Temperature dependent absorption spectroscopy of some tautomeric azo dyes and Schiff bases

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The spectral properties of several aromatic azo dyes of fundamental importance (4-phenylazo-1-naphthol, 1-phenylazo-2-naphthol and 2-phenylazo-1-naphthol) and Schiff bases (*N*-(2-hydroxy-1-naphthylmethylidene)aniline and *N*-(1-hydroxy-2-naphthylmethylidene)aniline) are investigated at temperatures down to 100 K. The observed spectral changes are interpreted in terms of the existing tautomeric equilibrium and hydrogen-bonding (H-bonding) with the solvent. In non-polar solvents the decrease in temperature leads, in all compounds except 4-phenylazo-1-naphthol, to a full transformation of the enol tautomeric form (*A*) to the quinone form (*H*). The temperature dependence of the equilibrium $A \rightleftharpoons H$ exhibits a shift around 240 K. In ethanol, due to intermolecular H-bonding, in the case of the azo dyes full transformation was not observed, while the behavior of the Schiff bases is the same as in non-polar solvents. The thermodynamic parameters of the equilibrium $A \rightleftharpoons H$ were estimated in both non-polar solvent and ethanol for all investigated compounds.

Introduction

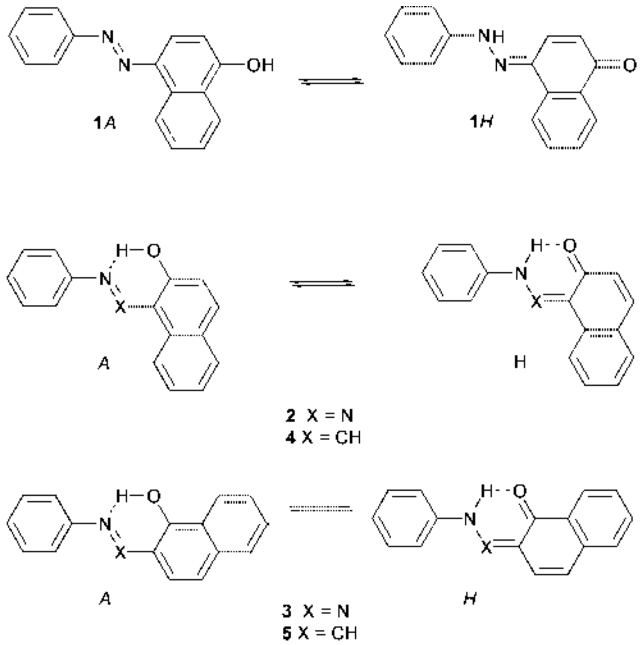
The application of aromatic azo dyes and Schiff bases for both conventional[1] and sophisticated "high-tech"[2,3] purposes are well-known. Their applications as optical sensors and for molecular memory storage are determined by the halo-, photo- and thermochromic properties and therefore attract considerable attention from both fundamental and applied points of view.[1–7] At the same time many of these compounds are tautomeric, and their tautomerism influences or even determines the properties mentioned above. In this respect the study of the factors (substituents, solvents, temperature, pH, UV-irradiation, *etc.*) determining the tautomeric equilibrium of azo dyes and Schiff bases is quite important.

The tautomeric compounds investigated in this paper, representing important basic structures for dye chemistry[1] are shown in Scheme 1. The dependence of their tautomeric ratios on the solvent and substituent effects has been intensively studied quantitatively in the last ten years.[8–12] However, there are only few studies describing temperature effect, especially the changes observed at low temperatures,[13–15] and then only qualitatively.

Therefore, the aim of the present study is to report the spectral changes of dyes **1**–**5** at both room and low temperatures, and to attempt an interpretation, in light of the available quantitative information about their tautomerism.[8–12] Main emphasis will be given to the absorption UV-Vis data, while the fluorescence data are used as supporting information. Their detailed interpretation in relation to the mechanism of proton transfer and dependence on solvent and substituent effects is in progress and will be submitted in a forthcoming paper.[16]

Experimental

All compounds studied were synthesized by standard procedures and purified by TLC or column chromatography. The solvents used—absolute ethanol (EtOH), cyclohexane (CH), methylcyclohexane (MCH) and toluene (T) were of extra pure grade.



