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Thermally Irreversible Photochromic Systems. Reversible Photocyclization of Non-Symmetric Diarylethene Derivatives

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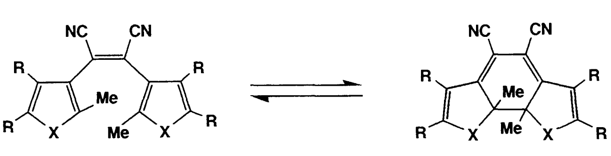
Non-symmetric diarylethenes with an indole ring on one end and a thiophene, a benzo[*b*]thiophene, or a pyrrole ring on the other end of the double bond were synthesized in an attempt to get thermally irreversible photochromic compounds having absorption bands at longer wavelengths. 2-(1,2-Dimethyl-3-indolyl)-3-(2,4,5-trimethyl-3-thienyl)maleic anhydride(**8a**) underwent photoinduced cyclization/ring-opening reactions with relatively high quantum yields (cyclization quantum yield: 0.15; ring-opening quantum yield: 0.40), and the both isomers were thermally stable. The closed-ring form had the absorption maximum at 595 nm with the edge extending to 760 nm. Cyclization/ring-opening reactions of **8a** and 2-(1,2-dimethyl-3-indolyl)-3-(2-methyl-3-benzo[*b*]thienyl)maleic anhydride (**9a**) were induced by Ar ion (488 nm) and He–Ne (633 nm) lasers.

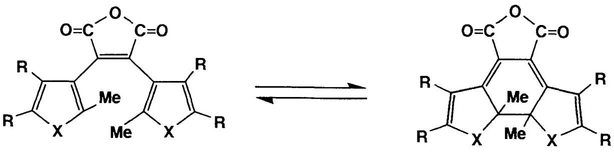
A photochromic material is characterized by its ability to undergo a reversible transformation between two different chemical forms. Such a transformation is induced by irradiation with an appropriate wavelength.[1] The instant image-forming property without processing has led to the consideration of the use in rewritable direct read after write memory systems.[2] Despite favorable situations provided by recent progress of optical memory technology, organic photochromic compounds have found little applications in optical information storage media. The limitation is due to the lack of suitable compounds which fulfill the requirements for the reversible recording media. Among the requirements the most important one is the thermal stability.[3]

Recently, a new type of thermally stable photochromic compounds, diarylethenes with heterocyclic rings, was developed such as 1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (**1a**), and 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (**3a**).[4] Compounds **1a**—**4a** are not thermochromic, even at 300 °C, and the colored closed-ring forms **1b** and **3b** are stable for more than 3 months at 80 °C.[2g] The compounds fulfill the most important condition for optical data storage media. The absorption edges of the closed-ring forms, however, do not extend to 700 nm. This precludes isomerization of the compounds by conventional diode laser light ($780<\lambda<840$ nm). The compounds lack the important requirement of photosensitivity at diode laser wavelengths.



1a, X=S; R=CH_3
2a, X=NCH_3;
R⌒R=CH=CH–CH=CH

1b, X=S; R=CH_3
2b, X=NCH_3;
R⌒R=CH=CH–CH=CH



3a, X=S; R=CH_3
4a, X=NCH_3;
R⌒R=CH=CH–CH=CH

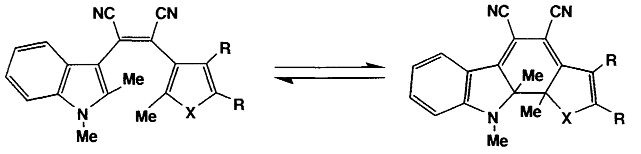
3b, X=S; R=CH_3
4b, X=NCH_3;
R⌒R=CH=CH–CH=CH

In order to gain access to compounds which have sensitivity at longer wavelengths, symmetric diarylethenes with various heterocyclic rings have been synthesized.[5] Replacing the thiophene rings with indole rings, i.e. 1,2-dicyano-1,2-bis(1,2-dimethyl-3-indolyl)ethene (**2a**) and 2,3-bis(1,2-dimethyl-3-indolyl)maleic anhydride (**4a**), shifts the absorption maxima to longer wavelengths. Compound **4b** has an absorption edge extending to 800 nm and the ring-opening reaction was effected with 780 nm diode laser. The closed-ring forms, **2b** and **4b**, were, however, thermally unstable, reverting in the dark to **2a** and **4a**. The absorption intensity of **4b** decreased to 50% of the initial intensity in 3 h at 80 °C. The thermal stability difference between the diarylethenes with thiophene and indole rings was interpreted by the difference in aromatic stabilization energy of the rings.[6]

In the present study, we synthesized unsymmetrically substituted non-symmetric diarylethene derivatives having an indole ring on one end and a thiophene, a benzo[*b*]thiophene, or a pyrrole ring on the other end of the double bond in an attempt to get thermally stable photochromic compounds having the absorption bands at longer wavelengths.

