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Thermally Irreversible Photochromic Systems. Reversible Photocyclization of 1,2-Diselenenylethene and 1,2-Diindolylethene Derivatives

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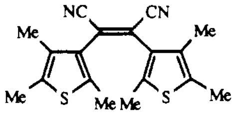
Diarylethene derivatives with selenophene or indole rings were synthesized in an attempt to obtain thermally stable photochromic compounds having the absorption bands at longer wavelengths and to confirm our previous theoretical prediction for molecular design of thermally irreversible photochromic compounds. The absorption maxima of the closed-ring forms of 2,3-bis(2,4,5-trimethyl-3-selenenyl)maleic anhydride (**6**) and 2,3-bis(1,2-dimethyl-3-indolyl)maleic anhydride (**10**) were observed at 565 and 620 nm, respectively. Although dicyano and maleic anhydride derivatives with selenophene rings showed thermally irreversible photochromic reactions with a relatively high quantum yield (0.3), the derivatives with indole rings underwent thermal ring-opening reactions in the dark. The closed-ring forms of the derivatives with selenophene rings kept the absorption intensity constant for more than 12 h at 80 °C, while the absorption intensity of the closed-ring form of the maleic anhydride derivative with indole rings decreased to 50% of the initial intensity in 3 h at 80 °C. 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, as predicted by our previous report, rather than a steric effect.

Introduction

Photochromic organic compounds have attracted a significant amount of attention because of their potential for use in optical memory media.[3,4] Although extensive work has been carried out,[5] 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, we[6] have reported a new type of thermally stable photochromic system, diarylethene derivatives having heterocyclic rings, such as 1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (1) or 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (2).



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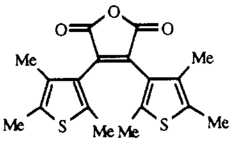

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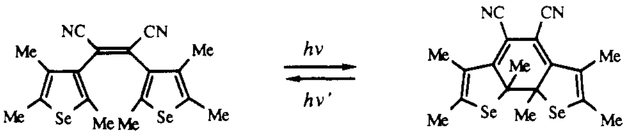
The compounds have no thermochromic property even at 300 °C and the colored closed-ring form is stable for more than 3 months at 80 °C. In addition, no detectable fatigue was observed for **2** even after 100 coloration and decoloration cycles in the absence of air. The absorption tail of the ring-closed form is, however, less than 700 nm.

In the present study, we synthesized diarylethene derivatives having selenophene or indole rings in attempting to obtain photochromic compounds having the absorption bands at longer wavelengths and to confirm our previous theoretical prediction[7] for molecular design of thermally irreversible photochromic compounds.

Results and Discussion

1. Diarylethene Derivatives with Selenophene Rings.

A cyano derivative having selenophene rings **3** was prepared by a self-coupling reaction of 2,3,5-trimethyl-4-(cyanomethyl)selenophene. The mixture of the trans and cis forms was dissolved in acetonitrile and exposed to ultraviolet light ($\lambda > 350$ nm). The irradiation converted the trans form to the cis form and led to the precipitation of the less soluble cis form, which was separated from the solution by filtration and purified by crystallization from a hexane-ether mixture. This material was used for further experiments.



3 **4**

Figure 1 shows the spectra of **3** 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 was observed. The replacement of thiophene rings[6] 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 ultraviolet absorption at 348 and 368 nm, and the initial cis form absorption was restored.

Figure 2, parts a and b, show the 360-MHz NMR spectra of methyl protons of **3** 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 cis 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 cis to trans 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 **3**. One conformer has two selenophene rings in mirror symmetry and the other C2 symmetry. The conversion of the cis form to the closed-ring form in the photostationary state was 87% based on the spectrum b.

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[1] Osaka University.
[2] Kyushu University.
[3] Hirshberg, Y. *J. Am. Chem. Soc.* **1965**, *78*, 2304.
[4] Heller, H. G. *IEEE Proc.* **1983**, *130*, 209.
[5] Brown, G. H., Ed. *Photochromism*; Wiley-Interscience: New York, 1971.
[6] Irie, M.; Mohri, M. *J. Org. Chem.* **1988**, *53*, 803.
[7] Nakamura, S.; Irie, M. *J. Org. Chem.* **1988**, *53*, 6136.

