Asymmetric Photocyclization of Diarylethene Derivatives

Tadatsugu Yamaguchi,[†] Kingo Uchida,[‡] and Masahiro Irie*

Contribution from the Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Higashi-ku, Fukuoka, 812, Japan

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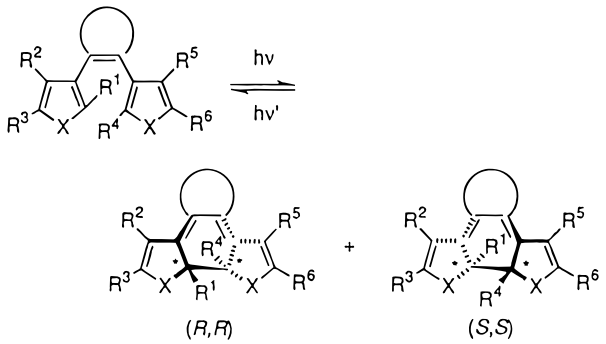
Abstract: Diarylethene derivatives, which have an optically active *l*- or *d*-menthyl group at the 2-position of benzo[*b*]thiophene ring, were synthesized. Irradiation with 450 nm light in solution led to the formation of diastereomer pairs of the closed-ring forms. The product ratio of the diastereomers was dependent on solvent polarity and temperature. In slightly polar (or polarizable) solvents, such as THF and toluene, an asymmetric photocyclization was observed. At −40 °C in toluene, a diastereomer excess as large as 86.6% was observed. The mechanism of the asymmetric photocyclization is discussed.

Introduction

Photochromic compounds characteristically exhibit two different chemical forms which are reversibly transformed form one to the other upon irradiation with light of appropriate wavelengths.[1] The instant image-forming property without processing has led to consideration of their use in a rewritable direct read-after-write medium.[2] The inherent drawback of the photochromic memory is a lack of readout stability. Photochromic reactions are, in general, induced in proportional to the number of photons absorbed by the medium. Therefore, the photochromic memory is destroyed after many readout operations. To avoid such inconvenience, it is indispensable to develop nondestructive readout methods.[3] One of the approaches is to introduce gated reactivity to the photochromic system.[4−6] Another approach is to discriminate between the two isomers using light which cannot induce the photochromic reactions. Changes in the reflective index,[7] infrared absorption,[8] and optical rotation[9] (or circular dichroism) can be detected with light of wavelengths longer than the electronic absorption bands.

Several photochromic compounds, which have chirooptical properties and change the optical rotation by photoirradiation, have been reported. Typical examples are highly substituted stilbenes[9] and fulgides[10] with helical asymmetry. They undergo photochromic reactions between the two forms with different optical rotations. Other examples are photochromic compounds with two chiral units (chirochromism)[11a] and those incorporated into chiral matrices, such as cholesteric liquid crystals[11b,c] or chiral polymers.[12]

Diarylethenes with heterocyclic rings undergo cyclization/ring-opening photochromic reactions. The photogenerated closed-ring form has either *S-S* or *R-R* asymmetric structure.



The enantiomers can be separated with a chiral high-performance liquid chromatography (HPLC) column (Daicel Chiralcel OD). For example, the enantiomer pairs of closed-ring forms of bis(2-methylbenzo[*b*]thiophen-3-yl)perfluorocyclopentene, 1,2-bis(2,4,5-trimethylthiophen-3-yl)perfluorocyclopentene, 1,2-bis(2,4-dimethyl-5-(4-methoxy-benzyl)thiophen-3-yl)perfluorocyclopentene, and 1-(1,2-dimethyl-3-indolyl)-2-(2-cyano-3,5-dimethylthiophen-4-yl)-*N*-(cyanomethyl)maleimide were detected.[13] When an optically active substituent such as a *l*- or *d*-methyl group is introduced to the above compounds, a diastereodifferentiating photocyclization is expected to occur under suitable conditions.[14,15] Martin et al.,[15] for example, reported such a diastereodifferentiation in the photosynthesis

[†] Interdisciplinary Graduate School of Engineering Sciences.
[‡] Institute of Advanced Material Study.
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(13) Enantiomer pairs of closed-ring forms of the following diarylethenes were separated with a chiral column (Daicel Chiralcel OD): 1,2-bis(methylbenzo[*b*]thiophen-3-yl)perfluorocyclopentene (eluent, hexane), 1,2-bis(2,4,5-trimethylthiophen-3-yl)perfluorocyclopentene (eluent, hexane), 1,2-bis(2,4-dimethyl-5-(4-methoxybenzyl)thiophen-3-yl)-perfluorocyclopentene (eluent, hexane/ethanol 99.4:0.6), and 1-(1,2-dimethyl-3-indolyl)-2-(2-cyano-3,5-dimethylthiophen-4-yl)-*N*-(cyanomethyl)maleimide (eluent, hexane/ethanol 4:1).

