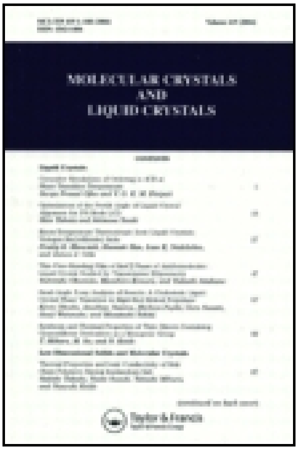

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photon Mode Color Display Device by Means of Isomerization of Chiral Azobenzene

S. Kurihara [a] , T. Yoshioka [a] , M. Moritsugu [a] , T. Ogata [a] & T. Nonaka [a]

[a] Department of Applied Chemistry and Biochemistry, Faculty of Engineering, Kumamoto University, Kumamoto, Japan

To cite this article: S. Kurihara, T. Yoshioka, M. Moritsugu, T. Ogata & T. Nonaka (2005): Photon Mode Color Display Device by Means of Isomerization of Chiral Azobenzene, Molecular Crystals and Liquid Crystals, 443:1, 69-78

To link to this article: http://dx.doi.org/10.1080/15421400500247276

Mol. Cryst. Liq. Cryst., Vol. 443, pp. 69–78, 2005
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500247276

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S. Kurihara
T. Yoshioka
M. Moritsugu
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T. Nonaka
Department of Applied Chemistry and Biochemistry, Faculty of Engineering, Kumamoto University, Kumamoto, Japan

*Photochromic compounds having plural chiral sites as well as azobenzene groups in a molecule was synthesized by reacting 4-, and 3-, 2-carboxy-4′-hexyloxyazobenzenes with isosorbide, and isomannide. A cholesteric liquid crystal (Ch LC) was induced by adding each chiral azobenzene compound in a nematic LC. Most azo dyes showed photochemical decrease in the helical twisting power (**HTP**) by UV irradiation. The change in **HTP** was related to the photochemical change in the molecular shape. Reversible control of the reflection wavelength of the Ch LC was achieved over a whole range of visible region by irradiation of UV and visible light.*

Keywords: chiral azobenzene; cholesteric liquid crystal; photoisomerization; selective reflection, switching

INTRODUCTION

Dissolving a chiral compound in a nematic LC causes a helical distortion, resulting in selective reflection of circular light corresponding to helical pitch and helical sense [1]. In such a Ch LC, the reciprocal of the helical pitch (1/p) is known to increase linearly with concentration of the chiral compound at lower concentration [1]. Here, helical twisting power (**HTP**) of the chiral compound can be defined as the slope of 1/p versus the concentration of the chiral compound. Therefore, if one

Address correspondence to S. Kurihara, Department of Applied Chemistry and Biochemistry, Faculty of Engineering, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan. E-mail: kurihara@gpo.kumamoto-u.ac.jp

can change **HTP** of the chiral compound photochemically, a change in the helical pitch will occur, realizing the photon mode color display device which responds only to an optical information without application of any external force such as an electric field. Several studies have been reported on the synthesis of chiral photochromic compounds in inducing a Ch phase, and controlling the wavelength of the selective reflection [2–12]. However, there is little report on the photon mode color display having rapid response over a whole visible region. Recently, we have reported the photochemical change in transparency as well as in the selective reflection of a Ch LC by photoisomerization of a chiral azobenzene compound doped in a host nematic LC [9]. The photochemical switching behavior was related closely to the photochemical change in **HTP** of the chiral azobenzene compounds. The larger the photochemical change in **HTP**, the faster was the photochemical switching [13]. Therefore, exploration of synthesis of the chiral azobenzene compounds showing larger photochemical change in **HTP** is significant in realizing such photon mode display devices.

In our previous works, the number of chiral groups introduced in a photochromic molecule influenced strongly the initial **HTP** value [13,14]. The azobenzene compounds substituted with two chiral groups at both ends of the azo-core were found to possess much larger initial **HTP** compared to the azobenzene compounds substituted with mono chiral group at one end of the azo-core. However, photochemical change in **HTP** of the di-substituted azobenzene compounds was smaller than that of the mono-substituted one [14]. Thus, an objective of this work is to synthesize chiral photochromic compounds having plural azobenzene groups and chiral sites in order to provide a chiral trigger having larger initial **HTP** value as well as larger photochemical change in **HTP**.