Results and Discussion

Diarylethene Derivatives with Dicyano Group. Substituted non-symmetric diaryldicyanoethenes having an indole ring on one end and a thiophene, a benzo[*b*]thiophene, or a pyrrole ring on the other end of the double bond were prepared by a coupling reaction of 3-(cyanomethyl)-1,2-dimethylindole and 3-(cyanomethyl)-2,4,5-trimethylthiophene, 3-(cyanomethyl)-2-methyl-benzo[*b*]thiophene or 3-(cyanomethyl)-1,2,4,5-tetramethylpyrrole, respectively.



5a, X=S; R=CH_3
6a, X=S;
$\widehat{\text{R R}}$=CH=CH-CH=CH
7a, X=NCH_3; R=CH_3

5b, X=S; R=CH_3
6b, X=S;
$\widehat{\text{R R}}$=CH=CH-CH=CH
7b, X=NCH_3; R=CH_3

In the case of a coupling reaction of equimolar (cyanomethyl)indole and (cyanomethyl)pyrrole approximately equal amounts of **7a** and **2a** were obtained. (Cyanomethyl)pyrrole reacted more efficiently with (cyanomethyl)indole than (cyanomethyl)pyrrole. The self coupling product of the pyrrole compounds, 1,2-dicyano-1,2-bis(1,2,4,5-tetramethyl-3-pyrrolyl)ethene, was formed in very low yield. The mixture of **7a** and its trans form, and **2a** and its trans form was separated by silica-gel chromatography using benzene as an eluent. The trans and cis mixture of the indolylpyrrolylethene derivative was dissolved in acetonitrile and exposed to ultraviolet-visible light (λ>350 nm). The irradiation converted a large part of the trans form to the cis form. The cis form was isolated by high-performance liquid chromatography (HPLC, 5 μm silica gel/benzene) and purified by recrystallization from a hexane–ether mixture.

The coupling reaction of equimolar (cyanomethyl)indole and (cyanomethyl)thiophene yielded the mixture of **5a**, **1a**, and **2a** (4:20:1 including the trans forms). The mixture was separated by the same procedure used for **7a**. Compound **6a** was also prepared by the similar coupling reaction as used for **7a**. The structures of the above compounds were fully characterized by spectroscopic methods.

Non-symmetric diarylethenes with the dicyano group underwent the cyclization to produce the cyclohexadiene-type derivatives.[7] Figure 1 shows the absorption spectral change of a dilute benzene solution of **5a** (1.0×10^{-4} mol dm^{-3}) by photoirradiation with 436 nm light. Irradiation of the yellow benzene solution in the presence of air with 436 nm light leads to the decrease of the absorption at 412 nm ($\varepsilon=1.0\times10^{4}$ l mol^{-1} cm^{-1}) and formation of a brown solution, in which a visible absorption at 549 nm ($\varepsilon=5.4\times10^{3}$ l mol^{-1} cm^{-1}) was observed. The closed-ring form **5b** shows a 37 nm bathochromic shift compared with **1b**. Isosbestic points are observed at 382 and 458 nm. The spectra indicate that the cis to trans isomerization is negligible when the sample is irradiated at 436 nm. Upon irradiation with light of wavelengths longer than 520 nm, the brown color of

