Photoswitching of Helical Twisting Power of a Chiral Diarylethene Dopant: Pitch Change in a Chiral Nematic Liquid Crystal

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Photostimulated reversible phase changes in liquid crystals potentially play a key role in molecular devices and optical display systems.[1,2] So far various types of photoresponsive liquid crystals have been reported. The first example is a cholesteric liquid crystal containing a cis−trans photoisomerizable azobenzene derivative, which shows a reversible pitch change by photoirradiation.[3] When azobenzene derivatives are doped to nematic liquid crystals, the liquid crystals undergo the switching between nematic and isotropic phases by the photoisomerization.[4] Other attractive photoresponsive systems are nematic liquid crystals containing photoactive chiral chromophores.[5−7] Photostimulated chiral property changes of the chromophores trigger the switching between the apparent nematic and chiral nematic (induced cholesteric) phases. In this communication we report on the development of an efficient and robust photochromic trigger, a chiral cyclohexane **1** having two diarylethenes, for the photoinduced large pitch change in the chiral nematic phase.

Compound **1** was prepared by reacting (1*R*,2*R*)-cyclohexanediamine (1 equiv) with the aldehyde derivative of the diarylethene.[8]

Upon irradiation with UV light, the two diarylethene chromophores transformed into closed-ring isomers, producing the mixture of **1C−O** and **1 C−C** isomers, as shown in Figure 1. The mixture of the colored isomers showed the absorption maximum at 541 nm in hexane. In the photostationary state under irradiation with 313-nm light, the main product was **1C−C** (~60%) and the rest was **1C−O** (~40%).[9] The colored isomers were stable at room temperature and never returned to the colorless form (**1O−O**) in the dark. Upon irradiation with >480-nm light, the mixture returned to initial **1O−O**. The photocoloration/decoloration cycles could be repeated more than 100 times while keeping the photochromic performance in hexane.

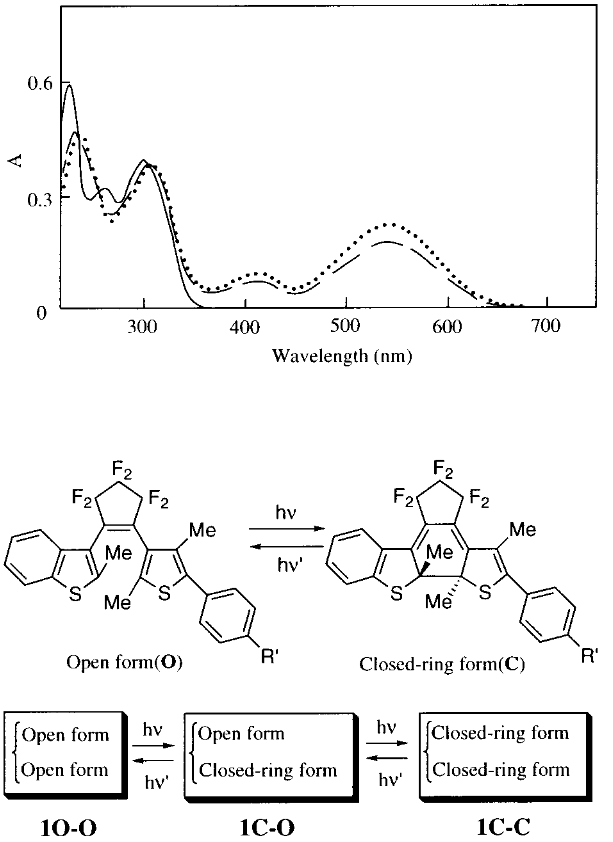
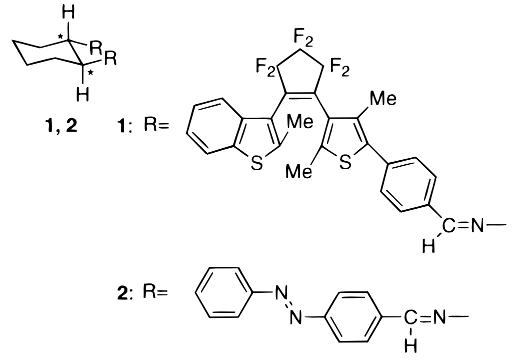


Figure 1. Photoisomerization of compound **1**. Absorption spectra of **1O−O** (—), in the photostationary state under irradiation with 313 nm (− −) and **1C−C** (···) in hexane (8.0×10^{-5} M).