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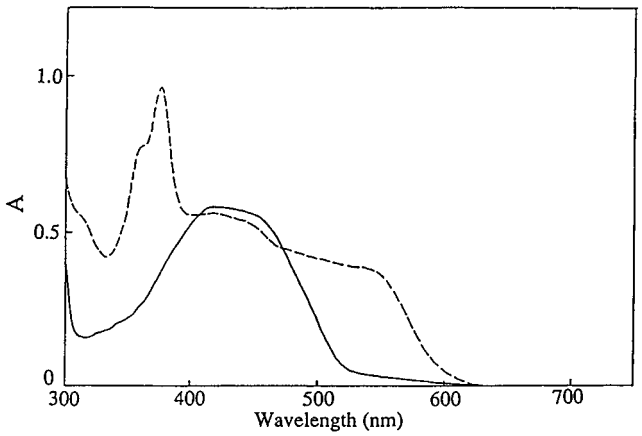
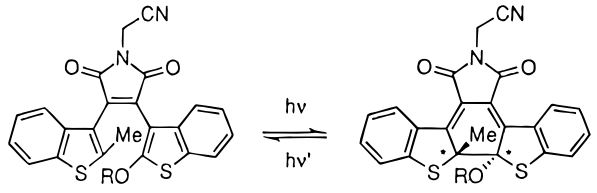


Figure 1. Absorption spectra of **1** in hexane (1.2×10^{-4} M) before (—) and after (- - -) irradiation with 450 nm light.

of helicenes. We have examined the photochemical asymmetric induction for the diarylmaleimide having a *l*- or *d*-menthyl group at the 2-position of benzo[*b*]thiophene ring (**1** and **2**).



Results and Discussion

Photochromic Reactions of Diarylethenes 1 and 2 in Hexane. Figure 1 shows the absorption spectral change of **1** in hexane. Upon irradiation with 450 nm light, the open-ring form **1a** (λ_{max} 417 nm, ϵ_{max} 4.3×10^3 M^{-1} cm^{-1}) converted to the closed-ring form **1b** with the absorption maxima at 538 nm (ϵ_{max} 7.4×10^3 M^{-1} cm^{-1}) and 375 nm (ϵ_{max} 1.5×10^4 M^{-1} cm^{-1}). The photoirradiated sample was analyzed with a conventional HPLC column (silica gel column, Wakosil 5 SIL). When the monitoring wavelength of the HPLC was 475 nm, which is the isosbestic point of the photoisomerization spectral change, three peaks were observed as shown in Figure 2a. The peak at the retention time of 38 min disappeared when the monitoring wavelength was shifted to 538 nm, where only the closed-ring form has the absorption band (Figure 2b). This result indicates that the peak at 38 min is due to the open-ring form and the peaks at 25 min and 28 min are due to the closed-ring forms. The reason why two peaks were observed for the closed-ring form is the following. As already noted, the conrotatory photocyclization of bis(benzo[*b*]thiophen-3-yl)-maleimide itself leads to the formation of *S,S* and *R,R* enantiomer pairs. When an optically active *l*-menthyl group is substituted at the 2-position of benzo[*b*]thiophene ring, the maleimide produces two *l*-*S,S* and *l*-*R,R* diastereomers. The two peaks are due to the diastereomers. We assigned the diastereomers that gave peaks at 25 and 28 min to the A and B isomers, respectively.

Figure 3 shows the absorption spectra of the isolated A and B isomers in hexane. The A and B diastereomers gave the same

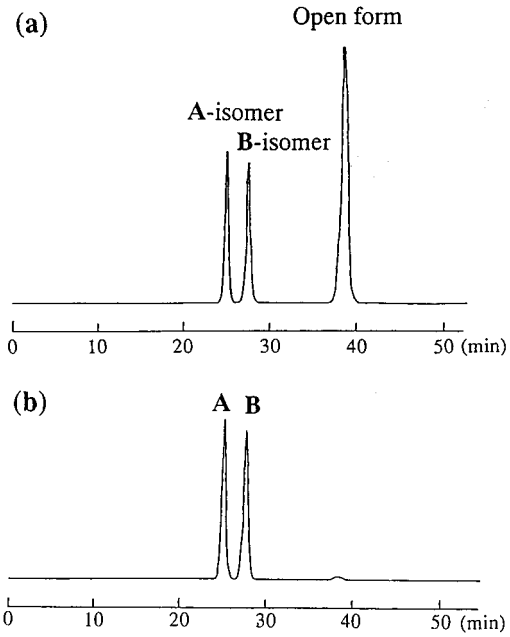


Figure 2. HPLC chart of **1** irradiated with 450 nm light in hexane: (a) monitored at 475 nm, (b) monitored at 538 nm. Eluent, hexane/ethyl acetate (90:10 volume ratio); flow rate, 3.0 mL min^{-1}.