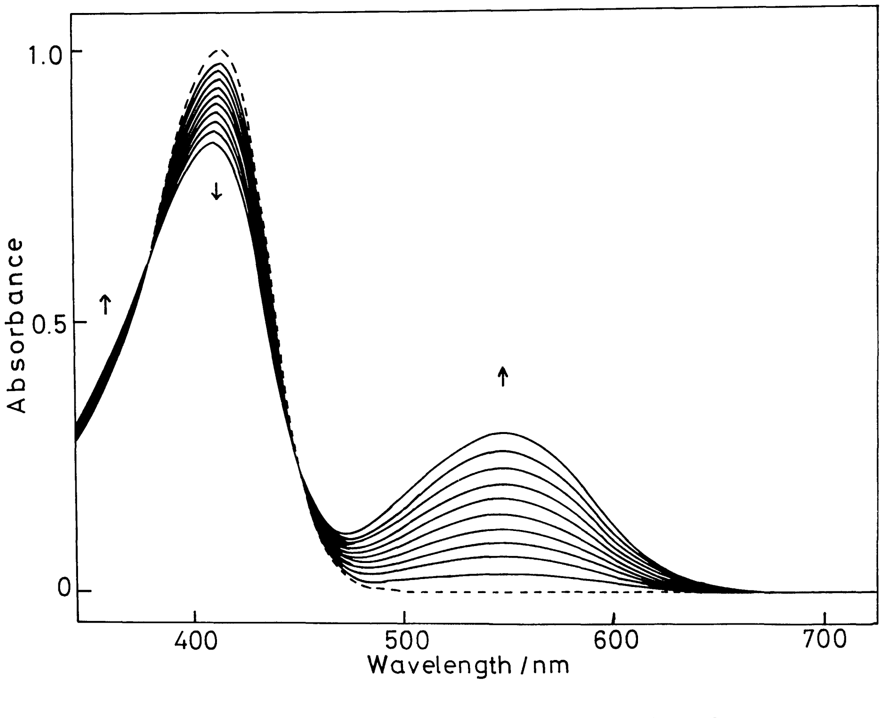


Fig. 1. Absorption spectral change of benzene solution of **5a** (1.0×10^{-4} mol dm^{-3}) (---) induced by irradiation with 436 nm light. Irradiation time; 25, 50, 80, 110, 150, 195, 261, 333, 471, and 855 s.

5b disappeared, and the initial cis form absorption was restored. The conversion of **5a** to **5b** at the photostationary state was estimated to be 55% by comparing the absorption intensity at 549 nm with that of **5b**, which was isolated from the photoirradiated sample by HPLC.

The absorption maximum of **1b** was observed at 512 nm,[1] while that of **2b** was 575 nm.[5] The absorption maximum of **5b** was in between those of **1b** and **2b**.[7] This indicates that donor-acceptor conjugation over two heterocyclic rings does not play an important role in this compound.

By replacing the thiophene ring of **5b** with a benzo[*b*]thiophene or a pyrrole ring, the absorption maximum of the closed-ring forms of the dicyano derivatives shifted to longer wavelengths, 558 and 575 nm, respectively. The absorption maxima and the conversions of the cis forms to the closed-ring forms at the photostationary state are summarized in Table 1. The conversions were determind by comparing the absorption maximum intensities at the photostationary state with those of the isolated closed-ring forms. The closed-ring forms were easily isolated from the photoirradiated samples by HPLC equipped with a visible absorption monitor. Conversions over 50% are observed for the non-symmetric dicyano derivatives. In order to shift the absorption band further to longer wavelengths and to prevent the cis to trans isomerization completely, the dicyano group was converted to an oxydicarbonyl group.

Table 1. Absorption Maxima of the Closed-Ring Forms and Photochromic Property of Non-Symmetric Diarylethenes in Benzene Solution

Compd	λ_{max}	Conversion[b]	Exciting wavelength
	nm	%	nm
5b	547	55	436
6b	558	50	440
7b	575	59	440
8b	595	58	491
8b[a]	578	70	450
9b	597	26	480
9b[a]	583	66	470

a) In hexane solution. b) At photostationary state.

Maleic Anhydride Derivatives. The dicyano derivatives were converted to maleic anhydride derivatives by hydrolysis with KOH in ethylene glycol monoethyl ether–water mixture. The 2,3-diarylmaleic anhydrides were purified by column chromatography using benzene as an eluent, and were recrystallized from a hexane–chloroform mixture.

Their structures were fully characterized by spectroscopic methods. The non-symmetric 2,3-diarylmaleic anhydride underwent cyclization reactions to produce the cyclohexadiene-type derivatives. Figure 2 shows the spectra of **8a** and **8b**, and the spectrum at the photostationary state under irradiation with 491 nm light in benzene. Upon irradiation with 491 nm light in the presence of air, the solution turned green and a new peak appeared at 595 nm (ε=5.5$\times$10^3 l mol^{-1} cm^{-1}). Isosbestic points are observed at 437 and

