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Light-induced structural changes in chiral liquid crystals

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Novel light-sensitive chiral dopants are studied as a light-sensitive component in chiral liquid crystals which may be used in tunable optical devices. Light-induced *cis–trans*- isomerization of chiral dopants results in changes of helical twisting power which translates into variations of helical pitch. Due to the light absorption in the liquid crystal cell the pitch variation is non-uniform across the cell, which leads, at first, to a deformation of cholesteric layers, and then to the formation of cholesteric bubbles. The sequence of structural changes has a distinct visual pattern and occurs at the surface close to the UV light source. Small deformations of cholesteric layers and bubbles are unstable and disappear after removing UV irradiation. The increasing size of the cholesteric bubbles results in better stability; large bubbles do not disappear after removing UV light. A theoretical model is suggested to describe the undulations of cholesteric layers.

1. Introduction

Chiral liquid crystals (CLCs) have attracted considerable recent attention as promising light switches, filters, and lasers [1–7]. CLCs are self-organized materials capable of forming planar helical structures when placed between glass plates coated with rubbed polyimide. Planar CLCs are one-dimensional, photonic band-gap structures for light with the same sense of polarization as a cholesteric helix. The pitch of the cholesteric helix is determined by chiral interactions between nematic molecules and chiral dopants. The selective reflection band (SRB) is centred at the wavelength $\lambda = nP$ while the width of the band is $\Delta\lambda = (\Delta n/n)\lambda$, where P is the pitch of the chiral liquid crystal [8], and $n = (n_e + n_o)/2$ is the average refractive index of the cholesteric planes which have a birefringence of $\Delta n = |n_o - n_e|$.

Optical properties of CLCs can be altered by dissolving optical switches (molecules changing their conformation under light irradiation) in cholesteric matrices. The most studied optical switches are azo compounds undergoing reversible *cis–trans*-isomerization under UV light irradiation. *Cis–trans*-isomerization alters both the shape and the effective polarity of the molecules. The rod like *trans*-isomers are transformed to bent-like *cis*-isomers during isomerization [4, 9]. The bulk properties of LCs and their alignment at the surface also change when isomerization of azo molecules occurs in the LC phase, owing to changes at the molecular level. The backward transition (from the *cis* to the *trans*) can be achieved by optical irradiation at a longer wavelength or by turning off the UV light. The rates of the forward (from the *trans* to the *cis*) and backward transformations depend on the material properties of the matrix, and are highest in matrices in which the viscosity is small.

The majority of azo-switches synthesized and studied to date are racemic compounds [10]. The isomerization of these molecules placed in a CLC matrix can only indirectly affect the pitch of CLCs by changing the order parameter and birefringence of the nematic layers. In this paper novel chiral azo compounds with chiral cholesterol groups attached to the azo fragment through a CONH bond are studied. The *trans*- and *cis*-isomers of these compounds must have different twisting powers in CLCs, but the magnitude of twisting power is relatively low. The helical structure of a CLC can be tightened by adding chiral dopants with higher twisting power non-sensitive to light irradiation. The isomerization of azo compounds will lead to changes in the concentration of *trans*- and *cis*-isomers and, therefore, to changes in the helical pitch P which can be determined from the equation:

$$p = \frac{1}{\beta_o c_o - \beta_{cis} c_{cis} - \beta_{trans} c_{trans}} \qquad (1)$$

where β_{cis}, c_{cis} and β_{trans}, c_{trans} are the helical twisting power (HTP) and the concentration of the *cis* and *trans* isomers, respectively. In this equation *cis*- and *trans*-isomers of azo compounds are assumed to produce a

