

Reversible Control of Pitch of Induced Cholesteric Liquid Crystal by Optically Active Photochromic Fulgide Derivatives

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(Received March 10, 1997; CL-970168)

Mixtures of nematic 4-cyano-4'-pentylbiphenyl and (*R*)-2,2'-dihydroxy-1,1'-binaphthyl-condensed fulgide derivatives form stable cholesteric liquid crystalline states. Photochromic reactions of them induced the change of their cholesteric pitch reversibly.

Special attention has been paid to controlling the properties of liquid crystals (LCs) by photochemical reactions of photochromic molecules.¹⁻⁹ While control of the cholesteric pitch is of particular interest, few examples have been reported.^{1,8,9} One recent elaboration reported by Schuster⁸ used a racemic mixture of an indolylfulgide with cholesteric LC induced by a nematic LC and a chiral dopant, and another one reported by Feringa⁹ used an enantiomer of a resolved stilbene derivative¹⁰ as the chiral dopant of a nematic LC. We here report that (1) fulgide derivatives **1** and **2** that have the inherent chiral nature worked as chiral dopants to induce the cholesteric phases by mixing them with a nematic LC, and (2) iterative irradiation of UV and visible light caused the large and repeated change of the cholesteric pitch. The former is the notable feature as the photochromic chiral dopant because we do neither have to worry about the racemization nor have to carry out the optical resolution.

Synthesis, structural characterization including the determination of the absolute configuration of the colored form, diastereoselective photochromic reaction,¹¹ and on/off switching of fluorescent nature by photochromism¹² of the fulgide derivatives **1** and **2** having the acetal structure of (*R*)-2,2'-dihydroxy-1,1'-binaphthyl have already been reported.

Mixtures of 4-cyano-4'-pentylbiphenyl (5CB), which is the representative of nematic LCs, and **1C** or **2C** formed cholesteric phases. A mixture was placed in a Cano's wedge-type glass cell ($\tan\theta$: 11.2×10^{-3}) at 30.0 °C, and the pitch length was determined from the observed line distances of the twist disclination (Cano's line). The pitch values of **1E** and **2E** were determined similarly after irradiation of >450-nm light to the LC cells. These cells were then irradiated with 366-nm light to afford the photostationary state (pss) (the ratio of E/C is *ca.* 20/80 - 15/85),^{11,13} and the pitch lengths were determined.

The absolute values of twisting power (β_M) of **1** and **2** were then calculated as the average of the reciprocal of the product of pitch (μm) and the concentration of the dopant (mol dm^{-3}) for three different concentrations.

In order to determine the sign of β_M of the fulgide derivatives,

Table 1. Cholesteric pitch values and β_M values of **1**, **2**, and **3** in 5CB at 30 °C^a

| | C | Pitch/ μm | | $\beta_M/\mu\text{m}^{-1} \text{ mol}^{-1} \text{ dm}^3$ | | |
|----------------------|------|----------------------|------|--|------|-------|
| | | E | pss | C | E | pss |
| 1 | 2.05 | 15.76 | 2.57 | -43.0 | -5.6 | -34.6 |
| 2 | 2.01 | 12.23 | 2.59 | -42.7 | -6.9 | -33.5 |
| 3^b | | | 3.24 | | | -22.5 |

^a Concentration of dopants: **1**; $1.12 \times 10^{-2} \text{ mol dm}^{-3}$. **2**; $1.15 \times 10^{-2} \text{ mol dm}^{-3}$. **3**; $1.41 \times 10^{-2} \text{ mol dm}^{-3}$.

^b Values for **3** are those just in 5CB.

