

## Photochromism of a Chiral Cyclohexane Having Two Diarylethene Chromophores. A Large Optical Rotation Change

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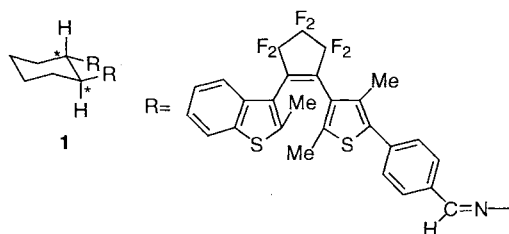
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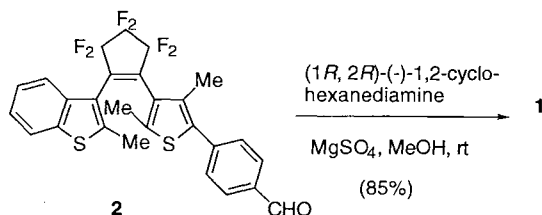
A chiral cyclohexane having two diarylethene chromophores was synthesized in an attempt to construct a molecule which shows a large optical rotation change by photoirradiation. Circular dichroism (CD) and optical rotation were found to change dramatically upon photoirradiation.

Photochromic molecules which show large optical rotation changes by photoirradiation are potentially useful for non-destructive readout in optical memories.<sup>1-5</sup> In a previous paper we have synthesized a chiral cyclohexane having two azobenzene chromophores, (*R, R*)-*N, N'*-bis[(4-phenylazophenyl) methylene]-1,2-cyclohexanediamine, which showed a large optical rotation change by photoirradiation.<sup>6</sup> The azobenzene chromophore undergoes a thermally reversible photochromic reaction. Therefore, the molecule can not be used for archival data storage. In this paper, we prepared a chiral cyclohexane having two diarylethene chromophores, which undergo thermally irreversible photochromic reactions.



Compound 1 was prepared by reacting (*1R, 2R*)-(-)-1,2-cyclohexanediamine (1 equiv.) with the aldehyde 2 (2 equiv.) and  $\text{MgSO}_4$  as shown in Scheme 1.<sup>7,8</sup> The crude product was purified by recrystallization with methanol to give compound 1<sup>9</sup> in 85% yield.

Figure 1 shows the absorption spectral change of 1 in n-hexane. The cyclohexane having two open-form diarylethenes (**1O-O**) showed the absorption maxima at 227 nm ( $\epsilon_{\text{max}} 7.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 299 nm ( $\epsilon_{\text{max}} 4.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). Upon



Scheme 1.

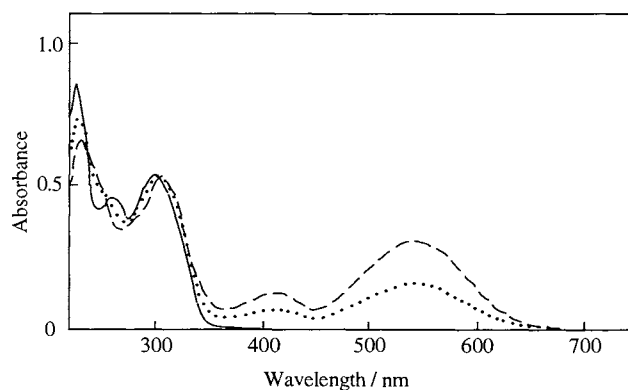
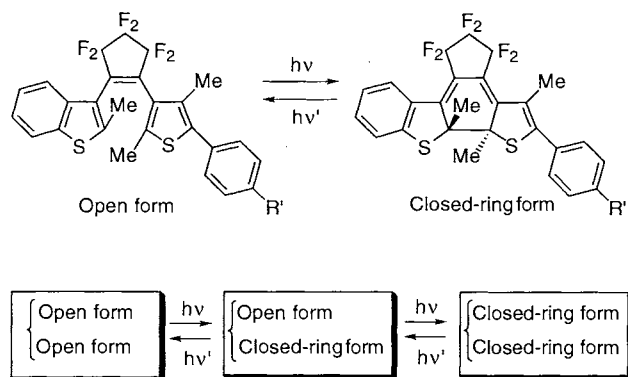
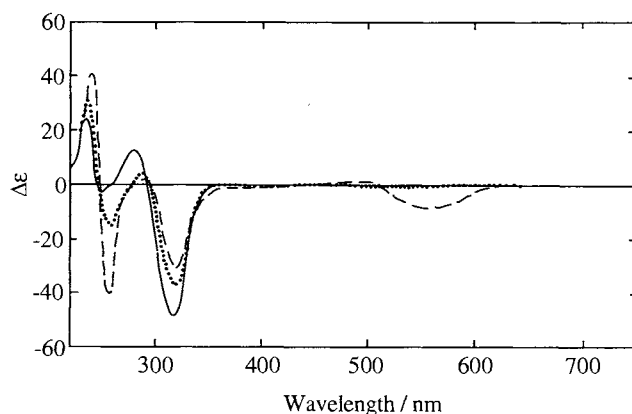


Figure 1. Absorption spectra for three isomers in n-hexane solution ( $1.1 \times 10^{-5} \text{ M}$ ); solid line **1O-O** form; dot line **1C-O** form; dash line **1C-C** form.