Scheme 1

The absorption spectra at room and higher temperatures (298–333 K) were recorded on a Varian Carry 50Bio UV-Vis spectrophotometer equipped with a Cotora thermostat (precision 1 K) in absolute ethanol. The low temperature spectra (100–300 K) were recorded on home-built spectrophotometer using a specially constructed 6 mm thick cell cooled by a

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Table 1 Spectral characteristics of compounds **1**–**5**

Comp.	Solvent	Temperature	X_H(%)	λ_{max} absorption spectra/nm		λ_{max} emission spectra/nm	Average quantum yield[a]	Quantum yield of *H*-form
				A-form	*H*-form			
1	Ethanol[b]	Room	12.4	411, 391sh	494sh, 471sh	566 structureless	8.9×10^{-5}	7.2×10^{-4}
		Low[c]	10.5	421, 402sh	510sh, 480sh, 440sh	552, 590	1.8×10^{-2}	1.7×10^{-1}
2	Ethanol	Room	38.4	414, 392sh	513sh, 478, 450sh	572 structureless	1.2×10^{-6}	3.1×10^{-6}
		Low	53.3	415, 394sh	515, 478, 450sh	555, 588	3.3×10^{-3}	6.2×10^{-3}
	CH	Room	33.1	414, 393sh	508, 473, 445	560 structureless	1.0×10^{-6}	3.0×10^{-6}
	MCH–T	Low	100		521, 490, 460sh	545, 575sh	3.8×10^{-3}	3.8×10^{-3}
3	Ethanol	Room	66.4	423	536sh, 497, 466sh	582 structureless	8.0×10^{-6}	1.2×10^{-5}
		Low	81.3	423	540sh, 530sh, 505, 473sh, 450sh	568, 599	7.0×10^{-3}	8.7×10^{-3}
	CH	Room	60.1	424	526sh, 492, 463sh	573	8.7×10^{-6}	1.4×10^{-5}
	MCH–T	Low	100		542, 506, 470sh	565, 600sh	5.0×10^{-3}	5.0×10^{-3}
4	Ethanol	Room	48.5	376	462, 441, 418sh	488, 510sh	5.0×10^{-5}	1.0×10^{-4}
		Low	100		465, 440, 416sh	479, 500sh well resolved	7.6×10^{-1}	7.6×10^{-1}
	CH	Room	8.3	376	460, 438sh	482, 509sh	2.2×10^{-5}	2.6×10^{-4}
	MCH–T	Low	100		460, 440, 415sh	480, 510sh well resolved	3.2×10^{-1}	3.2×10^{-1}
5	Ethanol	Room	59.8	383	481, 453, 422sh	509, 530sh	3.5×10^{-4}	5.7×10^{-4}
		Low	100		482, 455, 430sh, 406sh	500, 533sh	5.6×10^{-1}	5.6×10^{-1}
	CH	Room	17.3	383	481sh, 452, 429sh	505, 531sh, 588sh	1.5×10^{-4}	8.7×10^{-4}
	MCH–T	Low	100		483, 454, 431sh, 405sh	500, 526sh	4.1×10^{-1}	4.1×10^{-1}

[a] A value estimated as the average of several monitoring excitation wavelengths. [b] Absolute ethanol, the values X_H in 96% ethanol at room temperature for compounds **1**–**5** are as follows: 19.2, 42.0, 67.9, 52.6, 63.0. [c] In this table low temperature means 100 K for the absorption spectra and 90 K for the emission spectra.

Cryodyne (CTI Cryogenics) model 21 closed-cycle helium cryostat. An ordinary deuterium lamp was used as light source, the signal was detected by a PC2000 Miniature Fiber Optic Spectrometer (Ocean Optics Inc) and initially processed by OOIBase 32 (Ocean Optics Inc.) software. The temperature was measured with 2–3 K precision. At each temperature reference spectra of the solvent were recorded. EtOH and MCH–T 1 : 1 were used as solvents because they form a transparent glass upon cooling. All spectra were corrected for solvent contraction according to a procedure described in the literature.[17] The tautomeric fractions at low temperatures were estimated using previously published data for the tautomeric fractions, and individual spectra of the compounds studied at room temperature.[8–11,18]

Fluorescence spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer. For the low temperature measurements a liquid nitrogen-cooling device was used (keeping the temperature at approximately 90 K). Quantum yields were calculated by comparison with a solution of quinine in 0.5 M H_2SO_4.

