Solvatochromism, tautomerism and dichroism of some azoquinoline dyes in liquids and liquid crystals

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ABSTRACT

Absorption and emission spectra of three hetarylazoquinoline compounds with different substituents were examined in liquids and liquid crystalline solvents for the first time. The spectral features of the hetarylazoquinoline dyes were explained according to azo/hydrazone tautomerism in conjunction with the solvatochromic characteristic of the preferred tautomer. The nature and extent of solute–solvent interactions were described using Kamlet–Taft and Katritzky multiparameter polarity scales. It was observed that solvatochromic azo/hydrazone tautomerism depend on multiple solute-solvent interactions, in particular on specific interactions and the solvent ability to transport the hydrogen atom through the media. In addition, it was concluded that anisotropic hosts prevent shift of the tautomeric equilibrium toward the hydrazone form.

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1. Introduction

Hydroxy azo dyes are the most widely used class of coloring materials due to their massive application in various fields of science and technology. They are mainly used for coloring substrates in biological and medical studies and in the field of non-linear optics and optical data storage devices [1–3]. Many studies have been dedicated to synthesis and spectroscopic characterization of these dyes for improving their photophysical and photochemical features.

Some important investigations have been carried out on the synthesis and spectroscopic behavior of heteroarylazo dyes by Ertan and coworkers [4–7] and Karci [8]. In particular, synthesis and tautomerism of aryl and hetaryl azo derivatives with the 8-hydroxyquinoline have been explored by Amin [9] and Ahmed [10] and El-Bindary and co-workers [11] and other authors [12–14]. More recently, a good review article about synthesis and characterization of aryl and hetaryl azo compounds have been reported by Shawali [15]. Hetarylazoquinoline compounds have been put to much use in dye chemistry, and they have many scientific and industrial applications [12].

Some important phenomena in the solution chemistry of azo dyes include aggregation, tautomerism, as well as electrostatic, hydrophobic, acid/base and hydrogen bonding interactions. The importance of each process depends on structural and environmental factors [16–18]. Among these phenomena, azo-hydrazone tautomerism is quite interesting both from theoretical and practical standpoints. It is described by the intramolecular proton transfer between the phenol and imine groups in ground and/or excited state. Azo-hydrazone tautomerism has been extensively studied regarding color and other related industries. The azo-hydrazone tautomerism in solution and solid state is very interesting both from theoretical and practical point of view, as the tautomers possess different optical behavior and dyeing ability [19]. The hydrazone form that absorbs light at longer wavelengths was found to provide higher photoconductivity to dual-layered photoreceptors [20], hence the hydrazone tautomer is often commercially preferred. Moreover, a well-known photochromic cis–trans isomerization of azo compounds depends on the state of the tautomeric equilibrium, which can be directly influenced by the host media [21].

The azo-hydrazone tautomerism in hydroxy azo compounds has been known for many years and was reviewed several times [22]. Structural requirement for tautomerism is existence of a labile proton. This requirement is noticeable in the case of azo dyes, containing OH or NHR group, conjugated with azo group. Observation of

such tautomerism in solution depends on several factors such as solvent, temperature, concentration, and so on. However, principally the relative thermodynamic stability of the azo or hydrazone tautomer determines shift of the tautomeric equilibrium toward one of the tautomers [23].

The state of azo-hydrazone equilibrium in solution is closely related to the nature and degree of dye-solvent, specific and/or non-specific interactions [24]. Generally, hydrazone form is favored by polar media, and by electron-withdrawing substituents in the conjugated phenyl ring. The spectral changes observed for azo/hydrazone tautomerism arises from a relatively large dipole moment changes during transition from azo to hydrazone state that is stabilized in more polar solvents [25,26].

The guest−host interactions of azo dyes in liquid crystalline (LC) host have been the subject of much interest in recent years [27−29]. Such interest may arise from their optically switchable properties due to photochromic cis−trans isomerization in LC host. Dynamics inter-conversion between the cis−trans photostable states, under illumination, makes azo dyes potential candidate for use in molecular devices [30]. In fact, only azo tautomer is superior for cis−trans inter-conversion while presence of hydrazone tautomer diminishes it. In spite of extensive reports on the spectroscopic behavior of the tautomeric compounds in various environments, based on the authors literature review, anisotropic solvent effect on the azo-hydrazone tautomerism has attracted little attentions.

Spectroscopic methods, based on dye absorption and emission, give valuable information on contribution of different types of solute-solvent interactions using multi-parameter solvent polarity scales. It was shown that correlations of spectral properties are significantly improved by such multiparameter treatment [31]. This method allows various independent interactions to be characterized implicitly between solvent and solute ground, transition, and excited states. Knowledge of the spectroscopic properties of the azo compounds in liquid and liquid crystalline solutions is important for better understanding their photo-physical behavior in isotropic and anisotropic surrounding [32].

Present work was undertaken using non-polarized and polarized absorption and fluorescence spectroscopy for investigating three heteroarylazo compounds, with different substituents on benzothiazol moieties, in organic liquids and in liquid crystalline media. The unique absorption and emission spectra of the tautomeric species were used for characterizing the tautomers features and interactions in isotropic and anisotropic 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. Furthermore, this paper concerns the effect of different substituents on azo/hydrazone tautomerism. Such information is essential for design of new azo derivatives where one of the tautomers is preferentially dominant depending on the host environment, with the consequent optimization in the dye photophysical properties such as optical nonlinearity, photo switchability. The work reported here also provides information about the effect of anisotropic medium on azo/hydrazone tautomerism of the investigated compounds.

2. Experimental

2.1. Materials

All the isotropic organic solvents with high purity (spectroscopic grade) were obtained from Merck and their physical properties along with their polarity parameters are taken from Ref [33]. The solvents listed in the Appendix (see Table 1-A).

Four pure liquid crystals were used in our experiments as anisotropic hosts (Fig. 1). They are pentyl cyanobiphenyl (5CB),
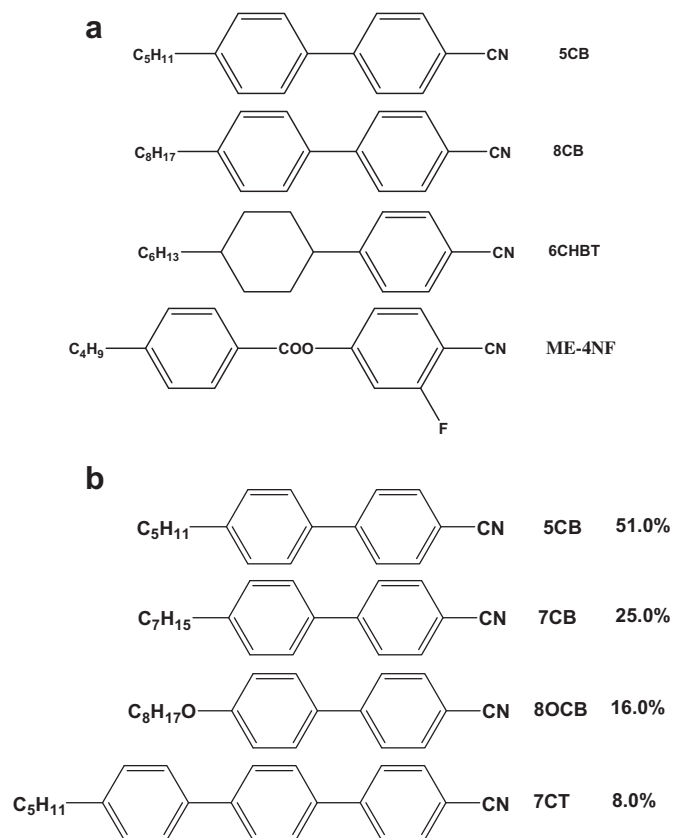

