Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Photochemical tuning of the helical structure of cholesteric liquid crystals by photoisomerization of chiral azobenzenes, and their structural effects

Teppei Yoshioka[a]; Md Zahangir Alam[a]; Tomonari Ogata[a]; Takamasa Nonaka[a]; Seiji Kurihara Corresponding author[a]
[a] Department of Applied Chemistry and Biochemistry, Faculty of Engineering, Kumamoto University, Kumamoto 860-8555, Japan

To cite this Article Yoshioka, Teppei , Alam, Md Zahangir , Ogata, Tomonari , Nonaka, Takamasa and Kurihara Corresponding author, Seiji(2004) 'Photochemical tuning of the helical structure of cholesteric liquid crystals by photoisomerization of chiral azobenzenes, and their structural effects', Liquid Crystals, 31: 9, 1285 — 1291

To link to this Article: DOI: 10.1080/02678290412331282118

URL: http://dx.doi.org/10.1080/02678290412331282118

LIQUID CRYSTALS, VOL. 31, NO. 9, SEPTEMBER 2004, 1285–1291

Taylor & Francis
Taylor & Francis Group

Photochemical tuning of the helical structure of cholesteric liquid crystals by photoisomerization of chiral azobenzenes, and their structural effects

TEPPEI YOSHIOKA, MD ZAHANGIR ALAM, TOMONARI OGATA, TAKAMASA NONAKA and SEIJI KURIHARA*

Department of Applied Chemistry and Biochemistry, Faculty of Engineering, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan

(*Received 24 November 2003; in final form 3 June 2004; accepted 4 June 2004*)

Several chiral azobenzene compounds having different chiral substituents were synthesized. A cholesteric phase was induced by mixing each chiral azobenzene compound with a host non-chiral nematic liquid crystal (E44). The helical twisting power (HTP) as well as the change in HTP by *trans-cis* photoisomerization of the chiral azobenzene compound was dependent on the structure of the chiral substituents. A compensated nematic phase was induced by combination of E44, a chiral azobenzene compound and a non-photochromic chiral compound. Reversible switching between the compensated nematic phase and cholesteric phase was brought about by *trans-cis* photoisomerization of the chiral azobenzene compound in the liquid crystalline systems. An azobenzene compound substituted with a menthyl group showed the highest efficiency as the trigger for the switching; this efficiency was related to the compactness of the chiral group substituted within the azobenzene core moiety.

1. Introduction

The cholesteric liquid crystalline (Ch) phase possesses a helical arrangement of the director, and the periodicity of the helical structure results in Bragg reflection known as selective reflection [1]. The wavelength of the selective reflection of the Ch phase is proportional to the pitch of the helical structure. The appearance of the Ch phase requires either a chiral mesogen or the addition of a chiral dopant to a non-chiral nematic LC. In the case of a Ch phase induced by doping with the chiral compound, the helical pitch P is inversely proportional to the concentration c. of the chiral dopant. The ability of the chiral dopant to twist the nematic phase is characterized by a helical twisting power HTP, defined as [1]

$$\mathrm{HTP}=1/(Pc). \qquad (1)$$

Therefore, if we change the HTP of the chiral dopant by external stimuli such as photoirradiation, a change in the helical pitch will also take place [2–10]. Several studies have been reported on the synthesis of chiral photochromic compounds as chiral dopants for inducing the Ch phase, and controling the wavelength of its selective reflection [3–11].

On the other hand, the Ch phase can be compensated by addition of a chiral dopant with an opposite twisting ability. We have reported a photochemically reversible switching between transparent and opaque, by using UV and visible (Vis) light irradiation on a compensated nematic LC in a glass cell with homogenous or homeotropic molecular orientation [10]. The compensated nematic LC was prepared by adding both a chiral azobenzene compound and a non-photochromic compound with opposite twisting ability in a low molecular mass non-chiral nematic LC. Transition between the compensated nematic phase and a cholesteric phase could be induced reversibly by photoisomerization of the chiral (azobenzene) molecules. This switching resulted from the difference in the HTP between the photoisomers, leading to a disruption of the compensated state. Therefore, it is expected that this photochemical change in HTP strongly influences the switching behaviour. Here, we have synthesized various kinds of chiral azobenzene compound to trigger the photochemical phase transition, and have investigated structural effects on the photochemical change in HTP as well as the rate of photochemical switching between transparent and opaque states.

