© 1998 The Chemical Society of Japan
Bull. Chem. Soc. Jpn., 71, 1101—1108 (1998)

Thermally Irreversible Photochromic Systems. Reversible Photocyclization of 2-(1-Benzothiophen-3-yl)-3-(2 or 3-thienyl)maleimide Derivatives

Kingo Uchida,* Yuichi Kido,† Tadatsugu Yamaguchi,†,# and Masahiro Irie*,†

Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Seta, Otsu 520-2194

†Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki 6-10-1, Fukuoka 812-8581

(Received October 6, 1997)

Non-symmetric diarylethenes that have a 1-benzothiophene ring on one end and a 2-thienyl or 3-thienyl group on the other end of the double bond of maleimide were synthesized in order to study the effects of the substitution position of the thiophene ring on the absorption bands and the reactivities. The open-and closed-ring forms of *N*-cyanomethyl-2-(2,4-dimethyl-5-phenyl-3-thienyl)-3-(2-methoxy-1-benzothiophen-3-yl)maleimide showed absorption bands at 420 and 563 nm in hexane, respectively. When 3-thienyl was changed to 2-thienyl, the absorption bands of *N*-cyanomethyl-2-(3,4-dimethyl-5-phenyl-2-thienyl)-3-(2-methoxy-1-benzothiophen-3-yl)maleimide shifted to 448 nm (the open-ring form) and 487 nm (the closed-ring form), respectively. The cyclization and ring-opening quantum yields were also dependent on the substitution position. The cyclization yield decreased from 0.30 to 0.03 by changing the position from 3- to 2-thienyl, while the ring-opening yield increased from 0.03 to 0.13. No absorption spectral change by photoirradiation was observed for *N*-cyanomethyl-2,3-bis(3,4-dimethyl-5-phenyl-2-thienyl)maleimide, which has two 2-thienyl groups.

Various kinds of diarylethenes that undergo thermally irreversible and fatigue-resistant photochromic reactions have been developed.[1] A theoretical consideration based on molecular-orbital theory has revealed that the thermal stability of both isomers of diarylethenes is attained by introducing aryl groups, which have low aromatic stabilization energies.[2] The theoretical prediction was confirmed by the synthesis of diarylethenes with various types of aryl groups.[3—12] When the aryl groups are furan, thiophene, or benzothiophene rings, which have low aromatic stabilization energies, the closed-ring forms are thermally stable and don't return to the open-ring forms in the dark.

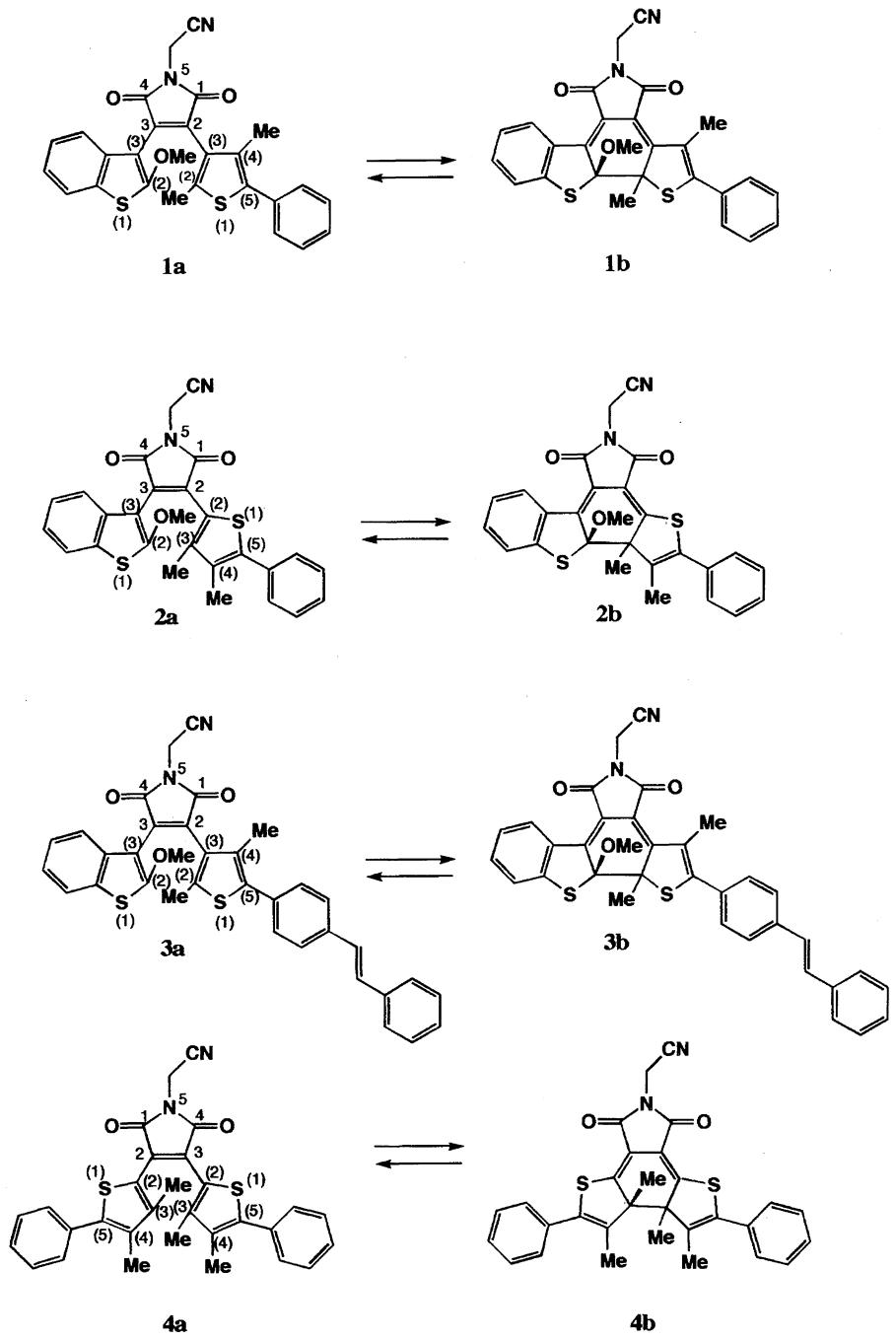
So far, the furan, thiophene, and benzothiophene rings were connected to the ethene moiety at the 3-position. The 1,2-bis(3-thienyl)ethenes convert to the cyclohexadiene derivatives with the absorption bands at longer wavelengths by photoirradiation. The red-shifts of the absorption bands are ascribed to extended π-conjugation in the closed-ring forms. The π-conjugation length depends on the connecting positions of the aryl groups. When the thiophene rings are attached to the ethene moiety at the 2-position, the π-conjugation length in the closed-ring forms becomes short and the absorption bands of the closed-ring forms are expected to shift to shorter wavelengths.[9]