Results and discussion

Two types of solvents have been used in this study—CH (MCH–T at low temperatures) and EtOH. The first one is nonpolar, without the possibility of specific interactions with the solute.† This presumably gives a better correlation with available gas phase quantum chemical results and a more pure effect when the temperature is changed. On the other hand EtOH is a polar solvent with comparable proton donor and proton acceptor abilities,[19] which allows two types of specific interactions (H-bonding) with both tautomeric forms of the solute.[20]

The spectral data collected in both solvents for both room and low temperatures are presented in Table 1. As seen from the table and in accordance with our previous results[8–11,18] *A*-forms exhibit absorption in the wavelength range 370–420 nm, while the *H*-forms absorb above 430 nm. Compounds **1**–**3** show weak emission in the 550–600 nm region, due to the *H*-form,[13,21] while compounds **4** and **5** emit strongly between 480 and 550 nm, which is in agreement with data for compound **4** published by Olivieri *et al.*[22]

As can be seen in Table 1, with the change of temperature both absorption and emission spectra exhibit a response that cannot be interpreted simply by considering the temperature effect on the tautomeric equilibrium. To explain the specific spectral features, the solvent effect also has to be taken into account, since the changes are different in CH and EtOH.

Spectral changes in CH and MCH–T

Ab initio quantum chemical calculations show a higher stability for the *A*-form in the gas phase, although the ground state energy difference between the *A* and *H*-form decreases in the direction **1** ⟶ **3** and **4** ⟶ **5**. For compound **3** the *H*-form is more stable (Table 2). In all cases the calculations indicate that the *H*-form is more polar. Therefore the increase of the medium polarity will lead to a decrease of the energy difference between both forms, favoring the more polar *H*-form.[23] These results are in agreement with molar fractions of *H*-form in CH at room temperature, estimated from the absorption spectra.[8–11,18] The content of the latter is in the 10–20% range for compounds **1**, **4** and **5**, while for compound **3**, the *H*-form dominates (~60%). However, cooling leads to a shift of this equilibrium towards the *H*-form in all cases, causing a decrease of the *A*-form (Figs. 1–3). At 100 K we have a complete disappearance of the *A*-form, except for compound **1**. These observations indicate an unusual temperature dependence of the $A \rightleftharpoons H$ equilibrium, which can be used to estimate the thermodynamic parameters of the process.

In Fig. 4 we have plotted the free energy differences $\Delta G°$ as a function of the temperature for compounds **1**, **2** and **5**. The estimated values for the entropy and enthalpy changes are collected in Table 3. For compounds **2**–**5** and to some extent for compound **1** these data appear to be the first values reported in the literature. In all cases it is interesting to note that there is a tendency towards two regions—one between 300 and 220–200 K and the second between 220 and 120–140 K. Below 140 K there is a third region, probably below the glass transition temperature, where we suspect the proton transfer reaction to be

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† The change of CH to CH–T (1 : 1) changes the molar fractions within 1–2%, which is within the frame of the precision of the method. Therefore we assume that although toluene has some ability as a proton donor it does not really effect the final results and conclusions in the case of compounds **1**–**5**.

Table 2 *Ab initio* (HF/6-31G**) quantum chemical data for compounds **1**–**5** in gas phase compared with the tautomeric constants in CH estimated from the experiment

Compound	$H - A$ energy difference/kcal mol^{-1}	μ/D	Reference	K_T (X_H/X_A)
1	1.53	1.18 *A*, 3.47 *H*	23	0.09
2	0.28	1.16 *A*, 2.03 *H*	23	0.49
3	−0.56	0.90 *A*, 1.32 *H*	23	1.51
4	1.80	2.31 *A*, 3.15 *H*	11	0.09
5	0.89	1.90 *A*, 3.09 *H*	18	0.20

