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STUDIES ON SYNTHESIS AND CHARACTERIZATION OF PHOTOCHROMIC DIARYLETHENE DERIVATIVES

(フォトクロミック ジアリールエテン誘導体の
合成と評価に関する研究)

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OSAKA UNIVERSITY

1991

PREFACE

This work presented in this thesis has been carried out under the guidance of Professor Koichiro Hayashi at the Institute of Scientific and Industrial Research, Osaka University and Professor Masahiro Irie at Institute of Advanced Material Study, Kyushu University.

The thesis is concerned with the syntheses and the characterizations of new photochromic diarylethene derivatives for rewritable optical data storage media.

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January, 1991

LIST OF PUBLICATIONS

The contents of this thesis are composed of the following papers.

(1) Thermally Irreversible Photochromic Systems.
Reversible Photocyclization of 1,2-Diselenenylethene and 1,2-Diindolylethene Derivatives.
Y. Nakayama, K. Hayashi, M. Irie
The Journal of Organic Chemistry, **55**, 2592-2596 (1990).

(2) Thermally Irreversible Photochromic Systems.
Reversible Photocyclization of Non-symmetrical Diarylethene Derivatives.
Y. Nakayama, K. Hayashi, M. Irie
Bulletin of the Chemical Society of Japan, **64**, (1991) in press.

(3) Thermally Irreversible Photochromic Systems.
Photoreaction of Diarylethene Derivatives with Imidazo[1,2-*a*]pyridine rings.
Y. Nakayama, K. Hayashi, M. Irie
Bulletin of the Chemical Society of Japan, **64**, (1991) in press.

(4) Thermally Irreversible Photochromic Systems.
Reversible Photocyclization of 1,2-Bis(benzo[*b*]thiophen-3-yl)ethene Derivatives.
K. Uchida, Y. Nakayama, M. Irie
Bulletin of the Chemical Society of Japan, **63**,1311-1315 (1990).

(5) Thermally Irreversible Photochromic Systems.
Effect of the Electron-donors on Diarylethene Derivatives in Photoreaction.
Y. Nakayama, K. Hayashi, M. Irie
in preparation.

(6) Color Change of 2,3-Di(2,3,4,5,6-pentafluorophenyl)-3-[2,3,5,6-tetrafluoro-4-(cyanomethyl)-phenyl]acrylronitrile by the Addition of Amines.
Y. Nakayama, K. Inukai, K. Hayashi, M. Irie
Bulletin of the Chemical Society of Japan, submitted for publication.

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GENERAL INTRODUCTION

Recently the magneto-optical recording media which have rewritable recording capability are beginning to become available. Organic rewritable media, such as pitt-forming media[1] and bump-forming media,[2,3] have been studied extensively. All media as for reported are based on a heat-mode optical recording principle. In order to utilize the versatile function of light fully, photon-mode recording method and media should be more extensively explored. Photon-mode recording will be advantageous in the sense of resolution, speed of writing, and multiplex recording capability. One of the candidates for the photon-mode and organic erasable recording media is a photochromic material.[4,5]

Photochromism is defined as a light induced transformation in a chemical species between two forms having different absorption spectra, and the compounds capable of this reaction are called photochromic molecules. Besides the absorption spectral change, the isomerization are always accompanied by certain physical property change, such as dipole moment and/or geometrical structural changes.

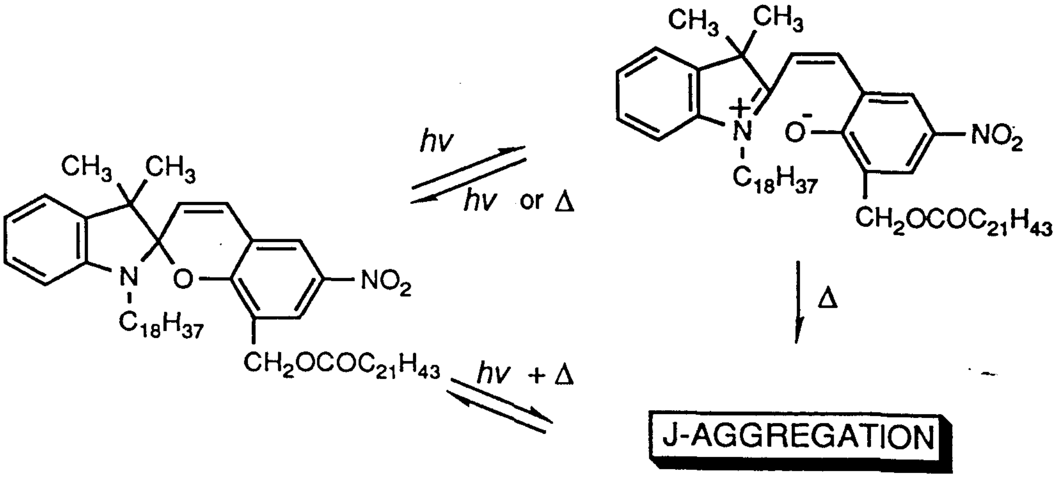
$$\mathrm{A} \underset{h\nu'}{\overset{h\nu}{\rightleftarrows}} \mathrm{B}$$

The instant image forming property without proceeding has led to the consideration of their use in rewritable direct read after write systems.[6] Despite favorable situations property by recent progress of optical memory technology, organic photochromic compounds have found little applications as optical information storage media. The limitation of the applications is due to the lack of suitable compounds which fulfill the requirements for the reversible recording medium[7,8] as following.

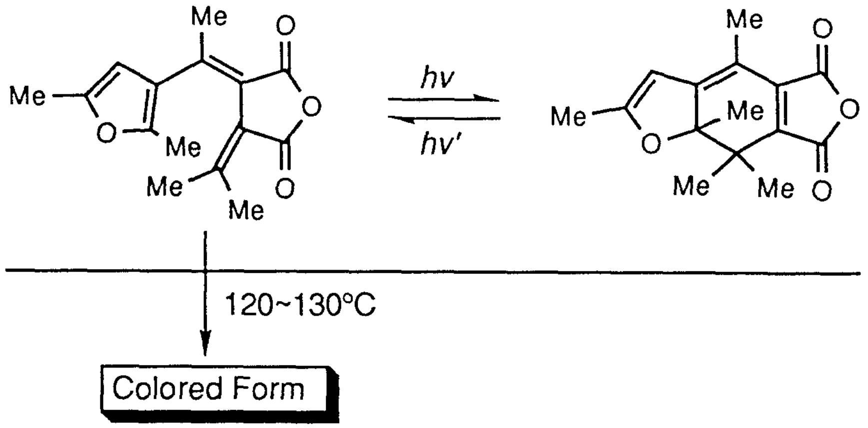
1) Archival storage capability (thermal stability).
2) Low fatigue (can be cycle many times without significant loss of performance.
3) Non-destructive read out capability.
4) Sensitivity at diode laser wavelength.
5) High sensitivity and rapid response.

Among the requirements, the more important ones are the thermal stability of both chemical forms, and the fatigue resistant property. Photochromic compounds so far reported have a drawback that one of the chemical forms is thermally unstable, and returns to the more stable form in the dark. In attempt to obtain the thermal stability of colored form, extensive work has been carried out.

For example, it has been reported that the monomeric photomerocyanin formed J-aggregate at temperature above 35°C under UV light, and the half decay period of the J-aggregate was 10^4 times longer than that of photomerocyanin form of conventional spiropyrans.[9]



Furthermore, although the closed-ring form of 3-furyl-fulgide has been reported to be thermally stable, the open ring form is rather unstable and shows irreversible thermochromism above 120°C.[10]



This thesis deals with the results obtained from the research on photochromic materials for rewritable optical data storage media.

Chapter 1 is concerned with symmetrical diarylethene derivatives, such as diselenenyl or diindolyl derivatives. The syntheses and the characterizations of diarylethene derivatives with selenophene or indole are mentioned. Effect of the electron-donors on diindolylethene derivatives also are mentioned.

In chapter 2 is dealt new non-symmetrical diarylethene derivatives. The syntheses and the characterizations of non-symmetrical diarylethene derivatives with indole ring on one end and thiophene, benzothiophene, or pyrrole ring on the other end are mentioned.

Chapter 3 deals with diarylethene derivatives with imidazo[1,2-*a*]pyridine rings. The syntheses and the characterizations of the symmetrical and non-symmetrical diarylethene derivatives with imidazo[1,2-*a*]pyridine rings are mentioned.

Chapter 4 refers to the new fluorine compound, 2,3-bis-(2,3,4,5,6-pentafluorophenyl)-3-[2,3,5,6-tetrafluoro-4-(cyano-methyl)phenyl]-acrylonitrile which was synthesized by applying the synthetic method of diarylethene derivatives. The coloration mechanism is studied by optical absorption, conductivity and product analyses. Structural requirements of the amines for the ion-pair formation are discussed.

References

(1) A. Kuroiwa, K. Namba, S. Asami, T. Aoi, and K. Takahashi, *Jpn. J. Appl. Phys.*, **22**, 340 (1983).
(2) M. C. Gupta and F. Strome, *J. Appl. Phys.*, **60**, 2932 (1986).
(3) N. E. Iwamoto, J. M. Halter, *Polym. preprint*, **29**, 47 (1988).
(4) S. Arakawa, H. Kaneko, and J. Seto, *Chem. Lett* , (1985) 1805.
(5) A. Morinaka, T. Yoshida, and N. Funakoshi, *Jpn. J. Appl. Phys. Suppl.*, **26**, 26 (1987).
(6) Y. Hirshberg, *J. Am. Chem. Soc.*, **78**, 2304 (1956).
(7) W. J. Tomlinson, *Appl. Optics.*, **24**,4609 (1984).
(8) H. G. Heller, *IEEE Proc.*, **1**, 209 (1983).
(8) E. Ando, J. Miyazaki, K. Morimoto, *Thin. Solid. Films.*, **133**, 21 (1985).
(9) H. G. Heller, *Chem. Ind.*, **18**, 193 (1978).

CHAPTER 1

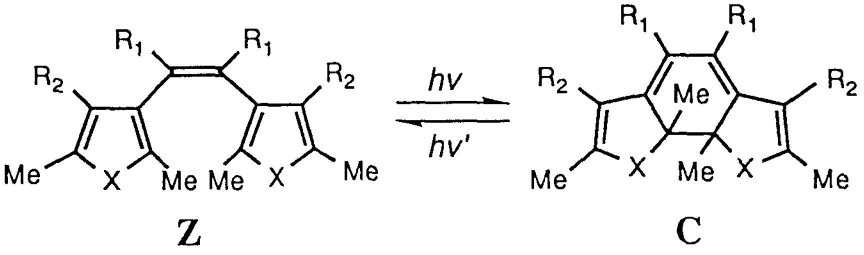
Reversible Photocyclization of Diselenenylrthene and Diindolylethene Derivatives

1.1 Introduction

Photochromic organic compounds have attracted a significant amount of attention because of their potential for use in optical memory media.[1,2] Although extensive work has been carried out,[3-12] the compounds still await practical application. Among the various requirements for optical memory media, the more important ones are the thermal stability of both isomers and the fatigue resistant property of the compounds. The coloration and decoloration cycles should be repeated many times without any loss of performance. Another important property is the sensitivity at diode laser wavelength ($780 < \lambda < 840$ nm).

Recently, Irie et al.,[13,14] have reported a new type of thermally stable photochromic system, diarylethene derivatives having heterocyclic rings, such as 1,2-dimethyl-1,2-bis(2,5-dimethyl-3-furyl)ethene (**1Z**), 1,2-dimethyl-1,2-bis(2,5-dimethyl-3-thienyl)-ethene (**2Z**), 1,2-dicyano-1,2-bis(2,3,5-trimethyl-3-thienyl)ethene (**3Z**), or 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (**4Z**).

The compounds have no thermochromic property even at 300°C and the colored closed-ring form is stable for more than 12 hours at 80°C. In addition, no detectable fatigue was observed for **4Z** even after 100 coloration and decoloration cycles in the absence of air. The absorption tail of the ring-closed form is, however, less than 700 nm.



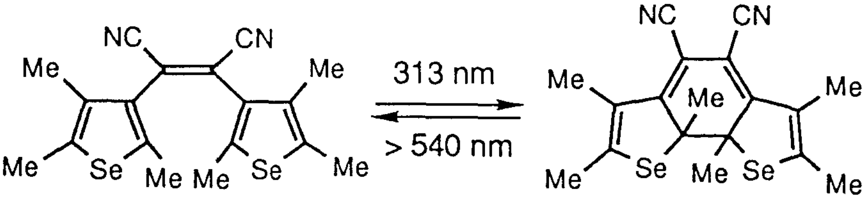
compound	X	R1	R2	λ_{max} / nm
1 C	O	Me	H	391
2 C	S	Me	H	431
3 C	S	CN	Me	512
4 C	S	COOCO	Me	560

This chapter describes that symmetrical diarylethene derivatives having selenophene or indole rings were synthesized in attempting to obtain photochromic compounds having the absorption bands at longer wavelengths.

1.2 Diselenenylethene Derivatives

1.2.1 Dicyano Derivative

A cyano derivative having selenophene rings **5Z** was prepared by a self-coupling reaction of two 2,3,5-trimethyl-4-(cyanomethyl)-selenophene. The mixture of *Z* and *E* form was dissolved in benzene and exposed to 313 nm and then > 520 nm light to convert the *E*



5Z **5C**

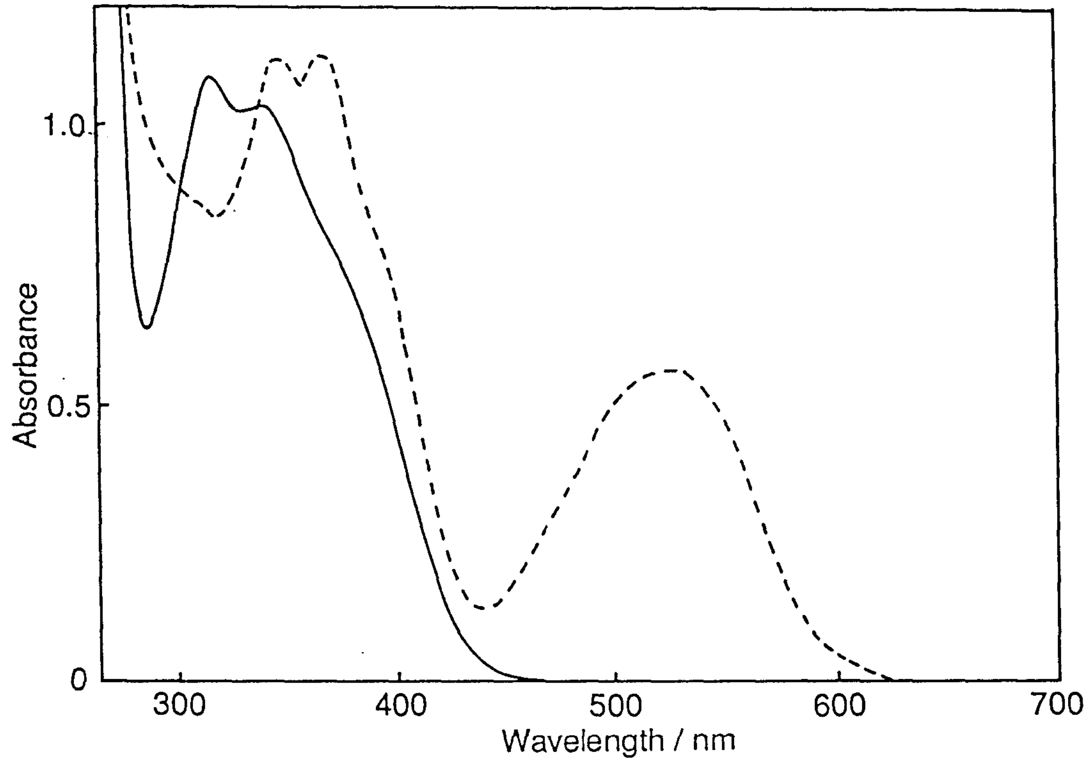


Figure 1-1. Absorption spectra of **5Z** ($1.6X10^{-4}$ mol dm^{-3}) (—) and in the photostationary state under irradiation with 313 nm light (- - -).

form to the *Z* form. The *Z* form was separated from the mixture of *Z* and *E* form by HPLC and purified by crystallization from a hexane-ether mixture. This material was used for further experiments.

Figure 1-1 shows the spectra of **5Z** before and after photoirradiation of 313 nm light in dilute benzene solution. Irradiation of the colorless benzene solution with 313 nm light led to the formation of a red solution, in which a visible absorption at 525 nm (ε: 5,000 dm^{3}mol^{-1}cm^{-1}) was observed. The replacement of thiophene rings[13] with selenophene ones shifted the absorption maximum to a longer wavelength by 13 nm. Upon visible irradiation ($\lambda > 520$ nm) the red color disappeared along with the

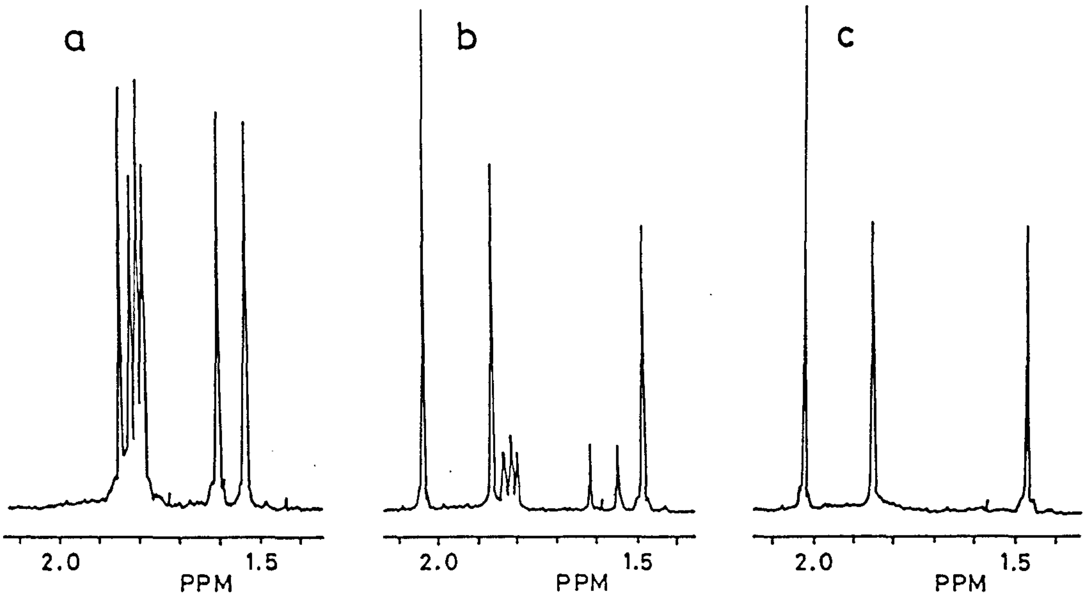
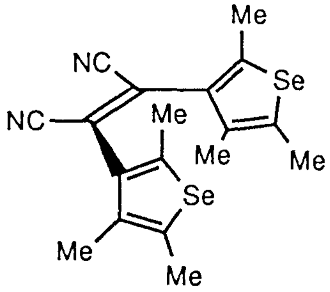


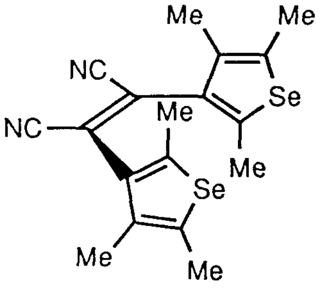
Figure 1-2. ^{1}H NMR spectra (360 MHz) of **5Z** in C_6D_6 ; (a) before irradiation; (b) in the photostationary state under irradiation with 313 nm light; (c) (b) - 0.87(a).

ultraviolet absorption at 348 and 368 nm, and the initial *Z* form absorption was restored.

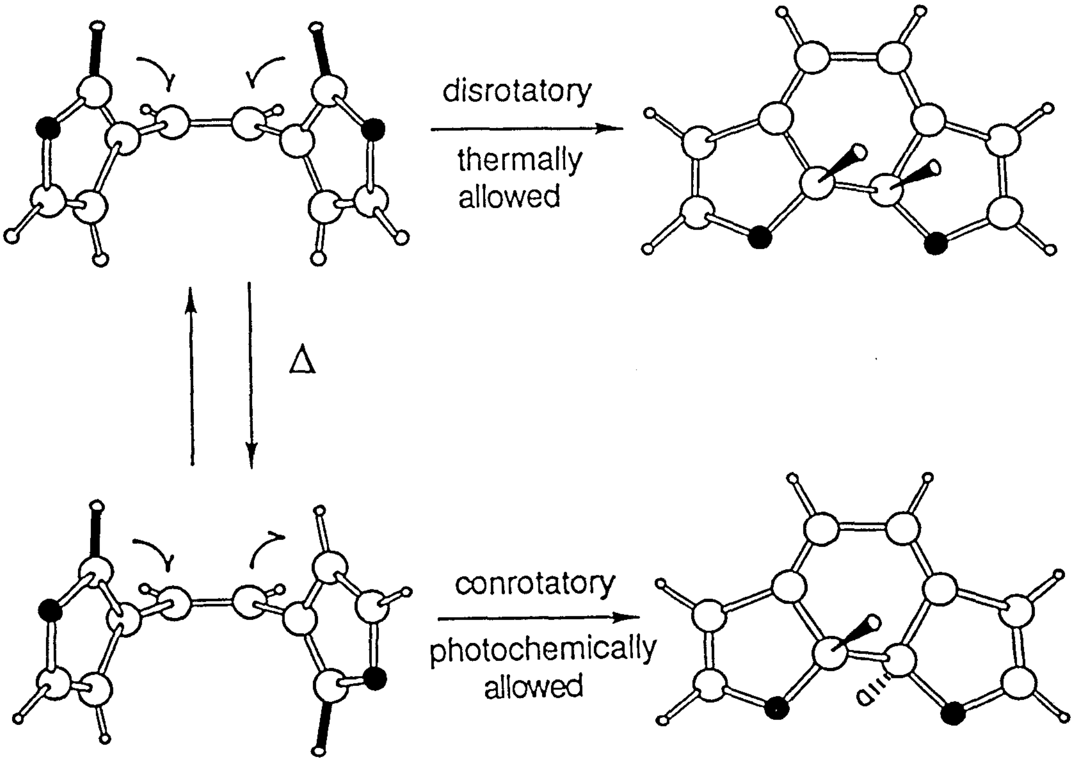
Figure 1-2, parts (a) and (b), show the 360-MHz NMR spectra of methyl protons of **5Z** in C_6D_6 before photoirradiation and in the photostationary state under irradiation with 313 nm light, respectively. Subtraction of the remaining methyl protons of the *Z* form yielded the spectrum (c). The absence of other signals except the three lines at 1.47, 1.85, and 2.03 ppm due to the closed-ring form indicates that the *Z* to *E* isomerization is negligible when the sample is irradiated with light of wavelength 313 nm.

The six lines observed before photoirradiation indicate the existence of two conformations in the compound **5Z**. One conformer has two selenophene rings in mirror symmetry (in parallel orientation) and the other C_2 symmetry (in anti-parallel orientation). The conversion of the *Z* form to the closed-ring form in the photostationary state was 87% based on the spectrum (b).