In this study, we synthesized diarylmaleimide derivatives with 3- and 2-thienyl groups, *N*-cyanomethyl-2-(2,4-dimethyl-5-phenyl-3-thienyl)-3-(2-methoxy-1-benzothiophen-3-yl)-maleimide (**1a**) and *N*-cyanomethyl-2-(3,4-dimethyl-5-phenyl-2-thienyl)-3-(2-methoxy-1-benzothiophen-3-yl)maleimide (**2a**), and examined the effect of the substitution positions of the thiophene groups to the maleimide moiety on their absorption bands and reactivities (Scheme 1).

Results and Discussion

Synthesis of *N*-Cyanomethyl-2-(2,4-dimethyl-5-phenyl-3-thienyl)-3-(2-methoxy-1-benzothiophen-3-yl)maleimide (1a) and *N*-cyanomethyl-2-(3,4-dimethyl-5-phenyl-2-thienyl)-3-(2-methoxy-1-benzothiophen-3-yl)maleimide (2a). Non-symmetrical diarylmaleimide derivatives, *N*-cyanomethyl-2-(2,4-dimethyl-5-phenyl-3-thienyl)-3-(2-methoxy-1-benzothiophen-3-yl)maleimide (**1a**) and *N*-cyanomethyl-2-(3,4-dimethyl-5-phenyl-2-thienyl)-3-(2-methoxy-1-benzothiophen-3-yl)maleimide (**2a**), were prepared by the method shown in Schemes 2 and 3. Figure 1 illustrates the absorption spectral change of a hexane solution of **1a** (λ_{max} 420 nm, ε 5300 M^{-1} cm^{-1}) (1 M = 1 mol dm^{-3}) by irradiation with 465 nm light. Irradiation of the hexane solution with the light led to a decrease of the absorption at 420 nm, and the formation of a red solution in which an absorption at 563 nm (ε 9520 M^{-1} cm^{-1}) is observed. Figure 2 illustrates the absorption spectral change of a hexane solution of **2a** (λ_{max} 448 nm, ε 8200 M^{-1} cm^{-1}) upon irradiation with 413 nm light. The absorption maximum of the photogenerated closed-ring form **2b** is 487 nm (ε 6750 M^{-1} cm^{-1}). The

Present address: Department of Applied Materials Science, College of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531.



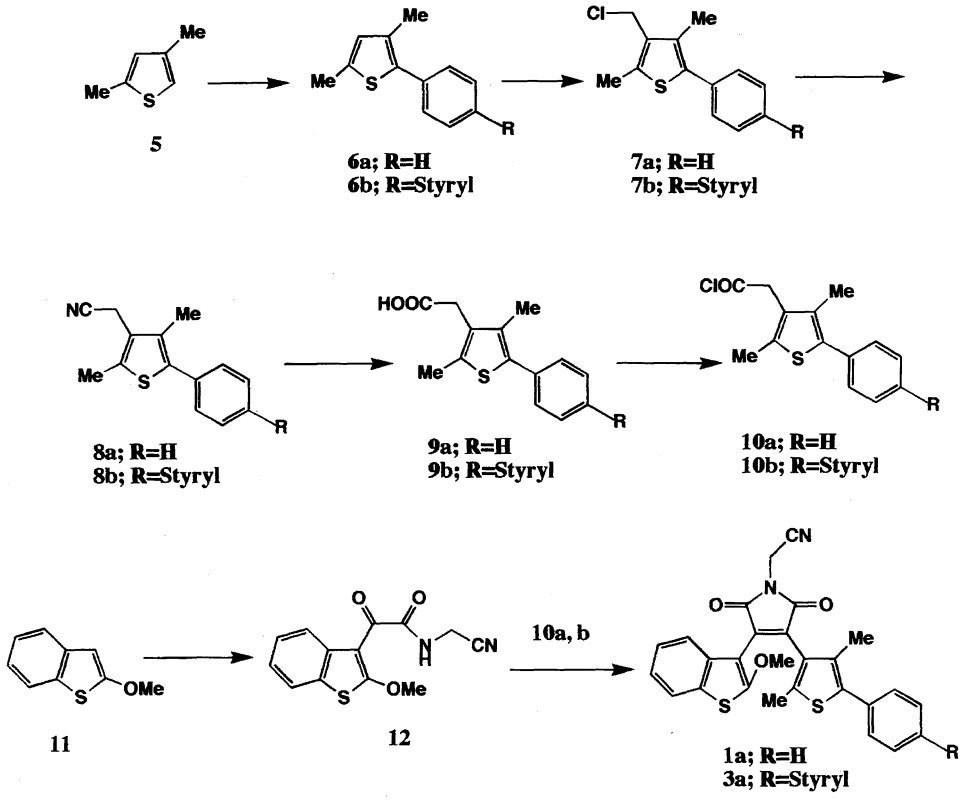
Scheme 1.

fractions of the closed-ring forms at the photostationary state under the above-mentioned conditions were 0.86 for **1b** and 0.31 for **2b**. Upon visible-light irradiation ($\lambda > 550$ nm) the red color disappeared along with a recovery of the absorption bands at 420 and 448 nm of open-ring forms **1a** and **2a**.

Thiophene substitution at the 2-position shifted the maximum of the closed-ring form **2b** (λ_{max} 487 nm) to a shorter wavelength compared with that of the closed-ring form **1b** (λ_{max} 563 nm), in which the thiophene was bound at the 3-position. The blue shift observed for **2b** suggests that the π-conjugation in the closed-ring form is localized in the cyclohexadiene structure.[9] In **1b**, π-conjugation is extended to the phenyl substituent, resulting in the red-shift of the absorption band.

