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Tautomeric behavior of some azoquinoline dyes in liquid and liquid crystalline media

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ABSTRACT

The absorption spectra of three azoquinolin-8-ol derivatives (*o-*, *m-*, *p*-cyano hydroxy azoquinolin dyes) were investigated in liquid and liquid crystalline solutions as a function of the solvent polarity. The spectral data of the dyes were compared in both ordinary liquid solvents and liquid crystalline media. Analysis of the spectral data was used to determine the azo and hydrazone forms in both the environments. The spectral shifts were correlated by Kamlet–Taft and Katritzky multi-parameter polarity scales. For the azoquinoline dyes, the azo form is almost entirely dominated in polar anisotropic hosts. In contrast, the compounds remain dominantly in hydrazone form in some polar solvents such as DMF. The polarized absorption spectra of the compounds in the anisotropic media were measured and their degree of anisotropies was determined.

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1. Introduction

Azo-hydrazone tautomerism in azo compounds is quite interesting both from theoretical and practical point of view and has been of particular interest [1–5]. The tautomeric behavior of a number of hydroxy azo dyes has been identified in various media [6–8]. It is described by the intramolecular proton transfer between nitrogen and oxygen atoms. The presence of azo/hydrazone tautomerism in these compounds influence considerably in their unique photo-physical properties, which is in turn strongly influenced by several factors including temperature, substituents structure and solvent polarity [9,10].

Azo-hydrazone tautomerism has been studied by various optical techniques, including electronic method. Due to the characteristic differences between the optical spectra of the dyes in azo and hydrazone forms, azo/hydrazone tautomeric behavior can be investigated from the electronic spectra. Therefore, electronic spectroscopy is one of the most applicable and successful techniques for investigating the azo/hydrazone tautomerism. Therefore, the both tautomers can be detected from the absorption spectra in the visible region.

Spectroscopic methods, based on absorption spectra, give valuable information on contribution of different types of solute–solvent interactions using multi-parameter solvent polarity scales [11–13]. Knowledge of the spectroscopic and solvation

properties of the azo compounds in isotropic and anisotropic nematic solvents is important for better understanding their photophysical behavior in isotropic and anisotropic surrounding.

In this work, the spectroscopic properties of *o*-, *m*-, *p*-cyano hydroxy azoquinolin dyes (see Supplementary Fig. 1a) in various organic solvents and in some anisotropic hosts with different polarities and polarizabilities were studied at room temperature. The hydroxy azoquinoline compounds investigated in this work possess an electron-withdrawing group, -C=N, attached to the phenyl ring. One of the principal aims of the investigation was to see how the location of -C=N group affects the spectral and tautomeric properties of the dyes.

The addition of a dye to a nematic host affects several host parameters, which is due to the strong mutual interactions between the dye and nematic molecules [14]. Therefore, the investigations of various kinds of guest–host systems are among the most important and needed in order to understand and provide further information about the intermolecular forces in anisotropic matrix. Among the many interesting properties of dye doped in liquid crystals, absorption anisotropy is one of the most important [15]. The guest–host interactions of azo dyes in liquid crystalline (LC) host have been the subject of much interest in recent years [16–18]. Such interest may arise from their optically switchable properties, due to photochromic *cis–trans* isomerization, in LC host.

As far as the authors are aware, no investigation on the azo/hydrazone tautomerism for the investigated dyes in various isotropic and anisotropic environments has been attempted. The most significance of this research is using polarized absorption method for investigation of the role of anisotropic media on the

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azo/hydrazone tautomerism. Therefore, this paper describes a comparative study on solvatochromic measurements in anisotropic and isotropic media. Moreover, this work is characterized by detailed quantitative studies on the nature and extent of solvent–solute interactions using correlations with multi-parameter solvent polarity scales.

2. Experimental

2.1. Materials

All the isotropic organic solvents with high purity were purchased from Merck and Fluka. Three pure liquid crystals were used in our experiments as anisotropic hosts. They are the pentyl cyanobiphenyl (5CB), octyl cyanobiphenyl (8CB), 4-*trans*-4*n*-hexyl-cyclohexyl-isothiocyanato-benzene (6CHBT), respectively (see Supplementary Fig. 1b). 8CB exhibits a smectic phase below the nematic to isotropic phase transition. In this work, the nematic mixtures of E7 (see Supplementary Fig. 1c) and 1751 with high and positive dielectric anisotropy were also used as anisotropic solvents. All the liquid crystalline materials were synthesized in the Institute of Chemistry of the Military Technical Academy, Warsaw, Poland.

