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Thermal Stability of Photochromic Bis((trifluoromethyl)thiazolyl)ethene Derivatives

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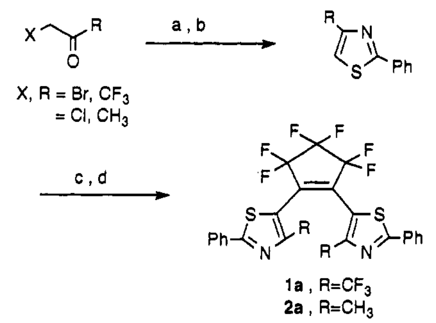
There has been considerable interest in the synthesis of photochromic compounds because of their potential use in optical data storage media.[1] Recently, Irie and his co-workers have been developing the thermally stable photochromic system, diarylethene derivatives such as 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride and 1,2-bis(2-methylbenzothiophene-3-yl)hexafluoro-1-cyclopentene. However, improvement in thermal stability of diarylethenes, particularly the light-induced ring-closed forms, is still one of the biggest problems to be overcome. On the other hand, a trifluoromethyl group often stabilizes the attached sp^3 carbon rather than the sp^2 carbon in the pericyclic reactions.[2] Therefore, an introduction of two trifluoromethyl groups into both of the terminal carbons in diarylethene systems is expected to increase the thermal stability of the light-induced ring-closed forms, where trifluoromethyl groups are attached to the photoinduced sp^3 carbons. As a part of our study on the fluorinated heterocycles,[3] we now demonstrate the synthesis and the thermal stability of the novel photochromic diarylethene, 1,2-bis(2-phenyl-4-(trifluoromethyl)thiazol-5-yl)hexafluoro-1-cyclopentene (**1a**).

2-Phenyl-4-(trifluoromethyl)thiazole was lithiated by butyllithium at −70 °C in THF, forming 5-lithio-2-phenyl-4-(trifluoromethyl)thiazole[4] which reacted with octafluorocyclopentene to give **1a** in 40% yield. Similarly, the 4-methylthiazolyl analogue **2a** was obtained in 55% yield by the reaction of 5-lithio-4-methyl-2-phenylthiazole, formed in situ from 4-methyl-5-phenylthiazole and butyllithium, with octafluorocyclopentene (Scheme I).

Scheme I[a]



[a] (a) Ph(C═S)NH$_2$, EtOH, reflux; (b) *p*-TsOH, toluene, reflux; (c) BuLi, THF, −70 °C to 20 °C; (d) octafluorocyclopentene.

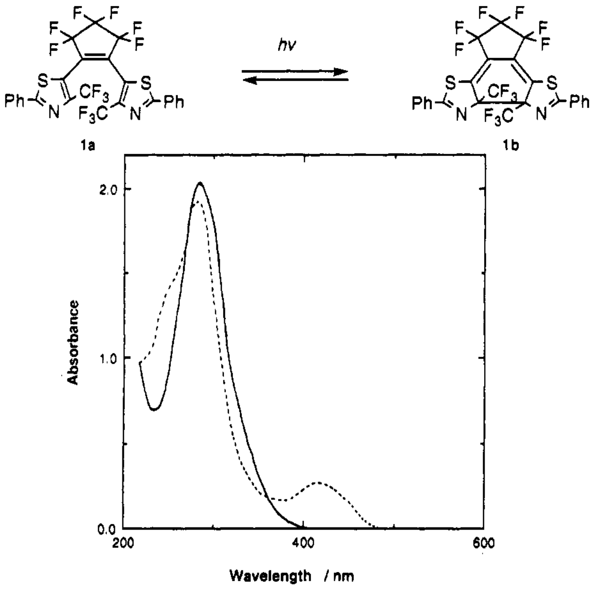


Figure 1. Absorption spectra of **1a** (1×10^{-4} M) (—) before photoirradiation and (- - -) in the photostationary state under irradiation with 330-nm light.

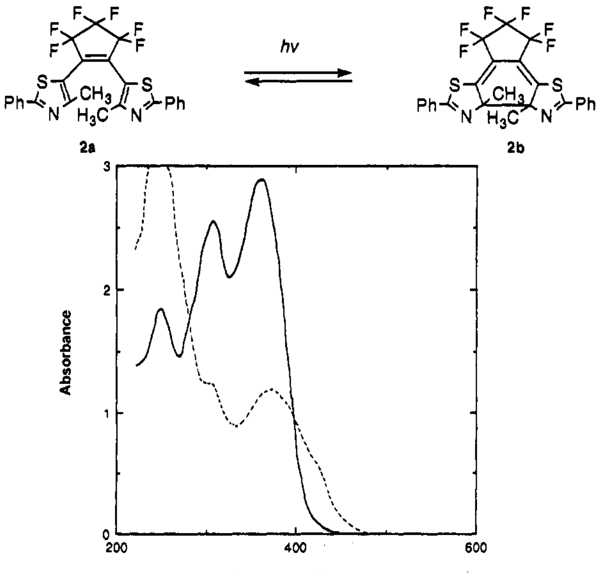


Figure 2. Absorption spectra of **2a** (1×10^{-4} M) (—) before photoirradiation and (- - -) in the photostationary state under irradiation with 330-nm light.

