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Excited state intramolecular proton transfer in some tautomeric azo dyes and schiff bases containing an intramolecular hydrogen bond

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Abstract

Photophysical properties of several basically important aromatic azodyes (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) all containing an intramolecular hydrogen bond were studied by both steady-state and time-resolved fluorescence spectroscopy with temperatures down to 98 K. It was found that the fluorescence results from the quinone form (H-form) only. The enol form (A-form) undergoes rapid excited state intramolecular proton transfer (ESIPT) resulting in the excited H-form. The compounds have relatively low quantum yields at room temperature, which increase considerably at low temperatures. Lifetime data at the different temperatures indicate that a substitution by both acceptor or donor groups on the para position in the phenyl ring decreases the deactivation rate and hence results in increased lifetime. © 2002 Published by Elsevier Science B.V.

Keywords: Tautomerism; Azonaphthols; Schiff bases; Fluorescence; Proton transfer

1. Introduction

Proton tautomerism plays an important role in many fields of chemistry and especially biochemistry [1–3]. It is well known that the proton transfer can occur in ground and/or excited state, but only during the last decade the excited state proton transfer has been subject of substantial interest [4–6]. Molecules giving rise to excited state tautomers by intramolecular proton transfer are often used as laser dyes, in higher energy radiation detectors and molecular memory storage devices, as fluorescent probes and polymer protectors [7–9].

Many salicylidene anilines (compound **1** in Scheme 1), being relatively simple in structure and exhibiting intramolecular proton transfer, have, therefore, attracted considerable attention from both experimental [10–13] and theoretical [14,15] points of view. However, the long time studies have not still answered all questions about the mechanism of ESIPT. At the same time there are only scattered fluorescence studies at room temperature [16,17] on the

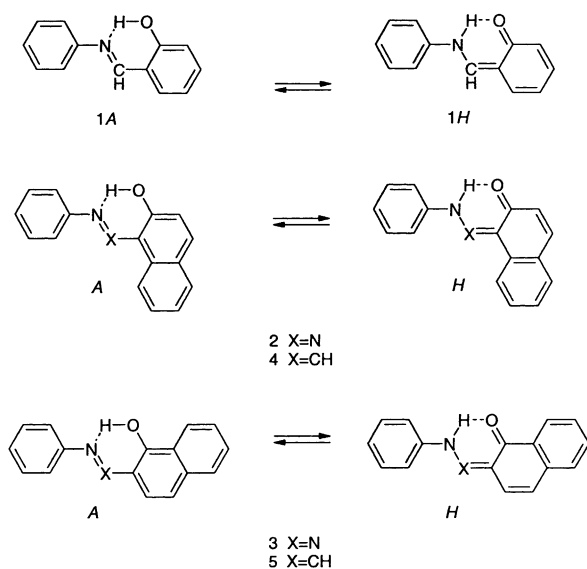
proton transfer in the anils of aromatic α -hydroxyaldehydes, where the tautomeric proton exchange occurs easily due to the smaller loss of aromaticity in the naphthalene fragment. Alarcón et al. [16] have reported fluorescence and absorption data for substituted hydroxybenzaldehydes and have found that emission comes only from the H-form. The enol-imine A-form undergoes rapid excited state intramolecular proton transfer (ESIPT) resulting in the keto H-form. At low temperatures, Guha et al. [13] investigated proton transfer reaction in 7-ethylsalicylidenebenzylamine and have suggested that this molecule exists in more than one structural form in most of the protic solvents. They also have found that the quantum yield increases when the solvent viscosity is increased.

In previous papers [18–22], we reported the absorption properties of compounds **2–5** (as shown below) as well as some fluorescence data over a large range of temperatures, in polar and non-polar solvents. In the present work, we have undertaken a systematic photophysical study of these compounds in respect of substituent effects on the efficiency of ESIPT and also in an attempt to suggest a simple scheme for this proton transfer. However, these compounds represent a special group of proton transfer systems, whose deactivation routes of the excited molecule are particularly

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Scheme 1.

complex. Therefore, now we cannot answer all questions in this respect, but the current study appears to outline the route for further detailed photophysical, photochemical and quantum chemical studies on the mechanism of proton transfer in compounds 2–5.

2. Experimental

All compounds studied were synthesised 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. At low temperatures EtOH and MCH/T 1/1 were used as solvents.

Room and low temperature UV–VIS absorption spectra were recorded and then processed as described [18].

Steady-state 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 of a solution of quinine in 1N H₂SO₄. The quantum yields of the studied compounds are low, and therefore, in order to remove the effects of possible impurities in the solvents as well as Raman scattering, the spectra of the solvents were recorded at the same conditions and then subtracted via an optimisation procedure.

