# DYNAMICS OF ORIENTATIONAL ORDERING IN A CHOLESTERIC LIQUID CRYSTAL MATRIX UNDER THE ACTION OF THE ELECTRICAL FIELD

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*The paper presents a study on the dynamics of molecular ordering in d.c. electrical field of a compensated cholesteric mixture of cholesteryl chloride - cholesteryl nonanoate CC/CN (1.9/1) wt. with the azodye, tetrazo-2,3'-dimethyl benzene β naphtol, used as optical marker. The order parameters of the dye were determined by measurements of the optical absorption anisotropy. The transition moment tensor components for the π-π\* transition of the azodye were determined by MO calculations in the frame of SCF-PPP method and those of the n-π\* transition by comparing the temperature dependence of the degrees of the optical absorption anisotropy of the π-π\* and n-π\* bands.*

## 1. Introduction

The measurement of the degree of optical absorption anisotropy of some molecules, dissolved in a liquid crystal, allows the determination of the order parameters in the liquid crystalline state [1-7]. The degree of the optical absorption anisotropy depends on two types of parameters: the molecular spectroscopic parameters, which depend on the polarization of the investigated bands and the parameters $S$ and $D$ of the orientational ordering of the molecules in the liquid crystal matrix, which are independent of the absorption band but are strongly dependent on the external fields.

To determine the order parameters are necessary enough absorption bands of different polarization and must be known the components of the transition moment tensor of these bands with respect to a $(x_i)$ molecule-fixed system. The components of the transition moment tensor can be determined using the method developed by Thulstrup, Eggers and Michl [8] in order to decompose the spectra into components of different polarizations, or the method used by Kuball et al. [2-6] for the determination of the $S$ and $D$ from the temperature dependence of the degree of the optical absorption anisotropy. In the former papers [9-11] we have used an other method, namely, the molecular orbitals (MO) calculation in the frame of SCF-PPP procedure. Knowing the spectroscopic parameters, the order parameters as well as their dynamics in different external conditions can be determined.

In this paper we present the dynamics of molecular ordering in d.c. electrical field of a compensated cholesteric mixture of cholesteryl chloride - cholesteryl nonanoate CC/CN (1.9/1) wt. As the mixture of cholesteryl chloride - cholesteryl nonanoate is transparent in the visible region of the spectrum, an azodye (tetrazo-2,3'-dimethyl benzene β naphtol) was used as optical marker. The ordering of the dye molecules was determined starting from the measurements of the degree of the optical absorption anisotropy (linear dichroism) of their π-π\* and n-π\* bands. The transition moment tensor components of the π-π\* band of the azodye were determined by MO calculations and those of the n-π\* band by the method proposed in [2]. From measurements of linear dichroism in the presence

of the electrical field the dependence of the order parameters $S_{ii33}$ on the electrical field was determined.

## 2. Theoretical background

A description of the orientational ordering in a liquid crystalline phase can be obtained by determining the order parameters of the molecules with respect to a chosen axis. Let be $X_i$ ($i = 1,2,3$) a space-fixed co-ordinate system and ($x_i$) the molecule-fixed co-ordinate system. The orientation of the molecular axis $x_i$ with respect to $X_i$ axis is characterized by the orientational distribution coefficients $g_{ijkl}$, in [2] as:

$$g_{ijkl} = \frac{1}{8\pi^2} \int f(\Omega) a_{ik} a_{jl} d\Omega \tag{1}$$

where $f(\Omega)$ is the distribution function of the molecules, $\Omega$ comprises the Eulerian angles $\theta, \varphi, \phi$ between the space-fixed $X_i$ co-ordinate system and the molecule-fixed $x_i$ co-ordinate system, and $a_{ik}$ are the elements of the orthogonal transformation matrix from the $X_i$ to the $x_i$ co-ordinate system. In a cholesteric phase the order can be also defined locally by using a local space-fixed co-ordinate system $(X_i')$ connected to the periodicity of the cholesteric phase [12]. For the moment, we take into account only the orientation of the molecules with respect to the $X_3$ axis, by considering a rotationally symmetric distribution around $X_3$ so that $g_{ii33} = <cos^2 \theta_{i3}>$. In this work, $X_3$ is the axis perpendicular to the cell electrodes (and in the same time the direction of the electric field in the electrical measurements) and $X_1$, $X_2$ are the axes in plane of the cell.

