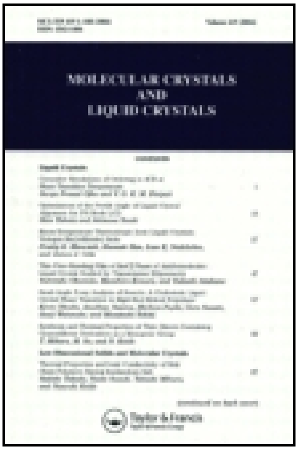

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Chiroptical Properties of Cholesteric Liquid Crystals Induced by Chiral Photochromic 3,3′-Dialkoxyazobenzenes

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Chiroptical Properties of Cholesteric Liquid Crystals Induced by Chiral Photochromic 3,3'-Dialkoxyazobenzenes

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The spectroscopic features and photoisomerization behaviors of chiral photochromic 3,3'-dialkoxyazobenzenes were evaluated in an isotropic solution and a nematic solvent. The effect of photoisomerization on the helical twisting power and handedness of these chiral dopants in induced cholesteric liquid crystals were studied. Depending on the distance of the chiral center from the azo-core, elongation of the helical pitch and reversion of the handedness upon *E-to-Z* photoisomerization were observed. These characteristics are interesting for optical devices based on light-controlled phase switching.

Keywords: azo compounds; chirality; cholesteric; photoisomerization

INTRODUCTION

The high photofatigue resistance and simplicity of photoisomerizable azobenzene molecules have made them potential phototriggers in optical devices based on light-controlled properties modification. One of the significant modification is the light-induced changes in helical pitches of cholesteric liquid crystals (LCs) which can be achieved by dissolving an achiral azobenzene in a cholesteric LC or by inducing a cholesteric phase using a chiral azobenzene doped into a nematic LC. Since the report on modification of cholesteric colors by Sackmann in 1971 [1], many efforts have been made to develop new materials with switchable chiroptical properties or new methods to optimize the performance of these photoswitchable molecular systems [2-5].

We have shown previously that the positional substitutions of an azobenzene molecule determine the conformations of the *E*- and *Z*-isomers which are crucial factors to influence the chiroptical properties of cholesteric LCs [6]. We extent our study to chiral azobenzenes to investigate their ability to induce cholesteric phases. To our knowledge, there have been no reports on chiroptical properties of 3,3'-substituted azobenzenes, whereas those of some 4,4'- and 2,2'-disubstituted azobenzenes have been reported [7]. We report here the photoisomerization behaviors of some novel chiral 3,3'-dialkoxyazobenzenes (**1-3** in Figure 1), their helical twisting powers in nematic LCs, and indicate the potential of these molecules as phototriggers for reversible chiroptical switching in liquid crystal systems.

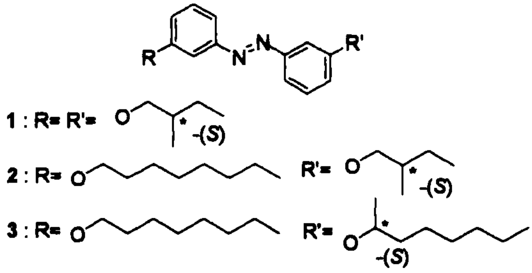

FIGURE 1 Chemical structure of the chiral azobenzenes used as dopants.

EXPERIMENTAL

The 3,3'-dialkoxyazobenzenes (**1-3**) were prepared by reacting 3,3'-dihydroxyazobenzene with chiral alcohols. Details of the synthesis and characterization will be reported elsewhere. The *E*- and *Z*-isomers were elucidated using HPLC with ethyl acetate and hexane (1: 9) solution as the eluent. The photoisomerization was performed using high pressure

Hg lamp (USH-500D) combined with suitable glass filters to sort out UV (365 nm) and visible (436 nm) light, and was studied in THF solutions and in a nematic LC.

These azobenzenes were dissolved in a nematic LC separately to give rise to cholesteric LCs. The induced helical pitch was measured using a wedge cell under a polarized microscope and the handedness of the helix was determined by observing the extinction zone upon rotating the analyzer [8] and checked by the contact method [9].

RESULTS AND DISCUSSION

The spectra of the *E*- and *Z*-isomers of **1** is shown in Figure 2. The *E* spectrum is characterized by low energy proximity of the π-π* band with λ_{max} at approximately 318 nm (ε= 1.7 x 10^4 cm^{-1} mol^{-1} dm^3), whereas the *Z* spectrum has a poorly defined π-π* band and a n-π* band centered at 438 nm (ε= 3.2 x 10^2 cm^{-1} mol^{-1} dm^3). The spectroscopic features are quite different from those of an unsubstituted or the corresponding *para*-substituted azobenzenes [6]. Similar spectra were found for **2** and **3**.