EXPERIMENTAL

Chiral azobenzene compounds (**Azo-Sor** and **Azo-Man**) were synthesized by the diazo-coupling reaction and following esterification with chiral diols in the presence of dicyclohexylcarbodiimide (DCC) in dichloromethane. Purification was carried out by column chromatography (silica gel, $CHCl_3$ as an eluent) and recrystallization from ethanol. A nonphotochromic chiral compound (**Chiral**) was synthesized according to a similar manner reported earlier [19]. Purification was carried out by column chromatography (silica gel, $CHCl_3$ as an eluent) and recrystallization from ethanol. A low molecular weight host LC (**E44**) was purchased from Merck Co. Ltd. Thermal phase transition behavior was examined by means of polarizing optical microscopic observation (POM, Olympus BHSP polarizing optical microscope; Mettler FP80 and FP82 hot stage and controller). The transmittance spectra were recorded with a Shimadzu UV-1600PC spectrometer. The irradiation 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 visible light irradiation (436 nm).

RESULTS AND DISCUSSION

For the synthesis of the chiral photochromic compounds, two chiral diols, isosorbide and isomannide, were chosen. Because, it had been reported that the chiral compounds derived from these two diols exhibited a good twisting ability [15,16]. Two types of chiral photochromic compounds were synthesized by reacting azobenzene compounds having a carboxyl group at 2-, 3-, or 4-position of the azo-core with isosorbide or isomannide termed as (*o*, *m*, *p*)-**Azo-Sor** (from isosorbide), (*o*, *m*, *p*)-**Azo-Man** (from isomannide), respectively (Fig. 1).

A Ch LC was induced by mixing each chiral azobenzene compound in **E44** (Merck Co.). **HTP**s of chiral azobenzene compounds and

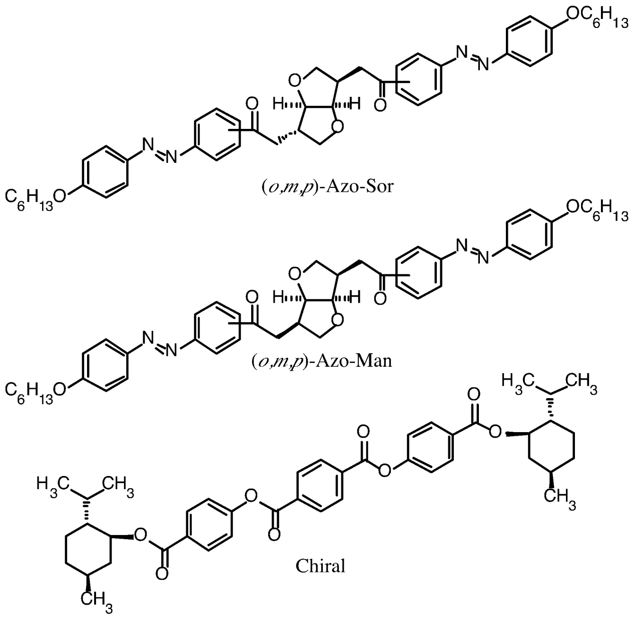

FIGURE 1 Chiral azobenzene compounds and non-photochromic chiral compounds used in this study.

non-photochromic chiral compound (**Chiral**) in **E44** were determined by the Cano's wedge method [17]. **HTP** of **Chiral** was $130 \times 10^8\,m^{-1}\,mol^{-1}\,g$-**E44**, and it was insensitive to UV and visible light irradiation, because of the absence of photo-functional group in **Chiral** molecule. **HTP**s of the chiral azobenzene compounds with or without UV irradiation are summarized in Table 1. The photoisomerization ratio in Table 1 was determined by comparing ^{1}H-NMR spectra before and after UV irradiation for 10 min. The yield of cis-form at the photostationary state was around 90% for all the chiral azobenzene compounds. As can be seen in Table 1, both *p*-type chiral azobenzene compounds have higher **HTP** than others, and the **HTP** values were decreased down to 20–30% of the initial value by UV irradiation, indicating the photochemical decrease in the **HTP** value of 80–70% relative to the initial **HTP** values. The initial **HTP** values and the magnitude of the photochemical decrease in the **HTP** value were larger than those obtained for mono- or di-substituted azobenzene dyes described above. Contrary to *p*-type dyes, *m*-type dyes showed a quite different behavior: that is, the **HTP** value of *m*-**Azo-Man**, and *m*-**Azo-Sor** were decreased and increased by UV irradiation, respectively.