Fig. 1. Molecular structures of the liquid crystalline hosts, a) pure liquid crystals, b) eutectic nematic mixture of E7.

octyl cyanobiphenyl (8CB), 4-trans-4-*n*-hexyl-cyclohexyl-iso-thiocyanato-benzene (6CHBT) and 4-butyl-benzoic acid 4-cyano-3-fluorophenyl 4-butylbenzoate (ME-4NF), respectively. 8CB exhibits a smectic phase below the nematic to isotropic phase transition. Note that the phase is monotropic for ME-4NF. In addition, two nematic mixtures of E7 (eutectic mixtures of cyanobiphenyls and terphenyl) and 1751 (mixture of six cyano esters with alkyl terminal chain) with high and positive dielectric anisotropy were used as anisotropic solvents. All the liquid crystalline materials were synthesized in the Institute of Chemistry of the Military Technical Academy, Warsaw, Poland.

The hetarylazoquinoline dyes were successfully synthesized in our laboratory according to the route summarized in Scheme 1 [12,13]. These dyes are 5-(2-benzothiazolylazo)-8-hydroxyquinoline (H-BTHQ) [9], and two *nitro-* and *methoxy-* substituted BTHQ dyes as 5-(6-*nitro*-2-benzothiazolylazo)-8-hydroxyquinoline (N-BTHQ) and 5-(6-*methoxy*-2-benzothiazolylazo)-8-hydroxyquinoline (M-BTHQ). The synthesized materials were characterized by conventional spectroscopic methods and were used as guest materials. Spectroscopic characterization performed as follow: The absorption spectra of the dyes were scanned on a Cary-100 UV−Vis. double-beam spectrophotometer. FT-IR spectra were recorded on a Shimadzu-8400 FT-IR spectrometer. ^{1}HNMR spectra were taken on a Brucker 500 MHz spectrometer in CDCl$_3$ using TMS as internal reference. Melting points were recorded with an Electro-thermal apparatus.

2.1.1. Preparation of 5-(2-benzothiazolylazo)-8-hydroxy quinoline

2-Aminobenzothiazole (2.0×10^{-3} mol, 0.300 g) was dissolved in glacial acetic acid: propionic acid mixture (2:1, 6.0 ml) and was quickly cooled in an ice/salt bath to 0−5 °C. The liquor was then added in portions during 15 min to a cold solution of nitrosyl
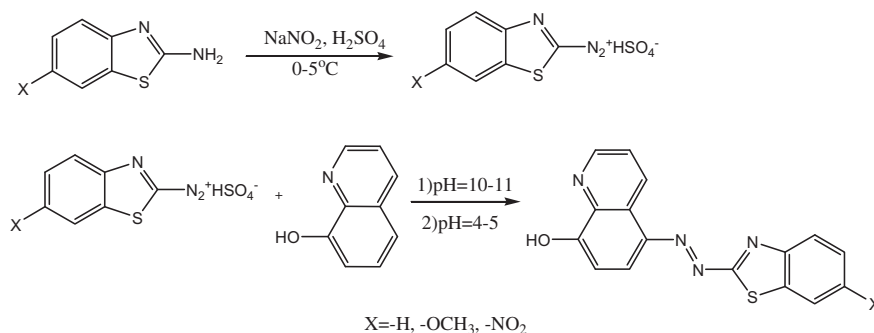
Scheme 1. Synthesis procedure used for preparation of the BTHQ dyes.

sulphuric acid (prepared from sodium nitrite (2.2 mmol, 0.15 g) and concentrated sulphuric acid (3 ml at 50 °C)). The mixture was stirred for an additional 3 h at the same temperature. Excess nitrous acid was destroyed by the addition of urea. After diazotization was complete, the diazo liquor was slowly added to vigorously stirred solution of 8-hydroxyquinoline (2.0×10^{-3} mol, 0.29 g) in Potassium hydroxide (2.0×10^{-3} mol, 0.112 g) and water (25 ml). The solution was stirred at 0–5 °C for 2 h and the pH of the reaction mixture was maintained at 10–11 by the simultaneous addition of 2.5% sodium hydroxide solution. In the end of procedure, the pH of reaction mixture was regulated at 4–5 by addition of 10% hydrochloric acid solution. After 30 min., the resulting solid was filtered, washed with cold ethanol and dried.

Recrystallization from DMF-H_2O gave dark red crystalline5-(2-benzothiazolylazo)-8-hydroxy quinoline (yield: 0.19 g, 62%; m.p. 238–240 °C). FT-IR (KBr): ν_{max}: 3436–3243(br, quinoline −OH), 1596(C=C), 1565(N=N), 1373(C−O) cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ 9.35 (1H, d, $J = 8$ Hz), 8.95 (1H, t), 8.42(1H, d, $J = 8.5$ Hz), 8.21(1H, d, $J = 8$ Hz), 8.09 (1H, d, $J = 8$ Hz), 7.94–7.44 (4H, m, Overlapped).

2.1.2. Preparation of 5-(6-nitro-2-benzothiazolylazo)-8-hydroxy quinoline

This dye was prepared from 6-nitro-2-amino-benzothiazole and 8- hydroxyquinoline as dark red crystals (yield: 0.19 g, 54%; m.p. 270 °C (dec.)). FT-IR (KBr): ν_{max}: 3400–3254 (br, quinoline −OH), 1610(C=C), 1584(N=O), 1518(N=N), 1325(N=O), 1375(C−O) cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ 9.33 (1H, d, $J = 8.5$ Hz), 8.98 (1H, t), 8.42(1H, d, $J = 8$ Hz), 8.23(1H, d, $J = 8.5$ Hz), 8.09 (1H, d, $J = 8$ Hz), 8.04–7.38 (3H, m, overlapped).

2.1.3. Preparation of 5-(6-methoxy-2-benzothiazolylazo)-8-hydroxy quinoline

This dye was prepared from 6-methoxy-2-amino-benzothiazole and 8- hydroxyquinoline as clear red crystals (yield: 0.27 g, 80%; m.p. 228–230 °C). FT-IR (KBr): ν_{max}: 3416–3284 (br, quinoline −OH), 1606(C=C), 1574(N=N), 1383(C−O) cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): 3.80(3H,s,OCH$_3$), 9.15 (1H, d,$J = 9.3$ Hz), 8.82(1H, d,$J = 9.3$ Hz), 7.88(1H, d, $J = 8$ Hz), 7.63(1H, d, $J = 7.5$ Hz),7.37–7.08 (4H, m, overlapped).

2.2. Measurement of absorption and fluorescence spectra

The absorption spectra of the dyes in liquid and liquid crystalline media were recorded on a double beam Shimadzu UV−Visible spectrophotometer (Model UV-2450 Scan) over a wavelength range between 300 and 800 nm at room temperature. Fluorescence spectra of the dyes in different hosts were studied on a JASCO FP-6200 spectrofluorometer with standard Quartz cuvettes. The uncertainties

in the measured wavelength of absorption and fluorescence maxima are ±0.1 nm and ±1 nm, respectively.