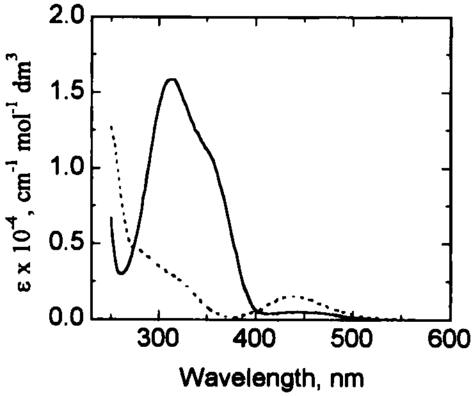

FIGURE 2 The absorption spectra of the pure *E*- (solid line) and *Z*-isomers (dotted line) of **1** in ethyl acetate/hexane (1:9) mixed solution.

From the spectroscopic feature, we can calculate the *Z*-fraction of the compounds when subjected to light. We compare the degree of photoisomerization of the azobenzenes in THF solutions and in a nematic DON-103 (T_{NI}= 74 °C) from the corresponding spectra, as shown representatively in Figure 3 for 1. Although part of the spectra overlapped with the absorption of the nematic LC, still we can estimate the *Z*-fraction by taking into account the absorbance of the pure nematic LC and the *ε* of the pure *E*- and *Z*-isomers.

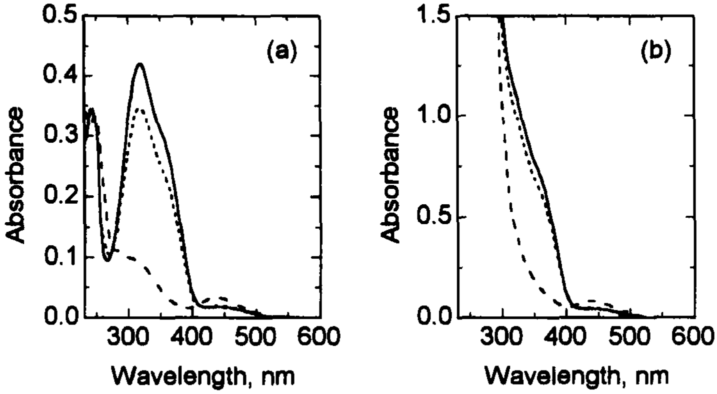

FIGURE 3 The absorption spectra of 1 before (solid line) and after illumination with UV (broken line) and visible light (dotted line) toward the photostationary states, (a) in THF and (b) in a nematic DON-103.

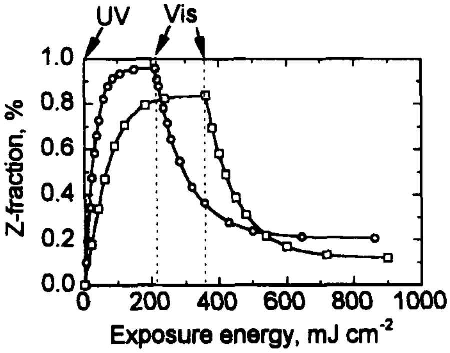

FIGURE 4 The change of *Z*-fraction as a function of exposure energy of UV and successively visible light for 1 in THF solution (circles) and in a nematic DON-103 (squares).

The evolution of the *Z*-fraction upon exposure energy of light is illustrated in Figure 4. At the photostationary state of UV light, the content of *Z*-isomers reached *ca*. 96 % and 84 % in THF and in the nematic LC, respectively, indicating a suppression of isomerization due to the viscosity of the LC matrix. On the other hand, photostationary state of visible light produced only 21 % and 12 % of *Z*-isomers, respectively. Based on the information of photoisomerizability, the effect of *E*-/*Z*-isomers on the induced cholesteric phases are elucidated.

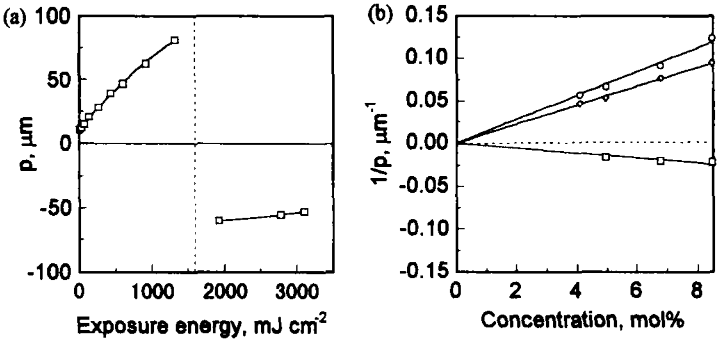

FIGURE 5 (a) The change of helical pitch length of 6.8 mol % of **1** in DON-103 upon photoisomerization with UV light and (b) the plots for the concentration of **1** versus reciprocal pitch length at the initial (circle) state, the photostationary states of visible (diamond) and UV (square) light.