Ichimura first reported photochemical increase in **HTP** value by photoisomerization of azobenzene dye having non-chiral and chiral groups at 2,2′- and 3,3′-positions, causing photochemical shortening of the helical pitch [8]. On the basis of semiempirical MOPAC calculation, they revealed that the chiral azobenzene molecule showing photochemical increase in **HTP** retained a rod-like molecular shape even after UV irradiation. MOPAC calculation seems to be an effective tool to clarify a conformational effect on the initial **HTP** value, and the photochemical change in **HTP**. Thus, the molecular aspect ratio defined as a ratio of molecular length to molecular width (**L**/**D**) of the azo dyes was estimated by semiempirical MOPAC calculation, as it is one of the important parameters contributing to an appearance of liquid crystalline molecular orientation. Therefore, it can be assumed that an intermolecular interaction between LC and azo dye molecules increases with an increase in **L**/**D** [1]. Consequently, the higher the **L**/**D** values, the larger will be the **HTP** values. Actually, the initial **HTP** value seems to be dependent on **L**/**D**, e.g., both *p*-type dyes have higher **L**/**D** than the others. In addition, the photochemical change in **HTP** may be explained as the difference in **L**/**D** between trans-form and cis-form. MOPAC calculation demonstrated that *m*-**Azo-Man** differed from the other dyes in changing **L**/**D** through the photoisomerization, contributing to the photochemical increase in **HTP**.

To control photochemically the helical structure of Ch LCs, we attempted first to use *p*-**Azo-Sor** and *p*-**Azo-Man**, because of larger

TABLE 1 **HTP** of **Azo-Sor** and **Azo-Man** having plural chiral sites and azobenzene groups doped in **E44** before and after UV irradiation (7.6 mW/cm^2) at 25°C

Azo	Tm (°C)	**HTP** ($\times 10^8$ m^{-1} mol^{-1} g-**E44**) before	after	Δ[1]	Change in **HTP** (%)	cis ratio at photo-stationary state (%)	Molecular aspect trans-form	ratio **L/D** cis-form
o-**Azo-Sor**	74	4.6	4.5	–0.1	–2	89	2.1	3.3
m-**Azo-Sor**	51	15.6	79.4	+64	+409	90	2.5	4.5
p-**Azo-Sor**	203	202	49	–153	–76	90	5.4	1.4
o-**Azo-Man**	104	60	35	–25	–42	89	3.0	2.2
m-**Azo-Man**	127	129	20	–109	–84	90	4.3	1.8
p-**Azo-Man**	187	141	17	–124	–88	90	4.4	1.6

[1] The difference (Δ) = HTP (after) – HTP (before)

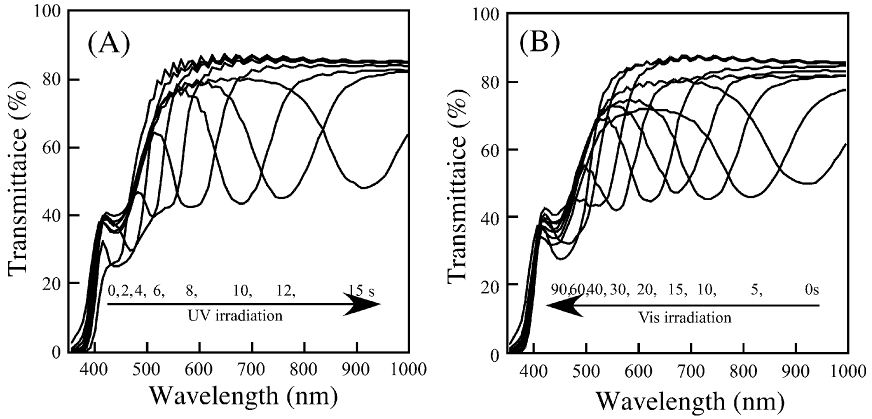

FIGURE 2 Changes in the selective reflection of the Ch LC of **E44**, **Chiral** and *m*-**Azo-Man** (80:8:12 wt%) by UV irradiation (7.6 mW/cm^2) (A) and following Vis light irradiation (14.3 mW/cm^2) (B) at 25°C.