*Author for correspondence;
e-mail: kurihara@gpo.kumamoto-u.ac.jp

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2004 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290412331282118

2. Experimental

2.1. *Materials*

Azobenzene compounds Azo-1–5 were synthesized by the diazo-coupling reaction of 4-aminobenzoic acid and phenol to give 4-carboxy-4′-hydroxyazobenzene. After etherification with hexyl bromide, esterification with appropriate chiral alcohols was carried out in the presence of dicyclohexylcarbodiimide (DCC) in dichloromethane. The product was purified by column chromatography (silica gel, $CHCl_3$ as eluant) and recrystallization from ethanol. The alcohols used were: (*S*)-(+)-octanol for Azo-1, (*S*)-(-)-1-phenylethanol for Azo-2, ethyl (*S*)-(-)lactate for Azo-3, (1*R*, 2*S*, 5*R*)-(-)-menthol for Azo-4, and cholesterol for Azo-5.

A non-photochromic chiral compound (Menth) was synthesized as follows. 4-Hydroxybenzoic acid was reacted with 3,4-dihydro-2H-pyran for protection of the hydroxy group. The product was then reacted with (1*S*, 2*R*, 5*S*)-(+)-menthol in the presence of DCC in dichloromethane to give 1-menthyl 4-(tetrahydropyran-2-yloxy)benzoate. This benzoate derivative was heated at 60°C for 4 h in the presence of pyridinium *p*-toluenesulphonate in ethanol to yield 2-menthyl 4-hydroxybenzoate. This benzoate derivative was condensed with terephthalic acid in the presence of DCC in dichloromethane to yield crude Menth. Purification was carried out by column chromatography (silica gel, $CHCl_3$ as eluant) and recrystallization from ethanol. The synthesized compounds were characterized by NMR, IR, and elemental analysis.

Azo-1: ^1H 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(cm^{-1}): 1600 (aromatic), 1709 (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%.

Azo-2: ^1H NMR ($CDCl_3$): δ(ppm) 0.8–1.8 (m, 14H, methylene), 4.0 (t, 2H, $ArOCH_2$–), 6.2 (m, 1H, COOCH–), 7.0–8.2 (m, 13H, aromatic). IR (cm^{-1}): 1600 (aromatic), 1714 (C=O). Anal. calcd for $C_{27}H_{30}N_2O_3$ C 75.3, H 7.02, N 6.51; found C 75.2, H 7.07, N 6.60%.

Azo-3: ^1H NMR ($CDCl_3$): δ(ppm) 0.9, 1.6 (m, 6H, methyl), 1.2–1.8 (m, 11H, methylene), 4.0 (t, 2H, $ArOCH_2$–), 4.2 (t, 2H, $COOCH_2$–), 5.3 (m, 1H, COOCH–), 7.0–8.2 (m, 8H, aromatic). IR(cm^{-1}): 1601 (aromatic), 1716, 1725 (C=O). Anal: calcd for $C_{24}H_{30}N_2O_3$ C 67.6, H 7.09, N 6.57; found C 67.5, H 7.00, N 6.68%.

Azo-4: ^1H NMR ($CDCl_3$): δ(ppm) 0.8–2.2 (m, 29H, methylene), 4.1 (t, 2H, $ArOCH_2$–), 5.0 (m, 1H, COOCH–), 7.0–8.2 (m, 8H, aromatic). IR(cm^{-1}): 1604 (aromatic), 1710 (C=O). Anal: calcd for $C_{29}H_{40}N_2O_3$ C 75.0, H 8.62, N 6.03; found C 74.7, H 8.58, N 6.15%.

Azo-5: ^1H NMR ($CDCl_3$): δ(ppm) 0.8–2.0 (m, 32H, methylene), 4.0 (t, 2H, $ArOCH_2$–), 4.9 (m, 1H, COOCH–), 7.0–8.2 (m, 8H, aromatic). IR(cm^{-1}): 1599 (aromatic), 1717 (C=O). Anal: calcd for $C_{46}H_{66}N_2O_3$ C 79.5, H 9.58, N 4.03; found C 79.3, H 9.52, N 4.09%.

Menth: ^1H NMR ($CDCl_3$): δ(ppm) 0.8–2.2 (m, 36H, methylene), 5.0 (m, 2H, COOCH–), 7.3–8.4 (m, 12H, aromatic). IR(cm^{-1}): 1064 (aromatic), 1708 (C=O). Anal: calcd for $C_{42}H_{50}O_8$ C 73.9, H 7.38, N 0; found C 73.7, H 7.40, N 0%.

A low molecular mass non-chiral nematic LC (E44) and chiral compounds (R811 and S811) were purchased from Merck Co. Ltd. and used as received.

2.2. *Characterization*

LC mixtures were prepared by mixing each azobenzene compound, Azo-*n*, and/or a non-photochromic chiral compound, Menth, into E44. The thermal phase transition behaviour of the compounds synthesized and the LC mixtures was examined by polarizing optical microscopy (POM, Olympus BHSP polarizing optical microscope, Mettler FP80 hot stage and and FP82 controller). Helical pitch was determined by the Cano's wedge method with or without photoirradiation [12].

