Substitution Effect on the Coloration Quantum Yield of a Photochromic Bisbenzothienylethene

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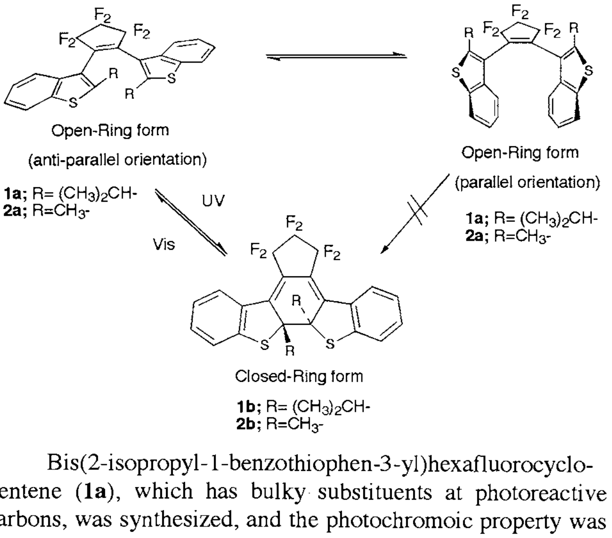
Introduction of isopropyl substituents to 2 and 2' positions of benzothiophene rings of bis(1-benzothiophen-3-yl)hexa-fluorocyclopentene increased the population of anti-parallel conformation, and enhanced the quantum yield of the cyclization reaction.

Photochromic molecules have attracted much attention because of their potential for the application to photonic devices.[1] For the application the molecules should have high coloration quantum yields. Diarylethenes undergo thermally irreversible photochromic reactions.[2-8] The molecules have two atrope conformers. One conformer has two aromatic rings in mirror symmetry (in parallel (p) orientation) and the other in C2 symmetry (in anti-parallel (a-p) orientation).[2-5] The cyclization reaction proceeds only from the a-p conformer. Although various types of diarylethene derivatives have been synthesized, the substituent effect on the conformation has not been reported. Control of the conformations by introducing bulky substituents has been successfully applied to fulgide derivatives.[9-14]

In this paper, we examined the effect of introduction of bulky isopropyl groups at 2 and 2' positions of bisbenzothienylethene on the conformation and the coloration quantum yield.



Bis(2-isopropyl-1-benzothiophen-3-yl)hexafluorocyclopentene (**1a**), which has bulky substituents at photoreactive carbons, was synthesized, and the photochromoic property was compared with bis(2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene (**2a**).[6]

Synthesis of **1a** was performed as follows. Butyllithium (15% hexane solution, 30.7 ml, 49.2 mmol) was added to the ether solution of 1-benzothiophene (6.0 g, 44.7 mmol), and the solution was refluxed for 1h. After the solution was cooled to 0 ℃, 2.27 ml of acetone(49.2 mmol) was added to form 7.25 g of 1-hydroxy-1-methylethyl-1-benzothiophene (**3**) (84%). Compound **3** (7.25 g, 35.5 mmol) was reduced to 3.54 g (19.6 mmol) of 2-isopropyl-1-benzothiophene (**4**) by mixing 2.23 g (58.8 mmol) of $LiAlH_4$ and 19.5 g (146 mmol) of $AlCl_3$ in 130 ml of ether for over night. The compound **4** (3.45 g, 19.6 mmol) was heated in the mixture of iodine (2.18 g, 8.6 mmol), periodic acid (0.68 g, 3.0 mmol), sulfuric acid (5 ml), acetic acid (50 ml) and water (37 ml) for 1.5 h at 70℃ to yield 5.26 g (17.4 mmol) of 3-iodo-2-isopropyl-1-benzothiophene (**5**) (89%). Diarylethene **1a** was synthesized by elimination reaction of octafluorocyclopentene and **5**. To the mixture of 5.26 g of **5** and 100 ml of THF, 10.9 ml of butyllithium hexane solution (17.4 mmol) was added at −60 ℃. Then, to the solution was added 0.61 ml (8.7 mmol) of octafluorocyclopentene to yield 4.58 g (11.9 mmol) of **1a** (69%).[15]

Figure 1 shows the ^1H NMR specta of **1a** and **2a**. In the spectrum of **2a**, the methyl signal of a-p conformer was observed at 2.21 ppm, while that of p conformer at 2.49 ppm. The intensity ratio of the two signals indicates that the relative population of a-p and p conformers is 65 : 35. The ^1H NMR spectrum of **1a** shows two sets of signals. The methyl signals of a-p conformer were observed at 0.25 and 1.19 ppm as two

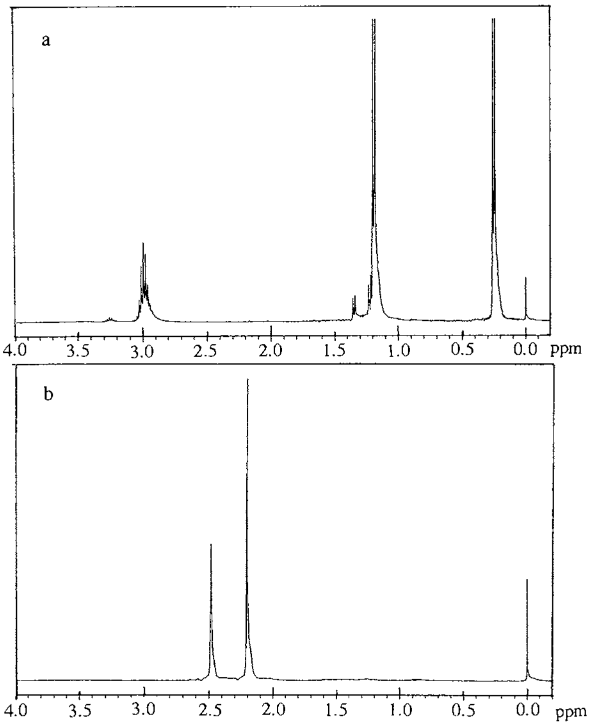


Figure 1. ^1H NMR spectra of **1a** (a) and **2a** (b) in $CDCl_3$ (400 MHz).