Parallel orientation


Anti-parallel orientation

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

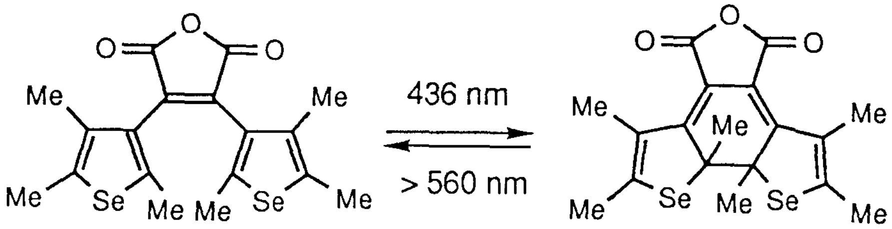


conformers. Ring closure reaction cannot proceed from parallel conformer because of the steric hindrance.

Although the introduction of selenophene rings shifted the absorption band of the closed-ring form of the dicyano derivative to a longer wavelength, the band is still shorter than 700 nm. In order to shift the absorption band further to longer wavelengths and to prevent the *Z* to *E* isomerization completely, the cyano groups were converted to an acid anhydride group.

1.2.2 Acid Anhydride Derivative

The cyano derivative was converted to the maleic anhydride derivative **6Z** by hydrolysis of **5Z** with KOH in ethylene glycol monoethylether-water mixture.



6Z

6C

Figure 1-3 shows the spectra of **6Z** before and after photoirradiation with 436 nm light in dilute benzene solution. Upon irradiation with 436 nm light, the solution turned brown and a new absorption peak appeared at 565 nm (ε: 5,600 $dm^3mol^{-1}cm^{-1}$). The absorption maximum shifts to a longer wavelength by only 5 nm in comparison with the thiophene derivative.[13] Upon exposure of the brown solution to the visible light (λ > 540 nm), the solution again became yellow and the initial absorption was restored.

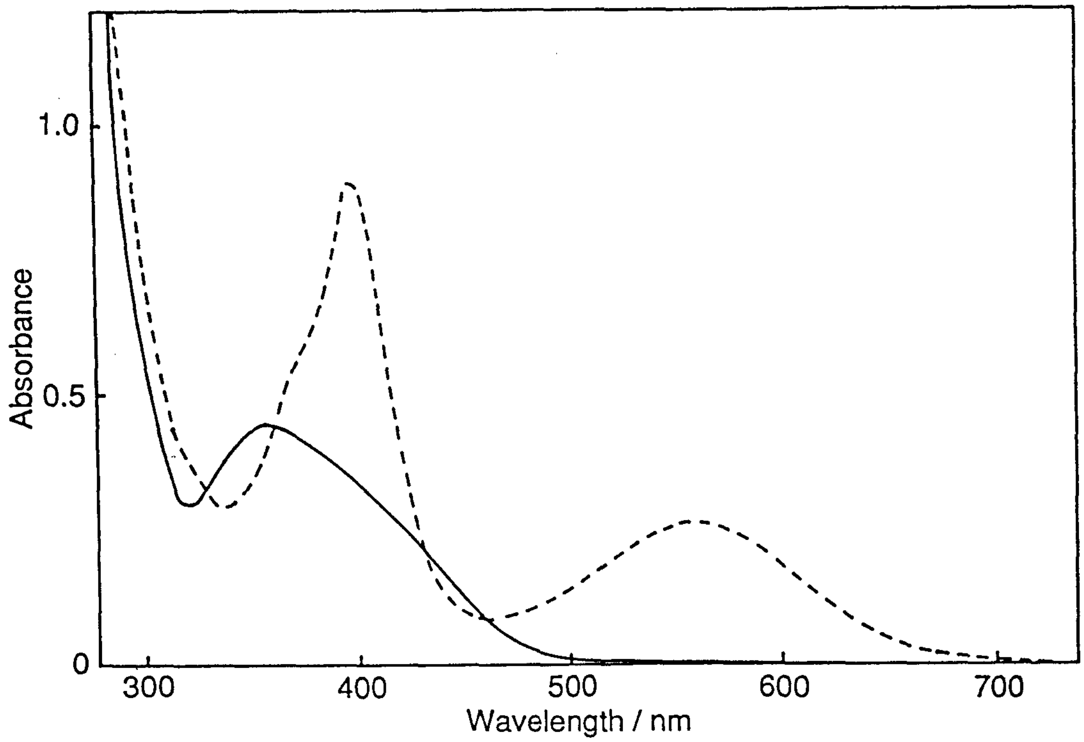


Figure 1-3. Absorption spectra of **6Z** (1.3×10^{-4} mol dm^{-3}) (—) and in the photostationary state under irradiation with 436 nm light (- - -).

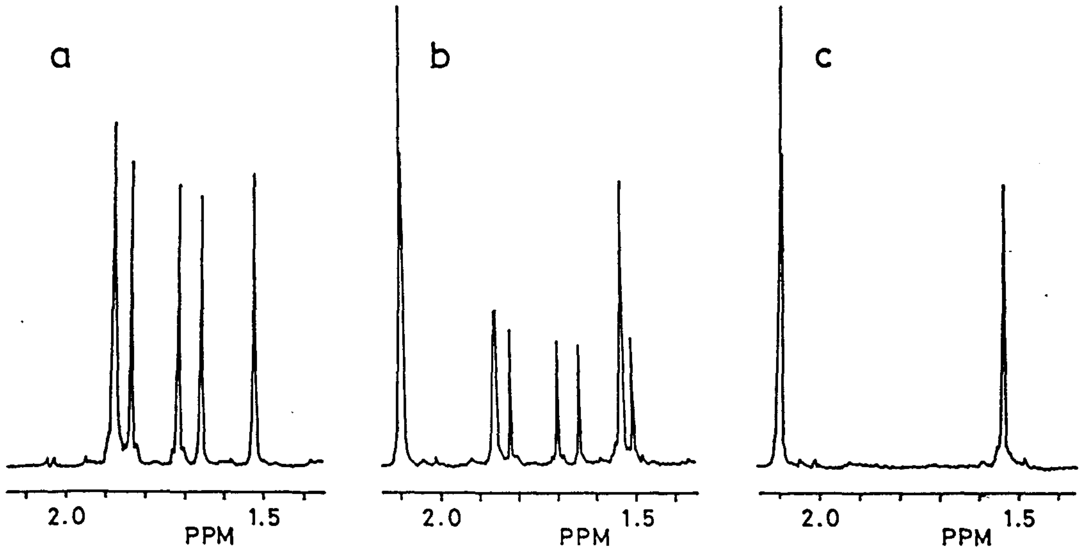


Figure 1-4. ^1H NMR spectra (360 MHz) of **6Z** in C_6D_6; (a) before irradiation; (b) in the photostationary state under irradiation with 436 nm light; (c) (b) - 0.54(a).

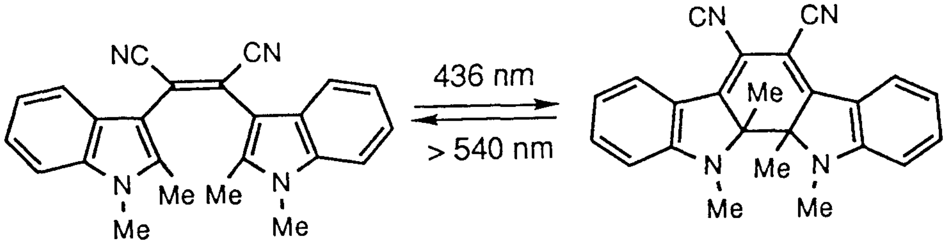
Figure 1-4 shows the NMR spectra of methyl protons of **6Z** in C_6D_6 before photoirradiation and in the photostationary state under irradiation with 436 nm light. Before photoirradiation, five lines, one of which at 1.88 ppm includes two different kinds of methyl groups, were observed. This indicates the existence of two conformers as described in the case of **5Z**. The conversion of the open-ring to closed-ring form in the photostationary state under irradiation with 436 nm light was obtained to be 54%. The conversion depended on the irradiation wavelength. When irradiated with 405 nm light, the conversion was less than 50%.

Although the introduction of selenophene groups shifted the absorption band of the closed-ring forms to longer wavelengths, the shifts was 13 nm in the case of the cyano derivative and was only 5 nm in the case of the maleic anhydride derivative in comparison with the thiophene derivatives.[13] The absorption tail of the closed-ring form of the maleic anhydride derivative is still shorter than 730 nm. The compounds have no sensitivity to the diode laser light ($780 < \lambda < 840$ nm). In order to shift the absorption band further to longer wavelengths, the selenophene groups were replaced with indole groups.

1.3 Diindolylethene Derivatives

1.3.1 Dicyano Derivative

The compound with indole groups were synthesized by a coupling reaction of two (1,2-dimethylindol-3-yl)acetonitriles, which were prepared by Mannich reaction of 1,2-dimethylindole. The mixture of the *E* and *Z* form were separated by a similar procedure as for the selenophene derivative.



7Z **7C**

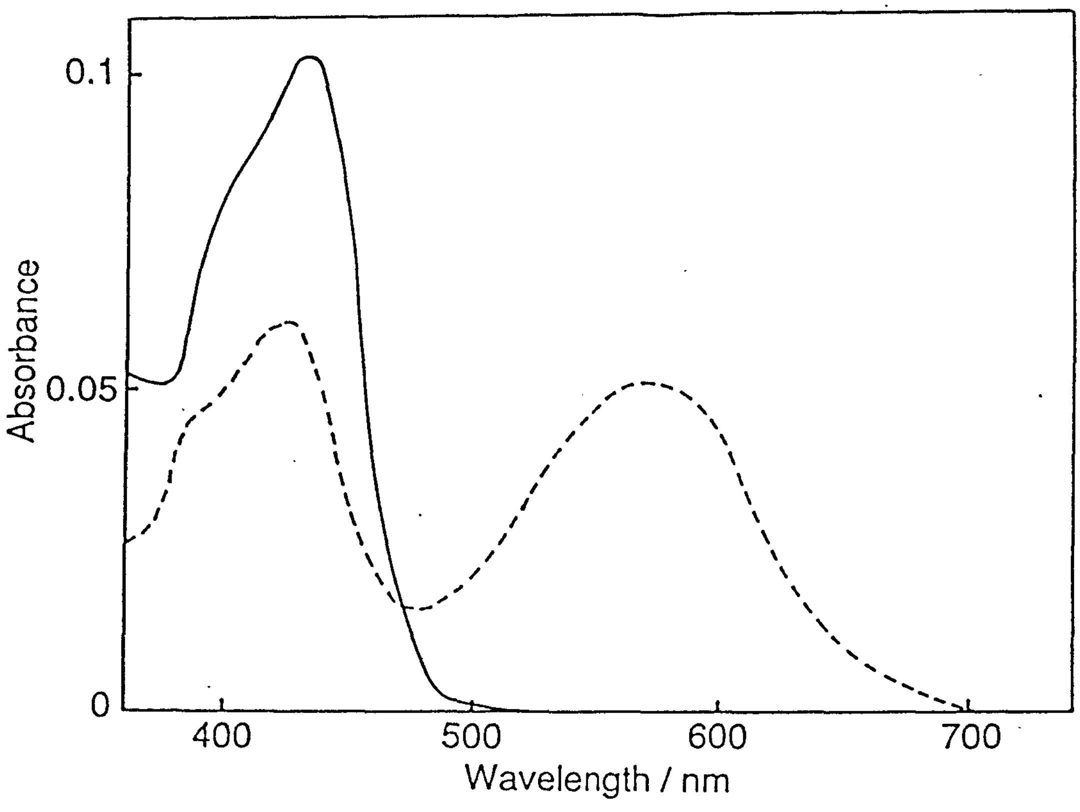
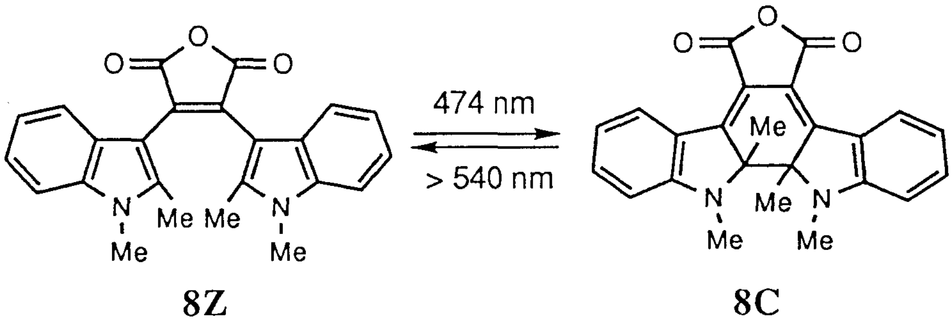


Figure 1-5. Absorption spectra of 7Z (—) and 7C (---) (0.7×10^{-5} mol dm^{-3}) in benzene.

Figure 1-5 shows the absorption spectra of 7Z and 7C in benzene solution. The closed-ring form was isolated by passing the photoirradiated sample through a silica gel column. The absorption maximum of the closed-ring form shifts to a longer wavelength by

55 nm in comparison with the selenophene derivatives **5C**. The conversion of the open-ring to closed-ring form in the photostationary state under irradiation with 436 nm light was estimated to be 8% by liquid chromatography measurement.

1.3.2 Acid Anhydride Derivative



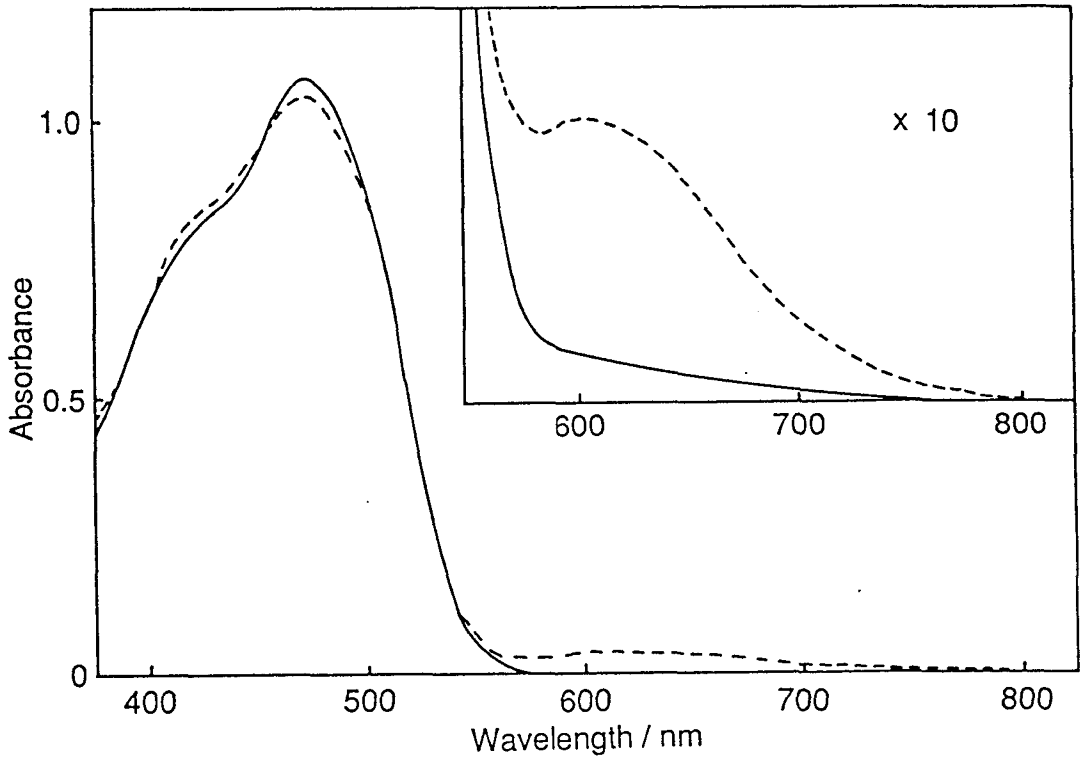
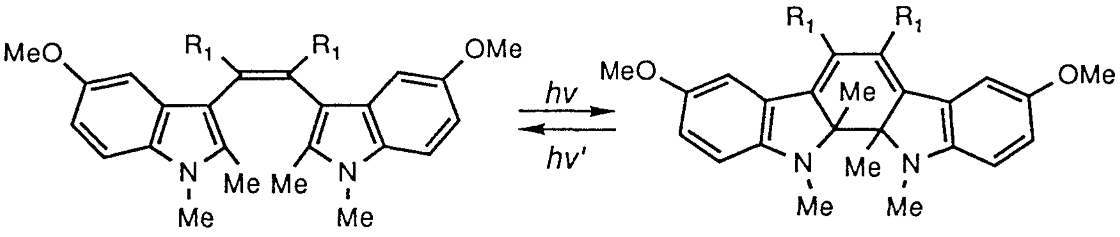


Figure 1-6. Absorption spectra of **8Z** (1.1×10^{-4} mol dm^{-3}) (—) and in the photostationary state under irradiation with 436 nm light (- - -).

The cyano derivative was converted to a maleic anhydride derivative **8Z** by the same method used for **6Z**.

Figure 1-6 shows the absorption spectra of **8Z** in benzene before photoirradiation and in the photostationary state under irradiation with 474 nm light. Upon irradiation with 474 nm light, a new absorption peak appeared at 620 nm. The absorption maximum shifts to red by 55 nm in comparison with selenophene derivatives **6C**. The absorption tail of the closed-ring form, **8C**, reaches 800 nm.

1.3.3 Effect of the Introduction of Electron-Donors



9Z, R1=CN
10Z, R1=COOCO

9C, R1=CN
10C, R1=COOCO

Figure 1-7 shows the absorption spectra of **9Z** in benzene solution before photoirradiation and in the photostationary state under irradiation with 440 nm light. Irradiation of **9Z** with 440 nm light led to the formation of the closed-ring form **9C**, in which a visible absorption at 610 nm (ε: 4,750 $dm^3mol^{-1}cm^{-1}$) was observed. The absorption maximum of the closed-ring form shifts to longer wavelength by 36 nm in comparison with **7C**. The compound had the sensitivity at the diode laser wavelength. The conversion of the open-ring to the closed-ring form in the photostationary state under irradiation with 440 nm light was estimated to be 7.4% by liquid chromatography measurement. The cyano derivative was converted to an maleic anhydride derivative **10Z**.

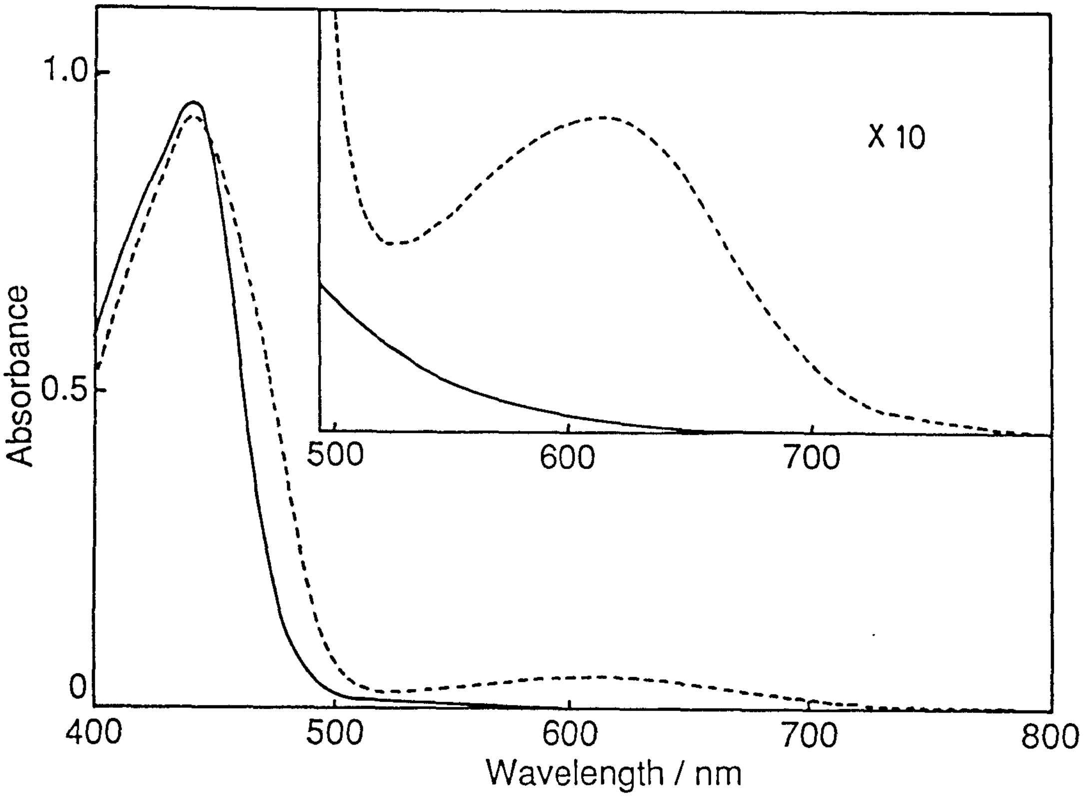


Figure 1-7. Absorption spectra of **9Z** ($1.0X10^{-4}$ mol dm^{-3}) (—) and in the photostationary state under irradiation with 440 nm light (- - -).

Upon irradiation with 490 nm light, a new absorption peak appeared at 660 nm (Figure 1-8). The absorption maximum shifts to red by 40 nm in comparison with **8C**. The value 660 nm for the λ_{max} is, to my knowledge, the largest one for that of the closed-ring form of diarylethene derivatives. The absorption tail of the closed-ring form, **10C**, reaches 840 nm.

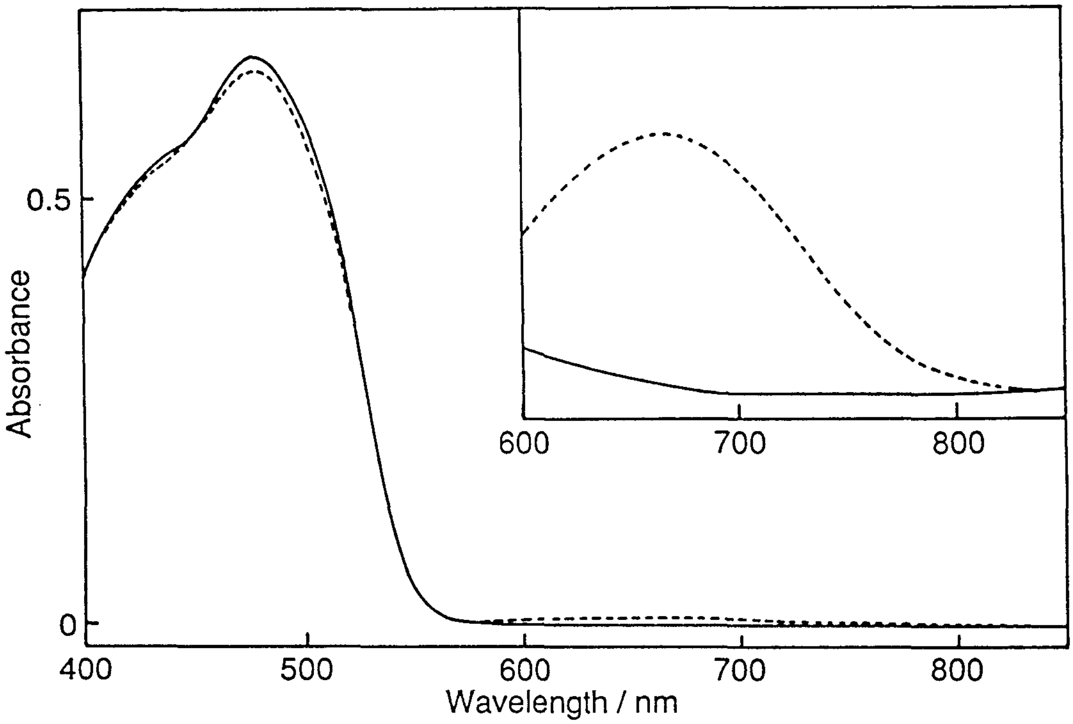


Figure 1-8. Absorption spectra of **10Z** (1.0×10^{-4} mol dm^{-3}) (—) and in the photostationary state under irradiation with 490 nm light (- - -).

