Regular Article

Effect of Alkyl Tail on the Visible Spectra and Order Parameters S of some Azo N-Ester-1,8-naphthalimide(ANEN) Disperse Dyestuff

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This research is an attempt to measure the effect of alkyl tail on the visible spectra and order parameters S of some azo N-ester-1,8-naphthalimide(ANEN) disperse dyestuff. For the first time, the visible absorption spectra of two azo N-ester-1,8-naphthalimide(ANEN) dyes with identical molecular size and diverse alkyl tails were obtained in liquids and liquid crystalline solvent. Ordinary organic solvents with different polarity and chemical nature (*i.e.* cyclohexane, 1,4-dioxane, tetrachloromethane, benzene, diethyl ether, chloroform, dichloromethane, 1-butanol, acetone, ethanol and methanol) accompanied by nematic liquid crystal matrix (5CB) were used. In the visible region of parallel aligned samples the intensity of the absorption bands was measured, thereby the dichroic ratios R and order parameters S of the dyes were determined. Then, the interaction of these dyes was investigated and compared with the anisotropic surroundings and those of the isotropic organic solvents. It was found that the electronic absorption spectra of the dyes in the alcoholic (methanol and/or ethanol) surroundings are shifted to red compared to that of the isotropic organic solutions. Thus, there are strong molecular interactions between the dye molecules and methanol molecules. Also, the electro-optical effects of the guest-host systems were investigated through polarized spectroscopic method.

Keywords: Azo N-ester-1,8-naphthalimide(ANEN) dyes, Dichroic ratio, Guest-host interactions, LD and ELD parameters

INTRODUCTION

Through several studies, it has been proved that the photo-physical behavior of a dissolved dye depends on the nature of its environment, such as the intensity, shape, and maximum absorption wavelength of the absorption band of dye in solution which is strongly related to the solvent-solute interactions and solvent nature. This effect is closely related to the nature and degree of dye-solvent interaction. Non-specific or specific solute-solvent interactions are dielectric enrichment and hydrogen-bonding respectively, can be cause of spectral shift in different solvents. The solvent dielectric constant, ε, and solvatochromic parameters could obtain the effect of solvent [1-5]. ε as a macroscopic property can give valuable information about the nature and strength of molecular interactions in liquid

solutions, furthermore the value of dielectric constant is strongly related both to chemical structure of a molecule and intermolecular interactions. The most important application of nematic liquid crystals is liquid crystal displays (LCDs) which is used in guest-host interactions [6-11].

It has to be mentioned that, this phenomenon is based on dichroic dye molecules dissolved in a nematic host and their orientations depend on the applied electric field, *i.e.* nematic molecules are able to orient dissolved dye molecules exactly parallel to their long axes. However, an additional amount of dye in a nematic host affects several host parameters, and this just happens due to the strong mutual interactions between the dye and nematic molecules [5]. Therefore, in order to understand and provide further information about the intermolecular forces in anisotropic matrix, several investigations on various kinds of guest-host systems among the most important requirements are needed. There are a lot

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of dye doped properties in liquid crystals among which absorption anisotropy is one of the most interesting.

The knowledge of the spectroscopic properties and solvation of ANEN dyes in isotropic and anisotropic uniaxial polar solvents is important to understand the effect of the ordinary and anisotropic surrounding on the dye photo-physical behavior. Nematic liquid crystals are those highly anisotropic materials which are owing to their large molecular anisotropy and intermolecular ordering. Oriented nematics form partially ordered structures and they are suited as anisotropic solvents for polarized spectroscopy. Besides, they are the qualified model systems for investigation of anisotropic intermolecular interaction (solute-solvent intermolecular interactions) [12]. Moreover, the intermolecular interaction of dye molecules surrounded by anisotropic molecules can be investigated by a suitable guest-host system.