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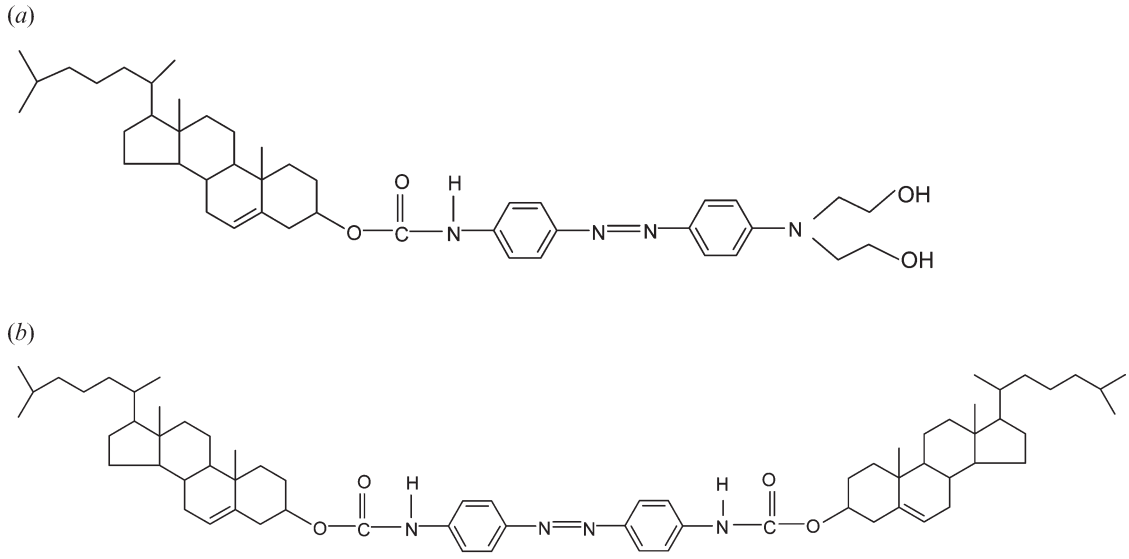

Figure 1. The chemical structure of a light sensitive compounds: (*a*) LSAZO1, (*b*) LSAZO2.

left-handed helix (negative HTP) and chiral dopants not sensitive to light produce right-handed helical structure (positive HTP).

2. Results and discussion

The CLC mixture contained three components: liquid crystal E63, liquid chiral dopant CB15 (both supplied by Merck), and light-sensitive chiral dopants LSAZO1 and LSAZO2 with the structures shown in figure 1. The synthesis of chiral dopants will be discussed in detail elsewhere. Owing to the presence of hydrogen-bonding CONH groups, the chiral dopants have relatively high melting temperatures (above 155°C) and a twisting power of about 1–3 μm^{-1}. This twisting power produces a left-handed helical pitch of about 20 µm at a concentration of about 4%. However, chiral dopants are difficult to dissolve in E63. The tighter pitch requires a higher concentration of chiral dopants. This significantly changes the thermodynamic properties of the liquid crystals and depresses the mesophase. In order to avoid using high concentrations of the chiral dopants, a third component, chiral dopant CB15, was added at a concentration of *c*. 40%, to yield a tighter right-handed pitch (*c*. 600 nm) without causing an appreciable change in the thermodynamic properties of the liquid crystalline mixture.

Low power UV irradiation of thin cells leads to a shift of the SRB. It requires about 15 min to shift the SRB from 800 to 740 nm. The helical pitch decreases because *cis*-isomers have low twisting power and therefore the influence of right-winding dopant CB15 increases. The morphology of the cell does not change. Removing UV irradiation results in a backward red shift of the SRB.

In thicker cells filled with the same CLC the increased dose of UV irradiation results in the formation of a 'crocodile skin' structure (figure 2) similar to the Helfrich distortions [11] observed in planar CLCs under an electric field. In contrast to Helfrich distortions of planar structure the 'crocodile skin' structure appears at the surface of the CLC close to the UV source. This becomes evident from microscopic observations of the CLC structure at different cross-sections of the sample.

The formation of the skin-like structure can be explained as follows. The intensity of the UV light irradiating the sample from the top, and inducing pitch

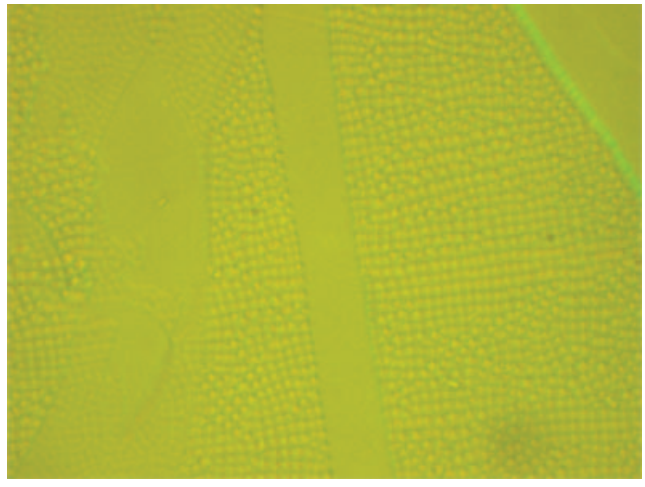

Figure 2. UV-induced structural changes, 'crocodile skin' structure..

