An Optically Active Diarylethene Having Cholesterol Units: A Dopant for Photoswitching of Liquid Crystal Phases

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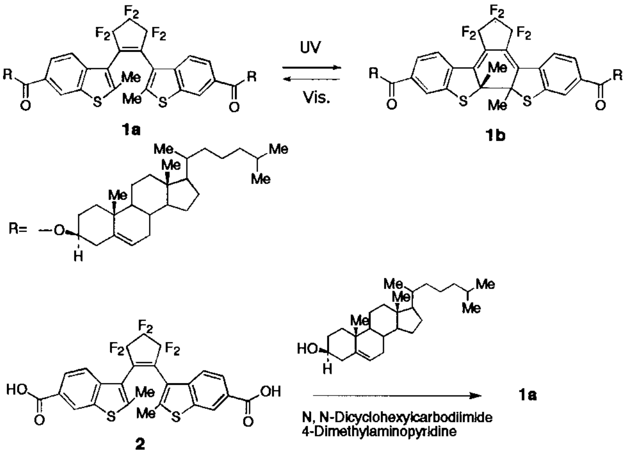
A diarylethene[1] having cholesterol units was synthesized in an attempt to use it as a dopant to control the phase of liquid crystals. By the addition of the diarylethene, 4-cyano-4'-pentylbiphenyl (K-15)(Tokyo kasei) nematic liquid crystal showed cholesteric liquid crystalline texture. Upon irradiation with UV light, the cholesteric phase was decomposed. The cholesteric phase was recovered by visible light irradiation. The reversible photoinduced-phase change was observed by alternate irradiation with UV and visible light.



Photoinduced reversible phase change of liquid crystals is a potentially useful technique to control optical properties of switching or display devices.[2] Such phase change can be induced by using photochromic compounds as dopants. As the first example, Sackmann reported on reversible color changes in cholesteric phases induced by photochemical cis-trans isomerization of dissolved azobenzene molecules.[3] Recently, the azobenzene derivatives[4] and photochromic thioindigo dyes[5] were also applied for the rapid switching of ferroelectric liquid crystals.

Sato et al.[6] investigated the photo-induced isomerization of azobenzene in compensated liquid crystals composed of cholesteryl chloride and cholesteryl nonanate, and found the transmittance of the liquid crystals was controlled by photoirradiation. Thereafter, a lot of photochromic compounds have been used as the photo-triggers that induce phase changes in liquid crystals.[7] On doping the photochromic compounds to thermotropic liquid crystals, thermal stability of both isomers of the photochromic compounds are desired. Recently, Feringa et al.[8] reported that a dithienylethene having chiral substituents could also be used as a dopant to induce the phase change. It is known that some of dithienylethenes lack the fatigue resistant property,[9] while diarylethenes that have benzothiophene rings have excellent fatigue resistance.[1]

Herein we have synthesized a bisbenzothienylethene derivative having two cholesteric units and doped it into K-15 liquid crystal in an attempt to induce the phase changes with high performance. The diarylethene (**1**)[10] was synthesized by condensation of diacid **2**[11] and 2 equivalent amount of cholesterol in the presence of dicyclohexylcarbodiimide as the dehydration regent.

The hexane solution of **1a** is colorless and the absorption maximum was observed at 318 nm (ε: 1.3 × 10^4 $M^{-1}cm^{-1}$). Upon irradiation with UV light, the hexane solution turned red-purple, producing the closed-ring isomer **1b** as shown in Figure 1. The colored isomer showed the absorption maximum at 543 nm. The colored isomer **1b** was stable even at 70 °C and never returned to the colorless isomer **1a** in the dark. Upon irradiation with visible light (λ > 480 nm), the color disappeared and colorless **1a** was regenarated. The photochromic reaction was also monitored by ^{1}H NMR spectra. The methyl signals of **1a** were observed at 2.25 and 2.52 ppm in $CDCl_3$. They were attributed to signals of anti-parallel and parallel conformations, respectively. The ratio of a-p to p conformations was 65 : 35, which is almost same as parent compound. Upon UV irradiation, a new signal appeared at 2.03 ppm, that is attributable to the methyl signal of closed-ring isomer **1b** and the signal disappeared by visible light irradi-

