



ELECTRIC FIELD EFFECT ON OPTICAL DICHROISM OF SOME AZODYES DISSOLVED IN COMPENSATED CHOLESTERIC LIQUID CRYSTAL

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abstract: In the paper are presented the results obtained in the study of the optical dichroism of some azodyes dissolved in a compensated mixture of cholesteryl chloride and cholesteryl-nonanoate under the electric field action. The electric field dependence of the order parameter S of the dyes is presented and discussed.

key words: liquid crystal; linear dichroism; order parameter

received: May 14, 2009

accepted: May 21, 2009

Introduction

The action of the electric field on the compensated mixtures of cholesteric compounds produces a change of molecular arrangement, known as cholesteric-nematic transition [1,2]. This transition appears in the cholesteric liquid crystals having a positive anisotropy of the dielectric constant. Studies on the optical transmission [3] of some cholesterics standing under the action of an electric field have also emphasized an hysteresis of the transmission, as well as the existence of the bistable behaviour of the cholesteric liquid crystals and their mixtures. Such behaviour must be connected with the orientational ordering of the molecules with respect to the applied electric field.

In this work are presented the results of the study on the optical absorption of some azo dyes, dissolved in a compensated cholesteric mixture, during the cholesteric-nematic transition. The dye and cholesteric liquid crystal molecules are together subjected to the electric field action which produces a collective movement that leads to the changes of molecular arrangement with respect to applied electric field direction. Firstly, the helical molecular arrangement axis is oriented perpendicular to the electric field direction and then produces an increase of the helical structure pitch [4,5]. Field values, greater than a critical value, E_c , of the electric field, produce a total unwinding of the helix and a homeotropic structure occurs. During the motion of the dye molecules, the probability of the optical

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transition, depending on the scalar product $|\mathbf{ME}|$ between the transition moment \mathbf{M} and the electric field \mathbf{E} of the electromagnetic wave, changes. In these conditions it is useful to estimate the dichroism of the optical absorption of the dyes, which gives us information about changes in molecular arrangement by measuring of the order parameter S of the dyes molecules.

The studies were carried out on the compensated mixture of cholesteryl chloride (CC) and cholesteryl nonanoate (CN), doped with azobenzene and other azodyes, derived from cumylphenol. The (CC/CN) mixture is transparent and the azodyes present two absorption bands ($\pi-\pi^*$ and $n-\pi^*$ respectively) in the visible range of spectrum, used in this experiment.

Experimental

The molecular structure of the dyes used in this work are presented in Fig. 1. The substituent Y is CH_3 in meta position ($m\text{-CH}_3$) for dye I, in para position ($p\text{-CH}_3$) for dye II, and OCH_3 for dye III ($m\text{-OCH}_3$), and dye IV ($p\text{-OCH}_3$). The dyes having a concentrations between 0.8% and 1% have been dissolved in the compensated cholesteric mixture of CC/CN, in proportion of 1.9/1 by wt. to assure the cholesteric-nematic transition at the room temperature (30°C). The (CC/CN-dye) mixtures have been encapsulated in the cells with plan parallel plates having a conductive layer deposited on them in order to apply the electric field. The thickness of the cells ($12\mu\text{m}$) and the dyes concentrations were chosen as they assure a good absorption signal. The transition cholesteric-nematic of the mixtures were controlled first with polarizing microscope. All the measurements were made at 30°C . The optical absorption was registered with an UV VIS Zeiss-Jena Spectrophotometer, in unpolarised light. The experimental set-up assures the propagation of the light by the cell (sample) perpendicular to the cell plates and along to the direction of the applied electric field.

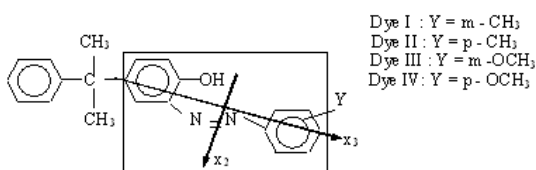


Fig. 1 The molecular structure of the dyes; x_2 and x_3 are molecular short and long axis.

Results and discussions

In Fig. 2 are presented the spectra of the (CC/CN-dyeII) mixture registered at constant temperature (30°C) for different values of the electric tension applied to the cell. The increasing of the electrical tension on the cell produces a decreasing of the optical absorption. For $U \geq 120\text{V}$ the optical absorption remains unmodified. Also, the action of the

electrical field on the mixture doesn't produce the bands displacement or deformations. This situation is similar for all studied mixtures.

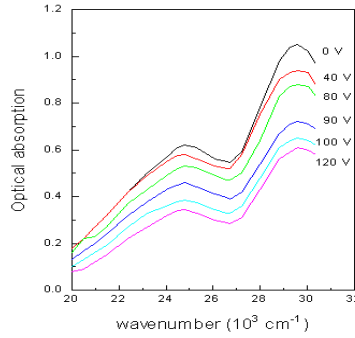


Fig. 2 Spectra of the (CC/CN - dyeII) mixture registered for different values of the electric tension.

The liquid-crystalline state is a partially ordered state. An uniaxially oriented state is characterised by the order parameters S and D [6÷8]. If (X_i) is the liquid crystal cell fixed co-ordinate system and (x_i) the molecule-fixed system, then $S=(1/2)\langle 3\cos^2\theta-1\rangle$, where θ is the angle between x_3 and X_3 , characterises the orientational ordering of the long molecular axis x_3 with respect to the X_3 axis of the liquid crystal matrix, and D is a measure for the deviation from a rotationally symmetric distribution of the molecules about this axis.

