Compound **2a** also underwent photochromism upon irradiation with UV and visible light in hexane (Fig. 1b). **2a** showed the absorption maximum at 280 nm ( $\varepsilon_{max} 2.35 \times 10^4 \, M^{-1} \, cm^{-1}$ ). Upon irradiation with 313 nm light, the diarylethene transformed into the closed-ring isomer **2b** ( $\varepsilon_{max} 1.68 \times 10^4 \, M^{-1} \, cm^{-1}$ ) at 435 nm. At the photostationary state, the conversion ratio from the opento the closed-ring isomer was 67%. Upon irradiation with light of wavelength longer than 440 nm, the closed-ring isomer returned



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Scheme 1. Photochromic reactions of diarylethenes.



**Scheme 2.** Synthesis of benzo[*b*]silole derivatives **1** and **2**. Reagents and conditions: (i) *n*-BuLi(1.1 equiv), THF at -78 °C; (ii) 1-(2-phenylbenzo[*b*]thiophen-3-yl)heptafluorocyclopentene(12%); (iii) 1-(2-phenyl-1-benzofuran-3-yl)heptafluorocyclopentene(13%).

to the original **2a**. The closed-ring isomer **2b** was stable at 25 °C in hexane, and it was also stable at 70 °C in toluene for more than 3 h.

The cyclization and cycloreversion quantum yields were measured for compounds **1a–2a** (Table 1). The data for the diarylethenes **3a–4a** are also shown in the table. The diarylethene **3a**, which has two benzo[*b*]thiophene rings, did not dissolve in hexane, and the absorption data of **3a** were determined in chloroform. The molar absorption coefficient of **1b** was determined from the combined data of the HPLC measurement and the absorption spectra. The closed-ring isomer diarylethene (**4b**), which has a benzofuran ring, shows an absorption maximum at 482 nm in hexane. By



Figure 2. Plot of logA versus time for first order process.



**Figure 1.** (a) Absorption spectra of **1a** (dotted line) and at the photostationary state (solid line) under irradiation with 313 nm light in hexane  $(3.02 \times 10^{-5} \text{ mol/L})$ . (b) Absorption spectra of **2a** (dotted line), **2b** (dashed line), and at the photostationary state (solid line) under irradiation with 313 nm light in hexane  $(2.94 \times 10^{-5} \text{ mol/L})$ .

changing an aryl unit from a benzofuran ring to a benzo[*b*]silole ring, the absorption maximum of the closed-ring isomer (**2b**) shifted to shorter wavelength by as much as 47 nm. Although the solvents of **1b** and **3b** were different, the same tendency was observed. For compound **3b**, by changing an aryl unit from a benzothiophene ring to a benzo[*b*]silole ring, the absorption maximum of the closed-ring isomer (**1b**) shifted to the shorter wavelength. The differences of the absorption band of the closed-ring isomers **1b–4b** originate from the differences of the aromaticity.

It was reported that the closed-ring isomer for 1,2-bis(2-methyl-1-benzofuran-3-yl)perfluorocyclopentene (**5a**) is 469 nm

Table 1			
Absorption charact	eristics and	quantum y	yields of 1–4

Compound (solvent)	$\epsilon/10^4dm^3mol^{-1}cm^{-1}$		Quantum yield	
	a	b	Cyclization	Cycloreversion
1 (hexane)	1.82 (277 nm)	1.31 (482 nm)	-	-
2 (hexane)	2.35	1.68	0.46	0.38
	(280 nm)	(435 nm)	(313 nm)	(436 nm)
3 (chloroform)	2.81	0.705	0.29	0.29
	(273 nm)	(524 nm)	(313 nm)	(524 nm)
4 (hexane)	3.42	1.80	0.39	0.27
	(277 nm)	(482 nm)	(313 nm)	(482 nm)



Figure 3. The ORTEP drawing of 1a. The ellipsoids represent 50% displacement of atoms.



Figure 4. The ORTEP drawing of 2a. The ellipsoids represent 50% displacement of atoms.

in hexane.<sup>9</sup> The closed-ring isomer of 1-(2-methyl-1-benzofuran-3-yl)-2-(2-methyl-1-inden-3-yl)perfluorocyclopentene (**6a**)<sup>10</sup> is 435 nm in hexane. By changing an aryl unit from a benzothiophene ring to an indene ring, the absorption maximum of the closed-ring isomer (**2b**) shifted to a shorter wavelength by as much as 34 nm. The hypsochromic effect is slightly larger for the benzo[*b*]silole ring than for the indene ring.