1.4 Thermal Stability of the Closed-Ring Forms

Figure 1-9 illustrates the thermal stability of the closed-ring forms, **5C**, **6C**, **7C**, **8C**, and **9C**, at 80°C in the dark. The value of *A*/*Ao* X 100 was plotted against storage time, where *Ao* is the initial absorbance of the closed-ring forms, and *A* the absorbance after *t* hours at 80°C. As seen in the Figure 1-9, the photogenerated closed-ring forms, **5C** and **6C**, are stable, and keep the absorption intensity constant for more than 12 h at 80°C, while the closed-ring forms

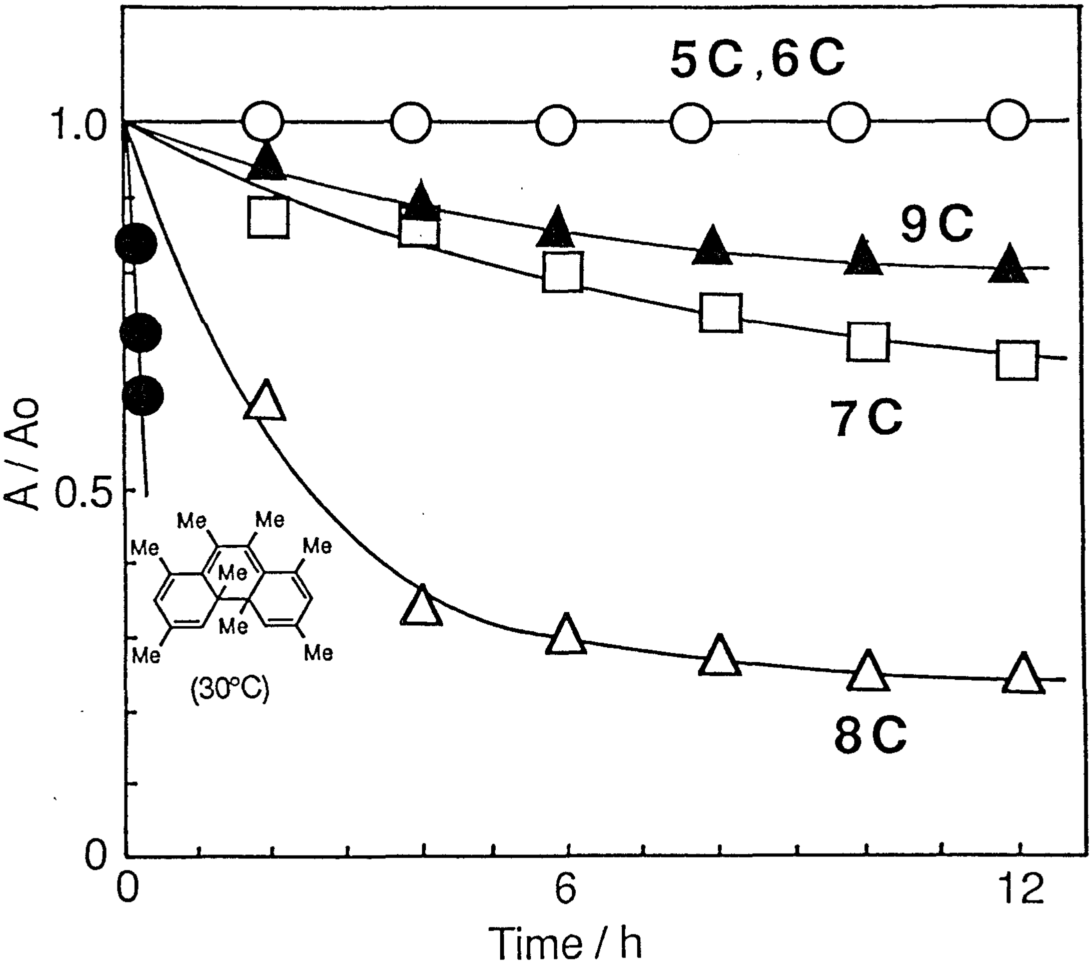


Figure 1-9. Thermal stability of the closed ring forms in toluene. Compounds 5C (○), 6C (○), 7C (□), 8C (△), and 9C (▲).

with indole groups are thermally unstable. Upon exposure of the dark red solution of **6C** to the visible light (λ > 520 nm), the solution again became yellow and the initial absorption was restored. The absorption intensity of the closed-ring form of the maleic anhydride derivative **8C**, decreases to 50% of the initial intensity in 3 h at 80°C. The photogenerated closed-ring form **9C**, became somewhat thermally stable in comparison with **7C**.

Thermal stability of a closed-ring form of methyl-substituted fulgide[5-9] is explained by the steric hindrance of methyl groups in the disrotatory ring-opening process. The adjacent two methyl groups in the photogenerated connecting bond of the closed-ring form is believed to prohibit the thermal disrotatory ring-opening reaction.[2] This interpretation dose not apply to the present system, in which compounds with similar steric hindrance, e.g. methyl-substituted indole (or pyrrole[18]) and methyl-substituted selenophene (or thiophene) derivatives, have different thermal stability. The steric repulsion between the methyl groups and the aryl rings possibly prevents the disrotatory ring-opening reaction of both the indole and selenophene derivatives. Ring opening reaction is allowed only in the conrotatory route even in the thermal process. Electronic effects need to be taken into account to explain the different thermal stability.

In 1989, Nakamura et al.[5] have carried out a theoretical study on the thermal stability of diarylethene derivatives. Semiempirical MNDO calculation of the state correlation diagrams of the reactions suggested that the thermal stability of the closed-ring form depends on aromatic stabilization energy of the aryl groups. When the aromatic stabilization energy is large in the course of ring-opening reaction, the closed-ring form is thermally unstable. The indole ring has appreciable aromatic stabilization energy.[5] This makes the closed-ring form thermally unstable. On the other hand, the aromatic stabilization energy of selenophene is rather low. The low energy stabilizes the closed-ring forms.

1.5 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.

It is not easy to compare quantitatively the fatigue resistance, i.e., haw many times coloration and decoloration cycles can be repeated without permanent product formation, because the property strongly depends on the environmental conditions, such as the solvent purity or matrix property.

Table 1-II. Fatigue Resistant Property of Diarylethene Derivatives.[a]

	irradiation wavelength,[a] / nm		repeatable
compound	coloring	bleaching	cycle no.[b]
5Z	313	546	10
6Z	346	546	75
6Z[c]	346	546	>100
7Z	436	546	>100
8Z	492	577	>100
furyl fulgide	366	546	21

[a] Irradiation was carried out in the presence of air. Concentration of the compounds were 1×10^{-4}M in benzene. [b] The cycle number when the colored intensity decreased to 80% of the first cycle. [c] In the absence of air.

I tried to measure qualitatively the fatigue resistant property of **5Z**, **6Z**, **7Z** and **8Z** in benzene in the presence and absence of air, as shown in Table 1-II. The number of repeatable cycles indicates the cycle number when the colored intensity decreased to 80% of the first cycle. Compounds **7Z** and **8Z** are fatigue resistant. Elimination of oxygen from the solution increased the number of repeatable cycles. The intensity of the closed-ring forms of compounds **7Z** and **8Z** did not show any detectable decrease even after 100 coloration / decoloration cycles.

1.6 Quantum Yields

The quantum yields of the cyclization and ring-opening reactions were measured in benzene solution. The quantum yields were determined 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. Mercury lines, which were isolated with a monochrometer, were used to induce the reactions. The light intensity was measured with a photometer, which was calibrated with a trisoxalatoferrate (III) chemical actinometer. Table 1-III and 1-IV summarize the results. The cyclization quantum yield of the selenophene derivatives was around 0.3, which is 3 times larger than the value observed in 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (**4Z**).[13] Replacement of selenophene rings with benzothiophene ones or indole ones decreased the quantum yield.

Table 1-III. Quantum Yields for Ring-closure in Benzene.

excitation wavelength, (nm)	compound			
	5Z	6Z	7Z	9Z
334	0.33	0.27	a	a
405	a	a	0.06	0.11

[a]Not measured.

Table 1-IV. Quantum Yields for Ring-Opening Reaction in benzene.

excitation wavelength, (nm)	compound 5C	6C	7C	9C
546	0.02	0.02	0.66	0.53
577	0.02	0.02	0.57	a
633	a	0.02	a	a

[a] Not measured.

The quantum yield of the benzothiophene derivatives or the indole derivatives is around 1/2 or 1/5 of that of selenophene derivatives, respectively. The quantum yield of **9Z** was 0.11 which is about twice larger than the value observed in **7Z**. Table 1-IV summarizes the ring-opening quantum yield.The quantum yield for the selenophene derivatives is independent of the excitation wavelength, while the quantum yield of the indole derivatives decreased with shifting the excitation wavelength to longer wavelengths. The quantum yield at 546 nm light was obtained to be 0.66, while it decreased to 0.57 at 577 nm. Similar wavelength dependence of the quantum yield was observed in the thiophene derivatives,[13] though the mechanism is not yet clear. The quantum yields for the cyclization of indole derivatives are smaller than their for the ring-opening reaction. This results are understandable because the cyclization is prohibited by the *Z*-*E* isomerization and ring-opening reaction.

The quantum yield of decoloration reaction of 3-furyl fulgide was reported to depend on the bulkiness of substituent at 7-position of the colored form. Adamantylidene furyl fulgide[19] has a quantum yield 5 times larger than that of isopropylidene furyl 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 dose 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.

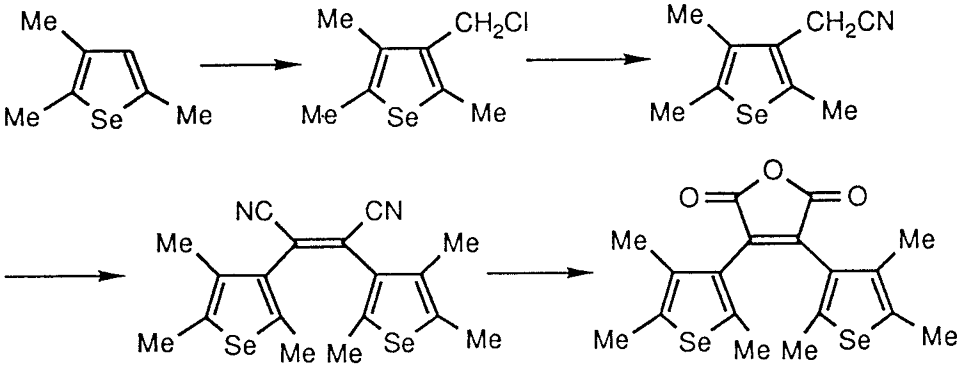
1.7 Experimental

IR spectra were measured with a Perkin Elmer Model 1618 spectrophotometer using KBr disks. ^{1}H NMR spectra were recorded in C_6D_6 or $CDCl_3$ using tetramethylsilane (0 ppm) as an internal standard with a 360-MHz NMR spectrometer (Brucker, WM-360), a 200-MHz NMR spectrometer (JOEL-FX 200), and a 60-MHz NMR spectrometer (JOEL PMX 60). ^{13}C NMR spectra (68 MHz) were recorded on JOEL JNM-GSX-270 spectrometer using $CDCl_3$ as the solvent with tetramethylsilane as an internal standard. Mass spectra and elemental analyses were performed in the Material Analysis Center of Osaka University. Melting points were determined by using a Gallenkamp melting point apparatus (MP-41). HPLC analysis was carried out on a JASCO 800 system. Stainless-steel columns (length, 250mm; i.d.,4.6mm, for analytical purposes, length, 250mm; i.d.,10.0mm, for preparative purposes) were slurry packed using silica gel (fine SIL-5). Absorption spectra were measured with a spectrophotometer (Shimadzu, MPS-200 and Hitachi, U-3410). A mercury lamp (Ushio, 1 kW) or a xenon-arc lamp (EWIG 500W) were used as a light source. The wavelengths of irradiated light was selected by passing the light through a monochrometer (Ritsu, MC-10N or Jobin Yvon H10-UV). A He-Ne laser was used for the light of 633 nm. Quantum yield was determined by measuring the rate of isomerization in the initial stage of the reaction at low concentration (absorbance at the irradiation wavelength < 0.2), and the light intensity was measured with a photometer (International Light, IL700 or IL1700) which was calibrated with a trioxalatoferrate (III) chemical actinometer.

The fatigue-resistant property was measured as follows. A benzene solution of each compound in the open-ring form was irradiated with light of an appropriate wavelength until the photostationary state was attained. The irradiation time depended on the compound, ranging from 1 to 5 min. Then, the closed-ring form was converted again almost completely (> 95%) to the open-ring form with light of a longer wavelength. It also took 1-5 min. The coloration / decoloration cycle was repeated.

Materials

1,2-Bis(2,3,5-trimethyl-3-selenenyl)maleic anhydride was synthesized from 2,3,5-trimethylselenophene[20,21] as follows.



4-Chloromethyl-2,3,5-trimethylselenophene.[22]

Chloromethyl methyl ether (403 g, 5 mol) was added dropwise to a solution of 2,3,5-trimethylselenophene (173 g, 1 mol) in 1 L of 1,2-dichloromethane at 0°C. To this solution was added, over a period of 1 h, $ZnCl_2$ (13 g, 0.2 mol), and then the solution was stirred for 1 h at room temperature. The reaction mixture was poured on ice. The aqueous solution was extract with $CHCl_3$, and the organic phase was dried over $MgSO_4$. Removal of the solvent and distillation of the residue under reduced pressure gave 2,3,5-trimethyl-4-(chloromethyl) selenophene in 25 % yield: bp 50-55 °C (0.5 mmHg); ^1H NMR ($CDCl_3$) δ 2.04 (s, 3H, $ArCH_3$), 2.35 (s, 3H, $ArCH_3$), 2.46 (s, 3H, $ArCH_3$), 4.30 (s, 2H, $ArCH_2Cl$).

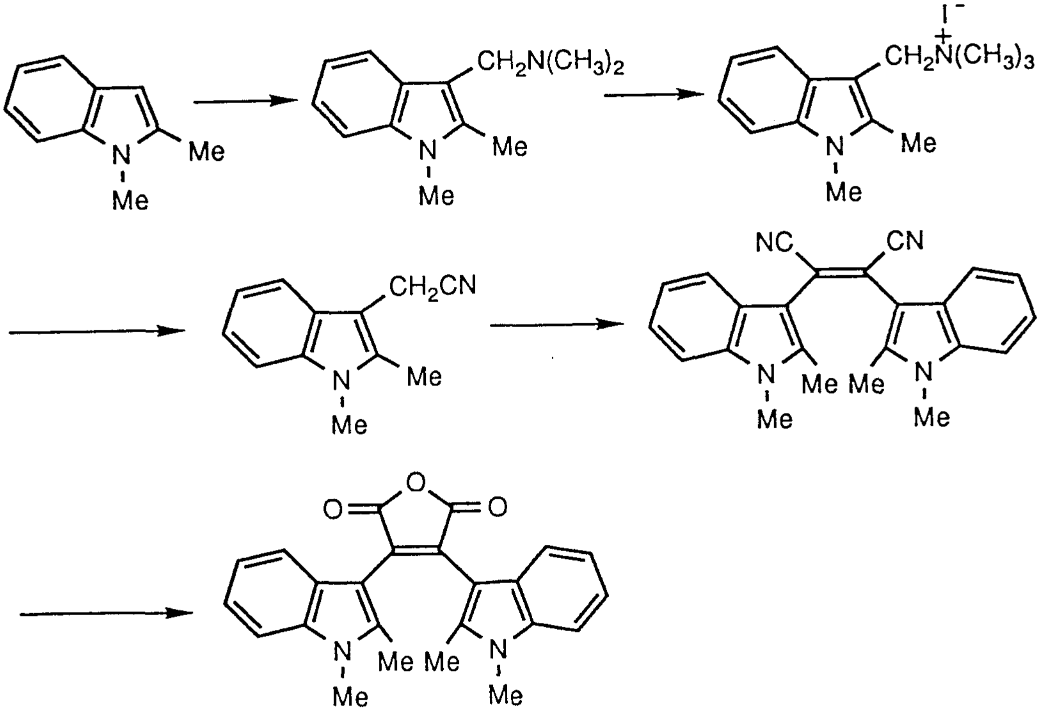
4-Cyanomethyl-2,3,5-trimethylselenophene.[23] This was prepared from 4-chloromethyl-2,3,5-trimethylselenophene by a similar procedure as used for 2,3,5-trimethyl-4-(cyanomethyl)-thiophene[13]: bp 75°C (0.3 mmHg); ^{1}H NMR ($CDCl_3$) δ 2.04 (s, 3H, $ArCH_3$), 2.35 (s, 3H, $ArCH_3$), 2.42 (s, 3H, $ArCH_3$), 3.38 (s, 2H, $ArCH_2CN$).

1,2-Dicyano-1,2-bis(2,3,5-trimethyl-3-selenenyl) ethene (5Z). To 1.3 mL of 50% NaOH aqueous solution containing tetrabutylammonium bromide (0.086 g, 0.3 mmol) was added, over a period 0.5 h, a mixture of 2,3,5-trimethyl-4-(cyanomethyl)- selenophene (1.4 g, 6.6 mmol), and CCl_4 (1.5 g, 0.01 mol) at 40°C. The solution was stirred for 1.5 h at 45°C. Then, the reaction mixture was poured into water. The aqueous solution was extracted with $CHCl_3$, and the organic phase was dried over $MgSO_4$. After the solvent was removed, the mixture of *Z* and *E* form was obtained in 31% yield by column chromatography on silica gel. The *Z* form was separated from the solution by HPLC and then purified by recrystallization from a hexane-ether mixture. mp 221-2°C; ^{1}H NMR (C_6D_6) δ 1.53, 1.60, 1.78, 1.80, 1.82, and 1.84 (s, 3HX6, $ArCH_3$); mass spectrum, m/e M^+ 420. Anal. Calcd. for $C_{18}H_{18}N_2Se_2$: C, 51.44; H, 4.32; N, 6.67; Se, 37.58. Found: C, 51.25; H, 4.00; N, 6.65.

2,3-Bis(2,3,5-trimethyl-3-selenenyl)maleic Anhydride (6Z).[24] This was prepared from 1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-selenenyl) ethene by a similar procedure as used for 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride.[14] **6Z** was isolated in 35% yield by column chromatography on silica gel. The crude product was purified by recrystallization from an ether-hexane mixture: mp 230-3°C; ^{1}H NMR (C_6D_6) δ 1.53, 1.66, 1.72, 1.84, and 1.88 (X2) (s, 3HX6, $ArCH_3$); mass spectrum, m/e M^+ 442.

Anal. Calcd for $C_{18}H_{18}O_3Se_2$: C, 49.11; H, 4.12; O, 10.90; Se, 35.87. Found: C, 49.39; H, 3.90.

1,2-Bis(1,2-dimethyl-3-indolyl)maleic anhydride was synthesized from 1,2-dimethylindole[25] as follows.



1,2-dimethyl-3-((dimethylamino)methyl)indole.[26] A mixture of 36mL of 25% aqueous dimethylamine and 40 mL of glacial acetic acid was cooled in an icebath. To the solution below 5°C were added 15 mL of 40% aqueous formaldehyde and then 1,2-dimethylindole (26.2 g, 0.18 mol). The reaction mixture was stirred gently until it became homogeneous. During the stirring the temperature rose to about 50°C. The reaction mixture was allowed to stand at room temperature for 24 h and then poured into a 400 mL aqueous solution containing 40 g of sodium hydroxide. The oily part was collected by extraction with ether. The ether extract was washed and dried with $MgSO_4$. Removal of the solvent and distillation of the residue gave 1,2-dimethyl-3-((dimethylamino)-methyl)indole in 38% yield; bp 105°C (0.5 mmHg).

1,2-Dimethyl-3-((dimethylamino)methyl)indole Methiodide.[26] To a solution of 9.1 g of 1,2-dimethyl-3-((dimetylamino) methyl)-indole in 40 mL of absolute ethanol was added in one portion 7.8g of methyl indole. The mixture was allowed to stand for 1 h at room temperature. Crystallization was completed by cooling, and the solid was collected and washed two times with absolute ethanol and three times with anhydrous ether. Nitrogen methiodide was isolate in 98% yield.

3-Cyanomethyl-1,2-Dimethylindole.[26] To a solution of 10 g of sodium cyanide in 100 mL of water was added 17.2 g of the methiodide, and the mixture was refluxed for 2.5 h. Both oily and solid parts were collected by extraction with ether. The ether solution was washed three times with water, dried over $MgSO_4$, filtered, and concentrated. After the ether was removed, 3-cyanomethyl-1,2-dimethylindole was isolated in 70 % yield by column chromatography on silica gel. The crude product was purified by recrystallization from an ether-hexane mixture.

1,2-Dicyano-1,2-bis(1,2-dimethyl-3-indolyl)ethene (7Z). This was prepared from 1,2-dimethyl-3-(cyanomethy)indole by a similar procedure as used for **5Z**. The coupling product was obtained as yellow crystals in 32% yield: mp 289-91°C; ^{1}H-NMR (C_6D_6) δ 1.91, 2.09 (s, 3HX2, $ArCH_3$), 2.65, 2.69 (s, 3HX2, NCH_3), 6.70-7.44 (m, 4HX2, $ArCH_3$); mass spectrum, *m/e* M^+ 364. HRMS *m/e* 364.1685, calcd for $C_{24}H_{20}N_4$ 364.1687. Anal. Calcd for $C_{24}H_{20}N_4$: C, 79.10; H, 5.53; N, 15.37. Found: C, 78.91;.H, 5.35; N, 15.28.

2,3-Bis(1,2-dimethyl-3-indolyl)maleic anhydride (8Z).[24] This was prepared from **7Z** by a similar procedure as used for **6Z**. Yield was 57 %: mp > 300°C; ^1H NMR ($CDCl_3$) δ 2.04, 2.11 (s, 3HX2, $ArCH_3$), 3.59, 3.62 (s, 3HX2, NCH_3), 6.91-7.36 (m, 4HX2, ArH); mass spectrum, *m/e* M^+ 384; HRMS *m/e* 384.1456, calcd for $C_{24}H_{20}N_2O_3$ 384.1473.