2.3. *Photoresponsive properties*

The LC mixtures were injected into a 5 μm glass cell having homogeneous or homeotropic alignment (EHC Co., Ltd.). During irradiation, changes in the helical structure were explored by monitoring transmitted light intensity through the samples with a diode laser (Suruga Seiki Co., 670 nm, 3 mW cm^{-2}). The photoirradiation was carried out by a 500 W high pressure Hg lamp (Ushio) equipped with a glass filter; UTVAF-35 (Sigma Koki Co.) for UV irradiation (366 nm), or SCF-42L (Sigma Koki Co.) for Vis irradiation (436 nm). The Ratio of the *trans* and cis-forms of the Azo-*n* compounds produced by the UV and Vis irradiation was determined by NMR spectroscopy.

3. Results and discussion

3.1. *Synthesis and properties of the chiral compounds*

Figure 1 shows structures of the chiral azobenzenes (Azo-*n*) and the non-photochromic chiral compounds (Menth, R811 and S811) used in this study. Azo-1 exhibits a cholesteric phase between 33 and 43°C only on cooling, and no LC phase was observed for the others. A cholesteric phase was induced by mixing each chiral azobenzene or the non-photochromic chiral compound in E44. A typical phase diagram of binary

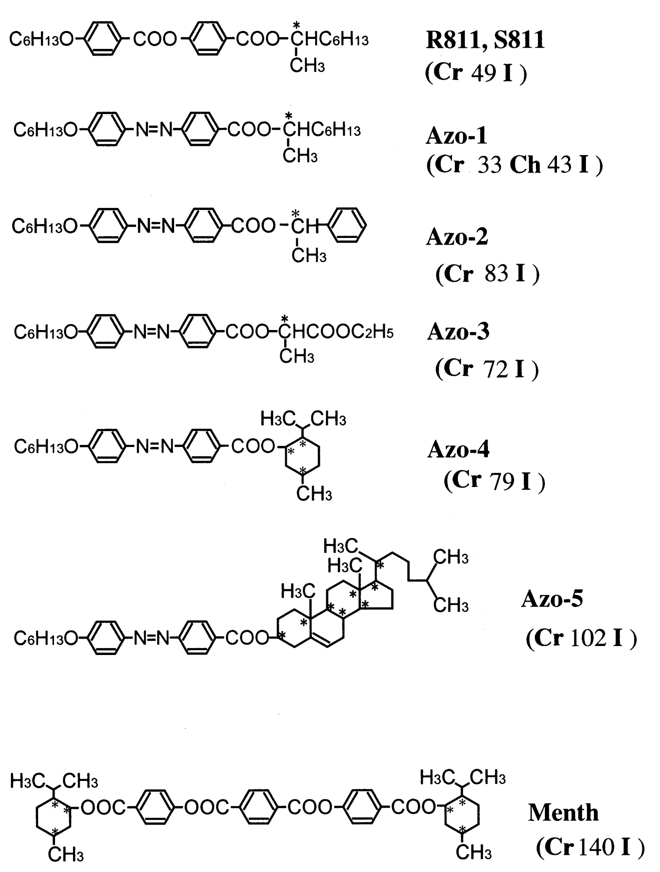

Figure 1. Structures and phase transition temperatures (°C) of the compounds.

mixtures of Azo-4 and E44, up to 10 wt% of Azo-4, is shown in figure 2. All the mixtures show the cholesteric phase only above room temperature, and the cholesteric to isotropic transition temperature decreases slightly with increasing concentration of Azo-4. Other LC mixtures containing Azo-*n* showed similar phase transition behaviour to that observed for binary mixtures consisting of Azo-4 and E44.

In such a binary cholesteric LC system consisting of a non-chiral host nematic LC and a chiral compound, the helical twisting power of the chiral compound, HTP, can be expressed by equation (1). It has been reported that the HTP of azobenzene compounds with chiral substituents is changed by photoirradiation [9, 10]. The azobenzene compounds are well known to show photochromism between the *trans*-form with a rodlike shape and the *cis*-from with a bent shape. Figure 3 shows changes in the absorption spectra of Azo-4 in methanol and in E44. The UV irradiation caused both a decrease in absorbance around 370 nm, and an increase in absorbance around 450 nm, indicating the *trans–cis*-photoisomerization of Azo-4 in both solutions.