The order parameters which describe the orientational order of the $x_i$ axes of the biaxial molecules with respect to $X_3$ are:

$$S_{ii33} = \frac{1}{2}(3g_{ii33} - 1) \qquad i = 1,2,3 \tag{2}$$

$$D = \frac{\sqrt{3}}{2}(2g_{2233} + g_{3333} - 1) \tag{3}$$

For an uniaxial matrix the parameter $D$ is determined by the biaxiality of the molecule i.e. $D = 0$ if the molecular axes $x_1$ and $x_2$ are distributed in a rotationally symmetric way around molecular $x_3$ axis (orientation axis).

The order parameters can be determined experimentally by measuring the degree of the optical absorption anisotropy. In our experiment, the direction of the incident light on the cell is $X_3$. In this case, the degree of the optical absorption anisotropy can be estimated as:

$$R(\nu) = 1 - \frac{A(\nu)}{A_{is}(\nu)} \tag{4}$$

where $A_{is}(\nu)$ is the absorption in the isotropic phase and $A(\nu)$ the absorption in mesophase, measured in linearly polarized light, perpendicularly to $X_3$. If we consider a rotational symmetric distribution of the molecules around $X_3$, the optical absorptions can be determined in unpolarized light.

The degree of the optical absorption anisotropy can be expressed, on the other hand, by [2]:

$$R(\nu,T) = a(\nu)S(T) + b(\nu)D(T) \tag{5}$$

where $a(\nu)$ and $b(\nu)$ are spectroscopic coefficients, depending on the band investigated, expressed by:

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

$$b(\nu) = \frac{\sqrt{3}}{2}(q_{22}(\nu) - q_{11}(\nu)) \tag{6}$$

where:

$$q_{ii} = \frac{\varepsilon_{ii}}{\sum_{j=1}^{3} \varepsilon_{jj}} \qquad (7)$$

$\varepsilon_{ii}$ are the components of the absorption tensor of the investigated band and are proportional to the squares $<M_i>^2$ of the electric dipole transition moment components with respect to the co-ordinate axis $x_i$ /13,14/, $S = S_{3333}$ and $D$ are the order parameters expressed by relations (2)-(3).

The spectroscopic coefficients $a(\nu)$ and $b(\nu)$ depend only on the polarisation of the investigated absorption band, characterised by $q_{ii}(\nu)$, and not depend on the temperature.

The orientational distribution coefficients $g_{ijkl}$, connect the molecular properties of molecules in an anisotropic distribution with measurable properties of the anisotropic sample which are described by a second rank tensor [2,4]. $g_{ijkl}$ and $q_{ii}$ depend on the choice of the co-ordinate system and in order to get the order parameters which characterize the orientation of the $x_i$ molecular axes, $q_{ii}$ must be expressed with respect to the molecule-fixed co-ordinate system $(x_i)$.

In order to determine the order parameters $S_{3333}$ and D from the linear dichroism measurements, two absorption bands are necessary for which the components $M_i$ of the transition moments with respect to the molecular axes $x_i$ must be different and known.

## 3. Experimental

The tetrazo-2,3'-dimethyl benzene $\beta$ naphtol dye (in concentration of 1%) has been dissolved in the compensated cholesteric mixture of cholesteryl chloride - cholesteryl nonanoate CC/CN (1.9-1 by wt. and $\Delta\varepsilon > 0$). The substances were synthesized in the Faculty of chemistry, University of Bucharest (Romania). The (CC/CN-dye) mixture has been encapsulated in a cell with plan parallel plates having a conductive layer ($In_2O_3$) deposited on them. The thickness of the cell (12 μm) and the dye concentration were chosen so as they ensure a good absorption signal. The heating of the sample was ensured by an oven, with a rate of about 1 °C/min. The phase transformations and texture of the sample were controlled with a polarizing microscope. The temperature was measured with a digital thermometer type TD 1300 with an accuracy of 0.1 °C. The temperature of the isotrop-cholesteric phase transition is $T_{ICh} = 50$ °C. The mixture remains in the cholesteric mesophase at the room temperature, presenting a dark conic focal texture. The phase transitions have been also investigated by measuring the optical absorption as function of temperature. The optical absorption was registered with an UV VIS Zeiss-Jena Spectrophotometer, in unpolarized light.

