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Photochemical tuning of the helical structure of cholesteric LC by photoisomerization of chiral azobenzene-based compounds

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Azobenzene compounds having either one or two chiral groups were synthesized. Mixing each chiral azobenzene compound in a host nematic liquid crystal induced a cholesteric phase. The helical twisting power (HTP) as well as the change in the HTP by trans-cis photoisomerization was depended on the structure of the chiral substituents. We discuss the structural effects of the chiral substituents on the photochemical change in HTP as well as a rate of the photochemical switching between transparent and opaque. In addition we propose a molecule design of chiral azobenzene compounds as the trigger for the switching of the helical structure of cholesteric liquid crystals.
Key words: chiral azobenzene, photoisomerization, helical twisting power, helical pitch, switching

1. INTRODUCTION

Recently, many studies have been focused on the synthesis of photoresponsive liquid crystals (LCs), in particular, cholesteric LCs. The cholesteric (Ch) LCs have a helical structure, reflect a wavelength of light corresponding to a helical pitch, and scatter a light. A combination of this unique optical properties and photochromism will enable us to provide optical devices such as optical memory, optical switching, chiro-optical switching [1-15]. Adding a chiral dopant in a host nematic LC can induce a Ch phase. In such a mixture system that consists of the nonchiral host nematic LC and the chiral compound, a reciprocal of the helical pitch (1/p) is known to increase linearly with a concentration of the chiral compound at lower concentration. A helical twisting power (HTP) of chiral compounds can be defined as the slope of the 1/p versus the concentration of the chiral compound in the system [16-17]. Therefore, one will be able to control the helical pitch of the induced Ch LCs by photochemical isomerization of photochromic compound with chiral substituents, resulting in a difference in the HTP of photoisomers.

In this paper, we describe synthesis of various kinds of chiral azobenzene compounds for trigger of the photochemical phase transition, and investigate the structural effects on the photochemical change in HTP as well as a rate of the photochemical switching between transparent and opaque. In addition, we propose a design of chiral azobenzene compounds as the trigger for the switching of the helical structure of Ch LCs such as changes in the helical pitch length in direction to shorter or longer wavelength, helical inversion of the helical structure, or phase transition between nematic and Ch phases.

2. EXPERIMENTAL

Structures of mono- and di-substituted azobenzene compounds (Azo-1-Azo-9) and nonphotochromic chiral compound (Menth) are shown in Fig. 1. Following alcohols were used for synthesis of chiral azobenzene compounds: (S)-octanol for Azo-1, (S)-1-phenylethanol for Azo-2, ethyl (S)-lactate for Azo-3, (1R, 2S, 5R)-menthol for Azo-4, cholesterol for Azo-5. Synthetic route of Azo-6-Azo-9 is shown in Scheme 1. Following chiral alcohols were used for synthesis of Azo-6-Azo-9: methyl (S)-lactate and methyl (R)-lactate

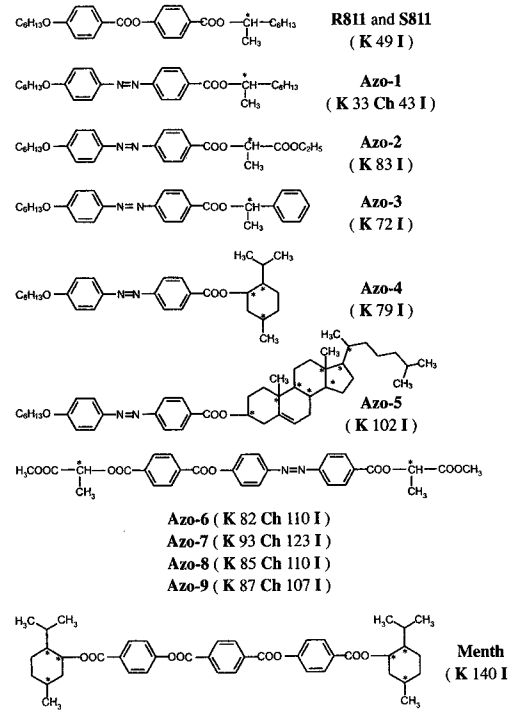


Fig. 1 Structures and phase transition temperatures (℃) of compounds.

for Azo-6, methyl (S)-lactate and methyl (S)-lactate for Azo-7, methyl (S)-lactate and methyl (RS)-lactate for Azo-8 and Azo-9.