Compound **1** was doped to a nematic liquid crystal, 4-cyano-4′-pentylbiphenyl (K-15) (Tokyo Kasei), and the

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(9) Three isomers were isolated by HPLC with an ODS column (Wako WS5C18; eluent, methanol).

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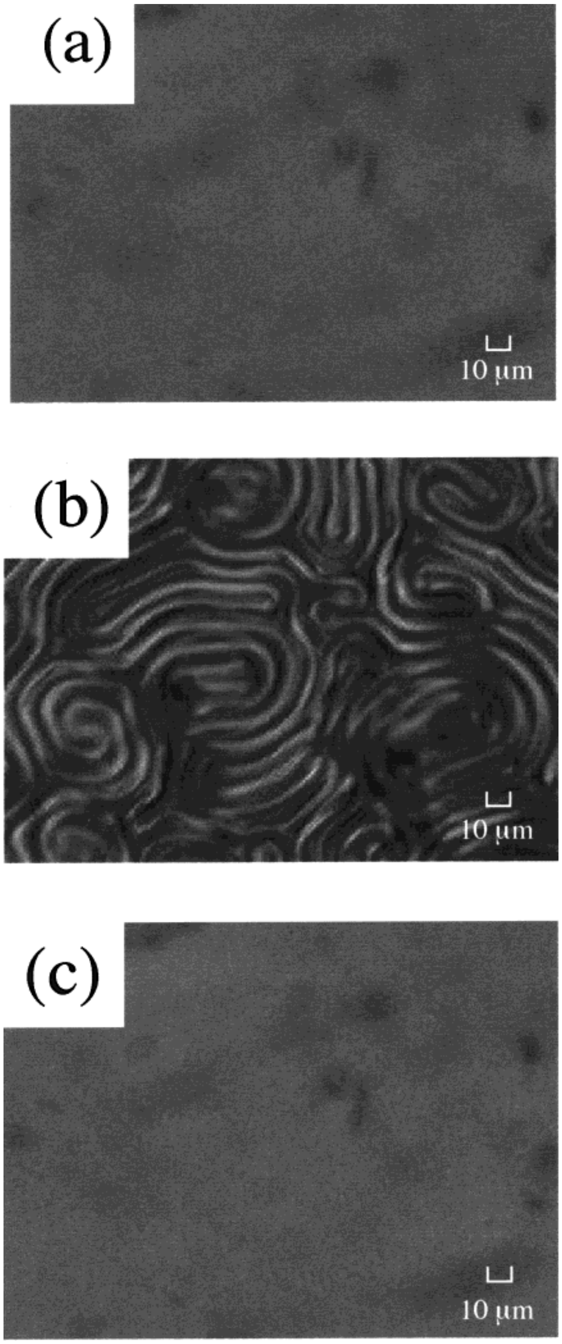

Figure 2. Photos of the K-15 liquid crystal containing 1.0 wt % compound **1** at 26 °C before (a), after irradiation with 254 nm light for 3 min (b), and after irradiation with >400 nm light for 3 min (c); viewed at ~100× magnification through cross polarizers between the covered lens and the microslide. The cell thickness was ~80 μm.

phase change (or the pitch change) of the liquid crystal was followed after UV/vis irradiation at 26 °C. The changes were monitored using a polarization microscope (Nikon OPTIPHOT2-POL). Irradiation was carried out with a mercury lamp (254 nm, 10 W), and a halogen lamp (λ > 480 nm, 100 W). The cell was constructed according to the method given in refs 5b and 10. The liquid-crystalline material K-15 showed a stable nematic texture even when 1.0 wt % **1O−O** was added, as shown in Figure 2a. When the content increased above 5.0 wt %, the texture clearly changed to a cholesteric fingerprint pattern. When the content of **1O−O** (inset 1) was less than 2 wt %, the liquid crystalline image was apparently a conventional nematic. The pitch of the chiral nematic phase is considered to be extremely large because of very weak helical twisting power of **1O−O**.

