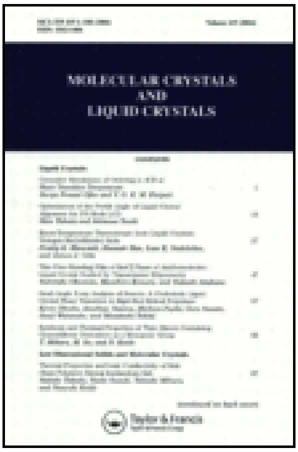

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PHOTOCHROMISM OF FULGIDES POSSESSING CHIRAL PROPERTIES

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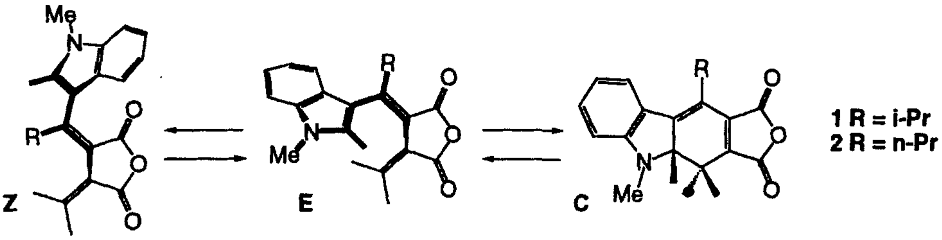
Abstract A thermally irreversible photochromic fulgide was resolved into enantiomers. A fulgide derivative that has the binaphthol moiety showed diastereoselective photochromic reactions. The change of chiral properties of these molecules by photochromic reactions were examined.

INTRODUCTION

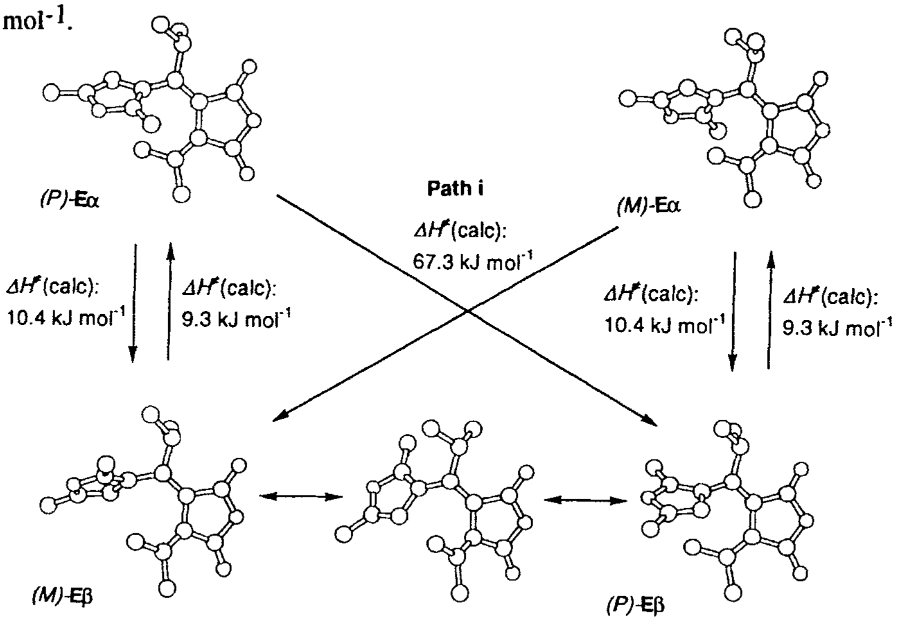
Among the organic photochromic compounds, thermally irreversible photochromic species such as fulgides[1] and diarylethenes[2] are expected to work as photochemical switches of materials for which one can control the function of the system by photoirradiation from outside. When the photochromic molecules are chiral, they show the change of chiral properties such as optical rotatory power and CD spectra, besides the usual properties that photochromic compounds are supposed to possess.



Fulgides are known to be chiral.[3] They exist as a mixture of equal amount of enantiomers both in solution and in the crystalline state. One way to have optically active fulgides in hand is therefore optical resolution. The other way is to introduce a chiral auxiliary to the fulgide to generate a mixture of diastereomers. The former is quite simple. However, once the racemization should occur, the laborious task of resolution will become nothing. To the contrary, we do not need to worry about the isomerization if the diastereomers form a set of thermally equilibrated system for the latter method. We can treat this system as one chemical species, yet the change of optical rotation and CD spectra by photochromic reaction are observable. We here show our results about these two methodologies applied to fulgides.