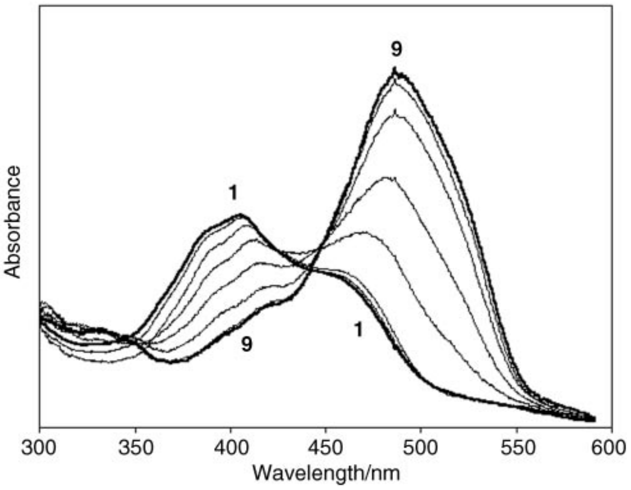

Fig. 1 Absorption spectra of compound **1** in MCH–T: 1—298, 2—270, 3—240, 4—220, 5—200, 6—180, 7—160, 8—140, 9—120 K. The first and last spectra are given in bold.

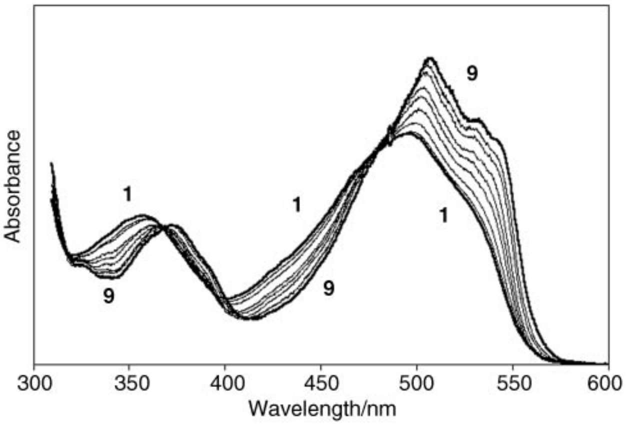

Fig. 2 Absorption spectra of compound **3** in MCH–T: 1—298, 2—270, 3—240, 4—200, 5—180, 6—160, 7—140, 8—120, 9—100 K. The first and last spectra are given in bold.

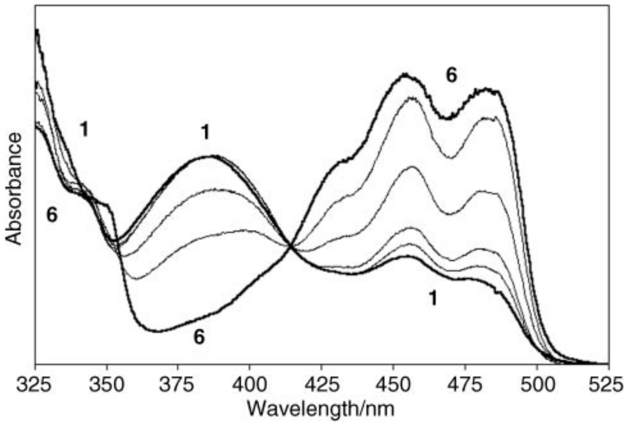

Fig. 3 Absorption spectra of compound **5** in MCH–T: 1—298, 2—230, 3—200, 4—180, 5—140, 6—100 K. The first and last spectra are given in bold.

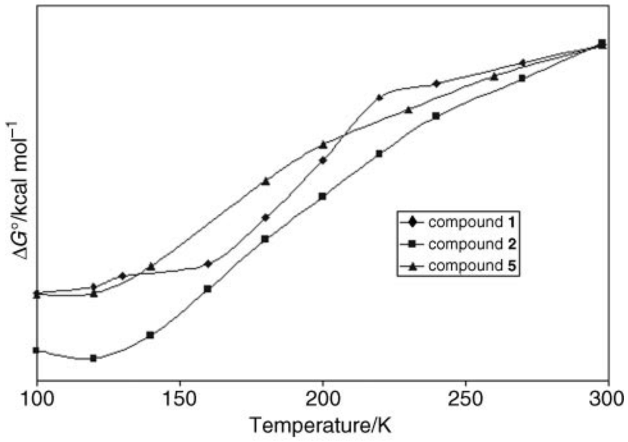

Fig. 4 $\Delta G°$ in compounds **1**, **2** and **5** as a function of the temperature for compounds **1**, **2** and **5** in non-polar solvent.