Lifetimes were measured using the time correlated single photon counting (TCSPC) technique [23]. The excitation source was a Coherent Mira 900 Ti:Sapphire laser which has a pulse width of ~3 ps. The output from the laser is frequency tripled to obtain the exciting wavelength of 294.6 nm. The energy is ~2 nJ/pulse. Fluorescence is collected from the sample through an optical system and is dispersed by a

Table 1
Fitted decay parameters^a of compound 5 in MCH/T

Temperature (K)	τ_1 (ns)	τ_2 (ns)	α_1	α_2	τ_{av} (ns)
98	4.64	1.61	75.63	24.96	3.91
123	2.68	1.04	85.36	14.64	2.43
173	0.27	—	—	—	0.27
223	0.09	—	—	—	0.09

^a Since, as stated in the text, the double exponential fit is not originating from the existence of real species in the matrix, in the discussion we use only average lifetimes (τ_{av}) calculated according to: $\tau_{av} = \alpha_1 \tau_1 + \alpha_2 \tau_2 / \alpha_1 + \alpha_2$, where α and τ are the corresponding relative amplitudes and decay lifetimes.

spectrometer on a MCP-PMT (Hamamatsu R3809U-50) detector. Decay data were recorded with the help of SPC-630 (Becker-Hickl) module and have been analysed using Fluofit software (Picoquant). All fits have χ^2 around 1, and residuals distributed randomly. Accuracy of the instrument was checked by recording the lifetimes of some standard compounds. Temperature is controlled and measured by a home-built system: accuracy in temperature measurements is ± 2 K.

Decay time measurements for compounds 2 and 3 were impossible because of their weak fluorescence. However, decay parameters for compounds 4 and 5 are summarised in Table 1 and Table 2. It should be pointed out that the decay fits with a double exponential function at low temperatures in both EtOH and MCH/T, which may be due to inhomogeneity of the matrix [24]. It cannot be attributed to the presence of more than one ground state conformers, as the excitation spectra and the measured lifetimes are independent of monitored emission. As seen from Table 1, the decrease in the major decay component is rather fast when the temperature is raised and finally can be fitted well with a monoexponential function.

3. Results and discussion

3.1. Photophysical parameters of unsubstituted compounds

The tautomeric behaviour of compounds 2–5 differs considerably from that of the corresponding azo phenols [3,25] and salicylidene anilines 1 [12,17], which exist mainly in the A-form at room temperature, even in polar solvents. Such a difference could be caused by the loss of aromaticity in going from A- to H-form, while in compounds 2–5 this effect is compensated by the transfer of aromaticity within the naphthalene fragment.¹

¹ In the azophenols and salicylidene anilines the number of delocalised electrons in the tautomeric phenyl ring is reduced from six to four in going to the H-form because two of those electrons are engaged in the strong C=N and C=O bonds. Thus, the phenyl ring loses much of its aromaticity. In the naphthalene compounds, this effect is compensated by the second aromatic ring [26].

Table 2

Spectral characteristics of some para substituted in the phenyl ring compounds in CH at room temperature

Dye	λ_{max} absorption spectra (nm)		λ_{max} emission spectra (nm)	Average quantum yield	Stokes shift (cm^{-1})	$\tau_{\text{av}}^{\text{a}}$ (ns)	η_{T} (%)
	A-form	H-form					
2	414 393sh	508 473 445	560	1.0×10^{-7}	1830 6300	—	—
2N(Me)₂	428	584sh 494 463	609 642sh	3.7×10^{-5}	700 6940	—	—
2NO₂	418	506sh 475 439sh	Non-Fl	Non-Fl	—	—	—
3	424	526sh 492 463sh	573	8.7×10^{-6}	1560 6130	—	—
4	376	460 438sh	482 509sh	2.2×10^{-5}	990 5850	1.85 3.11 ^c	21
4N(Me)₂	390	497sh 440sh 413	514 544sh 595sh	3.2×10^{-4}	670 6190	1.80	40
4NO₂	397	484sh	500 526sh 568sh	1.2×10^{-4}	660 5190	1.88	45
5	383	481sh 452 429sh	505 531sh 588sh	1.5×10^{-4}	990 6130	3.91 4.23 ^c	32
5N(Me)₂	405 384sh	505sh 471sh 433sh	518 550sh 593sh	1.5×10^{-3}	500 5390	3.40 0.12 ^b	84
5OMe	385	490sh 459sh	504 530sh 588sh	4.5×10^{-4}	570 6130	3.15	51
5CN	396	499sh 466sh 430sh	513 543sh 597sh	5.3×10^{-4}	550 5760	3.29	77
5NO₂	403	500sh 469sh	520 555sh 610sh	1.8×10^{-3}	770 5580	3.36 0.08 ^b	100

The Stokes shifts are given according to the long wavelength maximum of H-form (the values in italic are according to the maximum of A-form).