The open-ring form **2a**, on the other hand, gave an absorption band at a longer wavelength compared with **1a**. The π-conjugation in the open-ring form **2a** extends throughout the molecule, while in **1a** the π-conjugation is localized in the hexatriene structure.[9]

Figure 3 illustrates the thermal stability of the closed-ring forms, **1b** and **2b**, in a hexane solution at 70 °C in the dark. The value of A/A_0 was plotted against the storage time, where A_0 is the initial absorbance at the absorption maximum of the closed-ring forms and A is the absorbance after t hours at 70



Scheme 2.

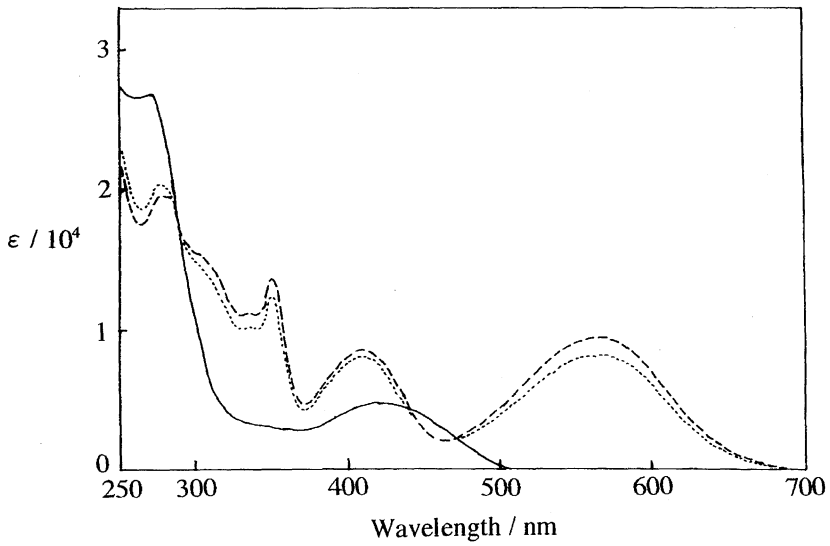
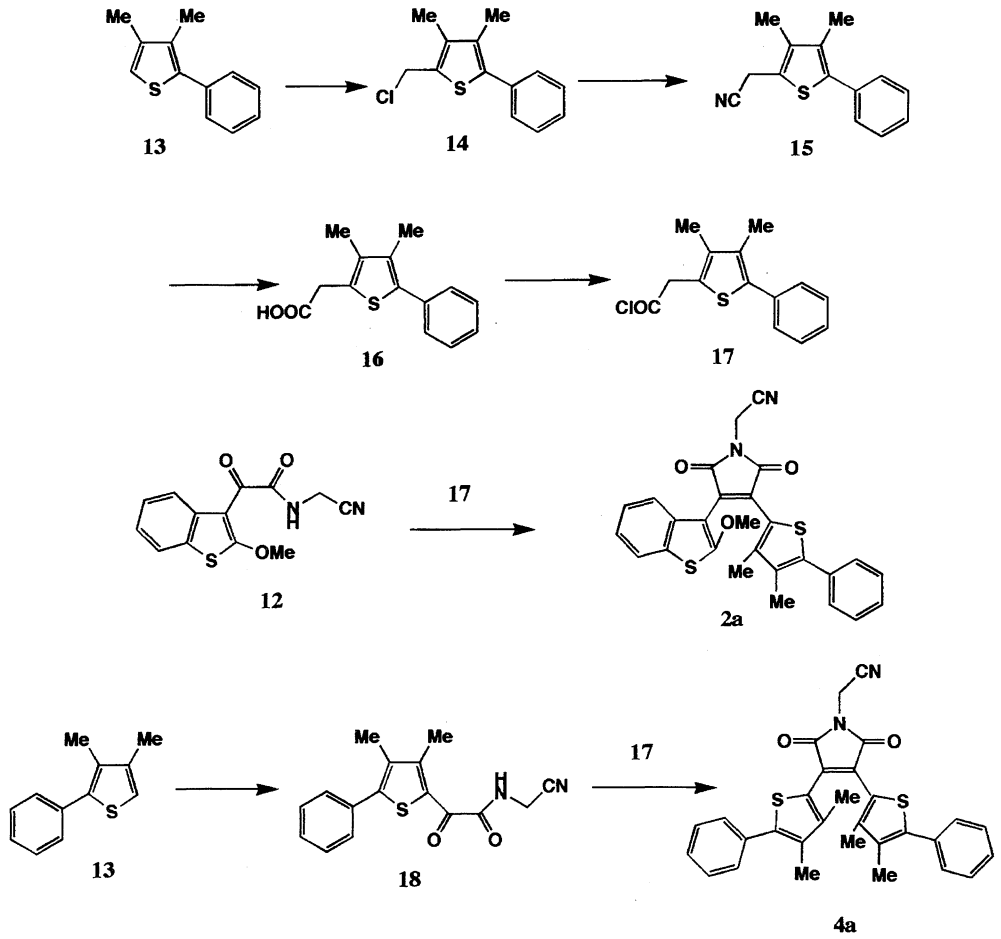


Fig. 1. Absorption spectra of **1a** (—), **1b** (- - -), and photostationary state (····) under irradiation with 465 nm light in hexane.

°C. As can be seen in Fig. 3, the absorption intensity of the photogenerated closed-ring form **2b** remains stable for 150 h, while the intensity of **1b** decreases in the presence of air. In the absence of air, the intensity of **1b** is stable for 150 h at the same temperature.

After storage for 150 h the samples were irradiated with visible light. Both **2b** and **1b** in the absence of air restored the initial absorbance, while **1b** in the presence of air could not return to the initial **1a** form. This result indicates that compound **1b** is decomposed in the presence of oxygen at 70 °C.

