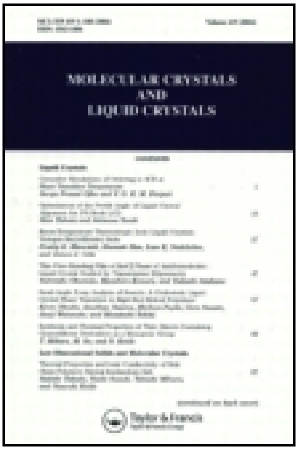

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Photochromic Reactions of Diarylethenes with Isopropyl Groups

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Photochromic Reactions of Diarylethenes with Isopropyl Groups

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Photochromic bisbenzothienylethene has two conformers, photo-reactive anti-parallel and inactive parallel ones. The cyclization quantum yield is dependent on the ratio of the two conformers. By the introduction of bulky substituents at 2-positions of the benzothiophene rings, the cyclization quantum yield increased along with the increase in the ratio of the anti-parallel conformer.

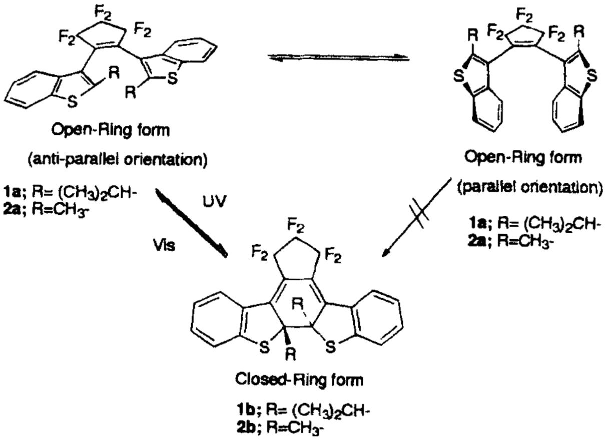
Keywords: Photochromism; Diarylethene; Substituent effect; Quantum yield; Conformation

INTRODUCTION

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 and fatigue resistant 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.

In this letter, we report the effect of introduction of bulky isopropyl groups at 2 and 2' positions of bisbenzothienylethene **1** on the conformation and the coloration quantum yield.



RESULTS AND DISCUSSION

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)hexafluoro-cyclopentene (**2a**) [6].

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

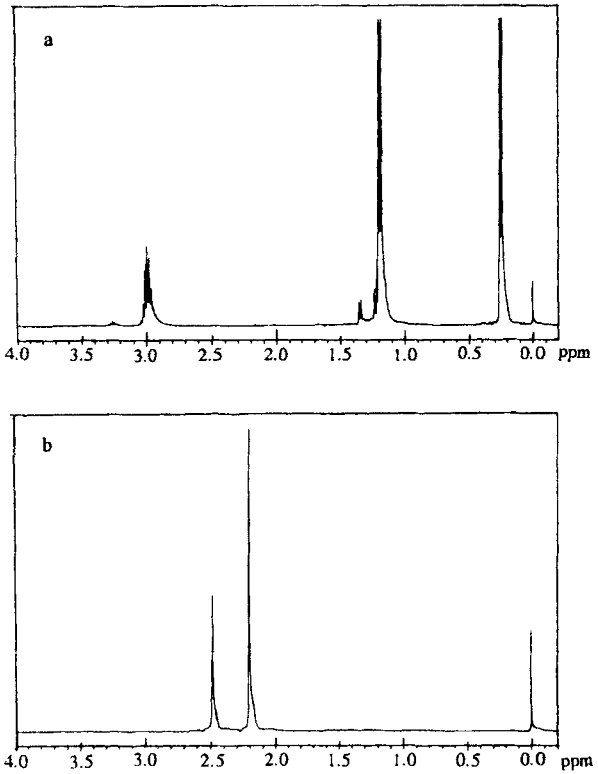


Figure 1. ^{1}H NMR spectra of **1a** (a) and **2a** (b) in $CDCl_3$ (400 MHz).

65 : 35. The ^{1}H 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 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 conformation. The ratio of anti-parallel and parallel conformers of **1a** was estimated to be 94 : 6.

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

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

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

Compound	Ratio of a-p : p obtained from eq. 1 at 298 K	Ratio of a-p : p observed in NMR spectra at 298 K
1a	84 : 16	94 : 6
2a	82 : 18	70 : 30

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.

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 cyclization and ring-opening reaction quantum yields of **1** and **2** were measured and summarized in Table 2. The quantum yields of the ring-opening reactions of **1b** and **2b** were similar to each other. The cyclization 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 cycliztion quantum yield.

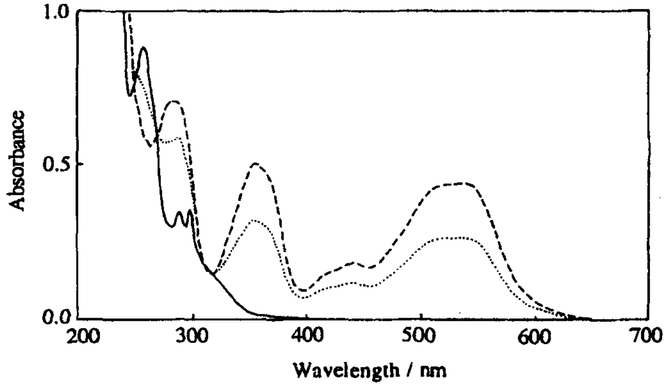


Figure 2. Absorption spectra of hexane solution of **1a** (5.0×10^{-5} mol/L) (———), **1b** (— — —), and the photostationary state (·········) under irradiation with 260 nm light.

Table 2. Absorption maxima and their coefficients of the open-ring and the closed-ring forms of bisbenzothienylethenes **1** and **2**, and the quantum yields in hexane.

	$\Phi_{a \to b}$		$\Phi_{b \to a}$
1a	0.80 (282 nm)	**1b**	0.34 (517 nm)
2a	0.55 (282 nm)	**2b**	0.36 (517 nm)

The open- and closed-ring isomers of the diarylethenes that have heterocyclic rings are known to be thermally stable. For example the closed-ring form **2b** is thermally stable even at 80 ℃ for 3 months [6]. Thermal stability of the closed-ring isomers **1b** was examined in Ar gas substituted hexane solution. After irradiation with 313 nm light, the colored solution was heated at 70 ℃ in an oven under dark. The absorbance of the closed-ring forms was monitored at the wavelength of absorption maximum. After 7 h. storage, the absorbance of **1b** was reduced to 0.83 of initial intensity as shown in Figure 3. Introduction of bulky isopropyl groups at the reactive positions reduced the thermal stability of the closed-ring isomers.

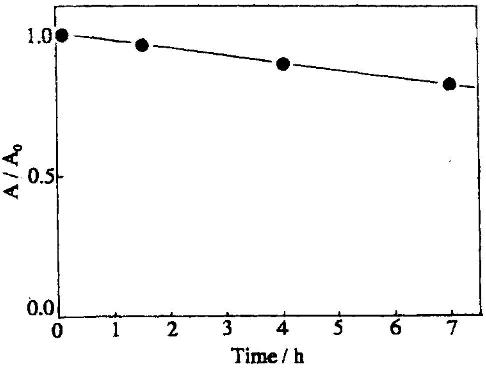


Figure 3. Thermal stability of the closed-ring isomer **1b** (—●—) in hexane at 70 ℃ in the presence of air.

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