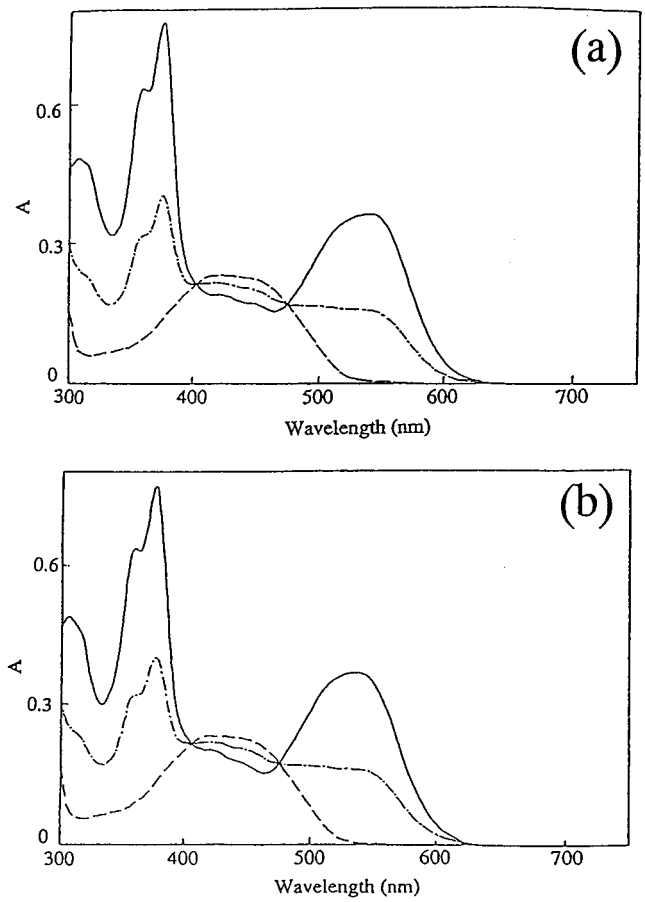


Figure 3. Absorption spectra of closed-ring form diastereomers in hexane ($c = 5.0 \times 10^{-5}$ M): (a) A-isomer (—), after irradiation with 570 nm light (- - -) and in the photostationary state under irradiation with 450 nm light (—•—); (b) B-isomer (—), after irradiation with 570 nm light (- - -) and in the photostationary state under irradiation with 450 nm light (—•—).

absorption maximum and coefficient. Both diastereomers returned to the open-ring forms upon irradiation with 570 nm light. When the sample was irradiated with 450 nm light, the

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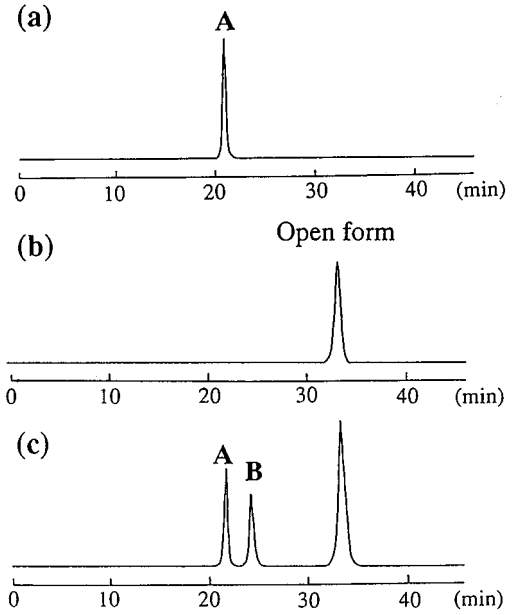

Figure 4. HPLC chromatograms of **1** monitored at 475 nm: (a) A diastereomer, (b) after irradiation with 570 nm light, (c) in the photostationary state under irradiation with 450 nm light in hexane.

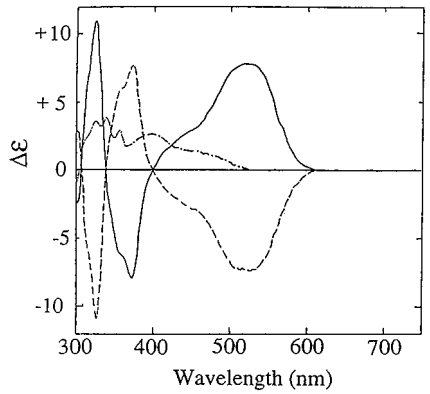

Figure 5. CD spectra of **1** in hexane: A diastereomer (—), B diastereomer (- - -), and open-ring form (—·—) at 23 °C.

open-ring isomers again converted to the closed-ring forms. The conversion was 42.5% in the photostationary state in both cases.

Contribution of the two diastereomers A and B to the spectral change shown in Figure 3a was examined by HPLC. Figure 4 shows the HPLC chromatograms monitored at 475 nm of the A isomer samples before (a) and after (b) irradiation with 570 nm light and after (c) irradiation with 450 nm light. The solid line absorption shown in Figure 3a is purely due to the A diastereomer. On the other hand, the absorption after irradiation of the open-ring form with 450 nm light is due to the mixture of A and B diastereomers. In the photostationary state under irradiation with 450 nm light in hexane, the ratio of A to B diastereomers was 1:1.