Quantum Yield. The quantum yields of cyclization and ring-opening reactions of **1** and **2** were measured in hexane at room temperature. Light of appropriate wavelength was isolated by passing light from a Xe lamp through a monochrometer, and used to induce the reaction. The results are summarized in Table 1. Both the cyclization and ring-opening quantum yields were found to depend on the substitution positions.[9] The quantum yield of the cyclization reaction of **1a** is 0.30, while the yield of **2a** is 0.03. Compound **1a**, in which the thiophene ring is bound at the 3-position to the maleimide moiety, has a large cyclization quantum yield.



Scheme 3.

Table 1. Absorption Maxima and Their Coefficients of the Open-Ring and Closed-Ring Forms of Diarylmaleimides, Quantum Yields of Cyclization and Ring-Opening Reactions in Hexane, and the Excitation Wavelengths

	λ_{max}/nm (ε_{max})	$\Phi_{a\rightarrow b}$		λ_{max}/nm (ε_{max})	$\Phi_{b\rightarrow a}$
1a	420 (5.30×10^3)	0.30 (465 nm)	**1b**	563 (9.52×10^3)	0.03 (563 nm)
2a	448 (8.20×10^3)	0.03 (413 nm)	**2b**	487 (6.75×10^3)	0.13 (487 nm)
3a	427 (6.10×10^3)	0.27 (465 nm)	**3b**	574 (1.47×10^4)	0.003 (574 nm)
4a	471 (1.35×10^4)	—	**4b**	—	—

The reactivity difference is considered to reflect the difference of the electron density in the reactive carbon and the conformation of the thiophene ring in the open-ring forms. The quantum yields of ring-opening reactions of **1b** and **2b** are 0.03 and 0.13, respectively. This result suggests that the localization of π-conjugation in the cyclohexadiene structure is effective to increase the ring-opening quantum yield.[12]

Fatigue Resistant Property. Fatigue resistance, i.e., how many times photo-cyclization and ring-opening reaction cycles can be repeated without loss of performance, is an indispensable property for practical applications. Hexane solutions of compounds **1** and **2** (in thin cells with light pass length of 2 mm) were irradiated alternatively with 457 nm light for 120 s and visible light ($\lambda > 550$ nm) for 120 s in the presence of air, and the absorption intensity of the closed-ring forms was plotted against the cycles, as shown in Fig. 4. The irradiation times were sufficiently long for these compounds to convert to the photostationary state and to the complete photobleached state, respectively. Both compounds **1** and **2** are fatigue resistant. The absorption intensity of **1b** decreased to 80% of the first cycle after 3000 times photocyclization/ring-opening reaction cycles. The absorption intensity of **2b** remained constant even after 3400 photoreaction cycles. The fatigue resistance property of **2** was superior to that of **1**. The photodegradation mechanism is considered to be the formation of endo-peroxides.[13] One of the reaction sites of α positions of the thiophene ring is substituted with an electron-withdrawing maleimide moiety in compound **2a**. This may prevent a side reaction.

Photochromic Properties of *N*-Cyanomethyl-2-[2,4-dimethyl-5-(4-styrylphenyl)-3-thienyl]-3-(2-methoxy-1-benzothiophen-3-yl)maleimide (3a) and *N*-Cyanometh-

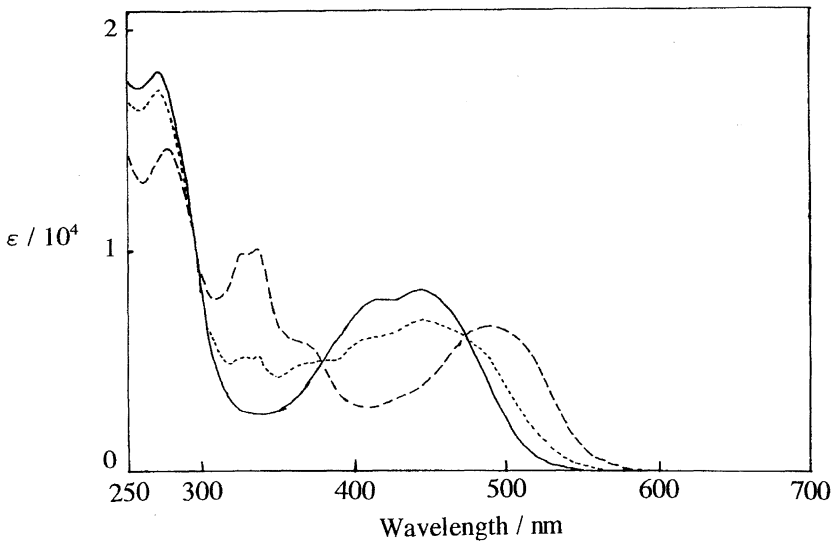


Fig. 2. Absorption spectra of **2a** (—), **2b** (- - -), and photostationary state (····) under irradiation with 410 nm light in hexane.

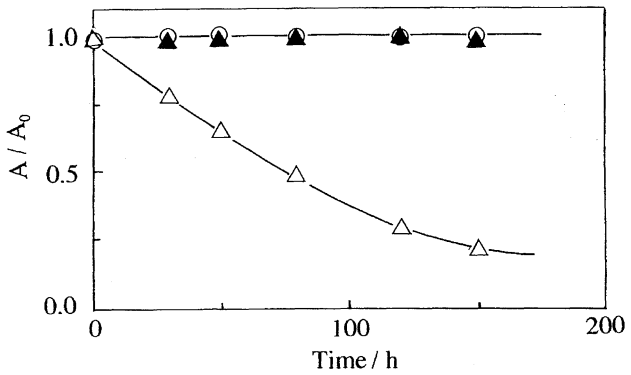


Fig. 3. Thermal stability of the closed-ring forms of **1b** (—△—) and **2b** (—○—) in hexane at 70 °C in the presence of air, and **1b** (—▲—) in the absence of air.

yl-2,3-bis(3,4-dimethyl-5-phenyl-2-thienyl)maleimide (4a). *N*-Cyanomethyl-2-[2,4-dimethyl-5-(4-styrylphenyl)-3-thienyl]-3-(2-methoxy-1-benzothiophen-3-yl)maleimide (**3a**) and *N*-Cyanomethyl-2,3-bis(3,4-dimethyl-5-phenyl-2-thienyl)maleimide (**4a**) were prepared in order to understand the effect of the π-conjugation length of the aryl group on the photochromic behavior. The synthetic methods are similar to those used for **1a** and **2a**. Figure 5 illustrates the absorption spectral change of a hexane solution of **3a** (λ_{max} 427 nm, ε 6100 M^{-1} cm^{-1}) upon irradiation with 465 nm light. The absorption maximum of the photogenerated closed-ring form **3b** is 574 nm (ε 14700 M^{-1} cm^{-1}). The fraction of the closed-ring form at the photostationary state was 0.88. The ε values at the absorption maximum of **3a** and **3b** are 1.15-times and 1.54-times larger than those of **1a** and **1b**, respectively. The introduction of a styryl group to the phenyl ring is effective to increase the absorption coefficient.