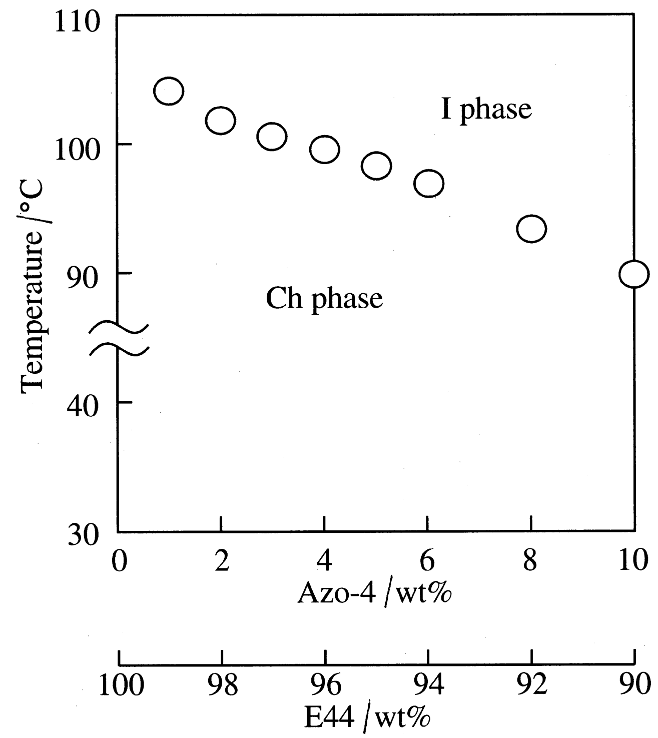

Figure 2. Thermotropic properties of mixtures of E44 and Azo-4.

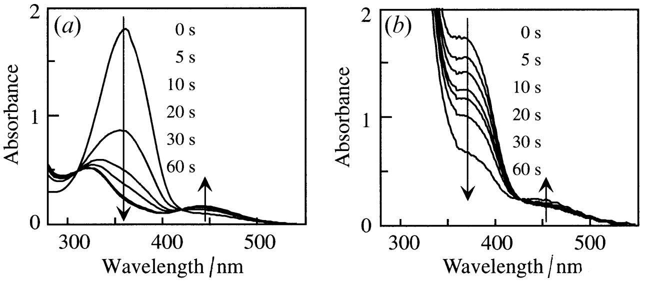

Figure 3. Changes in the absorption spectra of Azo-4 (*a*) in methanol and (*b*) in E44 at 5 wt% of Azo-4 under UV irradiation (7.6 mW cm^{-2}).

In figure 4 the reciprocal of the helical pitch of the induced Ch LC composed of E44 and Azo-4 is plotted as a function of the concentration of Azo-4 before and after UV irradiation. The HTPs of Azo-4 in E44 before and after UV irradiation can be estimated from equation (1) with the slopes shown in figure 4, because the reciprocal of the helical pitch is roughly proportional to the concentration of Azo-4. The slope after UV irradiation is smaller than that before UV irradiation. This implies that the HTP of the *cis*-form of Azo-4 is lower than that of its trans-form. The HTPs of both the *trans*- and *cis*-forms of Azo-*n* estimated in this way are given in the table. The HTPs of the

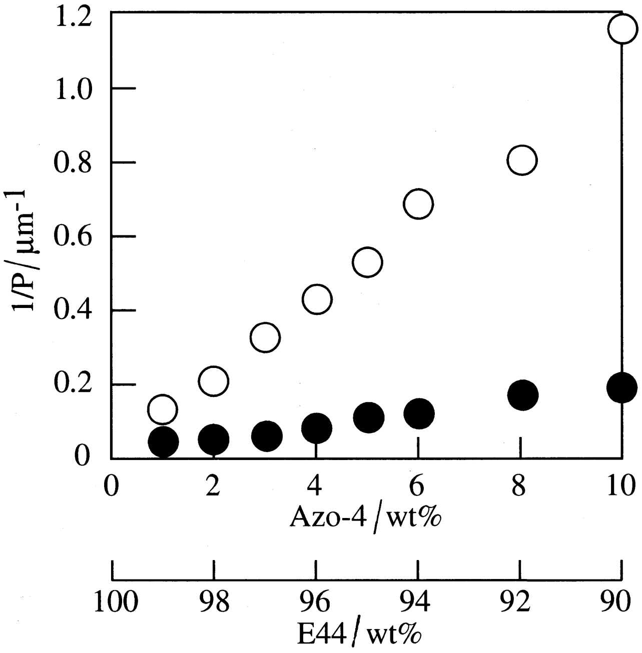

Figure 4. Changes in helical pitches of (E44/Azo-4) mixtures before (○) and after (●) UV irradiation (7.6 mW cm^{-2}, 3 min) at r. t.

cis-forms were smaller than those of the *trans*-forms for all the Azo-*n* compounds. It has been reported that the photochemical decrease and increase in HTP originates from the difference in the chemical structure of photoisomers [9, 13]. All Azo-*n* compounds are substituted at both the 4- and 4′-positions of the azobenzene moiety. The rod-like *trans*-form is more similar to conventional rod-like LC molecules than the *cis*-form. Therefore, the photochemical decrease in HTP under UV irradiation can be explained in terms of the change in the molecular shape by *trans*-*cis*-photoisomerization.