3-Cyanomethyl-1,2-dimethyl-5-methoxyindole.[27] To a chilled solution of dimethylamine (50 % aqueous, 2.64mL, 28.8mmol) and formalin (37% aqueous, 1.47mL, 18.9mmol) in glacial acetic acid (5.8mL) was added 5-methoxy-1,2-dimethylindole (3.2g, 18.3mmol) in three equal portions, at 0°C. After being warmed to room temperature and stirred for 4h, the solution was poured into ice water (75mL) and basified with 50% NaOH. Crude 5-methoxy-1,2-dimethyl gramine was extracted with ether (3X100mL), dried ($MgSO_4$), and concentrated. The gramine was used without further purification. Methyl iodide (3mL, excess) was added to a benzene (60 mL) solution of 5-methoxy-1,2-dimethyl gramine and placed in the dark overnight. The methiodide was filtered, dried under vacuum. The methiodide was used without further purification. A solution of 5-methoxy-1,2-dimethyl gramine methiodide, sodium cyanide (1.76g, 36.6mL), and ethanol (95%, 39mL) was refluxed under nitrogen until no more trimethylamine evolved (ca. 24h). The cooled solution was concentrated and chromatographed (benzene) to yield 5-methoxy-1,2-dimethylindole-3-acetonitrile (1.79g, 45.7% from 5-methoxy-1,2-dimethylindole: 60-MHz ^1H NMR ($CDCl_3$) 2.303 (s, 3H), 3.513 (s, 3H), 3.633 (s, 2H), 3.800 (s, 3H), 6.467-7.200 (m, 3H); IR (cm^{-1}); MS (EI) *m/e* (relative intensity) 214 (M^+, 100), 199 (75), 188 (14), 171 (35). HRMS *m/e* 214.1111, calcd for $C_{13}H_{14}N_2O_1$ 214.1105

1,2-Dicyano-1,2-bis(5-methoxy-1,2-dimethyl-3-indolyl) ethene (9Z). To 0.4mL of 50% NaOH aqueous solution containing tetra-n-buthylammonium bromide (26mg, 0.087mmol) was added, over a period 0.5h a mixture of 5-methoxy-1,2-dimethylindole-3-acetonitrile (0.435g, 2mmol) and carbon tetrachloride (0.29mL) and benzene (3.6mL) at 40°C. The solution was stirred for 3h at 45°C. Then, the reaction mixture was poured into water. The aqueous solution was dried ($MgSO_4$). After the solvent was removed and chromatographed (benzene). The cis form was separated with a HPLC and purified by recrystallization from a hexane-ether mixture yielding 170mg (39.4%): 360-MHz ^1H NMR ($CDCl_3$) 2.102 (s,6H), 3.355 (s,6H), 3.524 (s,6H), 6.610 (d, *J*=2.45Hz, 2H), 6.748 (dd, *J*=2.45 and 8.77Hz, 2H), 7.076 (d, *J*=8.77Hz, 2H); MS (EI) *m/e* (relative intensity) 424 (M^+,100), 409 (23), 394 (14) 212 (30). HRMS *m/e* 424.1901, calcd for $C_{26}H_{24}N_4O_2$ 424.1898.

1,2-Bis(5-methoxy-1,2-dimethyl-3-indolyl)maleic anhydride (10Z). 1,2-Dicyano-1,2-bis(5-methoxy-1,2-dimethyl-3-indolylethene (140mg, 0.33mmol) and ethylene glycol monoethyl ether 3.9mL were added to a solution of 1.85g of potassium hydroxide in 3.9mL of water. The solution was refluxed for 24h. The reaction mixture was poured into water and 20% hydrochloric acid aqueous solution was added until the mixture became acidic. The red precipitated was extracted with chloroform. The organic phase was dried ($MgSO_4$) and filtered. After the solvent was removed the maleic anhydride was isolated by column chromatography on silica gel (benzene). The crude product was purified by recrystallization from a ether-hexane mixture; 360-MHz ^1H NMR ($CDCl_3$) 2.142 (s, 6H), 3.310 (s, 6H), 3.589 (s, 6H), 6.478 (d, *J*=2.10Hz, 2H), 6.744 (dd, *J*=2.10 and 8.77Hz, 2H), 7.100 (d, *J*=8.77Hz, 2H); IR (KBr, cm^{-1}); MS (EI) *m/e* (relative intensity) 444

(M^+, 100), 429 (6), 400 (12), 372 (33); HRMS *m/e* 444.1668, calcd for $C_{26}H_{24}N_2O_5$ 444.1684.

1.8 References

(1) Y. Hirshberg, *J. Am. Chem. Soc.*, **78**, 2304 (1965).

(2) H. G. Heller, *IEEE Proc.*, **130**, 209 (1983).

(3) G. H. Brown, Ed. *Photochromism*; Wiley-Interscience: New York, 1971.

(4) A. Santiago, R. Becker, *J. Am. Chem. Soc.*, **90**, 3654 (1968).

(5) H. G. Heller, *Chem. Ind.* (London), **1978**, 193.

(6) H. G. Heller, S. Oliver, *J. Chem. Soc.,Perkin Trans.I.* **1981**, 197.

(7) P. J. Darcy, H. G. Heller, P. J. Strydom, J. Whittall, *J. Chem. Soc., Perkin Trans. I.* **1981**, 202.

(8) H. G. Heller, J. R. Langan, *J. Chem. Soc., Perkin Trans. I.* **1981**, 341.

(9) A. P. Glaze, S. A. Harris, H. G. Heller, W. Johncock, S. N. Oliver, P. J. Strydom, J. Whittall, *J. Chem. Soc., Perkin Trans. I.* **1985**, 957.

(10) K. Ulrich, H. Port, *Chem. Phys. Lett.*, **155**, 437 (1989).

(11) Y. Yokoyama, H. Hayata, H. Ito, Y. Kurita, *Bull. Chem. Soc. Jpn.*, **63**, 1607 (1990).

(12) H. Suzuki, A. Tomoda, M. Ishizuka, A. Kaneko, M. Furui, R. Matsushima, *Bull. Chem. Soc. Jpn.*, **62**, 3968 (1989).

(13) M. Irie, M. Mohri, *J. Org. Chem.* , **53**, 803 (1988).

(14) M. Irie, "Polymers in Information Storage Technology", Mittaled, K. L. Plenum. New York, **1989**, p105.

(15) A. Jaesehke, H. Muensch, H. G. Schmid, H. Friebobolin, A. Mannschreck, *J. Mol. Spec.*, **31**, 14 (1969).

(16) Y. Nakayama, K. Hayashi, M. Irie, *J. Org. Chem.*, **55**, 2592 (1990).

(17) K. Uchida, Y. Nakayama, M. Irie, *Bull. Chem. Soc. Jpn.*, **63**, 1311 (1990).

(18) S. Nakamura, M. Irie, *J. Org. Chem.*, **53**, 6136 (1988).

(19) Y. Yokoyama, Y. Goto, T. Inoue, M. Yokoyama, Y. Kurita, *Chem Lett.*, **1988**, 1049.

(20) C. Paal, *Ber.* **18**, 2255 (1885).

(21) M. V. Kudchadker, R. A. Zingaro, K. J. Irgolic, *Can. J. Chem.*, **46**, 1415 (1968).

(22) *Org. React*, **1942**, 1, 68

(23) K. Fukunaga, *Yukigoseikagaku.*, **33**, 774 (1975).

(24) M. A. Goldberg, E. P. Ordas, G. Carsch, *J. Am. Chem. Soc.*, **69**, 260 (1947).

(25) L. F. Fieser, H. Fieser, Reagents for Organic Synthesis, John-Wiley: New York, **1967**, p336.

(26) H. R. Snyder, E. L. Eliel, *J. Am. Chem. Soc.*, **70**, 1703 (1948).

(27) K. J. Drost, R. J. Jones, M. P. Cava, *J. Org. Chem.*, **54**, 5985 (1989).

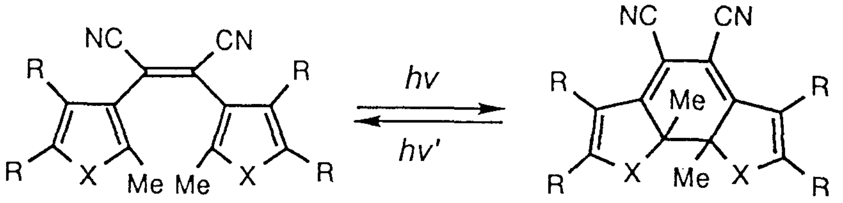
CHAPTER 2

Reversible Photocyclization of Non-symmetrical Diarylethene Derivatives

2.1 Introduction

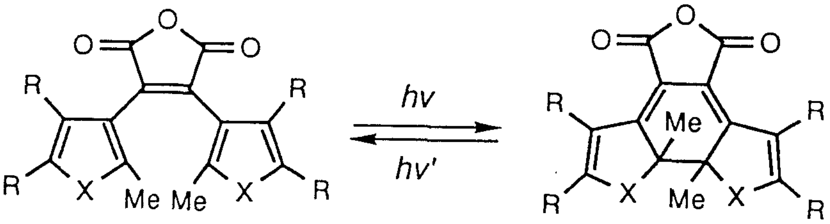
A photochromic material is characterized by its ability to undergo a reversible transformation between two different chemical forms. Such a transformation is induced by irradiation with an appropriate wavelength.[1] The instant image forming property without processing has led to the consideration of 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]

As mentioned in chapter 1, 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 (**3Z**), and 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (**4Z**).[4] Compounds **3Z**, **4Z**, **7Z**, and **8Z** are not thermochromic, even at 300°C, and the colored closed-ring forms **3C** and **4C** are stable for more than 3 months at 80°C.[2-g] 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 < λ < 840 nm).



3Z, X= S; R= CH_3
7Z, X= NCH_3;
R^R= CH=CH-CH=CH

3C, X= S; R= CH_3
7C, X=NCH_3;
R^R= CH=CH-CH=CH



4Z, X= S; R= CH_3
8Z, X= NCH_3;
R^R= CH=CH-CH=CH

4C, X= S; R= CH_3
8C, X= NCH_3;
R^R= CH=CH-CH=CH

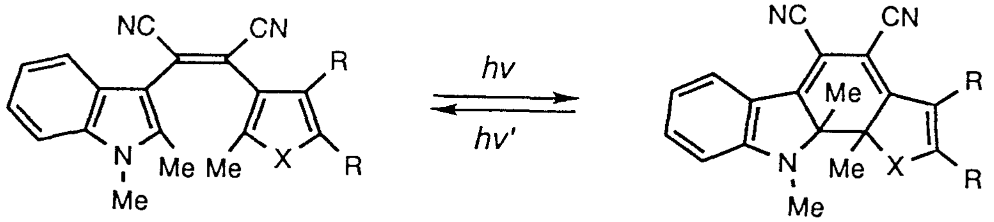
The compounds lack the important requirement of photo-sensitivity at diode laser wavelengths.

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-dimethly-3-indolyl)ethene (**7Z**) and 2,3-bis(1,2-dimethyl-3-indolyl)maleic anhydride (**8Z**), shifts the absorption maxima to longer wavelengths. Compound **8C** has an absorption edge extending to 800 nm and the ring-opening reaction was effected with 780 nm diode laser. The closed-ring forms , **7C** and **8C**, were, however, thermally unstable, reverting in the dark to **7Z** and **8Z**. The absorption intensity of **8C** 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 were interpreted by the difference in aromatic stabilization energy of the rings.[6]

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

2.2 Diarylethene Derivatives with Cyano Groups

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-methylbenzo[*b*]thiophene or 3-(cyanomethyl)-1,2,4,5-tetramethylpyrrole, respectively.



11Z, X=S; R=CH_3 **11C**, X=S; R=CH_3
12Z, X=S; R^R= CH=CH-CH=CH **12C**, X=S; R^R= CH=CH-CH=CH
13Z, X=NCH_3; R=CH_3 **13C**, X=NCH_3; R=CH_3

In the case of a coupling reaction of equimolar (cyanomethyl)-indole and (cyanomethyl)pyrrole approximately equal amounts of **11Z** and **3Z** 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 **13Z** and its trans form, and **7Z** and its trans form were separated by silica gel chromatography using benzene as an eluent. The trans and cis mixture of the indolyl-pyrrolylethene derivatives was dissolved in acetonitrile and exposed to ultraviolet-visible light ($\lambda > 350$ 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 um 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 **11Z**, **3Z**, and **7Z** (4 : 20 : 1 including the trans forms). The mixture was separated by the same procedure used for **13Z**. Compound **12Z** was also prepared by the similar coupling reaction as used for **13Z**. The structures of the above compounds were fully characterized by spectroscopic methods.

Non-symmetric diarylethenes with cyano group underwent the cyclization to produce the cyclohexadiene-type derivatives.[7] Figure 2-1 shows the absorption spectral change of a dilute benzene solution of **11Z** ($1.0\mathrm{x}10^{-4}$ 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 ($\varepsilon = 1.0\mathrm{x}10^{-4}$ L mol^{-1} cm^{-1}) and formation of a brown solution, in which a visible absorption at 549 nm ($\varepsilon = 5.4\mathrm{x}10^{3}$ L mol^{-1} cm^{-1}) was observed. The closed-ring form **11C** shows a 37 nm bathochromic shift compared with **3C**. 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 **11Z** disappeared, and the initial cis form absorption was restored.

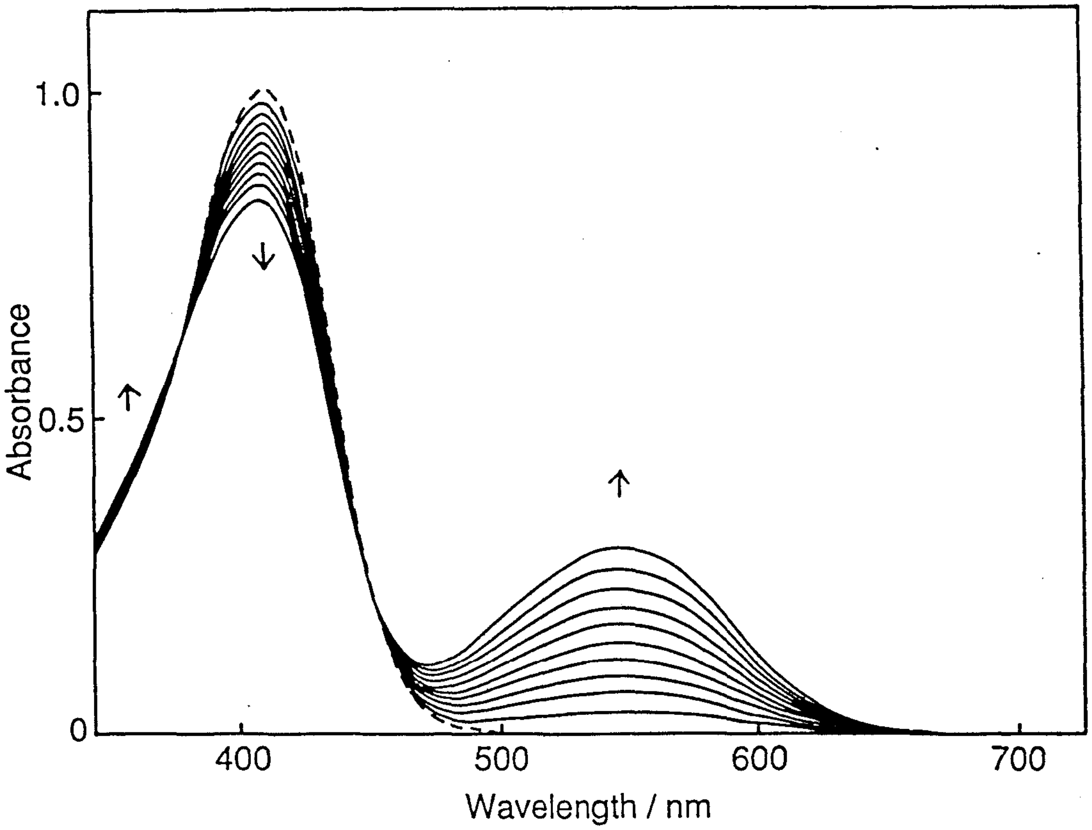


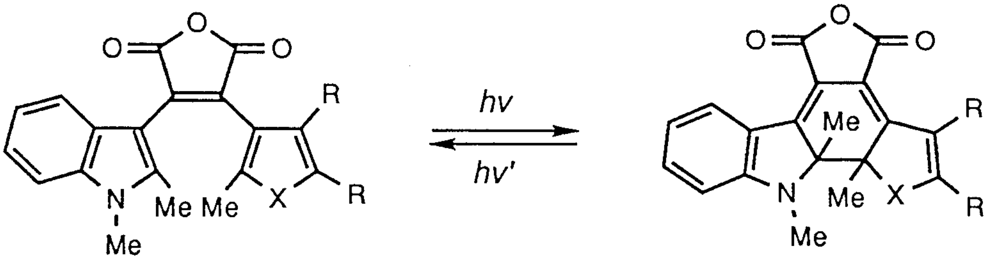
Figure 2-1. Absorption spectral change of benzene solution of (**11Z**) (1.0×10^{-4}mol dm^{-3}) (---) induced by irradiation with 436 nm light. Irradiation time; 25, 50, 80, 110, 150, 195, 261, 333, 471, and 855 sec.

The conversion of **11Z** to **11C** at the photostationary state was estimated to be 55% by comparing the absorption intensity at 549 nm with that of **11C**, which was isolated from the photoirradiated sample by HPLC.

The absorption maximum of **3C** was observed at 512 nm,[1] while that of **7C** was 575 nm.[5] The absorption maximum of **11C** was in between those of **3C** and **7C**.[7] This indicates that donor-acceptor conjugation over two heterocyclic rings dose not play an important role in this compound.

By replacing the thiophene ring of **11C** with a benzo[*b*]thiophene or 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 are summarized in Table 2-I. The conversions were determined 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. Conversion over 50% is 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.

2.3 Maleic Anhydride Derivatives



14Z, X=S; R=CH_3 **14C**, X=S; R=CH_3

15Z, X=S; R^R= CH=CH-CH=CH **15C**, X=S; R^R= CH=CH-CH=CH

The cyano derivatives were converted to maleic anhydride derivatives by hydrolysis with KOH in ethylene glycol monoethylether-water mixture. The 2,3-diarylmaleic anhydride were purified by the column chromatography using benzene as an eluent, and were recrystallized from a hexane-chloroform mixture.

Their structures were fully characterized by the spectroscopic methods. The non-symmetric 2,3-diarylmaleic anhydride underwent cyclization reactions to produce the cyclohexadiene-type derivatives.

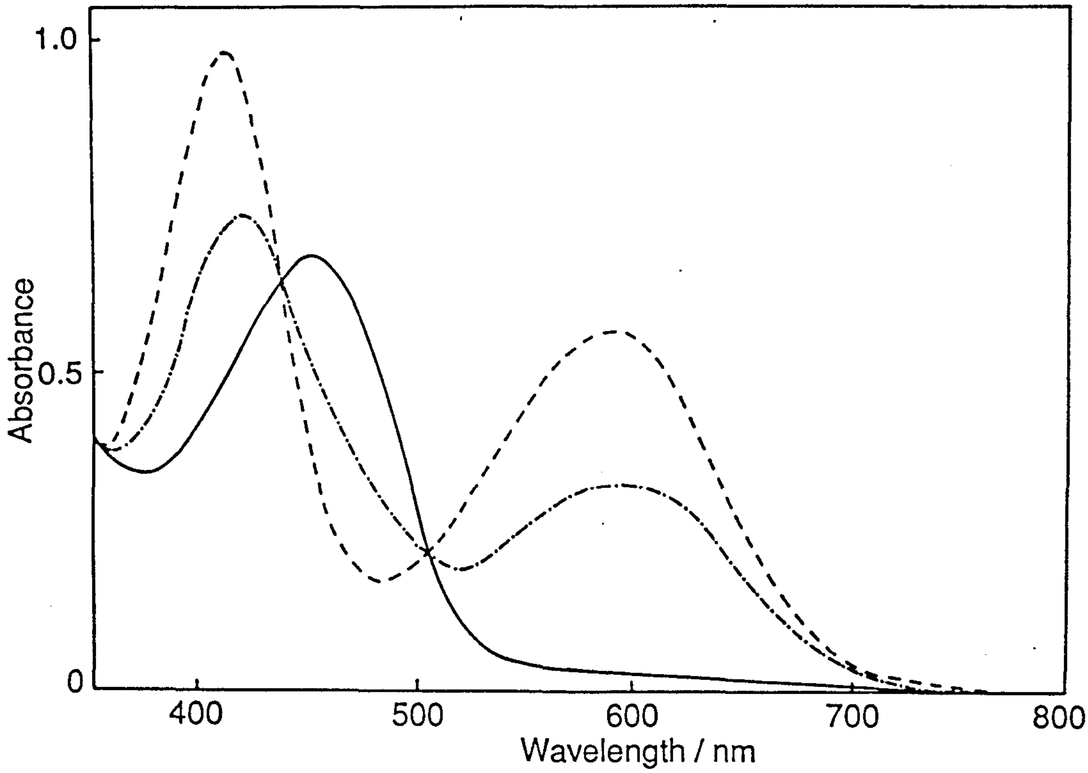


Figure 2-2. Absorption spectra of benzene solution of (**14Z**) (1.0×10^{-4} mol dm^{-3}) (—) and (**14C**) (1.0×10^{-4} mol dm^{-3}) (- - -) and a mixtyre of **14Z** and **14C** at the photostationary state (–·–) under irradiation with 491 nm light.

Figure 2-2 shows the spectra of **14Z** and **14C**, and the spectrum at the photostationary state under irradiation with 491nm 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 = 5.5×10^3 dm^{3}mol^{-1}cm^{-1}). Isosbestic points are observed at 437 and 504 nm. The absorption maximum shifts to longer wavelengths by

56 nm in comparison with the cyano derivative **11C**. On exposure to visible light (λ > 560 nm), the solution again became yellow, and the initial absorption of **14Z** was restored. The absorption maxima of **4C** and **8C** were observed at 560 nm and 620 nm, respectively.[4,5] the absorption maximum of **14C**, 595 nm, was in between those of **4C** and **8C**.

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 **15Z** underwent similar cyclization / ring-opening reactions upon irradiation with 488 and 633 nm lights.

Table 2-1 **Absorption Maxima of the Closed-ring Forms and Photochromic Property of Non-symmetric Diarylethenes in Benzene Solution.**

compound	closed form λmax (nm)	conversion yield (%)	exciting wavelength (nm)
11C	547	55	436
12C	558	50	440
13C	575	59	440
14C	595	58	491
14C[a]	578	70	450
15C	597	26	480
15C[a]	583	66	470

[a] In hexane

The absorption maxima of the closed forms of symmetric diarylethene showed red shifts with increasing electron-donating ability of the heterocyclic groups and with increasing the 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 ion 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 **11C** < **12C** < **13C**. The results suggests that donor-acceptor type interaction between hetrocyclic groups and the dicyano or the oxydicarbonyl group plays an important role in determining the position of absorption band.