2.3. Liquid crystal cell preparation

The guest−host cells were made by sandwiching the two optical glass plates (2×1.2 cm^2). The spacing between the plates was about 50 μm and was set by use of a Mylar spacer sheet. The plates were sealed together by a sealing material (e.g. epoxy resin glue). The planar orientation of the guest and host molecules was achieved by surface treatment of polyvinyl alcohol film coated on inner surface of the optical glass plates, followed by the rubbing process. The dye-doped liquid crystal samples were introduced into the cells by capillary action. The liquid crystal cell was checked under cross polarizers, and used in subsequent linear dichroism studies [34].

3. Results and discussion

3.1. Solvent effect on absorption and emission spectra of BTHQ dyes

The spectral characteristics and solvatochromic behavior of the BTHQ dyes in various organic solvents (23 solvents) were investigated at room temperature. The obtained spectral data are summarized in Table 1.

Fig. 2(a−c) presents absorption spectra of the BTHQ dyes (H-BTHQ, N-BTHQ, and M-BTHQ) in selected isotropic solvents. As it can be seen, the shape and maximum wavelength of the absorption spectra of the dyes are affected by the solvent polarity. The absorption spectra of BTHQs are strongly solvent dependent and show significant variation with increasing solvent polarity. Cyclohexane as a non-polar and non-associated solvent with very low dielectric constant ($\varepsilon = 2.02$) is the reference solvent in solvatochromic and tautomerism investigation. All the BTHQ dyes show simple transition band at shorter wavelengths in cyclohexane. On going from cyclohexane to the polar protic and aprotic solvents i.e. with increasing solvent polarity and acidity/basicity, generally, the absorption band at longer wavelengths dominate; however, these variation can not be interpreted and generalized confidently.

It is evident from the figure; the optical spectra of these dyes exhibit two distinct absorption bands in various liquid solvents. This feature can be attributed to the formation of azo/hydrazone tautomerism (Fig. 3), where the absorption band at longer wavelength region is due to the hydrazone formation.

Fig. 2(b) and (c) represents selected absorption spectra of N-BTHQ and M-BTHQ dyes, respectively. These two dyes show the same azo and hydrazone spectral characteristics, however, with some difference. It is obvious from the data in Table 1 that N-BTHQ is in hydrazone form in larger number of the solvents as compared

Table 1
Absorption and emission spectral data for the BTHQ dyes.

Solvent	H-BTHQ		N-BTHQ		M-BTHQ	
	$\tilde{\nu}_a$ (cm^{-1})	$\tilde{\nu}_f$ (cm^{-1})	$\tilde{\nu}_a$ (cm^{-1})	$\tilde{\nu}_f$ (cm^{-1})	$\tilde{\nu}_a$ (cm^{-1})	$\tilde{\nu}_f$ (cm^{-1})
Cyclohexane	23584.9	–	22831.1	20920.5	22321.4	–
Tetra chloromethane	23310.0	18797.0	22779.0	20080.3	22075.1	–
Toluene	22831.1	–	17889.1	–	21598.3	–
Benzene	23094.7	19802.0	21645.0	19723.9	21881.8	19157.1
Diethyl ether	23364.5	20720.8	22573.4	19646.4	22271.7	20527.1
1,4-Dioxane	22831.1	19685.0	21413.3	19305.0	21786.5	20138.6
Dichloromethane	22883.3	18484.3	21459.2	18382.4	21367.5	19011.4
Acetone	22727.3	19157.1	18518.5	16286.7	21881.8	–
DMF	17889.1	16366.6	16694.5	16366.6	18050.5	16393.4
DMSO	22123.9	19855.9	20661.2	–	20284.0	17825.3
Acetonitrile	18726.6	–	17574.7	–	18181.8	–
Decanol	18148.8	17093.1	16977.9	–	21276.6	19973.2
1-Heptanol	21834.1	19120.5	17094.0	17035.8	21276.6	18518.5
1-Butanol	17825.3	16806.7	17006.8	–	18450.2	17064.9
Benzyl alcohol	20491.8	–	18148.8	–	19607.8	–
Propionic acid	21834.1	–	20284.0	–	20661.2	–
Ethanol	17953.3	15151.5	17123.3	15290.5	17889.1	15128.6
Methanol	17985.6	–	17361.1	–	18214.9	16778.5

to H-BTHQ, while M-BTHQ shows hydrazone characteristics in a few numbers of the solvents.

The emission spectra of the investigated dyes in alcoholic solutions (ethanol and 1-butanol) are shown in Fig. 4a and b. It has been demonstrated that the azo tautomers are non-fluorescent in most cases and emission is only due to the hydrazone forms [22,35]. Detection of weak fluorescence in some of the BTHQ solutions indicates that small concentrations of the hydrazone tautomer are present. It means that the dye molecular structure, shape of spectrum and the peak position variations might be controlled by the solvent−dye interactions.

Apart from the solvent effect, the azo/hydrazone tautomerism is strongly influenced by the substituents structure and nature. The existence of an electron-donor substituent ($-OCH_3$) in the benzo-thiazol ring of the tautomeric system enhances the polarization of the molecule, and decreases the acidic character of the OH proton. Total effect evidently will be shift of the tautomeric equilibrium toward the azo form. The introduction of an electron acceptor substituent ($-NO_2$) will relatively stronger enhances charge transfer and formation of a donor−acceptor conjugated system. The direction of this change depends on the relative strength and position of the substituent, since the conjugated system formed has at both ends two substituents of similar nature. Therefore, we can expect a shift of the tautomeric equilibrium toward the hydrazone form. These explanations are in agreement with literature conclusions [36,37].

3.2. Correlation with multi-parameter solvent polarity scales

According to the results reported by Reeves and Kaiser [38] there is no correlation between empirical parameters reflecting the solvent polarity and the position of the azo-hydrazone tautomeric equilibrium. However, it was found that for the investigated dyes dependable correlations could be obtained between multiparameter polarity scales, Kamlet−Abboud−Taft (KAT) and Katritzky (KTZ) scales, and peak position of the absorption and emission bands. Such correlations characterize contribution of different type of solute-solvent interactions into the observed spectral features of the dyes [39]. The polarity scales were applied as:

$$A = A_o + aE_T(30) + b\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) + c\left(\frac{n^2 - 1}{2n^2 + 1}\right) \quad (1.a)$$

$$A = A_o + a' \cdot \alpha + b' \cdot \beta + c' \cdot \pi^* \quad (1.b)$$

A is the solute property (such as $\tilde{\nu}_a$, $\tilde{\nu}_f$ and $\tilde{\nu}_a - \tilde{\nu}_f$) and the coefficients a, a', b, b' and c, c' measure the relative susceptibilities of this property to the indicated solvent parameters. Katritzky et al. combined successfully Reichardt polarity function ($E_T(30)$) with the dielectric constant and index of refraction functions as a multi-parameter polarity scale. The KAT equation combines spectroscopic polarity scales including hydrogen bonding donor ability (HBD: α), hydrogen bonding accepting ability (HBA: β) and dipolarity/polar-izability (π^*) as a multiparameter scale. The KAT equation originally evaluates specific hydrogen bonding donor/acceptor interactions between solute and solvent, while the KTZ equation essentially evaluates dipolarity/polarizability interactions between solute and solvent [33].

It was found that partitioning the spectral data in reference to different spectral features of azo and/or hydrazone tautomers, give results that are more reliable. First, we have used all the solvents in multi-parameter analysis, and then according to statistical factors (larger coefficient of determination and smaller values for significance of F-test) and visual inspection we have removed inappropriate data in each set and selected the maximum number of data that satisfy the statistical criteria. Choice of the appropriate solvents in each group is very important in correlation of data and solvatochromic analysis. In fact, the solvents were selected according to the nature of intermolecular interactions and effect of these interactions on tautomeric equilibrium, rather than the bulk solvent properties. Because of tautomerism and solvent effect, three major regions including azo region, hydrazone region and an intermediate region can be identified through the absorption data analyses (Fig. 5). However, in correlation of fluorescence and stokes shift data, such partitioning cannot be used; It is due to the fact that just the hydrazone form demonstrates weak fluorescence emission.

