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Photochemical Switching between a Compensated Nematic Phase and a Twisted Nematic Phase by Photoisomerization of Chiral Azobenzene Molecules

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Introduction

Photochemically driven control of phase structures of liquid crystals has been widely studied in the field of optical devices such as optical memory, optical display, and optical switching.[1−13] Azobenzene compounds are well-known to show photochromism between trans form, with a rodlike shape, and cis form, with a bent shape. The *trans*-azobenzene molecules dissolve in a host liquid crystal without extreme disorganization effect on a molecular orientation of the host LC, while the *cis*-azobenzene molecules disorganize that of the host LC. This is explained as a result of the similarity of the molecular shapes between the *trans*-azobenzene molecules and the host LC molecules.

A few attempts have been reported on the photochemical control of cholesteric pitch by photoisomerization of chiral photochromic compounds such as stilbenes and flugides.[14−17] It was reported that the trans−cis photoisomerization of a guest azobenzene compound without chiral moiety caused a change in the cholesteric pitch of a host cholesteric LC.[18] There are few studies on the photoisomerization of azobenzene compounds with chiral moieties with respect to a reversible phase transition between nematic and cholesteric phases. The cholesteric phase has a helical structure, reflects a wavelength of light corresponding to the helical pitch, and scatters light. Therefore, if we can control photochemically the phase structure of the cholesteric phase, we might use the systems for the optical devices, or for switchable coatings. In this paper we describe the synthesis of chiral azobenzene compounds and experimental results on photochemical control of a phase transition between a nematic and a cholesteric phases.

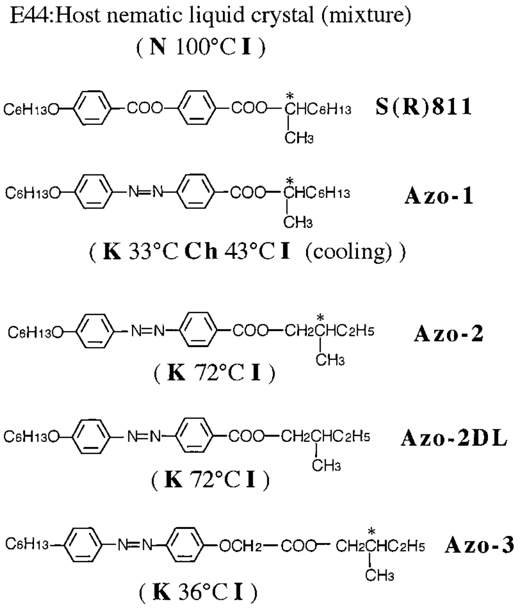

Figure 1. Structures and phase transition temperatures of compounds used in this study.

Results and Discussion

Figure 1 shows compounds used in this study. Three azobenzene compounds (**Azo-1**, **Azo-2**, and **Azo-3**) were synthesized by the diazo-coupling reaction, and following esterification with chiral alcohols.[19] The low molecular weight host liquid crystal (**E44**) and chiral dopants (**R-811** and **S-811**) are purchased from Merck. Co. Ltd. Other chemicals are commercially available.

A cholesteric phase was induced by mixing each chiral azobenzene compound in E44. In such a binary system consisting of a nonchiral host nematic LC and a chiral

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(19) Three chiral azobenzene compounds were identified by NMR, IR spectra, and elemental analysis. Data for **Azo-1**: ^{1}H NMR ($CDCl_3$) δ (ppm) 0.7−1.8 (m, 27H, methylene), 4.0 (t, 2H, $ArOCH_2$−), 5.0 (m, 1H, COOCH−), 7.0−8.2 (m, 8H, aromatic); IR (KBr) (cm^{-1}) 1720 ($\nu_{C=O}$). Anal. Calcd for $C_{27}H_{38}N_2O_3$: C, 73.9; H, 8.73; N, 6.39. Found: C, 73.8; H, 8.63; N, 6.63. Data for **Azo-2**: ^{1}H NMR ($CDCl_3$) δ (ppm) 0.8−2.0 (m, 20H, methylene), 4.0 (t, 2H, $ArOCH_2$−), 4.2 (m, 2H, $COOCH_2$−), 7.0−8.2 (m, 8H, aromatic); IR (KBr) (cm^{-1}) 1720 ($\nu_{C=O}$). Anal. Calcd for $C_{24}H_{32}N_2O_3$: C, 72.7; H, 8.13; N, 7.06. Found: C, 72.7; H, 8.13; N, 7.04. Data for **Azo-2**: ^{1}H NMR ($CDCl_3$) δ (ppm) 0.8−1.8 (m, 20H, methylene), 2.7 (t, 2H, $PhCH_2$−), 4.0 (m, 2H, $COOCH_2$−), 4.7 (s, 2H, OCH_2COO), 7.0−8.0 (m, 8H, aromatic); IR (KBr) (cm^{-1}) 1750 ($\nu_{C=O}$). Anal. Calcd for $C_{25}H_{34}N_2O_3$: C, 73.1; H, 8.34; N, 6.82. Found: C, 72.7; H, 8.13; N, 6.75.