0022-3263/90/1955-2592$02.50/0

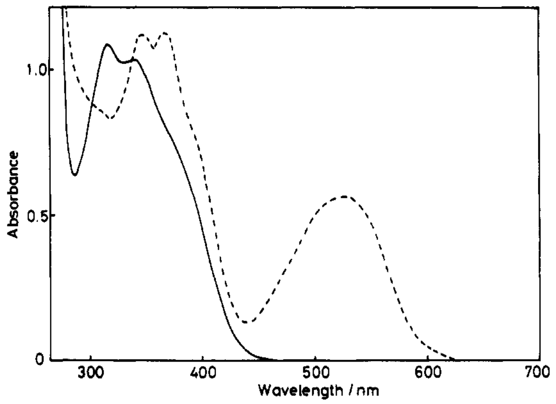


Figure 1. Absorption spectra of **3** (1.6×10^{-4} M) (—) and in the photostationary state under irradiation with 313-nm light (- -).

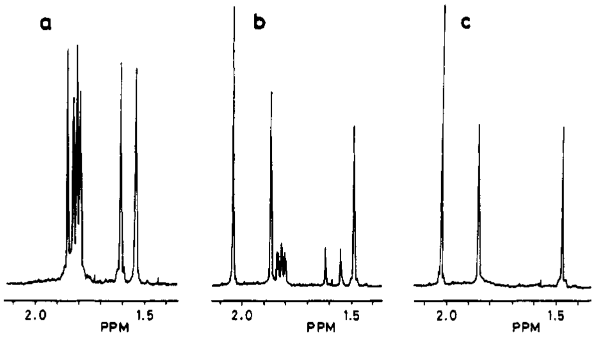
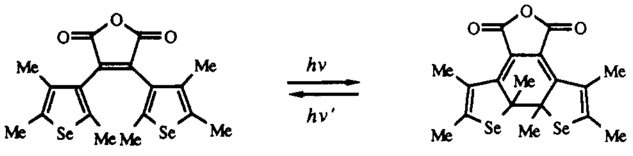


Figure 2. NMR spectra (360 MHz) of **3** in C_6D_6: (a) before irradiation; (b) in the photostationary state under irradiation with 313-nm light; (c) (b) − 0.87 (a).

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 cis to trans isomerization completely, the cyano groups were converted to an acid anhydride group. The cyano derivative was converted to the maleic anhydride derivative **5** by hydrolysis of **3** with KOH in ethylene glycol monoethyl ether–water mixture.



5 **6**

Figure 3 shows the spectra of **5** 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. The absorption maximum shifts to a longer wavelength by only 5 nm in comparison with the thiophene derivative.[6] Upon exposure of the brown solution to the visible light ($\lambda > 540$ nm), the solution again became yellow and the initial absorption was restored.

Figure 4 shows the NMR spectra of methyl protons of **5** 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 **3**. 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%.

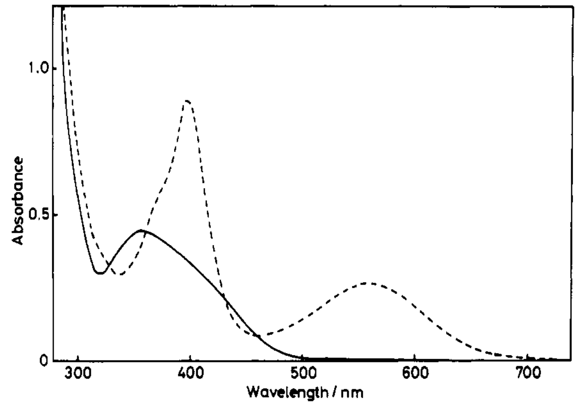


Figure 3. Absorption spectra of **5** (1.3×10^{-4} M) (—) and in the photostationary state under irradiation with 436-nm light (- -).