2.4 Solvent Effect

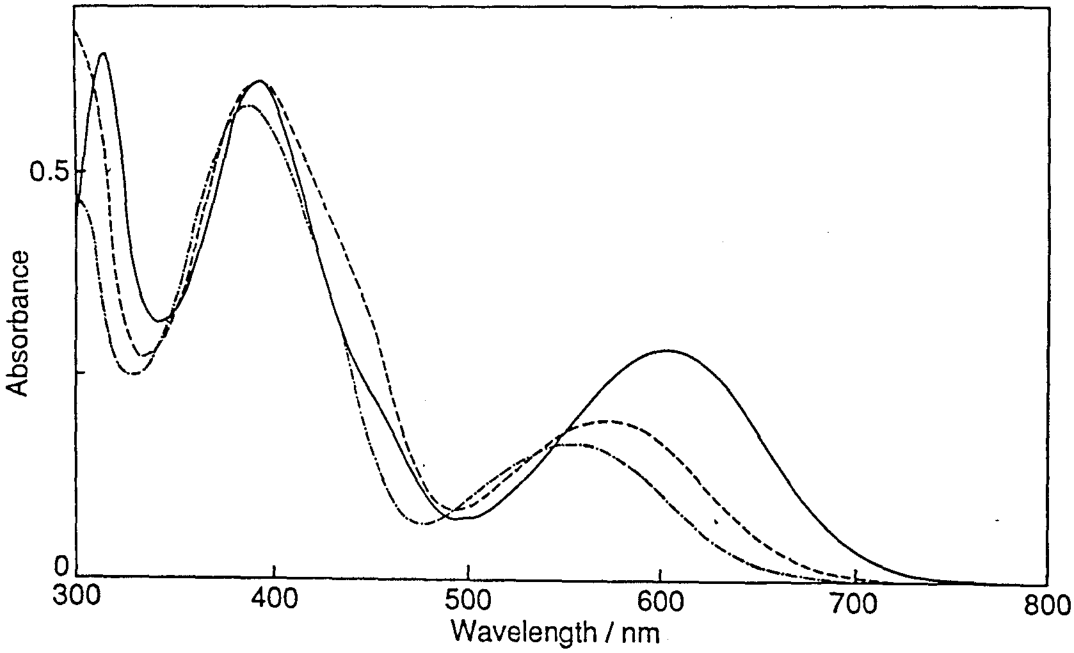


Figure 2-3. Absorption spectra of **13Z** + **13C** (total concentration, 1.0x10^{-4} mol dm^{-3}) at the photostationary state in hexane (-·-), in benzene (---) and in HMPA (—). Conversion from the open-ring to the closed-ring form was 39% in hexane, 44% in benzene, and 75% in HMPA. The absorption bands longer than 500 nm and at around 400 nm are ascribable to **13C**, and shoulders at around 450 nm to **13Z**.

The absorption spectrum of the closed-ring forms is dependent on the polarity of the medium. Figure 2-3 shows the absorption spectra of **13Z** + **13C** at the photostationary state in several solvents. The absorption maximum of **13C** 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-S_1 band of **13C** has charge-transfer character and the S_1 is polar state. The invariance of the second band of **13C** with solvent polarity suggests that the band is due to the transition to a less polar excited state.

2.6 Thermal Stability of Closed-ring Forms

Figure 2-4 illustrates the thermal stability of the closed-ring forms, **11C**, **12C**, **13C**, **14C**, and **15C** at 80°C in the dark. The value of A/Ao was plotted against storage time, where Ao is the initial absorbance at the absorption maximum of the closed-ring forms and A the absorbance after t hours at 80°C. As seen in the Figure 2-7, the photogenerated closed-ring forms **11C**, **12C**, **14C**, and **15C** are stable, and maintain absorption intensity for more than 12h at 80°C, whereas **13Z** is thermally unstable. The absorption intensity of **13C** decreases to 75 % of the initial intensity in 12 h at 80°C.

Recently, Nakamura et al., showed that the thermal stability of the closed-ring form of symmetric diarylethene derivatives is depended 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. **13C**, is thermally unstable.

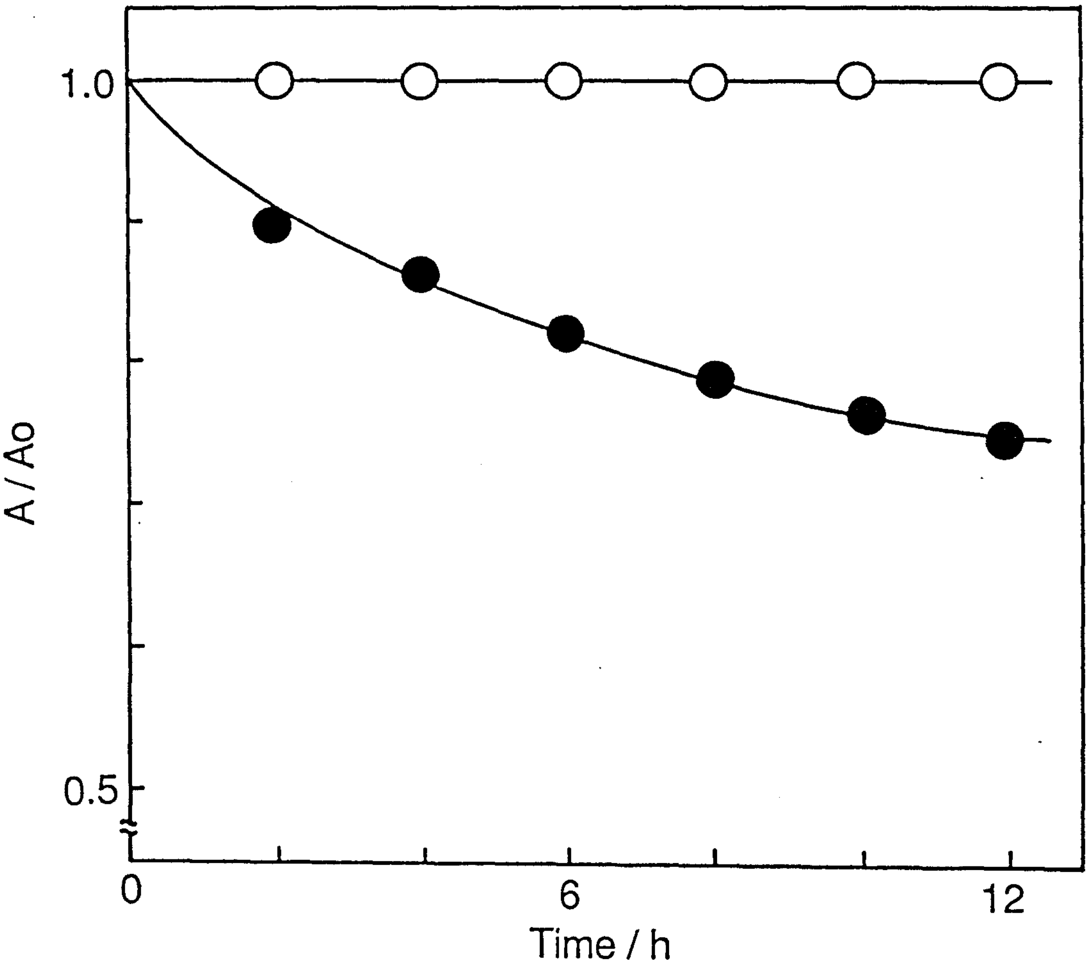


Figure 2-4. Thermal stability of the closed ring forms in benzene at 80°C in deaerated conditions. Compounds (**11C**) (○), (**12C**) (○), (**13C**) (●), (**14C**) (○), and (**15C**) (○)

2.6 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.

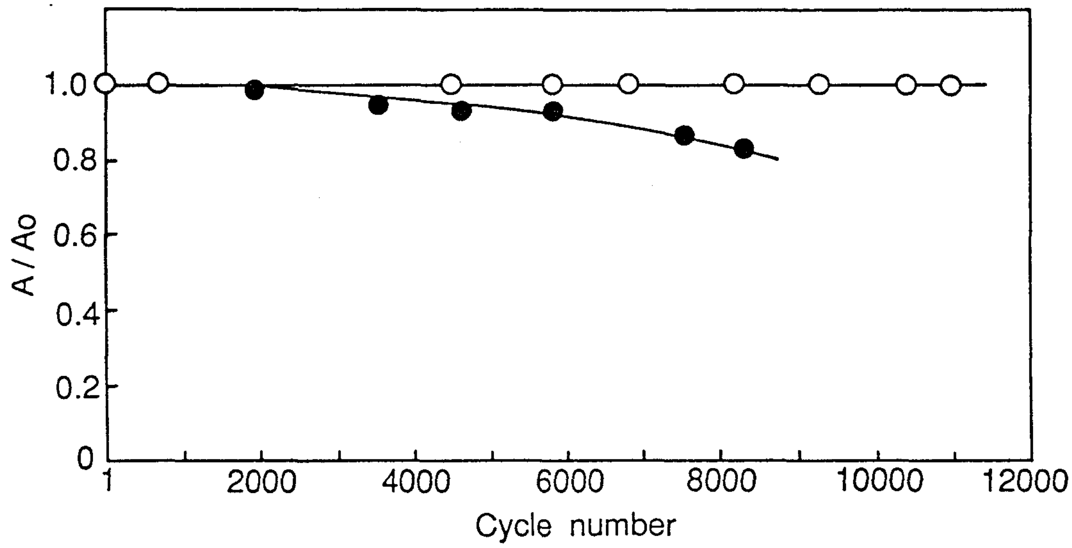


Figure 2-5 Fatigue resistant property of non-symmetric diarylethene derivatives. Compound (**11Z**) (●), (**14Z**) (○).

A benzene solution containing the compounds **11Z** and **14Z** (in a thin cell with light pass length of 2 mm) was irradiated alternatively with 436 nm and 546 nm light, and 491 nm and 633 nm light, respectively, in the absence of air. The irradiation times were long enough for the compound to convert to the photostationary state and to the complete photobleached state, respectively.

As seen in the Figure 2-5, the compounds **11Z** and **14Z** are fatigue resistant. In **11Z**, the intensity decreases to 80% of the first cycle after 8,000 times coloration / decoloration cycles. The absorption intensity of the closed-ring forms of compound **14Z** did not show any detectable decrease and remained constant even after 10,000 coloration / decoloration cycles.

2.7 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-III **Quantum Yields for Cyclization and Ring-opening Reaction of Non-symmetric Diarylethenes.**

	excitation wavelength / nm	solvent	
		benzene	hexane
11Z → 11C	405	0.08	a
14Z → 14C	405	0.06	0.15
	450	a	0.14
	490	0.05	a
11Z → 11C	546	0.56	a
14Z → 14C	546	0.40	a

aNot measured

Table 2-II summarizes the results. The cyclization quantum yields of **11Z** and **14C** in benzene are below 0.1. The value is similar to those observed for **7Z** and **4Z**. The cyclization quantum yield was strongly dependent on the polarity of solvents. The quantum yield in hexane is 3 times lager 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 **4Z** 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 state is responsible to the photocyclization.

The ring-opening quantum yields of **11C** and **14C** in benzene are quite high. The value of **14C** is 3 times lager than the value observed for the ring-opening reaction of **4C**. 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.

2.8 Experimental

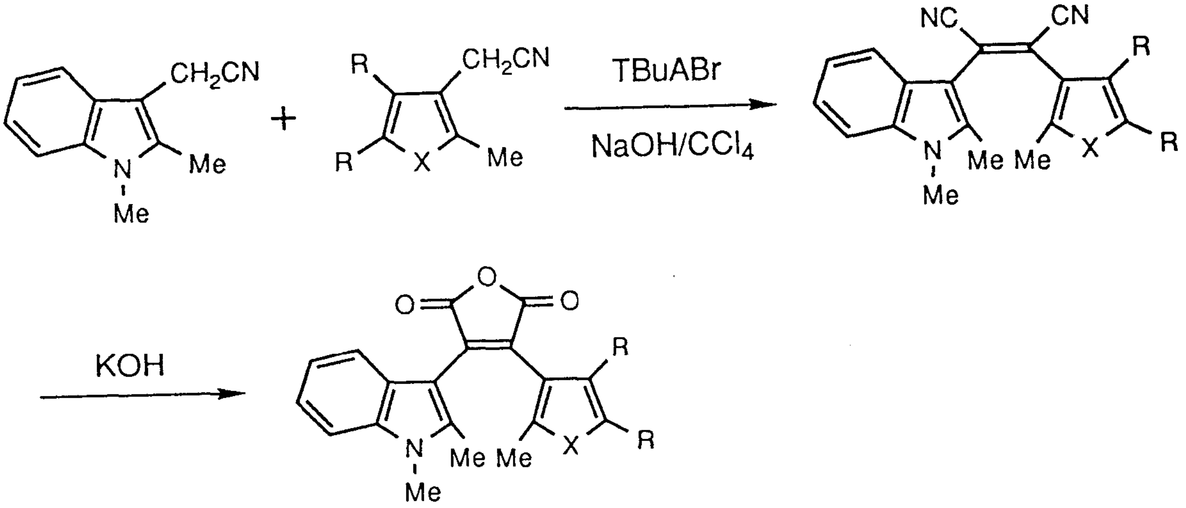
^{1}H NMR spectra (360MHz) were recorded in $CDCl_3$ with a Bruker WN-360 instrument. All chemical shifts were expressed in parts per million (ppm) downfield from internal tetramethylsilane. Mass spectra and elemental analyses were performed in the Material Analysis Center of Osaka University. High-performance liquid chromatography (HPLC) was carried out on a JASCO 800 instrument. For isolation and purification of samples, a column (10x250 mm) packed with silica gel (JASCO, Fine SIL-5) was used.

Absorption spectra were measured with a spectrophotometer (Shimadzu MPS-200). Photoisomerization were 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 (Jobin Yvon H10-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-dimethylindole5 3-(cyanomethyl)-2,4,5-trimethylthiophene,[4] 3-(cyanomethyl)-2methylbenzo[b]thiophene8 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-(2,3,5-trimethyl-3-thienyl)ethene (11Z). To a mixed solution of CCl_4 (1.58mL) and benzene (1.58mL) containing 0.07g (0.22mmol) of tetrabutylammonium bromide, 0.5g (2.7mmol) of 3-(cyanomethyl)-1,2-dimethylindole and 0.45g (2.7mmol) of 3-(cyanomethyl)-2,4,5-trimethylthiophene was added at 40°C 1.09mL of 50% NaOH aqueous solution. The reaction mixture was heated to 45°C for 3h, 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 mixture of **11Z** and its trans form, **3Z** and its trans form, and **4Z** and its trans form were separated by column chromatography on silica gel (30 um) using benzene as an eluent. The trans and cis mixtures of the indolyl-thienylethene derivatives was dissolved into acetonitrile and exposed to ultraviolet-visible light ($\lambda > 350$ 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 **11C** was also isolated by HPLC (5 µm silica gel / benzene). HPLC retention times (flow rate 1 mL/min): **11Z** 14.9 min, the trans form 7.9 min, **5C** 20.0 min. The cis form was further purified by recrystallization from a hexane-ether mixture yielding 0.1g (10%) of **11Z.** **11Z**: IR (KBr, cm^{-1}) 2240; ^{1}H NMR 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, 6.8Hz, 1H), 7.21 (dd, *J*=8.1, 6.8Hz, 1H), 7.25 (d, *J*=8.1 Hz, 1H), 7.39 (d, *J*=8.1Hz, 1H); MS, m/e (relative intensity) 345 (M$^+$, 100), 330 (45), 315 (17); HRMS, m/e 345.1320, calcd for $C_{21}H_{19}N_3S_1$ 345.1299. Anal. Calcd for $C_{21}H_{19}N_3S_1$: 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 (12Z). 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 1mL/min): **12Z** 13.0 min, the trans form 7.2 min, **12C** 9.3 min. **12Z**: IR (KBr, cm^{-1}) 2240; ^{1}H NMR 2.00 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 3.55 (s, 3H, CH_3), 6.99-7.70 (m, 8H); MS, m/e (relative intensity) 367 (M$^+$, 100); HRMS, m/e 367,1116, calcd for $C_{23}H_{17}N_3S_1$ 367.1142. Anal. Calcd for $C_{23}H_{17}N_3S_1$: 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 (13Z). This was prepared by a coupling reaction of 3-(cyanomethyl)-1,2-dimethylindole and 3-(cyanomethyl)-1,2,4,5-trimethyl-4-pyrrole, and isolated in 5 % yield. HPLC retention times (silica gel / benzene, flow rate 1 mL / min): **13Z** 19.8 min, the trans form 10.0 min. Isolation of **13C** by the silica gel column was failed. The conversion from **13Z** to **13C** at the photostationary state was estimated by measuring the HPLC intensity change of **13Z** by photoirradiation. **13Z**: IR (KBr, cm^{-1}) 2240; ^{1}H-NMR 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, 6.8Hz, 1H), 7.16 (dd, *J*=8.2,6.8Hz, 1H), 7.22 (d, *J*=8.2Hz, 1H), 7.27 (d, *J*=9.0Hz, 1H); MS, m/e (relative intensity) 342 (M^+, 100), 327 (57), 312 (12); HRMS, m/e 342.1875, calcd for $C_{22}H_{22}N_4$ 342.1843. Anal. Calcd for $C_{22}H_{22}N_4$: C, 77.16; H, 6.48; 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 (14Z). Compound **11Z** (630mg, 1.8 mmol) and ethylene glycol monoethyl ether (1.53mL) were added to a solution of 0.73g of potassium hydroxide in 1.53mL 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 **14Z** was isolated by HPLC (5 μm silica gel / benzene) and purified by recrystallization from a ether-hexane mixture, yielding 110 mg (16%) of **14Z**. HPLC retention times (flow rate 1 mL / min): **14Z** 8.8 min, **14C** 13.4 min. **14Z**: IR (KBr, cm^{-1}) 1760, 1820; ^{1}H NMR 1.87 (s, 3H, CH3), 1.95 (s, 3H, CH3), 2.17 (s, 3H, CH3), 2.25 (s, 3H, CH3), 3.70 (s, 3H, CH3), 7.03 (dd, J=8.1, 7.2 Hz, 1H), 7.13 (d, J=8.1Hz, 1H), 7.19 (dd, J=8.1, 7.2Hz, 1H), 7.26 (d, J=8.1Hz, 1H); MS, m/e (relative intensity) 365 (M^+, 100), 650 (8); HRMS, m/e 365.1103, calcd for $C_{21}H_{19}N_1O_3S_1$ 365.1085. Anal. Calcd for $C_{21}H_{19}N_1O_3S_1$: 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-benzothienyl)maleic Anhydride (15Z). This was prepared by the hydrolysis of **12Z.** HPLC retention tomes (flow rate 1mL / min): **15Z** 7.8 min, **15C** 5.6 min. **15Z**: IR (KBr, cm^{-1}) 1760; ^1H NMR 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/e 387 (M^+); HRMS, m/e 387.0954, calcd for $C_{23}H_{17}N_1O_3S_1$ 387.0928. Anal. Calcd for $C_{23}H_{17}N_1O_3S_1$: 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.

2.9 References

(1) a)H. Durr, *Angew. Chem.*, **101**, 427 (1989).
  b)H. Durr, H. Bouas-Laurent, Eds. Photochromism-Molecues and Systems, Elsevier Amsterdam, 1990.

(2) a)Y. Hirschberg, *J. Am. Chem. Soc.*, **78**, 2304 (1956).
  b)P. J. Darcy, H. G. Heller, P. J. Strydom, and J. Whittall, J. *Chem. Soc. Perkin Trans 1*, **1981**, 202.
  c)H. G. Heller, and J. R. Langan, *J. Chem. Soc., Perkin Trans* 2, **1981**, 341.
  d)H. G. Heller, *IEEE Proc.* **130**, 209 (1983), and references cited in.
  e)H. Suzuki, A. Tomoda, M. Ishizuka, A. Kaneko, M. Furui, and R. Matsushima, *Bull. Chem. Soc. Jpn.*, **62**, 3968 (1989), and references cited in.
  f)Y. Yokoyama, T. Iwai, N. Kera, I. Hitomi, and Y. Kurita, *Chem Lett.* **1990**, 263, and references cited in.
  g)M. Irie, Jpn. *J. Appl. Phys.*, **28-3**, 215 (1989).

(3) A. E. J. Wilson, *Phys. Technol*., **15**, 232 (1984).

(4) M. Irie and M. Mohri, *J. Org. Chem*., **53**, 803 (1990).

(5) Y. Nakayama, K. Hayashi, and M. Irie, *J. Org. Chem*., **53**, 6136 (1988).

(6) S. Nakamura and M. Irie, *J. Org. Chem*., **53**, 6136 (1988).

(7) R. M. Kellogg, M. B. Groen, and H. Wynberg, *J. Org. Chem*., **32**, 3093 (1967).

(8) K. Uchida, Y. Nakayama, and M. Irie, *Bull. Chem. Soc. Jpn*., **63** 1311, 1990.

(9) K. Sayo and M. Irie, Unpublished result.

(10) D. M. Young and C. F. Allene, *Org. Synth*., II, 219 (1943).

(11) W. Herz, R. L. Settine, J. Org. Chem., **24**, 201 (1959).

(12) M. A. Goldberg, E. P. Ordas, and G. Carsch, *J. Am. Chem. Soc*. **69**, 260 (1947).

CHAPTER 3

Photoreaction of Diarylethene Derivatives with Imidazo[1,2-*a*]pyridine Rings

3.1 Introduction

As mentioned in chapter 1, diarylethene derivatives with selenophene rings[1] have promising for optical data storage media, nevertheless they still lack several indispensable conditions, such as diode laser sensitivity and non-destructive read out capability. The absorption edges of the closed-ring forms are less than 720 nm. Replacement of the selenophene rings with indole ones, which have high electron-donating ability, shifted the absorption maximum of the closed-ring forms as much as 60 nm, and the absorption edge of the acid anhydride derivative reached 840 nm.[1] Although the compound has the sensitivity at the diode laser wavelength ($780 < \lambda < 830$ nm), the conversion of the open-ring to the closed-ring form in the photostationary state under irradiation with 490 nm light is less than a few percent, and the thermal stability of the closed-ring form is insufficient.

This chapter describes that a symmetrical diarylethene derivative with two imidazo[1,2-*a*]pyridine rings, which have higher electron-donating ability than indole ring, and a non-symmetrical one with imidazo[1,2-*a*]pyridine ring on one end and thiophene ring on the other end were synthesized in attempting to shift the absorption bands to longer wavelengths.

3.2 Symmetrical Diarylethene Derivatives

3.2.1 Absorption Spectra

A diarylethene derivative with two imidazo[1,2-*a*]pyridine rings was prepared by a self-coupling reaction[2] of two 3-(cyanomethyl)-2-methylimidazo[1,2-*a*]pyridine. The mixture of *Z* and *E* forms was dissolved in benzene and exposed to 490 nm light to convert the *E* form to the *Z* form. The *Z* form was separated from the mixture of *Z* and *E* forms by HPLC and purified by crystallization from a hexane-ether mixture.

