Reversible Optical Rotation Change According to the Enantiospecific Photochromic Reaction of [2.2]Metacyclophan-1-ene

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(Received April 19, 2004; CL-040431)

Chiral [2.2]metacyclophan-1-ene undergoes an enantiospecific photochromic reaction along with a photoreversible optical rotation change at the wavelength where both photoisomers never absorb. This enables us to carry out a non-destructive read-out of the photomemory made by the photochromic [2.2]metacyclophan-1-ene.

Organic photochromism is one of the most promising systems for molecular photomemory.[1] Photochromism is defined as the photoreversible structural change that occurs between two isomers with different absorption spectra. However, when the photomemory made by a photochromic compound is read-out by an absorption change, the compounds will get excited and the memory will get destroyed. Therefore, several attempts have been carried out for a non-destructive read-out of the photomemory made by photochromic compounds. In these systems, a read-out of the change in the chiral information according to the photochromic reaction is one of the most attractive systems. Since the chiral information, particularly that pertaining to optical rotation, can be read-out at the wavelength where both isomers never absorb,[1] reversible optical rotation changes, according to the photochromic reaction, have been studied and reported using fulgides, diarylethenes, etc.[2] In these systems, the chirality originates from the diastereoselective photochromic reaction (ring-closing reaction) affected by the internal chiral functional groups. Therefore, the diastereoselectivity is influenced by the reaction conditions such as temperature, media, state, concentration, etc.

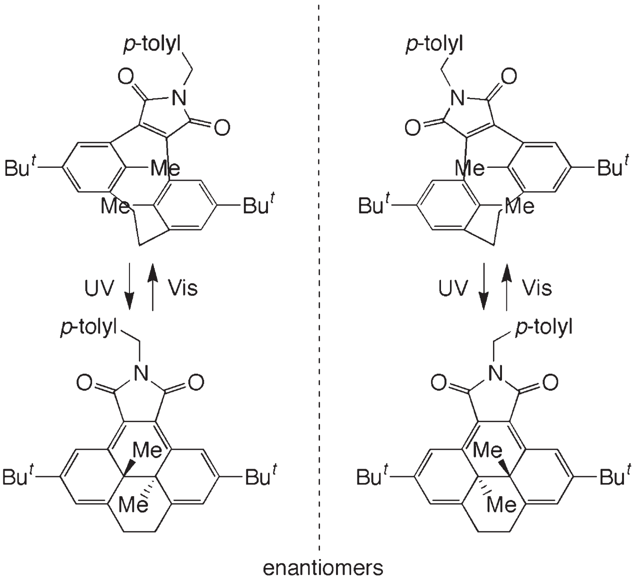

Figure 1. Enantiospecific photochromic reaction of enantiomers of [2.2]metacycophan-1-ene.

We have recently reported the enantiospecific photochromic reaction of [2.2]metacyclophan-1-ene (MCP-1-ene).[3,4] The MCP-1-ene has molecular chirality and its enantiomers are separable by HPLC with a chiral column.[4] Each enantiomer of MCP-1-ene undergoes cyclization with a UV irradiation to yield a pure enantiomer of tetrahydropyrene (THP). Upon visible irradiation, THP returns to the original MCP-1-ene enantiomer (Figure 1). These enantiomers never racemize even at 200 °C. Since there are steric hindrances between the inner methyl groups and the benzene rings, the ring flipping and the racemization process are inhibited. Thus, MCP-1-ene undergoes an enantiospecific photochromic reaction under any conditions. We examined the photoreversible optical rotation change by the photochromic reaction between MCP-1-ene and THP at the wavelength where both photoisomers never absorb.

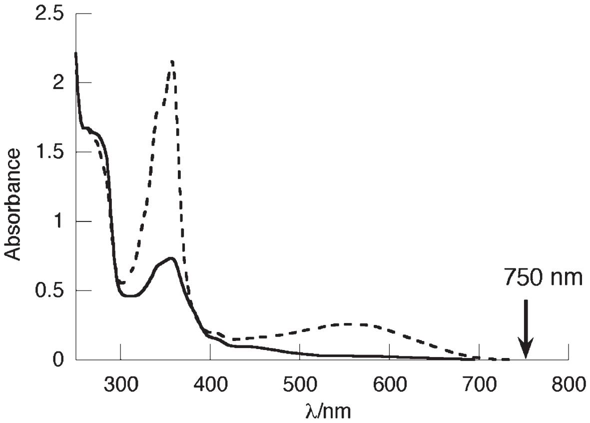

Figure 2. Absorption spectra of MCP-1-ene (solid line) and photostationary state at 313 nm (dotted line) (1.6×10^{-4} mol dm^{-3} in n-hexane).

Figure 2 shows the absorption spectral change of an n-hexane solution of MCP-1-ene upon irradiation with 313 nm light.[4] THP absorbs light at wavelength shorter than 720 nm; therefore, we chose two wavelengths of light, 750 and 880 nm light to measure the optical rotation to read-out this photochromic reaction.