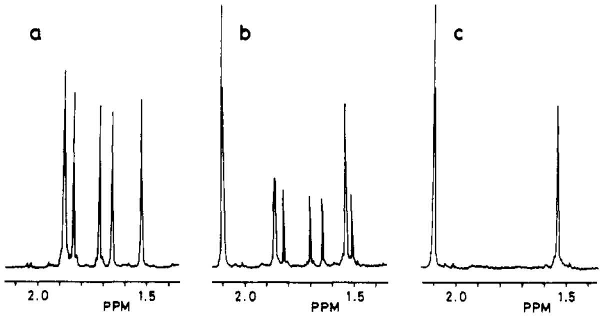
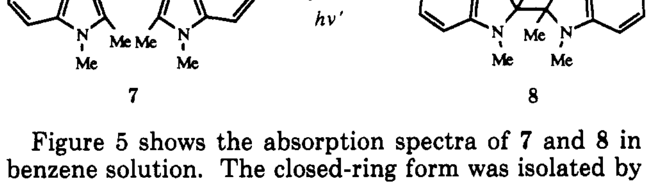


Figure 4. NMR spectra (360 MHz) of **5** in C_6D_6: (a) before irradiation; (b) in the photostationary state under irradiation with 436-nm light; (c) (b) − 0.54 (a).

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.[6] 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.

2. Diarylethene Derivatives with Indole Rings. 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 trans and cis form was separated by a similar procedure as for the selenophene derivative.



7 **8**

Figure 5 shows the absorption spectra of **7** and **8** 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 derivative **4**. The conversion of the

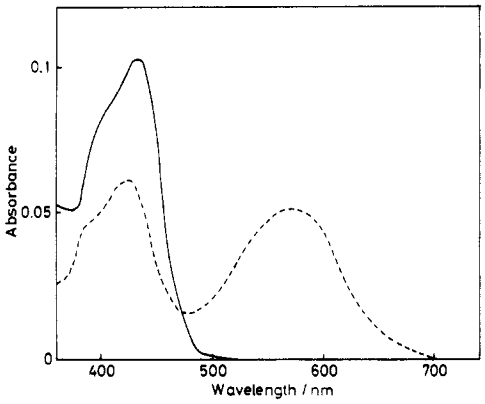


Figure 5. Absorption spectra of 7 (—) and 8 (- -) (0.7×10^{-5} M) in benzene.

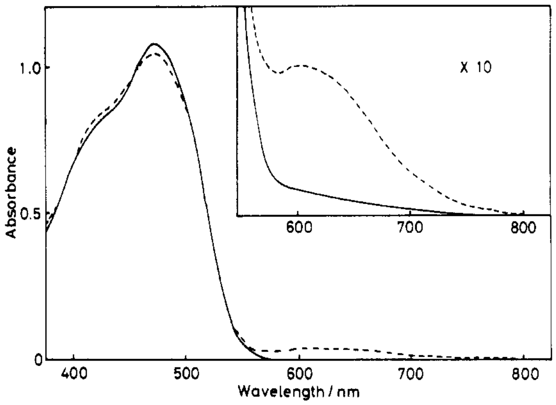
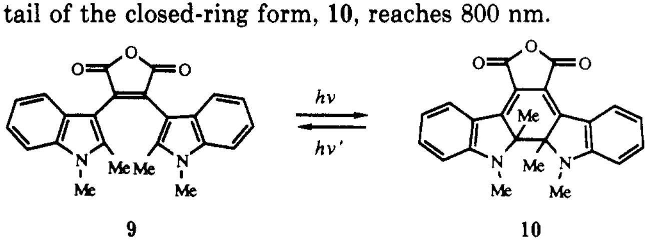


Figure 6. Absorption spectra of 9 (1.1×10^{-4} M) (—) and in the photostationary state under irradiation with 436-nm light (- -).

open-ring to the closed-ring form in the photostationary state under irradiation with 436-nm light was estimated to be 8% by liquid chromatography measurement.

The cyano derivative was converted to a maleic anhydride derivative by the same method used for 5.

Figure 6 shows the absorption spectra of 9 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 the selenophene derivative 5. The absorption tail of the closed-ring form, 10, reaches 800 nm.