inhibited. The first temperature region is representative of the liquid state of both solvents, while the second one includes the freezing points of MCH and T and could show the situation in a solid glass-like state. In general the second range is characterized by lower $\Delta H°$ and $\Delta S°$ values, the low $\Delta S°$ should be connected with the increased order of the solvent and with the poor solvation of the tautomers. In the temperature range 300–220 K the process is found to be exothermic and the values for compounds **1**–**3** keep the same trend as the heat of formation differences between both tautomers in gas phase.[23] In MCH–T with decreasing temperature the solute–solvent dipole–dipole interactions will increase leading to a higher degree of order. In this respect the changes of $\Delta S°$ in going from **1** to **3** confirm the expectations since in the case of compound **3** both tautomers are less polar. However, in all cases the $\Delta H°$ and $-T\Delta S°$ terms at room temperature are similar in magnitude, which means that there is a delicate interplay between the energetic and entropic effects, and further attempts to interpret these thermodynamic data in depth have the risk of overinterpretation.

Upon decreasing the temperature from 300 K to the freezing point, some differences between the spectra of **1**–**3** and **4**,**5** are worth noting. In the case of compounds **1**–**3** besides the well-resolved structure of the bands a strong bathochromic shift can be seen for the bands belonging to the *H*-form (Figs. 1 and 2, Table 1). According to some previous investigations[24] such changes can be attributed to the increased planarity of the molecules at low temperatures. It could also be expected to result from the more polar excited state of the *H*-form, a fact proven at room temperature in solvents of different polarity.[8–10] In the case of compounds **4** and **5** the decrease of the temperature only leads to well-resolved band structure and there is no spectral shift detected (Fig. 4). The same is observed at room temperature upon changing the solvent polarity.[11]

The emission spectra of the azo dyes and Schiff bases also show some differences. Emission bands of the azo dyes at room temperature are structureless, while at 90 K they show some sub-band structure, which is a mirror image of the corresponding pure *H*-form absorption spectrum at room temperature. In the case of **4** and **5** the emission bands at both room and low temperature have two well-defined sub-bands and a red tail.

Table 3 Thermodynamic parameters of the equilibrium $A \rightleftharpoons H$ in MCH–T and EtOH

Compound	MCH–T			EtOH		
	Temperature interval/K	ΔH°/kcal mol^{-1}	ΔS°/cal mol^{-1} K^{-1}	Temperature interval/K	ΔH°/kcal mol^{-1}	ΔS°/cal mol^{-1} K^{-1}
1	300–220	−0.115 ± 0.014	−4.60 ± 0.01	330–200	0.526 ± 0.033	−1.65 ± 0.11
	220–160	−3.20 ± 0.17	−18.5 ± 0.1			
2	300–220	−0.463 ± 0.004	−2.95 ± 0.02	300–200	−0.089 ± 0.012	−0.98 ± 0.05
	220–160	−0.836 ± 0.021	−4.71 ± 0.20			
3	300–220	−0.584 ± 0.021	−1.19 ± 0.09	300–200	−0.384 ± 0.034	−0.31 ± 0.17
	220–160	Very low correlation	Very low correlation			
4[a]	300–200	−0.198 ± 0.013	−5.43 ± 0.08	330–200	−0.598 ± 0.038	−2.18 ± 0.25
	200–140	−1.36 ± 0.15	−11.16 ± 0.78			
5	300–200	−0.481 ± 0.067	−4.76 ± 0.32	330–200	−0.664 ± 0.043	−1.43 ± 0.16
	200–120	−1.04 ± 0.22	−7.10 ± 1.54			

[a] The data published in ref. 11 for 96% ethanol are subject to a calculational error and must be divided by ln 10 to be comparable.

