MOLECULAR ORDERING IN THE NEMATIC STATE EVALUATED BY OPTICAL ABSORPTION ANISOTROPY MEASUREMENTS AND MO-SCF-PPP CALCULATIONS

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The paper presents the investigations on phase transitions of the mixtures of nematic liquid crystal 4-cyanophenyl-4'-pentyl benzoate and azodyes. The phase transitions have been detected by optical absorption in polarized light measurements. The experimental results are correlated with the theoretical values of the transition moment components of the azodyes, obtained by molecular orbitals (MO) calculations, performed in the frame of the SCF-PPP-CI method. The order parameters of the studied azodyes in the nematic matrix are determined from the degree of the optical absorption anisotropy. The order parameters of the azodyes in the nematic state of the mixture are presented as function of temperature.

1. Introduction

The temperature dependence of the optical absorption of the liquid crystals in different range of the spectrum is well known [1, 2]. The optical absorption of the liquid crystals and their mixtures in different phases are determined by various factors: the type of the mesophase, the molecular ordering, the transition moment of the investigated band, the refractive indices of the liquid crystal matrix, etc. [3-5]. The orientation of the dye molecules, dissolved in the nematic liquid crystal matrix, known as "guest-host" effect has been intensively studied [6-8]. These investigations had in view either the construction of the electrooptical display devices or the determination of the long range orientational order in the liquid crystals. A useful method of molecular ordering investigation is optical spectroscopy in polarized light. By using the polarized light, these investigations can provide information about the polarisation of the spectral bands as well as the order parameters of the substances dissolved in liquid crystals [9-11].

The work presents a study on the linear dichroism of the π-π* absorption band of a new series of azodyes. The azodyes have been oriented in the nematic liquid crystal 4-cyanophenyl-4'-pentyl benzoate. The aim of this work is to evaluate the order parameters of the molecules in the nematic matrix by using the temperature dependence of the linear dichroism of the azodyes.

For the determination of the order parameters there is the method developed by Kuball et al [9, 10], which takes in consideration the temperature dependence of the linear dichroism and a relation between S and D. In this work, we used another method which takes into account the values of the transition moment components of the π-π* absorption band of the azodyes, obtained by MO calculations performed in the frame of the SCF-PPP-CI method [15] and the measured degree of the optical absorption anisotropy [12-14].

2. Theoretical background

The molecular order in the nematic state can be described by using the orientational distribution coefficients [9, 10]

$$g_{ijkl} = \frac{1}{4\pi} \int f(\theta,\phi)\, a_{ik} a_{jl}\; sin\theta\; d\theta\, d\phi \tag{1}$$

where a_{ik}, a_{jl} are the elements of the orthogonal transformation matrix from molecule-fixed co-ordinate system x_i (where x_3 is taken as long molecular axis) and space-fixed system X_i, $f(\theta,\phi)$ is the orientational distribution function. A uniaxial system having the optical axis X_3 is characterised by the coefficients g_{ii33}, that connect the molecular properties to the measurable quantities.

By using the distribution coefficients, g_{ii33}, the molecular ordering can be evaluated by the order parameters:

$$S = \frac{1}{2}(3g_{3333} - 1) \tag{2}$$

$$D = \frac{3}{2}(g_{2233} - g_{1133}) \tag{3}$$

The order parameter S characterises the orientational ordering of the x_3 molecular axis with respect to the optical axis X_3, whereas the parameter D describes the anisotropy of the ordering.
The degree of the optical absorption anisotropy is experimentally determined by using the relation:

$$R(\nu) = \frac{A_3 - A_2}{A_3 + 2A_2} = \frac{\varepsilon_3 - \varepsilon_2}{\varepsilon_3 + \varepsilon A_2} \tag{4}$$

where A_3, A_2 represent the optical extinctions and ε_3, ε_2 the molar absorption coefficients, for light polarized parallel, respectively perpendicular to the optical axis of the matrix.

The molar absorption coefficients, ε_3 and ε_2, can be expressed as [14]:

$$\varepsilon_2 = \frac{M^2}{3}\left[1 - \frac{1}{2}(3q_{33} - 1)S - \frac{1}{2}(q_{22} - q_{11})D\right] \tag{5}$$

$$\varepsilon_3 = \frac{M^2}{3}\left[1 + (3q_{33} - 1)S + (q_{22} - q_{11})D\right] \tag{6}$$

where $q_{ii} = (M_{ii}/M)^2$ are the relative absorption coefficients, M_{ii} the transition moment components with respect to x_i molecular axis and $M^2 = \Sigma\, M_{ii}^2$

The theoretical values of the transition moment components are defined as [15]:

$$M_{ii} = \sqrt{2}\,e \int \varphi_o^* \left|\sum_\mu x_{i,\mu}\right| \varphi_n d\tau \tag{7}$$

where φ_o, φ_n are the orbitals implied in the electron transition and $x_{i,\mu}$ the co-ordinate of the atom μ with respect to the chosen co-ordinate system x_i.