Figure 5 shows the circular dichroism (CD) spectra of the A and B diastereomers in hexane. Negative and positive Cotton effects were observed for the A and B isomers, respectively. The two CD spectra have the same band shape but with different signs. Both have intense peaks at 537, 382, and 327 nm. The specific rotation $[\alpha]^{20}_{633}$ of the A isomer in hexane was +1300° and that of the B isomer was −1300°. The open-ring form had a rather weak induced CD spectrum. The specific rotation $[\alpha]^{20}_{633}$ of the open-ring form in hexane was about −50°. The large specific rotation of the closed-ring forms is based on their molecular asymmetric structure. The large specific rotation was detected at 633 nm, where the closed-ring form has no

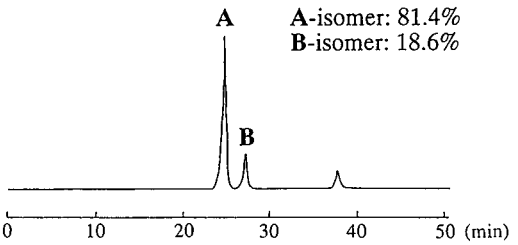

Figure 6. A HPLC chromatogram of **1** after irradiation with 450 nm light at 23 °C in a mixed solvents of hexane and THF (hexane/THF = 80.8:19.2 volume ratio).

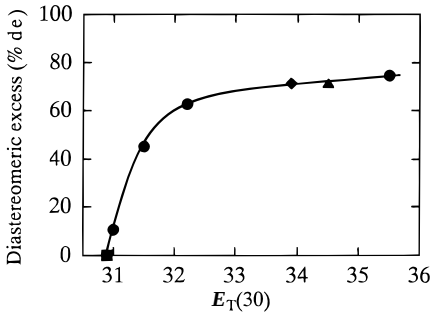

Figure 7. Polarity dependence of the percentage diastereomeric excess (% de) of **1**, in hexane/THF (●), hexane (■), toluene (◆), and benzene (▲).

absorption. This means that the recorded marks, the existence of the closed ring forms, can be read using a He−Ne laser without destruction of the closed-ring forms.

Asymmetric Induction. As shown in Figure 4c, photoirradiation of the open-ring form with 450 nm light produced equal amounts of A and B diastereomers in hexane. Any asymmetric induction was not discerned. However, the production ratio of the two diastereomers dramatically changed when a small amount of THF was added to the hexane solution. Figure 6 shows the HPLC of the photoirradiated sample with 450 nm light in a mixed solvent of hexane and THF (80.8:19.2 in volume ratio). The A diastereomer was predominantly produced, and the diastereomeric excess was as large as 62.8%.

The diastereomeric excess value depended on solvent polarity. Percentage diastereomeric excess (% de) increased with the increasing solvent polarity. The ratio of two diastereomers was measured in mixed solvents of hexane and THF and also in pure benzene and toluene. Figure 7 shows the relationship between % de and $E_T(30)$. Below an $E_T(30)$ of 30.9, asymmetric induction was not observed. The % de sharply increases above $E_T(30)$ of 30.9 and shows saturation above 33. The cyclization quantum yield was also depended on the solvent polarity.[16] A high yield of 0.23 in hexane ($E_T(30) = 30.9$) decreased to 0.056 in toluene ($E_T(30) = 33.9$).

Figure 8 shows the temperature dependence of % de in toluene. In toluene, the % de was found to increase at lower temperatures. At −40 °C, a % de value as high as 86.6% was observed. The asymmetric photocyclization in the photostationary state by irradiation with 450 nm light was confirmed by using pure A and B diastereomers as the starting compound at 23 °C, as shown in Figure 9. In these photoreactions, after 30 min of irradiation, the diastereomeric excess reached the photostationary value of 72.2% de.

The asymmetric cyclization reaction was observed in slightly polar (or polarizable solvents when an optically active menthyl substituent was introduced to the diarylethene. The asymmetric induction was not discerned in nonpolar hexane

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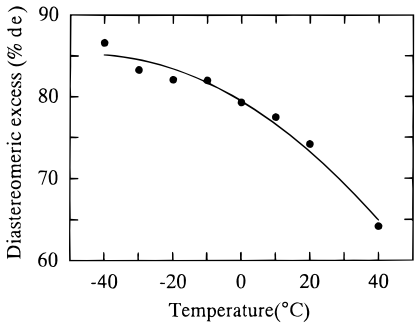

Figure 8. Temperature dependence of the percentage diastereomeric excess (% de) of **1** in toluene.

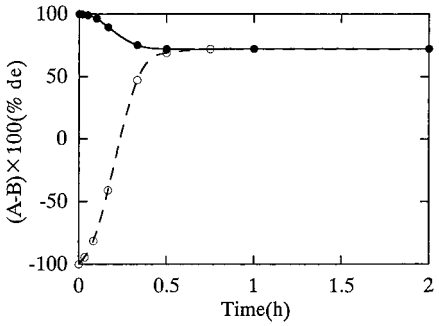

Figure 9. Diastereomeric excess (% de) of samples irradiated with 450 nm light in toluene at 23 °C (1.5×10^{-4} M): (●) starting from pure A diastereomer, (○) starting from pure B diastereomer.

solution. Thus, the solvent polarity plays an important role in the asymmetric induction.