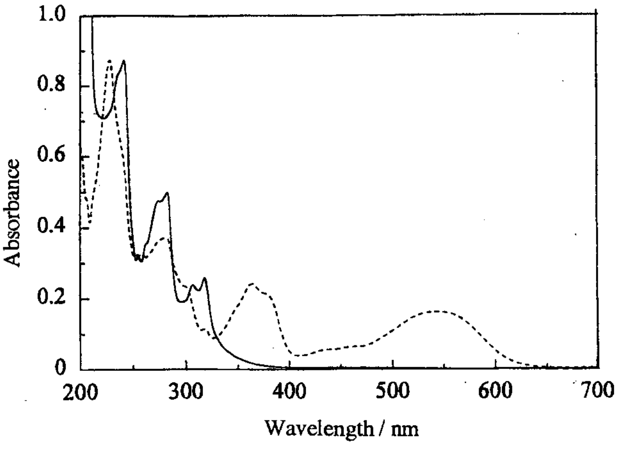


Figure 1. Photochromic reaction of diarylethene **1** in hexane before UV irradiation (solid line) and after UV irradiation (broken line).

Table 1. Pitch value and helical twisting power of the cholesteric phase formed by doping **1** in K-15 as determined by the Cano-Grandjean method.

Photochrome	Content / wt%	Pitch / mm	βM / μm^{-1}	Phase transition / ℃
1a	2.0	10	26	N* 35.7 I

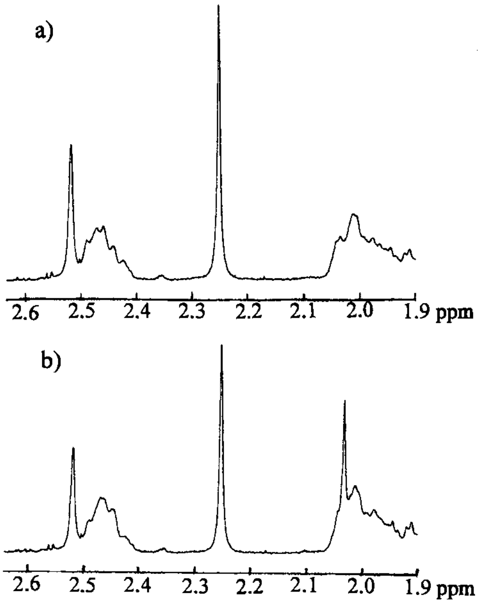


Figure 2. The ^{1}H NMR spectra of **1a** before UV irradiation (a) and after UV irradiation (b) in $CDCl_3$.

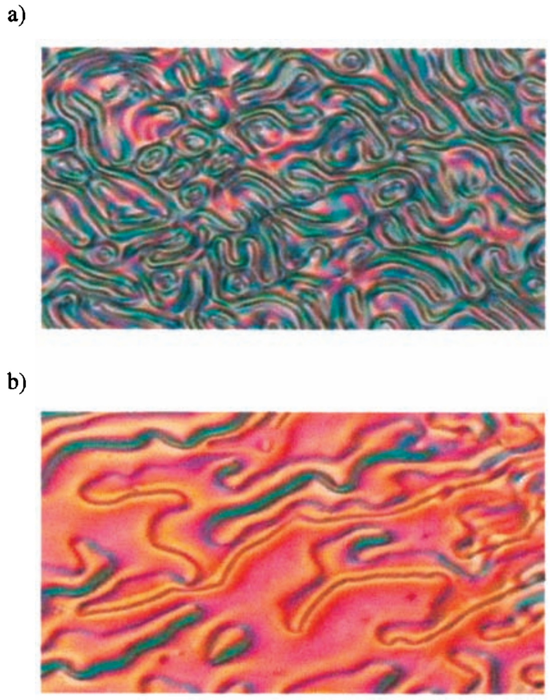


Figure 3. The texture of the twisted nematic and nematic liquid-crystalline phases; 2.0 wt% of **1** in K-15 at 34.8 ℃.
a) Cholesteric finger print texture. b) Nematic texture.

ation. Quantum yields of the photochromic reaction could not be obtained, because isolation of the closed-ring isomer by HPLC failed.