Taking into account the relations (5) and (6), the degree of absorption anisotropy can be expressed by:

$$R(\nu) = a(\nu)\, S + b(\nu)\, D \tag{8}$$

where

$$a(\nu) = (3q_{33} - 1)/2 \tag{9}$$
$$b(\nu) = (q_{22} - q_{11})/2 \tag{10}$$

The coefficients $a(\nu)$ and $b(\nu)$, depending on q_{ii}, contain information on the polarisation of the absorption bands and are temperature independent. The order parameters S and D are macroscopic parameters, characterising the uniaxial matrix and depend on temperature.

The distribution coefficients g_{ijkl}, the order parameters S and D, as well as the relative coefficients q_{ii} depend on the choice of the molecule-fixed system. In order to determine the order parameters S and D from the degree of anisotropy, $R(\nu)$, it is necessary to express q_{ii} with respect to x_i system.

3. Experimental

The molecular structure of azodyes is presented in Fig. 1. The substitute is $Y = CH_3$ in para position (p-CH$_3$) for dye D1, $Y = OCH_3$ in meta position (m-OCH$_3$) for dye D2, in para position (p-OCH$_3$) for dye D3, and $Y = OC_2H_5$ in para position (p-OC$_2$H$_5$) for dye D4.

The dyes have been dissolved in nematic liquid crystal 4-cyanophenyl-4'-pentyl benzoate (E5) found in the isotropic phase. The concentrations of the dyes have been of (0.1-1) % by wt. The (dye-E5) mixtures have been encapsulated in the cells of 12 μm in thickness. A planar orientation of the molecules was achieved by a conventional technique and controlled by microstructural observations with polarizing microscope. The cells were placed in a special hot stage inside the spectrophotometer. The electron spectra were registered with an UV VIS Zeiss Jena spectrophotometer, equipped with polarizers. The optical absorption was measured by using linear polarized light: parallel (A_3) and perpendicular (A_2) with respect to the optical axis of the samples. Also, the optical absorption A_3 and A_2 were measured as function of temperature at constant wavenumber (v_{max} of the π-π* absorption band of azodyes), in order to detect the phase transitions. The transition temperatures T_{IN} from isotropic phase into the nematic phase of the investigated mixtures are 46.5 ^{o}C (E5-D1 mixture), 45 ^{o}C (E5-D2 mixture), 43 ^{o}C (E5-D3 mixture) and 42 ^{o}C for (E5-D4 mixture).
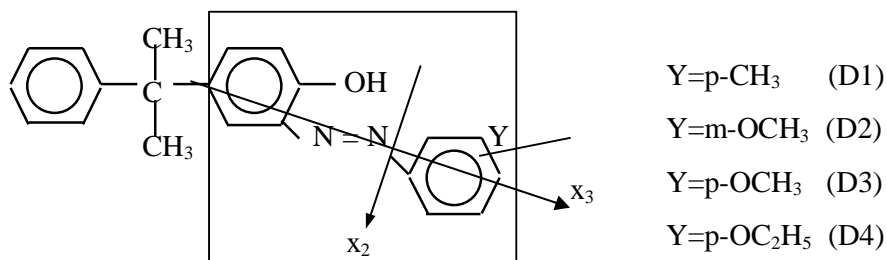

Fig. 1. The dye structure and associated x_i co-ordinate system.

4. Results and discussions

The investigated dyes present two absorption bands in the range of $(16-30)10^3 cm^{-1}$: a higher wavenumber band, corresponding to π-π* electronic transition and a lower wavenumber band corresponding to n-π* transition. The wavenumbers of the absorption maxima, taken as v_a for π-π* band and v_b for n-π* band, are listed in Table 1. These values remain unmodified in the isotropic phase and in the nematic phase of the (E5-dye) mixtures.
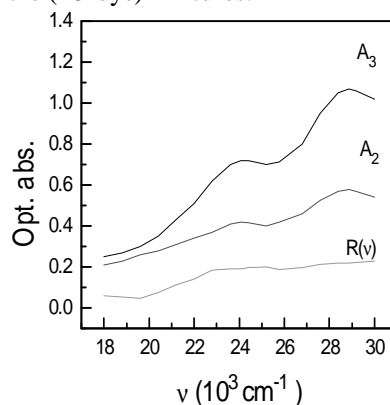

Fig. 2. The optical absorption in parallel (A_3) and perpendicular (A_2) polarized light to the optical axis of the nematic matrix, for the dye D1 (T = 34 ^{o}C); R(ν) – the optical absorption anisotropy.