OPTICAL RESOLUTION[4]

We have already clarified that an isopropyl-substituted furylfulgide exhibited enantiotopomerization behavior on variable-temperature experiments of ^{1}H NMR spectroscopy.[5,6] The process was monitored by the exchange of the enantiomeric sites of two methyl groups on the isopropyl group next to the furan ring. The activation enthalpy of enantiotopomerization is 52.9 kJ mol^{-1}. The process was elucidated by AM1 molecular orbital calculations (Scheme 1), and the calculated activation enthalpy is 51.5 kJ mol^{-1}.



SCHEME 1. Racemization pathway of an isopropyl-substituted furylfulgide (AM1 MO calculation)

On the basis of this result, we designed some fulgides that were supposed not to enantiotopomerize. Among them, only **1** was resolved into a pair of stable enantiomers at room temperature. The optical resolution was carried out using HPLC with a cellulose tris(3,5-dimethylphenylcarbamate) column (Daicel Chem. Ind., Ltd., Chiralcel OD-H) and 90/10 hexane – propan-2-ol (v/v) as eluent. We obtained the faster-moving enantiomer (**1E**$_f$, 99% ee) and slower-moving process (**1E**$_s$, 93% ee). At the photostationary state of 405-nm light irradiation, the proportion of the colored form is 81%, and no *Z*-form was observed during the photoirradiation. The absolute configuratin of **1E**$_f$ and **1E**$_s$ were determined by correlating to the binaphthol-condensed fulgide (*vide infra*), and **1E**$_f$ was proved to have P helical chirality of the substituents on the succnic anhydride part. The change of CD spectra between the photostationary states of 405-nm light (*E/C* = 19/81) and >580-nm light (only **1E**$_f$) is shown in Figure 1.

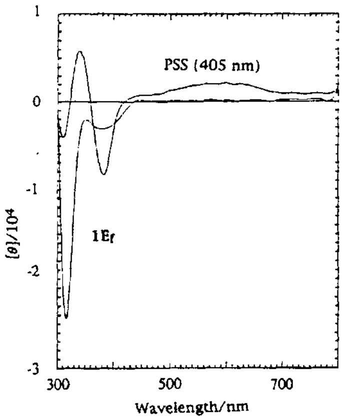


FIGURE 1. Change of CD spectra of **1E**$_f$ (2.1 X 10-4 mol dm-3, toluene)

We examined the degree of racemization during photoirradiation. When the 405-nm light was irradiated to its photostationary state, the enantiomeric excess of the *E*-form decreased gradually (Figure 2). Either of the *Z*-form produced in a hardly detectable amount or the hot-ground-state molecule generated at the last step of the photoreaction from the *C*-form to the *E*-form may be responsible for the enantiotopomerization.

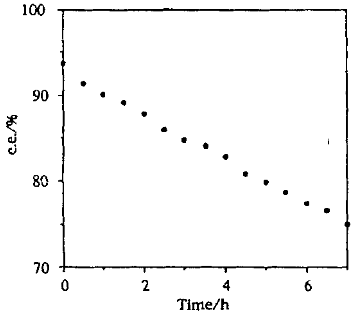


FIGURE 2. Photochemical racemization of **1E**$_f$ (in toluene, 1.47 x 10^{-4} mol dm^{-3}. Irradiation light: 405 nm, 0.69 mW cm^{-2})

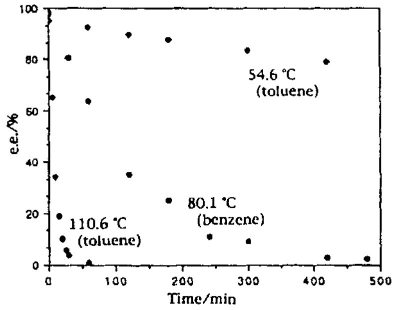


FIGURE 3. Thermal racemization of **1E**$_f$ (in toluene or benzene)

Thermal racemization of the resolved **1E** in aromatic hydrocarbon solvents at various temperatures were examined (Figure 3). From these experiments, we obtained the activation energy of racemization (*Ea*) to be 107 kJ mol^{-1}.

DIASTEREOSELECTIVE PHOTOCHROMISM[7]

Among the possible chiral auxiliaries, we chose 1,1'-bi-2-naphthol (binaphthol). Condensation of *(R)*-binaphthol to indolylfulgides **1E** and **2E** afforded **3E** and **4E**, respectively. To avoid the difficulty of separation, **3E** was converted to its colored form **3C**, and it was isolated.

As **3C** thus obtained was diastereomerically almost pure, we undertook the X-ray crystallographic analysis of a single crystal of **3C**.[8] The ORTEP diagram is shown in Figure 4. The absolute stereochemistry of the stereogenic quaternary carbon atom was determined in relation to the chirality of *(R)*-binaphthol.