2.2. Synthesis of the azoquinoline dyes

The azoquinoline dyes were successfully synthesized in our laboratory according to the route outlined in Scheme 1.

The purifying and drying of the compounds were performed according to the common procedure. The synthesized materials were characterized by conventional spectroscopic methods. The detail of the synthesis of the materials has already been reported [19]. Spectroscopic characterization utilized the following instrumentations: The absorption spectra of the compounds were scanned on a Cary UV-vis double-beam spectrophotometer (Model 100). FT-IR spectra were recorded on a Shimadzu Model



Scheme 1. Synthesis procedure used for preparation of the azoquinoline dyes.

FT-IR-8400. 1HNMR spectra were taken on a FT-NMR (500 MHz) Brucker versus TMS in CDCl₃ (Supplementary data Table 1). Melting points were recorded with an electro-thermal apparatus.

2.3. Liquid crystal cell preparation

The guest-host cell was made by sandwiching the solution between two optical glass plates ($2 \text{ cm} \times 1.2 \text{ cm}$). 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 spacing between the electrodes surfaces was 50 µm and was set by use of a Mylar. The introduction of the dissolved dye in nematic liquid crystal solvent was achieved by capillary action.

2.4. LD measurement

The polarized absorption spectra of the compounds in the liquid crystalline hosts were scanned on a Cary UV–vis double-beam spectrophotometer (Model 100) equipped with the sheet polarizers. The sample with homogeneous orientation of the guest and host molecules was mounted in a thermostated holder. Dichroic ratio *R* of the dissolved compound was obtained based on polarized absorption measurements [14,15]. The polarizer was rotated by 90°

Table 1

The maximum absorption wavelengths and the ratio of hydrazone/azo absorbances (A_h/A_a) of the azoquinoline dyes in isotropic and anisotropic solvents.