variations across the cell, changes with the distance from the upper glass in accordance with the equation

$$I(z) = I_o \exp(-z/l) \tag{2}$$

where $l = 1/c\varepsilon$; c is the concentration of the absorbing compound, and ε is the extinction coefficient of the chiral dopants.

Taking into account a high absorption inside the cell, the length l was estimated to be *c*. 6–8 μm. Immediately after turning on the UV light the twisting power of the chiral dopants is subject to irradiation-induced changes. At the beginning of the irradiation the *cis*-isomers are localized within a distance l from the irradiated surface. If the thickness of the cell is comparable to l, then the helical pitch changes uniformly across the sample. If the thickness of the cell is greater than l, a helical pitch gradient is developed across the cell. This results in a considerable distortion of cholesteric planes, predominantly those lying within l. The most energetically favourable deformation is the periodic change of the planarity of cholesteric layers (figure 3) and formation of undulations of cholesteric planes. Removing the UV light leads to a fast restoration of planarity of the CLCs due to the fast backward transformation of *cis*-isomers into *trans*-isomers.

Let us now prove that in-plane undulations of a cholesteric structure caused by non-uniform distribution of *cis*-isomers across the cell minimize the free energy of the system and lead to the appearance of a visible pattern with a period λ. The free energy density of the cell can be written as follows:

$$F(r) = \frac{1}{2}B\left[\frac{P(r)-P_o}{P_o}\right]^2 + \frac{1}{2}K\,\mathrm{grad}[\mathbf{d}(r)]^2 + [\chi_{cis}\Delta c_{cis}(r) + \chi_{trans}\Delta c_{trans}(r)](1 - c_{cis} - c_{trans}) \tag{3}$$

where P_o is an initial pitch before UV irradiation, $P(r)$ is a pitch caused by irradiation, $\mathbf{d}$ is a vector normal to the cholesteric planes, $B = K_{22}q^2$, $K = \frac{3}{8}K_{33}$; χ_{cis} and χ_{trans} are parameters describing the chiral interaction of azo dopants with the matrix. Equation (3) differs from the commonly used free energy expression by a last term describing chiral interactions with a nematic matrix. It is this term that relates to the undulations of cholesteric planes. Since the concentrations of azo dopants do not exceed 5%, equation (3) can be re-written:

$$F(r) = \frac{1}{2}B \times \left[\frac{P(r)-P_o}{P_o}\right]^2 + \frac{1}{2}K\,\mathrm{grad}[\mathbf{d}(r)]^2 + \chi_{cis}\Delta c_{cis}(r) + \chi_{trans}\Delta c_{trans}(r). \tag{4}$$

If deformations of cholesteric planes $[u(x, y, z)]$ are taken into account up to a second order [12], pitch $P(r)$ is related to these deformations through the equation

$$\frac{P(r)-P_o}{P_o} = \frac{\partial u(x,y,z)}{\partial z} - \frac{1}{2}\left\{\left[\frac{\partial u(x,y,z)}{\partial x}\right]^2 + \left[\frac{\partial u(x,y,z)}{\partial x}\right]^2\right\}. \tag{5}$$

If we take into account that the concentration of chiral dopants is related to helical pitch through equation (1), then equation (4) can be transformed into

$$F(r) = \frac{1}{2}K_{22}q^2 \times \left[\frac{\partial u(x,y,z)}{\partial z} - \frac{1}{2}\left\{\left[\frac{\partial u(x,y,z)}{\partial x}\right]^2 + \left[\frac{\partial u(x,y,z)}{\partial x}\right]^2\right\}\right]^2 + \frac{3}{16}K_{33}\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right)^2 + \frac{\chi_{cis}-\chi_{trans}}{\beta_{cis}-\beta_{trans}}\frac{q}{2\pi}\left[\frac{\partial u(x,y,z)}{\partial z}\right] - \frac{1}{2}\left\{\left[\frac{\partial u(x,y,z)}{\partial x}\right]^2 + \left[\frac{\partial u(x,y,z)}{\partial y}\right]^2\right\}. \tag{6}$$