When the liquid crystal containing 1.0 wt % **1O−O** was irradiated with UV light (254 nm) for 3 min, a cholesteric fingerprint texture gradually appeared (Figure 2b). Irradiation of the liquid crystal with UV light increased helical twisting power of the dopant. The fingerprint texture disappeared by irradiation with visible light (λ >400 nm) for 3 min (Figure 2c). Alternating irradiation with UV and visible light caused the reversible switching between the two images.

The pitch of the liquid crystalline phase was measured by the droplet method.[11] The same data was obtained with the Grandjean−Cano method.[12,13] Before irradiation with UV light, no disclination lines were observed with the droplet method. The pitch was longer than 40 μm. Upon irradiation with UV light, the concentric rings in the droplet gradually appeared. When the sample was irradiated with UV light for 3 min, the pitch decreased to 11.8 μm. Upon irradiation with >400 nm light for 3 min, the pitch again increased to >40 μm. The switching cycle was performed more than 50 times without deterioration of the liquid-crystalline phase.

Compound **1** is an efficient trigger for the switching. The pitch value indicates that the twisting power of the mixture of the closed ring isomers **1C−O** and **1C−C**, is much larger than that of **1O−O**. This photoresponsive behavior, UV light causing the decrease in the pitch, is different from the system containing a chiral bisimine-modified diarylethene.[7] When the two diarylethene units of **1** were in the open forms, the liquid crystalline phase apparently showed a nematic texture. Upon irradiation with UV light, the pattern changed to a cholesteric phase. On the other hand, the addition of small amount of bisimine-modified diarylethene caused a cholesteric phase. Upon irradiation with UV light, the phase changed to a nematic phase. The complementary property of the two systems may be useful to controlling the liquid crystalline phases.

The diarylethene choromophore showed a thermally irreversible and fatigue-resistant photochromic reaction. This means that both phases, the apparent nematic and chiral nematic (induced cholesteric) phases, remain stable even after long-term storage. To confirm the uniqueness of compound **1**, azobenzene derivative **2** was prepared.[14] The addition of 1.0 wt % **2E−E** (trans−trans isomer) to K-15 resulted in a chiral nematic phase at 26 °C, the pitch being calculated to be 12.0 μm. Irradiation of the sample with 366-nm light for 3 min increased the pitch to 22.1 μm.

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(10) The cell was constructed according to the refs 5b and 10. A thin Teflon spacer separated two covering lenses. The lenses were purchased from E.H.C. (Japan), they were coated with the polyimide for the surface alignment. The sample was filled with the capillary force.

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Compound **1** dramatically changed its optical rotation by UV/vis photoirradiation. The optical rotation value in the photostationary state under irradiation with 313-nm light ($[\alpha]^{25}_{669} = -600°$) was 5 times larger than that of **1O−O** ($[\alpha]^{25}_{669} = -110°$) in methanol. In contrast, compound **2** showed a small optical rotation change. The optical rotation value in the photostationary state under irradiation with 366-nm light was only half that of **2E−E**. Although the optical rotation value does not directly correlate with the twisting power force, the large increase in the value by UV irradiation observed for compound **1** is considered to play a role in the phase change.

In conclusion, we have demonstrated that a small amount of a chiral cyclohexane having two photochromic diarylethenes in a nematic liquid crystal K-15 induced a large and stable pitch change in the chiral nematic phase. The switching cycle was performed more than 50 times without deterioration of the liquid-crystalline phase.

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