The HTP of Azo-*n* before UV irradiation and its photochemical decrease (Δ in the table) are clearly dependent on the structure of chiral groups substituted within the Azo-*n* molecules. Azo-2 was found to exhibit the highest HTP among the Azo-*n* compounds, while the largest Δ was observed for Azo-4. Comparison of these results with the HTP and Δ of Azo-5 indicates that the number of chiral carbons in the chiral substituent is unlikely to contribute to both HTP and Δ. A cholesteric derivative is one of the commercially available chiral dopants [14]. However, Azo-5 surprisingly showed the lowest value not only of HTP but also of Δ. The cholesteryl group is well known to be a typical mesogenic group; thus, presumably intermolecular interactions between the cholesteryl moiety and the host LC molecules mainly influences the HTP and Δ values. Consequently, the photochemical change in the molecular shape of the azobenzene moiety has less influence on the HTP and Δ values.

The helical sense of the induced cholesteric phase is also given in the table. It was determined by comparing the wavelengths of the selective reflection of the induced cholesteric LC containing R811 or S811 before and after doping with each Azo-*n* [10]. All Azo-*n* compounds were found to give a left-handed helix when they were doped into E44. In the case of the synthesis of Azo-4, (1*R*,2*S*,5*R*)-(-)-menthol was used as the chiral alcohol. Therefore, (1*S*,2*R*,5*S*)-(+)-menthol was used for the synthesis of Menth in order to synthesize a non-photochromic chiral compound imparting a right-handed helical twisting ability to E44 as can be seen in the table.

3.2. *Photochemical switching behaviour*

Azo-*n* and Menth were found to induce the left- and right-handed helices respectively when they were doped into E44. Therefore, a compensated nematic phase can be obtained by mixing each Azo-*n* and Menth in E44. The photochemical decrease in the HTP of the Azo-*n*

Table. Changes in helical twisting power (HTP) of chiral azobenzenes in E44 before and after photoisomerization.

Sample	HTP $\times 10^8$ m^{-1} mol^{-1} g-E44			Change in HTP/%[b]	Helical sense[c]	*cis*-form at photostationary state/%[d]
	Before	After	Δ[a]			
Azo-1	32.0	20.9	11.1	−35	L	96
Azo-2	68.7	36.3	32.4	−48	L	97
Azo-3	36.6	19.9	16.7	−42	L	95
Azo-4	49.0	10.8	38.2	−78	L	94
Azo-5	10.7	10.5	0.2	−2	L	93
Menth	128	128	0	0	R	

[a] HTP (before)—HTP (after).

[b] $(-\Delta)$/HTP (before) × 100.

[c] L = left-handed helix; R = right-handed helix.

[d] Yield of cis form at photostationary state was estimated by change in NMR spectra before and after UV irradiation.

would disrupt the compensated state, causing a transition between the compensated nematic phase and a cholesteric phase. In the compensated nematic LCs, the concentration of E44 was constant at 80 wt%. The compositions of the E44/Menth/Azo-*n* mixtures prepared were 80/4.4/15.6 wt% for Azo-1, 80/9.2/10.8 wt% for Azo-2, 80/6.3/13.7 wt% for Azo-3, 80/7.2/12.8 wt% for Azo-4, and 80/1.5/18.5 wt% for Azo-5. All mixtures showed a schlieren texture between two glass slides in the dark, which indicates the nematic phase. The schlieren texture was transformed into a fingerprint texture by UV irradiation, and returned to the initial schlieren texture under Vis irradiation. Thus, a reversible phase transition between the compensated nematic and cholesteric phases could be brought about by UV and Vis irradiation.

Figure 5 shows changes in the transmittance of the E44/Menth/Azo-*n* LCs in a 5 μm glass cell with homeotropic alignment under UV and Vis irradiation at 25°C. The transmittance was measured by using a probe light from a diode laser (670 nm) without a polarizer; the reference was transmitted light intensity without the sample. Before UV irradiation, the transmittance of all samples was higher than 90%. The transmittance of the LCs containing Azo-*n* decreased on UV irradiation and was restored by subsequent Vis irradiation, except for the LC containing Azo-5. This switching has been explained in terms of changes in the LC structure between the homeotropic and focal-conic structures [10]. Thus, the compensated nematic LCs were transparent due to homeotropic structure in the glass cell with homeotropic alignment, while the focal-conic structure gave to the opaque state (figure 6).