If we further assume that helical pitch is modulated in the plane of the sample with a period λ, i.e.

$$u = u_0 \exp(-z\alpha)\cos\left(2\pi\frac{x}{\lambda}\right) \tag{7}$$

then after integration over x and z, and neglecting third and higher order terms, we get, for the free energy change F of the sample:

$$F = \frac{1}{2}\left(A\lambda - \frac{B}{\lambda} + \frac{C}{\lambda^3}\right)u_0^2[1-\exp(-\alpha L)]\Big/\alpha \tag{8}$$

where L is the sample thickness, $A = \dfrac{K_{22}q^2\alpha^2}{4}$, $B = \dfrac{\chi_{cis}-\chi_{trans}}{\beta_{cis}-\beta_{trans}}q$, $C = \dfrac{3}{2}K_{33}\pi^4$.

A period of modulation can be found by minimizing equation (8) over λ, producing a biquadratic equation

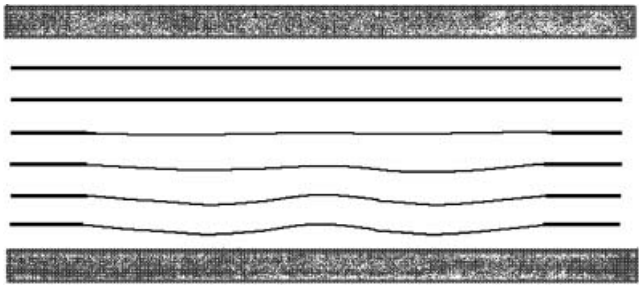

Figure 3. Undulations of cholesteric planes.

for λ:

$$A\lambda^4 + B\lambda^2 - 3C = 0. \quad (9)$$

The only positive root of this equation should be chosen as

$$\lambda = \left[\frac{(B^2 + 12AC)^{\frac{1}{2}}}{2A} - \frac{B}{2A}\right]^{\frac{1}{2}}. \quad (10)$$

If chiral interactions between matrix and chiral dopants do not change, equation (10) will reduce to

$$\lambda = \left(\frac{3C}{A}\right)^{\frac{1}{4}}. \quad (11)$$

Equation (11) is reminiscent of the Helfrich solution for distortions of cholesteric planes under an electric field [11]. However, the physical meaning of the general equation (10) is different from Helfrich's solution. Figure 4 shows the dependence of free energy on changes of chiral interactions of chiral dopants with the matrix, described by parameter B. All calculations were performed for the following set of CLC constants $K_{22}=0.3\times10^{-11}$ N, $K_{33}=10^{-11}$ N, $q=7\times10^{6}\,\mathrm{m}^{-1}$, $\alpha=q/20$. The strength of the interaction is proportional to $\frac{\chi_{trans}-\chi_{cis}}{\beta_{trans}-\beta_{cis}}q$. If $B=0$, the free energy change is not negative and, therefore, no changes in planar cholesteric structure should occur. Parameters χ and β are not independent. Increasing interaction of chiral dopant with a nematic matrix described by χ should probably result in a higher twisting power characterized by β. *trans*-Isomers interact more strongly with a nematic matrix and have a higher twisting power than *cis*-isomers. Increasing B leads to decreasing free energy and engenders modulations of the cholesteric planes.

An increase in the time of UV irradiation results in a higher concentration of *cis*-isomers near the surface, their diffusion deeper into the cell, and a propagation of the diffusion front away from the illuminated surface. Indeed, the rate of conversion of *trans*- into *cis*-isomers is much higher than the diffusion of *cis*-isomers away from the irradiated area. This stage is characterized by a transition from a 'crocodile skin' pattern to the nucleation and growth of cholesteric bubbles, which appeare on the surface closer to the UV source (figure 5). The morphological changes are totally reversible when the size of the bubbles is much smaller than the interdomain distance. Cholesteric bubbles gradually disappear after UV irradiation; most disappearing within three minutes after the UV irradiation is turned off. Bubbles are completely absent after 15–20 minutes. The proposed structure of an individual bubble is shown in figure 6. Cholesteric planes are significantly deformed, and when the deformation reaches a certain level, actual disclinations are formed. With a further increase of UV intensity the cholesteric bubbles coalesce and form stable structures including oil-streak defects. There are no visible changes of these structures for several days. Interestingly, somewhat similar domains with less visible internal structure were observed under laser-induced isomerization of non-chiral azo dopants [13]. A theoretical description of the bubbles can be developed in terms of the model for cholesteric walls suggested, for example, in [14], and is currently being developed.

