Synthesis of chiral azobenzene-based compounds for use in the photochemical tuning of the helical structure of liquid crystals

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We have synthesized azobenzene-based molecules containing either one or two chiral groups. A cholesteric phase can be induced by adding the chiral azobenzene compounds to a host nematic liquid crystal. We investigated the effects of the *trans–cis* photoisomerization of the chiral azobenzene compounds on the properties of the cholesteric phase, such as the helical pitch length. This can be increased or decreased by the photoisomerization of the chiral azobenzene compounds. We discuss the photochemically driven change in the helical pitch of the cholesteric phase with respect to structural effects involving the chiral groups.

1. Introduction

Recently, many studies have focused on the synthesis of photoresponsive liquid crystals (LCs), and in particular, cholesteric LCs. Cholesteric (Ch) LCs have a helical structure, reflect the wavelength of light corresponding to the helical pitch, and scatter light. This unique combination of optical properties coupled with photochromism will enable us to develop optical devices for use in optical memory, optical switching, and chirooptical switching [1–15]. Various photochromic compounds based on, for example, azobenzenes, flugides, and stilbenes have been investigated as photoresponsive Ch LCs [10–19]. Adding a chiral dopant to a host nematic LC can induce a Ch phase. In such a mixture, which consists of the non-chiral host nematic LC and the chiral compound, the inverse of the helical pitch $(1/p)$ is known to increase linearly with the concentration of the chiral compound for low concentrations. The helical twisting power (HTP) of chiral compounds can be defined as the slope of the plot of $1/p$ versus the concentration of the chiral compound [20, 21]. Therefore, it is possible to control the helical pitch of the induced Ch phase by the photochemical isomerization of the photochromic compound containing chiral substituents, if there is a difference in the HTP of the photoisomers. We have reported the photochemical control of the helical structure of an induced Ch phase containing a chiral azobenzene compound and a non-photochromic chiral dopant, by the photoisomerization of the chiral azobenzene compound [17].

Azobenzene compounds are well known to exhibit photochromism between the *trans*-form with a rod-like shape and the *cis*-form with a bent shape on irradiation using ultraviolet (UV) and visible (Vis) light. In our study, we used chiral azobenzene compounds having chiral and non-chiral substituents at the 4 and 4′-positons of the azobenzene core, and showed that the HTP of the *trans*-form of the chiral azobenzene compound was larger than that of the *cis*-isomer produced by UV irradiation. This means that the *trans* to *cis* photoisomerization necessarily resulted in an increase in the helical pitch of the induced Ch phase. We achieved photochemical control of the helical pitch of the induced Ch phases and could either increase or decrease the pitch by combining and varying the chirality of both the photochromic and non-photochromic chiral dopants and their concentrations. In addition, we demonstrated photochemical optical switching from transparent to opaque using the photochemical phase transition between a nematic and a Ch phase, and by an inversion of the chiral sense of the Ch phases.

Recently, Ruslim and Ichimura reported conformational effects on the photochemical change in the helical structure of Ch phases by the photoisomerization of azobenzene compounds having chiral groups at different positions. For most azobenzene-based compounds, such as 4,4′-disubstituted azobenzene-based compounds, an increase in the helical pitch of the Ch phases was brought about by *trans* to *cis* photoisomerization under UV light, while 3,3′-disubstituted-2,2′-dimethyl azobenzene-based compounds caused a decrease in the helical pitch on UV irradiation [22]. The photochemical