9 10

3. Thermal Stability of the Closed-Ring Forms. Figure 7 illustrates the thermal stability of the closed-ring forms, 4, 6, 8, and 10, at 80 °C in the dark. The value of $A/A_0 \times 100$ was plotted against storage time, where A_0 is the initial absorbance of the closed-ring forms, and A the absorbance after t hours at 80 °C. As seen in the Figure 7, the photogenerated closed-ring forms, 4 and 6, are stable, and keep the absorption intensity constant for more than 12 h at 80 °C, while the closed-ring forms with indole groups are thermally unstable. The absorption intensity of the closed-ring form of the maleic anhydride derivative decreases to 50% of the initial intensity in 3 h at 80 °C.

Thermal stability of a closed-ring form of methyl-substituted fulgide[8-12] 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.[4] This interpretation does not apply to the present system, in which compounds with similar steric hindrance, e.g. methyl-substituted indole (or pyrrole[7]) 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.

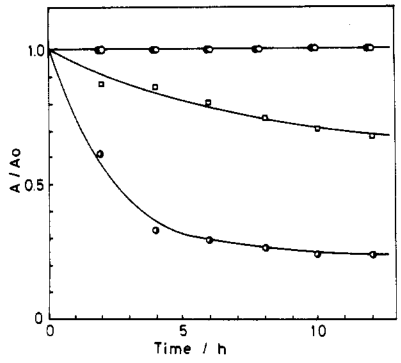


Figure 7. Thermal stability of the closed ring forms in toluene. Compounds 4 (●), 6 (○), 8 (□), and 10 (◑).

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

compd	irradiation wavelength[a]		repeatable cycle no.[b]
	coloring	bleaching	
3	313	546	10
5	334	546	75
5[c]	334	546	>100
7	436	546	>100
9	492	577	>100

[a] Irradiation was carried out in the presence of air. Concentration of the compounds was 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.

In a previous paper,[7] we have carried out a theoretical study on the thermal stability of diarylethene derivatives. Semiempirical MNDO calculations of the state correlation diagrams of the reactions suggested that the thermal stability of the ring-closed 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.[7] 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.

We also tried to measure qualitatively the fatigue resistant property of 3, 5, 7, and 9 in benzene in the presence and absence of air, as shown in Table I. The number of

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

(9) Heller, H. G.; Oliver, S. N. *J. Chem. Soc., Perkin Trans. 1* **1981**, 197.

(10) Darcy, P. J.; Heller, H. G.; Strydom, P. J.; Whittall, J. J. *Chem. Soc., Perkin Trans. 1* **1981**, 202.

(11) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 1* **1981**, 341.

(12) Glaze, A. P.; Harris, S. A.; Heller, H. G.; Johncock, W.; Oliver, S. N.; Strydom, P. J.; Whittall, J. *J. Chem. Soc., Perkin Trans. 1* **1985**, 957.

Table II. Quantum Yields for Cyclization in Benzene

excitation wavelength, nm	compd 3	compd 5	compd 7
334	0.33	0.27	*a*
405	*a*	*a*	0.06

[a] Not measured.

Table III. Quantum Yields for Ring-Opening Reaction in Benzene

excitation wavelength, nm	compd 4	compd 6	compd 8
546	0.02	0.02	0.66
577	0.02	0.02	0.57
633	*a*	0.02	*a*

[a] Not measured.

repeatable cycles indicates the cycle number when the colored intensity decreased to 80% of the first cycle. Compounds **7** and **9** are fatigue resistant. Elimination of oxygen from the solution increased the number of repeatable cycles. The intensity of the closed-ring forms of compounds **7** and **9** did not show any detectable decrease even after 100 coloration/decoloration cycles.

4. Quantum Yield. The quantum yields of the cyclization and ring-opening reactions were measured in benzene solution. Mercury lines, which were isolated with a monochrometer, were used to induce the reactions. Tables II and III 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.[6] Replacement of selenophene rings with indole ones decreased the quantum yield. The quantum yield of the indole derivatives is around $^1/_5$ of that of selenophene derivatives. Table III 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 derivative 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,[6] though the mechanism is not yet clear.