^a In MCH/T at 98 K.

^b At room temperature in MCH/T.

^c In ethanol at 100 K.

The experimental UV–VIS absorption spectral data support this finding—even in CH the absorption spectra at room temperature exhibit two distinct regions 370–420 nm and above 430 nm, which correspond to A- and H-forms, respectively [18–21]. Compounds **2** and **3** show emission maxima in the region 572–582 nm in ethanol and slightly blue shifted (560–573 nm) emission in CH. The quantum yield for compound **2** is fairly low, whereas it is larger by an order of magnitude for compound **3**. The low quantum yields could be explained by non-radiative decay paths to the low-lying $n\pi^*$ -states of the nitrogen atoms [27]. What is of more interest is the fact that the excitation spectra are identical irrespective of emission wavelength, which indicates that the observed emission originates from one tautomer only. At temperatures around 100 K in non-polar glass (MCH/T), the absorption spectra show a contribution from the H-form only [18]. At the same time, the excitation spectra are very similar

to the individual spectra of the pure H-form, which supports the hypothesis for emission of H-form. The lack of emission reported [25] for the A-form in dyes **2** and **3**, where the tautomeric proton is replaced by a methyl group, is one more proof in this respect.

In compounds **4** and **5**, absorption spectra reveal the presence of both A- and H-forms at room temperature and only of H-form at low temperatures in both ethanol and MCH/T [18]. The emission spectra show broad bands with maxima in the 480–510 nm range. The excitation spectra, being independent of the selected emission wavelength, show bands corresponding to both A- and H-forms at room temperature (Fig. 1). As expected, the quantum yield is significantly higher for these compounds. In agreement with the low temperature absorption spectra the excitation spectra at low temperatures contain bands corresponding to H-form only (Fig. 2).

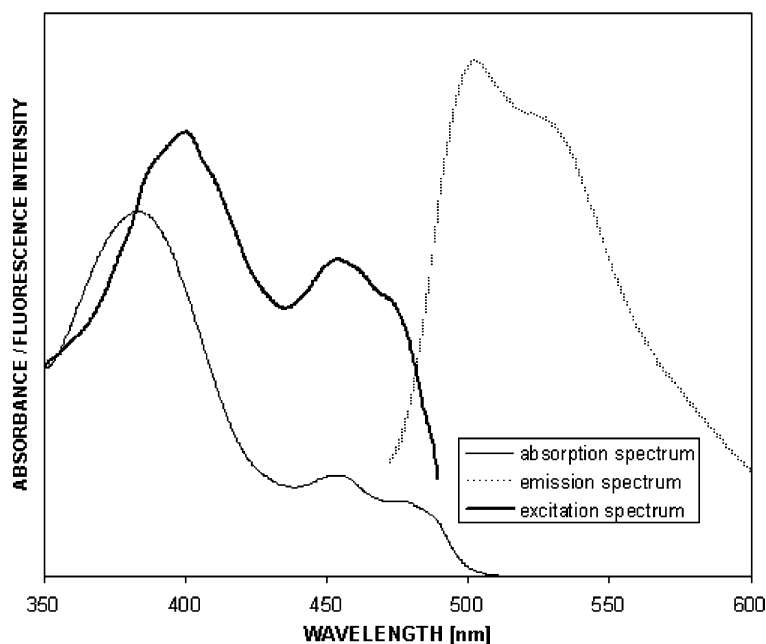


Fig. 1. Absorption, excitation and emission spectra of compound **5** in CH at room temperature.

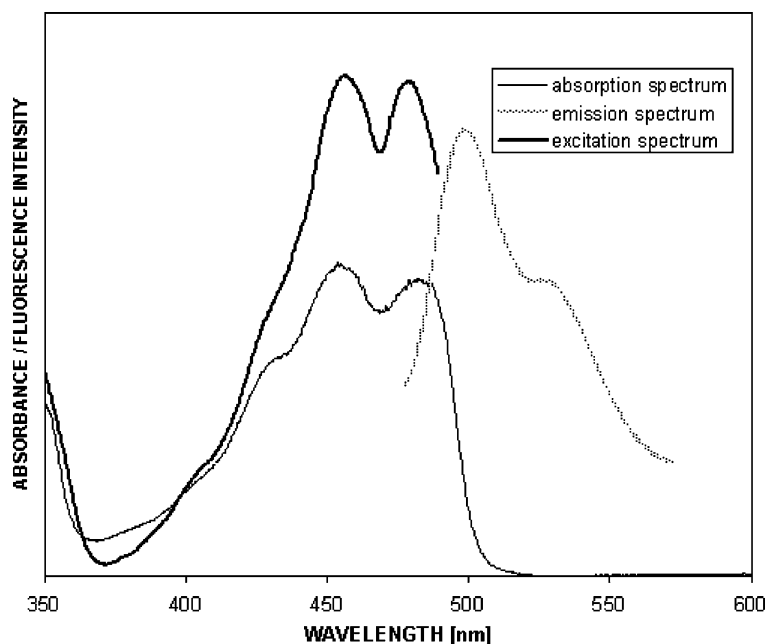
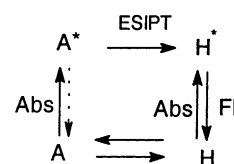