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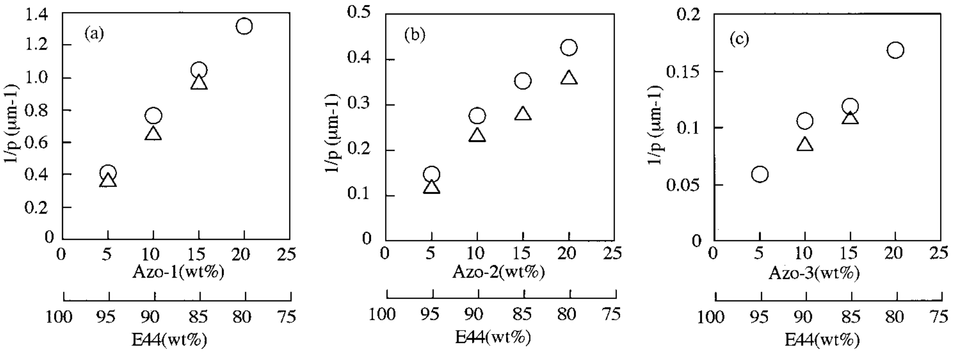

Figure 2. Changes in helical pitch as a function of the chiral azobenzene compounds in E44 before (○) and after (△) UV irradiation at 40 °C: (a) **Azo-1**, (b) **Azo-2**, and (c), **Azo-3**.

compound, the reciprocal of the helical pitch ($1/p$) is known to increase linearly with the concentration (c) of the chiral compound at lower c.[20,21] A twisting power of a chiral compound can be defined as the slope of the $1/p$ versus c. Figure 2 shows changes in the $1/p$ of the induced cholesteric LC's as a function of c in the dark and under ultraviolet (UV) irradiation (366 nm) to cause a trans–cis photoisomerization of the chiral azobenzene compounds for 30 min. The helical pitch was determined by the Cano's method.[21] The $1/p$ increases almost linearly with the increase of c. The twisting power of the chiral azobenzenes was on the order of **Azo-1** > **Azo-2** > **Azo-3**: 23×10^2 for **Azo-1**, 6.6×10^2 for **Azo-2** and 2.6×10^2 (μm^{-1} mol^{-1} g of **E44**) for **Azo-3** at 40 °C, respectively. The twisting power was decreased by increasing a distance between azobenzene moiety and chiral moiety. Similar results were previously reported.[22] The distance between the azo unit and the chiral center may be one of factors influencing the twisting power. A decrease in the $1/p$ was brought about photochemically by the UV irradiation. Namely, the trans–cis photoisomerization of all chiral azobenzene compounds caused a decrease in the helical pitch by 5–10%; e.g., the twisting powers of **Azo-1** before and after UV irradiation were 23×10^2 and 21×10^2 (μm^{-1} mol^{-1} g of **E44**), respectively.

Table 1. Changes in Helical Pitch Before and After UV Irradiation at 40 °C

	pitch (μm)	
sample (wt%)	in the dark	under UV
	E44/Azo-2	
(95:5)	6.86	8.51
(90:10)	3.62	4.28
(85:15)	2.84	3.47
(80:20)	2.35	2.78
	E44/S811/Azo-2DL	
(91.5:1.5:5)	6.67	6.61
(87.5:2.5:10)	4.14	4.07
(82.3:2.7:15)	3.63	3.53
(76.8:3.2:20)	3.35	3.16
	E44/Azo-1	
(95:5)	2.45	2.77
(90:10)	1.31	1.53
(85:15)	0.953	1.04
(80:20)	0.757	