Mechanism of the Asymmetric Induction. To reveal the asymmetric induction mechanism, we first examined which electronic state, ground or excited, contributes to the discrimination. The CD spectrum of the open-ring form was measured in hexane, hexane/THF mixture, and toluene. Any detectable difference was not observed. This indicates that in the ground state the solvent polarity does not affect the conformation of the open form. The right- and left-helical conformations are considered to be in equilibrium, and the relative population of the two conformations is equal even if the solvent polarity is changed. This was also confirmed by NMR measurements. Signal splitting, which is attributable to fixation of the conformation of the aryl groups, was not detected. These results indicate that the ground state conformation is not responsible for the asymmetric induction.

When the compound was photoexcited to the first excited singlet state, the compound can take two conformations, planar and twisted, as reported previously[16] and shown in Figure 10. The photocyclization reaction can proceed only form the planar conformation. In polar solvents photoexcitation brings about an intramolecular electron transfer (TICT) from the donor benzo[*b*]thiophene rings to the electron acceptor (methylcyano)-substituted maleimide moiety, and the charge-separated polarized state prefers the twisted conformation. The photocyclization reaction can not proceed from the twisted conformation. This mechanism explains the low cyclization quantum yield in polar solvents.[16]

In both planar and twisted conformations, diastereomeric right- and left-helical conformations coexist. The potential energies of the two conformer are, however, considered to be slightly different as shown in Figure 10. This potential energy difference can explain the solvent polarity dependence of the asymmetric induction as follows. In a nonpolar hexane solution, intramolecular charge transfer hardly occurs and the potential energy curves of the twisted conformation is higher than the energy curves of the planar conformations. Therefore, the photoexcited compounds dominantly convert to the planar conformations. In this case, discrimination between A and B diastereomer conformations is not attained because the excited compounds can not recognize the barrier difference between A and B conformations. In slightly polar solvents, on the other hand, the potential energy curve of the twisted conformation is lowered and starts to compete with the curves of the planar conformations. When the energy curve of the twisted conformation is located between the curves of the A and B conformations, as shown by the broken line of Figure 10, the cyclization reaction to B diastereomer is suppressed. During relaxation from the Franck−Condon state to relaxed fluorescent states, the excited molecule having the B conformation efficiently converts to the unreactive twisted conformation. The rate-limiting step that determines the % de is the formation process of the two conformer states. The subtle balance of the energy curves brings about the asymmetric induction and affects the yield of the closed-ring forms. As already reported,[17] a dithienylmaleic anhydride derivative converts to the closed-ring form much faster (<10 ps) than the main fluorescence lifetime (365 ps, 98%). The present diarylmaleimide derivative also has a similar lifetime of 554 ps in toluene. This fluorescence is considered to emit from one of the relaxed fluorescent states, which does not directly correlate to the cyclization reaction.

In order to know the energy barrier difference in the photoexcited state between A and B diastereomer formation, the temperature dependence of % de in toluene was analyzed. The quantum yields of formation of the A and B diastereomers, ϕ_A and ϕ_B, are the function of k_{un}, k_A, and k_B, where k_{un}, k_A, and k_B are the rate constants of decays from the Frank−Condon state through unreactive channels and formation of A and B diastereomers, respectively.

$$\phi_A = \frac{k_A}{k_{un} + k_A + k_B} \tag{1}$$

$$\phi_B = \frac{k_B}{k_{un} + k_A + k_B} \tag{2}$$

The product ratio of A and B diastereomers in the photostationary state, [A]/[B], is expressed as follows

$$\frac{[A]}{[B]} = \frac{\dfrac{\phi_A \epsilon_o}{\phi_o \epsilon_A}}{\dfrac{\phi_B \epsilon_o}{\phi_o \epsilon_B}} = \frac{\phi_A}{\phi_B} = \frac{k_A}{k_B} \tag{3}$$

where ϕ_o, ϵ_o, ϵ_A, and ϵ_B are the quantum yield of ring-opening reaction of diastereomers and the absorption coefficients of the open-ring form and the A and B diasteromers, respectively.

From the transition state theory, the rate constant is expressed by eq 4.

$$\bar{k} = \frac{kT}{h} \exp\left[-\frac{\Delta H^{\ddagger} - T\Delta S^{\ddagger}}{RT}\right] = \frac{kT}{h} \exp\left[-\frac{\Delta G^{\ddagger}}{RT}\right] \tag{4}$$

$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ stand for activation enthalpy and entropy, respectively. The ratio k_A/k_B is expressed as follows

