Thermally Irreversible Photochromic Systems. Reversible Photocyclization of 1,2-Bis(benzo[*b*]thiophen-3-yl)ethene Derivatives

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1,2-Bis(benzo[*b*]thiophen-3-yl)ethene derivatives, which possess thermally irreversible and fatigue resistant photochromic properties, were synthesized. *cis*-1,2-Dicyano-1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)ethene **1a** and 2,3-bis(2-methylbenzo[*b*]thiophen-3-yl)maleic anhydride **2a** underwent reversible photocyclization to produce red-colored closed-ring forms with λ_{max} at 507 nm and 544 nm, respectively. The closed-ring forms were stable for more than 3 weeks at 80 °C. The coloration/decoloration (ring closure/opening)cycles were able to be repeated more than 10^4 times with keeping the adequate photochromic performance.

The light induced reversible isomerization between two forms having different absorption spectra is referred as photochromism, and the compounds capable of this reaction are called photochromic molecules.

$$\mathrm{A} \underset{h\nu',\Delta}{\overset{h\nu}{\rightleftarrows}} \mathrm{B}$$

Recently, there is an increasing interest to use the organic photochromic molecules for optical data storage media. The conditions indispensable for the application of the photochromic molecules as optical data storage media are the thermal stability of both isomers and the fatigue resistant property of the compounds.

The compounds so far reported,[1–9] however, have a drawback that one of the chemical forms is thermally unstable and reverts to the more stable form in the dark. Although (*E*)-2-[2-(2,5-dimethyl-3-furyl)ethylidene]-3-(isopropylidene)succinic anhydride (furyl fulgide),[3–9] has been reported to be thermally stable, the open *E* form is rather unstable, and shows thermochromism above 120 °C.

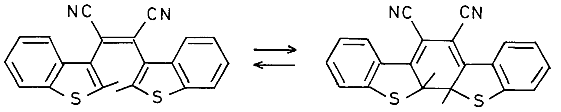
Recently we have developed a new type of photochromic compounds,[10] diarylethenes with heterocyclic rings, both isomers of which are thermally stable. The absorption tails of the closed-ring forms are, however, less than 700 nm. In the present paper, we have synthesized dicyano and acid anhydride derivatives of 1,2-bis(2-methylbenzo[*b*]thiophene-3-yl)ethene in attempting to shift the absorption maxima of the closed-ring forms to longer wavelengths. Although the absorption maxima showed unexpectedly blue shifts in comparison with those of corresponding 1,2-di(3-thienyl)ethenes, the compounds were found to have a remarkable fatigue resistant property and relatively high quantum yields.

Results and Discussion

1,2-Dicyano-1,2-bis(2-methylbenzo[*b*]thiophene-3-yl)ethene 1a. 1,2-Dicyano-1,2-bis(2-methylbenzo[*b*]thiophene-3-yl)ethene **1a** was prepared by the coupling reaction of two 2-methyl-3-(cyanomethyl)benzo[*b*]thiophene. The cis and trans isomers were separated by HPLC and purified by recrystallization from a hexane–benzene mixture.

Figure 1 shows the absorption spectral change of a benzene solution of **1a** (λ_{max}: 392 nm, ε: 7.7×10^3) by photoirradiation with 384 nm light. Irradiation of the benzene solution with 384 nm light led to the decrease of the absorption at 392 nm and the formation of a red solution, in which a visible absorption at 507 nm was observed (conversion; 52%). The absorption maximum showed a 5 nm blue shift in comparison with 1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene.

The photogenerated closed-ring form **1b** (λ_{max}: 507 nm, ε: 8.2×10^3) was stable.[11] The absorption spectrum at 507 nm remained constant for more than 3



1a **1b**

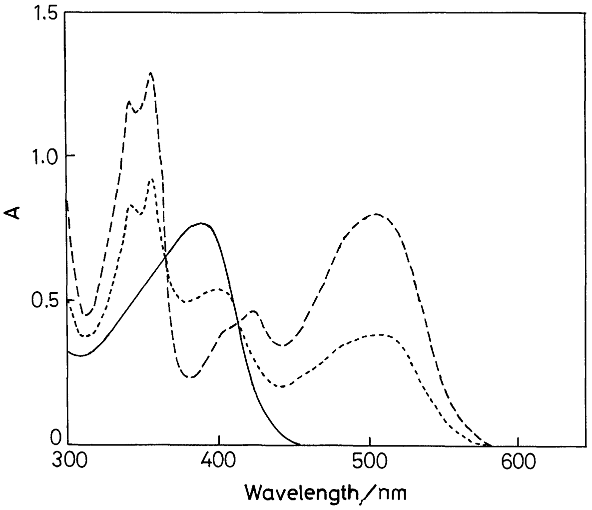


Fig. 1. Absorption spectral change of benzene solution of **1a** (1×10^{-4} M) (——), **1b** (– – –), and photostationary state (········) under irradiation with 384 nm light.