The change of the measured pitch length in a wedge cell for 6.8 mol % of **1** in DON-103 upon exposure of UV light is shown in Figure 5(a). The sign (-) represents left-handed sense of the cholesteric LCs and via versa. The pitch length increased, reached an infinite value (a compensated nematic phase), reversed the handedness and then decreased. Here the energy profile may not be in agreement with that indicated in Figure 4 due to the different in thickness of the wedge cell and is used only as an indicator to show the proceeding *E*-to-*Z* isomerization. However, with prolonged exposure of light, the same photostationary state should be obtained. Figure 5(b) shows the plot for the concentration of dopant (*C*) versus induced reciprocal pitch length (1/*p*) at the photostationary states of UV and visible light, from which we determined the helical twisting power (*β*) of the dopants through,

$$1/p = \beta C \tag{1}$$

The helical twisting powers at initial and each photostationary state of lights are summarized in Table 1. Before subjection to light the induced cholesteric LCs possess right-handed senses. Exposure to visible light decreased slightly the β because of small production of the Z-isomers (*ca.* 12 %). However, using the UV light, a large change of the pitch leading to reversion from a right-handed to a left-handed cholesteric LC can be found for **1** and **2**.

TABLE 1 Helical twisting power (β) of azobenzene dopants in DON-103 at initial state (β_{ini}), photostationary states of visible (β_{vis}) and UV (β_{UV}) light. The signs (-) and (+) represent left- and right-handedness of the pitches.

Dopant	β_{ini}	β_{vis}	β_{UV}
1	+1.4	+1.1	-0.28
2	+0.66	+0.52	-0.25
3	+4.1	+4.0	+3.4

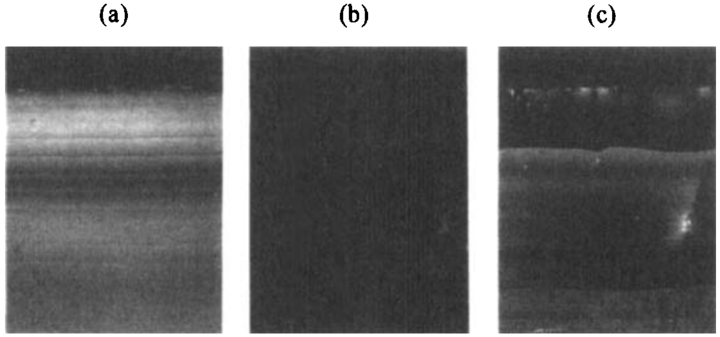

FIGURE 6 Grandjean-Cano lines of a wedge cell containing 8.5 mol % of **1** in DON-103 (a) before, (b) in the middle of and (c) at the photostationary state of UV light exposure. The photographs were taken under cross polarizers with the analyzer along the edge of the cell.
See Color Plate III at the back of this issue.

Figure 6 shows polarized photographs of the changes of the pitch and handedness of a 8.5 mol % of **1** in DON-103 filled in a wedge cell. The edge of the cell is located at the top of the photographs, along which the

Grandjean-Cano lines are (vertical lines in photograph (a)). Two consecutive lines represent one pitch. Notice that in the middle of UV light exposure (photograph (b)), the lines disappeared completely and the cell appeared dark due to the formation of a compensated nematic phase aligned homogeneously. Successive exposure of UV light toward the photostationary state again regenerated the lines (only two vertical lines in photograph (c)), corresponding to a much longer pitch with opposite handedness. In the case of **3**, only slight enlargement of the pitch was observed.

Since the photoisomerization features are similar for all the azobenzenes, the inversion seems to be dependent on the location of the chiral center with respect to the azo-core. It is to be noticed that the reversion of handedness of a cholesteric LC induced by a photosensitive dopant is usually the result of mixing two chiral dopants with opposite handedness so that the photochemical reaction of only one of the dopant can change the relative strength of their β [4, 5]. However, this in not the case here, because only a single chiral dopant was involved. Although a further study to elucidate the reversion mechanism is necessary, we assume that the *Z*-isomers of these 3,3'-disubstituted azobenzenes may have some different conformations [9] which should produce different molecular organizations with the LC molecules from that of the *E*-isomers. As a comparison, it should be mentioned that azobenzenes with *para*-substitutions were reported only to enlarge the pitch and some of *ortho*-substituted azobenzenes exhibited quite similar reversion of the handedness [10].

Additionally, these 3,3'-dialkoxyazobenzenes possess much longer *Z*-to-*E* thermal relaxation time when compared to those with *para*-substitutions and show excellent solubility in LCs compared to other azobenzenes. By utilizing this phenomenon, a photoswitching among three optical phases, right-handed cholesteric, nematic and left-handed cholesteric phases, can be realized since the photoisomerization process here is reversible with selective wavelength of the light.

CONCLUSION

Photochemical *E*-/*Z*-isomerization of chiral 3,3'-disubstituted azobenzenes results in photomodulation of macroscopic chirality of the

induced cholesteric phases. Selective modification of the chiral centers may results in creating phototriggers that display interesting photofunctionality, modulation of pitch length and reversion of the handedness. This characteristics may worth implementation to optical devices based on photoswitchable electro-optical properties.

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