The optical rotation (α) of the n-hexane solution (1.49×10^{-4} mol dm^{-3}, $c = 7.73 \times 10^{-3}$ g/100 mL) of enantiomer **A** of MCP-1-ene, which was in the first eluate of the chiral column chromatography,[5] was −0.0359° at 750 nm and −0.0246° at 880 nm, at a temperature of 20 °C (cell length = 1 dm).[6] The specific rotations of enantiomer **A** of MCP-1-ene calculated from these values were $[\alpha]_{750} = -470°$ and $[\alpha]_{880} = -320°$. On the other hand, the optical rotations of the *n*-hexane solution (1.92×10^{-4} mol dm^{-3}, $c = 9.55 \times 10^{-3}$ g/100 mL) of enantiomer **B** of MCP-1-ene in the second eluate at 750 nm and 880 nm were +0.0455 and +0.0307, respectively. The specific rotations of enantiomer **B** of MCP-1-ene were $[\alpha]_{750} = +480°$ and $[\alpha]_{880} = +320°$. The absolute specific rotation values of **A** and **B** were the same but their signs were opposite, indicating that **A** and **B** are enantiomers.

After UV irradiation with a super high pressure mercury lamp through a UV-D35 band-pass filter (350 ± 60 nm), the color of the solution changed from pale yellow to violet; this color change was indicative of the formation of THP. According to photocyclization, the optical rotations of each enantiomer changed. For example, that of enantiomer **A** at 750 nm became −0.1095° at a photostationary state (PSS). At this PSS, the conversion of MCP-1-ene to THP was 60%, as determined by the HPLC. As a result, the specific rotation of enantiomer **A** of THP ($[\alpha]_{750}$) can be calculated by the following equation:

$$\begin{aligned} -0.1095 &= 7.73 \times 10^{-3} \times 0.40 \times (-470) \times 100 \\ &\quad + 7.73 \times 10^{-3} \times 0.60 \times [\alpha]_{750} \times 100 \end{aligned} \tag{1}$$

Next, the specific rotation of enantiomer **A** of THP at 750 nm was calculated and the value $[\alpha]_{750}$ was estimated as −2050°. The specific rotation of **A** at 880 nm was determined as −870° in a manner similar to that described earlier. On the other hand, upon UV irradiation the optical rotations of enantiomer **B** at PSS became +0.133° and +0.0618 at 750 and 880 nm, respectively. The specific rotations of enantiomer **B** of THP were also calculated and the values were found to be +2000° and +870° at 750 and 880 nm, respectively. The optical rotations of enantiomers **A** and **B** returned to the initial values by visible light irradiations. Therefore, the optical rotations changed reversibly by the photochromic reactions. Such large specific rotations are not so unusual when compared with helicenes.[7] However, these reversible optical rotation changes according to the photochromic reaction are much larger than those of the reported photochromic compounds.[2] Hence the rigid fused ring structure of MCP-1-ene and THP and the 100% stereospecific photochromic reaction may enhance the optical rotation change.

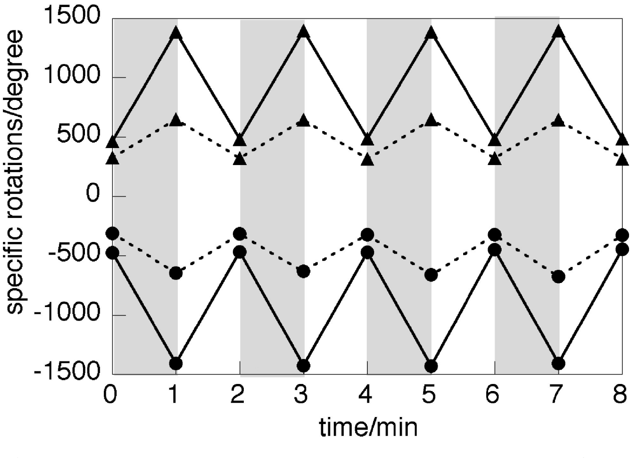

Figure 3. Specific rotation change of enantiomer **A** of [2.2]MCP-1-ene (circle, $c = 7.73 \times 10^{-2}$ g/100 mL in *n*-hexane) and that of enantiomer **B** (triangle, $c = 9.55 \times 10^{-2}$ g/100 mL in *n*-hexane) by alternate irradiation with 350 ± 60 nm light (gray, 1 min.) and >550 nm light (blank, 1 min). Solid and dotted lines indicate optical rotation change at 750 and 880 nm, respectively (cell length = 1 dm).

Figure 3 shows the reversible optical rotation changes of *n*-hexane solutions of enantiomers **A** and **B** by alternate irradiation with 350 ± 60 nm UV light (1 min) and >550 nm visible light (1 min.). Since the concentrations of the compound were assumed not to change, the specific rotations were calculated. The optical rotations were changed reversibly by the alternate photoirradiation.

In conclusion, the enantiospecific photochromic reaction of MCP-1-ene between THP drastically changes the optical rotation, and this change is photoreversible. We believe that this concept would enable us to use organic photochromic compound as a photomemory with a non-destructive read-out.

We thank Dr. Tadatsugu Yamaguchi of Fukuoka Industrial Technology Center for use of the JASCO P-1010 polarimeter. This work was partly supported by JSPS, Grant-in- Aid for Scientific Research (C) 16550126.

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5 DICEL Chiralpak AD-H was used as the chiral prepacked column for HPLC separation (hexane/2-propanol (100:1), 1 mL min^{-1}).

6 JASCO P-1010 polarimeter, 750 and 880 nm band-pass filters were used for measurement of optical rotation.

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Published on the web (Advance View) June 7, 2004; DOI 10.1246/cl.2004.844