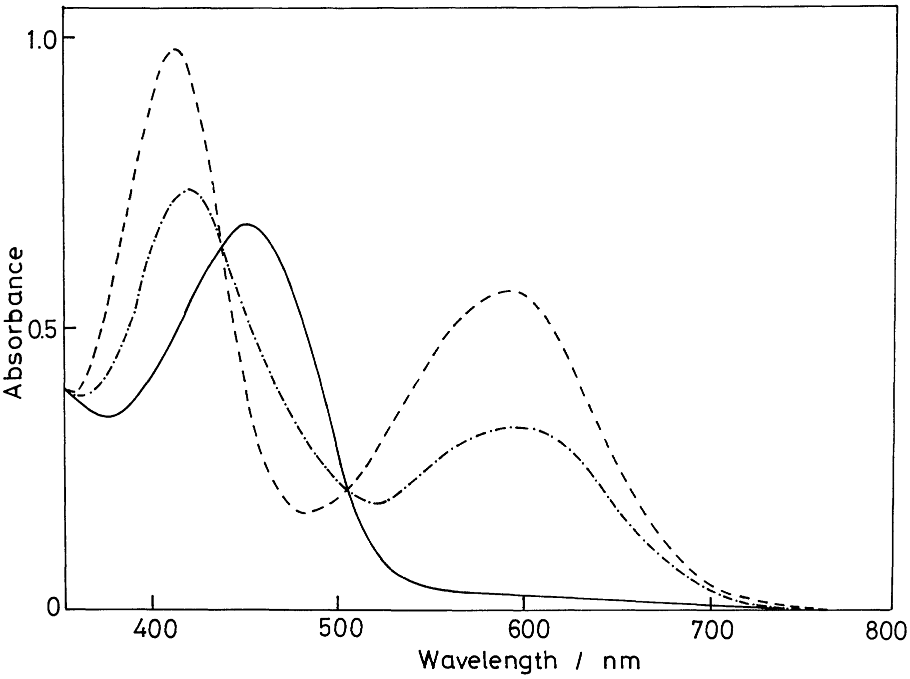
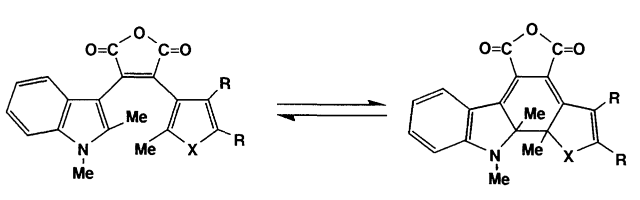


Fig. 2. Absorption spectra of benzene solution of **8a** (1.0$\times$10^{-4} mol dm^{-3}) (——) and **8b** (1.0$\times$10^{-4} mol dm^{-3}) (---) and a mixture of **8a** and **8b** at the photostationary stae (—-—) under irradiation with 491 nm light.



8a, X=S; R=CH$_3$
9a, X=S;
R⌒R=CH=CH-CH=CH

8b, X=S; R=CH$_3$
9b, X=S;
R⌒R=CH=CH-CH=CH

504 nm. The absorption maximum shifts to longer wavelengths by 56 nm in comparison with the dicyano derivative **5b**. On exposure to visible light ($\lambda>560$ nm), the solution again became yellow, and the initial absorption of **8a** was restored. The absorption maxima of **3b** and **4b** were observed at 560 nm and 620 nm, respectively.[4,5] The absorption maximum of **8b**, 595 nm, was in between those of **3b** and **4b**.

The cyclization reaction was also induced by irradiation with 488 nm light of Ar ion laser. The photogenerated green color disappeared on exposure to 633 nm He-Ne laser. Compound **9a** underwent similar cyclization/ring-opening reactions upon irradiation with 488 and 633 nm lights.

The absorption maxima of the closed forms of symmetric diarylethenes showed red shifts with increasing electron-donating ability of the heterocyclic groups and with increasing electron-accepting ability of 1,2-substituents by replacing the dicyano group with oxydicarbonyl group.[4,5,8] The absorption maxima of the closed-ring forms of dicyano derivatives increased in the following order; dithienylethene≈bis(benzo[*b*]thienyl)ethene<diselenenylethene<diindolylethene.[4,5,8] The maleic anhydride derivatives showed a bathochromic shift in comparison with the dicyano derivatives as much as 50 nm.

For the non-symmetric diarylethenes with an indole ring on one end of the double bond, the absorption maximum was also controlled by the electron-donating ability of the other heterocyclic rings. The absorption maximum showed red shift in the order of **5b**<**6b**<**7b**. The result suggests that donor–acceptor type interaction between heterocyclic groups and the dicyano or the oxydicarbonyl group plays an important role in determining the position of the absorption band.