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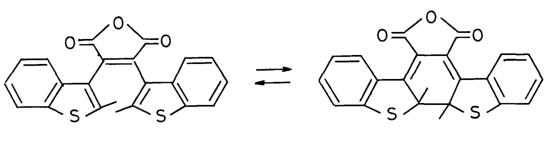
weeks at 80 °C. In addition, the cis form melts at 236 °C without changing the initial yellow color, and did not show any thermochromic reaction even at 300 °C.

2,3-Bis(2-methylbenzo[*b*]thiophen-3-yl)maleic Anhydride 2a. The acid anhydride derivative **2a** was prepared by hydrolysis of **1a** with KOH in a 2-methoxyethanol–water mixture. Compound **2a** is soluble in usual organic solvents such as benzene or chloroform.

Figure 2 shows the absorption spectra of **2a** ($\lambda_{\max}$: 417 nm, ε: 6.8×10^3) in benzene before photoirradiation and in the photostationary state under irradiation with 405 nm light. Upon irradiation with 405 nm light, the solution became dark red and a new absorption peak appeared at 544 nm (ε: 8.7×10^3). The absorption maximum shifts to longer wavelengths by 37 nm in comparison with the dicyano derivative **1b**. The absorption maximum is, however, 16 nm shorter than that of the closed-ring form of 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride. The new band is ascribable to the closed-ring form **2b** (conversion 48%).

The photogenerated closed-ring form was also thermally stable. Absorption intensity of the dark red-colored form remained constant for more than 3 weeks at 80 °C. Upon exposure of the dark red solution to the visible light (λ>500 nm), the solution again became yellow and the initial absorption was restored. The acid anhydride derivative **2a** did not show any thermochromic reaction. It melts at 239 °C without changing the initial color.



2a **2b**

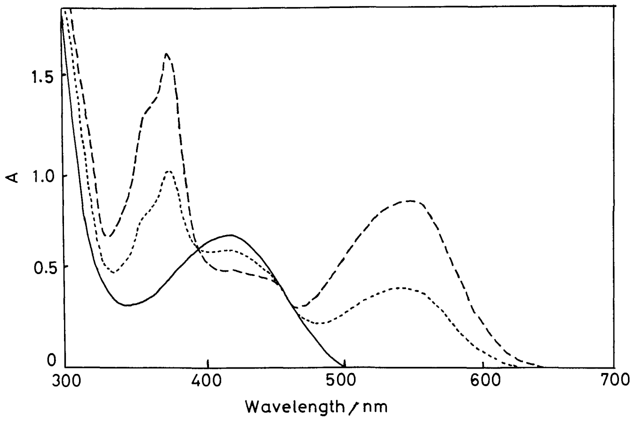


Fig. 2. Absorption spectral change of benzene solution of **2a** (1×10^{-4} M) (——), **2b** (– – –), and photostationary state (········) under irradiation with 405 nm light.

Table 1. Quantum Yield of Coloration and Decoloration in Benzene Solution

	Wavelength/nm	Quantum Yield
1a→1b	405	0.17
1b→1a	546	0.30
2a→2b	405	0.13
2b→2a	546	0.21

Quantum Yield. Table 1 shows the quantum yields of coloration and decoloration reactions of compound **1** and **2**. The quantum yields were determined in benzene by measuring the rate of isomerization in the initial stage of the reactions. The absorbance of the compounds at the irradiating wavelength was controlled to be less than 0.2. The light intensity was measured with a photometer, which was calibrated with a trisoxalatoferrate(III) chemical actinometer. The decoloration quantum yields of both compounds were larger than that observed for 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (quantum yield of decoloration: 0.15 in CCl_4).[10]

The quantum yield of decoloration reaction of furyl fulgide was reported to depend on the bulkiness of substituent at 7-position of the colored form. Adamantylidene furyl fulgide[12] has a quantum yield 5 times larger than that of isopropylidene furty fulgide. Bulky substituent was considered to increase the strain energy of the closed-ring form. This explanation cannot be applied to the present system, because the replacement of thiophene rings with benzo[*b*]thiophene rings does not bring about crowdness to the closed-ring form. The rigidness of the benzothienyl groups possibly introduces unstability to the closed-ring form, and increases the decoloration quantum yield.

