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Discontinuous change in the helical pitch of cholesteric liquid crystals by photoisomerization of a chiral azobenzene molecule

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This paper describes the discontinuous change in the helical pitch of a cholesteric liquid crystal (ChLC) by means of the photoisomerization of chiral azobenzene molecules under homogenous alignment conditions. A mixture of E44, R811 and Azo was prepared in the ratio 68/28/4, respectively. R811 and Azo have opposite twisting abilities such that they induce right- and left-handed helices, respectively when added to E44. The mixture was injected into a glass cell having a 2 or 5 μm cell gap, and treated for homogeneous molecular orientation. The wavelength of selective reflection from the ChLC was shifted to shorter wavelengths by the *trans-cis* photoisomerization of Azo. The change in the helical pitch was not only discontinuous, but also dependent on the cell thickness. The discontinuous change in the helical pitch was estimated to be almost the same as the half turn of the helical pitch in each cell gap, and was dependent on the number of helical half pitches in the glass cell. The homogeneous alignment condition affects the photochemical change in the helical structure of the ChLC system.

1. Introduction

Many studies have been reported on liquid crystals (LCs) containing azobenzene molecules in the field of optical materials for application in, for example, optical displays and optical memory [1–14]. Cholesteric liquid crystals (ChLCs) have a helical structure, and selectively reflect light of a wavelength proportional to the helical pitch. If we can control the helical pitch by external stimuli such as photoirradiation, change of temperature or application of an electric field, various optical devices can be prepared. A cholesteric phase can be induced in a host nematic liquid crystal by adding a chiral dopant. The ability of the chiral dopant to twist the nematic phase is given by the helical twisting power (HTP), β , where $\beta=1/(pc)$, in which p is the helical pitch length, and c is the concentration of the chiral dopant. The HTP of a compound is known to be sensitive to its molecular shape [15]. Thus, various photochromic compounds having chiral groups have been reported to exhibit different HTP values between photoisomers, providing a photochemical modulation of the helical structure of a ChLC induced by doping a host nematic LC with a chiral photochromic compound.

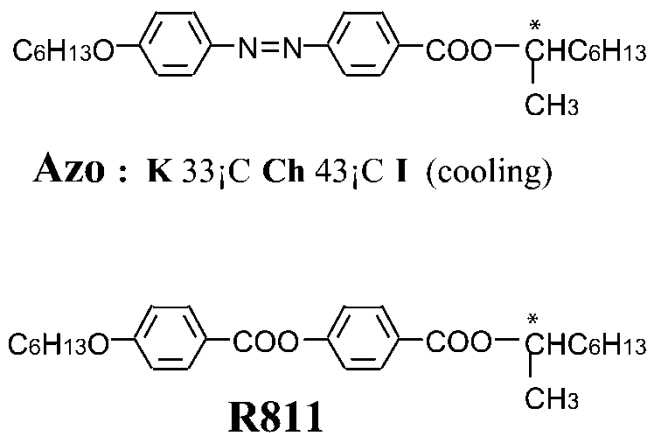
Recently, we reported the photochemical change in the helical pitch of a ChLC induced by doping with a chiral azobenzene compound and a non-photochromic chiral compound [16]. We studied the photochemical change of the helical pitch of the ChLC in a cell consisting of two glass plates coated with polyimide and rubbed to macroscopically align the LC molecules in a homogeneous molecular orientation, because this is suitable for the observation of the selective reflection of light. A significant influence of the molecular orientation and cell width on the photochemical change in the helical pitch of the ChLC was observed. In this paper, we describe the photochemical change in the helical pitch of the ChLC with respect to the molecular orientation and the cell width.

2. Experimental

The chiral azobenzene compound and the non-photochromic chiral compound used in this study, Azo and R811, are shown in the scheme. Azo was synthesized by the method reported earlier [16]. E44 was used as a low molar mass nematic host, because it exhibits a nematic phase over a wide range of temperature to 100°C. R811 and E44 were purchased from Merck Co., and used without further purification.

LC mixtures were prepared by adding Azo and/or R811 to E44. The LC properties of the mixture were

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Scheme. Chiral azobenzene, Azo, and non-photochromic chiral compound, R811.

examined by polarizing optical microscopy and differential scanning calorimetry. The LC mixtures were injected into a glass cell having either 2 or 5 μm cell gaps. The cells consisted of pairs of glass plates coated with polyimide and rubbed to provide homogeneous molecular orientation; they were purchased from EHC Co. Ltd. The transmittance spectra were recorded with a Simadzu UV-1600PC spectrometer. The helical pitch was determined by means of the Cano wedge method [17]. Photoirradiation was carried out using a 500 W high pressure Hg lamp (Ushio SX-UI 500H) equipped with a filter (Sigma Koki Co. UTVAF-35) for ultraviolet irradiation (366 nm).