| Solvent | o-Azoquinoline | | | <i>m</i> -Azoquinoline | | | p-Azoquinoline | | |
|----------------------|-----------------|-----------------------|-----------------------|------------------------|-----------------------|-----------------------|-----------------|-----------------------|-----------------------|
| | λ_{azo} | $\lambda_{hydrazone}$ | $A_{\rm h}/A_{\rm a}$ | λ_{azo} | $\lambda_{hydrazone}$ | $A_{\rm h}/A_{\rm a}$ | λ_{azo} | $\lambda_{hydrazone}$ | $A_{\rm h}/A_{\rm a}$ |
| Isotropic solvent | | | | | | | | | |
| Cyclohexane | 402 | - | ~ 0 | 389 | - | ~ 0 | 395 | - | ~ 0 |
| 1,4-Dioxane | 406 | - | ~ 0 | 396 | 502 | 0.06 | 404 | - | ${\sim}0$ |
| CCl ₄ | 403 | - | ~ 0 | 393 | 494 | 0.08 | 400 | - | ${\sim}0$ |
| Benzene | 403 | - | ~ 0 | 393 | 509 | 0.08 | 401 | - | ${\sim}0$ |
| Toluene | 404 | - | ${\sim}0$ | 393 | 508 | 0.07 | 400 | - | ${\sim}0$ |
| Chloroform | 402 | - | ${\sim}0$ | 392 | 502 | 0.12 | 406 | 479 | 0.52 |
| 2-Ethyl-1-hexanol | 409 | - | ${\sim}0$ | 400 | 505 | 0.17 | 421 | 476 | 1.66 |
| Dichloromethane | 402 | - | ${\sim}0$ | 393 | 497 | 0.07 | 382 | - | ${\sim}0$ |
| Benzyl alcohol | 411 | - | ${\sim}0$ | 400 | 432 | 0.58 | 416 | 427 | 0.96 |
| 2-Butanol | 409 | 511 | 0.09 | 400 | 461 | 0.42 | 434 | 469 | 1.15 |
| 1-Butanol | 402 | 513 | 0.16 | 403 | 478 | 0.58 | 414 | 491 | 0.60 |
| 2-Propanol | 408 | 511 | 0.12 | 398 | 478 | 0.35 | 412 | 469 | 0.59 |
| Acetone | 402 | - | ${\sim}0$ | 392 | 484 | 0.15 | 406 | 522 | 1.26 |
| Ethanol | 406 | - | ${\sim}0$ | 403 | 471 | 0.69 | 409 | 458 | 0.55 |
| Benzonitrile | 404 | - | ~ 0 | 394 | 496 | 0.22 | 406 | 522 | 1.35 |
| Methanol | 405 | 510 | 0.17 | 397 | 468 | 0.49 | 413 | 442 | 0.86 |
| Acetonitrile | 401 | 514 | 0.33 | 389 | 504 | 0.15 | 407 | 517 | 1.66 |
| DMF | 437 | 511 | 1.55 | 405 | 505 | 1.15 | 419 | 538 | 1.90 |
| DMSO | 416 | - | ${\sim}0$ | 409 | 497 | 0.14 | 417 | - | ${\sim}0$ |
| Acetic acid | 404 | - | ${\sim}0$ | 392 | 520 | 0.14 | 404 | 480 | 0.39 |
| NaOH (1 M) | - | 513 | ${\sim}0$ | 454 | 494 | 1.48 | - | 514 | ${\sim}0$ |
| Anisotropic solvents | | | | | | | | | |
| 5CB | 404 | - | ~ 0 | 392 | - | ~ 0 | 416 | - | ${\sim}0$ |
| 8CB | 409 | - | ${\sim}0$ | 399 | - | ~ 0 | 410 | - | ${\sim}0$ |
| 6CHBT | 409 | - | ${\sim}0$ | 392 | - | ~ 0 | 410 | - | ${\sim}0$ |
| E7 | 411 | - | ~ 0 | 396 | - | ${\sim}0$ | 400 | - | ${\sim}0$ |
| 1751 | 408 | - | ~ 0 | 393 | - | ${\sim}0$ | 395 | - | ${\sim}0$ |



Fig. 1. Absorption spectra of (a) *o*-azoquinoline, (b) *m*-azoquinoline, and (c) *p*-azoquinoline in various solvents: (1) cyclohexane, (2) EtOH, (3) ACN, (4) benzene, (5) DMF.

to record the absorbances in parallel and perpendicular directions to the rubbing direction of the cell, A_{\parallel} and A_{\perp} , respectively.

3. Results and discussion

3.1. Solvent effect on the absorption spectra of the hydroxy azoquinolin-8-ol dyes

The Kamlet–Taft solvent parameters π^* , α , and β were used to indicate the polarity and hydrogen bonding properties of the



Fig. 2. Absorption spectra of the azoquinoline dyes in DMF: (a) *o*-azoquinoline, (b) *m*-azoquinoline, and (c) *p*-azoquinoline.

organic solvents used in this work. The Kamlet–Taft parameters (α , β , and π^*) are summarized in Supplementary Table 2. α is the scale of solvent hydrogen bond donor ability (HBD), β is the scale of solvent hydrogen-bond acceptor ability (HBA). The π^* is a measure of 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 [13].

The visible absorption spectra of the hydroxy azoquinolin compounds (ca. 1×10^{-5} M) were obtained at room temperature in various organic solvents with different polarity. The selective spectral data are summarized in Table 1. Typically, Fig. 1(a–c) presents electronic absorption spectra of the azoquinoline compounds in five selected solvents. The absorption spectra of the compounds in cyclohexane, which is used as reference solvent, are also shown in the figures. The choice of cyclohexane as a base for solvatochromic behavior measurement was motivated by the following considerations. Cyclohexane is a non-polar and non-HBD/HBA solvent with very low dielectric constant (ε = 2.02) and its solvatochromic parameter values of cyclohexane are equal zero. Therefore, this solvent is a good reference in the solvatochromism investigations.