Fatigue Resistant Property. Fatigue resistance, i.e., how many times coloration and decoloration cycles can be repeated without loss of performance, is an important property required for photochromic compounds. The lack of this property is one of the reasons which have prevented so far their practical applications.

A benzene solution containing the compound **2** (3.7×10^{-4}M, in a thin cell with light pass length of 2 mm) was irradiated alternatively with 436 nm light for 25 s and 546 nm light for 15 s in the absence of air. The irradiation times, 25 s and 15 s, were long enough for the compound to convert to the photostationary state and to the complete photobleached state, respectively. The absorption intensity at 544 nm in the photostationary state remained constant even after 5000 times coloration/decoloration cycles, as shown in Fig. 3. The intensity decreases to 80% of the first cycle after 1.0×10^4 time coloration/decoloration cycles. In

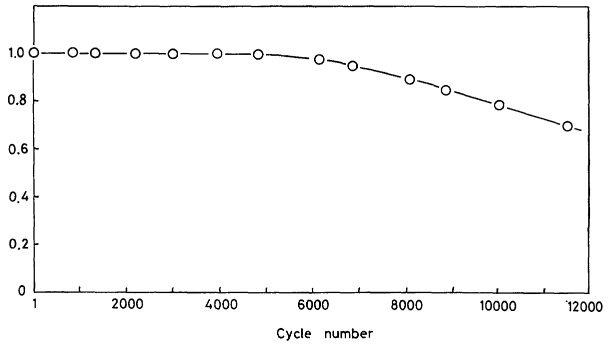
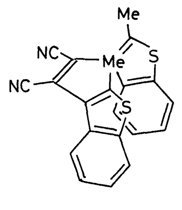


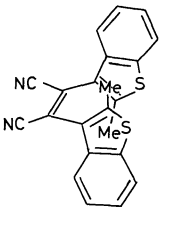
Fig. 3. Fatigue resistant property of **2a** in benzene solution.

the photostationary state of colorlation, almost 50% of the compounds converts to the closed-ring form. This means that the decomposition quantum yield is less than 1/40000. The reason why the quantum yield is so low, is not clear at present.

^{1}H NMR Spectrum. Figure 4 shows the ^{1}H NMR spectra of methyl protons of compound **1a** in CD_3OD at various temperatures. The broad signals are observed at δ 1.98 and 2.37 at room temperature. The two nonequivalent methyl protons indicate the existence of two atrope isomers in the compound. One conformer has two benzothiophene rings in mirror symmetry (in parallel orientation) and the other C_2 symmetry (in anti-parallel orientation).



parallel
orientation



anti-parallel
orientation

The intensity ratio of the two methyl protons depends on the temperature. At temperature below −20 °C, the relative intensity of the upper field signal increases. At −60 °C, the intensity ratio of the upper and the lower field signals is 1.13:1.00. Above room temperature, the line width of the signals increases, and the two signals collapse at 45 °C. At 60 °C, only a sharp single signal is observed. The line-shape change is explained by the interconversion of the two conformers, owing to the rotation of benzo[*b*]thienyl rings.

The activation energies of the conformational changes of **1a** and **2a** were estimated to be 67 kJ mol^{-1} and 71 kJ mol^{-1}, respectively by Jaeschke's method.[13] The rotational energy barriers of **1a** and **2a** are similar each other in spite of different substituents on the ethylene moiety.

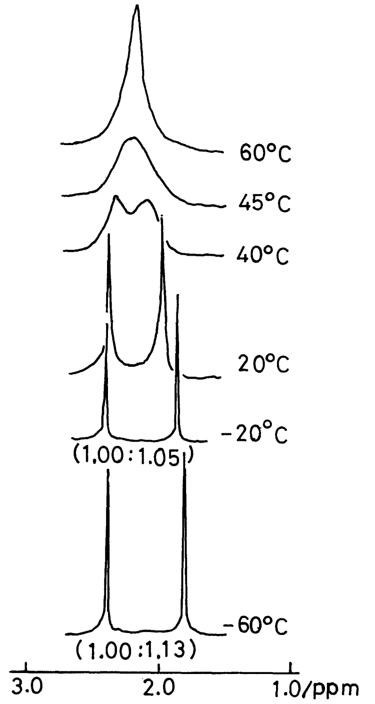


Fig. 4. Temperature dependence of ^{1}H NMR spectra of methyl protons of **1a** in CD_3OD.