Figure 1 shows the absorption spectra of a dichloromethane solution of **1a** before and after photoirradiation with 330-nm light. Photoirradiation causes absorption at 420 nm, which disappears instantly on exposure to light longer than 390 nm. In the ^{19}F NMR spectra of **1a**, before photoirradiation, three resonances are observed at 14.36, −35.00, and −54.70 ppm, and they are assigned to the CF_3 and two kinds of CF_2 groups, respectively. Upon irradiation, a new resonance appeared at 8.30 ppm along with a decrease of the intensity of the resonance at 14.36 ppm. Figure 2 shows the spectral change of a dichloromethane solution of **2a** by photoirradiation with 330-nm light. In the ^1H NMR spectra of **2a**, irradiation causes one new resonance which lies 0.66 ppm upfield from the methyl protons of **2a**. These new resonances at higher field, observed after irradiation, indicate the presence of the light-induced sp^3 carbon.[5] This result supports the idea that the ring-closed forms **1b** and **2b** are produced upon irradiation. In the photostationary state under irradiation with 330-nm light, the conversions of **1a** and **2a** into the

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[1] Yokoyama, Y.; Hayata, H.; Ito, H.; Kurita, Y. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1607. Suzuki, H.; Tomoda, A.; Ishizuka, M.; Kaneko, A.; Furui, M.; Matsusima, R. *Ibid.* **1989**, *62*, 3968.

[2] Dolbier, W. R., Jr.; Koroniak, H.; Burton, D. J.; Heinze, P. L.; Bailky, A. R.; Shaw, G. S.; Hansen, S. W. *J. Am. Chem. Soc.* **1987**, *109*, 219.

[3] Tanaka, K.; Mori, T.; Mitsuhashi, K. *Chem. Lett.* **1989**, 1115.

[4] 5-Lithio-2-phenyl-4-(trifluoromethyl)thiazole is highly reactive to various electrophiles; for example, the reactions with bromine, *p*-tolualdehyde, and benzaldehyde produced the corresponding products in 85, 89, and 87% yields, respectively.

[5] Nakayama, Y.; Hayashi, K.; Irie, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 202.

0022-3263/92/1957-3726$03.00/0

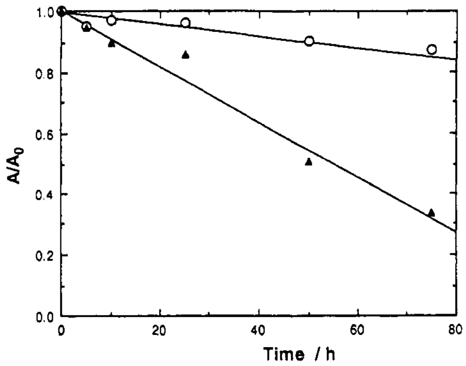


Figure 3. Thermal stability of **1b** and **2b** at 120 °C: (○) **1b**; (▲) **2b**.

corresponding **1b** and **2b** were estimated to be 20 and 15% on the basis of ^{19}F and ^1H NMR analyses, respectively. From Figures 1 and 2 it should be noted that introduction of trifluoromethyl group to the thiazole ring shifts the absorption of **1a** to the blue shifted. This shift makes the absorption at 420 nm of **1b** to be completely distinguished from those of **1a**.

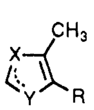
Thermal stability of **1b** and **2b** was estimated by heating a toluene solution of a mixture of **1b** (**1a**) or **2b** (**2a**) in the dark. On heating at 100 °C for 80 h, neither **1b** nor **2b** was converted to the ring-opened form **1a** or **2a**. The outstanding thermal stability of **1b**, compared to **2b**, was observed upon heating the sample to 120 °C. After 75 h, 87% of **1b** was recovered unchanged in contrast to only 34% for **2b**, as shown in Figure 3. It has been reported that the thermal stability of the diarylethene-type photochromic compounds can be improved by introducing aryl groups having a low aromatic stabilization energy.[6] The MNDO-estimated aromatic stabilization energy of thiazoles together with 3-methylfuran is summarized in Table I.[7] The stability of **1b** and **2b** can be explained by the low aromatic stabilization energy of thiazole ring and is expected to be larger than that of the corresponding bis(3-furyl)ethene derivatives. Moreover, the lower aromatic stabilization energy of 4-(trifluoromethyl)thiazole, compared to 4-methylthiazole, supports the rather stable **1b**. The estimated lower aromatic stabilization energy of 4-(trifluoromethyl)thiazole could be ascribed to the trifluoromethyl group destabilizing the thiazole ring in **1a** or stabilizing the sp^3 carbon in **1b**. Which effect is more important is now equivocal.