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change in the HTP of azobenzene-based compounds is closely related to their chemical structure and the change in their conformation, given that these is a difference in the intermolecular interactions between the *trans*- and *cis*-azobenzene molecules and the host LC. In this communication, we describe an approach to design chiral azobenzene-based compounds to act as trigger molecules for the control of the helical structure of Ch phases, i.e. bringing about effects, such as, either the increase or decrease of the helical pitch length, the inversion of the helical structure, or a phase transition between the nematic and Ch phases.
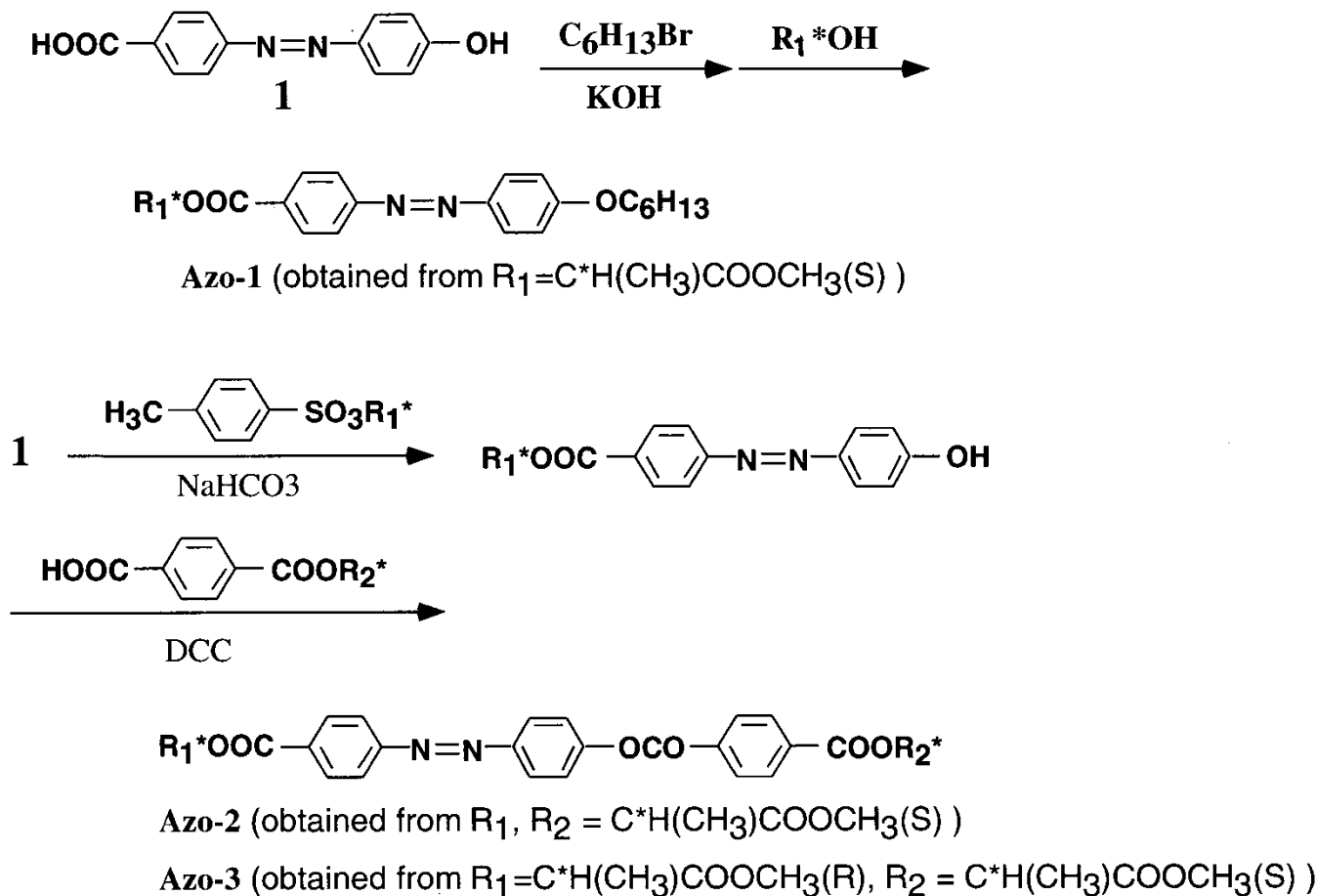
2. Experimental

We synthesized two di-substituted azobenzene-based compounds with chiral groups at the 4- and 4'-positions, one directly and the other separated by a phenyl group (Azo-2 and Azo3), and a third compound, Azo-1, having a chiral and a non-chiral group at the 4 and 4'-positions (see the scheme). Azo-1 was synthesized by the alkylation of 4-carboxy-4'-hydroxyazobenzene with 1-bromohexane, and subsequent esterification with

methyl (*S*)-lactate in the presence of dicyclohexyl-carbodiimide (DCC). Azo-2 was prepared by the esterification of 4-carboxy-4'-hydroxyazobenzene with methyl 2-[(4-methylphenyl)sulphonyl]oxypropionate, which is obtained by the reaction of *p*-toluenesulphonyl chloride and methyl (*S*)-lactate, in the presence of sodium bicarbonate in *N*,*N*-dimethylformamide [23]. This was followed by reaction with terephthalic acid methyl 2-(4-carboxylbenzoyloxy)propionate which is prepared from terephthanoyl chloride with methyl (*S*)-lactate [24]. Azo-3 was prepared according to the same method as Azo-2 but using methyl (*R*)-lactate instead of methyl (*S*)-lactate.