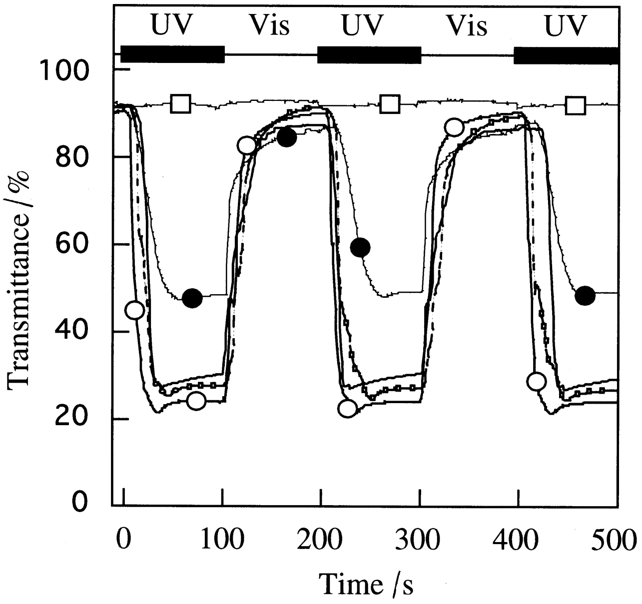

Figure 5. Changes in transmittance of the E44/Menth/Azo-*n* mixtures in a 5 μm homeotropic glass cell under UV and Vis light irradiation at r. t. (—●—) E44/Menth/Azo-1 = 80/4.4/15.6 wt%; (-----) E44/Menth/Azo-2 = 80/9.2/10.8 wt%; (———) E44/Menth/Azo-3 = 80/6.3/13.7 wt%; (—○—) E44/Menth/Azo-4 = 80/7.2/12.8 wt%; (—□—) E44/Menth/Azo-5 = 80/1.5/18.5 wt%.

The change in transmittance was clearly dependent on the kind of Azo-*n* compound. The switching rate of the LC containing Azo-4 was the fastest among the LC/Azo-*n* mixtures: the order of the switching rate was Azo-4 > Azo-2 ≈ Azo-3 > Azo-1 ≫ Azo-5. In addition, the higher the switching rate, the lower the minimum transmittance. The yield of the *cis*-form at the photostationary state under UV light was more than 90% for all Azo-*n* as given in the table, and no

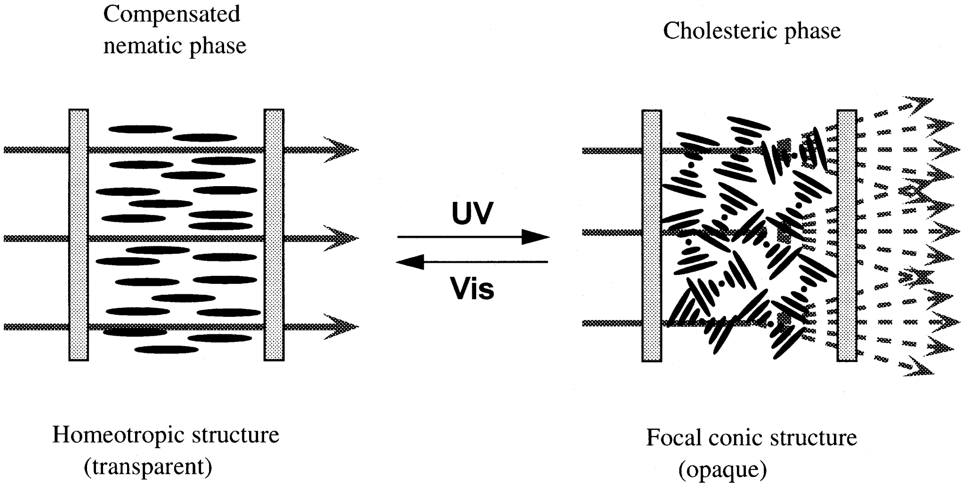

Figure 6. Schematic diagram of photochemical switching of the compensated nematic LC systems between transparent and opaque states.

difference was observed in the UV irradiation time required to achieve the photostationary state. Consequently, photochemical properties such as photoisomerization behaviour do not influence the switching properties. It can therefore be assumed that the order of efficiency as trigger for the switching is in the same order: Azo-4 > Azo-2≈Azo-3 > Azo-1 ≫ Azo-5. This order of efficiency is closely related to the photochemical change in HTP given in the table.