No spectral shift is observed as a function of the temperature. The sharp increase with decreasing temperature of the average quantum yields (two orders of magnitude) strongly suggests that the emission is due to the *H*-form, a conclusion in support of earlier investigations for compounds **2**,**3**,[21] and **4**.[22] Fluorescence data, both steady-state and time-resolved, for these compounds will be further investigated in a forthcoming publication.[16]

Spectral changes in EtOH

In ethanol two effects can be expected upon cooling—the change of the medium polarity and the effect of H-bonding with the solute. It should be noted that a decrease in temperature leads to substantial changes in solvent properties (increase in the polarity and viscosity). As a result the spectral changes observed in ethanol could be very sensitive to polarity and temperature effects on the one hand and the existing intra- and intermolecular H-bonding on the other. The *H*-form will be favored both by increased polarity and lower temperature as the results in non-polar solvents show. At the same time the increased polarity of the solvent may lead to weakening of intramolecular H-bonds and possibly to stronger intermolecular H-bonds.

While the situation with respect to intramolecular H-bonding in the case of compound **1** is clear (there is none), the situation for **2**,**3**, and **4**,**5** needs some additional explanation. The analysis of the available tautomeric constants at room temperature in various solvents,[8–11] performed by using the solvatochromic approach,[19] shows that although there are H-bonds in both types of compounds (**2**,**3** and **4**,**5**), these behave quite differently as a result of specific interactions with proton donor and proton acceptor solvents. For compounds **2** and **3** the proton donor and proton acceptor terms are of almost equal magnitudes, but with opposite signs, while for compound **4** the proton acceptor term tends to zero. This indicates that for compounds **2** and **3** the intramolecular H-bond is relatively weak and any reasonable proton acceptor solvent like ethanol can break it. Therefore the spectral changes are discussed for compounds **1**, **2**,**3**, and **4**,**5** separately.

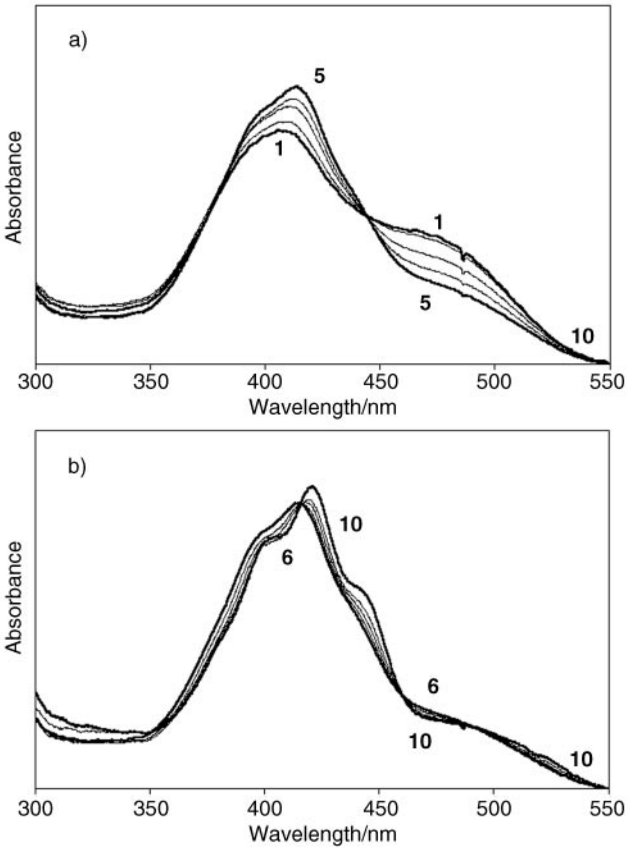

Fig. 5 Absorption spectra of compound **1** in ethanol: a) 1—298, 2—270, 3—240, 4—220, 5—200 K; b) 6—180, 7—160, 8—140, 9—120, 10—100 K. Spectra 1, 5, 6 and 10 are given in bold.

