

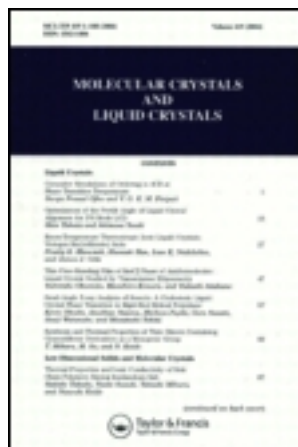
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Phase Transition of a Liquid Crystal Induced by Chiral Photochromic Dopants

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Phase Transition of a Liquid Crystal Induced by Chiral Photochromic Dopants

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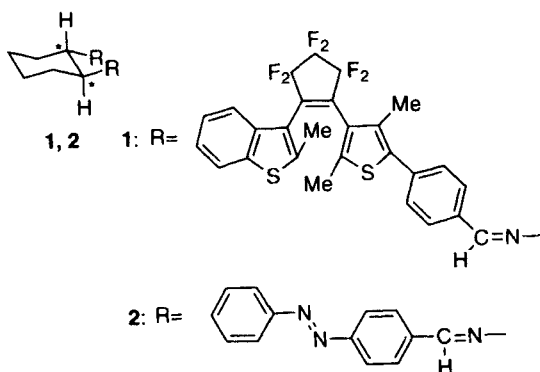
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A chiral cyclohexane having two photochromic diarylethene unit was synthesized in an attempt to use it as a dopant for a photoresponsive liquid crystal. A stable photoswitching between nematic and cholesteric phases could be induced by the addition of a small amount of the chiral cyclohexane to a nematic liquid crystal 4-cyano-4'-pentylbiphenyl (K-15).

Keywords: Photochromism; Diarylethene; Liquid Crystal; Chiral Dopant

INTRODUCTION

Photostimulated reversible phase changes in liquid crystals potentially plays a key role in molecular devices and optical display systems.^[1, 2] So far various types of photoresponsive liquid crystals have been reported. One of attractive photoresponsive systems is a nematic liquid crystals containing photoactive chiral chromophores.^[3-5] Photostimulated chiral property changes of the chromophores trigger the switching between nematic and chiral nematic (induced cholesteric) phases. In this paper we report on the development of an efficient and robust photochromic trigger, a chiral cyclohexane **1** having two diarylethenes, for the photoinduced nematic-cholesteric phase change.



RESULTS AND DISCUSSION

Compound **1** was prepared by reacting (1*R*, 2*R*)-cyclohexanediamine (1 equiv.) with the aldehyde derivative of the diarylethene (2 equiv.).^[6]

Upon irradiation with UV light, the two diarylethene chromophores transformed into closed-ring isomers, producing **1C-O**

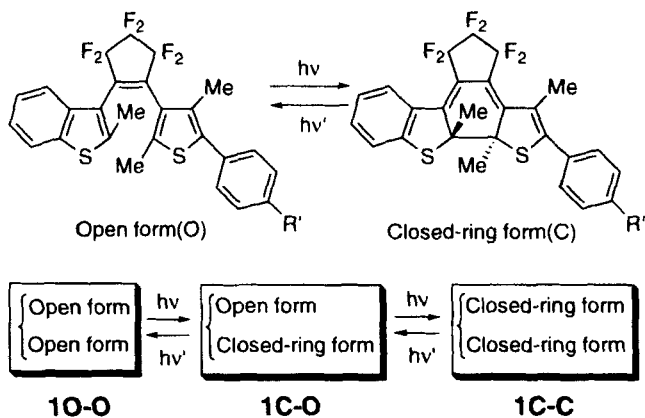


Figure 1. Photoisomerization of compound 1.

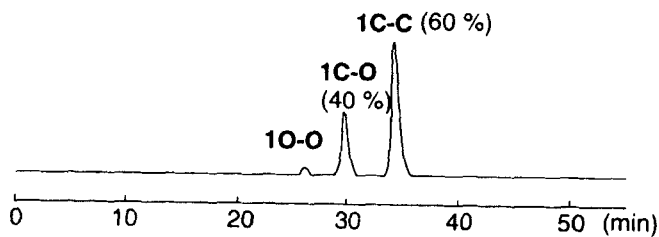


Figure 2. HPLC chart of 1 irradiated with 313 nm light.

and **1 C-C**, as shown in Figure 1 and 2. **1C-C** and **1C-O** showed the absorption maxima at 541 nm in hexane. In the photostationary state under irradiation with 313 nm light, the main product was **1C-C** (ca.

60 %) and the rest was **1C-O** (ca. 40 %)^[7]. 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, **1C-C** and **1C-O** returned to initial **1O-O**.

The optical rotation $[\alpha]_{669}^{25}$ ($c=1$, CH_3OH) of compound **1** changed dramatically by alternative irradiation with 313 nm and >480 nm light.^[6] 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.

Compound **1** was doped to a nematic liquid crystal, 4-cyano-4'-pentylbiphenyl (K-15), and the phase change of the liquid crystal was followed upon UV/Vis irradiation at 26°C. The phase transition was monitored using a polarization microscope (Nikon OPTIPHOT2-POL). Irradiation was carried out with a mercury lamp (254 nm, 10 W), and a halogen lamp ($\lambda>400$ nm, 100 W). The liquid-crystalline material K-15 showed the stable nematic texture even when 1.0 wt- % **1O-O** was added.

When the nematic liquid crystal containing 1.0 wt- % **1O-O** was irradiated with UV light (254 nm) for 1 min, a cholesteric fingerprint texture appeared. Irradiation of the sample with visible light ($\lambda>400$ nm) for 3 min. regenerated the nematic texture. Alternate irradiation with UV and Vis light caused the reversible switching between nematic and cholesteric phases.

The pitch of the liquid crystalline phase was measured by the droplet method (Table 1).^[8] Before irradiation with UV light no disclination lines were observed with the droplet method. The pitch was longer than 40 μm . When the sample was irradiated with UV light, the pitch decreased to 11.8 μm . Compound **1** is an efficient trigger for the switching between nematic and cholesteric phases.

Table 1. Pitch values of K-15 liquid crystals containing compound **1** (1.0 wt-%) and **2** (1.0 wt-%) at 26 °C as determined by the droplet method.

Compound	Pitch (μm)
10-O	>40
1 (Photostationary state sample) ^a	11.8
2E-E	12.0
2 (Photostationary state sample) ^b	22.1

^a The sample was irradiated with the 254 nm light.

^b The sample was irradiated with the 366 nm light.

The diarylethene chromophore showed a thermally irreversible and fatigue resistant photochromic reaction. This means that both phases, the nematic and cholesteric phases, remain stable even after long-time storage. To confirm the unique characteristic of compound **1**, azobenzene derivative **2** was prepared.^[9] The addition of 1.0 wt-% **2E-E** (trans-trans isomer) to K-15 resulted in a chiral nematic phases 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 .

In conclusion, we have demonstrated that a small amount of a chiral cyclohexane having two photochromic diarylethene in nematic liquid crystal K-15 can induce a stable photoswitching between nematic and cholesteric phases.

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