The compounds were characterized NMR, IR, elemental analysis, MS, DSC, and polarizing optical microscopy.

3. RESULTS AND DISCUSSION

3-1. HTPs of mono-substituted azobenzene group

Both HTPs of the trans and cis forms of Azo-n in E44 (Merck co.) estimated by Cano's wedge method and the helical sense of the induced cholesteric phase were given in Table I.

Table I. Changes in helical twisting power (HTP) of chiral azbenzenes for E44 befor and after photoisomerization.

Sample	HTP ($\times 10^8$ $m^{-1}mol^{-1}g$-E44)			Change in HTP (%)[2]	Helical sense[3]
	before	after	Δ[1]		
Azo-1	32.0	20.9	11.1	−35	L
Azo-2	68.7	36.3	32.4	−48	L
Azo-3	36.6	19.9	16.7	−42	L
Azo-4	49.0	10.8	38.2	−78	L
Azo-5	10.7	10.5	0.2	−2	L
Chiral	128	128	0	−	R

1) HTP (before) − HTP (after), 2) (−Δ) / HTP (before) × 100
3) L: Left-handed, R: Right-handed

The HTPs of the cis forms were smaller than those of the trans forms for all the Azo-n compounds. All Azo-n compounds are substituted at both 4 and 4'-positons of the azobenzene moiety. The rod-like trans form is more similar to the conventional rod-like LC molecules compared with cis form. Therefore, the photochemical decease in the HTP by UV irradiation can be explained in terms of the change in the molecular shape by the trans-cis photoisomerization. Both the HTP of Azo-n before UV irradiation and the magnitude of the photochemical decrease in the HTP (Δ in Table I) 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 likely not to contribute to both HTP and Δ. A cholesteric derivative is one of commercially available chiral dopants. However, Azo-5 surprisingly showed the lowest value not only in HTP but also in Δ. The cholesteryl group is well known to be a typical mesogenic group. Thus, it can be presumed that the intermolecular interaction between the cholesteryl moiety and the host LC molecules influences mainly the HTP and Δ values. Consequently, the photochemical change in the molecular shape of the azobenzene moiety gives less influence on the HTP and Δ values.

3-2. Photochemical switching behavior

Azo-n and Menth were found to induce the left- and the right-handed helices when they were doped into E44, respectively. 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 would break the compensated state, causing the phase 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, respectively. All mixtures showed the schlieren texture in two glass slides in the dark, indicating the nematic phase. The schlieren texture was transformed into the fingerprint texture by UV irradiation, and returned to the initial schlieren texture by Vis irradiation. This means that the reversible phase transition between the compensated nematic and the cholesteric phases could be brought about by UV and Vis irradiation.

Fig. 2 shows changes in the transmittance of the E44:Menth:Azo-n LCs in a 5-μm glass cell with the homeotropic alignment by UV and Vis irradiation at 25 ℃. The transmittance was measured by using a probe light from a diode laser (670 nm) without a polarizer, and the reference was a 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 was decreased by UV irradiation and restored by subsequent Vis irradiation, except for the LC containing Azo-5. This switching was explained in terms of change in the LC structure between the homeotropic and a focal conic structures [18]. Namely, the compensated nematic LCs were transparent due to the homeotropic structure in the glass cell with the homeotropic alignment, while the focal conic structure contributed the strong scattering of light (Fig. 3)

The change in the transmittance was clearly dependent on the kind of Azo-n compounds. The switching rate of the LC containing Azo-4 was the fastest among

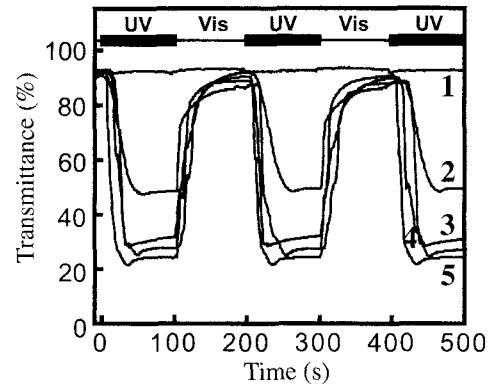


Fig. 2 Changes in transmittance of E44/Chiral/Azo-n ((1) Azo-5, (2) Azo-1, (3) Azo-3, (4) Azo-2, (5) Azo-4) mixtures in a homeotropic glass cell by UV and Vis light ittadiation at r. t.