Fig. 2. Absorption, excitation and emission spectra of compound **5** in MCH/T at 90 K.

In order to explain the observed spectral behaviour, we invoke the following simplified scheme involving both tautomers (Scheme 2).²

Excited A (A^*) undergoes a fast transformation to the excited H-form (H^*) and the emission results from the H-form



Scheme 2.

² In contrast to the salicylidene aniline (compound **1**) and the *o*-hydroxy azobenzene, compounds **3–5** always exist as tautomer mixture in solution at room temperature, i.e. the molecules are present in both A- and H-forms, as their relative stability depends on the solvent and/or temperature [18–21].

only, as observed. It explains the independence of the shape of emission from the excitation wavelength (i.e. excitation of A- or H-forms). The large values of the Stokes shifts of the emission compared to the absorption maxima of the A-forms confirm this hypothesis (Table 2). The low quantum yields, however, show that a substantial part of both A* and H* returns to the ground state through non-radiative deactivation.

Therefore, we tried to estimate from the excitation spectrum the relative fraction of the A-form molecules, which gets converted into the H-form through ESIPT. According to the scheme discussed earlier, in the case of ESIPT the excitation spectrum will have a contribution from both A- and H-forms with emission coming only from the H tautomer. In this case, as proved in the appendix, we can express the contributions of both forms in the following equations:

$$I_{\text{exc}}(\text{A}) = A_{\text{A}} \times Q_{\text{H}} \times \left(\frac{k_{\text{PT}}}{k_{\text{PT}} + k_{\text{d}}(\text{A})} \right) \quad (1)$$

$$I_{\text{exc}}(\text{H}) = A_{\text{H}} \times Q_{\text{H}} \quad (2)$$

where A_{A} and A_{H} are the measured absorbances at the maxima of A- and H-forms, respectively; $I_{\text{exc}}(\text{H})$ and $I_{\text{exc}}(\text{A})$ the excitation intensities at the same wavelengths; k_{PT} is ESIPT rate, and $k_{\text{d}}(\text{A})$ is the decay rate of the A-form and Q_{H} is the quantum yield of the H-form. Here we assumed that at the maximum of the A-form the contribution in the absorbance coming from the H-form is negligible (and vice versa), which is particularly true in the case of compounds **4** and **5** in non-polar solvents [19,22].

If we define $k_{\text{PT}}/k_{\text{PT}} + k_{\text{d}}(\text{A})$ as efficiency of the conversion of A* molecules to H* (η_{T}) from Eqs. (1) and (2)

follows:

$$\eta_{\text{T}} = \frac{I_{\text{exc}}(\text{A}) \times A_{\text{H}}}{I_{\text{exc}}(\text{H}) \times A_{\text{A}}} \times 100 \quad (3)$$

It is clear that in case of $k_{\text{PT}} \gg k_{\text{d}}(\text{A})$, the efficiency of transformation will tend to 100%. Using the Eq. (3), it was estimated that the efficiency of conversion for compound **4** is 21%, while for compound **5** it is 32%.

As reported in [18] and seen from Table 1, the quantum yields and lifetimes for compounds **4** and **5** in ethanol are higher in comparison with CH (MCH/T at low temperatures). This indicates the existence of intermolecular H-bonding with the solvent and its influence on the tautomeric proton exchange. Such an influence is substantial in the case of compound **4**, but slight in the case of compound **5**, where due to steric reasons solute–solvent intermolecular H-bonding is disturbed.