It was found that generally both KAT and KTZ polarity scales correlate the dyes spectral data acceptably. For KTZ equation, in order to have a comparable coefficients values (i.e. a', b' and c'), we have re-normalized and re-scaled the parameters for all the employed solvents. The correlated results for both the scales were obtained using the data quoted in Table 1 and multi-linear regression analysis. The regression analyses were listed in the Appendix (Tables 2-A−4-A).

The obtained result for the liquid solvents were transformed into percentage contributions and summarized in Table 2 for clarification. According to KAT correlations, Table 2, for all the dyes dipolarity/
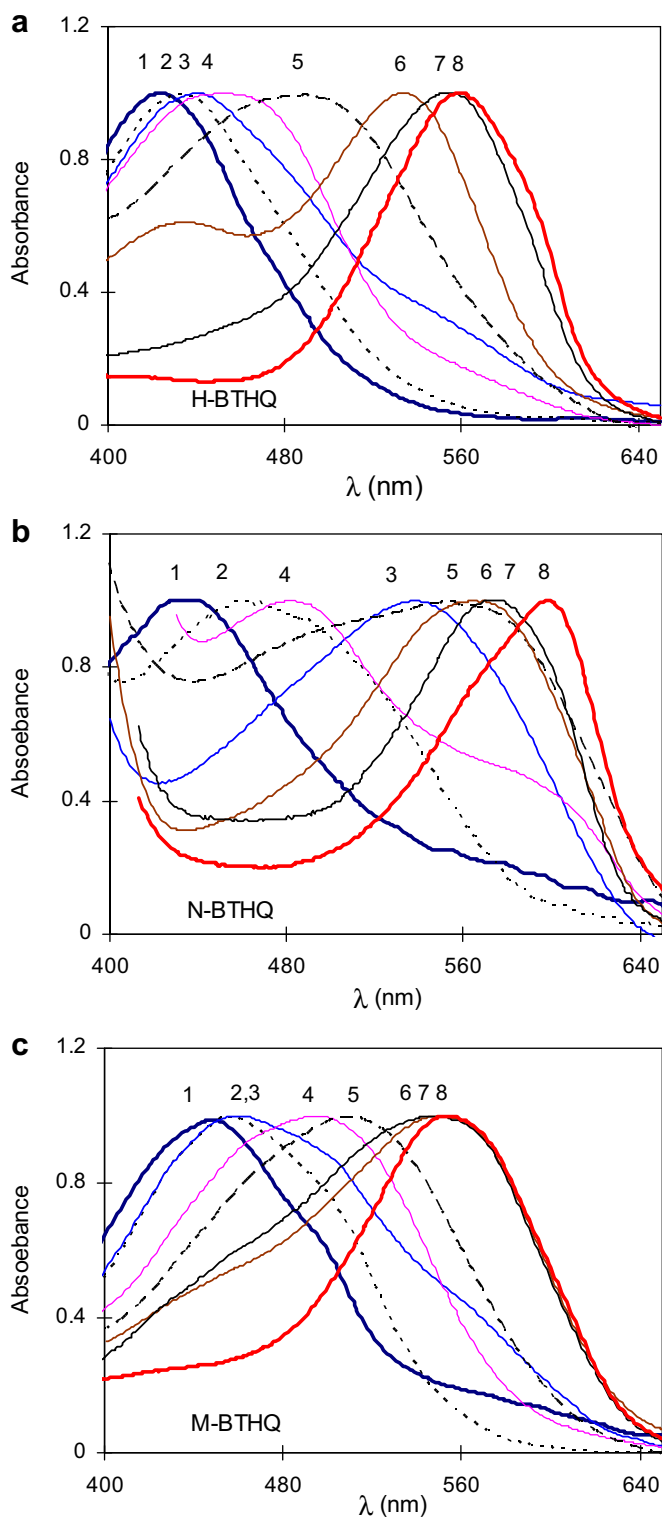
Fig. 3. Azo/hydrazone tautomerism.

region decreases, while number of solvents in azo region increases. It is in accordance with the conclusion that was made on substituent effect in previous section. As the data in this table show, going from ground state to excited state, in hydrazone region, dipolarity/polarizability contribution does not change considerably, while specific interaction contributions vary significantly.

As it can be seen from Table 2, KTZ multi-parameter correlation shows that, for absorption and emission data, generally, the value connected with $E_T(30)$ has the major effectiveness. It is in agreement with the results obtained from KAT correlations. However, contributions assigned to dipolarity and polarizability of the solvent cannot be ignored. Going from ground state to excited state, in hydrazone region, these contributions alter differently for different

Fig. 2. Normalized absorption spectra of the BTHQ dyes in 1) cyclohexane, 2) benzene, 3) acetone, 4) DMSO, 5) benzyl alcohol, 6) acetonitrile, 7) methanol, 8) DMF.
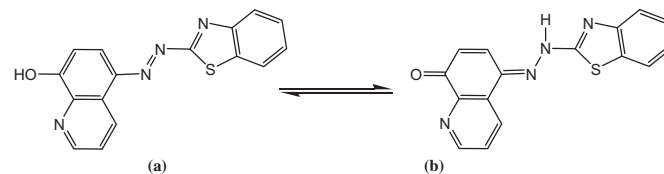
polarizability (π^*) interaction possesses the main contribution into spectral feature in azo region. This contribution decreases going to intermediate and, particularly, hydrazone regions. In contrast, contributions of hydrogen bond donor and/or acceptor abilities increase in these regions. It should be mentioned that going from N-BTHQ to H-BTHQ and M-BTHQ number of solvents in hydrazone
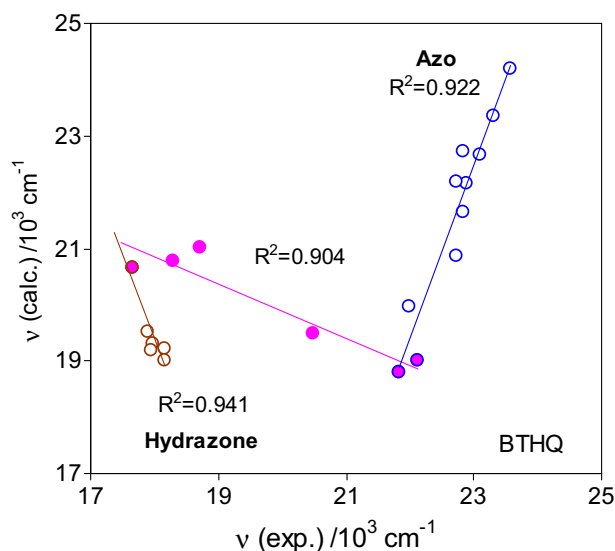

Fig. 4. Normalized emission spectra of the compounds in alcoholic solutions; a) ethanol, b) 1-butanol.

Fig. 5. Correlation between experimental and calculated values by KAT model for absorption band maxima of the BTHQ dye in different solvents.

dyes. It might be due to presence of different type of substituents that contribute differently in molecular resonance structures in ground and excited states.