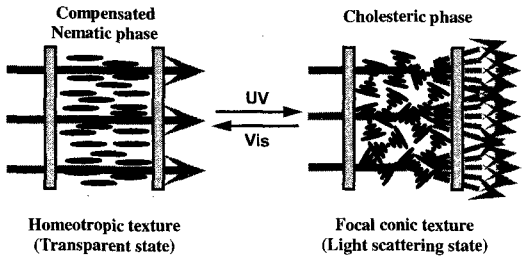


Fig. 3 Textures of the nematic and the cholesteric phases in the homeotropic glass cell by UV and Vis irradiation.

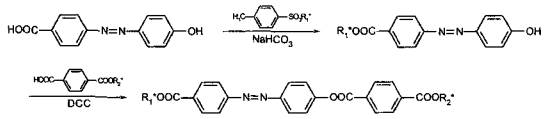
the LC mixtures containing other Azo-n compounds: the order of the switching rate was Azo-4 > Azo-2 ≒ Azo-3 > Azo-1 >> Azo-5. In addition, the higher the switching rate, the lower the minimum transmittance. The yield of the cis form at the photostationary state under UV light was more than 90 % for all Azo-n as given in Table I , and no difference was observed in the UV irradiation time required to be the photostationary state. Consequently, the photochemical properties such as photoisomerization behavior give no influence on the switching properties. Therefore, it can be assumed that the order of efficiency as the trigger for the switching is in the same order, Azo-4 > Azo-2 ≒ Azo-3 > Azo-1 >> Azo-5. This order of the efficiency is closely related to the photochemical change in the HTP given in Table I .

3-3. Synthesis and HTPs of di-substituted azobenzene group

In this section, we describe the synthesis and optical switching behavior of the di-substituted azobenzene in order to design the trigger molecules showing photochemical changes in the helical pitch length to shorter or longer wavelength.

We synthesized two di-substituted azobenzene compounds with chiral groups at 4- and 4'-positions directly and via a mesogenic group (Azo-6 and Azo-7 in Scheme 1). The synthetic route of di-substituted azobenzene compound group is shown in Scheme 1.

Azo-6 was prepared by esterification of 4-carboxy-4'-hydroxyazobenzene with methyl 2-[[(4-methylphenyl) sulfonyl] oxy] propionate, which is obtained by reaction



Azo-6 (R_1, R_2 = (S)-C*H(CH_3)$COOCH_3$)
Azo-7 (R_1 = (R)-C*H(CH_3)$COOCH_3$, R_2 = (S)-C*H(CH_3)$COOCH_3$)
Azo-8 (R_1 = (S)-C*H(CH_3)$COOCH_3$, R_2 = (RS)-C*H(CH_3)$COOCH_3$)
Azo-9 (R_1 = (RS)-C*H(CH_3)$COOCH_3$, R_2 = (S)-C*H(CH_3)$COOCH_3$)

Scheme 1 Synthesis of di-substituted chiral azobenzene compounds.

of *p*-toluenesulfonyl chloride and methyl (S)-lactate, in the presence of sodium bicarbonate in N, N-dimethylformamide [19], and subsequent reaction with terephthalic acid methyl 2(4-carboxylbenzoyloxy) propionate that is prepared from terephthanoly chloride with methyl (S)-lactate [20]. Azo-7 was prepared according to the same method as Azo-6 by the use of methyl (R)-lactate instead of methyl (S)-lactate as R1 group. The inversion of symmetry of methyl (S)-lactate for Azo-6 and methyl (R)-lactate for Azo-7 may be brought about via S_{N2} mechanism during the reaction of methyl 2-[[(4-methylphenyl) sulfonyl] oxy] propionate, resulting in the difference in the chiral symmetry of R1 group in Azo-6 and Azo-7.