More than 50% of the production of disperse dyestuffs is based on the amount of azo in the world. It should be mentioned that using this chromophore system and relatively, simple synthesis method for these dyestuffs enables them to produce a wide range of colors with high tensity and brightness from greenish yellow to cyan [13,14].

4-Amino-N-substituted-1,8-naphthalimides are significant intermediates for synthesis of monoazo disperse dyestuffs. These dyestuffs have been considered for dyeing polyester fibers [15-17].
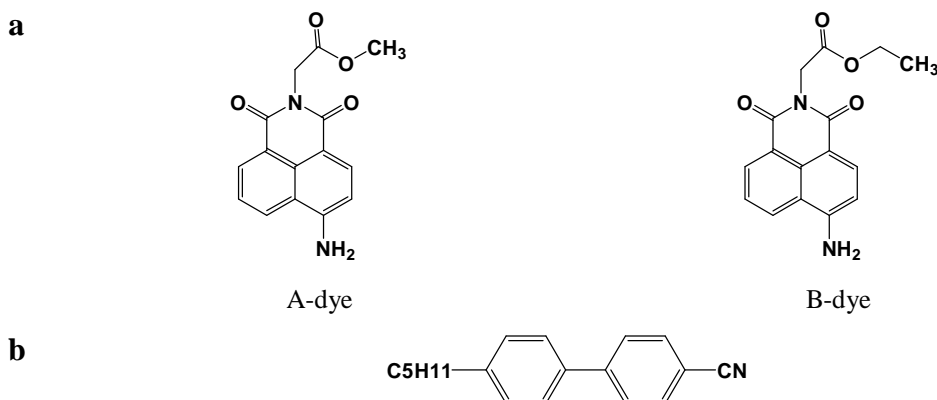
It was demonstrated that solvation of the guest molecules in liquid crystalline host could be affected by a specific anisotropic interaction related to the alignment by liquid crystal property as well as solvent polarity. Furthermore, it was found that the order parameters of dyes depend on the size, shape, polarity, and steric effect. To the best of our knowledge, there are few spectroscopic data about ANEN dyes specially the dyes studied in this work. The present study was undertaken to deduce of photo-physical properties of the two ANEN dyes, including various alkyl tails, in anisotropic and isotropic environments. These dyes are methyl 2-(6-amino-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)acetate (A-dye) and ethyl 2-(6-amino-1,3-dioxo-1H-benzo[de]isoquinolin-2 (3H)-yl)acetate (B-dye). In addition to these achievements, some spectroscopic data were reported for the first time. Also, linear dichroism (LD) and electric linear dichroism (ELD) of two ANEN dyes were obtained through employing polarized spectroscopic method.

EXPERIMENTAL

The Guest-Host Materials

ANEN dyes (Fig. 1a) were synthesized and purified according to the common procedure in our laboratory and utilized as solutes (guests). It must be taken into consideration that, all of the solvents except 5 CB (liquid crystal) were purchased from Merck. 5 CB (Fig. 1b) was supplied by institute of chemistry of the military technical academy, Warsaw, and Poland, and was used as the host. Dye-doped liquid crystal solutions were prepared by dissolving about 1 mg of the dye in 100 mg of the liquid crystal solvent (*i.e.* ~1% w/w).

Fig. 1. Molecular structure of the ANEN dyes (a) and nematic liquid crystal 5CB (b).
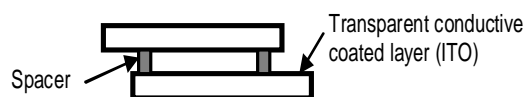
Liquid Crystal Cell Preparation

At this phase, first of all, for the measurement of the electro-optical effect and polarized absorption as a function of electric field strength, which is indium/tin oxide (ITO) coated, parallel glass plates (2×1.2 cm^2) were applied as transparent electrodes (Fig. 2).