These compounds were characterized using NMR, IR, and mass spectroscopies, elemental analysis, DSC, and polarizing optical microscopy.

3. Results and discussion

Azo-2 and Azo-3 were found to show a Ch phase, while Azo-1 showed only a melting transition at 72°C. This may be related to the difference in the chemical structures among the three azobenzene compounds,

Azo-1 (obtained from $R_1 = C^*H(CH_3)COOCH_3(S)$)

Azo-2 (obtained from R_1, $R_2 = C^*H(CH_3)COOCH_3(S)$)

Azo-3 (obtained from $R_1 = C^*H(CH_3)COOCH_3(R)$, $R_2 = C^*H(CH_3)COOCH_3(S)$)

Scheme. Synthesis of Azo-1, Azo-2 and Azo-3.

and specifically, that the phenylbenzoate group, (which is a conventional mesogenic core group) in Azo-2 and Azo-3 promotes liquid crystallinity. In addition, a difference in the phase transition temperatures between Azo-2 and Azo-3 was observed; Cr 93°C Ch 123°C I for Azo- 2, and Cr 82°C Ch 110°C I for Azo-3. Both compounds have the same chemical structure, but one of the chiral substituents differs in the sense of its chirality. The combination of differing chiral groups in the molecules may give different molecular packing as well as differing phase transition temperatures.

Figure 1 shows changes in the absorption spectra of Azo-2 in methanol on UV light irradiation. Before UV irradiation, there were two absorption bands in the visible region: an intense absorption band at 330 nm corresponding to the π–π* transition, and a weak band centred around 440 nm corresponding to the n–π* transition. The *trans* to *cis* photoisomerization of Azo-2 on UV irradiation gave a decrease and an increase in the absorption intensities at 330 and 440 nm, respectively. The *cis* to *trans* reverse photoisomerization was brought about on irradiation using visible light or thermally in the dark. Irradiation was performed using a 500 W high pressure mercury lamp (Ushio SX-U1500H) equipped with a filter—Sigma UTVAF35U for UV irradiation or Sigma SCF-42L for Vis irradiation. Other azobenzene-based compounds showed similar photoisomerization behaviour, except that the π–π* transition peak for Azo-1 was observed at 360 nm. In addition, all the azobenzene-based compounds in liquid crystal E44 (Merck) showed similar photoisomerization behaviour to that seen in methanol.
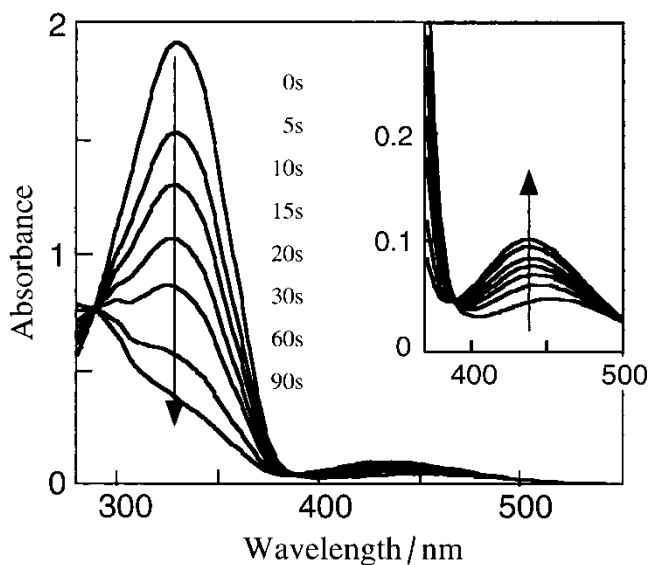