The absorption spectra of the closed-ring forms are dependent on the polarity of the medium. Figure 3 shows the absorption spectra of **7a**+**7b** at the photostationary state in several solvents. The absorption maximum of **7b** in hexane at 554 nm shifts to 574 nm in benzene. In hexamethylphosphoric triamide (HMPA), the closed-ring form has a deep blue color, and the absorption maximum is observed at 603 nm. The dramatic red-shift of the absorption band indicates that $S_0 \rightarrow S_1$ band of **7b** has charge-transfer character and the S_1 is polar state. The invariance of the second band of **7b** with solvent polarity suggests that the band is due to the transition to a less polar

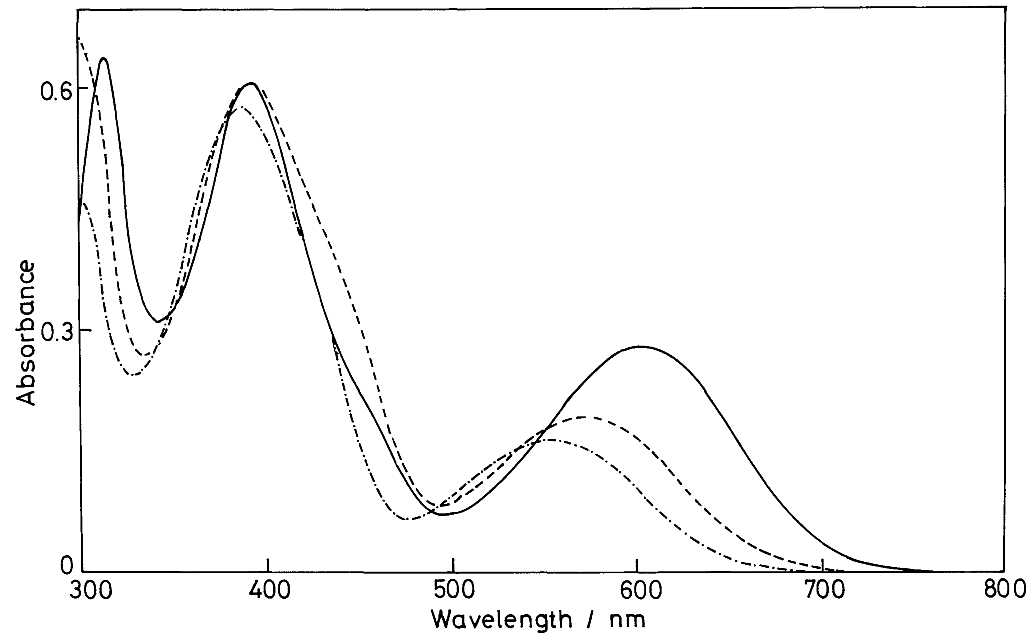


Fig. 3. Absorption spectra of **7a**+**7b** (total concentration, 1.0×10^{-4} mol dm^{-3}) at the photostationary state in hexane (—·—), in benzene (----), and in HMPA (——). Conversion from the open-ring to the closed-ring form was 39% in hexane, 44% in benzene, and 75% in HMPA. The absorption bands longer than 500 nm and at around 400 nm are ascribable to **7b**, and shoulders at around 450 nm to **7a**.

excited state.

Thermal Stability of Closed-Ring Forms. Figure 4 illustrates the thermal stability of the closed-ring forms **5b**, **6b**, **7b**, **8b**, and **9b** at 80 °C in the dark. The value of A/A_0 was plotted against storage time, where A_0 is the initial absorbance at the absorption maximum of the closed-ring form, and A the absorbance after t hours at 80 °C. As seen in Fig. 4, the photogenerated closed-ring forms, **5b**, **6b**, **8b**, and **9b** are stable, and maintain a constant absorption intensity for more than 12 h at 80 °C, whereas **7b** is thermally unstable. The absorption intensity of **7b** decreases to 75% of the initial intensity in 12 h at 80 °C.

In a previous paper,[6] we showed that the thermal stability of the closed-ring forms of symmetric diarylethene derivatives is dependent on the aromatic stabilization energy of the aryl groups. When the aryl groups of the compounds have low aromatic stabilization energy, the closed-ring forms are thermally stable, while they become thermally unstable when they contain benzene or pyrrole rings with high aromatic stabilization energy. The experimental results presented in this paper indicate that the closed-ring forms of non-symmetric diarylethenes are thermally stable when at least one of the heterocyclic rings has low aromatic stabilization energy. Note that the non-symmetric compound having aryl groups with high aromatic stabilization energy for both substituents, e.g. **7b**, is thermally unstable.

Quantum Yield. The quantum yields of cyclization and ring-opening reactions were measured in benzene and hexane solutions. A xenon lamp equipped with a monochromater (Jovin Yvon H10-UV) was used as the light source. The light intensity was determined with a photometer (International Light, IL-700). Table 2 summarizes the result. The cyclization quantum yields of **5a** and **8a** in benzene are below 0.1. The values are similar to those observed for **2a** and **3a**.