3.2. Substitution effect on the photophysical parameters of compounds **2**, **4** and **5**

The substituent effect on the tautomeric equilibrium in the hydroxy azonaphthols like compounds **2** and **3** is well studied [28]—the acceptor substituents in the phenyl ring preferentially stabilise the H-form, while electron donors favour the A-form. Due to the planarity of these molecules, there is full conjugation and engagement of the substituents in the overall electronic structure of the molecule. As seen from Table 2, the dimethylamino substituent in compound **2**, even though the equilibrium is shifted towards the A-form, leads to a sharp increase of the quantum yield. This is in contrast with the action of the nitro group, where no

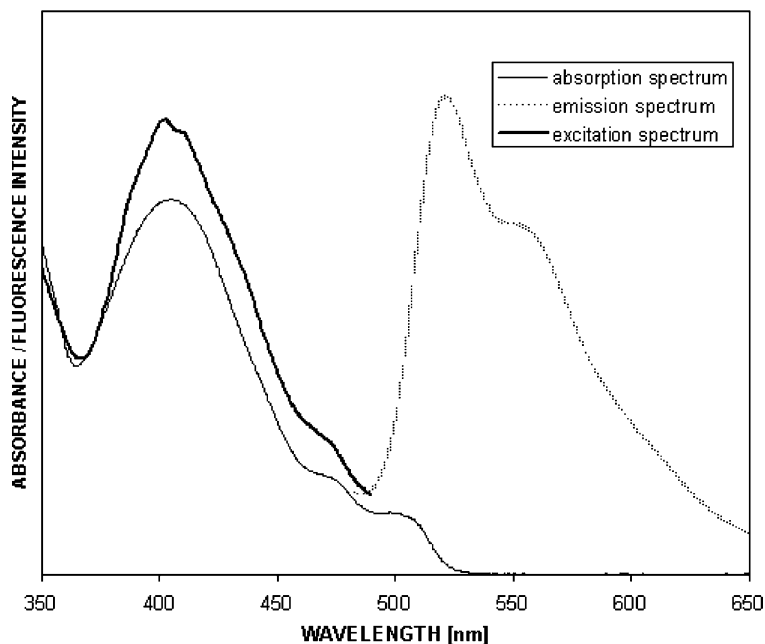


Fig. 3. Absorption, excitation and emission spectra of compound **5NO₂** in CH at room temperature.

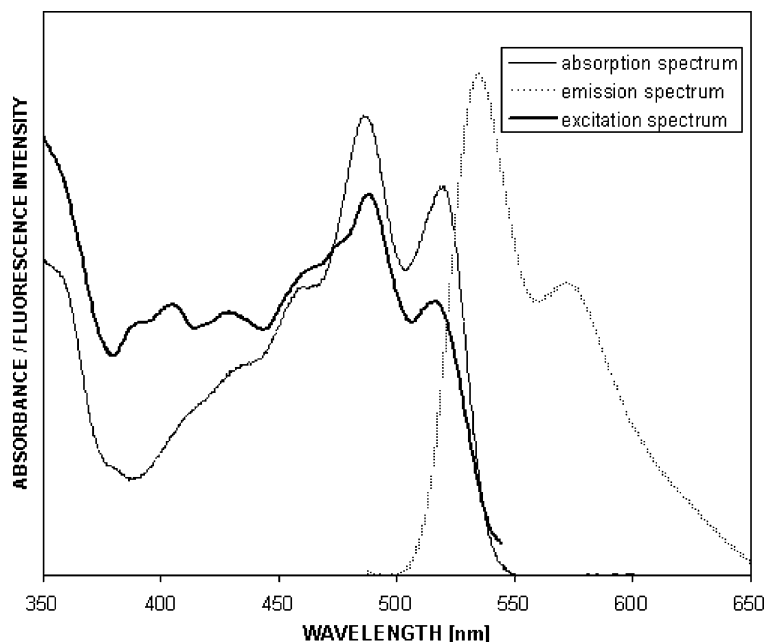


Fig. 4. Absorption, excitation and emission spectra of compound **5NO₂** in MCH/T at 90 K.

fluorescence at all is observed in the concentration range up to 10^{-4} M.

The situation changes in the case of compounds **4** and **5**. In the Schiff bases, the phenyl ring is twisted and its substituents are not fully conjugated with the rest of the molecule. Therefore, the tautomeric ratio does not depend, in general, on the electron action (donor or acceptor) of the substituent being primary determined by the relative polarity of both tautomers [19]. The tautomeric process, therefore, is localised on one naphthylmethylidene moiety as shown for salicylidene aniline **1** [14]. For that reason, we carried out the study of the substituent effect in CH, where, due to low polarity of the solvent, the relative dipole moments will not play an important role and we can assume that the tautomeric ratios in the substituted compounds are almost the same as in unsubstituted ones.

It is evident from Table 2 that in compound **4**, and especially in compound **5**, the substitution (independent of the type of substituent) leads to a substantial increase in the emission even at room temperature. The absorption and fluorescence spectra of **5NO₂** at room temperature presented in Fig. 3, show that in this case the non-radiative deactivation of A* is decreased in comparison with the unsubstituted dye (Fig. 1).