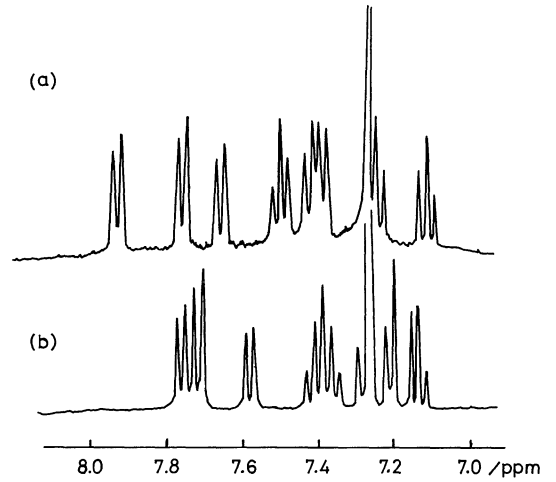


Fig. 5. ^{1}H signals of aromatic rings of **1a** (a) and **2a** (b) in $CDCl_3$ at −60 °C.

The ^{1}H signals of aromatic rings of **1a** and **2a** in $CDCl_3$ at −60 °C were shown in Fig. 5. The signals were assigned by using a proton decoupling technique. The results are summarized in Table 2. In the Table, the differences of chemical shifts between benzo[*b*]-thiophenyl moiety of compounds, **1a** and **2a**, and 3-methylbenzo[*b*]thiophene are listed in the brackets. Relatively large up-field shifts were observed in the protons at 4-position of benzo[*b*]thiophenyl groups in one conformation of **1a** and **2a**. The conformers

Table 2. Assignments of Aromatic Protons of Benzothiophenyl Groups of **1a** and **2a** at −60 °C (in $CDCl_3$ vs. TMS)

Position	**BT**	**1a**		**2a**	
		Anti-parallel	Parallel	Anti-parallel	Parallel
4	7.78	7.76 (−0.02) (d, J=7.7 Hz)	7.39 (−0.39) (d, J=7.9 Hz)	7.58 (−0.20) (d, J=7.6 Hz)	7.20 (−0.58) (d, J=8.0 Hz)
5	7.33	7.41 (0.08) (dd, J=7.7, 7.3 Hz)	7.11 (−0.22) (dd, J=7.9, 7.5 Hz)	7.36 (0.03) (dd, J=7.6, 7.2 Hz)	7.13 (−0.20) (dd, J=8.0, 7.1 Hz)
6	7.31	7.50 (0.19) (dd, J=7.8, 7.3 Hz)	7.25 (−0.06) (dd, J=7.9, 7.5 Hz)	7.40 (0.09) (dd, J=8.0, 7.2 Hz)	7.27 (−0.04) (dd, J=8.0, 7.1 Hz)
7	7.86	7.93 (0.07) (d, J=7.8 Hz)	7.66 (−0.20) (d, J=7.9 Hz)	7.76 (−0.10) (d, J=8.0 Hz)	7.72 (−0.14) (d, J=8.0 Hz)

BT; 2-Methylbenzo[*b*]thiophene. The difference of chemical shifts between **BT** and 1,2-bis(benzo[*b*]thiophen-3-yl)ethenes, **1a**, and **2a**, in each positions are listed in the brackets.

having up-field protons is attributable to parallel orientations, in the case that benzo[*b*]thiophene rings are nearly perpendicular to ethylene plane. These ^{1}H NMR data also support that there are two atropeisomers, parallel and anti-parallel conformations, in these compounds.

Temperature Dependence of Photoisomerization. According to Woodward–Hoffmann rule, photocyclization reaction of 1,3,5-hexatriene molecular framework proceeds in conrotatory mode. When aromatic rings are condensed into both 1,2- and 5,6-positions of the framework such as diarylethenes with two aromatic rings, the reaction course is further restricted. The reactions of the diarylethene derivatives proceed only from the anti-parallel conformers. Ring closure reaction cannot proceed from parallel conformer because of the steric hindrance. This suggests that the rate of photo-induced ring-closure reaction depends on the population of anti-parallel conformation. In order to confirm this assumption, we compared the rate of ring-closure reaction in methanol at −60 °C and 20 °C under the same irradiation conditions. Although the rate at −60 °C was slightly larger (1.1 times) than the rate at room temperature, it was difficult to conclude that the population difference is directly related to the reaction rate, because the difference is in the experimental uncertainty.