The cyclization quantum yield was strongly dependent on the polarity of solvents. The quantum yield in hexane is 3 times larger than the value observed in benzene. Similar solvent dependence of the quantum yield was observed for the thiophene derivatives.[4] The cyclization quantum yield of **3a** decreases from 0.13 to 0.003 by increasing the solvent polarity from hexane to acetonitrile.[9] These solvent dependences suggest that there exist two kinds of excited states with different polarity, and the less polar

Table 2. Quantum Yields for Cyclization and Ring-Opening Reactions of Non-Symmetric Diarylethenes

	Excitation wavelength	Solvent	
	nm	Benzene	Hexane
5a→**5b**	405	0.08	a)
8a→**8b**	405	0.06	0.15
	450	a)	0.14
	490	0.05	a)
5b→**5a**	546	0.56	a)
8b→**8a**	546	0.40	a)

a) Not measured.

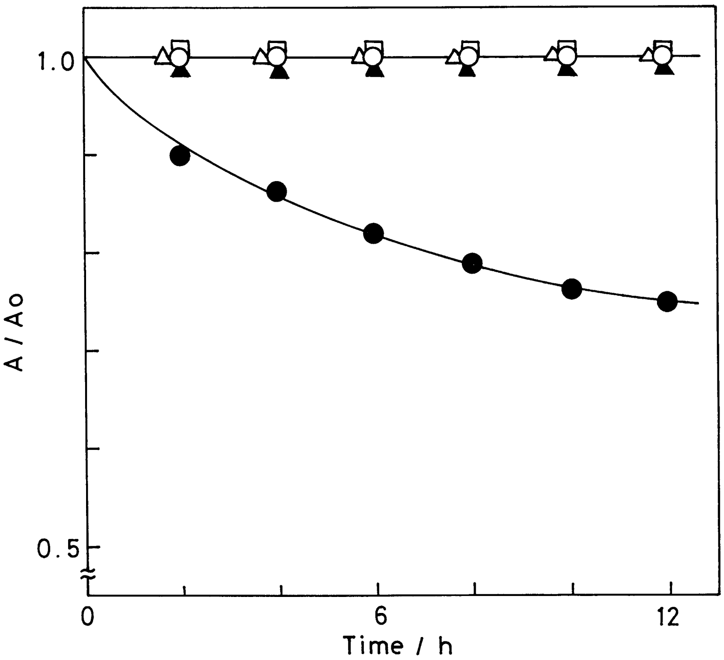


Fig. 4. Thermal stability of the closed ring forms in toluene at 80 °C in deaerated conditions. Compounds **5b** (□), **6b** (○), **7b** (●), **8b** (△), and **9b** (▲).

state is responsible to the photocyclization.

The ring-opening quantum yields of **5b** and **8b** in benzene are quite high. The value of **8b** is 3 times larger than the value observed for the ring-opening reaction of **3b**. Replacement of one of the thiophene rings with an indole ring increased the ring-opening quantum yield. Similar increase of the ring-opening quantum yield was observed for bis(benzo[*b*]thienyl)-ethene.[8] The introduction of a rigid indole (or benzo[*b*]thiophene) ring possibly destabilizes the closed-ring forms, and increases the ring-opening quantum yield.

Summary

Non-symmetric diarylethenes with an indolyl group on one end and a thienyl, a benzo[*b*]thienyl or a pyrrolyl group on the other end were synthesized. The diaryldicyano- and diaryl(oxydicarbonyl)ethenes **5a**, **6a**, **8a**, and **9a** underwent thermally irreversible photochromic reactions. Although these compounds still are not sensitive to wavelengths of diode lasers, both the open-ring and closed-ring forms have absorption bands in the visible region, and the cyclization/ring-opening reactions of **8a** and **9a** were induced by Ar ion (488 nm) and He–Ne (633 nm) lasers.

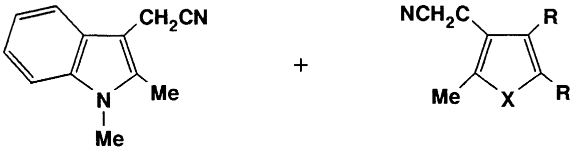
Experimental

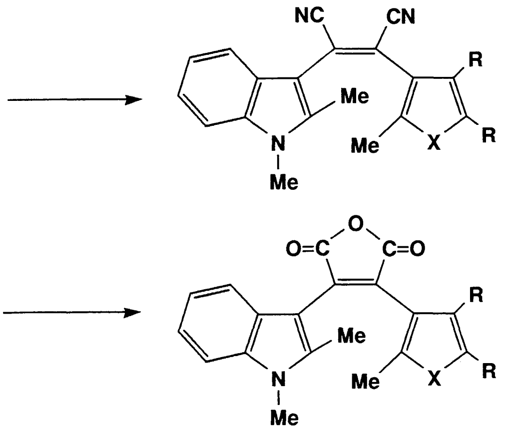
^{1}H NMR spectra (360 MHz) were recorded in $CDCl_3$ with a Brucker WN-360 instrument. All chemical shifts were expressed in parts per million (ppm) downfield from internal tetramethylsilane. Mass spectra and elemental analysis were performed in the Material Analysis Center of Osaka University. High-performance liquid chromatography (HPLC) was carried out on a JASCO 800 instrument. For isolation and purification of samples, a column (10×250 mm) packed with silica gel (JASCO, Fine SIL-5) was used.