The cyclization and ring-opening quantum yields of **3** were 0.27 and 0.003, respectively. Although the cyclization quantum yield was scarcely influenced by the styryl substituent, the ring-opening yield was strongly suppressed. The extension of π-conjugation in the aryl group suppresses the ring-opening yield, as observed for diarylethenes having oligothiophenes.[12]

Figure 6 shows that the absorption spectrum of **4a**. **4a** does not show any spectral changes upon irradiation with any wavelength. The absence of a spectral change indicates that photocyclization is ineffective, and that the ring-open-

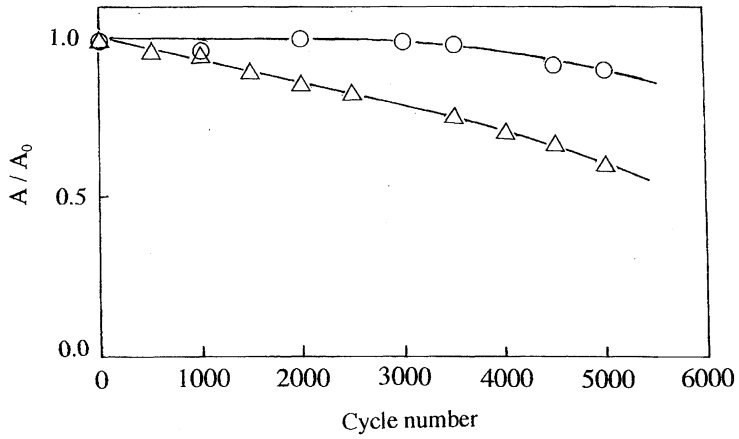


Fig. 4. Fatigue resistant property of **1** (—△—) and **2** (—○—) in hexane solution in the presence of air.

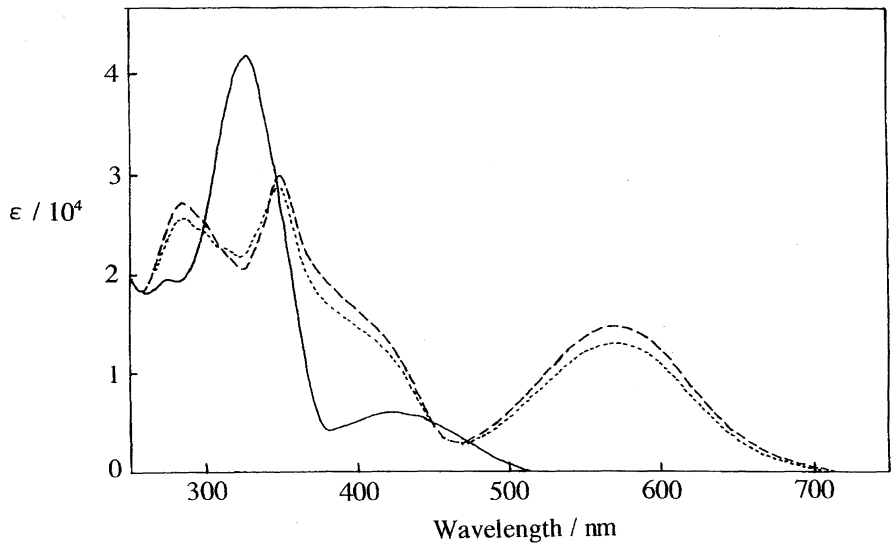


Fig. 5. Absorption spectra of **3a** (—), **3b** (- - -), and photostationary state (····) under irradiation with 465 nm light in hexane.

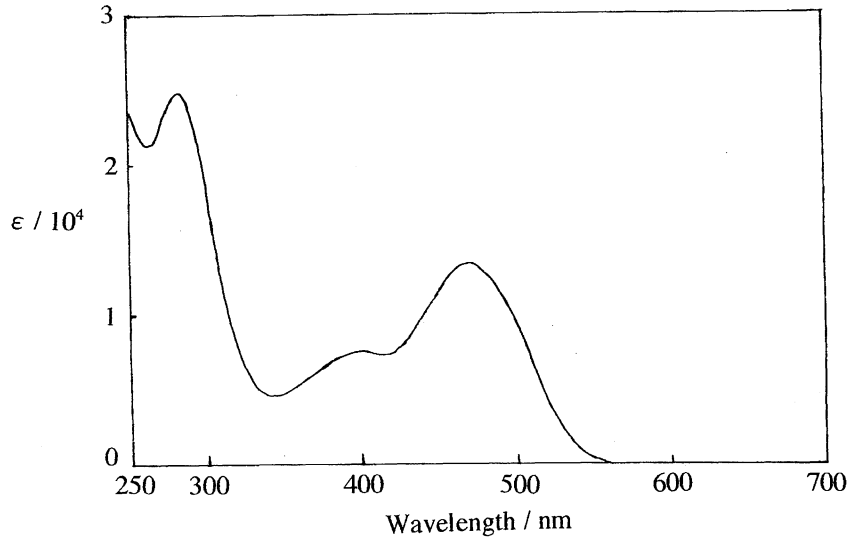


Fig. 6. Absorption spectrum of **4a** (—) in hexane.

ing quantum yield is high in this system. When the spectra of the open- and closed-ring forms overlap and the ring-opening quantum yield is higher than the cyclization quantum yield, the concentration of the closed-ring form at the photostationary state is considered to be negligible.