Experimental

Photoisomerization. A xenon-arc lamp (USHIO 500W) was used as a light source. The wavelengths of irradiated light were selected by passing the light through a monochrometer (Ritsu MC-10N).

Quantum yields were determined by measuring the rates of isomerization in the initial stage of the reaction at low concentration (absorbance at the measuring wavelength<0.2) and the light intensity was measured with a photometer (International Light, IL 700), which was calibrated with a trisoxalatoferrate(III) chemical actinometer.

Absorption spectra were measured with a spectrophotometer (Hitachi U-3410) and NMR measurement were carried out with a 200-MHz NMR spectrometer (JEOL-FX200) and a 360-MHz NMR spectrometer (Brucker WN-360).

Materials. 3-Chloromethyl-2-methylbenzo[*b*]thiophene: 2-Methylbenzo[*b*]thiophene (2.0 g, 0.014 mol) produced by thio-Claisen rearrangement[14] of thioethers, was added to a solution of chloromethyl methyl ether (33.0 g, 41 mmol) and 260 ml of dichloroethane. To the solution, $ZnCl_2$ (50 mg, 0.37 mmol) was added, and then the solution was stirred for 1 h. The reaction mixture was poured into water, and extracted with chloroform. Removal of the solvent gave 3-chloromethyl-2-methylbenzo[*b*]thiophene (2.4 g, 90%).

3-Cyanomethyl-2-methylbenzo[*b*]thiophene: 3-Chloromethyl-2-methylbenzo[*b*]thiophene (1.4 g, 7.7 mmol) was dissolved in 10 ml of benzene. To this solution was added 10 ml of aqueous solution containing sodium cyanide (2.5 g, 51 mmol) and tetrabutylammonium bromide. The solution was vigorously stirred at 60 °C for 2 h. The reaction mixture was poured into water, and extracted with benzene. Removal of the solvent and purification by silica gel chromatography gave 3-cyanomethyl-2-methylbenzo[*b*]thiophene in 74% yield (1.07 g).

^{1}H NMR ($CDCl_3$) δ=2.53 (3H, s, CH_3), 3.79 (2H, s, $-CH_2-CN$), 7.2—7.9 (4H, m, aromatic protons).

1,2-Dicyano-1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)ethene 1a: To 10 ml of 50% NaOH aqueous solution containing tetrabutylammonium bromide (30 mg, 0.1 mmol) was added a mixture of 3-cyanomethyl-2-methylbenzo[*b*]thiophene (1.0 g, 5.3 mmol), benzene (10 g), and CCl_4 (10 g). The solution was stirred for 1 h at 50—60 °C. The reaction mixture was poured into water and the product was extracted with benzene. After the solvent was removed, the mixture of cis and trans isomers of **1a** was purified and isolated in 39% yield by silica-gel chromatography. Cis and trans isomers (product ratio; 3:2) were separated by HPLC (Shimadzu, SCL-6B).

Cis isomer of **1a**: mp 235—236 °C; MS *m/z* 370 (M^+); IR (KBr) 2300 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ=1.98 (3H, s, CH_3), 2.37 (3H, s, CH_3), 7.1—7.9 (8H, m, aromatic protons). Found: C, 71.46; H, 3.62; N, 17.04%.Calcd for $C_{22}H_{14}N_2S_2$: C, 71.32; H, 3.81; N, 17.31%.

2,3-Bis(2-methylbenzo[*b*]thiophen-3-yl)maleic Anhydride 2a: Compound **1a** (0.83 g, 2.2 mmol) and 2-methoxyethanol (2.5 ml) were added to 3.0 ml of 50% KOH aqueous solution, and the solution was refluxed for 30 h. The reaction mixture was cooled to room temperature and poured into water, and 10% HCl was added until the solution became acidic. The yellow precipitate was extracted with benzene. After the benzene was removed, acid anhydride (118 mg, 0.3 mmol) was isolated in 14% yield by silica-gel column chromatography.

2a: mp 238—240 °C; MS *m/z* 390 (M^+); IR (KBr) 1710 cm^{-1} (COO); ^1H NMR ($CDCl_3$) δ=2.11 (3H, s, CH_3), 2.29 (3H, s, CH_3), 7.05—7.50 (6H, m, aromatic protons), 7.69 (2H, dd, *J*=9, 1 Hz). Found: C, 67.40; H, 3.66; S, 16.45%.Calcd for $C_{22}H_{14}O_3S_2$: C, 67.67; H, 3.61; S, 16.42%.

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