The estimated values for the efficiency of ESIPT (Table 2) show the same tendency—an increase in all studied cases of substitution, i.e. the effect is independent of the nature of the substituent.

The lifetime of compound **5** at room temperature is very short, but it was possible to estimate the lifetimes for the nitro and dimethylamino substituted dyes, i.e. the substitution

leads to increase of lifetime at room temperature. The decrease of the temperature leads to an increase of the quantum yields, mainly caused by decreasing the possibilities for non-radiative deactivation and partially by the increased content of the H-form (Fig. 4). It is worth noting, however, that in the case of para substituted compound **5**, there is no full conversion of the A- to H-form similar to the unsubstituted dye [18,22], a fact supported by the shape of the excitation spectrum in Fig. 4, since a band at 400 nm due to the A-form is still present. At low temperature, the quantum yields become essentially the same, following the same change of the lifetimes (Fig. 5). The decay curve for the nitro substituted compound **5** is shown in Fig. 6 as an example.³

As seen in Fig. 5 there is no obvious relation between the Hammett constants of the substituents, representing their electronic nature [30], and the measured lifetimes, i.e. the effect could be caused by the substitution itself only. It is possible that the introduction of a substituent on para position in the phenyl ring increases electronic interaction through the twisted phenyl ring (but not to full planarization [19]), which could lead to narrowing of the borders of twisting motion around the Ph–N bond and to an increase of the radiative deactivation. At low temperature, however, the molecules are “frozen” and the effect of the substituents disappears.

³ In the case of N(Me)₂ substituent the decay fits with decay function having a small rise time. As it contains dimethylamino group, the twisted intramolecular charge transfer (TICT) process [29] may be responsible for this rising component.

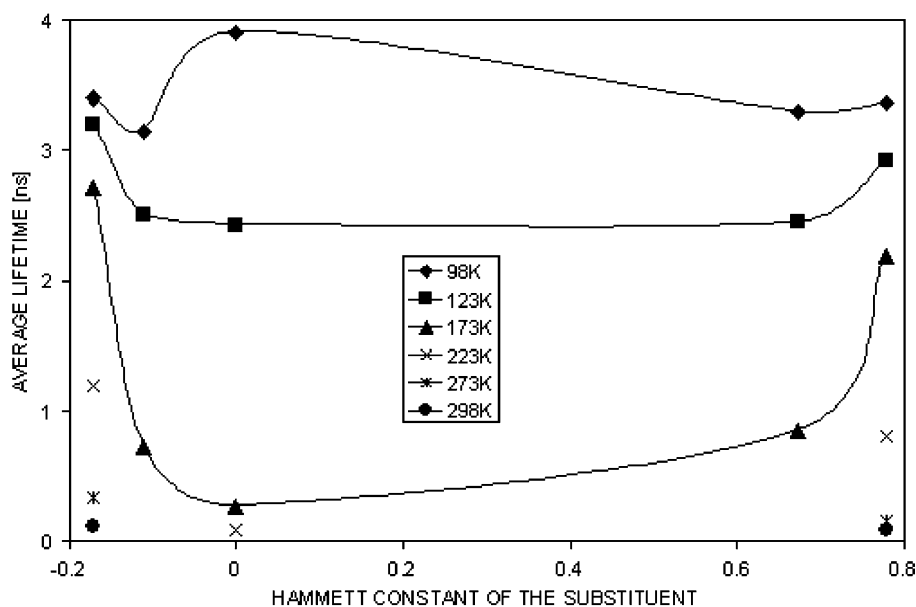


Fig. 5. Average lifetimes as a function of the temperature, for a number of different substituents.