The planar orientation of the guest and host molecules was achieved by surface treatment of a cast film of polyvinyl alcohol (Sigma) followed by the rubbing process. The space between the electrode surfaces was 50 µm and was set by a Mylar. The plates were sealed together with epoxy resin glue which is a sealing material. To introduce the dissolved dye in liquid crystal solvent (~1% w/w) capillary action was used. A two-part silver-loaded epoxy (RS components 567-604) and electrically conductive paint (RS components 555-156) both were employed to connect Copper wires. The liquid crystal cells were checked under crossed polarizers, and used in subsequent electric linear dichroism studies. The temperature of the cells was maintained at 25 °C.

LD and ELD Measurements

For the measurements of LD and ELD, initially, the absorption spectra of the dyes in the liquid crystalline host were scanned on a Carry UV-Vis double beam spectrophotometer (Mode 1100) equipped with the sheet polarizers. The samples with planar homogeneous orientation were mounted in a thermostat holder. Dichroic ratios R of the dyes were obtained on the basis of polarized absorption measurements. Respectively, the polarizer was rotated by 90° to record the absorbances in parallel and perpendicular directions to the rubbing direction of the cell (molecular alignment), A_{II} and $A_{\perp}$. The dichroic ratio was calculated by using $R = A_{II}/A_{\perp}$.

Contrast ratios CR of the dissolved dyes were obtained through using polarized spectroscopy in a guest-host system based on the homogeneous and homeotropic alignment. Polarized absorption spectra of the dissolved dyes were taken by the electric field on-off states (10 V, saturated voltage). Ratio between the maximum absorption in on and off states was calculated by using $R = A_{off}/A_{on}$ [5]. The mentioned spectrophotometer was used to scan the absorption spectra of the dyes in other solutions. The sample holder was a quartz spectrophotometer cell with the

Fig. 2. Cross-section of the experimental guest-host cell.

path length of 5 mm.

RESULTS AND DISCUSSION

The Solvent Effect on the Absorption Spectra

Analysis of solvent effect on electronic spectra of the dyes was measured on the basis of the solvatochromic parameters and the solvent electric permittivities. Since, the dye molecules with large dipole moment alter during transitions between two electronic states, the strong solvatochromic behavior is observed. Values of the solvatochromic parameters ($\pi*,\alpha,\beta$), including selected physical properties were obtained from literature and summarized in Table 1 [18,19].

$\pi*$ is a measure of the solvent dipolarity/polarizability which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect and correlated with the solvatochromic behavior values. The solvatochromic behavior of a dye is a shift in absorption wavelength due to the presence of solvent with different polarity, which is achieved as a result of the interaction between the solute and solvent molecules. β and α are respectively indices of solvent hydrogen-bond acceptor ability (HBA) and solvent hydrogen-bond donor ability (HBD).

The effect of anisotropic solvent (5CB) accompanied by isotropic organic solvents (non-polar, dipolar aprotic and polar protic) was examined at room temperature. Methanol, 1-butanol and ethanol were chosen as polar protic solvents, which exhibit strong hydrogen bond donor capability (high α value). Acetone, diethyl ether and 1,4-dioxane are dipolar aprotic solvent with the ability of very good hydrogen bond acceptor (high ß value), and poor hydrogen bond donor (low α value). Cyclohexane was used as a non-polar solvent with zero solvatochromic parameters ($\pi*, \alpha, \beta$). So, it is a very good origin for solvatochromic behavior determination. Tetrachloromethane, benzene, diethyl ether, chloroform and dichloromethane are relatively dipolar solvents and can be

Table 1. Permittivity, ε, Dipole Moment, μ, Dipole Correlation Factor, g, and Solvatochromic Parameters of the Selected Solvents at 22 °C, Taken from [1,21,22,25]