Analyses of Stokes shift data, using KAT and KTZ multiparameter polarity scales, confirm the same contributions on the way to

solvent reorientation process. It means that the solvent molecules reorient in such a way that support changing molecular interactions, and therefore parameters contributions, from ground state toward excited state. However, it should be noted that such correlation have been made with fewer number of data and therefore this conclusion should be generalized carefully. As the final remark, it should be noted that these correlations, as the associated standard error in evaluated parameters shows, just provide an overview of the solute−solvent interactions. It means that other process, like aggregate formation, ionization and acid−base reaction that may occur in the solvent media, should be considered.

3.3. Absorption and emission spectra of BTHQ dyes in the anisotropic media

The dye molecules may be incorporated into liquid-crystalline solvents without destruction of the order prevailing in the liquid-crystalline matrix. The anisotropic solute−solvent interaction leads to an appreciable orientation of the guest molecules with respect to the axis of preferred solvent alignment. The results may be useful as shown by the use of liquid crystals as anisotropic solvents for spectroscopic investigations of anisotropic molecular properties and intermolecular interactions. Ordered solvent phases such as liquid crystals have also been used as reaction media, particularly for photochemical reactions [40]. It was shown that azo/hydrazone tautomerism is not only affected by the solvent polarity and solute-solvent interactions, but also by the dye molecular structure and the media structure.

Table 2
Percentage contributions for the multiparameter scales for the BTHQ dyes.

Dye	Spectral feature[a]	P_α (%)	P_β (%)	$P_{\pi'}$ (%)	R^2	Prob. > F
Kamlet−Abboud−Taft multiparameter polarity scale						
H-BTHQ	Absorbance [*Azo*] (12)	31 (±7)	33 (±8)	36 (±9)	0.922	0.0001
	Absorbance [*Azo-Hydrazone*] (6)	11 (±12)	62 (±17)	27 (±14)	0.904	0.1405
	Absorbance [*Hydrazone*] (6)	3 (±14)	62 (±31)	35 (±41)	0.941	0.0870
	Fluorescence [*Hydrazone*] (8)	63 (±11)	18 (±12)	19 (±18)	0.943	0.0059
	Stokes shift [*Hydrazone*] (7)	3 (±4)	86 (±5)	11 (±5)	0.995	0.0005
N-BTHQ	Absorbance [*Azo*] (3)	0 (±0)	97 (±0)	3 (±0)	0.999	<0.0001
	Absorbance [*Azo-Hydrazone*] (8)	42 (±21)	30 (±8)	28 (±9)	0.904	0.0167
	Absorbance [*Hydrazone*] (6)	26 (±12)	35 (±39)	39 (±36)	0.921	0.1166
	Fluorescence [*Hydrazone*] (7)	31 (±8)	30 (±9)	39 (±9)	0.969	0.0093
	Stokes shift [*Hydrazone*] (5)	14 (±11)	65 (±15)	20 (±13)	0.968	0.2268
M-BTHQ	Absorbance [*Azo*] (11)	20 (±7)	15 (±8)	65 (±10)	0.914	0.0004
	Absorbance [*Azo-Hydrazone*] (7)	24 (±12)	9 (±18)	67 (±32)	0.623	0.3445
	Absorbance [*Hydrazone*]	–	–	–	–	–
	Fluorescence [*Hydrazone*] (8)	41 (±7)	2 (±8)	57 (±10)	0.950	0.0046
	Stokes shift [*Hydrazone*]	–	–	–	–	–

Dye	Spectral feature[a]	P_{ε_r} (%)	P_n (%)	$P_{E_T(30)}$ (%)	R^2	Prob. > F
Katritzky multiparameter polarity scale						
H-BTHQ	Absorbance [*Azo*] (8)	17 (±17)	5 (±12)	78 (±29)	0.916	0.0130
	Absorbance [*Azo-Hydrazone*] (5)	24 (±10)	34 (±30)	42 (±16)	0.917	0.3621
	Absorbance [*Hydrazone*] (5)	28 (±15)	61 (±33)	11 (±5)	0.968	0.2249
	Fluorescence [*Hydrazone*] (7)	15 (±42)	17 (±9)	68 (±18)	0.970	0.0087
	Stokes shift [*Hydrazone*] (7)	10 (±12)	13 (±11)	77 (±13)	0.952	0.0178
N-BTHQ	Absorbance [*Azo-Hydrazone*] (15)	22 (±10)	13 (±10)	65 (±8)	0.931	<0.0001
	Fluorescence [*Hydrazone*] (7)	31 (±4)	1 (±3)	68 (±4)	0.998	0.0002
	Stokes shift [*Hydrazone*] (5)	12 (±42)	17 (±14)	71 (±87)	0.946	0.2943
M-BTHQ	Absorbance [*Azo*] (16)	62 (±7)	7 (±8)	31 (±6)	0.950	<0.0001
	Absorbance [*Azo-Hydrazone*] (5)	22 (±39)	60 (±85)	17 (±11)	0.994	0.0965
	Absorbance [*Hydrazone*]	–	–	–	–	–
	Fluorescence [*Hydrazone*] (5)	25 (±18)	23 (±22)	52 (±24)	0.866	0.0128
	Stokes shift [*Hydrazone*]	–	–	–	–	–

[a] Number in parentheses denotes the number of data points used in correlations.

Table 3
Absorption spectral data for the BTHQ dyes in anisotropic hosts.

LC	$\bar{\varepsilon}$	$\bar{n}$	$\bar{\nu}_a^{H-BTHQ}$ (cm^{-1})	$\bar{\nu}_a^{N-BTHQ}$ (cm^{-1})	$\bar{\nu}_a^{M-BTHQ}$ (cm^{-1})
5CB	10.10	1.587	22123.9	20964.4	20202.0
8CB	7.93	1.570	22421.5	21505.4	20533.9
6CHBT	6.80	1.570	22624.4	22624.4	20576.1
E7[a]	9.8	1.592	22371.4	23696.7	21276.6
1751[a]	21.00	1.560	22727.3	22075.1	21739.1
FMN[b]	–	–	23201.9	21834.1	20491.8

[a] Nematic mixture.
[b] Monotropic LC.

The absorption and emission spectra of the BTHQ dyes were investigated in the liquid crystalline solvents. The spectral data together with selected physical properties of the nematic compounds used in this work are summarized in Table 3.

The mean dielectric constant and refractive index in the nematic phase can be calculated using the following equations [41]:

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

$$\bar{n} = \frac{1}{3}(n_e + 2n_o) \qquad (3)$$

where $\varepsilon_\parallel$ and $\varepsilon_\perp$ are dielectric constants parallel and perpendicular to the molecular axis, respectively. n_o and n_e are the ordinary and extraordinary refractive indices, respectively.

For all the investigated dyes no dependable, even very week, emission were detected in anisotropic media. The data in Table 3 show that the absorption maxima of the entire compounds appear to exist almost in azo region in the anisotropic solutions. Typical absorption spectra in the nematic media are shown in Fig. 6. The spectral variations demonstrate that influences of anisotropic environment on the solvation of the investigated compounds are complicated, and several interactions contribute to some extent, beside the liquid crystalline anisotropic interactions.

As it is evident, from Table 3, the spectral data does not show an expected variation on going from low polar to polar anisotropic solvents. Similarities in spectral behavior observed in the liquid crystalline hosts and some of the isotropic solvents (azo spectra), with different physical properties (e.g. cyclohexane) look uneven. In the same way differences in spectral behavior observed in the liquid crystalline hosts (azo spectra) and some other isotropic solvents (hydrazone spectra) with similar physical properties (e.g. Acetonitrile) seems anomalous. These observations cannot be explained based on regular solvatochromic behavior. In anisotropic hosts, the entire azo dyes exhibit an absorption band red shifted as compared to the compounds spectra in cyclohexane. In addition, the shapes of optical spectra are similar to polar ordinary liquid solvents in azo region. These results suggest that the dyes (in azo form) experience more polar environments in employed liquid crystals.