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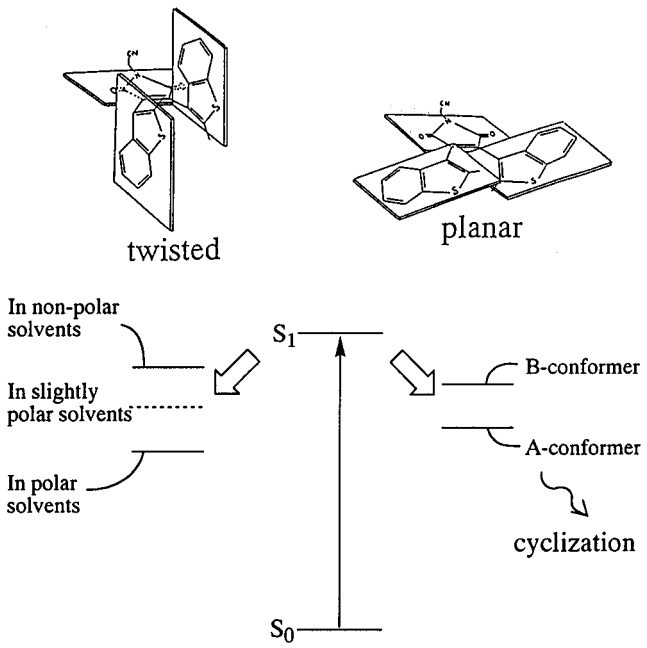


Figure 10. Schematic illustration of the energy levels of the photoexcited states.

$$\frac{k_A}{k_B} = \exp\left[-\frac{\Delta G_A^{\ddagger} - \Delta G_B^{\ddagger}}{RT}\right] = \exp\left[-\frac{\Delta H_A^{\ddagger} - \Delta H_B^{\ddagger} - T(\Delta S_A^{\ddagger} - \Delta S_B^{\ddagger})}{RT}\right] \quad (5)$$

The slope and intercept of Figure 11 gave the values of $\Delta H_B^{\ddagger} - \Delta H_A^{\ddagger} = 2.5$ kcal mol^{-1} and $\Delta S_B^{\ddagger} - \Delta S_A^{\ddagger} = -5.0$ cal mol^{-1} deg^{-1}.

The activation entropy difference of the A isomer is larger than and the activation enthalpy difference of A isomer is smaller than those of B isomer. Both entropy and enthalpy difference values indicate that the activation free energy difference of A isomer is smaller than that of B isomer and k_A is larger than k_B. In the temperature range examined, the diastereodifferentiating photocyclization is mainly controlled by the activation enthalpy.

For compound **2**, in which a *d*-menthyl group was substituted instead of an *l*-menthyl group, the B diastereomer became dominant and the other kinetic parameters were the same. This is another evidence that the optical active substituent is responsible to the asymmetric induction.

In toluene at 23 °C, the reversible circular dichroism changes of the photocyclization reaction were clearly observed as shown in Figure 12. Upon alternating irradiation with 450 and >570 nm light, the ellipticity reversibly changed. This is due to the difference in [A]/[B] at the photostationary state by irradiation with 450 nm. The different A/B ratio can be detected not only by CD but also by specific rotation. This means that this system can be potentially useful for nondestructive readout optical memory. At present, the problem is a rather small change in the value due to low conversion (~10%) in polar solvents.

Experimental Section

General. Solvents used were spectrograde and purified by distillation before use. Absorption spectra were measured with an absorption spectrophotometer (Hitachi, U-3410). A mercury lamp (Ushio, 500 W) and a xenon lamp (Ushio, 1 kW) were used as the light sources. Monochromic light was obtained by passing the light through a Toshiba cutoff filter (UV-35) and interference filters (KL-45 and KL-57).

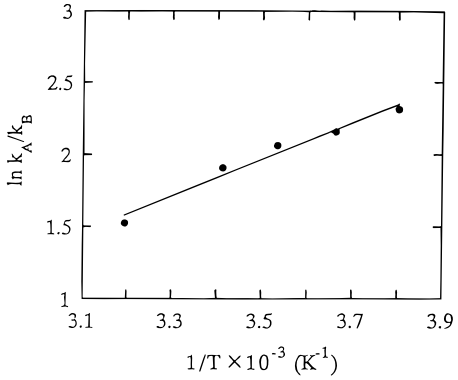


Figure 11. Temperature dependence of ln k_A/k_B where k_A/k_B were estimated from the concentration of A and B diastereomers in the photostationary state in toluene.

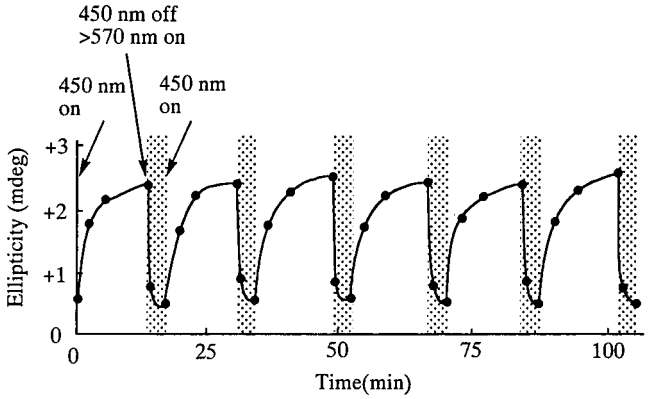


Figure 12. Reversible ellipticity change of **1** in toluene (1.2×10^{-4} M) at 23 °C by alternate irradiation with 450 nm light and >570 nm light: monitoring wavelength, 540 nm.