A *trans*-azobenzene molecule usually dissolves in a host LC without extreme perturbation effect on a molecular orientation of the host LC, because the *trans*-azobenzene molecule with rodlike shape is similar to that of the host LC molecule. A *cis*-azobenzene molecule with bent shape disorganizes the molecular orientation of the host LC. To explore the effect of the trans–cis photoisomerization of the chiral azobenzene compounds, the nonchiral azobenzene compound **Azo-2DL**, having the same chemical structure as **Azo-2**, was derived by esterification of the azobenzene intermediate with racemic alcohol. **S811** and **Azo-2DL** were added to **E44** in concentration ranges of 1.5–3.2 wt % and 5–20 wt %, respectively. The helical pitch was in a range of 3–6 μm. A little decrease in the helical pitch was brought about by the UV irradiation as given in Table 1, contrary to the photoisomerization effect of the chiral azobenzene compounds on the helical pitch. Comparison of the result for **Azo-2DL** with those of the chiral azobenzene compounds implies that the photochemical change in the helical pitch shown in Figure 2 may be related not only to the perturbation effect of the trans–cis photoisomerization on the molecular orientation, but also to photochemical change in an intermolecular interaction between the trans or the cis chiral azobenzene molecule and the host LC molecule. The higher twisting power of the *trans*-azobenzene molecule than that of the cis one is interpreted in terms of intermolecular interaction between the guest azobenzene molecule and the host LC molecule. The intermolecular interaction between the chiral *trans*-azobenzene molecule and the host LC molecule is higher than that between the chiral cis one and the host LC molecule, because of the similarity of their molecular shapes.

To reveal a helical sense of the induced cholesteric LC, two induced cholesteric LCs were prepared and their helical pitches compared. One is a cholesteric LC consisting of **R811**, **Azo-1**, and **E44**, the other contains **S811** instead of **R811**. **R811** and **S811** are reported to give right- and left-handed helical structures, respectively.[21] The sense of the helical structure induced by the chiral azobenzene **Azo-1** can be identified by measuring change in the helical pitch of the induced cholesteric LC containing **R811** or **S811** before and after doping of **Azo-1**. **Azo-1** gave a left-handed helical structure.

A compensated nematic LC can be prepared by mixing two chiral compounds with opposite twisting ability, in a host nematic LC. A mixture of **Azo-1, R811**, and **E44** (11.4:8.6:80 in wt %) which is abbreviated as **Azo-1/**

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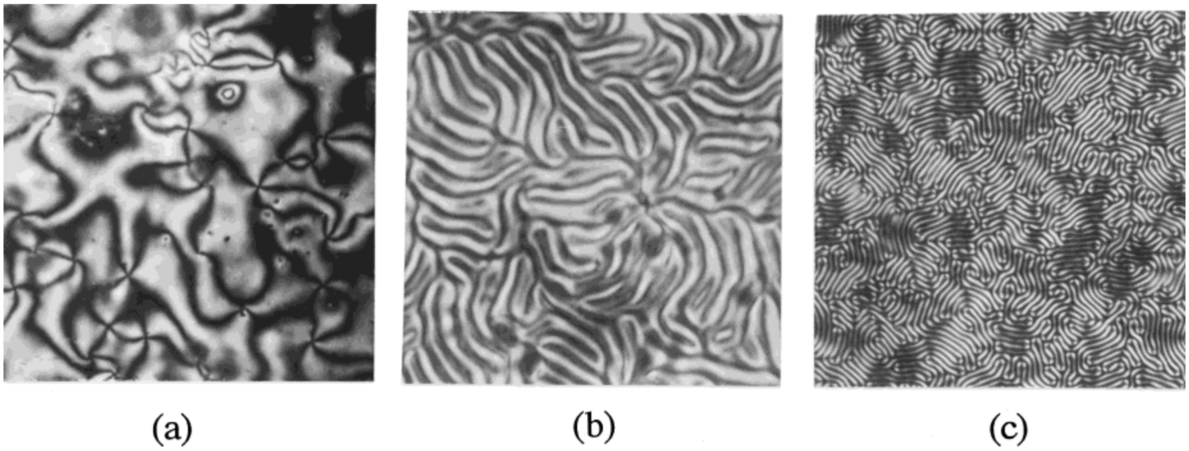

Figure 3. Polarized optical micrographs of the **Azo-1**/**R811**/**E44** mixture (11.4:8.6:80 wt %): (a) nematic phase at 65 °C, (b) cholesteric phase at 73 °C in the dark, and (c) cholesteric phase at 65 °C after UV irradiation. Magnification: 10 × 20.