It can be seen that the spectral profile considerably changed with the solvent polarity. The electronic spectra of the compounds in some organic solvents exhibit dual absorption bands. This feature can be attributed to the formation of azo/hydrazone tautomerism, where the absorption band at longer wavelength region is due to the hydrazone formation. The azo/hydrazone tautomerism is more obvious for the dyes dissolved in dimethylformamide (DMF), where the hydrazone form is dominated in this polar solvent (Fig. 2). DMF with high dielectric constant is known to enhance the medium basicity, and therefore, the azo form should be converted into its hydrazone form; i.e. the –NH group in the hydrazone form should be more stabilized in this solvent.



Percentage of different parameters contributions for Kamlet-Taft multiparameter scale.

| Dve | Absorbance | α | β | π^* |
|----------------|------------|---------|----------|----------|
| 290 | Hoborbance | | ۴ | |
| o-Azoquinoline | Azo | 34 (±3) | 62 (±4) | 4 (±3) |
| | Hydrazone | 19 (±9) | 40 (±16) | 41 (±19) |
| m-Azoquinoline | Azo | 19 (±4) | 69 (±6) | 12 (±5) |
| | Hydrazone | 57 (±5) | 7 (±6) | 36 (±9) |
| p-Azoquinoline | Azo | 1 (-) | 71 (±17) | 28 (±13) |
| | Hydrazone | 45 (±4) | 22 (±5) | 33 (±6) |



Fig. 3. Normalized absorption spectra of *m*-azoquinoline in alcohols: (1) EtOH, (2) 1-BuOH, (3) MeOH, (4) 2-BuOH and 2-PrOH, (5) 2EH, (6) BZOH.

Table 3

Percentage of different parameters contributions for Katritzky multiparameter scale.

| Dye | Absorbance | $P_{\rm ET}(30)(\%)$ | $P_{\varepsilon_{\mathrm{r}}}$ (%) | <i>P</i> _n (%) |
|----------------|------------|----------------------|------------------------------------|---------------------------|
| o-Azoquinoline | Azo | 11 (±3) | 26 (±5) | 63 (±32) |
| | Hydrazone | 24 (±0) | 34 (±0) | 42 (±0) |
| m-Azoquinoline | Azo | 67 (±10) | 18 (±9) | 15 (±8) |
| | Hydrazone | 66 (±8) | 19 (±4) | 15 (±5) |
| p-Azoquinoline | Azo | 52 (±11) | 23 (±10) | 25 (±6) |
| | Hydrazone | 48 (±4) | 45 (±6) | 7 (±2) |

In this work, the effect of acid and base media on the visible absorption maxima of the dyes was also investigated. It was observed that the absorption spectra of the compounds were very sensitive to basic solution, and the hydrazone form is entirely dominated in basic aqueous solution (0.1 M NaOH). In contrast, the azo form is totally dominated in acidic medium (acetic acid). A typical example for the dyes in basic solution is shown in Supplementary Fig. 2.

The spectral features of the compounds in polar protic solvents (alcohols) were obtained. As an example, Fig. 3 shows the absorption spectra of *m*-azoquinoline in the alcoholic solutions. In the protic solvents, the tautomeric equilibrium is shifted to the less polar tautomer. It could be due to the formation of inter-molecular H-bonding between the HBD solvents and –OH group in the azo form, which should mainly stabilize the less polar.

3.2. Correlation with multi-parameter solvent polarity scales

In this work, the Kamlet–Taft [13] and Katritzky [12] multiparameter equations were used for quantitative evaluation of the solvent effects:

$$\bar{\nu} = \bar{\nu}_0 + a' \times \alpha + b' \times \beta + c' \times \pi^* \tag{1}$$

$$\bar{\nu} = \bar{\nu}_{0} + a \times E_{\mathrm{T}}(30) + b \times \left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) + c \times \left(\frac{n^{2} - 1}{2n^{2} + 1}\right)$$
(2)

Table 4

The mean dielectric constants ($\tilde{\epsilon}$) and refractive indices (\tilde{n}) of the liquid crystals, taken from Ref. [18].

| Anisotropic host | Ē | n |
|-------------------|-------|-------|
| 6CHBT | 6.80 | 1.566 |
| 5CB | 10.10 | 1.587 |
| 6CB | 9.80 | 1.583 |
| 8CB | 7.93 | 1.570 |
| E7 ^a | 9.80 | 1.592 |
| 1751 ^a | 21.00 | 1.560 |

^a Nematic mixture.