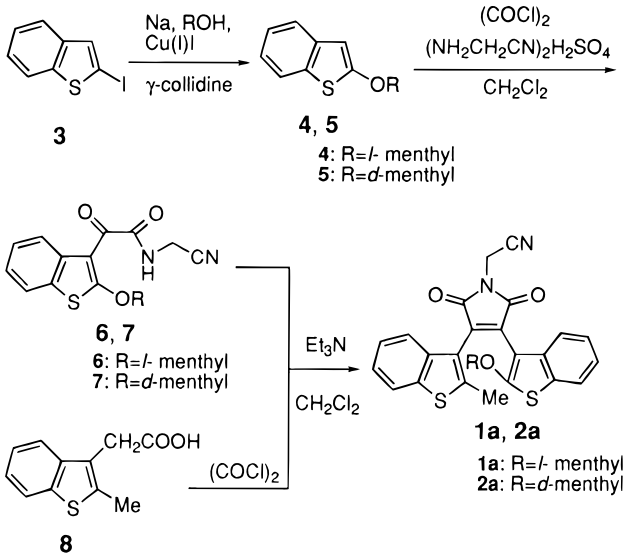
Fluorescence lifetimes were measured with a time-resolved spectrofluorometer (Hamamatsu, C4780). ^{1}H NMR spectra were recorded on JEOL-EX 270 (270 MHz) and Gemini 200 (200 MHz) spectrometers. The signals were expressed as ppm downfield from tetramethylsilane, used as an internal standard (δ value). Mass spectra were taken with a LUCY (version 2.22) mass spectrometer. Circular dichroism was measured with a JASCO J-720S spectrometer. The optical rotation was measured using a Union GIKEN PM-101 (633 nm light) polarimeter. The samples were not degassed. Optical purity of compounds was checked by chiral column (Daicel Chiralcel OD). A silica gel column (Wakosil 5SIL, Wako) was used to analyze diastereomers. HPLC was performed on a Shimadzu LC-6AD liquid chromatography coupled with a Shimadzu SPD-10AV spectrophotometeric detector.

Materials. 2-(2-Methylbenzo[*b*]thiophen-3-yl)-3-(2-*l*-menthoxybenzo[*b*]thiophen-3-yl)maleimide (**1**) and 2-(2-methylbenzo[*b*]thiophen-3-yl)-3-(2-*d*-menthoxybenzo[*b*]thiophen-3-yl)maleimide (**2**) were synthesized according to the following reaction route (Scheme 1). 2-Iodobenzo[*b*]thiophene (**3**) was prepared by the literature method.[18]

2-*l*-Menthoxybenzo[*b*]thiophene (4). A solution of *l*-menthol (16.01 g) in 2,4,6-trimethylpyridine (20 mL) was added to sodium (1.841 g). The solution was then stirred at 60 °C until the sodium dissolved. This solution was added to copper(I) iodide (1.647 g) and 2-iodobenzo[*b*]thiophene (**3**, 5.0 g), and the reaction mixture was stirred for 24 h at 110 °C. The copper was separated by filtration, and the filtrate was treated with 10% sodium thiosulfate solution. The product was extracted with ether from the reaction mixture, and the extracts were dried over sodium sulfate. The solvent was removed, and the residue was purified by a column chromatography to give **4** in 27 % yield: mp 104−105 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.82−1.76 (m, 16H), 2.22 (m, 2H), 2.30 (m, 1H), 4.03 (dt, $J = 4.3$, 10.6 Hz, 1H), 6.69 (s, 1H), 7.11−7.28 (m, 2H), 7.50 (d, $J = 10.6$ Hz, 1H), 7.59 (d, $J = 7.9$ Hz, 1H); MS, *m*/*z* (M^+) 288, ($M^+ - C_{10}H_{19}$) 150. Anal. Calcd for $C_{18}H_{24}OS$: C, 74.95; H, 8.38. Found: C, 75.05; H, 8.41.

(18) Gaertner, R. *J. Am. Chem. Soc.* **1952**, *74*, 4950.

Scheme 1



2-*l*-Menthoxy-3-(*N*-(cyanomethyl)oxamoyl)benzo[*b*]thiophene (6). A solution of sodium aminoacetonitrile (0.733 g) and triethylamine (1.0 mL) in dichloroethane (15 mL) was refluxed for 3 h. A 1,2-dichloroethane (15 mL) solution of **4** (0.500 g) was added dropwise to oxalyl chloride (0.325 g), and the solution was stirred for 3 h at 70 °C. The acid chloride solution was added dropwise to the amino-acetonitrile solution at room temperature. The mixture was stirred for 12 h at room temperature. The reaction mixture was poured into 1 M hydrochloric acid, the products were extracted with chloroform, and the extracts were dried over sodium sulfate. The solvent was removed, and the residue was purified by a column chromatography to give **6** in 92 % yield: mp 141−142 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.82−2.27 (m, 18H), 3.99−4.35 (m, 3H), 6.97−7.51 (m, 4H), 8.04−8.21 (m, 1H). Anal. Calcd for $C_{22}H_{26}O_3N_2S$: C, 66.30; H, 6.58; N, 7.03. Found: C, 66.27; H, 6.63; N, 7.01.