Experimental

^{1}H NMR spectra were recorded on a Varian Gemini-200 (200 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. The mass spectra (EI, 75 eV) were measured on a JEOL JMS-01-SG-2 mass spectrometer. The absorption spectra were measured using a Hitachi U-3410 spectrophotometer. Photoirradiation was carried out using an Ushio 500 W high-pressure Xenon arc lamp. Light of appropriate wavelength was isolated by passing the arc light through a monochrometer (Ritsu MC-10N). The quantum yields were determined by comparing the reaction yields of the diarylethenes in hexane against furyl fulgide in toluene.[14,15] The samples were not degassed.

3,5-Dimethyl-2-phenylthiophene (6a). To 60 ml of an ether solution containing 4.0 g (36 mmol) of 2,4-dimethylthiophene and 5.32 ml (42 mmol) of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) was added 26 ml of a *n*-BuLi hexane solution (1.6 M, 42 mmol) under a nitrogen atmosphere at −30 °C. The reaction mixture was stirred for 2 h at room temperature. To this reaction mixture was added 42 ml of an ether solution of zinc chloride (1.0 M), and the resulting mixture was stirred for 4 h. In another reaction flask, 3.3 ml (30 mmol) of iodobenzene and 340 mg of tetrakis(triphenylphosphine)palladium(0) were added to 20 ml of anhydrous tetrahydrofuran (THF), and the solution was stirred. To the THF solution was added the previous ether solution dropwise at room temperature. The reaction mixture was heated for 12 h at 50 °C and stirred overnight at room temperature. Water was added to the reaction mixture, and the reaction product was extracted with ether. The organic layer was washed with water, dried ($MgSO_4$), filtered, and evaporated. The residue was purified by column chromatography on silica gel (hexane) to give 6.1 g of 3,5-dimethyl-2-phenylthiophene (**6a**) in 90% yield.

6a: ^{1}H NMR ($CDCl_3$) δ = 2.25 (s, 3H), 2.45 (s, 3H), 6.59 (s, 1H), 7.20—7.60 (m, 5H). MS (*m/z*) 188 (M^+). Found: C, 76.49; H, 6.50%. Calcd for $C_{12}H_{12}S$: C, 76.55; H, 6.42%.

3,5-Dimethyl-2-(4-styrylphenyl)thiophene (6b). The coupling reaction of 2,4-dimethylthiophene (**5**) (2.8 g, 25 mmol) and 4-bromostilbene (5.0 g, 20 mmol) was performed by the same procedure as that described for compound **6a**. The crude product was purified by column chromatography on silica gel (hexane) to give 5.8 g of 3,5-dimethyl-2-(4-styrylphenyl)thiophene (**6b**) in 80% yield.

6b: ^{1}H NMR ($CDCl_3$) δ = 2.34 (s, 3H), 2.52 (s, 3H), 6.66 (s, 1H), 7.18 (d, 2H), 7.25—7.60 (m, 9H). MS (*m/z*) 290 (M^+).

3-Chloromethyl-2,4-dimethyl-5-phenylthiophene (7a). To a stirred solution of 3,5-dimethyl-2-phenylthiophene (1.5 g, 8.0 mmol) in 1,2-dichloromethane (16 ml) was added chloromethyl methyl ether (1.5 ml) and $ZnCl_2$ (10 mg) with cooling in an ice bath, and then stirred for 30 min at the temperature, followed by stirring for 30 min at room temperature. The reaction mixture was poured into water. Extraction with ether, washing with water, drying with magnesium sulfate, and evaporation afforded crude 3-chloromethyl-2,4-dimethyl-5-phenylthiophene. This compound was used for cyanation without further purification.

7a: ^{1}H NMR ($CDCl_3$) δ = 2.32 (s, 3H), 2.53 (s, 3H), 4.59 (s, 2H), 7.34—7.60 (m, 5H).

3-Chloromethyl-2,4-dimethyl-5-(4-styrylphenyl)thiophene (7b). The reaction of 3,5-dimethyl-2-(4-styrylphenyl)thiophene **6b** (700 mg, 2.4 mmol) and chloromethyl methyl ether (3.8 ml) was performed by the same procedure as that described for compound **7a**. The crude product was used for following cyanation without further purification.

7b: ^{1}H NMR ($CDCl_3$) δ = 2.31 (s, 3H), 2.48 (s, 3H), 4.55 (s, 2H), 7.12 (d, 2H), 7.25—7.60 (m, 9H).

3-Cyanomethyl-2,4-dimethyl-5-phenylthiophene (8a). A mixture of **7a**, tetrabutylammonium bromide (310 mg, 1 mmol), and sodium cyanide (560 mg, 11.4 mmol) in water (10 ml) was refluxed for 3 h. After cooling to ambient temperature, the reaction mixture was extracted with ether (30 ml×3). The combined organic layer was dried ($MgSO_4$), filtered and evaporated in vacuo. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 8/2) to give 210 mg of 3-cyanomethyl-2,4-dimethyl-5-phenylthiophene (**8a**) in 45% (from 3,5-dimethyl-2-phenylthiophene) yield.

8a: ^{1}H NMR ($CDCl_3$) δ = 2.18 (s, 3H), 2.38 (s, 3H), 3.50 (s, 2H), 7.26—7.62 (m, 5H). MS (*m/z*) 227 (M^+).

3-Cyanomethyl-2,4-dimethyl-5-(4-styrylphenyl)thiophene (8b). The conversion of **7b** to 3-cyanomethyl-2,4-dimethyl-5-(4-styrylphenyl)thiophene (**8b**) was performed by a procedure like that described for compound **8a**. The residue was purified by column chromatography on silica gel (hexane/chloroform = 7/3) to give 1.1 g of **8b** in 46% (from **6b**) yield.

8b: ^{1}H NMR ($CDCl_3$) δ = 2.29 (s, 3H), 2.47 (s, 3H), 3.56 (s, 2H), 7.14 (d, 2H), 7.25—7.60 (m, 9H). MS (*m/z*) 329 (M^+). Found: C, 80.08; H, 5.82; N, 4.23%. Calcd for $C_{22}H_{19}NS$: C, 80.20; H, 5.81; N, 4.25%.