Fig. 4. Absorption spectra of the azoquinoline dyes ((a) *o*-azoquinoline, (b) *m*-azoquinoline, and (*c*) *p*-azoquinoline) in the liquid crystalline solvents: (1) 8CB, (2) 5CB, (3) 6CHBT, (4) E7.

where $\bar{\nu}$ is the solute property (band maximum in cm⁻¹) and the coefficients *a*, *a'*, *b*, *b'* and *c*, *c'* are the relative susceptibilities of $\bar{\nu}$ to the indicated solvent parameters. The Kamlet–Taft equation originally evaluates specific hydrogen bonding donor/acceptor interactions between solute and solvent, while the Katritzky equation essentially evaluates dipolarity/polarizability interactions between solute and solvent. The Kamlet–Taft equation combines spectroscopic polarity scales including hydrogen bonding donor ability (α), hydrogen bonding accepting ability (β) and dipolarity/

Table 5

The dichroic ratios (R) and the order parameters (S_{dye}) of the azoquinoline dyes in the anisotropic media.

| LC | o-Azoquinoline | | <i>m</i> -Azoq | uinoline | p-Azoquinoline | |
|-------|----------------|------------------|----------------|------------------|----------------|------------------|
| | R | S _{dye} | R | S _{dye} | R | S _{dye} |
| 5CB | 1.49 | 0.14 | 1.51 | 0.14 | 1.32 | 0.10 |
| 8CB | 1.47 | 0.13 | 1.67 | 0.18 | 2.31 | 0.30 |
| 6CHBT | 1.69 | 0.19 | 1.62 | 0.17 | 2.42 | 0.32 |
| E7 | 1.37 | 0.11 | 1.53 | 0.15 | 2.38 | 0.31 |
| 1751 | 1.75 | 0.20 | 1.32 | 0.10 | 1.65 | 0.18 |

polarizability (π^*) as a multiparameter scale. It was found that generally both Kamlet–Taft and Katritzky polarity scales correlate the spectral data of each synthesized dye acceptably. The correlated results for both the scales (Supplementary data Tables 3 and 4) were obtained using the data quoted in Table 1 and multi-linear regression analysis. The obtained result for the solvents were transformed into percentage contributions and summarized in Tables 2 and 3 for clarification.

According to Kamlet–Taft correlations, for the dyes, the solvent hydrogen-bond acceptor ability (β) possesses the main contribution into spectral feature in azo region. In contrast, this contribution decreases in hydrazone regions, irregularly. As it can be seen from Table 3, except for *o*-azoquinoline, the Katritzky multi-parameter correlation shows that the value connected with $E_{\rm T}(30)$ has the major effectiveness. However, contributions assigned to dipolarity and polarizability of the solvent cannot be ignored. In hydrazone region, these contributions alter differently for different dyes.

3.3. Absorption spectrum of the azoquinoline dyes in anisotropic hosts

The mean dielectric constant and refractive index in the nematic phase can be calculated using:

$$\bar{\varepsilon} = \frac{1}{3} (\varepsilon_{\parallel} + 2\varepsilon_{\perp}) \tag{3}$$

$$\bar{n} = \frac{1}{3}(n_{\rm e} + 2n_{\rm o}) \tag{4}$$

where ε_{\parallel} and ε_{\perp} are dielectric constants parallel and perpendicular to the molecular axis, respectively. n_0 and n_e are the ordinary and extraordinary refractive indices, respectively. As it can be seen, the investigated compounds experience a wide range of polarity and polarizability in anisotropic media (Table 4). Therefore, in this investigation we might be able to determine the role of dipole–dipole interactions between the dye and the nematic media.

The anisotropic solvation characteristics of the investigated dyes in liquid crystals with various polarity and polarizability were investigated at room temperature. The selective spectral data in the anisotropic media are also summarized in Table 1. Fig. 4(a-c) shows the visible absorption spectra of the dyes in various liquid crystalline hosts (0.1%, w/w). The absorption spectra of the compounds in cyclohexane, which is used as reference solvent, are also shown in the figures. As it can be seen, the compounds appear to exist almost in its azo form in the anisotropic solution. Interestingly, the similarities of the spectra behavior (azo form) observed in the polar nematic hosts and cyclohexane with remarkable dissimilar physical properties cannot be explained based on regular solvatochromic behavior.