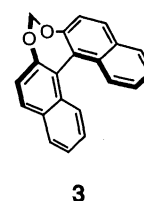
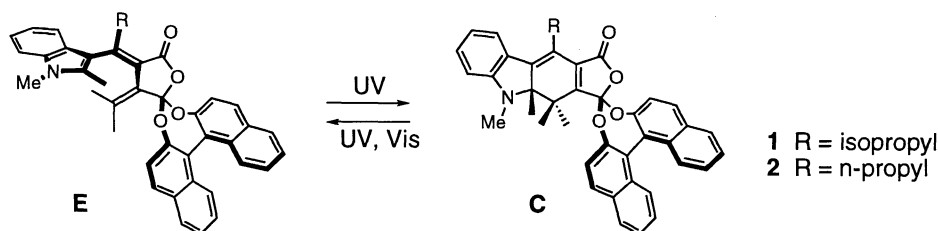
equal amount of 5CB containing methylene acetal of (*R*)-binaphthol **3** ($0.622 \times 10^{-2} \text{ mol dm}^{-3}$, pitch/ μm = 7.07; **3** is reported to have the minus β_M ¹⁴) and 5CB containing **1C** ($1.115 \times 10^{-2} \text{ mol dm}^{-3}$, pitch/ μm = 2.05) was mixed, and the pitch was calculated. As the pitch was 3.16 μm which is practically equal to the predicted value (3.18 μm) if the β_M values of **3** and **1C** have the same sign, the sign of β_M of **1C** was proved to be minus.¹⁵

The sign of β_M of **1E** was determined by observing the change of pitch of the initial a few ten seconds when the cell containing **1C** and 5CB was irradiated with visible light. As the pitch lengthened monotonously, the sign of β_M of **1E** was also found to be minus. Results are summarized in Table 1.

As the contribution of the chiral quaternary carbon atom of the C-form to its β_M is considered to be small, its β_M mainly comes from the binaphthol moiety. Because the β_M values are twice as large as that of **3**, the total molecular shapes of **1C** and **2C** also contribute to their minus helical senses. To the contrary, the helical array of the substituents on the furandione ring of the E-form should affect β_M largely. It has been shown that the major two conformational isomers of the E-forms have *P*-helicity.¹¹ As the (*R*)-binaphthyl unit has *M*-helicity, it was offset by the *P*-helicity of the indole moiety to some extent, and the E-forms showed the small minus β_M values.

The change of the pitch was repeated for many times by photochromic reactions between the E-form and the pss, though the difference of the pitch decreased gradually¹⁶ (Figure 1).

In summary, we have shown that (1) the chiral fulgide derivatives worked as the chiral dopants to induce the cholesteric



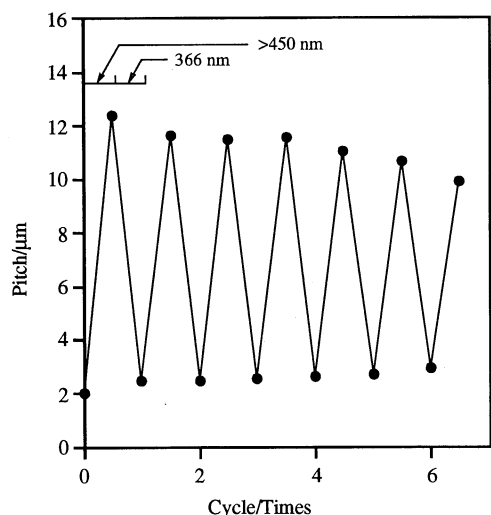


Figure 1. Reversible change of pitch of the cholesteric phase of 5CB induced by **2** by photoirradiation. c : $1.22 \times 10^{-2} \text{ mol dm}^{-3}$. Starting with **2C** at 30°C . Irradiation time; $>450 \text{ nm}$: 5 min, 366 nm : 60 min.

phases when doped with the nematic LC, and (2) their photochromic reactions induced the reversible and large change of the pitch values of the cholesteric phases. Since fulgide derivatives do not change their structures thermally, the induced cholesteric phases are stable as long as the exciting light is absent.

This work was supported by Tokuyama Science Foundation and Nissan Science Foundation which are greatly acknowledged. We also thank Chisso Corporation for generous gift of 5CB.

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- 13 Both **1** and **2** do not generate the Z-forms during the photochromic reactions.¹¹
- 14 G. Solladie and R. G. Zimmermann, *Angew. Chem., Int. Ed. Engl.*, **23**, 348 (1984).
- 15 The predicted value of the pitch was $5.77 \mu\text{m}$ if the sign of β_M of **1C** is different from that of **3**.
- 16 The fatigue resistivity of binaphthol-condensed indolylfulgide in 5CB was inferior to that in PMMA.¹¹