initial **HTPs** and larger photochemical change in **HTP**. However, a phase separation was brought about by mixing *p*-**Azo-Sor** or *p*-**Azo-Man** in **E44** even at a concentration of 3 wt% to **E44**. Contrary to *p*-type dyes, *m*-**Azo-Man** was miscible even higher than 10 wt% of

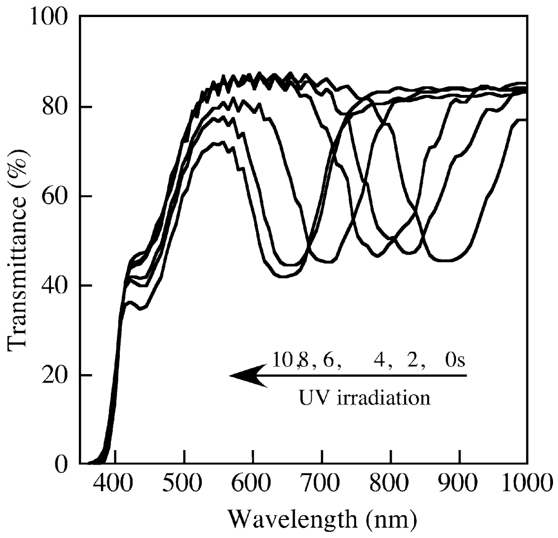

FIGURE 3 Change in the selective reflection of the Ch LC of **E44**, **Chiral** and *m*-**Azo-Sor** (80:8:12 wt%) by UV irradiation (7.6 mW/cm^2) at 25°C.

the concentration in **E44**. Both *p*-type azo dyes have higher melting point; 203°C for *p*-**Azo-Sor** and 187°C for *p*-**Azo-Man**. The phase separation may be related to higher molecular aspect ratio, causing strong molecular interaction between the azo dye molecules, and high melting point.

A mixture consisting of *m*-**Azo-Man**, **Chiral** and **E44** (12:8:80 wt%) showed a Ch phase above room temperature up to 72°C; Ch • 72°C • I. This Ch LC was injected into a glass cell with 5 μm cell gap, which consisted of two glass plates coated with polyimide and rubbed to provide uniaxially parallel molecular orientation in plane. Prior to use azo dyes for photochemical modulation of the helical structure, it should be noted that the disorganization effect of azo dyes results in photochemical phase transition of a LC phase into other LC or an isotropic phase [18]. To avoid the photochemical phase transition as unfavorable side-effect, it is preferred to add azo dye as small concentration as possible. Therefore, **Chiral** was used for adjusting initial reflection wavelength. Both *m*-**Azo-Man** and **Chiral** provided a Ch phase having a left handed helical structure, and the Ch LC containing both *m*-**Azo-Man** and **Chiral** also possessed the left handed helical structure.

Changes in transmittance spectra of the Ch LC by UV irradiation at 25°C was shown in Figure 2(A). Before UV irradiation, only an extreme low transmittance was observed shorter than 400 nm corresponding to π-π' absorption band of azo chromophore. However, the purple color was recognized with the naked eye, indicating the reflection of light around 400 nm as can be seen in Figure 4. UV irradiation resulted in the shift of the selective reflection to longer wavelength, and the wavelength became longer than 900 nm by irradiation for 15 s. The selective reflection returned to the initial state by visible light irradiation as shown in Figure 2(B). Thus, a reversible shift of the selective reflection over a whole visible region could be achieved by UV and visible light irradiation.