Solvent	Permittivity	Dipole moment	$g = \dfrac{\mu_{eff}^2}{\mu^2}$	β	α	π^*
Cyclohexane	2.02	0.0	1.0	0.00	0.00	0.00
1,4-Dioxane	2.21	0.4	~1.0	0.37	0.00	0.57
Tetrachloromethane	2.24	0	~1.0	0.10	0.00	0.28
Benzene	2.27	0.0	~1.0	0.10	0.00	0.55
Diethyl ether	4.2	1.3	1.1	0.47	0.00	0.24
Chloroform	4.8	1.15	1.1	0.10	0.20	0.69
Dichloromethane	8.93	1.55	1.1	0.10	0.13	0.73
1-Butanol	17.51	1.74	3.3	0.84	0.84	0.47
Acetone	20.56	2.7	1.3	0.48	0.08	0.71
Ethanol	24.55	1.71	2.9	0.77	0.83	0.54
Methanol	32.66	1.71	2.8	0.66	0.98	0.60
5CB[a]	$\bar{\varepsilon} = 10.8$	4.8	0.5	0.72	0.15	0.88

[a]Liquid crystalline host.

proper intermediates for the present study.

The optical characterization of the dyes in the nematic matrix (~1% w/w) together with those obtained in ordinary organic solvents with different polarity and chemical nature was investigated. The main absorption band of the dyes in visible region corresponds to a transition moment largely parallel to the long axis of the molecules due to π-π^* transition (localized in the azo group). The spectral position of the correspondent band is influenced by the nature of the solvent [20]. The electronic absorption spectra of the ANEN dyes at the room temperature and in different solvents are shown in Figs. 3a and 3b.
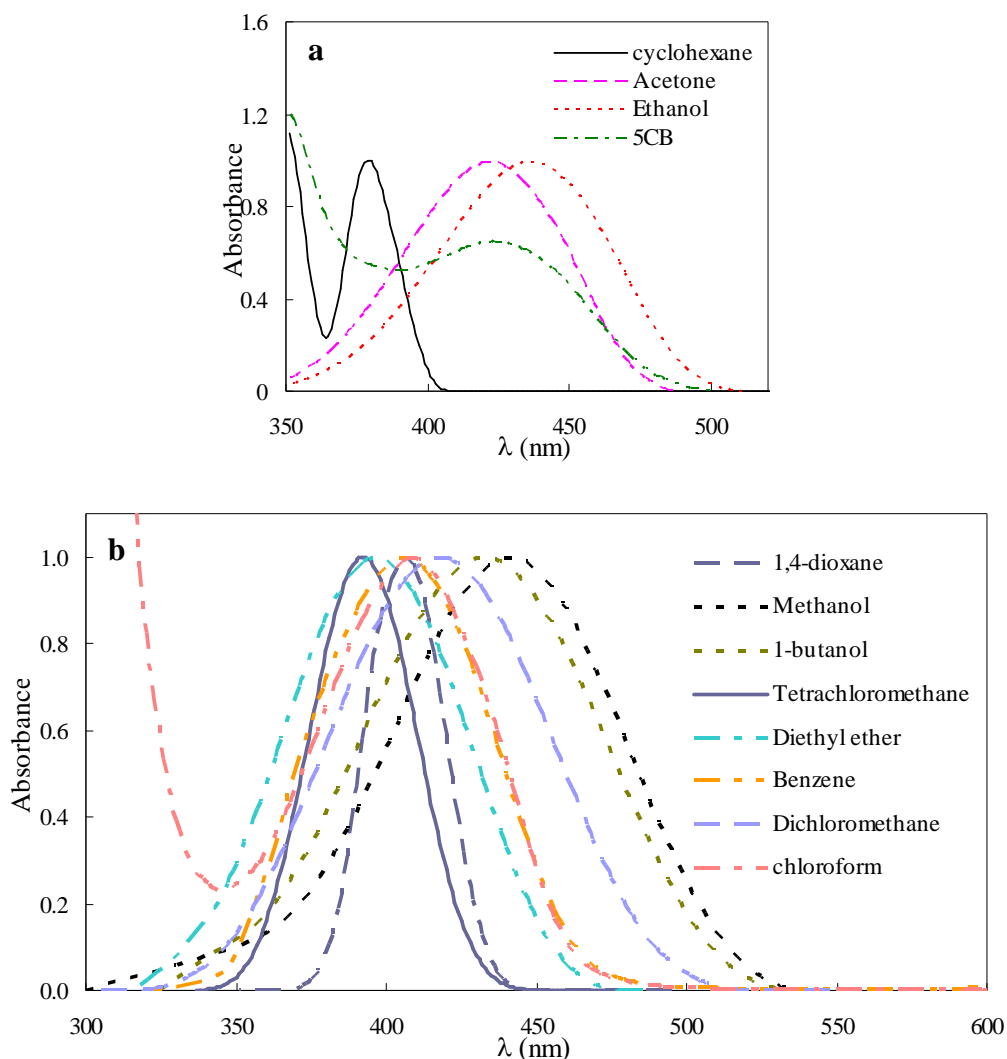
As it is observed, the absorption spectra of the dyes in methanol, ethanol and 1-butanol are shifted to the red as compared to the dye spectra in the other isotropic solutions and nematic matrix. It thus, indicated a relatively strong guest-host interaction between the dyes and the alcoholic host environment.