2,4-Dimethyl-5-phenyl-3-thiopheneacetic Acid (9a). A mixture of compound **9a** (2.0 g, 8.8 mmol) and 50 ml of concentrated hydrochloric acid was refluxed for 5 h. After cooling, the mixture was extracted with ether. The extracts were dried over $MgSO_4$ and concentrated in vacuo to give 246 mg of 2,4-dimethyl-5-phenyl-3-thiopheneacetic acid (**9a**) (12 %).

9a: ^{1}H NMR ($CDCl_3$) δ = 2.13 (s, 3H), 2.35 (s, 3H), 3.50 (s, 2H), 7.23—7.60 (m, 5H). MS (*m/z*) 246 (M^+).

2,4-Dimethyl-5-(4-styrylphenyl)-3-thiopheneacetic Acid (9b). The hydrolysis of **8b** (1.0 g, 3.0 mmol) was performed by a procedure as that described for compound **9a** to form 63 mg of 2,4-dimethyl-5-(4-styrylphenyl)-3-thiopheneacetic acid (**9b**) in 6% yield.

9b: ^{1}H NMR ($CDCl_3$) δ = 2.28 (s, 3H), 2.46 (s, 3H), 3.54 (s, 2H), 7.13 (d, 2H), 7.25—7.60 (m, 9H). MS (*m/z*) 348 (M^+).

***N*-Cyanomethyl-2-methoxy-1-benzothiophene-3-glyoxylamide (12).** A dichloromethane solution (130 ml) containing 7.9 mg (37 mmol) of aminoacetonitrile sulfate and 10.5 ml (75 mmol) of triethylamine was refluxed for 3 h. In another flask, 2.5 ml (28 mmol) of oxalyl chloride was added to a 1,2-dichloroethane solution (85 ml) of 2-methoxy-1-benzothiophene (3.1 g, 19 mmol) and refluxed for 3 h. To this reaction mixture the dichloromethane solution was added and stirred for 12 h at room temperature. The reaction mixture was extracted with chloroform (100 ml) after the addition of 50 ml of 2 M HCl. The organic layer was dried ($MgSO_4$), filtered and evaporated in vacuo. The residue was recrystallized from ethyl acetate to give 2.8 g (10.2 mmol) of *N*-cyanomethyl-2-methoxy-1-benzothiophene-3-glyoxylamide (**12**) in 54% yield.

12: ^{1}H NMR ($CDCl_3$) δ = 4.16 (s, 3H), 4.28 (d, 2H), 7.10—8.30 (m, 4H). MS (*m/z*) 274 (M^+). Found: C, 57.07; H, 3.53; N, 10.05%. Calcd for $C_{13}H_{10}N_2O_3S$: C, 56.93; H, 3.65; N, 10.22%.

***N*-Cyanomethyl-2-(2,4-dimethyl-5-phenyl-3-thienyl)-3-(2-methoxy-1-benzothiophen-3-yl)maleimide (1a).** To a benzene solution (30 ml) containing 123 mg (0.5 mmol) of **9a**, 0.11 ml (1.25 mmol) of oxalyl chloride was added. The mixture was stirred for 1 h, followed by 1h of refluxing. After evaporating benzene and excess oxalyl chloride in vacuo, 10 ml of a 1,2-dichloroethane solution containing 137 mg (0.5 mmol) of **12** and 5 ml of triethylamine was added dropwise. After stirring for 40 h at 30 °C, the reaction mixture was extracted with chloroform (100 ml) following the addition of 50 ml of water. The organic layer was washed with 50 ml of 2 M HCl, dried ($MgSO_4$), filtered, and evaporated in vacuo. The residue was purified by thin-layer chromatography on silica gel (hexane/ethyl acetate = 7/3) to give 95 mg of **1a** in 46% yield.

1a: Mp 101—102 °C; ^{1}H NMR ($CDCl_3$) δ = 2.10 (s, 6H), 3.77 (s, 3H), 4.58 (s, 2H), 7.22—7.70 (m, 9H). MS (*m/z*) 484 (M^+). Found: C, 66.76; H, 4.50; N, 5.46%. Calcd for $C_{27}H_{20}N_2O_3S_2$: C, 66.92; H, 4.16; N, 5.78%.

***N*-Cyanomethyl-2-[2,4-dimethyl-5-(4-styrylphenyl)-3-thienyl]-3-(2-methoxy-1-benzothiophen-3-yl)maleimide (3a).** *N*-Cyanomethyl-2-[2,4-dimethyl-5-(4-styrylphenyl)-3-thienyl]-3-(2-methoxy-1-benzothiophen-3-yl)maleimide (**3a**) was synthesized from **10b**, which was produced from 174 mg of **9b** (0.5 mmol) and 137 mg of **12** (0.5 mmol) by a same procedure as that used for **1a**. The crude product was purified by thin-layer chromatography on silica gel (hexane/ethyl acetate = 7/3) to give 137 mg of **3a** in 47% yield.

3a: Mp 204—205 °C; ^{1}H NMR ($CDCl_3$) δ = 2.05 (s, 3H), 2.08 (s, 3H), 3.77 (s, 3H), 4.58 (s, 2H), 7.11 (d, 2H), 7.25—7.70 (m, 13H). MS (*m/z*) 586 (M^+). Found: C, 71.45; H, 4.53; N, 4.75%. Calcd for $C_{35}H_{26}N_2O_3S_2$: C, 71.65; H, 4.47; N, 4.78%.

2-Chloromethyl-3,4-dimethyl-5-phenylthiophene (14). Chloromethylation was carried out from 1.5 ml of chloromethyl methyl ether and 1.5 g of 3,4-dimethyl-2-phenylthiophene (**13**) (8.0 mmol) by the same procedure as that used for **7a**. The crude product was used for cyanation without further purification.

14a: ^{1}H NMR ($CDCl_3$) δ = 2.10 (s, 3H), 2.13 (s, 3H), 4.72 (s, 2H), 7.20—7.40 (m, 5H).

2-Cyanomethyl-3,4-dimethyl-5-phenylthiophene (15). The

conversion of **14** to 2-cyanomethyl-3,4-dimethyl-5-phenylthiophene (**15**) was performed by the same procedure as that described for compound **8a**. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 19/1) to give 163 mg of **15** in 45% (from **13**) yield.