For compound **1**, quantum chemical calculations show[20] that methanol‡ acts as a proton acceptor solvent interacting with both tautomeric forms, but stabilizing the *A*-form more. However, the increase of polarity narrows the ground state energy difference between the tautomeric forms. The experimental facts are in line with this finding—at room temperature the *A*-form is indeed dominant (Table 1). The conclusion is confirmed by the solvatochromic approach[19] showing the proton acceptor term to be almost three times higher than the proton donor term. The increase in temperature up to 333 K leads to an enhanced *H*-form content and the opposite trend should be expected at low temperatures. As is observed from Fig. 5a at temperatures down to 200 K the proportion of the *A*-form increases (to 88% at 200 K) as the spectral changes proceed through a well-defined isosbestic point at 440 nm. In Fig. 5b we show the changes below 200 K. The intensities remain essentially the same, but a strong bathochromic shift is observed for all bands and a well-resolved fine band structure is evident. It is possible that due to increased viscosity and the strong intermolecular H-bonds, where EtOH is acting as proton acceptor, both tautomeric forms (*A* and *H*) are in a frozen condition, without the possibility of proton exchange *i.e.* the tautomeric proton is fixed. The observed spectral changes below 200 K could be explained by the existence of different ethanol–dye complexes (even three new isosbestic points at 416, 460 and 490 nm are formed). A shift in the emission spectra and a change of

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‡ In the case of compounds studied the same behaviour is assumed for the ethanol molecule.

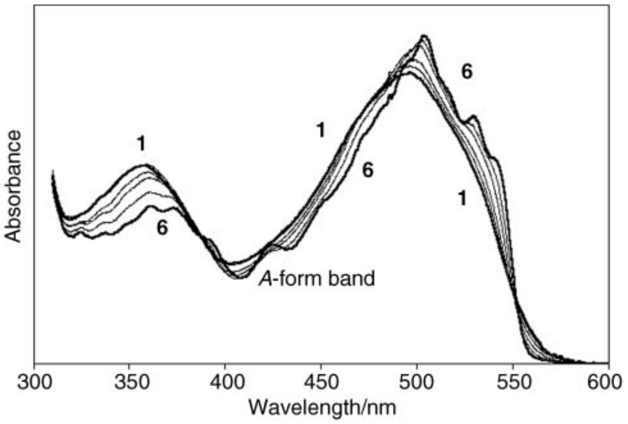

Fig. 6 Absorption spectra of compound **3** in ethanol: 1—298, 2—260, 3—220, 4—180, 5—140, 6—100 K. The first and last spectra are given in bold.

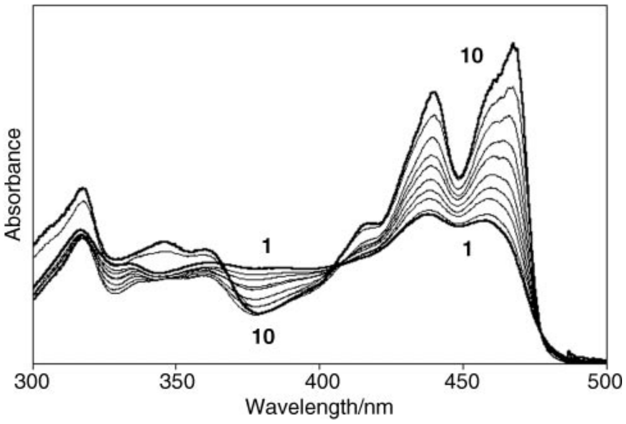

Fig. 7 Absorption spectra of compound **4** in ethanol: 1—298, 2—270, 3—240, 4—220, 5—200, 6—180, 7—160, 8—140, 9—120, 10—100 K. The first and last spectra are given in bold.

its shape is also observed, but the excitation spectrum remains very similar to the absorption spectrum of the *H*-form, which confirms that the *H*-tautomer remains in the mixture.

For compounds **2** and **3** at room temperature tautomeric constants are very close and an increase of the temperature up to 333 K leads to very slight changes in favor of the *A*-form. These changes are more evident for compound **3**, where due to steric hindrance the intermolecular H-bonding will be more easily disturbed. At these conditions it could be expected that instead of intramolecular H-bonding, where the ethanol molecules are acting as proton donors, an intermolecular H-bond, where ethanol acts as a proton acceptor (breaking the intramolecular H-bond), is formed. With decreasing temperature the equilibrium shifts slightly towards the *H*-form and again changes for compound **3** are more substantial (Fig. 6). It could be expected that at low temperature the intramolecular H-bonds are broken and stronger H-bonds are established between tautomers and the solvent, fixing them in the same way as observed for compound **1**. As seen from Fig. 6 in the case of compound **3** at 140 K a well-resolved structure and a bathochromic shift of the *H*-bands is observed. However, the band belonging to the *A*-form is still evident at 423 nm, showing that the conversion of the *A*- to the *H*-form is not complete. This fact becomes more clear by comparing Figs. 2 and 6.