Table 1. Calculated and observed ratio of anti-parallel conformer (a-p) and parallel conformer (p) of open-ring form of diarylethenes

Compound	Heat of formation(kJ / mol)		Energy difference between a-p and p (kJ / mol)	Ratio of a-p : p obtained from eq. 1	Ratio of a-p : p observed in NMR spectra
	a-p	p			
1a	-836.62	-832.61	4.01	84 : 16	94 : 6
2a	-758.66	-754.85	3.81	82 : 18	65 : 35

Table 2. Absorption maxima and their coefficients of the open-ring and the closed-ring forms of bis(benzothienyl)ethenes, and the quantum yields in hexane.

	λ_{max} / nm (ε_{max})	$\Phi_{a\to b}$		λ_{max} / nm (ε_{max})	$\Phi_{b\to a}$
1a	299 (7200), 258 (20800)	0.52 (313 nm)	**1b**	535 (8800)	0.34 (517 nm)
2a	258 (14000)	0.35 (313 nm)	**2b**	517 (9100)	0.35 (517 nm)

doublet signals, and the methine signal at 2.99 ppm as septet. The methyl signals of parallel conformers of **1a** were observed at 1.22 and 1.35 ppm.

The septet methine proton of p conformer was detected at 3.26 ppm. The high field methyl signal (0.25 ppm) indicates that a methyl group is faced to the benzothiophene ring in the anti-parallel orientation. The ratio of anti-parallel form and parallel form of **1a** was estimated to be 94 : 6.

To know the possibility to estimate the relative population of the two conformers, we calculated the heat of formation of the both conformers by use of an AM1 program of MOPAC Ver. 6. Calculated results were summarized in the Table 1. The populations of both conformers, ρ_p and $\rho_{a\text{-}p}$, were calculated from Boltzmann distribution equation (eq. 1), and also listed in the Table 1.

$$\rho_p / \rho_{a\text{-}p} = e^{-\Delta E/RT} \qquad (1)$$

As can be seen in Table 1, introduction of isopropyl groups to the aryl moieties increases the relative stability of the photoreactive anti-parallel conformer. However, large difference as observed in the ^{1}H NMR measurement was not obtained in the relative populations calculated at 298 K.

Figure 2 illustrates the absorption spectral change of the hexane solution of **1a** (5.0 × 10^{-5} mol / L) by UV irradiation. Photoirradiation with 260 nm light in the presence of air led to decrease of the absorption at 258 nm (ε 20800 $M^{-1}cm^{-1}$) and the formation of a red solution, in which a new band appeared at 535 nm (ε 8800 $M^{-1}cm^{-1}$). The quantum yields, the absorption maxima of the open-ring and the closed-ring forms, and their absorption coefficients are summarized in Table 2.

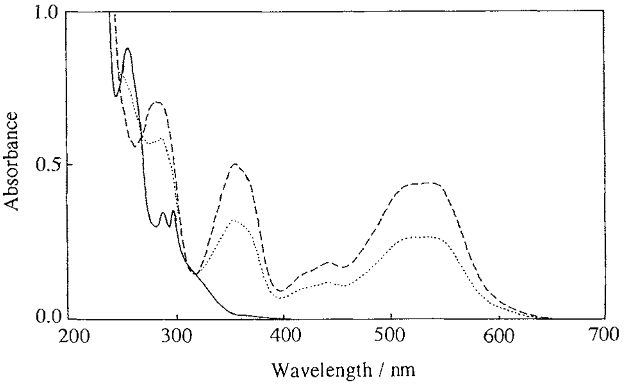


Figure 2. Absorption spectra of hexane solution of **1a** (5.0× 10^5 mol/ L) (———), **1b** (— — —), and the photostationary state (············) under irradiation with 260 nm light.

The quantum yields of ring-opening reactions of **1b** and **2b** were similar to each other. The ring-closure coloration quantum yield increased from 0.35 to 0.52 by the introduction of the isopropyl groups. The increase in the relative population of the anti-parallel conformer increased the coloration quantum yield.

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15 **1a:** colorless needles; mp 189.3-189.4 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.25 (d, 6H, J=7.0 Hz (a-p)), 1.19 (d, 6H, J=7.0 Hz (a-p)), 1.22 (d, 6H, J=7.0 Hz (p)), 1.35 (d, 6H, J=7.0 Hz (p)), 3.00 (sep, 2H, J=7.0 Hz (a-p)), 3.26 (sep, 2H, J=7.0 Hz (p)), 7.13 (ddd, 1H, J=8.0, 7.0, 1.0 Hz (p)), 7.17 (ddd, 1H, J=7.5, 7.0, 1.0 Hz (p)), 7.30 (dd, 1H, J=8.0, 7.0 Hz (a-p)), 7.39 (dd, 1H, J=7.5, 7.0 Hz (a-p)), 7.56 (dd, 1H, J=8.0, 1.0 Hz (p)), 7.61 (dd, 1H, J=7.5, 1.0 Hz (p)), 7.69 (d, 1H, J=8.0 Hz (a-p)), 7.72 (d, 1H, J=7.5 Hz (a-p)). ; MS (m / z) 524 (M+). Found: C, 61.68; H, 4.23%. Calcd. for $C_{27}H_{22}F_6S_2$: C, 61.83; H, 4.20%.