Absorption spectra were measured with a spectrophotometer (Shimadzu MPS-200). Photoisomerization was carried out in solution in the presence of air. A Ushio mercury lamp (1 kW) or a EWIG XC-500 xenon lamp equipped with a monochromater (Jovin Yvon 10H-UV) were used as the light sources. Quantum yields were determined by measuring the rate of isomerization in the initial stage of the reaction at low concentration (absorbance at the irradiation wavelength<0.2). The light intensity was measured with a photometer (International Light IL700).

Materials. 3-(Cyanomethyl)-1,2-dimethylindole,[5] 3-(cyanomethyl)-2,4,5-trimethylthiophene,[4] 3-(cyanomethyl)-2-methylbenzo[*b*]thiophene,[8] and 3-(cyanomethyl)-1,2,4,5-tetramethylpyrrole[10,11] were prepared by the reported procedures.

A general procedure for the preparation of 1,2-diaryl-1,2-dicyanoethenes and 2,3-diarylmaleic anhydrides is illustrated by the following scheme.





1,2-Dicyano-1-(1,2-dimethyl-3-indolyl)-2-(2,4,5-trimethyl-3-thienyl)ethene(5a). To a mixed solution of CCl_4 (1.58 ml) and benzene (1.58 ml) containing 0.07 g (0.22 mmol) of tetrabutylammonium bromide, 0.5 g (2.7 mmol) of 3-(cyanomethyl)-1,2-dimethylindole and 0.45 g (2.7 mmol) of 3-(cyanomethyl)-2,4,5,-trimethylthiophene was added at 40 °C 1.09 ml of 50% NaOH aqueous solution. The reaction mixture was heated to 45 °C for 3 h, and then cooled to room temperature. The solution was poured into water, and the aqueous layer was extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and filtered. After the solvent was removed, the mixtures of **5a** and its trans form, **1a** and its trans form, and **3a** and its trans form were separated by column chromatography on silica gel (30 μm) using benzene as an eluent. The trans and cis mixture of the indolylthienylethene derivative was dissolved into acetonitrile and exposed to ultraviolet-visible light (λ>350 nm). The irradiation converts a large part of the trans form to the cis form. After evaporation of the solvent, the trans and the cis forms were isolated by column chromatography (HPLC, 5 μm silica gel/benzene). The closed-ring form **5b** was also isolated by HPLC (5 μm silica gel/benzene). HPLC retention times (flow rate 1 ml min^{-1}): **5a** 14.9 min, the trans form 7.9 min, **5b** 20.0 min. The cis form was further purified by recrystallization from a hexane–ether mixture yielding 0.1 g (10%) of **5a**.

5a: IR(KBr, cm^{-1}) 2240; ^{1}H NMR δ=1.92 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 3.63 (s, 3H, CH_3), 7.10 (dd, J=8.1, 6.8 Hz, 1H), 7.21 (dd, J=8.1, 6.8 Hz, 1H), 7.25 (d, J=8.1 Hz, 1H), 7.39 (d, J=8.1 Hz, 1H); MS m/z (rel intensity) 345 (M^+, 100), 330 (45), 315 (17); HRMS Found: m/z 345.1320. Calcd for $C_{21}H_{19}N_3S$: M, 345.1299. Anal. Calcd for $C_{21}H_{19}N_3S$: C, 73.01; H, 5.54; N, 12.16; S, 9.28%. Found: C, 73.06; H, 5.40; N, 12.15%.

1,2-Dicyano-1-(1,2-dimethyl-3-indolyl)-2-(2-methyl-3-benzo[*b*]thienyl)ethene (6a). This was prepared by a coupling reaction of 3-(cyanomethyl)-1,2-dimethylindole and 3-(cyanomethyl)-2-methylbenzo[*b*]thiophene, and isolated in 19% yield. HPLC retention times (silica gel/benzene, flow rate 1 ml min^{-1}): **6a** 13.0 min, the trans form 7.2 min, **6b** 9.3 min.