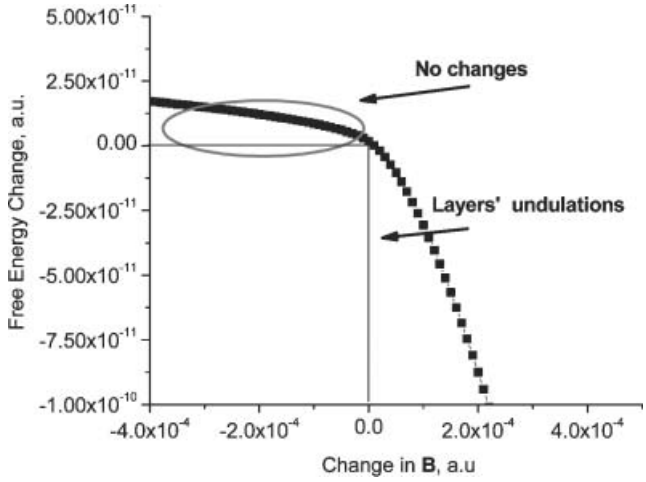

Figure 4. Free energy change of a CLC sample as a function of chiral interactions.

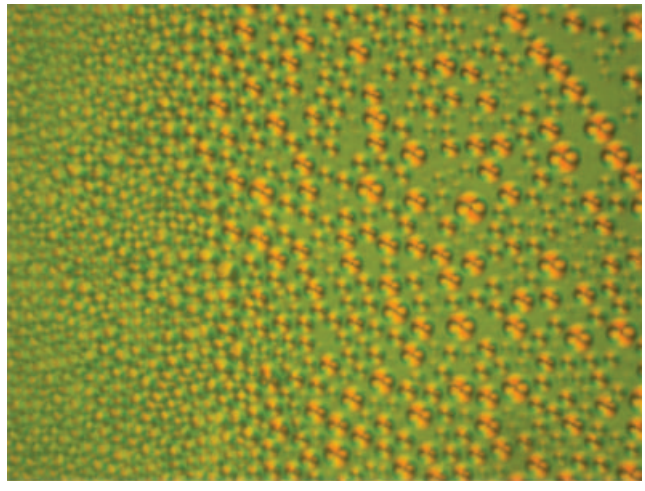

Figure 5. Transformation of 'crocodile skin' structure into cholesteric bubbles.

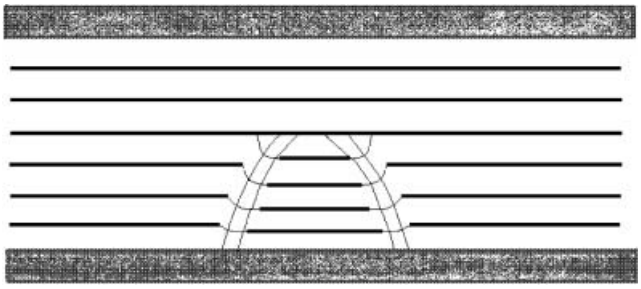

Figure 6. Proposed structure of a cholesteric bubble.

3. Conclusions

Reversible tuning of the selective reflection band in CLCs doped with chiral azo dyes is observed over a wide spectral range under mild UV irradiation. A sequence of structural changes occurs with the increasing dose of UV irradiation. At low UV doses distortions of the cholesteric planes are fully reversible. At higher levels of UV irradiation small cholesteric bubbles grow and form stable structures persisting inside the cells for a long time after the UV light is removed, despite the reversibility of the *trans-cis* isomerization. A model describing distortions of the cholesteric planes in terms of CLC elastic constants, helical twisting powers and chiral interactions of *cis*- and *trans*-isomers with the matrix is developed. This model can be directly applied to reversible undulations, but cannot be used to describe the growth of cholesteric bubbles containing defects. The energy of singularities of the chiral nematic should be taken into account in describing the latter. This study is underway and will be presented in a separate publication.

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