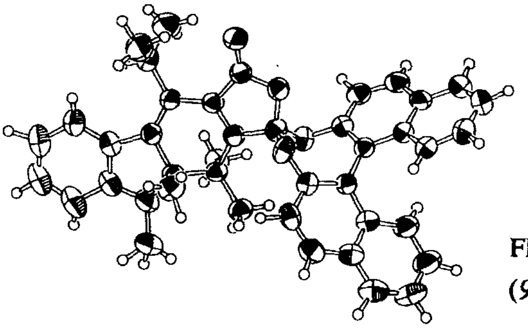
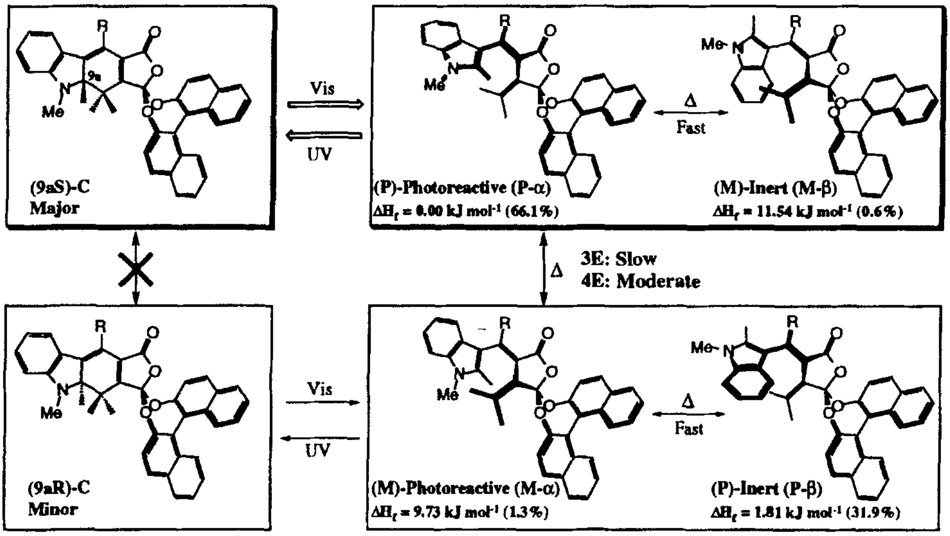


FIGURE 4. X-ray structure of (*9aS*)-**3C** (major diastereomer)

The possible conformational isomers and their stability were predicted by AM1 molecular orbital calculations for **5E**, a methyl-substituted compound (Scheme 2). There are four stable conformers. The most stable one has the P helical chirality about the substituents on the anhydride-ortho-ester moiety, and photocyclization-possible conformation (P-α conformation). The second one also has the P chirality, but it has cyclization-impossible arrangement of the indole ring (P-β). The third one has the M helical chirality and cyclization-possible conformation (M-α). The fourth one has M chirality and cyclization-impossible conformation (M-β). The probable population of the conformers at 298K was calculated by neglected the entropy terms, and is shown in Scheme 2. From the study to obtain activation enthalpy values between the conformational isomers of a furylfulgide by AM1 calculation, the activation enthalpy of conformational change between P-α and M-β, and P-β and M-α are predicted to be low (Scheme 1). The exchange of conformers between P-α and M-α corresponds to the enantiotopomerization of the indolylfulgides **1E** and **2E**.



3: R = i-Pr, **4**: R = n-Pr, **5**: R = Me

SCHEME 2. Stable conformers and their population of **5E** obtained by AM1 calculations

Change of absorption spectra and ^{1}H NMR spectra during photochromic reactions of **3** and **4** were shown in Figures 5 – 8. For the *n*-propyl-substituted **4E**, the NMR spectrum before 366-nm light irradiation showed that there were two conformational isomers (57/43). At the photostationary state of 366-nm light irradiation (*E/C* = 14/86), the C-form consisted of two diastereomers (95/5). These results strongly indicate that not only one of the conformational isomers of **4E** produced the major diastereomer of **4C** but both did. After the visible-light irradiation, the initial mixture of conformational isomers of **4E** was restored.

The photochromic reactions of the isopropyl-substituted **3** were initiated from **3C**. The ratio of diastereomers was 98/2 before visible-light irradiation. After irradiation when **3C** completely changed to **3E**, the ratio of conformational isomers of **3E** was 96/4 that reflected the ratio of the diastereomers of **3C**. At the thermal equilibrium, the ratio of the conformational isomers of **3E** changed to 48/52.