Scheme 2. Three isomers of compound 1.

irradiation with UV light (313 nm), the diarylethene chromophores transformed into closed-ring isomers independently, producing **1C-O** and **1C-C**, as shown in Scheme 2. Three isomers, **1O-O**, **1C-O** and **1C-C** were isolated by HPLC (Wako Wakosil 5C18, methanol) and their electronic absorption and CD spectra were measured. **1C-O** showed the absorption maxima at 230 nm ( $\epsilon_{\text{max}} 6.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), 303 nm ( $\epsilon_{\text{max}} 4.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), 411 nm ( $\epsilon_{\text{max}} 5.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 542 nm ( $\epsilon_{\text{max}} 1.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). **1C-C**, which has two closed-ring forms, showed the maxima at 238 nm ( $\epsilon_{\text{max}} 5.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), 306 nm ( $\epsilon_{\text{max}} 4.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), 412 nm ( $\epsilon_{\text{max}} 1.1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 542 nm ( $\epsilon_{\text{max}} 2.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). In the photostationary state



**Figure 2.** CD spectra for three isomers in n-hexane; solid line **1O-O**; dot line **1C-O**; dash line **1C-C**.

under irradiation with 313 nm light, the main product was **1C-C** (60%) and the rest was **1C-O** (40%). Upon irradiation with light longer than 480 nm, **1C-C** and **1C-O** forms returned again to **1O-O** form.

Figure 2 shows CD spectra of **1**. Three isomers, **1O-O**, **1C-O** and **1C-C**, gave three distinct spectra. In the wavelength region longer than 500 nm only **1C-C** gave the CD spectrum. The visible CD spectrum disappeared when **1C-C** converted to **1C-O**. The spectrum is not ascribed to induced CD effect, because the cyclohexane having a single closed-ring form did not give the CD spectrum and the CD maximum at 558 nm is different from the absorption spectral maximum at 542 nm. Induced

spectral intensity is proportional to the absorption spectral intensity ( $\epsilon$ ) and its maximum position is identical to that of the absorption spectrum. The **1C-C** form has the maximum at 558 nm (negative) and about 480 nm (positive) in CD spectrum. The spectral shape indicates a weak exciton coupling effect.

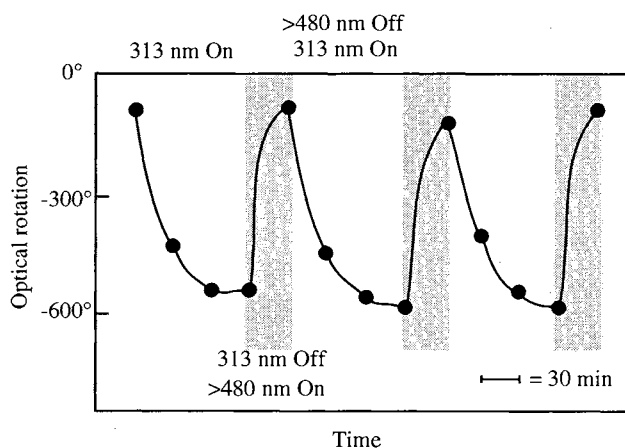
Figure 3 shows the optical rotation change by photoirradiation in methanol. The optical rotation  $[\alpha]_{669}^{25}$  ( $c=1$ ,  $\text{CH}_3\text{OH}$ ) changed dramatically by alternative irradiation with 313 nm and >480 nm light. The optical rotation value in the photostationary state under irradiation with UV light was 5-times larger than that of the VIS irradiated sample, which contained only **1O-O**. This is ascribed to the difference in the ratio of the isomers by irradiation with 313 nm light and >480 nm light. The specific rotation  $[\alpha]_{669}^{25}$  of **1O-O**, **1C-O** and **1C-C** were determined to be  $-110^\circ$ ,  $-360^\circ$  and  $-670^\circ$ , respectively. In the photostationary state under irradiation with 313 nm, 60% of **1** was in **1C-C** form and the rest was in **1C-O**. Therefore, the optical rotation decreased close to  $-600^\circ$ . On the other hand, upon irradiation with light longer than 480 nm, all molecules returned to **1O-O**, and the optical rotation increased to  $-110^\circ$ .

In conclusion, a chiral cyclohexane having two diarylethene chromophores underwent thermally irreversible photochromic reactions and showed a large optical rotation change from  $-110^\circ$  to around  $-600^\circ$  with 313 nm and >480 nm light.

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## References and Notes

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9. **1**: mp 132-133  $^\circ\text{C}$ ,  $^1\text{H}$  NMR(200 MHz,  $\text{CDCl}_3$ )  $\delta$  1.43-2.45(m, 26H), 3.39 (s, 2H), 7.14-8.20 (m, 16H); MS,  $m/z$   $M^+$  1151,  $M^+$  1150. Anal. Found: C, 62.62; H, 4.28; N, 2.50%. Calcd for  $\text{C}_{60}\text{H}_{46}\text{F}_{12}\text{N}_2\text{S}_4$ : C, 62.60; H, 4.03; N 2.43%.



**Figure 3.** Reversible ellipticity change  $[\alpha]_{669}^{25}$  ( $c=1$ ,  $\text{CH}_3\text{OH}$ ) of **1** ( $1.2 \times 10^{-4}$  M) by alternate irradiation with 313 nm light and >480 nm light.