Table 1. The wavenumbers of the absorption maxima and coefficients $q_{ii}(\nu_a)$ for the investigated dyes.

Dye	ν_a (10^3 cm^{-1})	ν_b (10^3 cm^{-1})	$q_{11}(\nu_a)$	$q_{22}(\nu_a)$	$q_{33}(\nu_a)$
D1	29.67	25.0	0	0.040	0.959
D2	30.30	25.0	0	0.063	0.937
D3	28.08	25.0	0	0.041	0.958
D4	27.92	25.0	0	0.042	0.957

The optical absorption of the azodyes presents a linear dichroism in the nematic phase of the mixtures. The Fig. 2 presents the optical absorption $A_3(\nu)$ and $A_2(\nu)$ as well as the degree of the optical absorption anisotropy $R(\nu)$ of the dye D1, measured as function of the wavenumber ν, at T=34°C in the nematic state. The degree of the optical absorption anisotropy $R(\nu)$ is positive in the visible range of the spectrum for all studied dyes. This suggests that the transition moment of these absorption bands is preferentially oriented along the long molecular axis, x_3. The phase transition of the (E5-dye) mixtures were detected by recording the temperature dependencies of A_3, or A_2 at the same wavenumber, corresponding to the maximum (ν_a) of the π-π[8] band of the azodyes. The Figs. 3 and 4 present the temperature dependence of the optical absorption $A_3(\nu_a)$ and $A_2(\nu_a)$ for $\nu_a = 29.67 \times 10^3$ cm^{-1}, measured at the heating and the cooling of the (E5-D1) mixture. All studied mixtures show the same behaviour: in the isotropic phase, the value A_{iso} of the absorption $A_3(\nu_a)$ or $A_2(\nu_a)$ remains constant with the increase of the temperature and is smaller than in the solid state. At the isotropic-nematic temperature T_{IN}, A_3 and A_2 show an absorption peak. The ascendent part of the peak corresponds to a metastable state, when the nematic droplets appear and the descendent part to the enlargement of the droplets, which induces the stable nematic state.
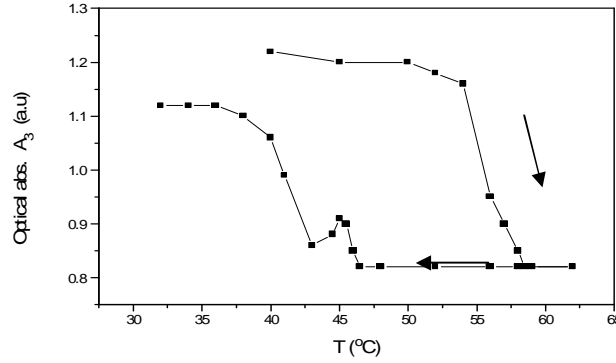
Fig. 3. The temperature dependence of the optical absorption A_3 (ν_a) for (E5-D1) mixture.

In the stable nematic phase $A_3 > A_{iso}$ and $A_2 < A_{iso}$. This fact can be explained by considering the uniaxiality of the matrix (D = 0), when the relations (5)-(6) are

$$\varepsilon_3 = \varepsilon_{iso}[1 + S(3q_{33} - 1)] \tag{11}$$

$$\varepsilon_2 = \varepsilon_{iso}[1 - S(3q_{33} - 1)/2] \tag{12}$$

and in the isotropic phase, $\varepsilon_{iso} = M^2/3$. The increasing of the S parameter in the mesophase means that $\varepsilon_3 > \varepsilon_{iso}$, and $\varepsilon_2 < \varepsilon_{iso}$ if ($3q_{33} - 1$) > 0. This condition was verified by calculation of the transition moment components M_{ii}, corresponding to the π-π* band of the dyes. The values of M_{ii} were obtained by MO calculations performed in the frame of the SCF-PPP-CI method, applied only for the π-π* transitions [14]. The calculations were performed [13] by considering only the conjugated part of the dye molecule (surrounded part in Fig. 1). The calculations were carried out in the co-ordinate system x_i, indicated in Fig. 1, where x_3 has been chosen as long axis of the conjugated part (or orientation axis).

The values of the coefficients $q_{ii} = (M_{ii}/M)^2$, calculated with respect to x_i system are summarised in Table 1 and correspond to the absorption maxima ν_a of the dyes. The q_{ii} values show that the π-π* transitions of the investigated azodyes are polarized in the (x_2, x_3) plane and the transition moment is preferentially oriented along the x_3 axis. The higher values of q_{33} accomplish the relation $(3q_{33} - 1) > 0$, that explains the dependencies presented in the Figs. 3 and 4. Because q_{ii} is a molecular property, which is not affected by external conditions, the shape of the absorptions A_2 and A_3 depends only on the temperature dependence of the order parameter S.