Table 1 also shows the cyclization and cycloreversion quantum yields. Those of compound 1 could not be measured because the closed-ring isomer **1b** is unstable at room temperature in solution. Those of compound **2** could be measured. The values for diarylethene **2** are similar to those for the reference compound **4** in hexane. The cyclization quantum yield of **5** is 0.38 in hexane. The benzofu-

ran derivative **5a** has the methyl unit at the reactive carbon atoms. By changing the methyl unit to the phenyl unit, the cyclization quantum yield of **4** become slightly larger than that of **5**. For compound **3**, the cyclization quantum yield is slightly smaller than that of compound **4**.

The previous works on 1,1-dimethyl-2-phenylbenzo[*b*]silole<sup>17</sup> showed that the compound had a high fluorescence quantum yield ( $\Phi_{\rm fl}$ =0.55(300 nm)) in dichloromethane. But the fluorescence quantum yields of **1a** and **2a** are 0.054 and 0.010 (313 nm) in hexane, respectively.<sup>19</sup> These diarylethenes have a perfluorocyclopentene moiety, and they are not good groups of fluorescent properties due to their strong deficient-electronic function. The fluorescence quantum yield of **2b** is 0.003 (313 nm) in hexane.

intensity reversibly changed upon irradiation with UV and visible light.

A single crystal 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.<sup>20</sup> The drawing shows that this diarylethene has benzo[*b*]thiophene and benzo[*b*]silole rings. The aryl moieties are in an anti-parallel conformation, and the distances between the reactive carbon atoms are 0.386 nm (C1–C17) and 0.374 nm (C36–C52). The distances are suitable for the molecule to undergo the photochromic reaction in the crystal.<sup>9</sup> The colorless crystals of **1a** were irradiated with 365 nm light, and the crystal color became pale violet. After the colored crystals were allowed to stand for 3 days, the crystal color became colorless.

Figure 4 shows the ORTEP drawing of 2a.<sup>21</sup> The drawing shows that this diarylethene has benzofuran and benzo[*b*]silole rings. The aryl moieties are in an antiparallel conformation, and the distances between the reactive carbon atoms are 0.386 nm (C1–C17) and 0.374 nm (C36–C52). The colorless crystals of 2a were irradiated with 365 nm light, and the crystal became brown. After the colored crystals were irradiated with >440 nm light, the crystal became colorless.

In conclusion, new photochromic compounds having a benzo[*b*]silole unit were synthesized and their photochromic reactivity was examined in solution. Although the benzofuran derivative (**2b**) showed thermal stability at 70 °C in toluene, the benzo[*b*]thiophene derivative (**1b**) showed thermal instability at 25 °C in hexane. They showed photochromism in single-crystalline phase. Further modification of the benzo[*b*]silole derivatives is now in progress in our laboratory, and the reason why the diarylethene **1b** is thermally unstable will be clarified.

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### Supplementary data

Supplementary data associated with this Letter can be found, in the online version, at doi:10.1016/j.tetlet.2011.08.063.

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- 20. Crystal data for **1a**: C<sub>35</sub>H<sub>24</sub>F<sub>6</sub>SSi, MW = 618.69, triclinic, space group *P*1, *a* = 10.5709(8) Å, *b* = 10.8900(8) Å, *c* = 28.972(2) Å, *a* = 95.2270(10)°,  $\beta$  = 91.9470(10)°,  $\gamma$  = 117.5680(10)°, *V* = 2933.3(4)Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.401 g cm<sup>-3</sup>, *R*<sub>1</sub> = 0.0523 for 11921 observed reflections with *l* > 2*σ*(*l*) from 32078 unique reflections. CCDC deposition number: 825052.
- 21. Crystal data for **2a**:  $C_{35}H_{24}F_6OSi$ , MW = 602.63, triclinic, space group  $P\bar{1}$ , a = 10.3316(7) Å, b = 10.9624(8) Å, c = 28.891(2) Å,  $\alpha = 94.9020(10)^\circ$ ,  $\beta = 91.8890(10)^\circ$ ,  $\gamma = 116.7640(10)^\circ$ ,  $V = 2901.5(4)Å^3$ , Z = 4,  $D_c = 1.380$  g cm<sup>-3</sup>,  $R_1 = 0.0528$  for 11747 observed reflections with  $I > 2\sigma(I)$  from 31626 unique reflections. CCDC deposition number: 825051.