15: ^{1}H NMR ($CDCl_3$) δ = 2.15 (s, 3H), 2.16 (s, 3H), 3.78 (s, 2H), 7.30—7.45 (m, 5H). MS (*m/z*) 227 (M^+).

3,4-Dimethyl-5-phenylthiophene-2-acetic Acid (16). Hydrolysis of **15** (1.05 g, 4.6 mmol) was performed by the same procedure that as described for compound **9a** to form 203 mg of 3,4-dimethyl-5-phenylthiophene-2-acetic acid (**16**) in 21% yield.

16: ^{1}H NMR ($CDCl_3$) δ = 2.12 (s, 3H), 2.18 (s, 3H), 3.81 (s, 2H), 7.25—7.45 (m, 5H). MS (*m/z*) 246 (M^+).

***N*-Cyanomethyl-2-(3,4-dimethyl-5-phenyl-2-thienyl)-3-(2-methoxy-1-benzothiophen-3-yl)maleimide (2a).** *N*-Cyanomethyl-2-(3,4-dimethyl-5-phenyl-2-thienyl)-3-(2-methoxy-1-benzothiophen-3-yl)maleimide (**2a**) was synthesized from **17** produced from 123 mg of **16** (0.5 mmol) and 137 mg of **12** (0.5 mmol) by the same procedure as that used for **1a**. The crude product was purified by thin-layer chromatography on silica gel (hexane/ethyl acetate = 7/3) to give 95 mg of **2a** as an orange oil in 40% yield.

2a: Orange oil, ^{1}H NMR ($CDCl_3$) δ = 1.64 (s, 3H), 2.05 (s, 3H), 3.94 (s, 3H), 4.60 (s, 2H), 7.19—7.70 (m, 9H). MS (*m/z*) 484 (M^+). Found: C, 66.89; H, 4.66; N, 5.91%. Calcd for $C_{27}H_{20}N_2O_3S_2$: C, 66.92; H, 4.16; N, 5.78%.

***N*-Cyanomethyl-3,4-dimethyl-5-phenyl-2-thiopheneglyoxylamide (18).** *N*-Cyanomethyl-3,4-dimethyl-5-phenyl-2-thiopheneglyoxylamide (**18**) was synthesized from 940 mg of **12** (5.0 mmol) by the same procedure as that used for **12**. The crude product was purified by recrystallization from ethyl acetate to give 470 mg (1.6 mmol) of **18** in 32% yield.

18: ^{1}H NMR ($CDCl_3$) δ = 2.17 (s, 3H), 2.55 (s, 3H), 4.25 (s, 2H), 7.30—7.45 (m, 5H), 7.75 (s, 1H). MS (*m/s*) 298 (M^+). Found: C, 64.30; H, 4.53; N, 9.07%. Calcd for $C_{16}H_{14}N_2O_2S$: C, 64.43; H, 4.70; N, 9.40%.

***N*-Cyanomethyl-2,3-bis(3,4-dimethyl-5-phenyl-2-thienyl)maleimide (4a).** *N*-Cyanomethyl-2,3-bis(3,4-dimethyl-5-phenyl-2-thienyl)maleimide (**4a**) was synthesized from **17** produced from 148 mg of **16** (0.6 mmol) and 179 mg of **18** (0.6 mmol) by the same procedure as that used for **1a**. The crude product was purified by thin-layer chromatography on silica gel (hexane/ethyl acetate = 7/3) to give 121 mg of **4a** in 40% yield.

4a: Mp 114—115 °C; ^{1}H NMR ($CDCl_3$) δ = 1.78 (s, 6H), 2.19 (s, 6H), 4.58 (s, 2H), 7.30—7.50 (m, 10H). MS (*m/z*) 508 (M^+). Found: C, 70.68; H, 4.98; N, 5.26%. Calcd for $C_{30}H_{24}N_2O_2S_2$: C, 70.84; H, 4.76; N, 5.51%.

This work was supported in part by a Grant-in-Aid for Scientific Research (C) No. 09640692 from the Ministry of Education, Science, Sports and Culture and by CREST of Japan Science and Technology Corporation (JST).

References

1) M. Irie, "Photoreactive Materials for Ultrahigh Optical Density," ed by M. Irie, Elsevier, Amsterdam (1994), p. 1.
2) S. Nakamura and M. Irie, *J. Org. Chem.*, **53**, 6136 (1988).
3) M. Irie and M. Mohri, *J. Org. Chem.*, **53**, 803 (1988).
4) K. Uchida, Y. Nakayama, and M. Irie, *Bull. Chem. Soc. Jpn.*, **63**, 1311 (1990).
5) Y. Nakayama, K. Hayashi, and M. Irie, *J. Org. Chem.*, **55**, 2592 (1990).
6) M. Hanazawa, R. Sumiya, Y. Horikawa, and M. Irie, *J. Chem. Soc., Chem. Commun.*, **1992**, 206.
7) S. L. Gilat, S. H. Kawai, and J.-M. Lehn, *Chem. Eur. J.*, **1**, 275 (1995).
8) T. Yamaguchi, K. Uchida, and M. Irie, *J. Am. Chem. Soc.*, **119**, 6066 (1997).
9) K. Uchida and M. Irie, *Chem. Lett.*, **1995**, 969.
10) S. Iwata, Y. Ishihara, C.-P. Qian, and K. Tanaka, *J. Org. Chem.*, **57**, 3726 (1992).
11) M. Irie, K. Sakemura, M. Okinaka, and K. Uchida, *J. Org. Chem.*, **60**, 8305 (1995).
12) M. Irie, T. Eriguchi, T. Takada, and K. Uchida, *Tetrahedron*, **53**, 12263 (1997).
13) H. Taniguchi, A. Shinpo, T. Okazaki, F. Matsui, and M. Irie, *Nippon Kagaku Kaishi*, **1992**, 1138.
14) Y. Yokoyama and Y. Kurita, *Nippon Kagaku Kaishi*, **1992**, 998.
15) Y. Yokoyama and Y. Kurita, *Synth. Org. Chem. Jpn.*, **49**, 364 (1991).