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Substituent Effects of 1,2-Bis(2-thienyl)perfluorocyclopentenes

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The 1,2-Bis(2-thienyl)perfluorocyclopentenes that reversibly change color from colorless to yellow by UV irradiation were synthesized. Methyl and bromo substituents at 5-positions of the thiophene rings were effective to shift the absorption bands of the open-ring forms to longer wavelengths. Methyl-substitution at 4-positions shifted the absorption bands of the closed-ring forms to longer wavelength.

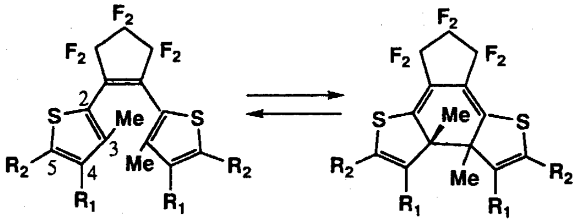
Introduction

Although a great number of photochromic compounds have been reported,$^{1)}$ the compounds which turn yellow upon UV irradiation are quite rare. Chromene$^{2)}$ and spironaphthoxazine with pyrazine ring$^{3)}$ are such a few examples. When we apply photochromic compounds to full color display, it is strongly desired to develop new yellow-developing compounds.

Diarylethenes containing heterocyclic rings undergo photo-induced reversible electrocyclic reactions to produce closed-ring forms that absorb light at longer wavelengths.$^{4\text{-}9)}$ Recently, we have reported on a new diarylperfluorocyclopentene which turns yellow upon UV irradiation.$^{10)}$ The compound, 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene, has thiophene rings that are bound to perfluorocyclopentene moiety at their 2-positions. The substituent effects of 1,2-bis(3-thienyl)ethenes$^{8)}$ and 1,2-bis(3-benzo[b]thienyl)ethenes$^{9)}$ have already been reported, but the substituent effects of 1,2-bis(2-thienyl)ethenes have not yet been studied. In this paper, we report on the substituent effects of 1,2-bis(2-thienyl)ethene derivatives.

Results and Discussion

1,2-Bis(3-methyl-2-thienyl)perfluorocyclopentene **1a**, 1,2-bis(3,4-dimethyl-2-thienyl)perfluorocyclopentene **2a**, 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene **3a**, and 1,2-bis(5-bromo-3-methyl-2-thienyl)perfluorocyclopentene **4a**, were synthesized by addition-elimination reactions of perfluorocyclopentene with appropriate 2-lithiothiophenes.$^{11)}$



1a: R_1=H, R_2=H
2a: R_1=Me, R_2=H
3a: R_1=H, R_2=Me
4a: R_1=H, R_2=Br

1b: R_1=H, R_2=H
2b: R_1=Me, R_2=H
3b: R_1=H, R_2=Me
4b: R_1=H, R_2=Br

Figure 1 illustrates the absorption spectral changes of a hexane solution of **1a** (5.0×10^{-5} M (=mol dm^{-3})) by UV irradiation. Photoirradiation with 334 nm light in the presence of air led to decrease of the absorption at 320 nm (ε : 1.0×10^{4} M^{-1} cm^{-1}) and formation of a yellow solution, in which a new band appeared at 431 nm (ε : 5.8×10^{3} M^{-1} cm^{-1}). This band is ascribable to the closed-ring form **1b**. ^{1}H-NMR spectra gave three new signals at 1.45 (s), 5.70 (d, J=6 Hz), and 6.19(d, J=6 Hz) ppm upon UV irradiation. They are assigned to the methyl signal (δ =1.45 ppm) and the olefinic proton signals (δ =5.70 and 6.19 ppm), respectively, of the closed-ring form. The ^{1}H-NMR signals and the new visible absorption band disappeared by irradiation with light of wavelength > 440 nm. At a photostationary state under irradiation with 334 nm light, the ratio of the closed-ring to the open-ring forms was 81:19.