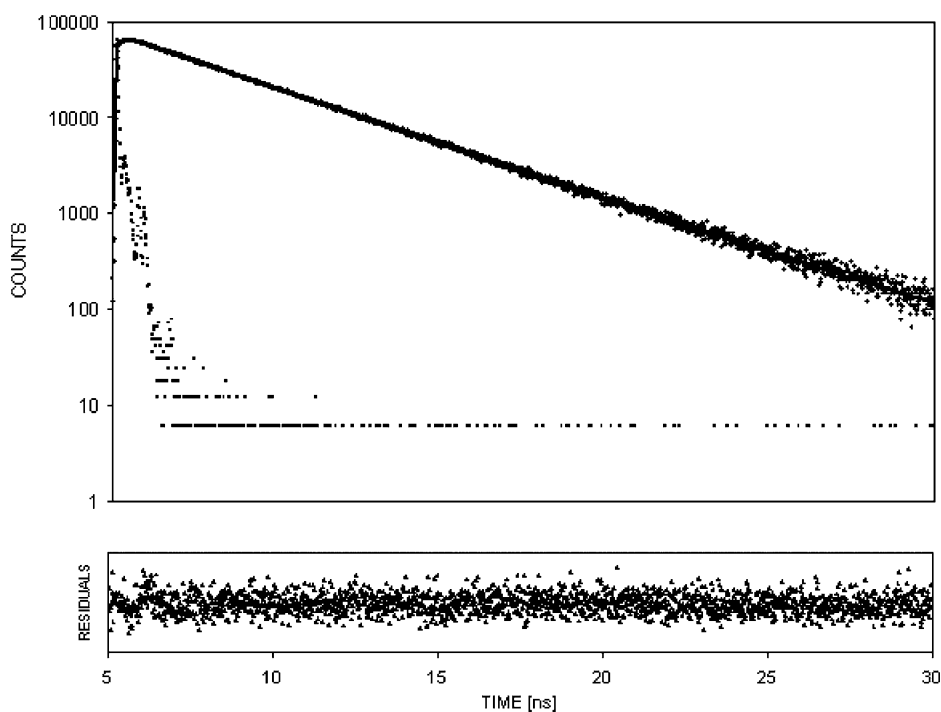


Fig. 6. Two exponential fitted decay curve for NO_2 substituted compound **5** in MCH/T at 98 K (excitation wavelength is 294.6 nm; emission wavelength is 550 nm).

4. Conclusion

In this paper, we study the photophysical properties of some tautomeric compounds containing intramolecular H-bonding as a function of the temperature and substitution. At room temperature both the A- and the H-forms are presented in the ground state, but the fluorescence arises

from the H-form only. The large Stokes shift, and the shape of the excitation spectra, give a clear indication of a fast proton transfer reaction in the excited state, which converts the excited A^* -state to the H^* -form. This proton transfer reaction competes with non-radiative processes and its efficiency could be estimated on the basis of a simple kinetic scheme. The mechanism of the non-radiative deactivation

is not clear, but it was observed that substituents on para position in the phenyl ring appear to reduce this pathway.

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Appendix A

In this appendix we study the tautomeric scheme proposed in the main text in somewhat more detail, and we derive Eqs. (1) and (2). The basic idea is that when the *A* form gets excited, it rapidly transforms to the excited *H* form, which then decays, partly by fluorescence, to the ground state. The ground states then establish equilibrium again.

The set of kinetic equations satisfied by the various components is the following:

$$\begin{aligned}\frac{dn_A}{dt} &= -(W_A(\lambda) + k_f)n_A + k_A n_{A^*} + k_r n_H \\ \frac{dn_{A^*}}{dt} &= W_A(\lambda)n_A - (k_A + k_{PT})n_{A^*} \\ \frac{dn_H}{dt} &= k_f n_A - (W_H(\lambda) + k_r)n_H + k_H n_{H^*} \\ \frac{dn_{H^*}}{dt} &= W_H(\lambda)n_H - k_H n_{H^*} + k_{PT}n_{A^*}\end{aligned}\quad (\text{A.1})$$

In these equations n_i is the number of particles *i* present, k_A is the decay rate of A^* , which is the sum of the inverse radiative life time and nonradiative processes (except the PT reaction), similar considerations hold for k_H . The functions W are the probabilities for excitation, dependent on the excitation wavelength λ , and related to the absorption spectrum. k_{PT} is the excited state proton transfer rate, we assume that there is no back-reaction, since excited state proton transfers are usually very rapid.

Although it is possible to solve this set of equations to get the full time-dependent solutions, for the purpose of this paper finding the stationary state is sufficient. Since fluorescence comes only from the *H* state, we need to calculate n_{H^*} to find the fluorescence intensity. In the stationary state all the left-hand side members of Eq. (A.1) are set to zero, and we get:

$$n_{A^*} = \frac{W_A(\lambda)}{k_A + k_{PT}} n_A \quad (\text{A.2})$$

from the second equation. From the first we then get:

$$n_H = \frac{W_A(\lambda)k_{PT} + k_f(k_A + k_{PT})}{k_r(k_A + k_{PT})} n_A \quad (\text{A.3})$$

and from the last we find

$$\begin{aligned}n_{H^*} &= W_H(\lambda) \frac{W_A(\lambda)k_{PT} + k_f(k_A + k_{PT})}{k_r k_H(k_A + k_{PT})} n_A \\ &\quad + \frac{k_{PT}W_A(\lambda)}{k_H(k_A + k_{PT})} n_A\end{aligned}\quad (\text{A.4})$$

and finally we need to use that the sum of all the particles has to remain equal to the total number of particles present: N , to get the number of particles of each component.