3. Results and discussion

A Ch phase was observed for E44 containing Azo or R811 at room temperature. Azo and R811 yield left- and right handed helices, respectively, when they are doped in E44 [16]. According to the equation $\beta = 1/(pc)$, the reciprocal of the helical pitch is proportional to the concentration of the chiral dopant. Thus, the helical pitch can be controlled by varying the amount of chiral compound added to the host nematic LC.

Figure 1 shows changes in the transmittance spectra of E44 containing Azo and/or R811 in the glass cell with a 5 μm cell gap. A mixture of E44 and R811, in the weight ratio 68/28, showed a Ch phase from room temperature to 75°C. The minimum transmittance was observed around 530 nm, indicating the selective reflection in this wavelength region. Next, Azo was added to the E44/R811 mixture to give a mixture of E44, R811 and Azo in the weight ratio 68/28/4. This mixture also showed a Ch phase from room temperature to 75°C. It appears that the addition of Azo to the E44/R811 mixture does not destabilize liquid crystallinity, because there is no difference in the clearing

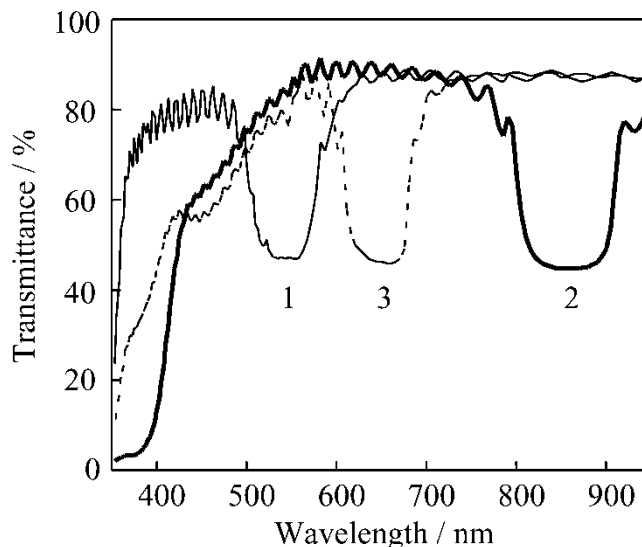


Figure 1. Change in the selective reflection wavelength of E44 containing chiral compounds, R811 and Azo. 1: a mixture of E44/R811(68/28); 2: a mixture of E44/R811/Azo(68/28/4); 3: a mixture of E44/R811/Azo(68/28/4) after UV irradiation (366 nm, 6.4 mW cm^{-2} , 30 s) at room temperature.

temperatures of the mixtures with and without Azo. However, the addition of Azo caused a shift of the wavelength of selective reflection to longer wavelengths, around 850 nm, indicating an unwinding of the helix in the E44/R811/Azo mixture. This increase in the helical pitch may be attributed to the opposite helical twisting ability of R811 and Azo with respect to each other. In addition, a decrease in the transmittance due to the absorption by Azo was observed in the ranges from 450 to 500 nm and shorter than 400 nm, corresponding to $n-\pi$ and $\pi-\pi^*$ transitions of the Azo chromophore.

Ultraviolet (UV) irradiation transforms *trans*-Azo into *cis*-Azo and a decrease and increase in the transmittance corresponding to $n-\pi$ and $\pi-\pi^*$ transitions, respectively, can be seen in figure 1 (curve 3). Furthermore, a shift of the wavelength of selective reflection to shorter wavelengths was brought about by UV irradiation. Azobenzene compounds are well known to exhibit *trans-cis* photoisomerization: *trans*-Azo has a rod-shape, while *cis*-Azo has a bent-shape. We reported that the HTP values of *trans*-chiral azobenzenes were larger than those of the *cis*-isomers produced photochemically. The photochemical change in HTP between the photoisomers causes the photochemical shift of the wavelength of selective reflection of the E44/R811/Azo mixture to a shorter wavelength. The photochemical change in the HTP of Azo may be closely related to the difference in the molecular shape between the *trans*- and *cis*-Azo isomers.