6a: IR(KBr, cm^{-1}) 2240; ^{1}H NMR δ=2.00 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 3.55 (s, 3H, CH_3), 6.99—7.70 (m, 8H); HRMS Found: m/z 367.1116. Calcd for $C_{23}H_{17}N_3S$: M, 367.1142. Anal. Calcd for $C_{23}H_{17}N_3S$: C, 75.18; H, 4.66; N, 11.43; S, 8.72%. Found: C, 75.23; H, 4.52; N, 11.37%.

1,2-Dicyano-1-(1,2-dimethyl-3-indolyl)-2-(1,2,4,5-tetramethyl-3-pyrrolyl)ethene (7a). This was prepared by a coupling reaction of 3-(cyanomethyl)-1,2-dimethylindole and 3-(cyanomethyl)-1,2,4,5-trimethylpyrrole, and isolated in 5% yield. HPLC retention times (silica gel/benzene, flow rate 1 ml min^{-1}): **7a** 19.8 min, the trans form 10.0 min. Isolation of **7b** by the silica-gel column was failed. The conversion from **7a** to **7b** at the photostationary state was estimated by measuring the HPLC intensity change of **7a** by photoirradiation.

7a: IR(KBr, cm^{-1}) 2240; ^{1}H NMR δ=1.72 (s, 3H, CH_3), 1.77 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 3.19 (s, 3H, CH_3), 3.63 (s, 3H, CH_3), 7.03 (dd, *J*=9.0, 6.8 Hz, 1H), 7.16 (dd, *J*=8.2, 6.8 Hz, 1H), 7.22 (d, *J*=8.2 Hz, 1H), 7.27 (d, *J*=9.0 Hz, 1H); MS *m/z* (rel intensity) 342 (M$^+$, 100), 327 (57), 312 (12); HRMS Found: *m/z* 342.1875. Calcd for $C_{22}H_{22}N_4$: M, 342.1843. Anal. Calcd for $C_{22}H_{22}N_4$: C, 77.16; H, 6.48; N, 16.36%. Found: C, 77.42; H, 6.68; N, 16.26%.

2-(1,2-Dimethyl-3-indolyl)-3-(2,4,5-trimethyl-3-thienyl)maleic Anhydride (8a).[12] Compound **5a** (630 mg, 1.8 mmol) and ethylene glycol monoethyl ether (1.53 ml) were added to a solution of 0.73 g of potassium hydroxide in 1.53 ml of water. The solution was refluxed for 24 h. The reaction mixture was poured into water and 20% hydrochloric acid was added until the mixture became acidic. The red precipitate was extracted with $CHCl_3$. The organic phase was dried over $MgSO_4$ and filtered. After the solvent was removed **8a** was isolated by HPLC (5 µm silica gel/benzene) and purified by recrystallization from a ether–hexane mixture, yielding 110 mg (16%) of **8a**. HPLC retention times (flow rate 1 ml min^{-1}): **8a** 8.8 min, **8b** 13.4 min.

8a: IR(KBr, cm^{-1}) 1760, 1820; ^{1}H NMR δ=1.87 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 7.03 (dd, *J*=8.1, 7.2 Hz, 1H), 7.13 (d, *J*=8.1 Hz, 1H), 7.19 (dd, *J*=8.1, 7.2 Hz, 1H), 7.26(d, *J*=8.1 Hz, 1H); MS *m/z* (rel intensity) 365 (M$^+$, 100), 650 (8); HRMS Found: *m/z* 365.1103. Calcd for $C_{21}H_{19}NO_3S$: M, 365.1085. Anal. Calcd for $C_{21}H_{19}NO_3S$: C, 69.02; H, 5.24; N, 3.83; O, 13.13; S, 8.77%. Found: C, 68.89; H, 5.01, N, 3.57%.

2-(1,2-Dimethyl-3-indolyl)-3-(2-methyl-3-benzo[*b*]thienyl)maleic Anhydride (9a). This was prepared by the hydrolysis of **6a**. HPLC retention times (flow rate 1 ml min^{-1}): **9a** 7.8 min, **9b** 5.6 min.

9a: IR(KBr, cm^{-1}) 1760; ^{1}H NMR δ=2.09 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 3.62 (s, 3H, CH_3), 6.97—7.72 (m, 8H); MS *m/z* 387 (M$^+$); HRMS Found: *m/z* 387.0954. Calcd for $C_{23}H_{17}NO_3S$: M, 387.0928. Anal. Calcd for $C_{23}H_{17}NO_3S$: C, 71.30; H, 4.42; N, 3.62; O, 12.39; S, 8.27%. Found: C, 71.26; H, 4.33; N, 3.33%.

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