On the other hand, the helical pitch of a cholesteric LC is known to be dependent on temperature [1]. In addition, it has been reported that the *trans–cis*-photoisomerization of azobenzene molecules doped in LC systems causes a transformation from the LC phase to an isotropic phase due to the disruption of the LC molecular orientation [15]. Ikeda *et al.* reported the photochemical change in helical structure caused by the combination of temperature dependence of the helical pitch and the photochemical disruption effect of the azobenzene molecules [11]. Therefore, it is valuable to determine the temperature dependence of the helical pitch of the Ch LC containing Azo-*n*, in order to explore the mechanism of switching between the transparent and opaque states. The temperature dependence of the helical pitch of the Ch LC consisting of E44 and Azo-4 (98/2 wt%), and the UV light intensity effect on the change in the helical pitch at 20°C is shown in figure 7. No temperature dependence of the helical pitch was observed, while it was increased five times by UV irradiation. These results indicate that the change in helical pitch can be explained in terms of the change in intermolecular interaction between the chiral azobenzene molecules and the LC molecules, rather than the disorganization effect.

Shibaev *et al.* have extensively studied photochemical modulation of the helical structure of polymeric Ch LCs. They reported a photochemical shift of the selective reflection wavelength to longer wavelengths by more than 50 nm, by *trans-cis*-photoisomerization of azobenzene molecules containing a menthyl group doped in to polymeric Ch LCs [7*b*]. In this study Azo-4, having a menthyl, group also showed good performance as a trigger for switching. It is difficult, at present time, to explain adequately the relationship between the chemical structure of the azobenzene molecule and its efficiency as the trigger. However, the compactness of the chiral group may be an important factor influencing the switching. Thus, the effects of large chiral groups, such as the cholesteryl group, are mainly due to the intermolecular interactions with the LC molecules as described previously. In contrast to the cholesteryl group, compact chiral groups would not themselves interact significantly with LC molecules. In the case of chiral azobenzene compounds with relatively compact chiral groups, the azobenzene moiety is expected to play a major role in the intermolecular interaction with LC molecules. Therefore, the change in molecular shape from rod-shape to the bent-shape of the azobenzene moiety causes a significant effect on the HTP of the chiral azobenzene compounds, leading to higher efficiency as trigger for the switching.

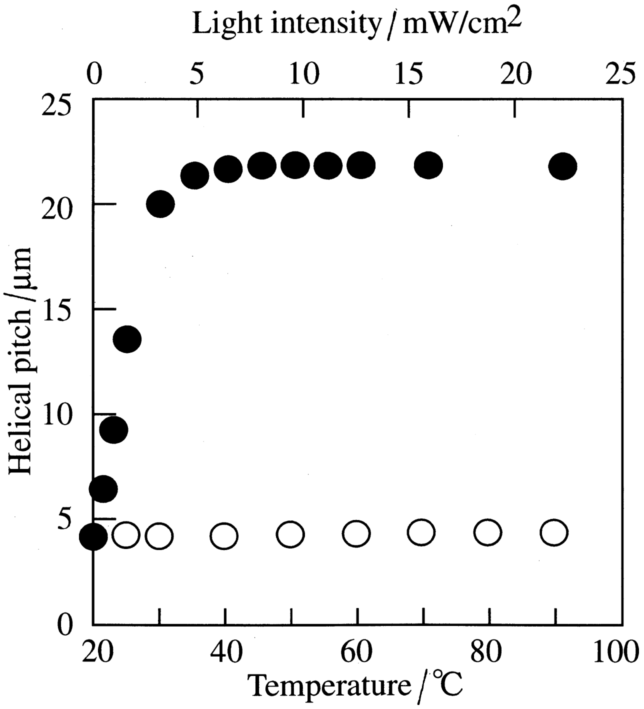

Figure 7. Temperature dependence of the helical pitch of the E44/Azo-4 (98/2 wt%) mixture (○); and the change in helical pitch under UV irradiation for 3 min at 20°C with various light intensities (●).

Figure 8 shows the change in transmittance of a mixture consisting of E44, Menth and Azo-4 (80/7.2/12.8 wt%) under UV irradiation of various light intensities. The switching rate was improved by an increase in the light intensity. The change in the helical pitch of cholesteric LCs was found to depend strongly on the UV and visible light intensity, as can be seen in figure 6. The switching rate was thus increased due to the light intensity effect on the change in the helical pitch.

In conclusion, the efficiency of Azo-*n* as trigger for the reversible switching between transparent and opaque states depends on the structure of chiral substituents within the azobenzene compounds. Azo-4, with a menthyl moiety as a chiral substituent, was found to show higher switching efficiencies. The compactness of the chiral substituent is an important features. The time required for switching from the