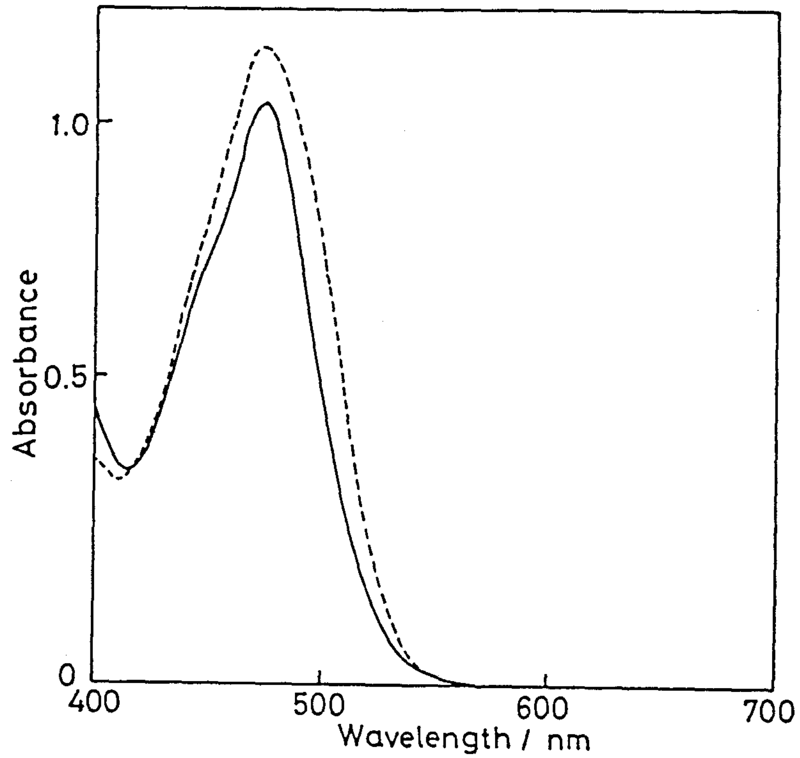
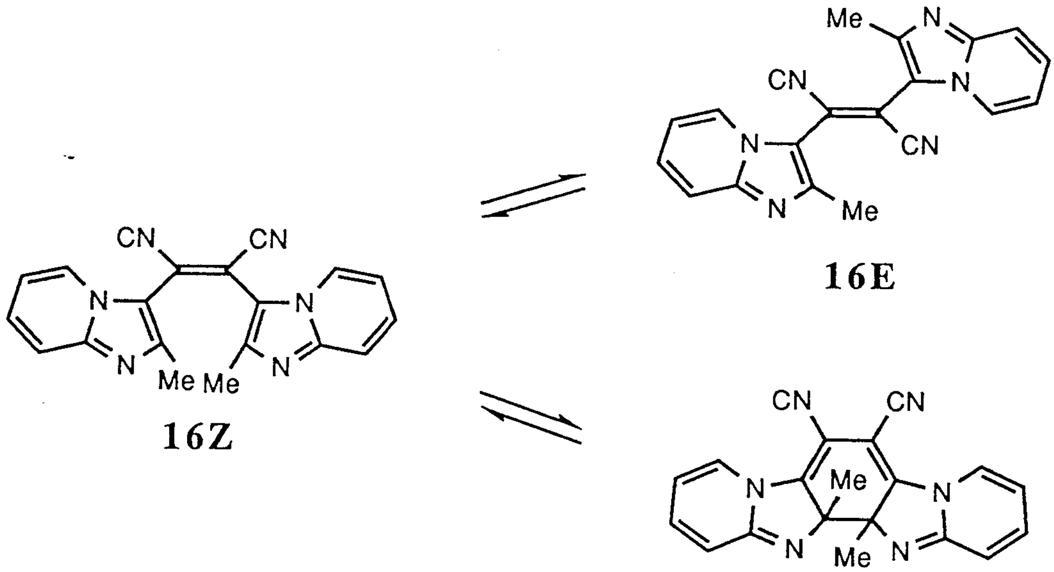


Figure 3-1. Absorption spectra of **16Z** (6.8×10^{-5} mol dm^{-3}) (—) before photoirradiation and (- - -) in the photostationary state under irradiation with 475 nm light.



16Z

16E

16C

The *Z* form, **16Z**, was irradiated in benzene (6.8x10^{-5} mol dm^{-3}) in the presence of air with 475 nm light, and the reaction was followed by absorption and HPLC measurements (silica gel column, 1:1 chloroform-acetone). Figure 3-1 shows the spectra of **16Z** before and after photoirradiation with 475 nm light in the dilute benzene solution. The absorption maximum of **16Z** was observed at 475 nm and the molar absorption coefficient was 15,000 dm^{3}mol^{-1} cm^{-1}. The absorption maximum shifts to a longer wavelength as much as 40 nm in comparison with *Z* form of 1,2-dicyano-1,2-bis(1,2-dimethy-3-lindolyl)ethene (**7Z**).[1] Upon irradiation with 475 nm light, the intensity of the absorption in 420-550 nm region increases. Any new absorption was not observed at longer wavelengths. It was inferred from the NMR measurement that the absorption intensity change is due to the *Z*-*E* isomerization from **16Z** to **16E**. Under the photostationary state, the *Z* to *E* ratio was estimated by HPLC to be **16E**/**16Z**=33/67. A ring-closure reaction was not discerned even after prolonged irradiation with lights of 420-550 nm wavelengths.

3.2.2 ^{1}H NMR Spectra

Figure 3-2 a-1 and b show the 270-MHz ^{1}H NMR spectra of methyl protons of **16Z** in $CDCl_3$ before and after photoirradiation with 475 nm light in benzene solution, respectively. Figure 3-2 a-2 shows the signals of methyl protons of **16Z** in $CDCl_3$ at -25°C. At this temperature, the sharp singlet splits into two peaks at 2.19 and 2.21 ppm. The two methyl protons indicate the existence of two atropisomers in the compound **16Z**. A similar line-shape change was reported for dibenzothiophene derivatives.[3] One conformer has two imidazo[1,2-*a*]pyridine rings in mirror symmetry (in parallel orientation) and the other C_2 symmetry (in anti-parallel orientation).

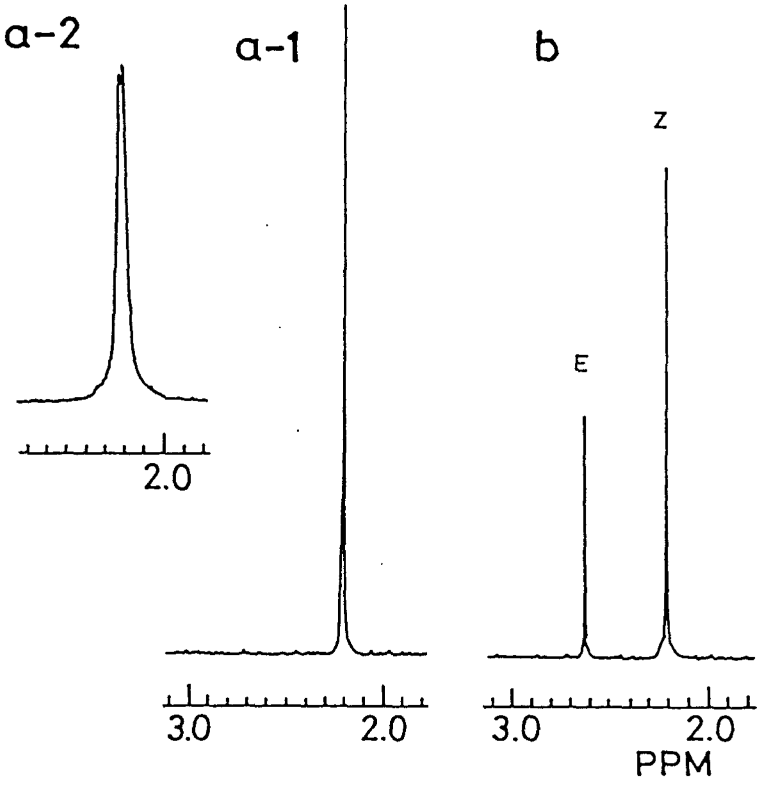
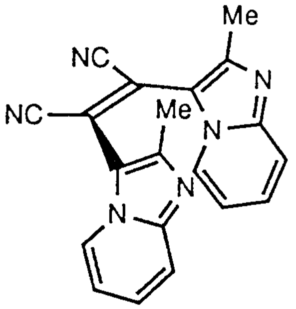
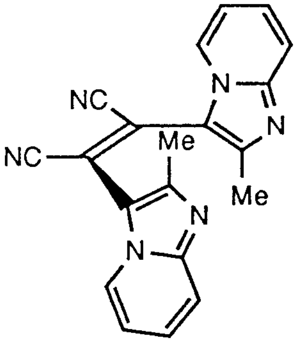


Figure 3-2. ^{1}H NMR spectra (360-MHz) of **16Z** in $CDCl_3$: (a-1) before irradiation at room temperature; (a-2) at - 25°C; (b) after irradiation with 475 nm light.



parallel
orientation



anti-parallel
orientation

After photoirradiation a new signal appeared at 2.63 ppm (fig. 3-2). The absence of other signals except the one line indicates that the signal is ascribable to the *E* form and the ring-closure reaction is negligible. The assignment was further confirmed by the ^{13}C NMR measurement. Any signal ascribable to sp^3 carbons was not discerned after photoirradiation.

3.3 Non-symmetrical Diarylethene Derivatives

3.3.1 Absorption Spectra

A diarylethene derivative with imidazo[1,2-*a*]pyridine ring on one end and thiophene ring on the other end was prepared by a cross-coupling reaction[4] of 3-(cyanomethyl)-2-methylimidazo[1,2-*a*]pyridine[5] and 4-(cyanomethyl)-2,3,5-trimethylthiophene.[2] The mixture of *E* and *Z* forms was dissolved in benzene and exposed to the light longer than 450 nm. The irradiation is expected to converted the *E* form to the *Z* form. The *Z* form was separated by HPLC and purified by crystallization from a hexane-ether mixture.

The *Z* form, **17Z**, was irradiated in benzene (1.25×10^{-4} M) in the presence of air with 450 nm light, and the reaction was followed by absorption and HPLC measurement (silica gel column, chloroform).

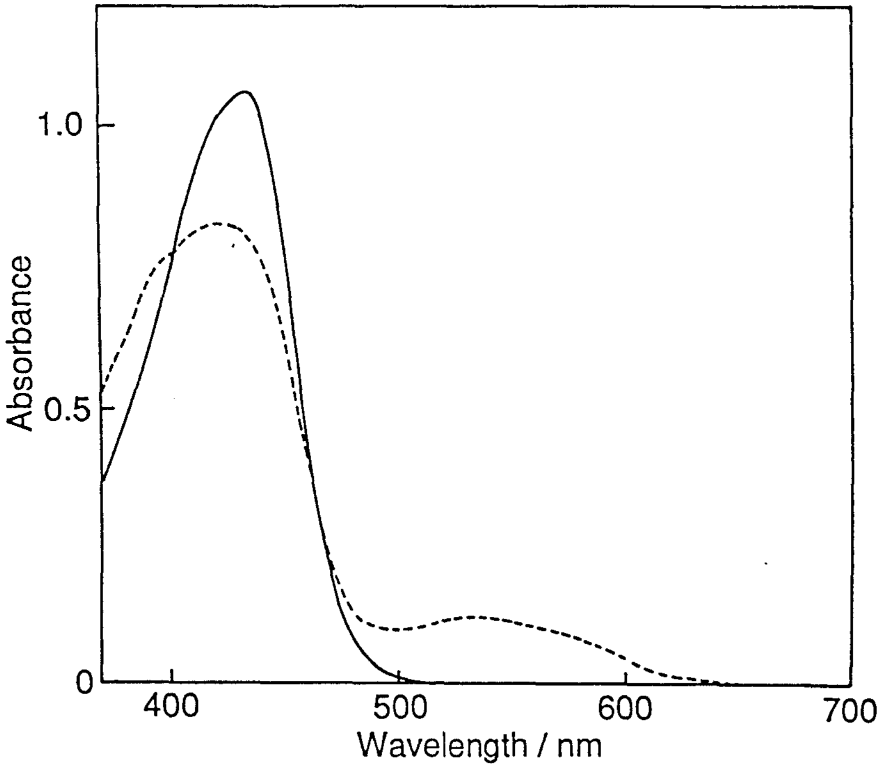


Figure 3-3. Absorption spectra of **17E** (1.25×10^{-4} mol dm^{-3}) (—) before photoirradiation and (- - -) in the photostationary state under irradiation with 450 nm light.

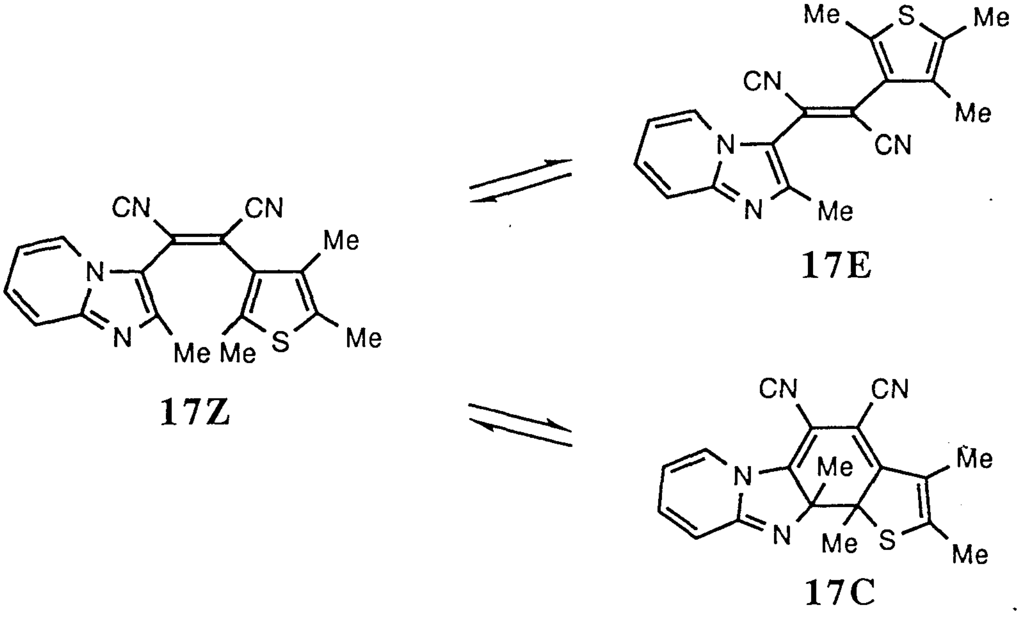


Figure 3-3 shows the spectra of **17Z** before and after photoirradiation with 450 nm light. Irradiation of the yellow benzene solution with 450 nm light led to the formation of a red solution, in which a visible absorption was observed at 535 nm and a shoulder at 580 nm. The visible absorption was ascribed to the closed-ring form, **17C**, from the NMR measurement.

The replacement of one of imidazo[1,2-*a*]pyridine rings with a thiophene ring enables the diarylethene to undergo the ring-closure reaction. The absorption maximum wavelength is 23 nm longer than that of the dithienylethene derivative.[3] The conversion from **17Z** to **17C** in the photostationary state under irradiation with 450 nm light was estimated to be 30% by HPLC analysis.

The irradiation was also accompanied with a *Z*-*E* isomerization from **17Z** to **17E**. In the photostationary state, the contents of each isomer were estimated by HPLC as **17Z** (40%), **17C** (30%) and **17E** (30%). The yield of the closed-ring form depended on the irradiation wavelength. When the solution was irradiated with 425 nm light, the conversion was decreased to less than 15%.

3.3.2 ^{1}H NMR Spectra

The ^{1}H NMR spectra (360-MHz) of **17Z** in C_6D_6 before photoirradiation and after irradiation with 450 nm light are shown in Fig.3-4 a and b. Before photoirradiation, 4 lines were observed at 1.41, 1.50, 1.62, and 1.96 ppm, which are assigned to the **17Z** form. Upon irradiation with 450 nm light, new 8 lines appeared at 1.43, 1.56, 1.83, 1.87, 2.00, 2.20, and 2.62 ppm along with a decrease of the intensity of the 4 lines. The eight lines observed after photoirradiation indicate the co-existence of three isomers, **17Z**, **17C** and **17E**. The assignments are shown in the figure.

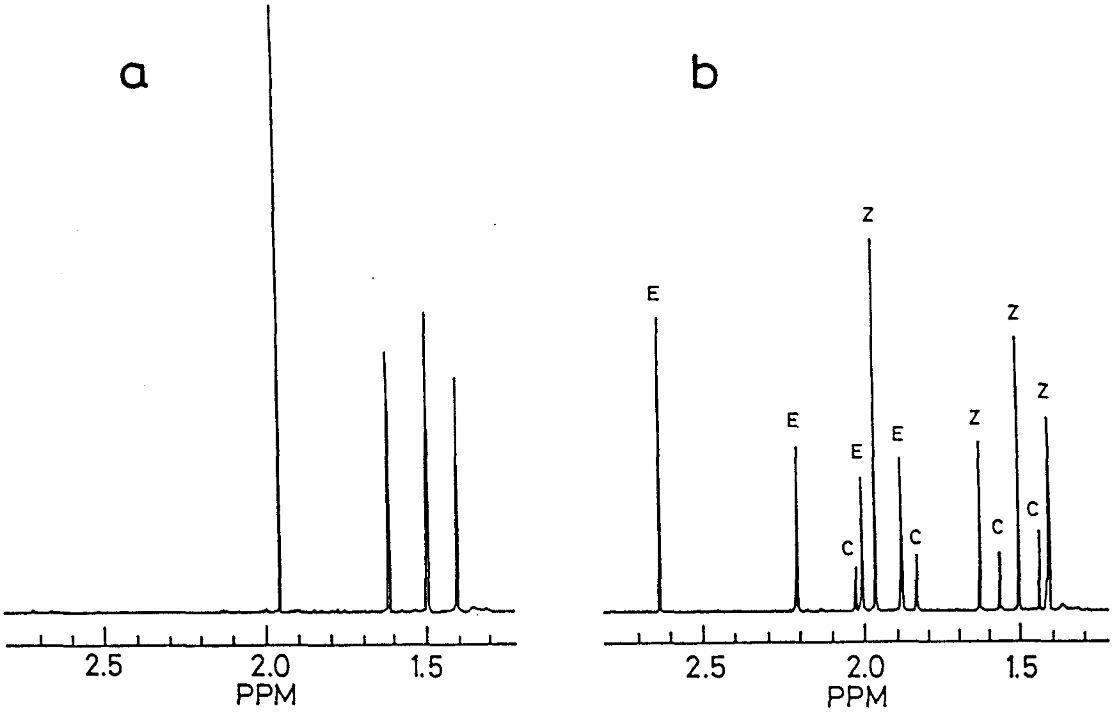


Figure 3-4. ^{1}H NMR spectra (360-MHz) of **17Z** in C_6D_6: (a) before irradiation; (b) after irradiation with 450 nm light.

Figure 3-5 a and b show the 68-MHz ^{13}C NMR spectra of methyl carbon of **17** in $CDCl_3$ before photoirradiation and after irradiation with 450 nm light, respectively. Before photoirradiation, 4 lines were observed at 12.86, 13.09, 14.32, and 14.77 ppm, which are due to **17Z** form. Upon irradiation, new 8 lines appeared at 12.57, 13.12, 13.19, 13.92, 14.11, 14.74, 16.17, and 17.01. These 8 lines may be classified into two groups (13.12, 13.19, 14.74, and 16.17 ppm) and (12.57, 13.92, 14.11, and 17.01 ppm). The former is assigned to the *E* form, **17E**, and the latter to the closed-ring form, **17C**. The other two lines at 29.69 and 53.88 ppm observed after photoirradiation indicate the existence of sp^3 carbon after photoirradiation. This result confirms that closed-ring form, **17C**, was formed by photoirradiation.

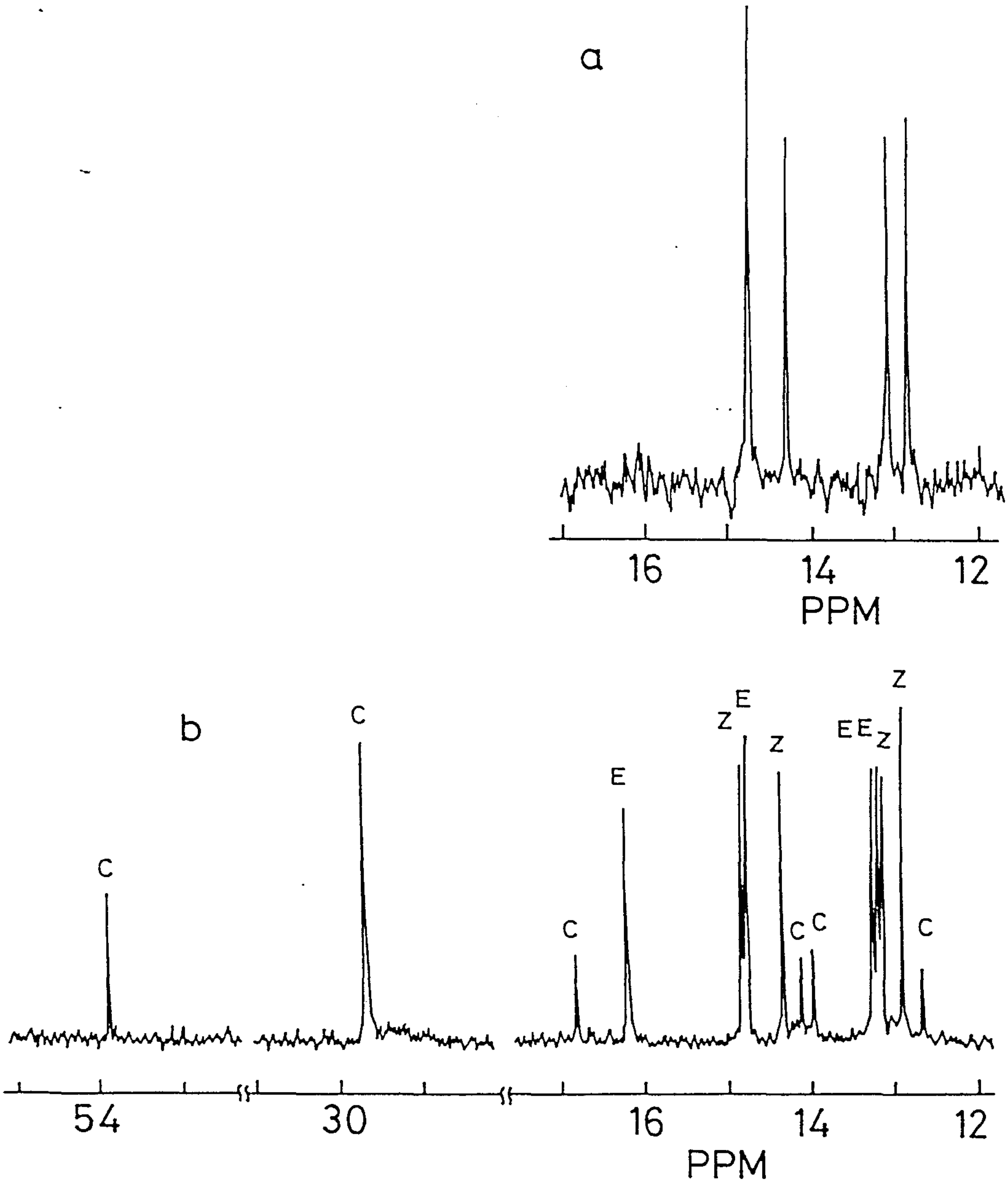


Figure 3-5. ^{13}C NMR spectra (68-MHz) of **17Z** in $CDCl_3$; (a) before irradiation; (b) after irradiation with 450 nm light.