Figures 2-4 illustrate the absorption spectral changes of hexane solutions of **2a** (λ_{max} : 326 nm, ε : 1.0×10^{4} M^{-1}cm^{-1}), **3a** (λ_{max} : 336 nm, ε : 1.3×10^{4} M^{-1}cm^{-1}), and **4a** (λ_{max} : 338 nm, ε : 1.3×10^{4} M^{-1}cm^{-1}), by irradiation with ultraviolet light. The

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Dedicated to Professor Hitoshi Takeshita on the occasion of his retirement

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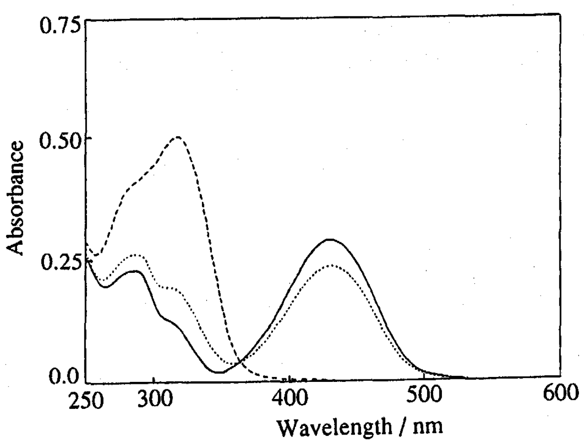

Fig. 1 Absorption spectra of **1a** (5.0×10^{-5} M)(– – –), **1b**(———), and at the photostationary state(·······) upon irradiation with 334 nm light in hexane.

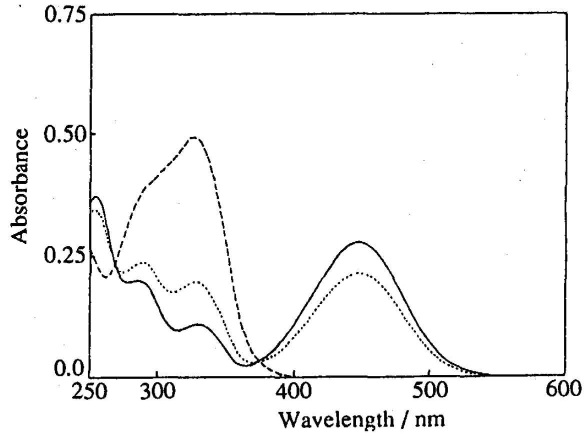

Fig. 2 Absorption spectra of **2a** (5.0×10^{-5} M)(– – –), **2b**(———), and at the photostationary state(·······) upon irradiation with 334 nm light in hexane.

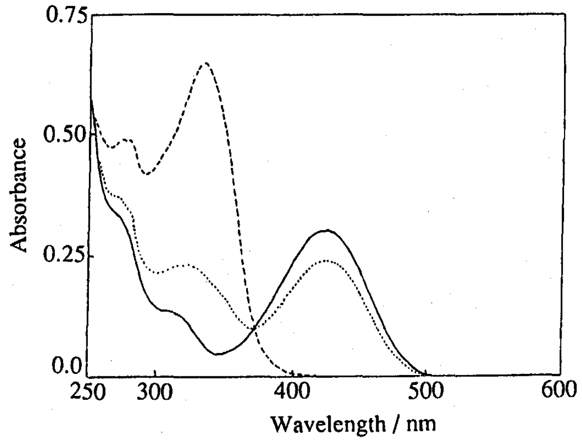

Fig. 3 Absorption spectra of **3a** (5.0×10^{-5} M)(– – –), **3b**(———), and at the photostationary state(·······) upon irradiation with 366 nm light in hexane.

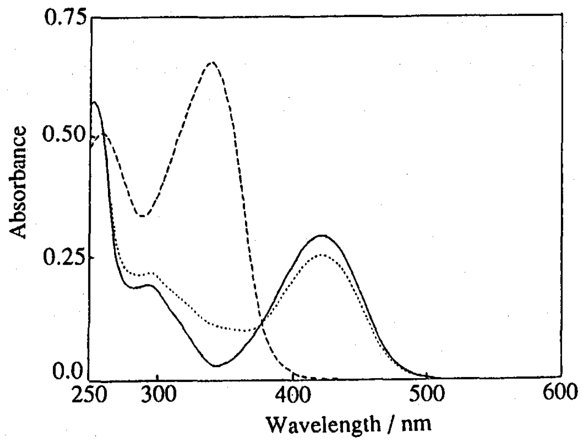

Fig. 4 Absorption spectra of **4a** (5.0×10^{-5} M)(– – –), **4b**(———), and at the photostationary state(·······) upon irradiation with 334 nm light in hexane.

absorption maxima of the photogenerated closed-ring forms, **2b** - **4b**, are 450 nm (**2b**, ε : 5.6×10^3 $M^{-1}cm^{-1}$), 425 nm (**3b**, ε : 5.8×10^3 $M^{-1}cm^{-1}$), and 421 nm (**4b**, ε : 5.8×10^3 $M^{-1}cm^{-1}$), respectively. The fractions of the closed-ring forms at a photostationary state under irradiation with ultraviolet light were 0.77 for **2b** (irradiation wavelength, 334 nm), 0.79 for **3b** (366 nm), and 0.86 for **4b** (334 nm).