We can restrict ourselves to the simple case where we can use excitation wavelengths in the non-overlapping parts of *A* and *H*. We first consider excitation of *H* itself, and subsequently the independent excitation of *A*.

Setting $W_A(\lambda) = 0$, we only excite *H*, no proton transfer takes place, and we expect to find the usual quantum yield of *H*.

If $W_A(\lambda) = 0$, the above equations reduce to

$$n_{A^*} = 0 \quad (\text{A.5})$$

$$n_H = \frac{k_f}{k_r} n_{A^*} \equiv K n_A \quad (\text{A.6})$$

where K is the ground state equilibrium constant, and

$$n_{H^*} = W_H(\lambda) \frac{K}{k_H} n_A \quad (\text{A.7})$$

Now we use again that the sum of all the particles has to be equal to N , to get

$$n_A = N \left[1 + K + W_H(\lambda) \frac{K}{k_H} \right]^{-1} \quad (\text{A.8})$$

so that we get for n_{H^*}

$$n_{H^*} = \frac{KW_H(\lambda)}{(1 + K)k_H + KW_H(\lambda)} \quad (\text{A.9})$$

Finally we assume that we have no saturation effects, so that we can neglect $KW_H(\lambda)$ in the denominator of the above expression, to get

$$n_{H^*} = \frac{KW_H(\lambda)}{(1 + K)k_H} \quad (\text{A.10})$$

We can write this in terms of the quantum yield Q_H of *H* if we multiply this expression with the intrinsic fluorescence lifetime τ_H , so that

$$I = \tau_H^{-1} n_{H^*} = \frac{K}{1 + K} W_H(\lambda) Q_H \quad (\text{A.11})$$

where I is the fluorescence intensity.

Note that if $K = 0$, meaning that there is no *H* present, we cannot get fluorescence from *H*, whereas if $K \rightarrow \infty$ we get the maximum amount, since only *H* is present initially in the ground state.

Next we study the case where $W_H(\lambda) = 0$. Then the equations reduce to:

$$\begin{aligned}
 n_{A^*} &= \frac{W_A(\lambda)}{k_A + k_{PT}} n_A \\
 n_H &= \frac{W_A(\lambda)k_{PT} + k_f(k_A + k_{PT})}{k_r(k_A + k_{PT})} n_A \\
 n_{H^*} &= \frac{k_{PT}W_A(\lambda)}{k_H(k_A + k_{PT})} n_A
 \end{aligned} \quad (\text{A.12})$$

Again making use of the conservation of total number of particles, we now get

$$n_{H^*} = \frac{k_r k_{PT} W_A(\lambda)}{(1 + K)k_r(k_A + k_{PT})k_H + W_A(\lambda)(k_r k_H + k_{PT}k_H + k_r k_{PT})} \quad (\text{A.13})$$

We will once more assume that saturation effects can be neglected, to get

$$n_{H^*} = \frac{k_{PT}W_A(\lambda)}{(1 + K)(k_A + k_{PT})k_H} \quad (\text{A.14})$$

so that we now get for the fluorescence intensity

$$I = \frac{1}{1 + K} \frac{k_{PT}}{k_A + k_{PT}} W_A(\lambda) Q_H \quad (\text{A.15})$$

Note that this equation has the correct properties: if $K = 0$, we now get the maximum effect, whereas when $K \rightarrow \infty$ the intensity goes to zero, since there is initially no A present to excite.

This gives us the limiting cases we need to derive the Eqs. (1) and (2).

In absence of light the number of A particles is $N/(1 + K)$, and of H particles it is $KN/(1 + K)$. Absence of saturation effects means that this number is not appreciably decreased, and the equilibrium is not shifted by photochemical effects. For the light intensities used in the experiments this is a good approximation. We get for the intensity of the excitation spectrum when there is no overlap between the absorption spectra:

$$\begin{aligned}
 I(\lambda) &= \tau_H^{-1} n_{H^*} \\
 &= \frac{\tau_H^{-1}}{k_H} \left[\frac{NKW_H(\lambda)}{1 + K} + \frac{NW_A(\lambda)}{1 + k} \frac{1}{1 + k_A/k_{PT}} \right] \quad (\text{A.16})
 \end{aligned}$$

We finally note that the absorption spectrum is given by

$$A(\lambda) \propto \left[\frac{NKW_H(\lambda)}{1 + K} + \frac{NW_A(\lambda)}{1 + K} \right] \quad (\text{A.17})$$

which immediately leads to the equations used in the main body of the paper.

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