For the electrical measurements, the experimental set-up assured the propagation of the light along the direction of the applied on the cell d.c. electrical field. The electric tension applied on the cell had the values between 0 and 60 V, which correspond to the electrical fields of $(0\div5)\times10^6$ V/m and the measurements were made at room temperature (21 °C). The cholesteric-nematic transition in electrical field has been investigated with a polarizing microscope as well as by determining the saturation value of the optical absorption for each value of the applied electrical field.

## 4. Results and discussion

### 4.1. Spectroscopic properties

The tetrazo-2,3'-dimethyl benzene $\beta$ naphtol dye with the molecular structure presented in Fig. 1 shows, in the visible range of the spectrum, a $\pi$-$\pi^*$ band centred on the wavenumber $\nu_a = 23.68\times10^3 cm^{-1}$ and a n-$\pi^*$ band characterised by two maxima at $\nu_b = 16.4\times10^3$ $cm^{-1}$ and $\nu_c = 15.2\times10^3$ $cm^{-1}$ respectively.

The polarisation of the $\pi$-$\pi^*$ band has been determined by MO-SCF-PPP calculations and that of the n-$\pi^*$ band by comparing the linear dichroism of the $(\nu_a)$ and $(\nu_c)$ bands.
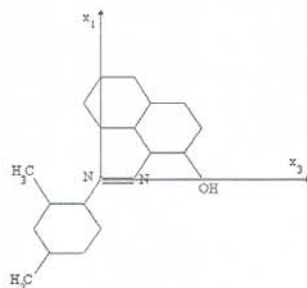
Fig. 1 The molecular structure of the azodye tetrazo-2,3'-dimethyl
benzene $\beta$ naphtol and molecule-fixed coordinate system $(x_i)$.

Fig. 2(a) presents the temperature dependence of the optical absorptions $A(v_a, T)$ and $A(v_c, T)$ of the dye dissolved in cholesteric mixture of CC/CN, recorded at the fixed wavenumbers $v_a$ and $v_c$. The measurements were made in the range 55 °C - 29 °C, i.e. in the isotropic phase and cholesteric mesophase. The optical absorptions $A(v_a, T)$ and $A(v_c, T)$ have a significant dependence on temperature. At the isotrop-cholesteric transition temperature $T_{ICh} = 50$ °C, $A(v_a, T)$ and $A(v_c, T)$ they present an increase with respect to their values in the isotropic phase which suggests the fact that the cholesteric state has a structural anisotropy in comparison with the isotropic phase. In the cholesteric state the increase of the $A(v_a, T)$ and $A(v_c, T)$ is less important.

Fig. 2(b) presents the temperature dependence of the experimental values $R(v_a, T)$ and $R(v_c, T)$, determined with (4) by using the values of optical absorptions from Fig. 2(a) and $A_{is}(v_a) = 0.91$, $A_{is}(v_c) = 0.38$. It can be observed that the linear dichroism of the two bands passes at the temperature $T_{ICh}$ from null values, in the isotropic phase, to negative values, in the cholesteric phase. Because the $\pi$- $\pi^*$ transition of the dye is polarized in the molecular plane (as it pointed by the MO-SCF-PPP calculations), the negative values of $R(v_a, T)$ and $R(v_c, T)$ suggest the fact that the molecules of the dye in CC/CN matrix have the tendency to orientate their $x_3$ axis not in the $X_3$ direction but especially perpendicularly to $X_3$.
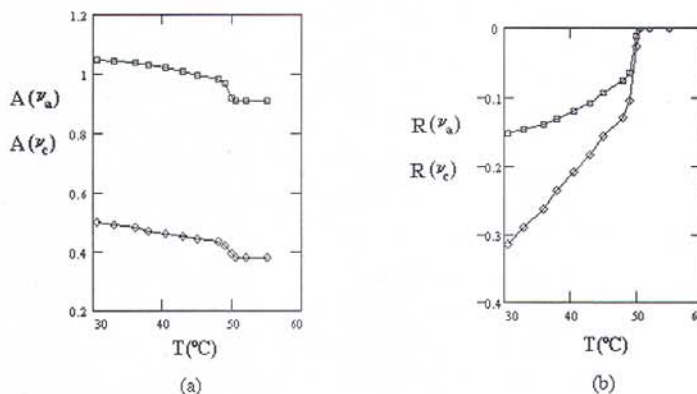