Table 1 summarizes the wavelengths of absorption maxima of the open- and closed-ring forms, determined experimentally, and predicted by calculation using a ZINDO program of CAChe system. The calculated spectral shifts by methyl-substitution qualitatively agreed with the observed results.

When methyl groups were substituted at R_1 positions of 2-thienyl moiety, the absorption spectrum of the closed-ring form **2b** showed bathochromic shift in comparison with the closed-form **1b**. But no substituent effect was observed for open-ring form **2a** in comparison with **1a**. The substitutions at R_2 positions with methyl groups or bromine, on the other hand, showed bathochromic (and hyperchromic) shifts of the absorption bands of open-ring forms, **3a** and **4a**. To explain these results, we calculated the electron densities of HOMO and LUMO orbitals of **1a** and **1b** by using MOPAC program of CAChe system. The calculated results are shown in Fig. 5.

In the closed-ring forms, electron densities at 4-positions in HOMO were low. Therefore, the substituent effect can not be explained by the density charge at the 4-positions. In **2b**, two methyl groups come to very close each other, giving rise to strain in closed-ring form skeleton. The strain may increase the degree of conjugation of 1,4-bis(vinylthio)-butadiene structure in some extent. The electron densities at 5-positions are relatively high. Introduction of electron donating substituents will destabilize the

Table 1 Absorption Characteristics of Dithienylethenes

Open-ring form	λ_{max} / nm (ε / 10^4 $M^{-1}cm^{-1}$)	$(\lambda_{max}/nm)_{calcd}$	Closed-ring form	λ_{max} / nm (ε / 10^4 $M^{-1}cm^{-1}$)	$(\lambda_{max}/nm)_{calcd}$
1a	320 (1.0)	253	**1b**	431 (0.58)	340
2a	326 (1.0)	249	**2b**	450 (0.56)	354
3a	336 (1.3)	260	**3b**	425 (0.58)	341
4a	338 (1.3)	-	**4b**	421 (0.58)	-

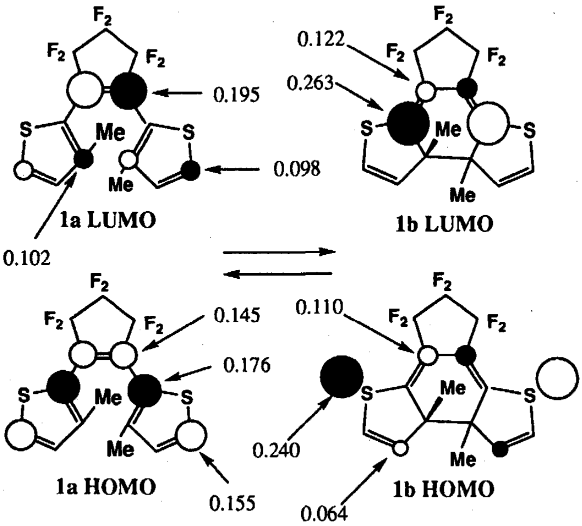

Fig. 5 HOMO and LUMO orbitals and their electron densities of dithienylethene **1**

HOMO orbital, resulting in the bathochromic shift of the absorption bands of the open-ring forms. Bromine substituents produced similar effect as methyl substituents in both **3a** and **4a**.

The thermal stability of the closed-ring forms **1b**-**4b** was measured in heptane in the presence of air at room temperature. Optical densities of these isomers remained almost constant after 100 h. The closed-ring forms of dithienylperfluorocyclopentenes **1b**-**4b** were stable irrespective of the substituents on the thiophene rings.[12)]

Experimental

Absorption spectra were measured with an absorption spectrometer (Hitachi U-3410). ^{1}H NMR spectra were recorded on Varian-Gemini-200(200 MHz) spectrometer in $CDCl_3$. Photoirradiation was carried out by using a USHIO 500 W high-pressure mercury lamp as the exciting light source. Mercury lines at 334 and 366 nm were isolated by passing the light through a monochrometer (Ritsu MC-10N). The spectral characteristics were also supported by the calculation using a ZINDO program of CAChe system .