In conclusion, the thermally stable novel bis(thiazolyl)ethene **1a** carrying two trifluoromethyl groups on the 4-position of both thiazole rings was synthesized, and the trifluoromethyl group resulted in a blue-shifted absorption in the ultraviolet spectra of **1a** and increased the thermal stability of the ring-closed **1b**. These properties are expected to be useful in a new series of photodevices.

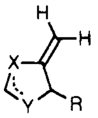
Experimental Section

Melting points are uncorrected. Ultraviolet and infrared spectra were recorded on JASCO Ubest-50 and Report-100 spectrophotometers, respectively. ^1H and ^{19}F NMR spectra were taken on a JEOL JNM-GX270 (270 MHz) spectrometer, using TMS and trifluoroacetic acid as internal and external standards, respectively, the chemical shifts being given in δ ppm downfield. THF was freshly distilled under nitrogen from sodium benzophenone ketyl.

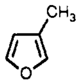
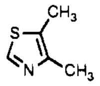
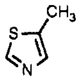
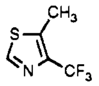
Table I. Aromatic Stabilization Energy: Difference in the Energy between A and B



A



B

compounds	energy (kcal/mol)[a]	compounds	energy (kcal/mol)[a]
	10.58		15.31
	9.54		12.90

[a] Difference in heat of formation between A and B, estimated by the MNDO calculation in MOPAC Ver.5.01; see ref 7.

2-Phenyl-4-(trifluoromethyl)thiazole was prepared by the literature method.[8] Photoirradiation was carried out with a 500-W mercury lamp. Light around 330 nm was selected by passing the light through a ultraviolet transmitting, visible absorbing filter (UV-330) and light longer than 390 nm through a sharp cut filter (L-39).

1,2-Bis(2-phenyl-4-(trifluoromethyl)thiazol-5-yl)hexafluoro-1-cyclopentene (1a). To a solution of THF (30 mL) containing 2-phenyl-4-(trifluoromethyl)thiazole (1.0 g, 4.4 mmol) was added butyllithium (2.3 mL, 2.0 M hexane solution) dropwise at −70 °C. After having stirred for 30 min at −70 °C, octafluorocyclopentene (0.42 g, 2.0 mmol) was added dropwise to the reaction mixture. After being stirred for 3 h at room temperature, the reaction mixture was quenched with water, extracted with diethyl ether, and dried ($MgSO_4$). Removal of the solvent left a residue, which was chromatographed on silica gel (eluent, hexane–ethyl acetate, 50:1) to give the crude product. Recrystallization from ethyl acetate–hexane gave 0.49 g (40%) of **1a** as yellow plates: mp 155–156 °C; ^{19}F NMR ($CDCl_3$) δ 14.36 (s, 6 F, CF_3), −35.00 (br, 4 F, CF_2), −54.70 (pentet, 2 F, CF_2); IR (KBr) 3050 (Ph), 1200–1120 cm^{-1} (CF_3, CF_2). Anal. Calcd for $C_{25}H_{10}F_{12}N_2S_2$: C, 47.63; H, 1.60; N, 4.44. Found: C, 47.52; H, 1.85; N, 4.28.

1,2-Bis(4-methyl-2-phenylthiazol-5-yl)hexafluoro-1-cyclopentene (2a). The similar procedures to the above using 4-methyl-2-phenylthiazole produced 55% of **2a**. Recrystallization from ethyl acetate–hexane gave pale yellow needles of **2a**: mp 105–105.5 °C; ^1H NMR ($CDCl_3$) δ 7.90–7.95 (m, 4 H), 7.45–7.50 (m, 6 H), 2.18 (s, 6 H, CH_3); ^{19}F NMR ($CDCl_3$) δ −32.70 (t, 4 F), −54.46 (pentet, 2 F); IR (KBr) 3050 (Ph), 3000–2950 (CH_3), 1150–1120 cm^{-1} (CF_2). Anal. Calcd for $C_{25}H_{16}F_6N_2S_2$: C, 57.46; H, 3.09; N, 5.36. Found: C, 57.74; H, 3.26; N, 5.43.

Thermal Stability of the Ring-Closed Compounds 1b and 2b. A toluene solution of **1a** (1×10^{-5} M) was irradiated for 5 min through a ultraviolet transmitting, visible absorbing filter (UV-330) with a 500-W mercury lamp. The absorbance at 427 nm (A_0 in Figure 3), ascribed to **1b**, was observed. The solution in a sealed tube was heated at 120 °C in the dark. After 5, 10, 25, 50, and 75 h, the absorbances at 427 nm (A in Figure 3) were observed. On the basis of UV analysis, 3% of **1a** decomposed after 75 h; however, the decomposition products were not identifiable.

The similar procedures using **2a** were carried out and the absorbances at 450 nm were observed. After heating at the 120 °C for 75 h, 21% of **2a** was estimated to decompose.

Registry No. **1a**, 141062-95-5; **1b**, 141062-97-7; **2a**, 141062-96-6; **2b**, 141088-03-1; 2-phenyl-4-(trifluoromethyl)thiazole, 137929-12-5; octafluorocyclopentene, 559-40-0; 4-methyl-2-phenylthiazole, 1826-17-1.

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