The HTPs of the trans and cis forms of Azo-6 and Azo-7 for E44 estimated and the helical sense of the induced cholesteric phase was given in Table II. The HTPs were -15 x 10^8 for Azo-6 and -64 x 10^8 $m^{-1}mol^{-1}$ g-E44 for Azo-7. Fig. 4 shows changes the helical pitch of E44 doped with 2 wt% of Azo-6 or Azo-7 by UV irradiation. The helical pitch of E44 doped with Azo-7 was increased by UV irradiation, indicating the decrease in the HTP by the trans-cis photoisomerization. On the contrary, the helical pitch of E44 containing Azo-6 was clearly found to decrease by the trans-cis photoisomerization. The HTP of cis-form (stationary state) are -21 x 10^8 for Azo-6 and -46 x 10^8 for Azo-7.

Table II. Changes in helical twisting power (HTP) of chiral azbenzenes for E44 befor and after photoisomerization.

Sample	HTP (× 10^8 $m^{-1}mol^{-1}g$-E44)			Change in HTP (%)[2]	Helical sense[3]
	before	after	Δ[1]		
Azo-6	15.5	20.9	-5.4	+35	L
Azo-7	64.3	46.1	18.2	-28	L
Azo-8	18.3	11.7	6.6	-36	R
Azo-9	34.6	32.9	1.7	-4.9	L

1) HTP (before) − HTP (after), 2) (- Δ) / HTP (before) × 100
3) L: Left-handed, R: Right-handed

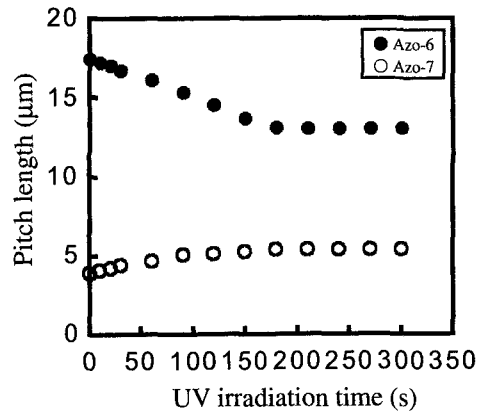
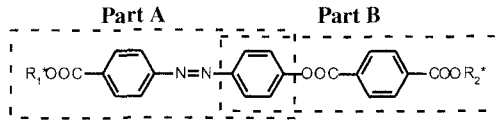


Fig.4 Changes in helical pitch of E44 containing each chiral azobenzene compound by UV irradiation(7.6 mW/cm^2) at r. t.

In order to discuss why the results occurred, we synthesized two chiral azobenzene compounds (Azo-8 and Azo-9) in Scheme 1. Azo-8 and Azo-9 were pre-

Table III. HTPs of the *trans*- and *cis*-forms of azobenzene-based compounds.



Compound	Part A				Part B				Total			
	observed		estimated		observed		estimated		observed		estimated	
	trans	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*
Azo-6			+ 18	+ 12			- 35	- 33	- 15	- 21	- 17	- 21
Azo-7			- 18	- 12			- 35	- 33	- 64	- 46	- 53	- 45
Azo-8	+ 18	+ 12					0	0	+ 18	+ 12		
Azo-9			0	0	- 35	- 33			- 35	- 33		

pared according to the same method as Azo-6 and Azo-7 by the use of following lactates: methyl (S)-lactate as R1 group and methyl (RS)-lactate as R2 group for Azo-8, and methyl (RS)-lactate as R1 group and methyl (S)-lactate as R2 group for Azo-9 respectively. The HTPs of both the trans and cis forms of Azo-8 and Azo-9 in E44 were given in Table II. On the bases of the results given in Table II, one can calculate separately HTP of part A and part B of the azobenzene compounds, (Table III).