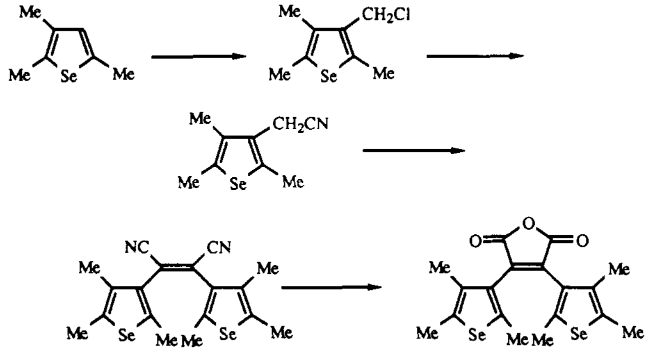
5. Summary. Diarylethene derivatives with selenophene or indole rings were synthesized. The dicyano and maleic anhydride derivatives with selenophene rings, **3** and **5**, showed a thermally irreversible photochromic reaction with a relatively high quantum yield. The conversion of the dicyano derivative 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 55 nm to longer wavelengths. The maleic anhydride derivative had the absorption tail extending to 800 nm. The very high quantum yield was observed for the ring-opening reaction of the dicyano derivative with indole rings **8**. 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.

Experimental Section

^{1}H NMR spectra were recorded in C_6D_6 with a 360-MHz NMR spectrometer (Brucker, WM-360). Absorption spectra were measured with a specrophotometer (Shimadzu, MPS-200). A mercury lamp (Ushio, 1 kW) was used as a light source. Mercury lines were isolated by passing the light through a monochrometer (Ritsu, MC-10N). 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).

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(2,4,5-trimethyl-3-selenenyl)maleic anhydride was synthesized from 2,3,5-trimethylselenophene[13,14] as follows.



2,3,5-Trimethyl-4-(chloromethyl)selenophene.[15] 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 extracted 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); ^{1}H NMR ($CDCl_3$) δ 2.04 (s, 3 H, $ArCH_3$), 2.35 (s, 3 H, $ArCH_3$), 2.46 (s, 3 H, $ArCH_3$), 4.30 (s, 2 H, $ArCH_2Cl$).

2,3,5-Trimethyl-4-(cyanomethyl)selenophene.[16] This was prepared from 2,3,5-trimethyl-4(chloromethyl)selenophene by a similar procedure as used for 2,3,5-trimethyl-4-(cyanomethyl)-thiophene:[6] bp 75 °C (0.3 mmHg); ^{1}H NMR ($CDCl_3$) δ 2.04 (s, 3 H, $ArCH_3$), 2.35 (s, 3 H, $ArCH_3$), 2.42 (s, 3 H, $ArCH_3$), 3.38 (s, 2 H, $ArCH_2CN$).

1,2-Dicyano-1,2-bis(2,3,5-trimethyl-3-selenenyl)ethene (3). To 1.3 mL of 50% NaOH aqueous solution containing tetra-*n*-butylammonium 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 trans and cis form was obtained in 31% yield by column chromatography on silica gel. The mixture product was dissolved in acetonitrile and then exposed to ultraviolet light ($\lambda > 350$ nm). The cis form precipitated was separated from the solution by filtration 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, 1.84 (9 H, $ArCH_3$); 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.

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

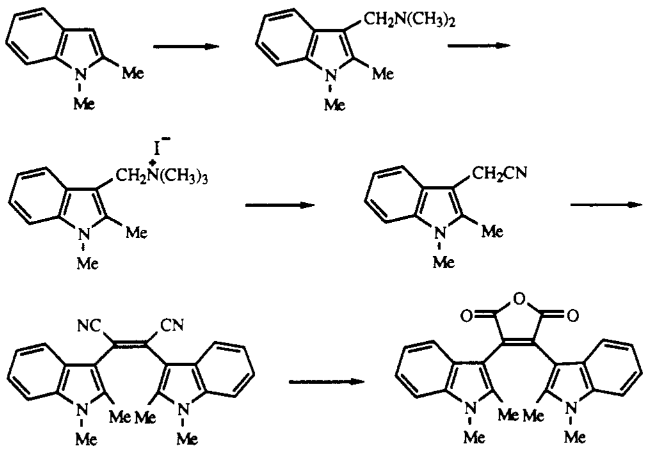
(14) Kudchadker, M. V.; Zingaro, R. A.; Irgolic, K. J. *Can. J. Chem.* **1968**, *46*, 1415.