The maximum absorption wavelengths of the dyes in liquid crystal solvent (~1% w/w) and their solvatochromic behavior between 5CB (anisotropic solvent) and cyclohexane (isotropic solvent) are shown in Tables 2 and 3.

It is interesting to notice the relatively large redshifts of 45-47 nm in the absorption maxima of liquid crystalline host in comparison to the non-polar solvent and more interesting large red shifts of 63 nm in methanolic host. The origin of the redshift observed for the dyes in the methanolic solvent with small dipole moment about 1.7 D can be due to the relatively strong molecular interaction between the dye molecules and the alcoholic surroundings [21].

In addition, methanol (and two other alcohols) can make H-bond with the dye molecules that could be very effective in the solvation of the dye molecules in the alcoholic host and strong solute-solvent interaction. In spite of similarity of the shape of the bands in acetone (aprotic solvent) and ethanol (protic solvent), maximum wavelengths of the dyes are very different from each other. The differences between maximum wavelengths of the dyes in protic and aprotic solvents suggest that the H-bond has a major effect on their absorption spectra in the isotropic medium.

Figure 4 illustrates the variation of λ_{max} (nm) obtained from the absorbance spectra of the dyes which is a function of dielectric constant (ε) of different isotropic solvents associated with anisotropic host. The mean of dielectric

Fig. 3. Visible absorption spectra of the dyes in different solvents; both dyes possess the same spectra, a) cyclohexane, acetone, ethanol and 5CB b) 1,4-dioxane, tetrachloromethane, benzene, diethyl ether, chloroform, dichloromethane, 1-butanol, methanol.

constant in nematic phase of 5CB was calculated by using the following equation

$$\bar{\varepsilon} = \frac{1}{3}\left(\varepsilon_{\text{II}} - \varepsilon_{\perp}\right) \qquad (1)$$

Of this account, this is the location in which ε_{II} and $\varepsilon_{\perp}$ are respectively dielectric constants parallel and perpendicular to the molecular axis. Moreover, for taking literature value, approximately about 10.8 was obtained for the mean of dielectric constant at 22 °C [22].
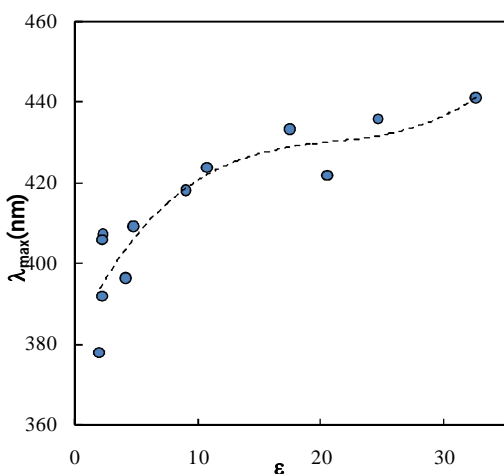
As seen, there is a relatively large solvatochromic behavior in liquid crystal and cyclohexane solutions. It was noted that a maximum value of λ_{max} was obtained for the dyes in alcoholic host and a minimum was obtained for the dyes in the non-polar solvent. On the basis of several studies, it is truly known that polar liquid solvents such as methanol and ethanol are strongly associated because of dipole-dipole interactions and hydrogen bonding [23,24]. All of the solvents except cyclohexane, tetrachloromethane, 1,4-dioxane and benzene demonstrate a parallel molecular