These findings can be supported by a qualitative analysis of the thermodynamic data for EtOH shown in Table 3. In general $\Delta H^\circ_{\mathrm{EtOH}}$ can be presented as the sum of a gas phase value and a solvation term, *i.e.* eqn. (1).

$$\Delta H^\circ_{\mathrm{EtOH}} = \Delta H^\circ_{A-H} + \Delta H^\circ_{\mathrm{solv}} \qquad (1)$$

If we assume ΔH°_{A-H} to be equal to $\Delta H^\circ_{\mathrm{MCH-T}}$, the values of $\Delta H^\circ_{\mathrm{solv}}$ will be a measure for the intermolecular H-bond strength in the case of the compounds studied.§ These values are estimated to be 0.457, 0.374 and 0.200 kcal mol^{-1} for compounds **1**, **2** and **3** respectively, showing that the intermolecular H-bonding is stronger in the case of compound **1**. The positive sign might suggest that the intermolecular H-bonding leads to increased solvation of the *A*-form, its influence being defined by the action of EtOH as a proton acceptor and the possibility of breaking the intramolecular H-bond.

Finally for compounds **4** and **5** at room temperature in EtOH the tautomeric ratios are similar to those of **2** and **3** (see Table 1). Elevation of the temperature leads to an increase in the *A*-form proportion, the opposite happens upon freezing the samples *i.e.* the spectral changes over the whole temperature interval (from 333 to 100 K) are unidirectional. The spectral evidence for the existence of the *A*-form disappears at 160–140 K; the structure of the complicated *H*-band becomes very well-resolved and there is no bathochromic shift (Fig. 7). Obviously, in this case the intramolecular H-bonding, is strong enough to be broken by the solvent. In other words ethanol is acting as a proton donor solvent only (as shown by quantum chemical calculations)[11] and consequently both the increased polarity of the medium and the decreased temperature stabilize the more polar *H*-form. This interpretation is also strongly supported by the fact that almost identical positions of the emission bands are observed at room and low temperatures. As a result, proton exchange between the tautomers is not disturbed. According to a recent study on the thermochromism of tautomeric Schiff bases,[25] the $A \longrightarrow H$ shift is attributed to formation of *H*-dimers. However, we did not find any spectral evidence for the existence of dimers in compounds **4** and **5** in the concentration range up to 10^{-4} M. The spectral changes in ethanol where the formation of dimers is impossible are the same as in MCH–T, an observation in strong support of our hypothesis.

Conclusions

The main conclusion that can be drawn from the spectroscopic data presented in this paper is that the tautomerization reaction of compounds **2**–**5**, which involves besides the electronic rearrangement a short distance proton transfer process, still takes place at low temperatures, even though there is a sudden change of thermodynamic parameters around 200 K. For compound **1**, however, the proton is transferred over a much longer distance, and apparently this process becomes severely inhibited at lower temperatures. This makes it likely that at least in this transfer mechanism, somehow the dynamics of the environment also plays an important role.

The sudden change at around 200 K in MCH–T remains somewhat mysterious, since we expect the glass transition temperature for the mixture to be closer to 100 K. The melting points of MCH (146 K), and T (178 K) are also below this point and the glass transition temperature for the pure compounds are well below it (85 and 112 K respectively). Apparently there is no direct connection with either of those temperatures, and there is no indication that the reaction rate slows down to the point that equilibrium between the tautomers is no longer fully established. This means that there is indeed a shift in thermodynamic parameters at the point indicated, which in turn could imply that upon cooling and shrinkage of the solvent the solutes are forced in different configurations. This interpretation is supported by the fact that for compound **1** we appear to get several species below this temperature.

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§ This interpretation is only qualitative because: $\Delta H^\circ_{\mathrm{MCH-T}}$ also includes a solvation term, albeit very small, and $\Delta H^\circ_{\mathrm{solv}}$ includes an additional solvation contribution coming from the higher polarity of EtOH.

Time-resolved experiments, based on the fluorescence properties of these compounds should shed more light on these problems.

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