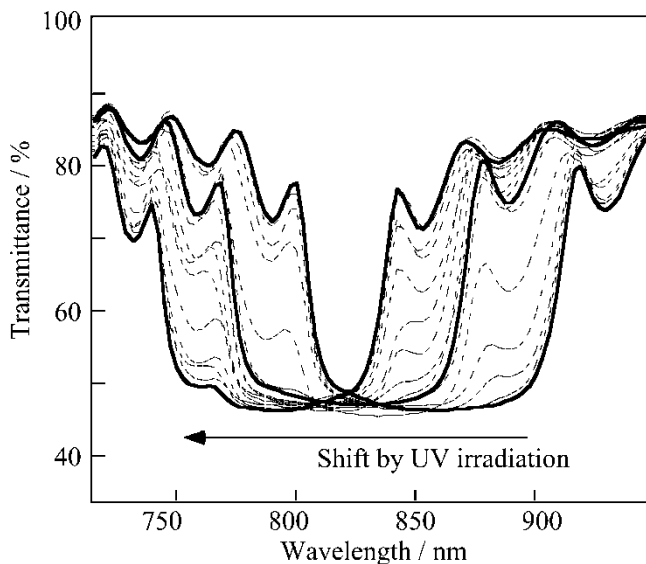


Figure 2. Changes in selective reflection wavelength under UV irradiation (366 nm , 0.32 mW cm^{-2}) of the E44/R811/Azo=68/28/4 mixture in a $5\text{ }\mu\text{m}$ homogeneous glass cell at room temperature.

As can be seen in figure 1, the *trans-cis* photoisomerization of Azo in the E44/R811/Azo mixture on UV irradiation shifted the selective reflection to a shorter wavelength. The photochemical decrease in the HTP of Azo resulted in an increase in the total HTP of the mixture, so that the helical pitch length was reduced. Figure 2 shows changes in the transmittance spectra of the E44/R811/Azo mixture in the glass cell with a $5\text{ }\mu\text{m}$ cell gap. Before UV irradiation, the selective reflection

was centered on 865 nm . The transmittance intensities at longer and shorter wavelengths decreased and increased under UV irradiation, respectively and are shown as dotted lines in figure 2. Consequently, the wavelength of the minimum transmittance changed discontinuously from 865 to 820 nm . Further UV irradiation caused a similar change in the transmittance spectra, and shifted the wavelength from 820 to 780 nm .

It is worthwhile to evaluate the helical pitch length and the number of pitches in the glass cell. In order to evaluate the helical pitch p , an average refractive index of E44, n , was determined to be 1.57 by using a wedge-shaped cell. From the equation $\lambda=np$, where λ represents the wavelength of reflected light, p can be estimated. The helical pitch decreased on UV irradiation as follows: 551 , 522 , and 497 nm for selective reflection centered at 865 , 820 and 780 nm respectively. Based on the helical pitches estimated, the number of helical pitches in the $5\text{ }\mu\text{m}$ glass cell were 9.1 , 9.6 and 10.1 , respectively.

Figure 3 shows changes in the transmittance spectra of the E44/R811/Azo mixture in glass cells with cell gaps of 2 and $5\text{ }\mu\text{m}$. The helical pitches and the number of helical pitches in each gap were evaluated from the minimum transmittance wavelength in figure 3, and are given in the table. The number of helical pitches in each cell is approximately equal to an integral multiple of half turns of the helical pitch as given in the last column of the table. As mentioned already, the helical pitch of the ChLCs was determined by means of the Cano wedge method [17, 18]. In a thin wedged cell treated for homogeneous orientation, the discontinuous lines are