Table 2. Maximum absorption wavelengths of the dyes in isotropic and Anisotropic Solvents
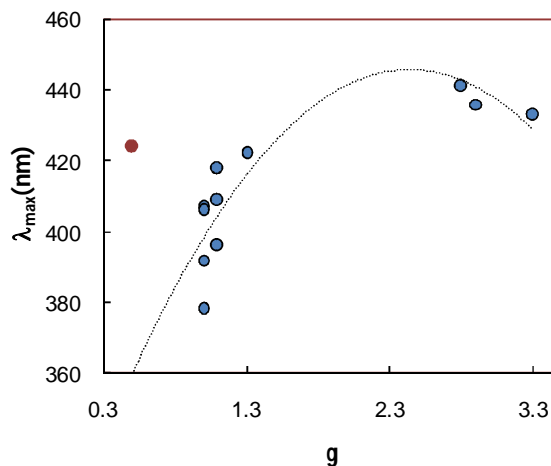
Dye Solvent	Dye A	Dye B
	λ_{max} (nm)	
Cyclohexane	378	378
1,4-Dioxane	407	407
Tetrachloromethane	392	392
Benzene	406	406
Diethyl ether	396	396
Chloroform	409	409
Dichloromethane	418	418
1-Butanol	433	433
Acetone	422	422
Ethanol	436	436
Methanol	441	441
5CB	423	425

Table 3. Dichroic Ratio R, Contrast Ratio (CR), Degree of Anisotropy and Solvatochromic Behavior Between 5CB and Cyclohexane Measured for the ANEN Dyes in the Oriented Nematic Solvent at 22 °C

Dye	λ_{max} (nm)	R	CR	S_{dye}	Solvatochromic behavior (nm)
A	423	2.22	1.95	0.29	45
B	425	2.09	1.82	0.27	47

Fig. 4. Variation of λ_{max} of the dyes A or B as a function of solvent dielectric constant, ε. A mean dielectric constant for 5CB was chosen to be about 10.8.

Fig. 5. Variation of λ_{max} of the dyes in different solvents as a function of the dipole correlation factor, g (5CB has been highlighted using red bullet). The g values for the solvents are available in Table 2 .

dipole association (*i.e.* g > 1), while the nematic liquid crystal 5CB displays a significant anti-parallel molecular association (g ~0.5) [22], which cause a remarkable reduction in effective dipole moment (see Table 1). The Kirkwood correlation factor (g) is a measure of molecular association between a reference molecule and its nearest neighbors. The departure of g value from unity is indicative of molecular association. Figure 5 displays the variation of λ_{max} obtained from the absorbance spectra of the dyes as a function of dipole correlation factor, $g = \mu^2 e_{ff}/\mu^2$, for the polar solvents together with anisotropic host 5CB. Only a small variation is observed in Fig. 5 to represent the position of the absorption bands as a function of g. Also, the dipole correlation factor g can be considered as a measure of solvent-solvent interaction.