Based on the helical sense of chiral azobenzene compounds, the chiral configuration of methyl lactate of part A of Azo-7 is the same with that of Azo-8, while Azo-6 is opposite. Therefore, the HTP of part A of Azo-6 and Azo-7 can be estimated as the HTP of Azo-8 in Table II. The HTP of the part B of Azo-6 and Azo-7 can be estimated by subtracting the HTP owing to part B from the HTP of Azo-9; -35 x 10^8 and -33 x 10^8 for trans- and cis- Azo-9. The chiral configuration of part B of both Azo-6 and Azo-7 are the same, because the same intermediate compound was used for preparation of both compounds as shown in Scheme 1. The observed and estimated HTPs of Azo-6 and Azo-7 are not the same exactly, but they show a similar tendency. This estimation is based on the assumption that both HTP of the parts A and B are independent each other. This implies that the total HTP of the compounds is equal to summation of each HTP. A little deviation between the observed total HTP and the estimated one for Azo-6 may arise from an interaction between the parts A and B.

4. CONCLUSION

The efficiency as trigger for the reversible switching between transparency and opaque was formed to be dependent evidently on the structure of chiral groups substituted within the azobenzene molecules.

The combination of chiral substituents and their chemical structure are important factors to design a photochemical trigger molecule for tuning macroscopic helical structure of Ch LCs. Not only the changes in the helical pitch length in direction to shorter or longer wavelength, but also the helical inversion and phase transition between nematic and Ch phases will be achieved photochemically by varying structure as well as chirality of substituents attached to the azobenzene core group.

REFERENCES

[1] H. J. Cole, R. Simon, Polymer, 26, 1801 (1985).
[2] M. Eich, J. H. Wendroff, B. Reck, H. Ringsdorf, Macromol. Chem. Rapid Commun., 8, 59 (1987).
[3] T. Ikeda, O. Tsutsumi, Science, 268, 1873 (1995).
[4] H. Akiyama, M. Momose, K. Ichimura, S. Yamamura, Macromolecules, 28, 288 (1995).
[5] A. Natansohn, P. Rochon, A. P. Pezolet, D. Brown, S. To, Macromolecule, 27, 2580 (1994).
[6] L. Corvazier, Y. Zhao, Macromolecules, 32, 3195 (1999).
[7] J. Stumpe, T. Fischer, M. Rutloh, R. Rosenhauer, J. G. Meier, Proc. SPIE., 3800, 150 (1999).
[8] S. Kurihara, A. Sakamoto, T. Nonaka, Macromolecules, 31, 4648 (1998).
[9] Y. Onogi, T. Hayashi, Y. Mizushima, M. Yamamoto, Nippon Kagaku Kaishi., 8, 815 (1990).
[10] S. Z. Janichi, G. B. Schuster, J. Am. Chem. Soc., 117, 8524 (1995).
[11] B. L. Feringa, N. P. M. Huck, H. A. van Doren, J. Am. Chem. Soc., 117, 9929 (1995).
[12] Y. Yokoyama, T. Sagisaka, Chem. Lett., 687 (1997).
[13] M. Brehmer, J. Lub, P. van de Witte, Adv. Mater., 10, 1438 (1998).
[14] A. Y. Bobrovsky, N. I. Boiko, V. P. Shivaev, Liq. Cryst., 25, 679 (1998).
[15] A. Y. Bobrovsky, N. I. Boiko, V. P. Shivaev, J. Springer, Adv. Mater., 12, 1180 (2000).
[16] C. B. Escher, D. Fliegner, G. Heppke, H. Molsen, Ber. Bunsenges. Phys. Chem., 95, 1233 (1991).
[17] H. Finkelmann, H. Z. Stegmeyer, Naturforsch, 28a, 799 (1973).
[18] S. Kurihara, S. Nomiyama, T. Nonaka, Chem. Mater., 12, 9 (2000).
[19] A. Omenat, R. A. Hikmet, J. Lub, P. van der Sluis, Macromolecules, 29, 6730 (1969).
[20] P. Bezou, A. Pacreau, J-P. Vairon, Tetrahedron Lett., 36, 2995 (1995).

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