R811/E44, showed a nematic phase below 73 °C and the cholesteric phase between 73 and 83 °C. Higher than 83 °C, the mixture was in an isotropic phase. To clarify the phase transition from the compensated nematic to the cholesteric phases, we measured temperature dependence of the twisting power of **R811** and **Azo-1**, respectively. The twisting power of **R811** and **Azo-1** decreased slightly with temperature, and there is a little difference in their temperature dependence. The difference in the temperature dependence of the twisting power may be related to the appearance of the cholesteric phase.

The trans–cis photoisomerization of the chiral azobenzene compounds decreased the twisting power by about 10% as can be seen in Figure 1. Therefore, it might be expected that the trans–cis photoisomerization in the compensated nematic LC containing both the chiral azobenzene **Azo-1** and the nonphotochromic chiral compound **R811** results in the twisting ability, because the photochemical decrease in the twisting power of **Azo-1** breaks the compensated state. Figure 3 shows the polarized optical micrographs of the **Azo-1/R811/E44** mixture before and after UV irradiation at 65 °C. Before the UV irradiation the mixture showed a schlieren texture, indicating the compensated nematic phase as shown in Figure 3a, while a fingerprint texture indicating transformation into helical structure was observed after the UV irradiation (Figure 3c). A fingerprint texture for the same mixture taken at a cholesteric phase (73 °C) in the dark is also shown in Figure 3b. It is clear that there is a significant difference in the helical pitch between the helical structures shown in parts b and c of Figure 3; helical pitches are 10 μm for Figure 3b and 3.3 μm for Figure 3c, respectively. Therefore, the photochemically induced helical structure does not result from a depression of the phase transition temperature between the compensated nematic phase and the cholesteric phase, owing to the perturbation effect of the trans–cis photoisomerization. The estimated helical pitch, based on the photochemical decrease in the twisting power (10%), is 12 μm. The observed helical pitch after irradiation (3.3 μm) was much shorter than the estimated one (12 μm). Sackmann reported that the decrease in the helical pitch was brought about by the trans–cis photoisomerization of achiral azobenzene molecule in a host cholesteric LC.[18] Actually, the photoisomerization of **Azo-2DL** resulted in the decease in the helical pitch as given in Table 1. This photochemical effect on the helical pitch might be one of causes for the large decrease in the helical pitch by UV irradiation beyond expectation, adding to the photochemical change in the twisting power between trans form and cis form. The photochemically induced cholesteric phase scattered light strongly compared to the compensated nematic phase before UV irradiation.

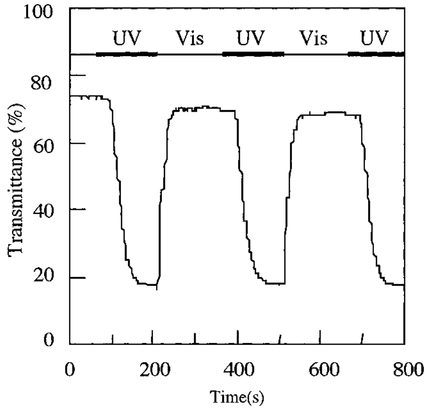

Figure 4. Changes in the transmittance of the **Azo-1**/**R811**/**E44** mixture (11.4:8.6:80 wt %) by UV and vis irradiation at 40 °C.

Figure 4 shows a change in the transmittance of the **Azo-1/R811/E44** mixture by UV and visible (vis) light irradiation with 75-W high-pressure mercury lamp equipped with glass filters UTVAF-35 (Sigma Koki Co.) for UV irradiation (366 nm) and SCF-42L (Sigma Koki Co.) for vis irradiation (436 nm) at 40 °C. The **Azo-1/R811/E44** mixture was injected into two glass plates. The film thickness was about 5 μm. The transmittance was measured by using a probe light from a diode laser (670 nm) without polarizer, and reference was a transmitted light intensity without the sample. Before UV irradiation, the transmittance was kept about 75%. The transmittance was decreased by the UV irradiation, and restored by subsequent vis irradiation. A similar reversible change in the transmittance was achieved by the irradiation at 65 and 30 °C. The response time and the light scattering intensity were found to depend on the irradiation temperatures.

In summary, the photochemical reversible phase transition between the nematic and the cholesteric phases was achieved by the trans–cis photoisomerization of **Azo-1** in the compensated nematic LC. The nematic phase was transparent, while the photochemically induced cholesteric phase scattered light strongly. The photochemical change in the light scattering property will be candidates as various optical materials such as optical shutter, optical display, and photocontrollable coatings.

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