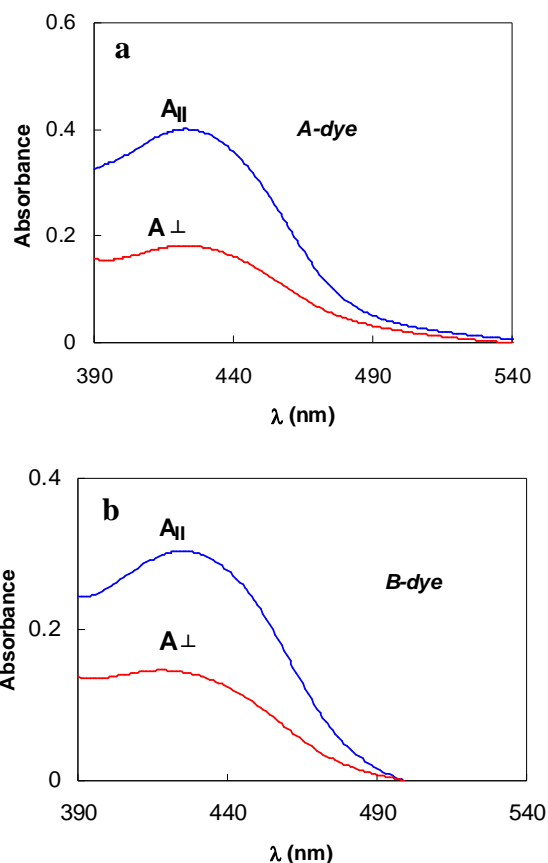## Order Parameter of the Dye-Liquid Crystal Mixture

As revealed in Figs. 6a and 6b, the polarized absorption spectra of the ANEN dyes dissolved in parallel-aligned liquid crystal (5CB) are shown at room temperature. The dichroic ratios ($A_{II}/A_{\perp}$) of the dyes were also determined from the absorption of light polarized parallel (A_{II}), it is perpendicular ($A_{\perp}$) to the alignment of nematic and has been complied in Table 3.

The ANEN dyes applied in this study have a relatively planar shape, besides the direction of the transition dipole moment of the dye molecules is not largely parallel to the long molecular axis. Since, the transition moment vector between two electronic states (π-π^* transition) of these molecules does not lie within the molecular plane, a relationship between the absorption anisotropy and the order parameter (S) of the guest molecules dissolved in oriented nematic host can be derived (see Eq. (2)), moreover, it is provided that the transition moment vector is along the long molecular axis. All order parameters will be calculated based on above assumption.

$$S = \frac{A_{II} - A_{\perp}}{A_{II} + 2A_{\perp}} \quad (2)$$

The order parameter is related to the dichroic ratio, R, as follows:

$$S = \frac{R - 1}{R + 2} \quad (3)$$

Fig. 6. Polarized absorption spectra of the ANEN dyes in the oriented nematic solvent of 5CB (~1% w/w) at 22 °C. (a) A-dye, (b) B-dye.

According to Table 3, it can be seen that dye B has the lower linear dichroism with respect to the other dye investigated here. This is a consequence of the presence of an excess methyl group attached to the esteric group. It should be noted that the dichroic ratio essentially depends on two factors, *i.e.* the alignment of the dye in the nematic host and the angle between transition dipole moment and the dye long molecular axis.
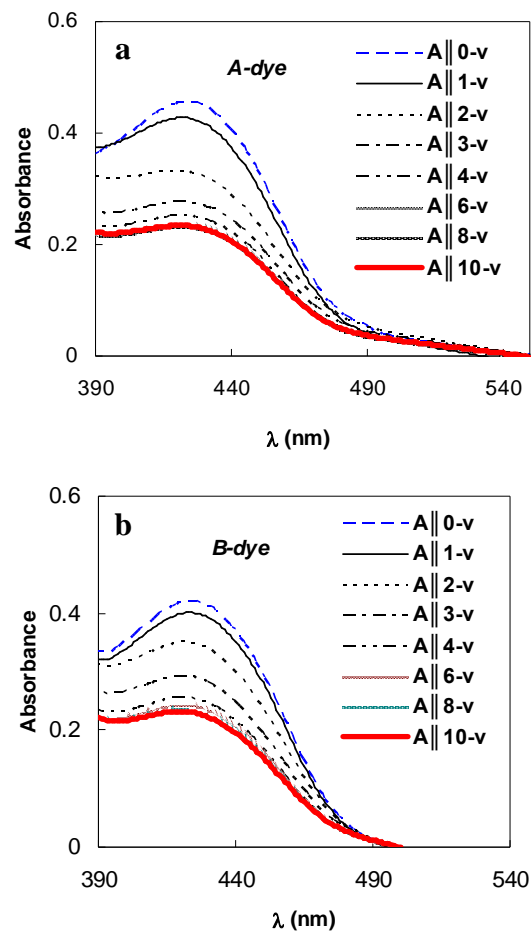
ELD Measurements