(a)                                      (b)

Fig. 2 The temperature dependence: (a) of the optical absorptions $A(v_a)$ ( —□— ) and $A(v_c)$
( —◇— ) and (b) of the degrees of the optical absorption anisotropy $R(v_a)$ ( —□— )
and $R(v_c)$ ( —◇— ), of the azodye tetrazo-2,3'-dimetil benzene $\beta$ naphtol,
dissolved in CC/CN, measured at $v_a = 23.68 \times 10^3 cm^{-1}$ and $v_c = 15.2 \times 10^3$ $cm^{-1}$, respectively.

The values of the components $M_i$ of the dipole transition moment for the $\pi$-$\pi^*$ transition have been determined by molecular orbitals (MO) calculations in the frame of SCF-PPP method by using the procedure from [15]. The MO calculations have been made in the molecular system $(x_i)$

presented in Fig. 1, where $(x_1, x_3)$ is the molecular plane, $x_3$ axis has the -N=N- direction and $x_2$ is axis out of plane. The calculated components of the dipole transition moment of the $\pi$-$\pi^*$ transition are $M_1 = -1.53$, $M_2 = 0$, $M_3 = -1.35$ and $M = (\Sigma M_i^2)^{1/2} = 2.04$. The value $M_2 = 0$ indicates that the $\pi$-$\pi^*$ transition is polarized in the molecular plane. In this way, the values of $q_{ii}(\nu_a) = (M_1/M)^2$ as well as $a(\nu_a)$ and $b(\nu_a)$ have been determined and are presented in table 1.

Table 1

The polarizations of the absorption bands ($q_{ii}$) and the spectroscopic coefficients (a,b) for the bands $\nu_a$, $\nu_c$

| Absorption band | $q_{11}$ | $q_{22}$ | $q_{33}$ | a | b |
|---|---|---|---|---|---|
| $(\nu_a)$ | 0.563 | 0 | 0.439 | 0.157 | -0.487 |
| $(\nu_c)$ | 0.820 | 0 | 0.180 | -0.230 | -0.710 |

The values of $q_{ii}(\nu_c)$ have been obtained by comparing the $R(\nu_a,T)$ and $R(\nu_c,T)$ values, using the procedure proposed in [2].

Taking account of the relations (5)-(6), and considering the transitions polarized in the $(x_1,x_3)$ molecular plane, the degree of the optical anisotropy of the two investigated bands can be expressed as :

$$R(\nu_a,T) = (1/2)[3q_{33}(\nu_a)-1] S(T) - (\sqrt{3}/2)[1- q_{33}(\nu_a)] D(T) \qquad (8)$$

$$R(\nu_c,T) = (1/2)[3q_{33}(\nu_c)-1] S(T) - (\sqrt{3}/2)[1- q_{33}(\nu_c)] D(T) \qquad (9)$$

In order to determine the value of $q_{33}(\nu_c)$, the experimental dependence $R(\nu_a,T) = \Phi(R(\nu_c,T))$ is required. The experimental values $R(\nu_a,T)$, $R(\nu_c,T)$ obtained at the same temperature, represent a point in a $[R(\nu_a,T), R(\nu_c,T)]$ plane. This experimental dependence is presented, by squares, in the Fig. 3.