In our experiment we consider the direction of the electric field as X_3 . The light through the cell is propagating in the X_3 direction of the applied electric field. The cholesteric matrix is considered as being rotationally symmetric around the applied electric field direction. In this case the measurement can be performed in unpolarised light, because the absorption of the light polarized in X_1 or X_2 direction is the same ($A_1=A_2$). In these conditions, for an absorption band, the anisotropy $R(\nu)$ of the absorption can be valued by:

$$R(\nu)=1-\frac{A_2}{A_{iso}} \quad (1)$$

where A_{iso} is the absorption in the isotropic state.

Theoretically, taking account of the order parameters S and D , the dichroism $R(\nu)$ can be expressed as [6]:

$$R(\nu) = A(\nu)S + B(\nu)D \quad (2)$$

where $A(\nu)$ and $B(\nu)$ depend on the transition moment components M_i of the considered band and are given by:

$$A(\nu) = \frac{1}{2}(3q_{33} - 1) \quad (3)$$

$$B(\nu) = \frac{\sqrt{3}}{2}(q_{22} - q_{11}) \quad (4)$$

where $q_{ii} = M_i^2 / M^2$ and $M^2 = \sum M_i^2$.

The spectroscopic coefficients $A(\nu)$ and $B(\nu)$ in (2) depend on the polarisation of the investigated absorption band and are temperature independents. The order parameters S and D depend on external factors (electric field, temperature).

Fig. 3 presents the ratio A_2/A_{iso} of the optical absorptions of the dyes, as function of the applied electric tension on the cell. The A_2 and A_{iso} are values corresponding to the maximum of the π - π^* band of each dye. During the cholesteric-nematic transition can be observed a significant decrease of A_2/A_{iso} for all dyes.

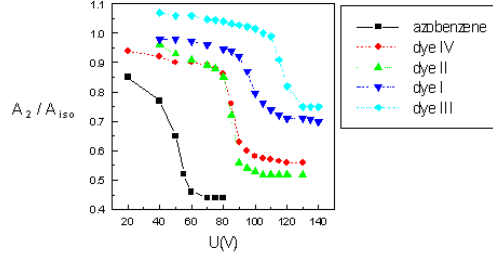


Fig. 3 A_2/A_{iso} as function of the applied electric tension on the cell.

This result may be explained by the fact that in condition of homeotropic alignment, resulting as a consequence of the cholesteric-nematic transition, the x_3 axis of the dyes molecules tends to be orientated preferentially along the X_3 axis of the liquid crystal matrix. In this case, if the transition moment \mathbf{M} is oriented along the x_3 molecular axis, the probability of the optical transition, depending on the scalar product $[\mathbf{M}\mathbf{E}_2]$ between the transition moment \mathbf{M} and the electric field component \mathbf{E}_2 of the electromagnetic wave, must decrease during the cholesteric-nematic transition which would produce the decrease of the optical absorption A_2 . The decrease of A_2/A_{iso} shown in Fig. 3 suggests this fact, i.e. the transition moment \mathbf{M} is aligned in the direction of the long molecular axis x_3 . These experimental results are in good agreement with the theoretical values of the transition moment components M_i ($i=1,2,3$), corresponding to the π - π^* band of each dye, determined by MO calculations performed in the frame of the SCF-PPP-CI method [9].

According to the theoretical results, the transition moment components are in relation $M_3 \gg M_2$ and $M_1 = 0$. As consequence, the values of the spectroscopic coefficients $A(\nu)$ and $B(\nu)$ will be $A(\nu) \gg B(\nu)$, and the relation (2) becomes:

$$R(\nu) = A(\nu)S \quad (5)$$

By measurement of $R(\nu)$ and calculation of $A(\nu)$, using data from [9], we have determined the order parameters S .

The dependencies of the dyes order parameters S as function of the electric tension applied to the cell are presented in Fig. 4. It can be observed three regions in these graphs. In the first region, corresponding to the small values of the electric tension, order parameters have small values. This reveals a weak response to electric field action. In the second region, for the tensions higher than a threshold value U_{th} , the S parameters have a significant increase, which corresponds to the cholesteric-nematic transition. In the third region the order parameters have a slower increase and they tend to a saturation value S_{max} .

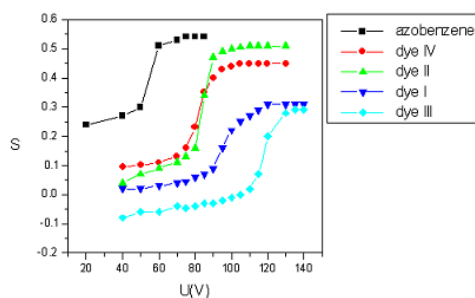


Fig. 4 The orientational order parameters of the dyes as function of the electric tension.

The evolution of the dyes order parameters depend on the dyes structure. The order parameters of the dyes I-IV are lower in comparison with azobenzene, due to the bulky substituent $C_6H_5-C(CH_3)_2$ meta substituted versus azo group. Also, taking account of the second substituent ($Y=CH_3, OCH_3$) it can be observed that the meta substitution (dye I and III) determines a lower S parameter in relation to the para substitution (dye II and IV). The values of S_{max} show a better final orientation of the parasubstituted dyes in comparison with the metasubstituted dyes. All these point out a difficulty in the molecular orientation of the metasubstituted dyes.

Conclusions

The electric field produces significant changes of the optical absorption of the dyes dissolved in the compensated cholesteric mixture. This is due to the changes of molecular arrangement under the electric field action. By evaluating the optical dichroism of the dyes in these conditions, we determined the order parameters of the dyes which give a measure of the electric field effect on the cholesteric-dye mixture.

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