The spectral behavior of the investigated compounds in nematic solvents should have multiple origins, and several interactions contribute to some extent. Therefore, the influence of anisotropic medium on the solvation of the compound should be complicated. It should be concluded that, the spectral features in the nematic hosts might depends on several factors such as solvent polarity,



Fig. 5. Polarized absorption spectra of the azoquinoline dyes ((a) *o*-azoquinoline, (b) *m*-azoquinoline, and (c) *p*-azoquinoline) in 5CB.

viscosity, molecular packing, host rigidity and polarizability. Therefore, the anisotropic medium provides a relatively rigid, packed and polarizable environment for the solute molecules, and thus prevents azo/hydrazone tautomerism.

3.4. Linear dichroism of the hydroxy azoquinolin-8-ol dyes

The polarized absorptions spectra of the compounds were recorded in parallel-aligned liquid crystal cells and their dichroic



Fig. 6. Polarized absorption spectra of the azoquinoline dyes ((a) *o*-azoquinoline, (b) *m*-azoquinoline, and (c) *p*-azoquinoline) in 8CB.

ratios were obtained. The dichroic ratios $(R=A_{\parallel}/A_{\perp})$ of the dyes dissolved in the nematic host were calculated from the absorption of light polarized parallel (A_{\parallel}) and perpendicular (A_{\perp}) to the liquid crystal alignment (rubbing direction). The dichroic ratio directly relates to the orientational order parameter, S_{dye} , for the transition moment of dye absorption which is responsible for the color of the dye. The orientational order parameter of the dye dissolved in oriented nematic host can be determined from the expression:

$$S_{\rm dye} = \frac{R-1}{R+2} \left(\frac{1}{(1/2)(3\cos^2\beta - 1)} \right)$$
(5)

This equation can be used to evaluate the order parameter of the dye if the angle β is known [14]. If the transition moment vector between two electronic states of the dye is directed along its long molecular axis (i.e. β = 0), Eq. (5) reduces to:

$$S_{\rm dye} = \frac{R-1}{R+2} \tag{6}$$

The angle between the absorption oscillator and the long molecular axis (β) is unknown for the dyes under study. If we assume β = 0, and estimate the order parameter of the dye dissolved in the nematic host by using Eq. (6). However, for these dyes $\beta \neq 0$, so the term of "*degree of anisotropy*" could be applied instead of order parameter.

Polarized absorption spectra of the compounds dissolved in parallel-aligned nematic hosts were recorded at room temperature. Typically, Figs. 5 and 6 show the polarized absorption spectra of the compounds in 5CB and 8CB, respectively. The dichroic ratios and degree of anisotropies of the compounds were complied in Table 5. The low values of these parameters for the investigated dyes in the ordered anisotropic host might be related to the several factors, i.e. the dye molecular structure, the intermolecular interactions between the dye and liquid crystal molecules, and the angle between the transition dipole moment and the long molecular axis. Moreover, the alignment properties of the guest–host systems can be affected by the molecular structures of the dyes. In other words, the director orientation can be altered by shape, size and structure of the dye over long distances.

4. Conclusions

The synthesized hydroxy azoquinolin-8-ol dyes were used in this research. The spectral data show the importance of location of CN group attached to the aromatic skeleton in these compounds. The spectral behavior of the compounds and the ratio of azo/hydrazone mixture are largely changed by the position of this electron-attracting group.

The experimental result indicated that the strong azo/hydrazone tautomerism occurred in some polar solvents such as DMF. This phenomenon is more evidence for *m*-azoquinoline. However, in solvents of low polarity, the azo form is dominated. Interestingly, the compounds appear to exist almost entirely in its azo form in the anisotropic media (both the polar and low polar). In conclusion, the anisotropic solvents provide relatively rigid, packed and polarizable media for the dye molecules, and therefore, prevent azo/hydrazone tautomerism.

According to the dichroism results obtained in the present work the dichroic ratios *R* of the dyes are larger than one. This means that the absorption bands for these dyes could be considered as parallel transition (i.e. $\pi - \pi^*$).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2011.11.020.

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