Reverse shift of the selective reflection to shorter wavelength was carried out by UV irradiation on a Ch LC consisting of *m*-**Azo-Sor**, **Chiral** and **E44** (12:8:80 wt%). The initial reflection wavelength was about 900 nm, and became 620 nm by UV irradiation after 10 s (Fig. 3). It is interesting here to compare the results with *m*-**Azo-Man** and *m*-**Azo-Sor**. The UV irradiation on the Ch LC containing *m*-**Azo-Man** changed the reflection band shape to broader and higher transmittance, whereas little change in the band shape was observed for the Ch LC containing *m*-**Azo-Sor**. The **L/D** molecular aspect ratio of *m*-**Azo-Man** and *m*-**Azo-Sor** decreased and increased by the trans-to-cis photoisomerization, respectively. The change in reflection

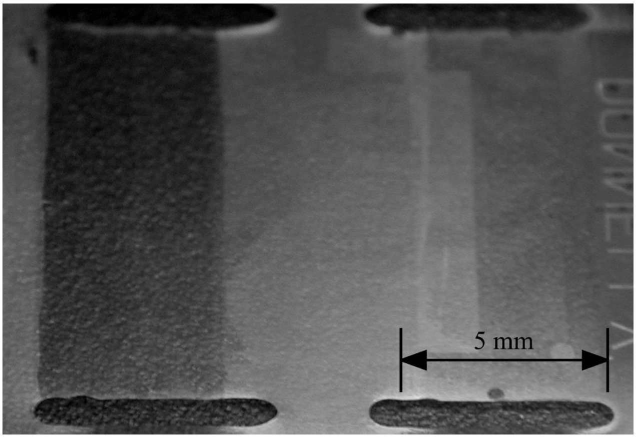

FIGURE 4 Change in the reflection color of the Ch LC of **E44**, **Chiral** and m-**Azo-Man** by varying UV irradiation time 0 (left, blue), 4 (middle, green), and 10 s (right, red).

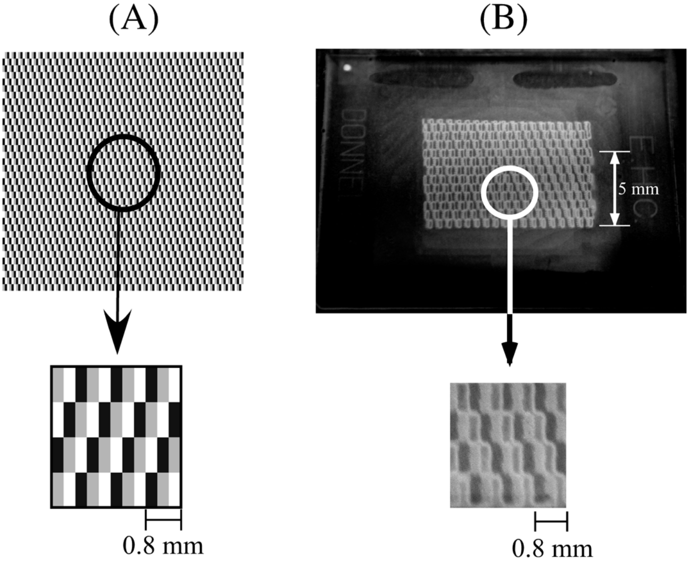

FIGURE 5 Gray mask (A) and RGB patterning of the Ch LC of **E44**, **Chiral** and m-**Azo-Man** obtained by UV irradiation for 10 s through the gray mask at 25°C (B).

band shape may be interpreted in terms of photochemical change in the molecular aspect ratio, facilitating liquid crystalline molecular orientation. Consequently, the helical structure of the Ch LC containing *m*-**Azo-Sor** is more stable than the Ch LC containing *m*-**Azo-Man** under UV irradiation.

Figure 4 shows colors reflected from the Ch LC containing *m*-**Azo-Man** by varying UV irradiation time as 0, 4, and 10 s. Before irradiation, the color was purple, and it turned to green and red, corresponding to the shift of the reflection wavelength (Fig. 2(A)). The color could be also adjusted by varying light intensity with gray mask as can be seen in Figure 5 (A and B). The resolution of the color patterning was estimated to be 70–100 μm by patterning experiments with the use of photo-mask.

CONCLUSION

A combination of rigid chiral diol core and azobenzene groups provides an effective trigger molecule for the photochemical modulation of the helical structure of Ch LCs. Semiempirical MOPAC calculation revealed that the molecular aspect ratio, **L**/**D**, is significant for ascribing photochemical change in the twisting ability of the chiral azobenzene compounds. The reversible change in the selective reflection was achieved over a whole range of visible region by UV and visible light irradiation for several tens second.

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