As the absolute stereochemistry of the major diastereomer of **3C** has been determined as shown in Figure 4, the major conformational isomer right after visible-light irradiation should be P-α because the photoreactions of fulgides obey the Woodward-Hoffmann rules. After thermal equilibration, the conformational isomers observed by ^{1}H NMR are P-α and P-β. Irradiation of 366-nm light to this mixture afforded **3C** only from **3E** with P-α conformation.

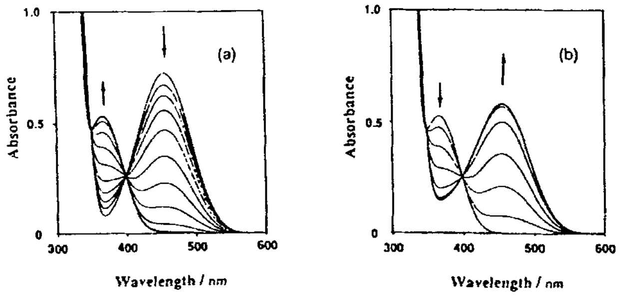


FIGURE 6. Absorption spectral change of **3** in toluene
(a) 495 nm irradiation to **3C**
(b) 366 nm irradiation to **3E**

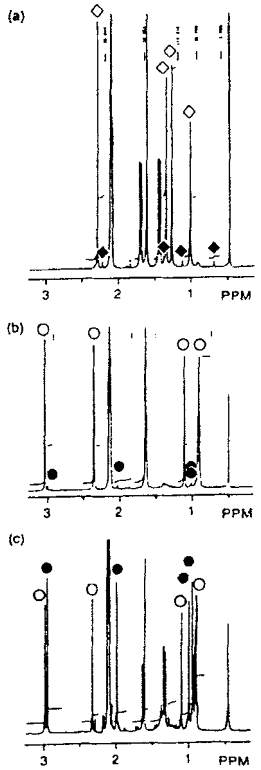


FIGURE 5. Change of ^{1}H NMR spectra of **3** in toluene-d_8
(a) **3C** before irradiation (◇: major, ◆: minor)
(b) after 495 nm irradiation (○: major, ●: minor)
(c) **3E** at thermal equilibrium

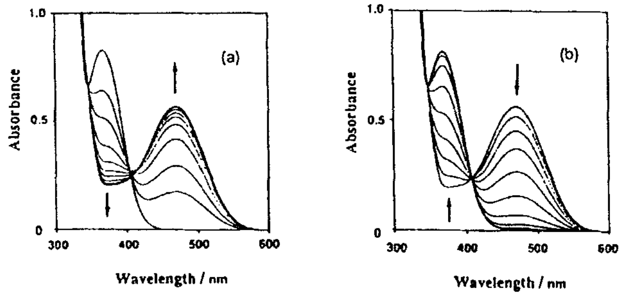


FIGURE 8. Absorption spectral change of **4** in toluene
(a) 366 nm irradiation to **3E**
(b) 495 nm irradiation to pss

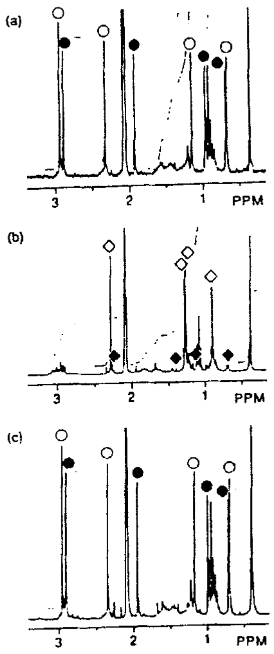


FIGURE 7. Change of ^{1}H NMR spectra of **4** in toluene-d_8
(a) **4E** at thermal equilibrium (○: major, ●: minor)
(b) pss of 366 nm irradiation (◇: major, ◆: minor)
(c) after 495 nm irradiation

These results indicate, together with the results of AM1 calculation, that the interconversion between P/M-α and M/P-α and/or P/M-α and P/M-β is quite fast for **4E**, and very slow for **3E**. As one diastereomer of the colored form is afforded predominantly from the mixture of conformational isomers of the colorless form for **4**, we would like to name this phenomenon as "*Diastereoselective Photochromism*".

Since their colorless and colored forms contain the optically active binaphthol moiety, the properties arising from the optical activity of the photochromic molecules (such as optical rotation, ORD, and CD), should change by photochromic reactions. Their specific optical rotation at D-line spectrum of sodium ($[\alpha]_D$) in toluene are -543° (**3E**) and -122° (photostationary state), and -572° (**4E**) and -186° (photostationary state). Changes of optical rotation values were also observed in PMMA films.

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