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Photoswitching of Helical Twisting Power by Chiral Diarylethene Dopants

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Photoswitching of Helical Twisting Power by Chiral Diarylethene Dopants

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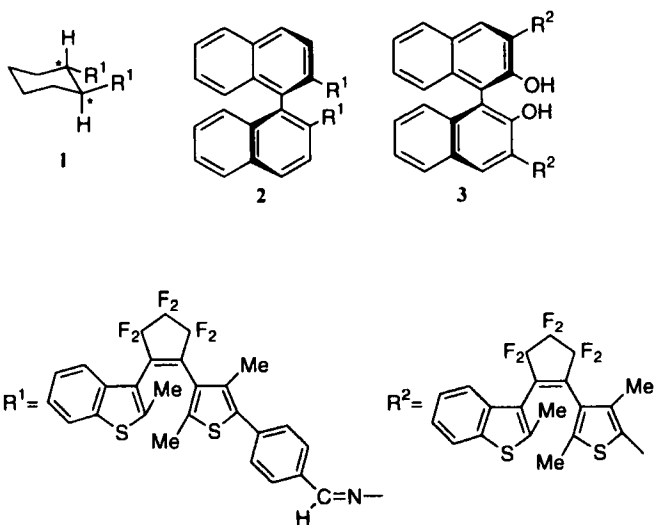
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Photochromic chiral compounds having two diarylethene units were synthesized in an attempt to use them as dopants for photoresponsive liquid crystals. Stable photoswitching of the photochromic dopants induced large pitch changes of chiral nematic liquid crystals composed of K-15 and a small amount of the chiral dopants.

Keywords: Photochromism; Diarylethene; Liquid Crystal; Chiral Dopant

INTRODUCTION

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. One of attractive photoresponsive systems is a nematic liquid crystal containing photoactive chiral chromophores.^{[3][7]} Photostimulated chiral property changes of the chromophores trigger the switching between the apparent nematic and chiral nematic (induced cholesteric) phases. In this paper we report on the development of efficient and robust photochromic triggers, chiral compounds **1-3** having two diarylethenes, for the photoinduced large pitch changes in the chiral nematic phase.

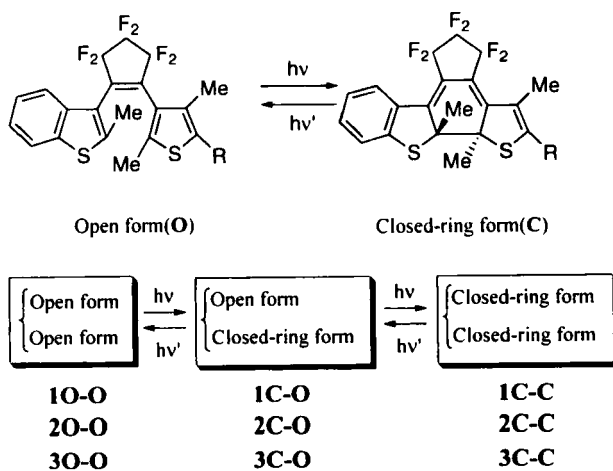


RESULTS AND DISCUSSION

Compounds **1-3** containing two photochromic diarylethene units were synthesized in an attempt to use them as dopants for photoresponsive liquid crystals. Compounds **1-3** were prepared according to the method described before.^[8]

Compounds **1-3** underwent reversible photoisomerizations in methanol by alternate irradiation with UV and visible light. The chiral cyclohexane having two open-ring diarylethenes (**1O-O**) converted into two kinds of closed-ring isomers by irradiation with 313 nm light. In the photostationary state, the main product was **1C-C** (60 %) and the rest was **1C-O** (40 %).^[8]

The binaphthyl having two open-ring form diarylethenes (**2O-O**) showed the absorption maximum at 318 nm in methanol. Upon irradiation with 313 nm light, the diarylethene chromophores transformed into closed-ring isomers independently, producing **2C-O** (26 %), **2C-C** (26 %) and **2O-O** (48 %). The mixture of the three isomers showed the maximum at 546 nm.



The binaphthyl having two open-ring form diarylethenes (**3O-O**) showed the absorption maximum at 298 nm in methanol. Upon irradiation with 313 nm light, the diarylethene chromophores also transformed into closed-ring isomers independently, producing **3C-O** and **3C-C**. The mixture of the two isomers showed the maximum at 537 nm. In the photostationary state under irradiation with 313 nm light, the main product was **3C-O** (72 %) and the rest was **3C-C** (10 %) and **3O-O** (17 %).

Table 1. Pitch values of the K-15 liquid crystals containing compounds **1-3** (2.0 wt-%) at 26 °C as determined by the droplet method.

Compound	Pitch (μm)
1 (Open form)	23.7
1 (Photostationary state sample) ^a	7.9
2 (Open form)	28.5
2 (Photostationary state sample) ^a	24.4
3 (Open form)	>100
3 (Photostationary state sample) ^a	24.1

^a The sample was irradiated with 254 nm light.

Compounds **1-3** were doped into a nematic liquid crystal, 4-cyano-4'-pentylbiphenyl(K-15), and the phase changes (or the pitch changes) of the liquid crystals were followed after UV/ Vis. irradiation at 26 °C. The pitch of the liquid crystalline phase was measured by the droplet method.^{[9],[10]} Table 1 shows pitch values of K-15 liquid crystals

containing compounds **1-3** (2.0 wt- %). Compound **1** is an efficient trigger for the switching as reported in a previous paper.¹⁷⁾ Compound **2** is not an effective trigger for the pitch change.

Compound **3** was a best trigger for the switching. Before irradiation with UV light, no disclination lines were observed for the liquid crystal containing compound **3**. The droplet showed a schrielen texture. Upon irradiation with 254 nm light, the concentric rings in the droplet gradually appeared. When the sample was irradiated with the UV light for 3 min, the pitch decreased to 24.1 μm . Upon irradiation with > 400 nm light for 3 min, the concentric rings disappeared. The pitch again increased to > 100 μm .

Compound **1** changed its optical rotation by UV/ Vis. photoirradiation . The optical rotation value in the photostationary state under irradiation with 313 nm light($[\alpha]_{669}^{25}$ -600°) was 5 times larger than that of **10-O**($[\alpha]_{669}^{25}$ -110°) in methanol. Compound **3** also changed its optical rotation by UV/Vis photoirradiation. The specific rotation values($[\alpha]_{669}^{25}$ (c=5, ethyl acetate)) of **30-O** and the photostationary state sample by irradiation with 254 nm light were 0° and -28°, respectively. Although the optical rotation value does not directly correlate with the twisting power force, the decrease of the optical rotation value is considered to play a role in the pitch change.

In conclusion, we have demonstrated that a small amount of chiral binaphthyl **3** having two photochromic diarylethene units in nematic liquid crystalline K-15 can induce a stable photoswitching between apparently nematic and cholesteric phases.

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