All these observations indicate that the interactions between the solute and the anisotropic solvent, i.e. the anisotropic solvation, are complex; however, their overall contributions prevent the formation of the hydrazone type species. Perhaps, it can be attributed to the relatively rigid and packed alignment of the host molecules.

Apart from polar interaction (dipole–dipole and H-bonding), van der Waals interactions (steric and dispersive) may have important contribution in the solute alignment in the liquid crystalline host. The components of anisotropic hosts have highly polarizable molecular characteristics due to extended distribution of π-electrons along the molecular skeleton. Therefore, there is an extra π–π interaction between the aromatic systems of the solute and the
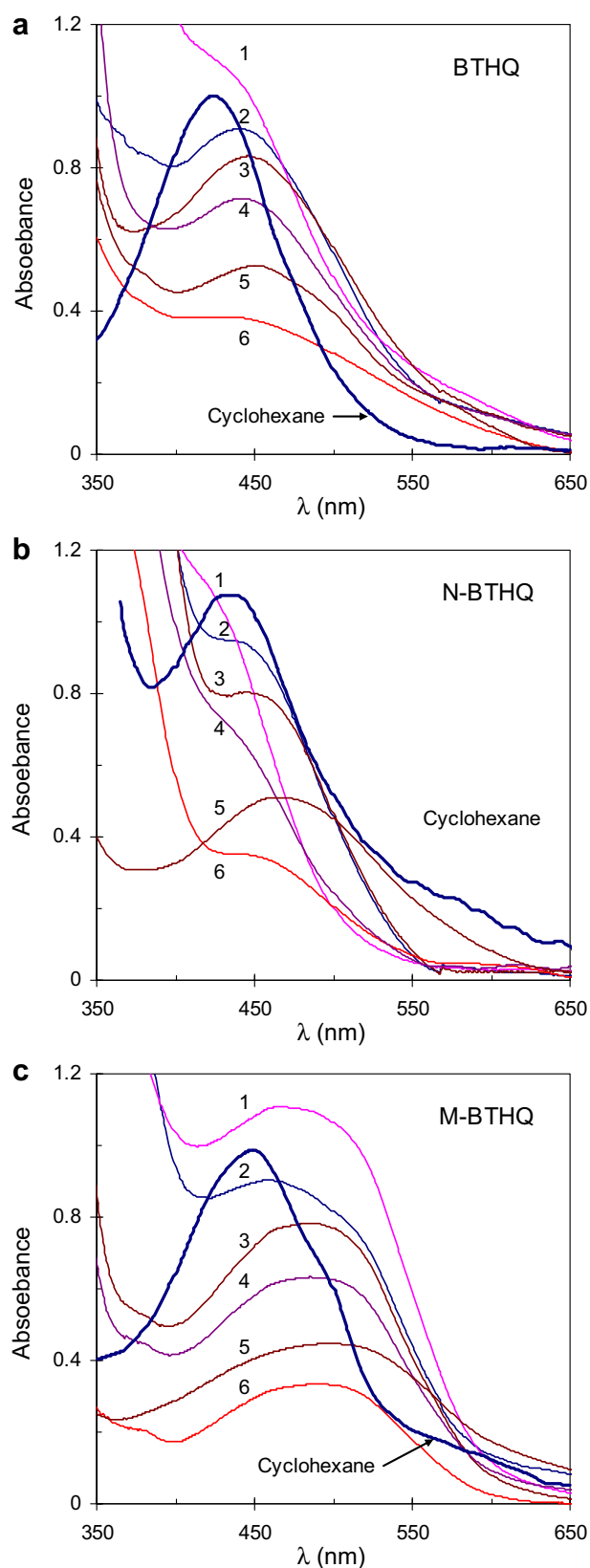
Fig. 6. Absorption spectra of the BTHQ dyes in the liquid crystalline hosts; 1) nematic mixture of E7, 2) nematic mixture of 1751, 3) 8CB, 4) 6CHBT, 5) 5CB, 6) ME-4NF.

anisotropic host, which can play an important role in alignment and mobility of the guest molecule.

In summary, the spectral changes in the anisotropic hosts depend on several factors such as solvent polarity, viscosity, molecular packing, polarizability and host rigidity. Therefore, here in contribution into azo/hydrazone tautomerism the anisotropic media provide relatively rigid, packed and polarizable environment for the solute molecules that prevent azo/hydrazone tautomerism.

3.4. Linear dichroism of BTHQ dyes

As it was verified in previous section, all the investigated azo dyes appear in azo form in anisotropic hosts. Therefore, optical polarization measurements in oriented anisotropic solvents give important information about the dyes in azo form. Polarized absorption spectroscopy provides information on the orientation of the dyes molecules, the transition moment directions and the polarization of electronic absorption bands. The linear dichroism (LD) of a sample is defined as the difference in absorbance between two linearly polarized beams of light possessing electric vector perpendicular to each other. The polarized absorption spectra of the dye dissolved in the anisotropic hosts were measured using parallel-aligned guest−host cells. The dichroic ratio ($R = A_{\parallel}/A_{\perp}$) of the dye was calculated from the absorption of light polarized parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the liquid crystal alignment (rubbing direction).

Although, the dye dissolved in the anisotropic host align, approximately, parallel to the nematic director, the direction of each dye molecule can deviate from the direction of the director, **D** (Fig. 7). Here **M** is the direction of the dye long molecular axis; **T** is transition moment of the dye that makes an angle β with **M**. The molecule makes an angle θ with the nematic director.

The dichroic ratio directly relates to the orientational order parameter S_{dye} for the transition moment. The value of S_{dye} may differ from the order parameter of the molecular axis S_M. This is the case when there is an angle β between the transition moment and the long molecular axis (Fig. 7). The order parameter of the dye in oriented nematic host can be determined from the expression:

$$S_{dye} = \frac{R-1}{R+2}\left(\frac{1}{1/2(3\cos^2\beta - 1)}\right) \qquad (4)$$

If the transition moment vector of the dye is directed along its long molecular axis (i.e. $\beta = 0$), Eq. (4) reduces to:

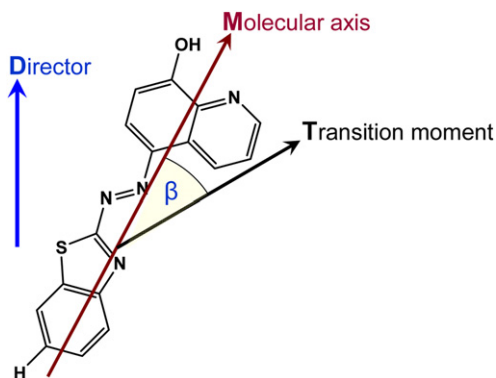**Fig. 7.** Deviation of the dye long molecular axis axis, M, and transition moment, T, from the nematic director, D.