The experimental dependence was fitted with a theoretical one, by using the expressions (8)-(9) for $R(\nu_a,T)$ and $R(\nu_c,T)$ and assuming a relation between $S$ and $D$. Because $D = 0$, if $S = 0$ and $S = 1$, we have proposed for $D$ a dependence of the type:

$$D(S) = (\sqrt{3}/2)(1-S)S^\gamma m \qquad (10)$$

where $\gamma$ and m are parameters which determine the form of theoretical dependence. We have found that the best form corresponds to $\gamma = 1/2$. The experimental dependence was fitted by calculating $R(\nu_a,T)$ and $R(\nu_c,T)$, given by the relations (8)-(9), with varying the parameters $q_{33}(\nu_c)$ and m.
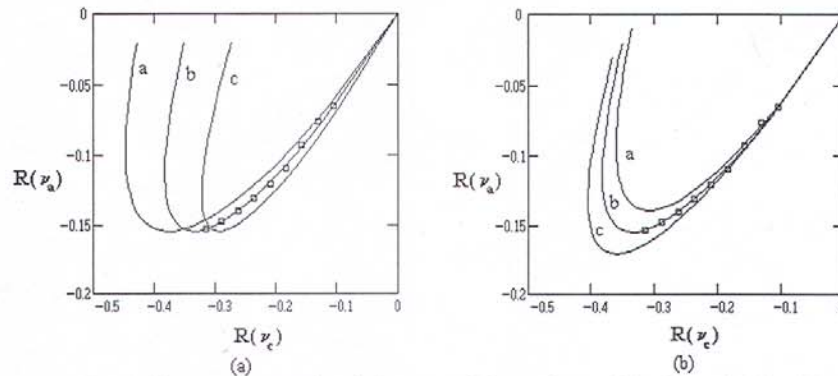


Fig. 3 The experimental and theoretical dependences $R(\nu_a,T) = \Phi(R(\nu_c,T))$.
Experimental points are represented by squares ( —□— ); solid curves represent
the computer simulated dependence: (A) for m = 1.23 and $q_{33}(\nu_c) = 0.12$ (a),
$q_{33}(\nu_c) = 0.18$ (b), $q_{33}(\nu_c) = 0.24$ (c) and (B) for $q_{33}(\nu_c) = 0.18$ and m = 1.13 (a),
m = 1.23 (b) and m = 1.33 (c).

In Fig. 3(a) are presented by squares the experimental points and by solid curves the theoretical dependencies for three values $q_{33}(v_c) = 0.12, 0.18, 0.24$ and $m = 1.23$. In Fig. 3(b) the same dependencies are presented for $q_{33}(v_c) = 0.18$, but different values of m ($m = 1.13, 1.23$ and $1.33$).

By examining the fits in Fig. 3, one concludes that the transition $(v_c)$ is characterised by $q_{11}(v_c) = 0.82$, $q_{22}(v_c) = 0$ and $q_{33}(v_c) = 0.18$ (Table 1).

## 4.2 Dynamics of orientational ordering in an electrical field

The behaviour of the molecules in the presence of the electrical field can be studied by analyzing the dependence of order parameters $S_{ii33}$ on the electrical field. The order parameters were determined from the measurements of the optical absorption in electrical field. In order to do this determination, the optical absorptions $A_e(v_a)$ and $A_e(v_c)$, corresponding to the wavenumbers $(v_a)$ and $(v_c)$ have been measured in the presence of the electrical field applied on the sample at a constant temperature.

Fig. 4(a) presents the optical absorption parameters $A_e(v_a)$ and $A_e(v_c)$, measured at room temperature (21 °C) in the cholesteric mesophase, as a function of the electrical field. The decrease of the absorption values indicates the presence of the cholesteric-nematic transition. In Fig. 4(b) is shown the evolution of the linear dichroism $R_e(v_a)$ and $R_e(v_c)$ as a function of the electrical field, estimated with the help of (4) by using the values $A_e(v_a)$ and $A_e(v_c)$ and $A_{is}(v_a) = 0.91$, $A_{is}(v_c) = 0.38$.