The photogenerated closed-ring form, **17C** was thermally stable. Any changes of the absorption intensity at 535 nm was not observed even at 80°C. The absorption intensity remained constant for more than 24h, at 80°C.

3.4 Quantum Yield

Quantum yields for the cyclization and the ring-opening reactions of **17** were determined in benzene solution in the presence of air at 25°C. Table 3-I summarized the results. The cyclization quantum yield of the imidazo[1,2-a]pyridine-thiophene derivative **17Z** at 405 nm was 0.06, which is similar value observed for 1,2-dicyano-1,2-bis(1,2-dimethyl-3-indolyl)-ethene[1] and 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride[2]. The quantum yield of the ring-opening reaction at 546 nm was obtained to be close to unity. The value is 8 times larger than that observed for dithienylethene derivative.[2] The large value is possibly due to the steric strain of closed-ring form, especially the strain of the imidazo[1,2-a]pyridine ring.[1,3]

Table 3-I. Quantum Yields for Ring-Closure and Ring-Opening Reactions in Benzene Solution

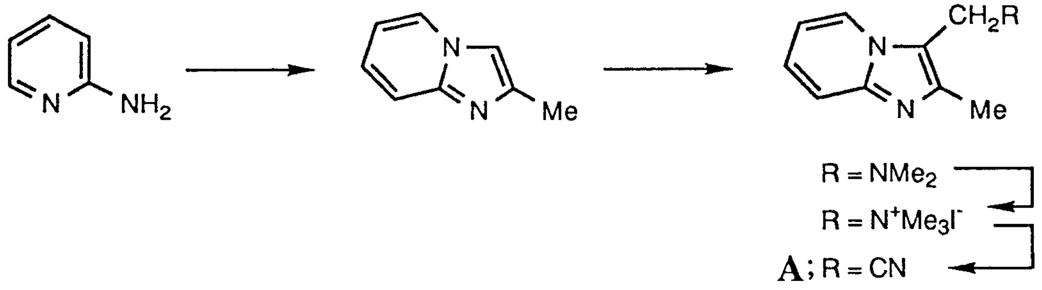
Reaction	Excitation wavelength / nm	Quantum yield
17Z → **17C**	405	0.06
17C → **17Z**	546	1.00

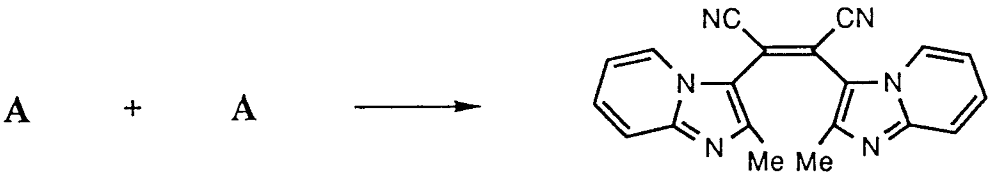
3.5 Experimental

General Method

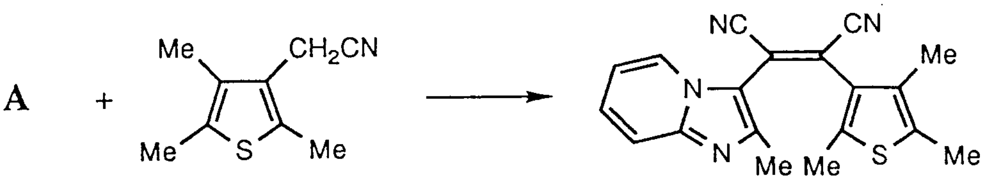
IR spectra were measured with a Perkin Elmer Model 1618 spectrophotometer using KBr disks. ^1H NMR spectra (360 MHz) were recorded with a Bruker WN-360 spectrometer. Samples were measured in C_6D_6 or $CDCl_3$ using the tetramethylsilane (0 ppm) as an internal standard. ^{13}C NMR spectra (68 MHz) were recorded on JOEL JNM-GSX-270 spectrometer using $CDCl_3$ as the solvent with tetramethylsilane as an internal standard. Mass spectra and elemental analyses were performed in the Material Analysis Center of Osaka University. Melting points were determined by using a Gallenkamp melting points apparatus (MP-41). HPLC analysis was carried out on a JASCO 800 system. Stainless-steel columns (length, 250 mm; i.d., 4.6mm, for analytical purposes, length, 250mm; i.d., 10.0mm, for preparative purposes) were slurry packed using silica gel (Fine SIL-5). Absorption spectra were measured with a Shimadzu MPS-200 instrument. Photoirradiation was carried out with a EWIG XC-500 Xenon lamp. The wavelength of light was selected by passing the light through a monochrometer (Jobin Yvon H10-UV). Quantum yield 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) and the light intensity was measured with a photometer (international Light IL1700).

Materials





16Z



17Z

2-Methylimidazo[1,2-*a*]pyridine.[9] A mixture of 11.3g (0.12 mol) of 2-aminopyridine and 11.1g (0.12 mol) of chloroacetone in 120 mL of ethanol was heated under reflux for 20h. The ethanol was removed by evaporation, and the residual material was dissolved in 100 mL of water. The aqueous solution was extracted with dichloromethane (4x20 mL). The dichloromethane extracts were washed with water (20 mL). The aqueous solutions were combined, and adjusted to pH11.5-12 by the addition of 50% sodium hydroxide (ca.12 mL). The basic aqueous solution was extracted with dichloromethane (3X20 mL). The dichloromethane extracts were combined and washed with water (20 mL). The aqueous solution was cooled with ice and was adjusted to pH7 by the addition of 6N hydrochloric acid (ca. 20 mL). After the solution was allowed to stand overnight, the solid that precipitated was isolated by filtration, washed with water and dried. Recrystallization from dichloromethane-methanol gave 5.6g (0.042 mol) (35%) of 2-methylimidazo[1,2-*a*]pyridine. bp 120°C / 0.35mmHg. ^{1}H NMR ($CDCl_3$), 2.45 (s, 3H, $ArCH_3$), 7.00 (dt, *J*=1.1 and 6.8Hz, 1H), 7.09 (ddd, *J*=1.4, 6.8 and 9.4Hz, 1H), 7.32 (s, 1H), 7.49 (d, *J*=9.4Hz, 1H), 8.01 (dt, *J*=6.5 and 1.1Hz, 1H).

3-[(Dimethylamino)methyl]-2-methylimidazo[1,2-*a*] pyridine. A mixture of 5.6g (0.042 mol) of 2-methylimidazo[1,2-*a*]pyridine 4.45g (0.055 mol) of dimethylamine hydrochloride and 1.64g (0.055 mol) of paraformaldehyde in 40 mL of methanol was heated under reflux for 1.5 h with stirring. Thereafter, the mixture was evaporated. Upon cooling to ambient temperature, the reaction mixture was acidified by the addition of concentrated hydrochloric acid (ca.4mL) and stirred for 18h. The solid was isolated by filtration and washed with methanol and finally ether. After drying the solid was dissolved in 52 mL of hot water. The aqueous solution was adjusted to pH 11-12 by adding 50% sodium hydroxide. The mixture was cooled to 0°C and extracted with dichloromethane (3X20 mL). The extracts were combined and washed with aqueous NaCl solution (20 mL). The dichloromethane was removed under reduced pressure to give an oil of 3-[(dimethylamino)methyl]-2-methylimidazo[1,2-*a*]pyridine 7.9g (0.042 mol) (100%). This material was used without further purification. ^{1}H NMR ($CDCl_3$), 2.22 (s, 6H, NCH_3), 2.44 (s, 3H, $ArCH_3$), 3.65 (s, 2H, $ArCH_2N$), 6.75 (td, *J*=7.0 and 1.1Hz, 1H), 7.13 (ddd, *J*=1.1, 6.8 and 9.0Hz, 1H), 7.49 (d, *J*=9.0Hz, 1H), 8.17 (d, *J*=7.2Hz, 1H).

2-Methyl-3-[(trimethylammonio)methyl]imidazo[1,2-*a*] pyridine Iodide. 3-[(Dimethylamino)methyl]-2-methylimidazo[1,2-*a*]pyridine 7.9g (0.042 mol) was dissolved in 58 mL of ethanol. To the ethanol solution at 0°C was added dropwise with stirring 6.6g (0.047 mol) of methyl iodide. The reaction mixture was stirred at ambient temperature overnight. The solid that formed was isolated by filtration and washed with ethanol (10 mL) and finally ether (35 mL). After drying, 14.0g (0.042 mol) (100%) of 2-methyl-3-[(trimethylammonio)methyl]imidazo[1,2-*a*]pyridine iodide was obtained.

3-(Cyanomethyl)-2-methylimidazo[1,2-*a*]pyridine. A mixture of 14.0g (0.042 mol) of 2-methyl-3-[(trimethylammonio) methyl]imidazo[1,2-*a*]pyridine iodide and 2.16 g (0.044 mol) of sodium cyanide in 120 mL of N,N-dimethylformamide was heated on a steam bath for 1 h with stirring. The mixture was poured into ice / water (360 mL) and stirred for 1h. The solid was isolated by filtration, washed with water, and dried. Recrystallization from acetonitrile gave 2.4g (0.014 mol)(33 %) of 3-(cyanomethyl)-2-methylimidazo[1,2-*a*]pyridine. IR (KBr) 2246 cm^{-1}; Mass spectrum (EI) m/e (relative intensity), 171(M^+,100), 156(M^+-Me,29), 145(M^+-CN, 37); ^{1}H NMR ($CDCl_3$), 2.47 (s, 3H, $ArCH_3$), 3.98 (s, 2H, $ArCH_2CN$), 6.91 (t, *J*=6.8Hz, 1H) 7.24 (t, *J*=7.9Hz, 1H), 7.57 (d, *J*=9.0Hz, 1H), 7.94 (d, *J*=6.8Hz, 1H); mp 157-9°C; Found : C, 70.31; H, 5.23; N, 24.46%. Calcd for $C_{10}H_9N_3$: C, 70.16; H, 5.30; N, 24.54%.

1,2-Dicyano-1,2-bis(2-methylimidazo[1,2-a]pyridin-3-yl) ethene (16Z). To 1.1 mL of 50% NaOH aqueous solution containing tetrabutylammonium bromide (0.07 g, 0.2 mmol) was added over a period 0.5h a mixture of 3-(cyanomethyl)-2-methylimidazo[1,2-*a*]pyridine (462 mg, 2.7 mmol) and carbon tetrachloride (0.79 mL, 8 mmol), benzene 0.79 mL and acetone 1.0 mL at 40°C. The solution was stirred for 3h at 45°C. Then the reaction mixture was poured into water. The aqueous solution was extracted with $CHCl_3$ and the organic phase was dried over $MgSO_4$. After the solvent was removed, the mixture of *Z* and *E* form was obtained in 79% yield by column chromatography on silica gel. The mixture of *Z* and *E* forms was dissolved in benzene and then exposed to 490 nm light. The *Z* form was separated from the solution by HPLC and then purified by recrystallization from a hexane-ether mixture. mp 250-2°C; IR (KBr) 2211 cm^{-1}; ^1H NMR[6] ($CDCl_3$), 2.21 (s, 6H, $ArCH_3$), 6.75 (td, *J*=6.8 and 1.3Hz, 2H), 7.27 (ddd, *J*=1.4, 6.5 and 8.3 Hz, 2H), 7.53 (d, *J*=9.7 Hz 2H), 7.54 (d, *J*=6.8Hz, 2H); ^1H NMR (C_6D_6), 2.02 (s, 6H), 5.77 (td, *J*=6.8 and 1.4Hz, 2H), 6.31 (ddd, *J*=8.6, 7.2 and 1.4Hz, 2H), 6.71 (d, *J*=6.8Hz, 2H), 7.07 (d, *J*=8.6Hz, 2H); mass spectrum (EI) m/e (relative intensity) 338 (M^+, 100) 323 (M^+-Me, 8); Found : C, 70.93; H,3.98; N, 24.83%. Calcd for $C_{20}H_{14}N_6$: C,70.99; H,4.17; N,24.84%.

1,2-Dicyano-1-(2-methylimidazo[1,2-*a*]pyridin-3-yl)-2-(2,3,5-trimethylthiophen-3-yl)ethene (17Z). This was prepared by a cross-coupling reaction of 3-(cyanomethyl)-2-methylimidazo[1,2-*a*]pyridine and 4-(cyanomethyl)-2,3,5-

trimethylthiophene[2] and isolated in 18% yield, mp>300°C; IR (KBr) 2215 cm^{-1}; ^1H NMR[7] ($CDCl_3$), 1.79 (s, 6H), 2.00 (s, 6H), 2.12 (s, 6H), 2.18 (s, 6H), 6.88 (td, *J*=6.8 and 1.4 Hz, 2H), 7.39 (ddd, *J*=1.4, 6.8 and 9.0Hz, 2H), 7.58 (d, *J*=8.6Hz, 2H), 7.87 (td, *J*=6.8 and 1.1Hz, 2H); ^1H NMR (C_6D_6), 1.41 (s, 6H), 1.50 (s, 6H), 1.62 (s, 6H), 1.96 (s, 6H), 6.05 (td, *J*=6.8 and 1.1Hz, 2H), 6.49 (ddd, *J*=7.6, 6.8 and 1.1Hz, 2H), 7.22 (d, *J*=7.6Hz, 2H), 7.33 (d, *J*=6.8Hz, 2H); ^{13}C NMR ($CDCl_3$), 12.86, 13.09, 14.32, 14.77, 113.00, 113.75, 114.383, 114.529, 116.01, 117.38, 119.59, 124.08, 127.15, 128.85, 130.26, 132.55, 137.69, 146.88, 147.95; mass spectrum (EI) m/e (relative intensity), 332(M^+,100), 317(M^+-Me,63); Found : C, 68.58; H, 4.96; N, 16.71%. Calcd for $C_{19}H_{16}N_4S_1$: C, 68.65; H, 4.85; N, 16.85%.

3.6 References and Notes

(1) Y. Nakayama, K. Hayashi, M. Irie, *J. Org. Chem.*, **55**, 2592 (1990).

(2) M. Irie, M. Mohri, *J. Org. Chem.*, **53**, 803.(1988).

(3) K. Uchida, Y. Nakayama, M. Irie, *Bull. Chem. Soc. Jpn.*, **63**, 1311 (1990).

(4) Y. Nakayama, K. Hayashi, M. Irie, *Bull. Chem. Soc. Jpn.*, (1991) in press.

(5) J. J. Kaminski, J. A. Bristol, S. Puchalski, R. G. Lovey, A. J. Elliott, H. Guzik, D. M. Solomon, D. J. Conn, M. S. Domalski, S. Wong, E. H. Gold, J. F. Long, P. J. S. Chiu, M. Steinberg, A. T. Mcphail, *J. Med. Chem.*, **28**, 876 (1985).

(6) **16E** form: ^1H NMR ($CDCl_3$) 2.21 (s, 3H), 2.35 (s, 3H), 2.52 (s, 3H), 7.05 (td, *J*=6.8 and 1.1 Hz, 1H), 7.43 (ddd, *J*=10.1, 6.8 and 1.1 Hz, 1H), 7.69 (d, *J*=10.1 Hz, 1H), 8.20 (d, *J*=6.8 Hz, 1H); ^1H NMR (C_6D_6) 1.87 (s, 3H), 2.00 (s, 2H), 2.20 (s, 2H), 2.62 (s, 2H), 6.08 (td, *J*=7.2 and 1.4 Hz, 2H), 6.54 (ddd, *J*=7.9,

7.2 and 1.4 Hz, 2H), 7.33 (d, *J*=7.2 Hz, 2H), 7,71 (d, *J*=7.9 Hz, 2H)

(7) **17E** form: ^{1}H NMR ($CDCl_3$) 2.63 (s, 6H), 7.07 (td, *J*=6.8 and 1.1 Hz, 2H), 7.46 (ddd, *J*=1.4, 6.8 and 9.0 Hz, 2H), 7.72 (d, *J*=9.0 Hz, 2H), 8.30 (d, *J*=6.5 Hz, 2H); ^{1}H NMR (C_6D_6) 2.56 (s, 6H), 6.10 (td, *J*=1.4 and 6.8 Hz, 2H), 6.55 (ddd, *J*=1.4, 7.0, and 8.8 Hz, 2H), 7.33 (d, *J*=8.6 Hz, 2H), 7.79 (d, *J*=7.2 Hz, 2H)

CHAPTER 4

Color Change of 2,3-Bis(2,3,4,5,6-Pentafluorophenyl)-3-[2,3,5,6-tetrafluoro-4-(cyanomethyl)phenyl]acrylonitrile by the Addition of Amines

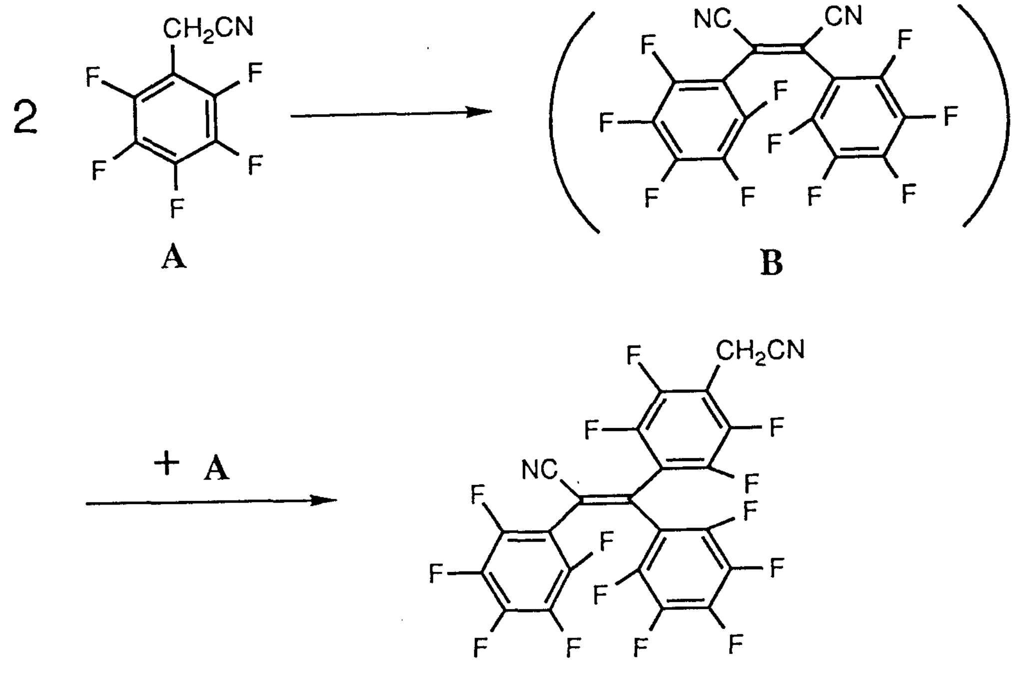
4.1 Introduction

Molecular complexes of macrocyclic polyethers have been utilized in various directions, such as selective extraction, separation and transport of guest molecules, phase transfer catalyses or models of vital systems.[1-6] In spite of such explosive development of host-guest complexes, much less attention has been paid to ion-pair complexes.[7,8]

The ion-pair formation in less polar solvents via an intermolecular proton transfer is also expected to be useful for recognition of ionizable molecules, such as amines. In the present study, we studied structural requirements for the ion-pair formation by using 2,3-bis(2,3,4,5,6-pentafluorophenyl)-3-[2,3,5,6-tetrafluoro-4-(cyanomethyl)phenyl]acrylonitrile (**18E**) as a proton donating molecule. The compound **18E** formed ion-pair complexes with various amines in organic solvents along with a brilliant red coloration. The ion-pair formation depends on the structure of the amines and the nature of the solvents. The association constants (K_a) for the formation of ion-pair complexes between **18E** and various amines have been determined to reveal what kind of properties control the complex formation.

4.2 Synthesis

2,3-Bis(2,3,4,5,6-pentafluorophenyl)-3-[2,3,5,6-tetrafluoro-4-(cyanomethyl)phenyl]acrylonitrile (**18E**) was prepared by a self-coupling reaction of two 2,3,4,5,6-pentafluoro-1-(cyanomethyl)-benzenes (**A**) followed by replacement of a cyano group by another molecule of **A**. The reaction process is presumed as follows.[9,10]



A

B

18E

Isolation of the intermediate **B** was failed. The self coupling product **B** and the active fluorine atom at 4 position of **A** is considered to react easily each other to produce **18E**.[11,12] Compound **18E** was obtained as a the mixture of *E*/*Z* isomer. The mixture was dissolved in benzene and exposed to ultraviolet light (>280 nm). The *Z* form was efficiently converted to *E* form by the irradiation. The *E* form was isolated by high-performance liquid chromatography and purified by recrystallization from a benzene-hexane mixture. The structure of the product was determined on the basis of mass spectra, NMR spectra, and material analysis whose data are presented in the experimental section.

4.3 Formation of ion-pair complexes and absorption spectral changes

The absorption spectra of 2,3-bis(2,3,4,5-pentafluorophenyl)-3-[2,3,5,6-tetrafluoro-4-(cyanomethyl)phenyl]acrylonitrile (**18E**) in 300-650 nm region were measured at 20°C in benzene solution in the absence and presence of various amines.