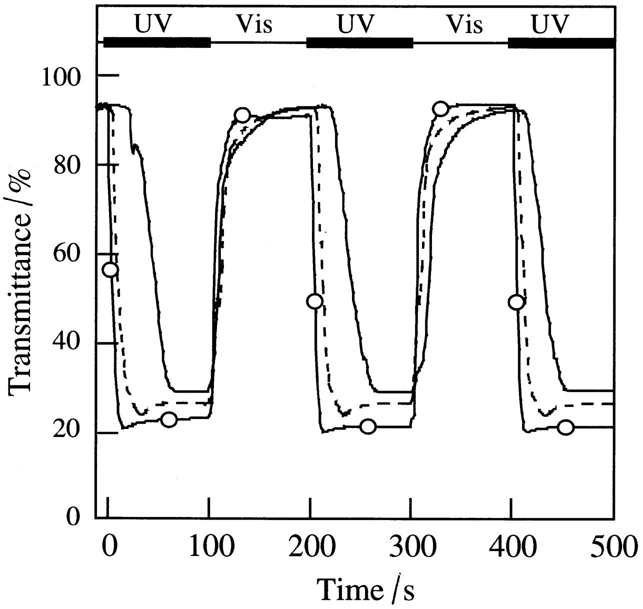

Figure 8. Changes in transmittance of E44/Menth/Azo-4 mixtures in a 5 μm homeotropic glass cell under UV and Vis irradiation with various light intensities at 25°C. (———) UV 0.8, Vis 2.1 mW cm^{-2}; (-----) UV 3.2, Vis 8.3 mW cm^{-2}; (—○—) UV 8.5, Vis 22.3 mW cm^{-2}.

transparent to opaque state, and the reverse process, was a few seconds. The transmittance of the opaque state was 20%, and consequently the contrast between the transparent and opaque states was about 4. The switching rate and contrast are still not satisfactory. The exploration of chiral photochromic compounds with higher HTP and higher photochemical change in HTP will be required for further improvement of the switching performance.

References

[1] De Gennes, P. G., and Prost, J., 1993, *The Physics of Liquid Crystals* (New York: Oxford University Press), Chap. 6.

[2] Sackmann, E., 1971, *J. Am. chem. Soc.*, **93,** 7088.

[3] Janichi, S. Z., and Schuster, G. B., 1995, *J. Am. chem. Soc.*, **117,** 8524.

[4] (*a*) Feringa, B. L., Huck, N. P. M., and van Doren, H. A., **1995**, *J. Am. chem. Soc.*, **117**, 9929; (*b*) van Doren, B. L., van Gelder, M. B., Huck, N. P. M., and Feringa, B. L., 2003, *Adv. funct. Mater.*, **13**, 319.

[5] (*a*) Yokoyama, Y., and Sagisaka, T., 1997, *Chem. Lett.*, 687; (*b*) Sagisaka, T., and Yokoyama, Y., 2000, *Bull. chem. Soc. Jpn.*, **73**, 191.

[6] (*a*) Brehmer, M., Lub, J., and van de Witte, P., 1998, *Adv. Mater.*, **10**, 1438. (*b*) van de Witte, P., Brehmer, M., and Lub, J., 1999, *J. mater. Chem.*, **9**, 2087.

[7] (*a*) Bobrovsky, A. Y., Boiko, N. I., and Shibaev, V. P., 1998, *Liq. Cryst.*, **25**, 679; (*b*) Bobrovsky, A. Y., Boiko, N. I., Shibaev, V. P., and Springer, J., 2000, *Adv. Mater.*, **12**, 1180; (*c*) Bobrovsky, A. Y., and Shibaev, V. P., 2002, *Adv. funct. Mater.*, **12**, 367.

[8] Tamaki, N., 2001, *Adv. Mater.*, **13,** 1135.

[9] (*a*) Ruslim, C., and Ichimura, K., 2001, *Adv. Mater.*, **13**, 37; (*b*) Ruslim, C., and Ichimura, K., 2001, *Adv. Mater.*, **13**, 641; (*c*) Ruslim, C., and Ichimura, K., 2000, *J. phys. Chem. B.*, **104**, 6529.

[10] (*a*) Kurihara, S., Nomiyama, S., and Nonaka, T., 2000, *Chem. Mater.*, **12**, 9; (*b*) Kurihara, S., Nomiyama, S., and Nonaka, T., 2001, *Chem. Mater.*, **13**, 1992.

[11] Lee, H.-K., Doi, K., Harada, H., Tsutsumi, O., Kanazawa, A., Shiono, T., and Ikeda, T., 2000, *J. phys. Chem.*, **104,** 7023.

[12] Escher, C. B., Flinger, D., Heppke, G., and Molsen, H., 1991, *Ber. Bunsenges. phys. Chem.*, **95,** 1233.

[13] Kurihara, S., Yohioka, T., Ogata, T., Zahangir, A. D., and Nonaka, T., 2003, *Liq. Cryst.* (in the press).

[14] Hochgesand, R., Plach, H. J., and Sage, I. C., 1989, *Merck.Co.* (data sheet).

[15] Tazuke, S., Kurihara, S., and Ikeda, T., 1987, *Chem. Lett.*, 911.