The electro-optical effect of the dissolved dyes in the anisotropic host was also measured by using a parallel-aligned guest-host cell with the thickness of d = 50 μm, and their contrast ratios (A_{off}/A_{on}) were obtained. At this instance, A_{off} is the absorbance at the absorption maximum

wavelength in the off state and A_{on} represents the same thing in the on state. Figures 7a and 7b display the polarized absorption spectrum of nematic solution of A and B dyes at different alternating electric field strength (5 kHz). It is observed that the intensity of the spectrum (without changing its shape) decreases as the voltage increases. In a voltage of 10 V, a minimum absorption of the dye was recorded. With zero electric field, the liquid crystal molecules were in a uniform parallel orientation and the dye molecules were parallel to the nematic director. The contrast ratios, CR, of the dyes were obtained and listed in Table 3. It should be noted that, as A_{on} is an electric field direction dependent quantity and its value also depends on anchoring energy of the surface, the dichroic ratio R and the contrast ratio CR values are slightly different. However, the obtained contrast ratio values were smaller than the dichroic ratios in the dyes. It can be seen that A-dye has the higher dichroic ratio (or contrast ratio) and order parameter. This is a consequence of the presence of excess methyl group attached to the esteric group which causes B-dye to be less ordered than A-dye. It is thoroughly reported that, as the structure, size and shape of the dye and liquid crystalline solvent molecules are compatible, the dye molecules can be incorporated into the liquid crystalline matrix without disrupting its order. Therefore, the alkyl tail has an important influence on the alignment properties of the guest-host system.

CONCLUSIONS

Absorption spectroscopy of ANEN dyes that could be interesting and important for all fields of color technology, was studied and reported for the first time for all fields of color technology, absorption spectroscopy of ANEN dyes was studied and reported. The visible absorption spectra of the dyes were found to exhibit a strong solvent dependence representing a regular variation with the dielectric constants of the solvents and could be explained on the basis of solvatochromic behavior. The solute-solvent and anisotropic interactions significantly contribute to the dye spectra in liquid and liquid crystal solutions, while the solvent-solvent interaction has a minor effect on the absorption spectra of the dyes. For each dye in liquid crystalline solutions, due to the strong molecular interactions between the dye

Fig. 7. Polarized absorption spectra of (A, B-dyes) in the oriented nematic solvent of 5CB (~1% w/w) and in different alternating electric field strength (5 kHz).

molecules and liquid crystal matrix, positive solvatochromic behavior was found. It was discovered that the solvatochromic behavior of dyes in alcoholic solutions is higher than that in other solutions. Solvatochromic and maximum absorption spectra of both dyes were completely the same as that one which reveals that excess methyl group has no effect on these parameters. According to the results of dichroism obtained in the present study, it has to be considered that the dichroic ratios R of the dyes are larger than one. This means that the absorption bands of these dyes may be considered as parallel transition (*i.e.* π-π*). Also, the alignment properties of the guest-host system can be affected by the molecular structure of the dye. In other words, the direct of orientation can be altered by shape, size

and structure of the dye over long distances. Consequently, although the process of considering or reasoning about the excess methyl group in dye-B makes the long axes of the molecule more prolonged than that in dye-A, the mentioned group makes it more disordered than dye-A.

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