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

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

2,3-Bis(2,4,5-trimethyl-3-selenenyl)maleic Anhydride (5).[17] 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.[6] **5** 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, 1.88 (×2) (18 H, $ArCH_3$); 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[18] as follows.



1,2-Dimethyl-3-((dimethylamino)methyl)indole.[19] A mixture of 36 mL of 25% aqueous dimethylamine and 40 mL of glacial acetic acid was cooled in an ice bath. 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.[19] To a solution of 9.1 g of 1,2-dimethyl-3-((dimethylamino)methyl)indole in 40 mL of absolute ethanol was added in one portion 7.8 g of methyl iodide. 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.

1,2-Dimethyl-3-(cyanomethyl)indole.[19] To a solution of 10g 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, 1,2-dimethyl-3-(cyanomethyl)indole was isolated in 70% yield by column chromatography on silica gel. The crude product was purified by recrystallization from a ether-hexane mixture.

1,2-Dicyano-1,2-bis(1,2-dimethyl-3-indolyl)ethene (7). This was prepared from 1,2-dimethyl-3-(cyanomethyl)indole by a similar procedure as used for **3**. 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, 3 H × 2, Ar CH_3), 2.65, 2.69 (s, 3 H × 2, NCH_3), 6.70-7.44 (m, 4 H × 2, Ar CH_3); mass spectrum, *m/e* M^+ 364. HRMS *m/e* 364.16850, calcd for $C_{24}H_{20}N_4$ 364.16868.

2,3-Bis(1,2-dimethyl-3-indolyl)maleic anhydride (9).[17] This was prepared from **7** by a similar procedure as used for **5**. Yield was 57%: mp >300 °C; ^{1}H NMR ($CDCl_3$) δ 2.04, 2.11 (s, 3 H × 2, Ar CH_3), 3.59, 3.62 (s, 3 H × 2, NCH_3), 6.91-7.36 (m, 4 H × 2, Ar H); mass spectrum, *m/e* M^+ 384; HRMS *m/e* 384.14564, calcd for $C_{24}H_{20}N_2O_3$ 384.14727.

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[17] Goldberg, M. A.; Ordas, E. P.; Carsch, G. *J. Am. Chem. Soc.* **1947**, *69*, 260.

[18] Fieser, L. F.; Fieser, H. *Reagents for Organic Synthesis*; John-Wiley: New York, 1967, p 336.

[19] Snyder, H. R.; Eliel, E. L. *J. Am. Chem. Soc.* **1948**, *70*, 1703.

Flash Vacuum Thermolysis of 2,3-Dihydro-1,4-oxathiin: Synthesis, Photoelectronic Spectroscopy, and Dienophilic Reactivity of Thioxoethanal[1,2]

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Thioxoethanal has been generated in the gas phase by flash vacuum thermolysis of 2,3-dihydro-1,4-oxathiin. Its characterization was performed by chemical trapping and photoelectron spectroscopy (PES). The PE HeI-HeII study led to the conclusion that thioxoethanal was obtained, with ethylene, as the only thermolysis product at 720 °C. At higher temperatures, a cleavage into methanethial and carbon monoxide was observed. The results from this PE study, as well as MNDO calculations, indicate a very weak interaction between the formyl and thioformyl moieties of the molecule through the σ C-C bond. The HOMO sulfur lone pair is only slightly stabilized by the inductive effect of the carbonyl group. These conclusions account for the observed dienophilic reactivity of thioxoethanal.

In contrast to ethanedithial (**1**) which has received much attention,[3] thioxoethanal (**2**), remains a poorly characterized compound. Ethanedithial, **1**, as well as most α-dithiones,[4] has been shown, from theoretical and experi-

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