By knowing the values of the spectroscopic coefficients $a(v_a)$, $b(v_a)$, $a(v_c)$ and $b(v_c)$ (Table 1) and using the relations (2-3), (8-9) and the condition $\Sigma g_{ii33} = 1$, there were determined the order parameters $S_{1133}$, $S_{2233}$ and $S_{3333}$, which describe the orientational order of the molecular axes $x_i$ ($i = 1,2,3$) with respect to $X_3$.
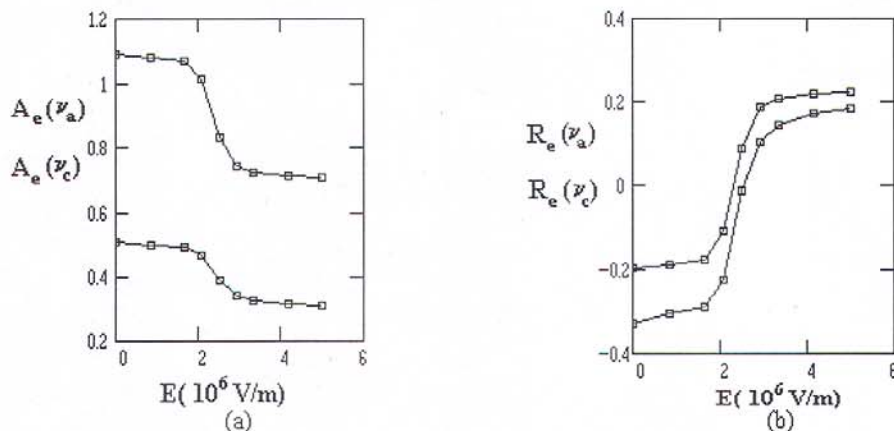


Fig. 4 (a) The optical absorptions $A_e(v_a)$ (—□—) and $A_e(v_c)$ (—◇—) and (b) the degree of the optical absorption anisotropy $R_e(v_a)$ (—□—) and $R_e(v_c)$ (—◇—), measured at room temperature (21 °C), as a function of the intensity of the applied electrical field.

Fig. 5 presents the order parameters $S_{1133}$, $S_{2233}$ and $S_{3333}$ as function of the electrical field. It can be observed that the order parameter $S_{2233}$, which characterise the orientation of the out of plane $x_2$ molecular axis, passes from positive values to negative values. This feature suggests the tendency of the $x_2$ axes of the molecules to be perpendicular to $X_3$. The saturation values of the order parameters point out that $S_{3333} > S_{1133}$. This behaviour of the order parameters in the presence of the electrical field is in accordance with the mechanism of the cholesteric-nematic transition reported in the literature [16].
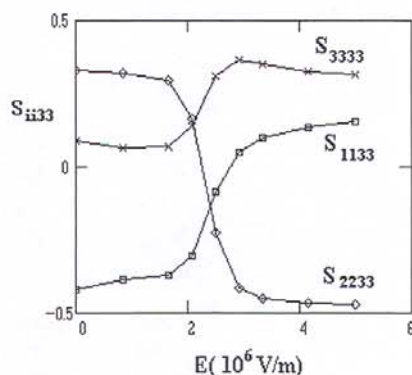
*Fig. 5 The order parameters $S_{ii33}$ (i = 1,2,3) which characterize the orientational ordering of the molecular axes $x_i$ with respect to $X_3$, measured at the room temperature (21 $^\circ$C), as a function of the electrical field intensity.*

## 5. Conclusions

We have studied the isotrope-cholesteric transition and the cholesteric-nematic transition in d.c. electrical field of the cholesteric mixture of cholesteryl chloride - cholesteryl nonanoate CC/CN (1.9/1 by wt.) with the azodye tetrazo-2,3'-dimethyl benzene $\beta$ naphtol, by using the measurements of the degree of the optical absorption anisotropy $R(v)$. Because $R(v)$ depends on the order parameters, which are affected by different external fields, any transformation of the liquid crystal matrix which influences the ordering is reflected in the $R(v)$ values. We have determined the dependence of the order parameters $S_{ii33}$ on the intensity of the electrical field which characterize the orientational order of the molecular axes $x_i$ of the dyes molecules with respect to the electrical field. This was performed by measuring $R(v)$ of two absorption bands of the dye in the presence of the electrical field. The dependence of $S_{ii33}$ on the electrical field intensity is in agreement with the mechanism of the cholesteric-nematic transition.

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