Figure 1. Changes in absorption spectra of Azo-2 in methanol on UV irradiation (11.5 mW cm^{-2}) at room temperature.
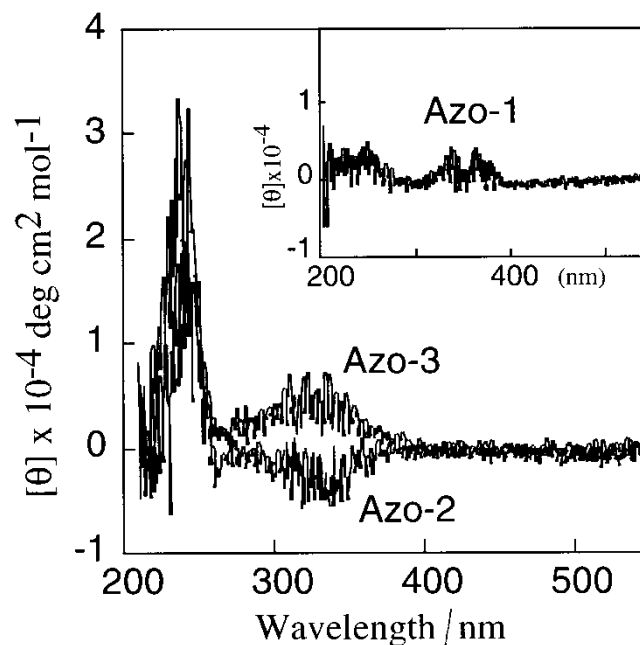

Figure 2. CD spectra of the azobenzene-based compounds in methanol.

Circular dichroic (CD) spectra of Azo-2 and Azo-3 in methanol are given in figure 2. The bands around 250 nm for both Azo-2 and Azo-3 are positive, whereas the bands around 330 nm are opposite in sign: positive for Azo-3 and negative for Azo-2. The CD spectrum of Azo-1 is shown in the insert in figure 2. Comparison of these spectra allows us to assign the band around 250 nm, which is absent in the spectrum of Azo-1, to the azo-phenyl benzoate group containing methyl lactate as the R_2 substituent (part B in the table). In addition, the bands around 330 nm can be mainly assigned to the π–π* transition associated with the azo-phenyl group having the methyl lactate group as the R_1 substituent (part A in the table). Although methyl (S)-lactate was used in Azo-1 and Azo-2 as the R_1 substituent, the sign of the bands associated with the π–π* transition of the azo chromophore are opposite in sign, as can be seen in figure 2. The introduction of R_1 into Azo-1 was carried out by the reaction of 4-carboxyl-4′-hydroxyazobenzene with methyl (S)-lactate in the presence of DCC, whereas Azo-2 was synthesized via the esterification of 4-carboxyl-4′-hydroxyazobenzene with methyl 2-[(4-methylphenyl)sulphonyl]oxypropionate. The inversion of the symmetry of methyl (S)-lactate may occur during the S_N2 reaction with methyl 2-[(4-methylphenyl)sulfonyl]-oxypropionate, resulting in a difference in the chiral symmetry of the R_1 group in Azo-1 and Azo-2.

The chiral sense and HTP of the azobenzene-based compounds in a low molecular mass nematic LC were determined using the Cano wedge method. E44 (Merck.)

Table. Helical twisting powers ($\times 10^8 \, \text{m}^{-1} \text{mol}^{-1}$ g-E44) of the *trans*- and *cis*-forms of azobenzene-based compounds.

Part A

R$_1$OCO—⟨◯⟩—N=N—⟨◯⟩—OC$_6$H$_{13}$

R$_1$OCO—⟨◯⟩—N=N—⟨◯⟩—OCO—⟨◯⟩—COOR$_2$* **Part B**

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-1	−29	−13							−29	−13		
Azo-2			+29	+13			−35	−33	−15	−21	−6	−20
Azo-3			−29	−13			−35	−33	−64	−46		

was used as the host low molecular mass nematic LC. All the azobenzene-based compounds gave a left-handed helical structure when they were added to E44. The values of HTP were -29×10^8 for Azo-1, -15×10^8 for Azo-2 and $-64 \times 10^8 \, \text{m}^{-1} \text{mol}^{-1}$ g-E44 for Azo-3 in the dark, respectively. Here, the negative sign represents the left-handed helical structure. Figure 3 shows changes in the helical pitch of E44 doped with 2 wt% of each azobenzene-based compound on UV irradiation. The helical pitches of the mixtures of E44 doped with Azo-1 and Azo-3 increased on UV irradiation, indicating a decrease in the HTP resulting from the *trans* to *cis* photoisomerization. By contrast, the helical pitch of the mixture of E44 and Azo-2 was clearly found to decrease following the *trans* to *cis* photoisomerization. The values of HTP of the *cis*-form (stationary state) are -13×10^8 for Azo-1, -21×10^8 for Azo-2 and $-46 \times 10^8 \, \text{m}^{-1} \text{mol}^{-1}$ g-E44 for Azo-3.