Materials.

1,2-Bis(3-methyl-2-thienyl)perfluorocyclopentene (1a): To 100 ml of an ether solution containing 2-bromo-3-methylthiophene(9.86 g, 56 mmol) was added 35 ml of a hexane solution (1.6 M, 56 mmol) at -60 ℃ in 5 min, and the solution was stirred for 1h at the low temperature. Then 5.9 g of perfluorocyclopentene(28 mmol) was added to the reaction mixture at -60 ℃, and the solution was further stirred for 1h at same temperature. The reaction was stopped by the addition of a dilute hydrochloric acid. The reaction product was extracted with ether. The organic layer was washed with water, dried over $MgSO_4$, and evaporated. The residue was subjected to column chromatography on silica gel, and hexane elution gave 1.23 g of 1,2-Bis(3-methyl-2-thienyl)perfluorocyclopentene (**1a**) in 12% yield. **1a:** pale yellow prisms; mp 69-70 ℃. Anal. Found: C, 49.13; H, 2.61%. Calcd for $C_{15}H_{10}F_6S_2$: C, 48.91; H, 2.72%. MS (*m/z*) 368 (M+); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.77 (6H, s, Me), 6.85 (2H, d, *J*=5 Hz, aromatic protons), 7.45 (2H, d, *J*=5 Hz, aromatic protons).

1,2-Bis(3,4-dimethyl-2-thienyl)perfluorocyclopentene (2a). n-Butyl lithium hexane solution (1.6 M, 18.4 mmol) was added to a solution of 3,4-dimethylthiophene (2.0 g, 18 mmol) of diethyl ether (50 ml) at room temperature under a nitrogen atmosphere and the reaction mixture was refluxed for 1 h. After cooled down to - 30 ℃, perfluorocyclopentene (1 ml, 9 mmol) was added. The reaction mixture was warmed up to room temperature and treated with dilute hydrochloric acid, and the product was extracted with diethyl ether. After the removal of diethyl ether, the product **2a** was purified by silica gel chromatography(hexane) and isolated in 45% yield. **2a:** pale yellow plates; mp 98-99 ℃. Anal. Found: C, 51.71; H, 3.82%. Calcd for $C_{17}H_{14}F_6S_2$: C, 51.51; H, 3.53%. MS (*m/z*) 396 (M+); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.65 (6H, s, Me), 2.10 (6H, s, Me), 7.13 (2H, s, aromatic protons).

1,2-Bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene (3a). The coupling reaction of 2,4-dimethylthiophene (7.7 g, 69 mmol) and perfluorocyclopentene (4.6 ml, 34 mmol) was performed by the procedure as described for **2a**. The crude product was purified by silica gel chromatography(hexane) to give 6.8 g of 1,2-Bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene (**3a**) in 50% yield. **3a:** pale yellow prisms; mp 129-130 ℃. Anal. Found: C, 51.31; H, 3.66%. Calcd for $C_{17}H_{14}F_6S_2$: C, 51.51; H, 3.53%. MS(*m/z*) 396(M+); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.72 (6H, s, Me), 2.44 (6H, s, Me), 6.51 (2H, s, aromatic protons).

1,2-Bis(2-bromo-4-methyl-5-thienyl)perfluorocyclopentene (4a): Benzyltrimethylammonium tribromide (BTMA Br_3)[13)] (400 mg, 1.03 mmol) and $ZnCl_2$ (ca. 100 mg) were added to a solution of 1,2-Bis(3-methyl-2-thienyl)perfluorocyclopentene (**1a**) (180 mg, 0.5 mmol) in acetic acid (5 ml). The mixture was stirred at room temperature for 2h until the disappearance of the orange color of the reagent. Aqueous $NaHCO_3$(5%, 1 ml) was added to the mixture. The products were extracted with hexane (10 ml x 3) . The combined organic layer was dried ($MgSO_4$) and purified by column chromatography on silica gel (hexane) to give 260 mg of 1,2-Bis(2-bromo-4-methyl-5-thienyl)perfluorocyclopentene (**4a**) in 99% yield. **4a:** pale yellow prisms; mp 91-93 ℃. Anal. Found: C, 34.04; H, 1.49%. Calcd for $C_{15}H_8Br_2F_6S_2$: C, 34.22; H, 1.52%. MS(*m/z*) 526(M+); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.81 (6H, s, Me), 6.84 (2H, s, aromatic protons).

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