The Fig. 5 presents the temperature dependence of the optical absorption anisotropy $R(\nu_a)$, for π - π* band of the dyes, calculated with the relation (4). According to relation (8), it must be observed that the values $R(\nu_a)$ are affected by the orientational ordering of the dye molecules in the nematic matrix. Both order parameters S and D can be in principle determined from $R(\nu)$ measurements of two polarized bands, for which the orientation of the transition moments are different and known in advance [9,10]. This isn't the case of the studied dyes, as we have information only about the π-π* absorption band. Because the π-π* absorption band of the investigated dyes is characterised by $a(\nu_a) \gg b(\nu_a)$, as derived from q_{ii} values, $R(\nu_a)$ was approximated by :

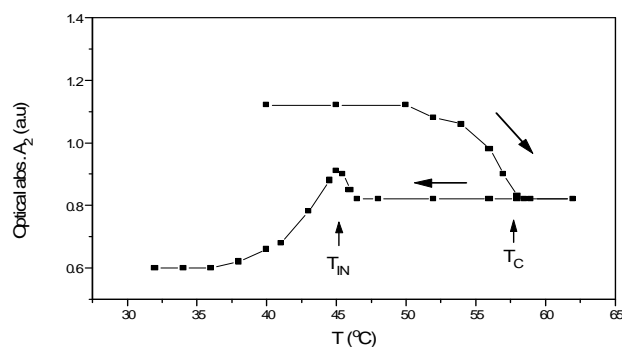$$R(\nu_a) = a(\nu_a) \, S \tag{13}$$

Fig. 4. The temperature dependence of the optical absorption A_2 (ν_a) for (E5-D1) mixture.
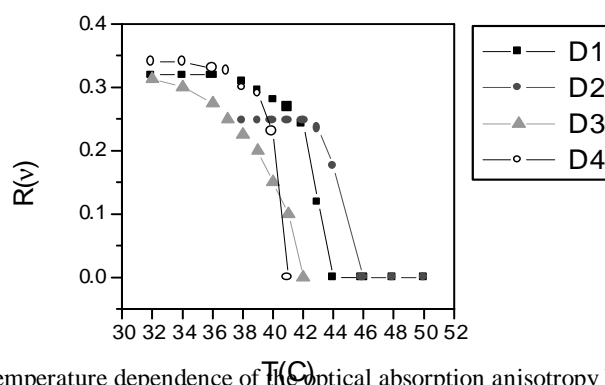

Fig. 5. The temperature dependence of the optical absorption anisotropy $R(\nu_a)$ of the dyes.

Using the theoretical values of q_{ii} and the optical absorption anisotropy $R(\nu_a)$, the order parameters S of the dyes molecules in the E5 matrix were calculated with (9) and (13).

In Fig. 6, the order parameters of the dyes in nematic matrix are presented as function of reduced temperature T/T_{IN}. The values of S differ at the same reduced temperature, depending on the nature and position of the substitute Y with respect to the axis x_3. At the reduced temperatures $T/T_{IN} > 0.95$, the parasubstituted dyes D1, D3 and D4 have a lower order parameter than dye D2, i.e. they show a poorer orientation at higher temperatures in comparison with D2. At the reduced temperatures $T/T_{IN} < 0.95$, the dyes D1, D3 and D4 are more efficiently oriented than the dye D2. This effect can be attributed to the guest-host interactions, rather than to the effect of the length of the Y substitute of the dyes.
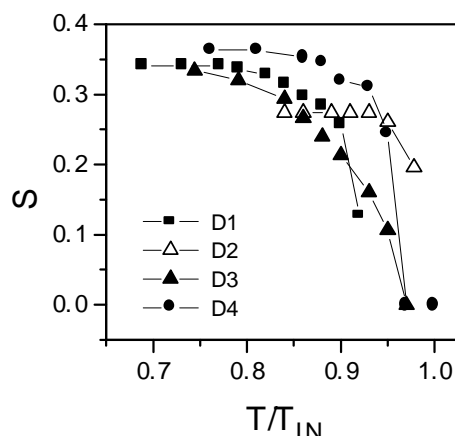
Fig. 6. The order parameters of the dyes D1-D4 in nematic matrix as function of the reduced temperatures T/T_{IN}.

5. Conclusions

By measuring the optical absorption in polarized light we have determined the anisotropy of the optical absorption for some azodyes dissolved in nematic solvent 4-cyanophenyl-4'-pentyl benzoate. The degree of the optical absorption was used to evaluate the order parameter S of the dye molecules in nematic matrix. In order to calculate the parameters S, other information, concerning the polarisation of the absorption bands, are needed. The information on the polarisation of the π-π^* absorption band of the investigated dyes was obtained from the values of the transition moment components of the π-π^* absorption band, got by MO calculations performed in the frame of the SCF-PPP-CI method.

Acknowledgements

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