Based on the results given in figure 3, we can calculate separately the HTP values of part A and part B of the azobenzene-based compounds, see the table. As mentioned already, the initial HTPs of the *trans*-form were -29×10^8 for Azo-1, -15×10^8 for Azo-2 and -64×10^8 for Azo-3. The HTP of Azo-1 may be attributed to part A of the molecule, because Azo-1 has only one chiral group which is in the 4-position. Thus, the HTPs of part A of *trans*- and *cis*-Azo-1 are considered to be -29×10^8 and -13×10^8, respectively.

Based on the CD spectra, the chiral configuration of the methyl lactate of part A of Azo-3 is the same as that of Azo-1, while Azo-2 is in the opposite sense. Therefore, the HTP of part A of Azo-2 and Azo-3 can
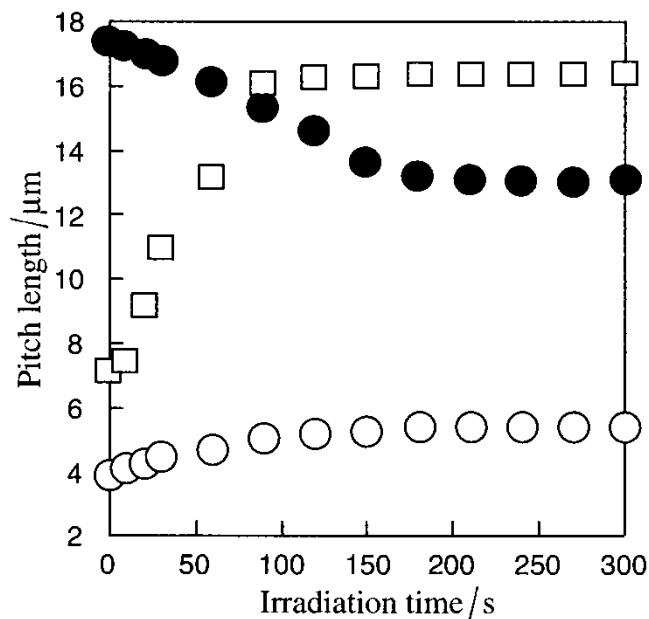

Figure 3. Changes in the helical pitch of the Ch phase containing each Azo-based compound dissolved in E44 on UV irradiation. (□): Azo-1. (●): Azo-2. (○): Azo-3.

be estimated, see the table. Azo-3 exhibited a larger HTP than Azo-1; this means that the HTPs of parts A and B of Azo-3 have the same helical twisting ability, giving the left-handed helical structure. Thus, it is assumed that the HTP of part B of Azo-3 can be estimated by subtracting the HTP attributed to part A from the measured HTP of Azo-3; i.e. -35×10^8 and -33×10^8 for the *trans*- and *cis*-forms of Azo-3, respectively. The chiral configuration of part B of both Azo-2 and Azo-3 are the same, because the same chiral intermediate was used for the preparation of both compounds, see the scheme. Indeed, both Azo-2 and Azo-3 showed a similar CD peak at around 250 nm corresponding to the phenyl benzoate group containing a methyl lactate substituent. Thus, the HTP of part B of Azo-2 is the same as that of part B of Azo-3; i.e. -35×10^8 and -33×10^8 for the *trans*- and *cis*-forms, respectively. Finally, the value of the HTP of Azo-2 can be estimated to be -6×10^8 and -20×10^8 for the *trans*- and *cis*-forms, respectively, by summing the estimated HTPs of parts A and B of Azo-2. The observed and estimated HTPs are not exactly the same but show a similar tendency. Specifically, the HTP of the *trans*-form is smaller than that of the *cis*-form. This estimate is based on the assumption that both HTPs of parts A and B are independent of each other. This result implies therefore that the measured HTP of the compound is equal to the summation of each HTP. A small deviation between the observed HTP and the estimated value for Azo-2 may arise from an interaction between parts A and B.

It has been reported that chiral dopants having a more similar structure to that of the host LC molecules exhibit relatively larger HTPs [25, 26]. The phenyl benzoate group in the Azo-2 and Azo-3 compounds is found in many mesogenic groups. This molecular shape effect contributes to the larger HTP for part B and the small difference in HTP for part B between the *trans*- and *cis*-forms. In addition, the results indicate that the combination of chiral substituents and their chemical structures is important in designing a molecule to provide the photochemical trigger for changing and tuning the macroscopic helical structure of Ch LCs. Not only can changes, both increases and decreases, in the helical pitch length be achieved photochemically, but so can helical inversion and phase transitions between nematic and Ch phases by varying the structure as well as the chirality of the substituents attached to the azobenzene core.

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