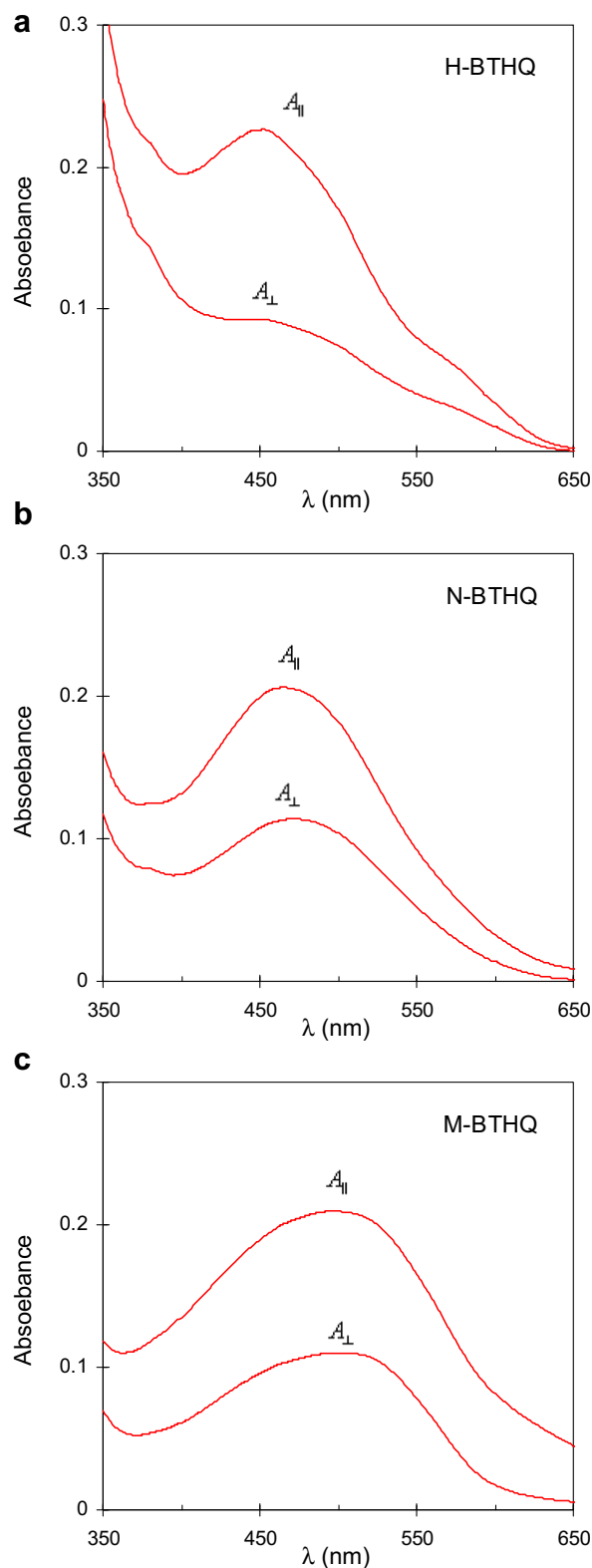**Fig. 8.** Polarized absorption spectra of BTHQ dyes in 5CB anisotropic host.

$$S_{dye} = \frac{R-1}{R+2} \qquad (5)$$

For the investigated dyes, we assume that $\beta = 0$, and estimate the order parameter of the dye dissolved in the anisotropic hosts

Table 4
Dichroic ratios and degree of anisotropies obtained for the dyes in the anisotropic hosts.

LC	H-BTHQ		N-BTHQ		M-BTHQ	
	R	S	R	S	R	S
5CB	1.9	0.23	1.8	0.21	1.9	0.23
8CB	1.7	0.18	1.4	0.13	2.2	0.29
6CHBT	1.7	0.18	1.6	0.18	1.5	0.14
E7[a]	1.8	0.22	1.4	0.12	1.8	0.22
1751[a]	1.8	0.21	1.7	0.19	1.6	0.18

[a] Nematic mixture.

by means of Eq. (5). However, for investigated dyes $\beta \neq 0$, so the term of "degree of anisotropy" should be applied instead of order parameter.

Polarized absorption spectra of the BTHQ dyes doped in parallel-aligned liquid crystalline hosts were recorded at room temperature using guest–host cells with the thickness of $d = 50$ μm. Fig. 8 shows selected polarized spectra of the compounds in selected liquid crystalline host. The dichroic ratios and the degree of anisotropies of the azo dyes were calculated and summarized in Table 4.

The low values of R and S_{dye} for the dyes in the ordered nematic hosts might be related to the several factors, i.e. the dye molecular structures, the intermolecular interactions between the dye and liquid crystal molecules, and the angles between the transition dipole moments and the long molecular axes. Moreover, the structure and shape of the dyes and liquid crystalline molecules are not compatible. Errors in the measured dichroic ratios due to imperfect alignment of the liquid crystal and dye molecules should be considered and estimated to be less than 5 %.

As the data in Table 4 shows, dichroic ratios, R, and degrees of anisotropy, S_{dye}, do not significantly differ for the dyes with different substituents. The molecular structures of the investigated dyes in azo form are approximately planer. Therefore, according to the dichroism result ($A_{\parallel} - A_{\perp} > 1$), the transition moments of the dyes almost lay within their molecular planes and the electronic transitions are $\pi - \pi^*$ transitions in nature.

4. Conclusions

The absorption and emission spectra of three 5-(2-benzothiazolylazo)-8-hydroxyquinoline dyes with different substituent were examined in a series of liquid and liquid crystal-line solvents. The spectral features of the dyes were interpreted as presence of azo/hydrazone tautomerism in conjunction with the solvatochromic characteristic of the preferred tautomer.

The nature and extent of solute-solvent interactions were characterized using correlation with Kamlet–Abboud–Taft and Katritzky multiparameter solvent polarity scales. The results reveal the azo/hydrazone tautomerism cannot be directly interpreted by multiparameter survey. However, multiparameter analyses of the spectral data in selected sets of the solvents associated with azo or hydrazone spectral regions provide valuable information about the solvent effect on the azo/hydrazone tautomerization. The results of such analyses show that solvatochromic azo/hydrazone tautomerism depend on multiple solute-solvent interactions, especially on specific interactions. Moreover, the solvent should be able to transport the hydrogen atom through the media. It means that the host media should have moderate HBD and HBA characteristics and should not be strictly associated.

Moreover, the data show the importance substituent type attached to the aromatic skeleton in these compounds. An electron-donor substituent ($-OCH_3$) in the benzothiazol ring of the tautomeric system shifts the tautomeric equilibrium toward the azo form; while introduction of an electron acceptor substituent ($-NO_2$) move the tautomeric equilibrium toward the hydrazone form. In addition, the absorption and emission spectral features of the dyes and the linear dichroism in some ordered liquid crystalline hosts were investigated.

It was observed that the anisotropic hosts, which provide relatively rigid, packed and polarizable environments for the solute molecules, prevent shift of the tautomeric equilibrium toward the hydrazone form. Moreover, positive absorption anisotropies for these dyes in liquid crystalline solution, i.e. $R > 1$, indicate that the transition moments lay in plane of the azo form and thus the transitions are $\pi - \pi^*$ type.

Appendix

Table A-1
Physical properties and polarity parameters for the solvents used.

