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OPTICAL ABSORPTION ANISOTROPY OF SOME AZODYES, DETECTED BY UV-VIS SPECTROSCOPY IN POLARIZED LIGHT

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abstract: The work presents a study on the optical absorption anisotropy (linear dichroism) of the π-π* absorption band of a series of azodyes. The azodyes have been oriented in the nematic liquid crystal 4-cyanophenyl-4'-pentyl benzoate. The linear dichroism of the dye molecules in the nematic matrix is also evaluated as function of the temperature.

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1. Introduction

The anisotropy of the optical absorption of the molecules can be detected only if the molecules are oriented, for example in an anisotropic solvent like the liquid crystal. The orientation of the dye molecules, dissolved in the nematic liquid crystal matrix, is also known as "guest-host" effect and has been intensively studied [6÷8]. The optical absorption of the liquid crystal-dye 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.[1÷5]. A useful method in the investigation of the anisotropy of the optical absorption (linear dichroism) is UV-VIS spectroscopy in polarized light. By using the polarized light, these investigations can provide information about the polarisation of the spectral bands as well as order parameters of the substances dissolved in liquid crystals [8÷11].

This work presents a study of the linear dichroism of the π-π* absorption band of a 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 temperature dependence of the linear dichroism of the azodyes as well as the influence of the nature, position of the substitutes and of the molecular ordering of the dyes molecules in the liquid crystal solvent.

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2. Experimental

The molecular structures of azodyes are presented in Fig. 1. The substitute is Y=CH_3 in para position (p-CH_3) for dye C1, Y=OCH_3 in meta position (m-OCH_3) for dye C2, in para position (p-OCH_3) for dye C3, and Y=OC_2H_5 in para position (p-OC_2H_5) for dye C4. The x_i is the coordinate system associate to the dye molecule, where x_3 is designated as long molecular axis.

The dyes, with the concentrations of (0.1-1)% by wt., have been dissolved in nematic liquid crystal 4-cyanophenyl-4'-pentyl benzoate (E5). The (E5-dye) 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.

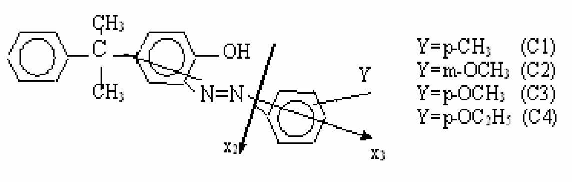

Fig. 1 *The dye structure and associated x_i coordinate system.*

The electron spectra have been registered with an UV-VIS Specord Zeiss Jena spectrophotometer and the light has been polarized by using the polarizing filters. The optical absorption has been measured by using linear polarized light: parallel (A_3) and perpendicular (A_2) with respect to the optical axis (X_3) of the samples (X_i are the associated axes of the nematic matrix, where X_3 represent the preferential orientation of the molecules). Also, the optical absorption A_3 and A_2 were measured as function of temperature at constant wavenumber ν_a ($\nu_a=\nu_{max}$ of the π-π* absorption band of azodyes). The transition temperatures T_{IN} from isotropic phase into the nematic phase of the investigated mixtures are presented in the Table 1. The temperatures T_{NI} have been detected by measurements of (A_2) and (A_3) and confirmed by microstructural observations in polarized light.

3. Results and discussions

The investigated dyes present two absorption bands in the visible range, 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 ν_a for π-π* band and ν_b for n-π* band, are listed in the Table 1. These values remain unmodified in the isotropic phase and in the nematic phase of the (E5-dye) mixtures. The liquid crystal used as solvent has an insignificant absorption in the visible range of the spectrum.

Table 1 The wavenumbers of the absorption maxima and the transition temperatures T_{IN}

Dye	ν_a (10^3cm^{-1})	ν_b (10^3cm^{-1})	T_{IN} °C
C1	29.67	25.0	46.5
C2	30.30	25.0	45.0
C3	28.08	25.0	43.0
C4	27.92	25.0	42.0

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 C1, measured as function of the wavenumber ν, at T=34°C in the nematic state.