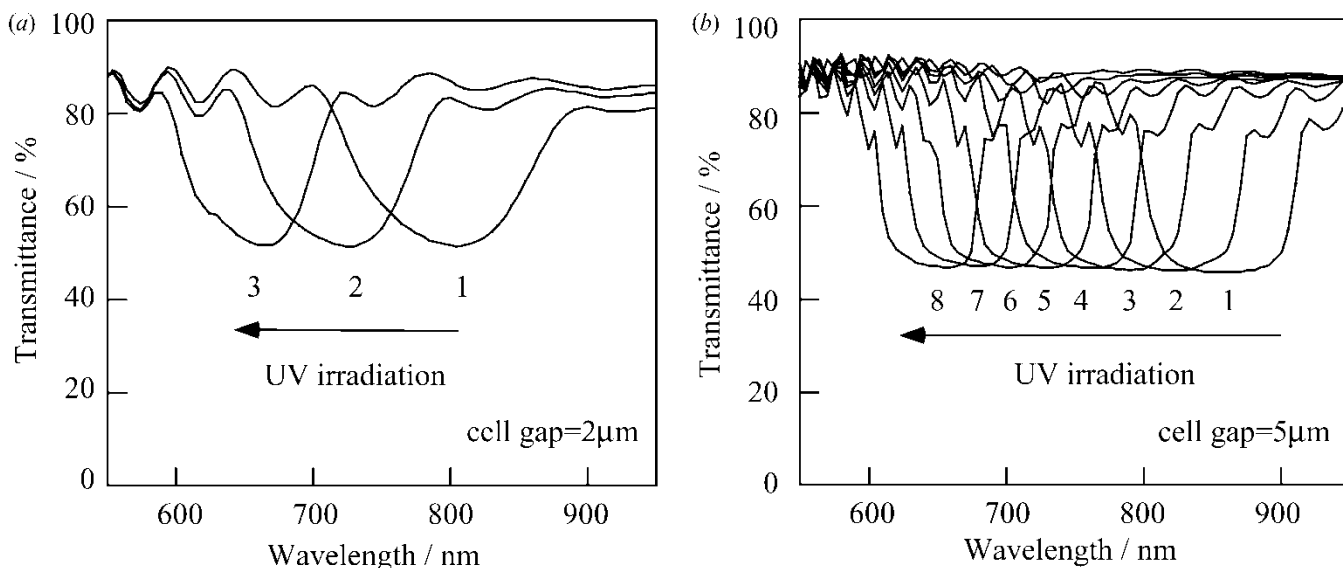


Figure 3. Changes in the selective reflection wavelength under UV irradiation (366 nm , 6.4 mW cm^{-2}) of the E44/R811/Azo=68/28/4 mixture in (a) $2\text{ }\mu\text{m}$ and (b) $5\text{ }\mu\text{m}$ homogeneous glass cells at room temperature.

Table. Changes in the number of pitches in the homogenous glass cells with 2 or 5 μm cell gaps as a function of UV irradiation time.

Curve	Irradiation time/s	Cell gap/ μm	l/nm	Pitch ^a / μm	Cell gap Pitch
1 ^b	0~2	2	805	0.513	3.9
2	4~6	2	730	0.465	4.4
3	9~	2	660	0.420	4.8
1 ^c	0	5	865	0.551	9.1
2	0.5	5	820	0.522	9.6
3	2	5	780	0.497	10.1
4	4~5	5	750	0.441	10.5
5	7~9	5	720	0.459	10.9
6	11~13	5	690	0.433	11.5
7	15~22	5	668	0.420	11.9
8	24~	5	645	0.411	12.1

^aPitch was calculated from $l=np$, where n is 1.57, which is an average refractive index of the Ch liquid crystal. The n value used was obtained experimentally for E44.

^bCurve numbers from figure 3 (a).

^cCurve numbers from figure 3 (b).

observed, and separate domains with n and $(n+1)$ half turns of helices. This means that the helical pitch is changed by a half-pitch between two homogeneously oriented glass plates. In addition, discontinuous lines were observed between two parallel polished plates if one uses a ChLC with gradient twisting ability [18]. Therefore, it is reasonable to expect that the helical pitch was varied by a half-pitch unit, even in two parallel solids having homogeneous alignment, when the photochemical change in the helical pitch of the ternary ChLC occurred. Actually, a discontinuous line was observed on the boundary between areas with and without UV irradiation as shown in figure 4. In addition, the increment of the change in the helical pitch in the 5 μm glass cell was smaller than that in the 2 μm glass cell. The number of half turns increases with the increase in the cell gap, resulting in the reduction of the increment with increase of the cell gap. Consequently, increasing the cell gap shortened the UV irradiation time required for one half-turn change. Indeed, a ChLC in a 25 μm glass cell was found to show a change in helical pitch of several half turns by UV irradiation applied only for a second.

4. Summary

We have examined the photochemical change of the helical structure of a ChLC in a homogenous glass cell caused by *trans-cis* photoisomerization. A discontinuous change in the helical pitch by a half-turn was brought about by photoisomerization of the chiral azobenzene component of the ChLC in the homogenous glass cell. The increment of the discontinuous change in the helical pitch, and the irradiation time

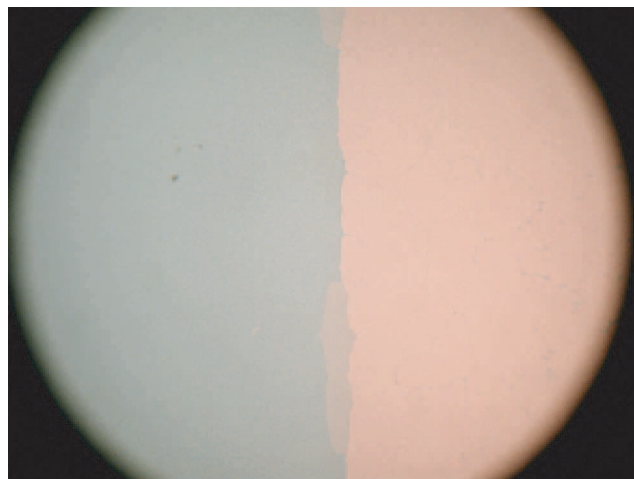


Figure 4. Polarizing optical micrograph of the E44/R811/Azo mixture with and without UV irradiation. Left side: no UV; right side: with UV.

required for the one half turn change, were influenced significantly by the molecular orientation and cell width.

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