Solvent	$E_T(30)$	ε	n	α	β	π^*
Cyclohexane	30.9	2.02	1.4260	0.00	0.00	0.00
Tetra chloromethane	32.4	2.24	1.4602	0.00	0.10	0.21
Toluene	33.9	2.38	1.4969	0.00	0.11	0.49
Benzene	34.3	2.28	1.5010	0.00	0.10	0.55
Diethyl ether	34.5	4.34	1.8290	0.00	0.47	0.24
1,4-Dioxane	36.0	2.22	1.4220	0.00	0.37	0.49
THF	37.4	7.58	1.4072	0.00	0.55	0.55
Trichloromethane	39.1	4.89	1.4459	0.20	0.10	0.69
Dichloromethane	40.7	8.93	1.4242	0.13	0.10	0.73
Benzonitrile	41.5	25.20	1.5282	0.00	0.41	0.90
Acetone	42.2	21.01	1.3590	0.08	0.48	0.62
DMF	43.2	38.25	1.4300	0.00	0.69	0.88
DMSO	45.1	47.24	1.4790	0.00	0.76	1.00
Acetonitrile	45.6	35.94	1.3441	0.19	0.40	0.66
Decanol	47.7	8.00	1.4370	0.70	0.82	0.45
2-Propanol	48.4	19.92	1.3772	0.76	0.84	0.48
1-Heptanol	48.5	11.30	1.4240	0.64	0.96	0.39
Hexanol	48.8	13.00	1.4180	0.67	0.94	0.40
1-Butanol	49.7	17.40	1.3990	0.84	0.84	0.47
Benzyl alcohol	50.4	12.70	1.5404	0.60	0.52	0.98
Acetic acid	51.7	6.17	1.3719	1.12	0.45	0.64
Ethanol	51.9	24.30	1.3610	0.86	0.75	0.54
Methanol	55.4	33.70	1.3290	0.98	0.66	0.60

$E_T(30)$: Reichardt empirical polarity parameter; ε: dielectric constant; n: refractive index; α: hydrogen bonding acceptor ability polarity scale; β: hydrogen bonding donor ability polarity scale; π^*: dipolarity/polarizability polarity scale.

Table A-2
KAT and KTZ multiparameter survey for H-BTHQ dye.

Scale	Spectral feature[a]	Intercept	a, a' (cm^{-1})	b, b' (cm^{-1})	c, c' (cm^{-1})	R^2	Prob. > F
KAT	Absorbance [Azo] (12)	23615.32 (±119.45)	−738.99 (±171.53)	−792.44 (±204.62)	−879.42 (±214.25)	0.922	0.0001
	Absorbance [Azo-Hydrazone] (6)	12107.09 (±2190.72)	1388.02 (±1523.71)	8008 (±2218.53)	3497.66 (±1814.78)	0.904	0.1405
	Absorbance [Hydrazone] (6)	17741.42 (±591.09)	−37.57 (±164.73)	731.5 (±364.84)	−410.76 (±485.63)	0.941	0.0870
	Fluorescence [Hydrazone] (8)	20168.66 (±944.73)	−5358.45 (±956.8)	1525.59 (±1046.94)	−1601.26 (±1504.87)	0.943	0.0059
	Stokes shift [Hydrazone] (7)	5200.21 (±150.87)	−150.06 (±229.94)	−4541.97 (±273.92)	−577.84 (±254.07)	0.995	0.0005
KTZ	Absorbance [Azo] (8)	25295.61 (±648.7)	−347.94 (±338.84)	92.06 (±246.62)	−1595.38 (±582.02)	0.916	0.0130
	Absorbance [Azo-Hydrazone] (5)	12117.43 (±5391.53)	3420.04 (±1429.88)	−4765.64 (±4300.3)	5943.42 (±2243.54)	0.917	0.3621
	Absorbance [Hydrazone] (5)	3926.35 (±8038.83)	4552.81 (±2516.05)	10019.55 (±5386.26)	−1843.45 (±813.03)	0.968	0.2249
	Fluorescence [Hydrazone] (7)	23802.43 (±1763.87)	−884.42 (±2410.94)	956.47 (±498.03)	−3935.06 (±1048.84)	0.970	0.0087
	Stokes shift [Hydrazone] (7)	10252.11 (±1541.17)	−604.48 (±692.47)	−731.32 (±636.09)	−4441.87 (±759.86)	0.952	0.0178

[a] Number in parentheses denotes the number of data points used in correlation.

Table A-3
KAT and KTZ multiparameter survey for N-BTHQ dye.

Scale	Spectral feature[a]	Intercept	a, a' (cm^{-1})	b, b' (cm^{-1})	c, c' (cm^{-1})	R^2	Prob. > F
KAT	Absorbance [Azo] (3)	22831.05 (±0)	0 (±0)	−557.33 (±0)	17.74 (±0)	0.999	<0.0001
	Absorbance [Azo-Hydrazone] (8)	26793.2 (±1213.4)	−9363 (±4603.15)	−6714.83 (±1720.93)	−6355.8 (±1953.3)	0.904	0.0167
	Absorbance [Hydrazone] (6)	14156.77 (±2551.55)	1151.32 (±527.36)	1526.85 (±1721.45)	1685.94 (±1569.3)	0.921	0.1166
	Fluorescence [Hydrazone] (7)	21612.62 (±468.35)	−2788.19 (±706.98)	−2735.86 (±834.33)	−3481.99 (±820.93)	0.969	0.0093
	Stokes shift [Hydrazone] (5)	2737.06 (±267.54)	496.73 (±384.93)	−2267.76 (±514.22)	700.25 (±467.17)	0.968	0.2268
KTZ	Absorbance [Azo-Hydrazone] (15)	29448.33 (±1991.55)	−2097.9 (±909.2)	1205.13 (±927.55)	−6262.74 (±793.13)	0.931	<0.0001
	Fluorescence [Hydrazone] (7)	27035.82 (±462.57)	−2101.01 (±249.36)	79.09 (±189.62)	−4648.89 (±300)	0.998	0.0002
	Stokes shift [Hydrazone] (5)	5995.06 (±3611.66)	−638.58 (±2217.16)	911.44 (±732.77)	−3734.5 (±4617.36)	0.946	0.2943

[a] Number in parentheses denotes the number of data points used in correlation.

Table A-4
KAT and KTZ multiparameter survey for M-BTHQ dye.

Scale	Spectral feature[a]	Intercept	a, a' (cm^{-1})	b, b' (cm^{-1})	c, c' (cm^{-1})	R^2	Prob. > F
KAT	Absorbance [Azo] (11)	22835.06 (±190.15)	−643.15 (±204.87)	−460.44 (±238.87)	−2037.14 (±307.78)	0.914	0.0004
	Absorbance [Azo-Hydrazone] (7)	8396.31 (±5733.76)	3786.6 (±1895.79)	1367.04 (±2835.34)	10419.09 (±4970.87)	0.623	0.3445
	Absorbance [Hydrazone]	−	−	−	−	−	−
	Fluorescence [Hydrazone] (8)	21552.67 (±427.63)	−2505.3 (±437.7)	−128.09 (±501.39)	−3506.21 (±588.74)	0.950	0.0046
	Stokes shift [Hydrazone]	−	−	−	−	−	−
KTZ	Absorbance [Azo] (16)	27796.65 (±1064.41)	−4089.31 (±458.68)	487.93 (±508.97)	−2063.96 (±401.35)	0.950	<0.0001
	Absorbance [Azo-Hydrazone] (5)	−16804.75 (±71067.98)	12314.94 (±21208.11)	33121.56 (±46736.79)	−9518.46 (±5916.27)	0.994	0.0965
	Absorbance [Hydrazone]	−	−	−	−	−	−
	Fluorescence [Hydrazone] (5)	22257.78 (±2319.77)	−1107.22 (±792.25)	991.42 (±959.82)	−2290.32 (±1072.69)	0.866	0.0128
	Stokes shift [Hydrazone]	−	−	−	−	−	−

[a] Number in parentheses denotes the number of data points used in correlation.

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