2-Methyl-3-benzo[*b*]thienylacetic acid (**8**) was prepared according to the procedure described before.[19]

3-(2-Methyl-3-benzo[*b*]thienyl)-4-(2-*l*-menthyl-3-benzo[*b*]thienyl)-*N*-(cyanomethyl)maleimide (1). A solution of 2-methyl-3-benzo[*b*]-thienylacetic acid (**8**) (0.922 g) in dry benzene (40 mL) was added dropwise to oxalyl chloride (1.422 g), and the solution was stirred for 2 h at room temperature and refluxed for 1 h. The solvent and excess oxalyl chloride were removed in vacuo, and the residue was dissolved in 1,2-dichloroethane (25 mL). The acid chloride solution was added dropwise to a 1,2-dichloroethane (25 mL) solution containing 2-*l*-menthoxy-3-(*N*-(cyanomethyl)oxamoyl)benzo[*b*]thiophene (**6**, 1.365 g) and triethylamine (15 mL). The solution was stirred for 48 h at room temperature. The reaction mixture was poured into 1 M HCl, the product was extracted with chloroform, and the extracts were dried over sodium sulfate. The solvent was removed, and the residue was purified by column chromatography to give compound **1** in 71 % yield: mp 103−104 °C; ^{1}H NMR (270 MHz) δ 0.55−2.41 (m, 21H), 3.62−3.74 (s, 1H), 4.51 (s, 2H), 6.88−7.63 (m, 8H); MS *m*/*z* ($M^+ - C_{10}H_{19}$) 430. Anal. Calcd for $C_{33}H_{32}O_3N_2S_2$: C, 69.69; H, 5.67; N, 4.93. Found: C, 69.85; H, 6.05; N, 4.94.

Closed form (A) for 1: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.68−1.67 (m, 16H), 2.03 (s, 3H), 2.28−2.38 (m, 2H), 4.18−4.23 (m, 1H), 4.60 (s, 2H), 7.15−7.39 (m, 2H), 7.51−7.54 (m, 1H), 7.67−7.71 (m, H), 9.15−9.25 (m, 2H); $[\alpha]^{20}_{633} = +1300°$.

Closed form (B) for 1: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.67−1.67 (m, 16H), 2.03 (s, 3H), 2.28−2.40 (m, 2H), 4.17−4.23 (m, 1H), 4.60 (s, 2H), 7.15−7.39 (m, 2H), 7.52−7.55 (m, 1H), 7.68−7.72 (m, 1H), 9.17−9.24 (m, 2H); $[\alpha]^{20}_{633} = -1300°$.

2-*d*-Menthoxybenzo[*b*]thiophene (5). The synthetic procedure was the same as that for **4** except *d*-menthol was used instead of *l*-menthol. For **5**: mp 104−105 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.82−1.74 (m, 16H), 2.22 (m, 1H), 2.26 (m, 1H), 4.03 (dt, J = 4.1, 10.0 Hz, 1H), 6.38 (s, 1H), 7.11−7.29 (m, 2H), 7.47−7.61 (m, J = 10.6 Hz, 2H). Anal. Calcd for $C_{18}H_{24}OS$: C, 74.95; H, 8.39. Found: C, 74.72; H, 8.34.

2-*d*-Menthoxy-3-(*N*-(cyanomethyl)oxamoyl)benzo[*b*]thiophene (7). The synthetic procedure was the same as that for **6** except 2-*d*-menthoxybenzo[*b*]thiophene was used instead of 2-*l*-menthoxybenzo-[*b*]thiophene. For **7**: mp 141−142 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.80−1.80 (m, 16H), 2.04−2.27 (m, 2H), 3.99−4.05 (m, 3H), 6.87−6.90 (m, 1H), 7.20−7.41 (m, 2H), 7.53−7.57 (m, 1H), 8.22−8.25 (m, 1H). Anal. Calcd for $C_{22}H_{26}O_3N_2S$: C, 66.30; H, 6.58; N, 7.03. Found: C, 66.25; H, 6.60; N, 6.96.

3-(2-Methyl-3-benzo[*b*]thienyl)-4-(2-*d*-menthyl-3-benzo[*b*]thienyl)-*N*-(cyanomethyl)maleimide (2). The synthetic procedure was the same for **1** except 2-*d*-menthoxy-3-(*N*-(cyanomethyl)oxamoyl)benzo[*b*]-thiophene was used instead of 2-*l*-menthoxy-3-(*N*-(cyanomethyl)-oxamoyl)benzo[*b*]thiophene. For **2**: mp 103−104 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.63−2.56 (m, 21H), 3.65−3.82 (m, 1H), 4.60 (s, 1H), 6.94−7.72 (m, 8H). Anal. Anal. Calcd for $C_{33}H_{32}O_3N_2S_2$: C, 69.69; H, 5.67; N, 4.93. Found: C, 69.74; H, 5.87; N, 4.64.

JA970200J

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