Diarylethene **1a** was doped into a nematic liquid crystal, K-15 to form a stable cholesteric phase (Figure 3a) and the texture was monitored using polorization microscope (Olympus BH-2). In order to obtain a stable cholesteric phase, the addition of 1–2 wt% of **1a** was needed. The phase transition temperature of chiral nematic to isotropic phase (N*-I) of the mixture of **1a** (2.0 wt%) and K-15 was 35.7 °C. The pitch and helical twisting power were determined by the droplet method[12] and the Grandjean-Caro method.[13] The result is summarized in Table 1. When the mixture was irradiated with UV light (254 nm) for 60 s at 34.8 °C, the chiral nematic phase disappeared and a nematic phase texture was observed (Figure 3b). The N-I phase transition temperature of the photoirradiated sample was 35.5 °C, which was similar to N*-I phase transition temperature. Irradiation with visible light (λ > 480 nm) for 1 or 2 s, finger print texture of cholesteric phase was regenerated. The cycle could be repeated more than 50 times without deterioration of the liquid-crystalline phase.

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References and Notes

1 M. Irie and M. Mohri, *J. Org. Chem.*, **53**, 803 (1988); M. Irie and K. Uchida, *Bull. Chem. Soc. Jpn.*, **73**, 985 (1998); S. H. Kawai, S. L. Gilat, and J-M. Lehn, *Chem. Eur. J.*, **1**, 285 (1995); G. M. Tsivgoulis and J-M. Lehn, *Chem. Eur. J.*, **2**, 1399 (1996).
2 H. Duerr and H. Bouas-Laurent, “Photochromism Molecules and Systems,” Elsevir, Amsterdam (1990).
3 E. Sackmann, *J. Am. Chem. Soc.*, **93**, 7088 (1971).
4 M. Negishi, O. Tsutsumi, T. Ikeda, T. Hiyama, J. Kawamura, M. Aizawa, ans S. Takehama, *Chem. Lett.*, **1996**, 319.
5 L. Dinescu and R. P. Lemieux, *J. Am. Chem. Soc.*, **119**, 8111 (1997).
6 S. Sato and H. Ueda, *Denshitsuushin-Gakkai-Ronbunshi*, **J-62-C**, 179 (1979).
7 T. Ikeda and O. Tsutsumi, *Science*, **268**, 1873 (1995); T. Ikeda, T. Sasaki, and K. Ichimura, *Nature*, **428**, 361 (1993).
8 C. Denekamp and B. L. Feringa, *Adv. Mater.*, **10**, 1082 (1998).
9 M. Irie, T. Lifka, K. Uchida, S. Kobatake, and Y. Shindo, *Chem. Commun.*, **1999**, 747.
10 **1a:** Transparent plates; mp 202.1–203.9 °C ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.86–2.50 (84H, m), 2.25 (6H, s (a-p)), 2.52 (6H, s (p)), 7.54 (2H, d, J = 8.4 Hz (p)), 7.65 (2H, d, J = 8.4 Hz (a-p)), 7.85 (2H, d, J = 8.4 Hz (p)), 8.04 (2H, d, J = 8.4 Hz (a-p)), 8.32 (2H, s (p)), 8.40 (2H, s (a-p)), IR(KBr); 1710 cm^{-1}, Anal. Found: C, 73.14; H, 7.93%. Calcd for $C_{79}H_{102}O_4F_6S_2$: C, 73.33; H, 7.96%.
11 M. Irie, O. Miyatake, K. Uchida, and T. Eriguchi, *J. Am. Chem. Soc.*, **116**, 9894 (1994).
12 S. Canau, P. le Roy, and F. Debeauvais, *Mol. Cryst. Liq. Cryst.*, **23**, 278 (1973).
13 F. Grandjean, *C. R. Hebd. Seances Acad. Sci.*, **71**, 172 (1921); R. Cano, *Bull. Soc. Fr. Mineral*, **91**, 20 (1968).