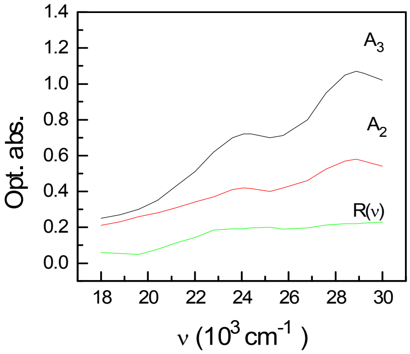

Fig. 2 *The optical absorptions (A_3) and (A_2) of the dye C1, measured at T=34°C; $R(\nu)$* – the optical absorption anisotropy

The degree of the optical absorption anisotropy $R(\nu)$ is positive in all the visible range of the spectrum for C1. This suggests that the transition moment of absorption bands is preferentially oriented along the long molecular axis, x_3. Such behaviour is encountered for all the investigated dyes.

By measuring the values of A_3, or A_2 at the fixed wavenumber ν_a as function of temperature we found a sensitive temperature dependence of them. The Figs.3 and 4 present the temperature dependence for the optical absorptions $A_3(\nu_a)$ and $A_2(\nu_a)$ measured in the heating and in the cooling of the (E5-C1) mixture. In the solid state, the absorption $A_3(\nu_a)$ or $A_2(\nu_a)$ decreases with the increase of the temperature. At the transition temperature from the solid to the isotropic liquid state, $A_3(\nu_a)$ and $A_2(\nu_a)$ have an important decrease. In the isotropic liquid phase, the values of the $A_3(\nu_a)$ and $A_2(\nu_a)$ remains constant and smaller than in the solid state. In the cooling, at the isotrop-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 appear the nematic droplets and the downward part to the expansion of the droplets, which induces the stable nematic state. All studied mixtures present the same behaviour. This dependence is explaned by the relations (3) and (4), by taking in consideration the order parameter S which increase in the nematic state.

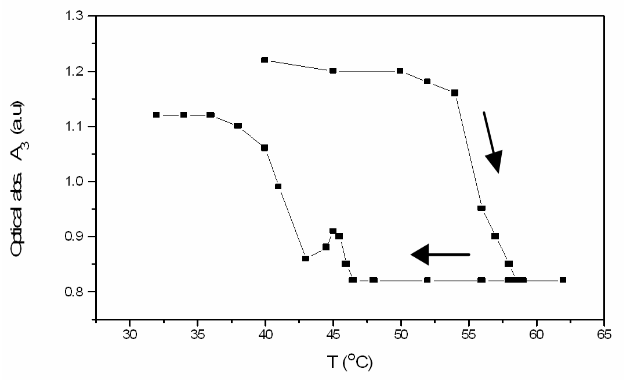

Fig. 3 *The temperature dependence of the optical absorption $A_3(\nu_a)$ for (E5-C1) mixture.*

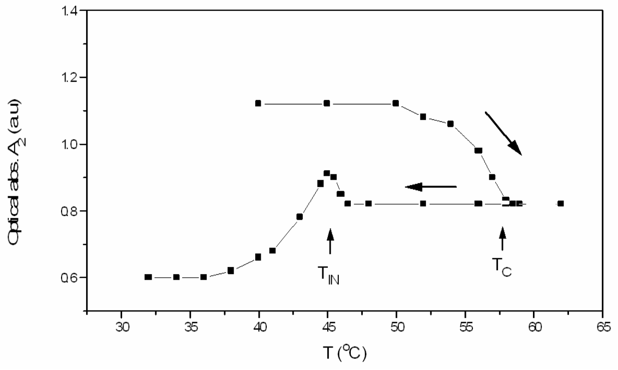

Fig. 4 *The temperature dependence of the optical absorption $A_2(\nu_a)$ for (E5-C1) mixture.*

The Fig. 5 presents the temperature dependence of the optical absorption anisotropy $R(\nu_a)$, measured for the maxima ν_a of the π-π^* band of the investigated dyes. Experimentally, $R(\nu_a)$ is evaluated with the relation:

$$R(\nu_a) = \frac{A_3(\nu_a) - A_2(\nu_a)}{A_3(\nu_a) + 2A_2(\nu_a)} \tag{1}$$

which can be also written as:

$$R = \frac{\varepsilon_3 - \varepsilon_2}{\varepsilon_3 + 2\varepsilon_2} \tag{2}$$

where ε_3, ε_2 represent the molar absorption coefficients, for light polarized parallel, respectively perpendicular, to the optical axis of the nematic matrix. Theoretically they are expressed by the relations [6÷8]:

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

$$\varepsilon_3 = \frac{M^2}{3}\left[1 + (3q_{33} - 1)S + (q_{22} - q_{11})D\right] \tag{4}$$

where $q_{ii}=(M_{ii}/M)^2$, M_{ii} are the transition moment components with respect to x_i molecular axis and $M^2=\Sigma M_{ii}^2$; S is the order parameter which describes the orientation of the long molecular axis x_3 with respect to the optical axis X_3 of the matrix and D describes the order anisotropy. Taking into account the relations (2)-(4), the degree of absorption anisotropy can be expressed as:

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

where $a(\nu)=(3q_{33}-1)/2$ and $b(\nu)=(q_{22}-q_{11})/2$ are spectral coefficients depending on the q_{ii} values of the absorption band and comprise informations on the polarisation of the absorption bands. They dont depend on the temperature. The parameters S and D in (5) characterise the matrix structure and depend on the temperature. As consequence, the temperature dependence of the $R(\nu_a)$ values in Fig. 5 is due only to the temperature dependence of the molecular ordering.

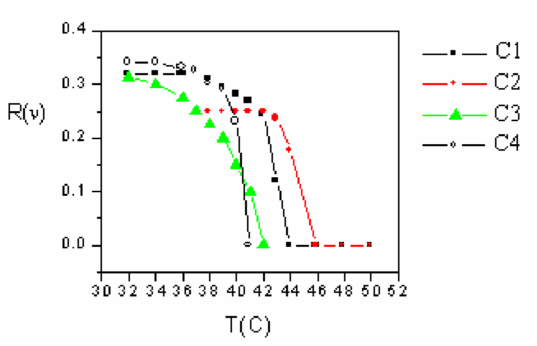

Fig. 5 *The temperature dependence of the optical absorption anisotropy $R(\nu_a)$*

The condition D=0 is accomplished if the liquid crystal matrix is uniaxial, having X_3 as optical axis and experimentally, the absorption A_3 and A_2 are measured in the linear polarized polarized light, parallel and perpendicular respectively to the optical axis X_3. In these conditions:

$$R(\nu) = a(\nu)\,S \tag{6}$$

In the Fig. 5 it can be observed that in the isotropic state, $R(\nu_a)=0$ because of the absence of the ordering (S=0), in according with (6). At the phase transition temperature, T_{IN}, $R(\nu_a)$ increase significantly, that indicates the anisotropy of the nematic state structure($S\neq0$). In the nematic state, the value of the $R(\nu_a)$ depend on the orientation of the dye molecules which is determined by the structure of the dye, particularly by the position of the substitute Y with respect to the long molecular axis x_3. As consequence, the parasubstituted C3 dye ($Y=p\text{-}OCH_3$) has superior values of S and $R(\nu_a)$ as against metasubsituted C2($Y=m\text{-}OCH_3$) dye. In the same time, the values of $R(\nu_a)$ depend of the nature of Y. This can be seen in the Fig.5, where the dye C4($Y=p\text{-}OC_2H_5$) has a better $R(\nu_a)$ than dye C3($Y=p\text{-}OCH_3$). On the other hand, the values of the R(ν) are positive in the vizible spectral range for all investigated dyes. According to relation (6), the pozitive values of $R(\nu_a)$ prove that the transitions moments are preferentially oriented along the long molecular x_3 of the dyes molecules and $a(\nu) > 0$.

Conclusions

By measuring the optical absorption in polarized light we can conclude that the anisotropy of the optical absorption of the studied azodyes is positive, depending on the nature of the substitute and his position with respect to the long molecular axis of the dye molecule. Also, the detection of the temperature dependence of the optical absorption in polarized light, depending on the molecular ordering, is a sensitive method to determine the phase transitions temperatures.

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