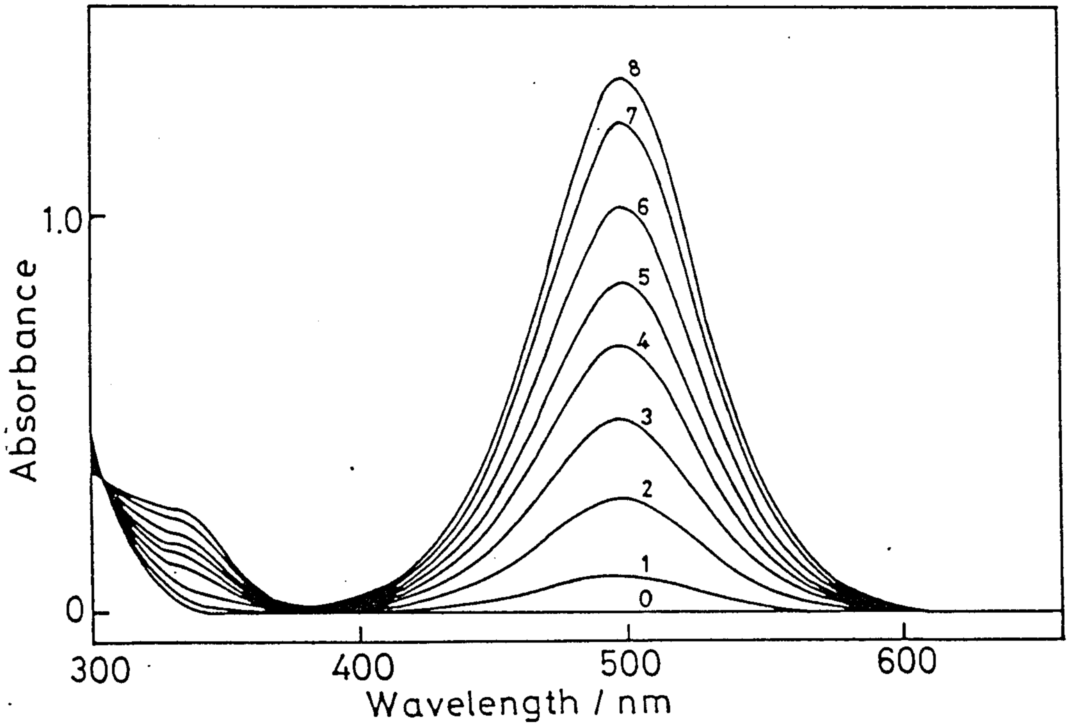
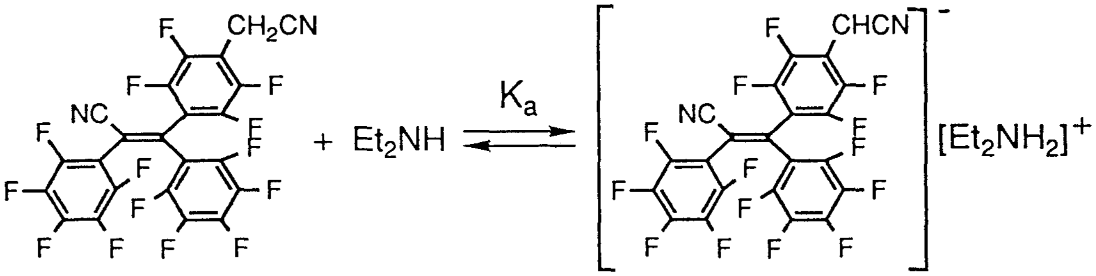


Figure 4-1. Absorption spectra of **18E**-Et_2NH system in benzene. [**18E**]=3.4x10^{-5}mol dm^{-3}, 0: [Et_2NH]=0mol dm^{-3}; 1: [Et_2NH]=3.4x10^{-2} mol dm^{-3}; 2: [Et_2NH]=6.8x10^{-2} mol dm^{-3}; 3: [Et_2NH]=1.0x10^{-1} mol dm^{-3}; 4: [Et_2NH]=1.4x10^{-1} mol dm^{-3}; 5: [Et_2NH]=1.7x10^{-1} mol dm^{-3}; 6: [Et_2NH]=2.4x10^{-1} mol dm^{-3}; 7: [Et_2NH]=3.4x10^{-1} mol dm^{-3}; 8: [Et_2NH]=5.1x10^{-1} mol dm^{-3}.

Figure 4-1 shows a typical absorption spectral change of a dilute benzene solution of **18E** ($[\mathbf{18E}]_0=3.4\times10^{-5}$ mol dm^{-3}) by the addition of Et_2NH. The benzene solution turns red in the presence of small amount of Et_2NH. An absorption maxima is observed at about 500 nm. The maximum gradually shifts to 503 nm with increasing the amount of Et_2NH.[13,14] An isosbestic point is observed at 305 nm in the absorption spectrum.

The absorption spectrum maintained a constant intensity, so far the solution being stored in the dark at room temperature. The addition of H^+ (H_2SO_4, HCl) to the reaction mixture decreased the absorption intensity and the initial colorless solution was obtained. The absorption spectrum of 2,3,4,5,6-pentafluoro-1-(cyanomethyl)-benzene **A** was not affected by the addition of amines. These results suggest that the absorption observed at around 500 nm is ascribable to the ion-pair complex of **18E** with the amine by proton transfer, as shown below.



Bazavluk et al[8] reported a similar ion-pair formation for heptafluoro-2-naphthol and aliphatic amines system in undecane.

4.4 Association Constants Measurements

The association constants and the molar absorption coefficients of the complexes of **18E** with various amines ($[\mathbf{18E}]_0=2.2\times10^{-5}$ mol dm^{-3}) are shown in Table 4-I. These values were determined by using the U.V./vis spectrophotometric method.[15,16]

Table 4-I. **Association constants and molar absorption coefficients of complexes of 18E with amines in benzene solution.**

Entry	Amine	K_a mol dm^{-3}	$10^4\varepsilon$ dm^{3}mol^{-1}cm^{-1}
1	n-PrNH$_2$	10.0	4.2
2	n-BuNH$_2$	7.8	4.3
3	cyclohexylamine	11.1	4.5
4	Et$_2$NH	22.0	4.2
5	n-Pr$_2$NH	4.0	4.5
6	i-Pr$_2$NH	6.8	4.5
7	n-Bu$_2$NH	4.3	4.4
8	Et$_3$N	3.4	3.8
9	aniline	n.d.	n.d.
10	pyridine	n.d.	n.d.
11	Et$_2$NH[a)]	30.0	4.7
12	Et$_2$NH[b)]	13.6	4.7
13	n-Pr$_2$NH[a)]	13.4	4.8

a) in CH_2Cl_2. b) in hexane.

Aromatic amines, such as aniline and pyridine do not make ion-pair complexes with **18E**. This is possibly due to the low basicity. The association constant has a tendency to decrease in the order: primary > secondary > tertiary amines. This order agrees with the observation for the charge transfer complex formations.[17,18] Primary amines, n-PrNH$_2$ and n-BuNH$_2$, have large association constants, which are around twice the corresponding secondary amines. Among the secondary amines, Et$_2$NH has an extraordinary large association value, which is 5 times larger than the values of n-Pr$_2$NH and n-Bu$_2$NH. A simple steric hindrance explanation[21,22] that large alkyl groups prohibit the close approach of the amines to **18E** can not be applied to the present system, because the large association constant is observed for cyclohexylamine and the value of Et$_3$N is close to the values of n-Pr$_2$NH and n-Bu$_2$NH. The large value for Et$_2$NH and cyclohexylamine suggests that **18E** has a site which recognizes the difference in the shape between cyclohexylamine and *n*-Pr_2NH, and the site favorably accepts Et_2NH. Such a steric requirement to allow close approach is considered to play an important role in the proton transfer process.

The association value is also dependent on the solvent polarity. The value increases with the increases in the solvent polarity. It is worthwhile to note that along with the increases in the association constants the difference in the values between Et_2NH and *n*-Pr_2NH decreases in polar CH_2Cl_2. In polar solvents, large stabilization in the ion-pair states possibly diminishes the energy barrier difference in the recognition process.

4.5 Coloration Mechanism

In order to confirm the ion-pair mechanism for the coloration, we measured conductivity[19] of CH_2Cl_2 solution containing **18E** and Et_2NH.

Figure 4-2 shows the conductivity change of a dilute CH_2Cl_2 solution of **18E** by the addition of Et_2NH (a) and the change of the optical density at λmax (510 nm) of the same solution (b). Addition of Et_2NH increased the absorption intensity along with the increases in the conductivity. Although slight increase in the conductivity is observed even in the absence of **18E**, the value is much smaller than the value in the presence of **18E**. Both the conductivity value and the intensity of the absorbance showed a saturation behavior above 0.3 mol dm^{-3} of amine. The good correlation between the conductivity and the absorption intensity clearly indicates that the coloration is due to the formation of ion-pair between **18E** and the amine.

Product analysis also supported the ion-pair formation. The colored form was quenched in CH_2Cl_2 by deuterium chloride and then **3** was analyzed. One of the cyano methyl protons of **18E** was found to be replaced by a deuterium atom.[22]

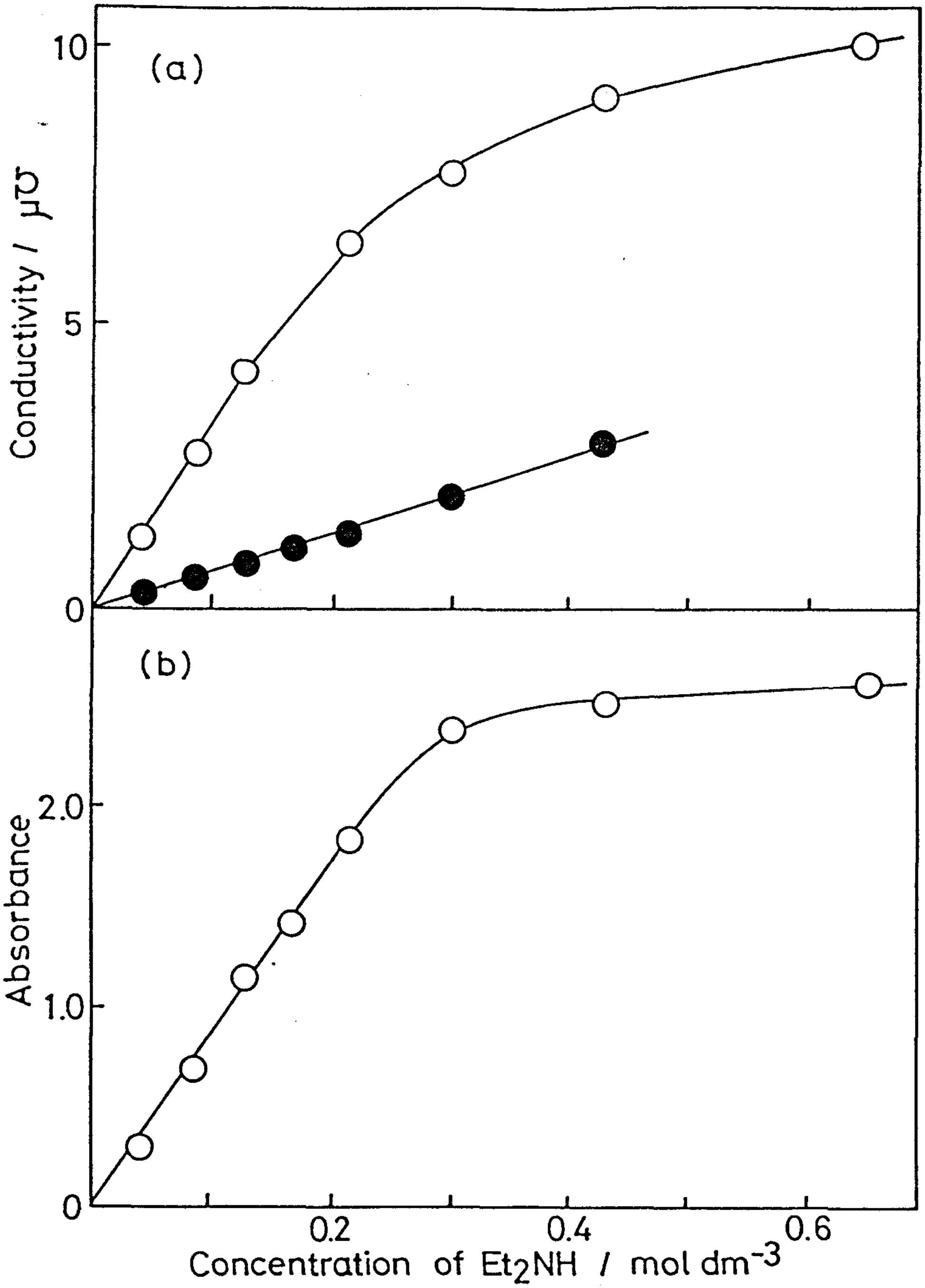


Figure 4-2. (a) Conductivity change of **18E**-Et_2NH system in CH_2Cl_2. (○), with **18E** (4.3×10^{-5} mol dm^{-3}); (●), without **18E**. (b) Absorption intensity change of **18E**-Et_2NH system in CH_2Cl_2 at 510 nm.

This is unambiguous evidence that a proton is transferred from CH_2CN group of **18E** to the amine.[23-25]

The compound **18E** also interacts with many compounds with basic nature to produce red colored solutions, such as ethers, THF, or alcohols. When **18E** in solid state was placed in the THF vapor, the solid turned to red. By evacuating THF from the solid, the solid again returned to colorless state. It was possible to repeat the coloration/decoloration cycles many times.

4.6 Experimental

General Methods

IR spectra were measured with a Shimadzu IR-408 spectrophotometer. ^1H NMR spectra (360MHz) and ^{13}C NMR spectra (91 MHz) were recorded in $CDCl_3$ with Bruker WN-360 instrument. All chemical shifts are reported in parts per million (δ) downfield from internal tetramethylsilane. ^{19}F NMR were recorded on a Bruker WN-360 instrument at 339MHz and are reported in ppm from internal trichlorofluoromethane. Mass spectra and elemental analyses were performed in the Material Analysis Center of Osaka University. HPLC analysis was performed on a JASCO 800 system. Absorption spectra were measured with a Shimadzu MPS-200 instrument. Photoisomerization was performed by a mercury lamp (Ushio, 1kw), associated with filter (aqueous solution of $CuSO_4$ and Toshiba UV-28 glass filter), as a light source. Ion-pair complex formation constants (association constant) (K_a) were determined by using the U.V./vis spectrophotometric method.[15,16] K_a and molar absorption coefficients (ε) of the complexes are obtained from the plots of $[\mathbf{18E}]_0\,[A]_0/OD$ values vs $[A]_0$ values.(equation 2)

$$\frac{l\ [\mathbf{18E}]_0\,[A]_0}{OD} = \frac{1}{\varepsilon}[A]_0 + \frac{1}{\varepsilon K_a} \qquad (2)$$

In the equation, OD is the optical density of the solution and *l* is the cell width (1cm). Conductivity was measured with a autobalance universal bridge instrument (WAYNE KERR B642).

Materials

All amines were obtained commercially and were purified by distillation.

2,3,4,5,6-Pentafluoro-1-(Cyanomethyl)benzene.

(A).[26,27] NaCN (9.2g, 0.19mol) and tetrabutylammonium chloride (0.108g, 0.39mmol) was dissolved in 32.8 mL of water. To this solution was added 2,3,4,5,6-pentafluoro-1-(bromomethyl)benzene (10.0g, 38mmol) in 32.8mL of THF, and stirred for 10 min. The reaction mixture was poured into water and then the product was extracted with ether. Removal of the ether and distillation of the residual under vacuum gave 2,3,4,5,6-pentafluoro-1-(cyanomethyl)benzene in 63% yield : bp.101°C; ^{1}H NMR (CDCl$_3$), 3.71 (s); ^{13}C NMR (CDCl$_3$), 104.17-104.69, 114.38, 135.70-136.21, 139.50-139.85, 143.03-143.55, 146.83-146.94; ^{19}F NMR (CDCl$_3$), -160.73 (m, 2F), -152.51 (m, 1F), -141.65 (m, 2F); IR (KBr) 2260 cm^{-1} (-CN); MS (EI) m/e (relative intensity) 207 (M$^+$, 100), 188 (M$^+$-F, 35), 181 (M$^+$-CN, 28); Found : C, 46.40; H, 0.97; N, 6.76; F, 45.87%. Calcd for $C_8H_2N_1F_5$: C, 46.64; H, 0.87; N, 6.52; F, 45.75%.

2,3-Bis[2,3,4,5,6-Pentafluorophenyl]-3-[2,3,5,6-tetrafluoro-4-(Cyanomethyl)phenyl]acrylonitrile.

(18E).[9,10] To 2.9mL of 50% NaOH aqueous solution containing tetrabutylammonium bromide (0.195g, 0.6mmol) was added, over a period 0.5h a mixture of 2,3,4,5,6-pentafluoro-1-(cyanomethyl)-benzene (A) 3g (14.5mmol) and CCl$_4$ 2.25mL (23.3mmol) at 40°C. The solution was stirred for 1.5h at 45°C. Then, the reaction mixture was poured into water. The aqueous solution was extracted with $CHCl_3$, and the organic phase was dried over $MgSO_4$. After the solvent was removed, the mixture of *E* and *Z* forms of **18E** was obtained in 4.7% yield by column chromatography on silica gel using THF/hexane (1:1) and then benzene as the eluting solvent. The *Z*/*E* mixture was dissolved in benzene and exposed to ultraviolet light (>280 nm). The *Z* form converted to *E* form by the irradiation. The *E* form was separated by HPLC[28] and then purified by recrystallization from a benzene-hexane mixture. The *E* form was obtained in 4% yield., mp.135°C: ^1H NMR ($CDCl_3$), 5.83 (s); ^{19}F NMR ($CDCl_3$)[29], -159.60 (m, 2F), -159.28 (m, 2F), -149.84 (m, 1F), -148.90 (m, 1F), -139.75 (m, 2F), -139.46 (m, 2F), -138.80 (m, 2F), -134.18 (m, 2F); MS (EI) m/e (relative intensity), 572 (M^+, 100), 405 (M^+-C_6F_5, 14); IR (KBr) 2240 cm^{-1} (-CN); Found : C, 48.02; H, 0.52; N, 4.94%, Calcd for $C_{23}H_2N_2F_{14}$: C, 48.27: H, 0.35; N, 4.90; F, 46.48%.

4.7 References and Notes

(1) R. M. Izatt and J. J. Christensen, Eds.; Academic Press: New York, **1978**, 1.

(2) F. Voegtle, *Top. Curr. Chem.*, **98**, 1 (1981)., **101**, 1 (1982).

(3) M. Hiraoka, Crown Compounds; Elsevier: New York,**1982**, 1.

(4) G. W. Gokel and S. H. Korzeniowski, Macrocyclic Polyether Synthsis; Spring-Verlag: New York, **1982**, 1.

(5) F. Voegtle and E. Weber, *Top. Curr. Chem.*, **121**, 1 (1984).

(6) R. M. Izatt, J. S. Bradshow, S. A. Nielsen, J. D. Lamb J. J. Christensen and D. Sen, *Chem. Rev.*, **85**, 271 (1985).

(7) T. K. Pal, G. K. Mallik, T. Ganguly, and S. B. Banerjee, *Bull. Chem. Soc. Jpn.*, **62**, 3315 (1989).

(8) Y. A. Bazavluk, A. N. Delnov and G. S. Denisov, *Zh. Priki. Spektrosk*, **48**, 799 (1988).

(9) M. Irie and M. Mohri, *J. Org. Chem.*, **53**, 803 (1988).

(10) Y. Nakayama, K.Hayashi, and M. Irie, *J. Org. Chem.*, **55**, 2592 (1990).

(11) J. M. Birchall and R. N. Haszeldine, *J. Chem. Soc.*, **1961**, 3719.

(12) M. Zupan and B. Sket, *Isr. J. Chem.*, **17**, 92 (1978).

(13) J. A. Riddic and W. B. Bunger, Organic Solvents. Techniques of Chemistry Vol.II,3rd ed. Wily-Interscience, New York, 1970.

(14) H.Fujiwara, T.Takaba, Y.Yamazaki and Y.Sasaki, *J. Chem. Soc., Faraday Trans. 1*, **75**, 79 (1979).

(15) L. Forlani and P. E. Todesco, *J. Chem. Soc. Perkin Trans. 2*, **1980**, 313

(16) R. Foster, Organic Charge-Transfer Complexes, Academic Press, London (1969).

(17) R. Foster, *J. Chem. Soc.*,**1960**,1075.

(18) O. D. Bonner and G. B. Woolsey, *Tetrahedron*, **24**, 3625 (1968).

(19) J. O. Singh, J. D. Anunziata and J. J. Silber, *Can. J. Chem.*, **63**, 903 (1985).

(20) A. S. N. Murthy and A. P. Bhardwaj, *J. Chem. Soc., Faraday Trans. 2*, **78**, 1811 (1982).

(21) M. F. Mayahi and H. A. Hussain, *J. Indian. Chem. Soc.*, L, **1973**, 34.

(22) The determination was performed by mass spectra.

(23) S. Bruckenstein and A. Saito, *J. Am. Chem. Soc.*, **87**, 698 (1965).

(24) E. A. Yerger and G. M. Barrow, *J. Am. Chem. Soc.*, **77**, 4474 (1955).

(25) G. M. Barrow, *J. Am. Chem. Soc.*, **78**, 5802 (1956)

(26) K. Fukunaga, *Yuki gosei kagaku Kyokai Shi*, **33**, 774 (1975).

(27) R. Filler and S. M. Woods, *Org. Syn.*, **57**, 80 (1977).

(28) Conditions of HPLC analysis is as follows: Column JASCO Fine SIL (silica gel) 4.6x250 mm for analytical purposes: Elution, benzene: Flow rate, 1 mL: retention time: **18E**, 4.3 min and **18Z**, 5.3 min: Column JASCO Fine SIL (silica gel) 10.0x250 mm for preparative purposes.

(29) **18Z**, ^{19}F NMR ($CDCl_3$), -159.25 (m, 2F), -159.10 (m, 2F), -149.60 (m, 1F), -147.96 (m, 1F), -140.05 (m, 2F), -138.37 (m, 2F) -138.12 (m, 2F), -135.78 (m, 2F).

CONCLUSION

The aim of the present research was to study the syntheses and the characterizations of new photochromic diarylethene derivatives for rewritable optical data storage media.

The important results mentioned in each chapter of this thesis are summarized as follows.

Chapter 1 is concerned with a symmetrical diarylethene derivatives, such as diselenenyl, diindolyl derivatives. Diarylethene derivatives with selenophene or indole were synthesized. The dicyano and maleic anhydride derivatives with selenophene rings showed a thermally irreversible photochromic reaction with a relatively high quantum yield. The conversion of the dicyano derivative with selenophene to the closed-ring form was obtained to be 87% under irradiation with 313 nm light. Replacement of the selenophene rings with indole ones shifted the absorption maximum by over 55 nm to longer wavelengths. The maleic anhydride derivative with methoxy groups had the absorption tail extending to 840 nm. The very high quantum yield was observed for the ring-opening reaction of the dicyano derivative. The difference in thermal stability between the diarylethenes with selenophene and indole rings was interpreted by the difference in aromatic stabilization energy of the two rings rather than a steric effect.

In chapter 2 is dealt new non-symmetrical diarylethene derivatives. 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 underwent thermally irreversible photochromic reactions. Although these compounds still are not sensitive to wavelength of diode laser, both the open-ring and closed-ring forms have absorption bands in the visible region, and the cyclization / ring-opening reactions of the compounds were induced by Ar ion (488 nm) and He-Ne (633 nm) lasers. The coloration / decoloration (ring closure / opening) cycles were able to be repeated more than 10,000 times with keeping the adequate photochromic performance.

Chapter 3 deals with diarylethene derivatives with imidazo[1,2-*a*]pyridine rings were synthesized. The symmetric diarylethene derivatives with two imidazo[1,2-*a*]pyridine rings underwent only the *Z*-*E* photoisomerization. The ring-closure reaction was not observed. On the other hand, the non-symmetrical diarylethene derivative with imidazo[1,2-*a*]pyridine ring on one end and thiophene ring on the other end underwent both the *Z*-*E* isomerization and the ring-closure reaction. The absorption maximum showed a bathochromic shift as much as 23 nm in comparison with that of dithienyl-ethene derivative. A quantum yield close to unity was observed for the ring-opening reaction.

Chapter 4 refers to the new fluorine compound, 2,3-bis(2,3,4,5,6-pentafluorophenyl)-3-[2,3,5,6-tetrafluoro-4-(cyanomethyl)phenyl]-acrylonitrile which was synthesized by applying the synthetic method of diarylethene derivatives. A benzene solution of the compound turns into a brilliant red color by the addition of aliphatic amines. The coloration mechanism was studied by optical absorption, conductivity and product analyses. It has become apparent that ion-pair formations with the amines by proton transfer reactions were responsible for the coloration. Structural requirements of the amines for the ion-pair formation were discussed.

Several important knowledges obtained through the present investigation on the utilization of photochromic diarylethene system would open the new field of optical data storage media.

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