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ARTICLE *in* JOURNAL OF PHOTOCHEMISTRY AND PHOTOBIOLOGY A CHEMISTRY · NOVEMBER 2002

Impact Factor: 2.5 · DOI: 10.1016/S1010-6030(02)00274-5

ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 153 (2002) 67–76

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Ground and excited state proton transfer reaction of two new *o*-hydroxy Schiff bases in some protic solvents at room temperature and 77 K

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Received 29 March 2002; received in revised form 25 June 2002; accepted 10 July 2002

Abstract

The ground and excited state proton transfer processes of two new *o*-hydroxy Schiff bases, 7-phenylsalicylidene benzylamine (PSBA) and 7-ethylsalicylidene aniline (ESA), have been studied by means of absorption, steady state and time-resolved fluorescence spectroscopy in some protic solvents at room temperature and 77 K. The behaviour of PSBA and ESA has been investigated in neutral and basic conditions. In pure methanol and ethanol two ground state species have been detected in the case of PSBA only. These are: (1) the intramolecularly hydrogen bonded enol and (2) the species which is intermolecularly hydrogen bonded to solvent. After excitation the PSBA preferentially forms the zwitterion while the ESA undergoes excited state intramolecular proton transfer (ESIPT) to form a keto tautomer along with the zwitterion in each of the solvents studied. In the solid matrix at room temperature and at 77 K both the compounds show ESIPT. From the nanosecond measurements we have estimated the proton transfer decay rates in the case of PSBA. Our theoretical calculation at the AM1 level of approximation shows that the ground singlet state has rather large activation barrier both in the cases of PSBA and ESA. The barrier height is much lower on the corresponding excited singlet surface. The process is predicted to be endothermic in the ground state and exothermic in the excited singlet state.

Keywords: Proton transfer; Schiff bases; Protic solvents

1. Introduction

The photophysical behaviour of (hydroxyphenyl)benzoles (HPBs), salicylidene anilines (SAs), (hydroxyphenyl)benzothiazoles (HPBTs), (hydroxyphenyl)benzimidazole (HPBI) and related molecules is shown to be different in polar protic solvents as compared to that observed in nonpolar and aprotic solvents [1–10]. The photo tautomers of the molecules have been demonstrated to be less efficiently produced in alcohols and water as compared to nonpolar solvents due to intermolecular hydrogen bonding interaction with solvent molecules [4,5]. As a result different emitting forms such as neutral, anion, cation and tautomers of different stability are observed depending upon the nature and polarity of the solvents, suggesting a complex excited state proton transfer equilibrium [1–3]. The formation of different rotameric forms, *cis* and *trans* as well as zwitterionic tautomers have been proposed in the literature [1–3,8].

A large Stokes shift due to keto tautomers followed by a normal emission due to enol form is usually registered in the emission spectra of such molecules. A strong normal emission along with a tautomer emission was reported for HPBI in polar solvents. This is due to the coexistence of two intramolecularly hydrogen bonded rotamers, the *cis*-enol and *trans*-enol forms in the ground state. It is suggested that the phototautomer can only be obtained by the electronic excitation of the *cis*-enol form. The *trans*-enol form is responsible for the normal emission and does not undergo an excited state intramolecular proton transfer (ESIPT). It is generally accepted that the stable form of SAs in the ground state is the *cis*-enol form, with an intramolecular hydrogen bond between the hydroxyl group and the nitrogen atom. Upon photoexcitation to the first excited singlet state, it undergoes an ultrafast proton transfer from the hydroxyl group to the nitrogen, due to the electronic redistribution in the excited state. The proton transfer generates a keto tautomer in the excited singlet state [1,11–16]. Highly polar hydrogen bonding solvent, water can show different behaviour compared to alcoholic solvents [17,18]. Brucker

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PII: S1010-6030(02)00274-5

et al. [16] found the *cis*- and *trans*-enol forms in equilibrium in the ground state in neutral ethanolic solution in the case of 4,5-dimethyl-2(2′-hydroxyphenyl)imidazole (DMHI). In neutral aqueous media they have detected both the *trans*-enol and keto forms. It is suggested that the presence of three isomers of DMHI is due to the specific interactions with the solvent molecules with the differential stabilization of these dipolar species in polar protic media. In the first excited singlet state, the *cis*-enol form of DMHI undergoes ESIPT to produce keto tautomer. These observations are quite different from that observed in the case of HBI. HBI exhibits two different intramolecularly hydrogen bonded isomers in the ground electronic state in the aqueous media, excitation of which leads to the formation of the keto tautomer and emission of the normal isomer [19]. The occurrence of both normal and tautomer emissions of HBI seems to be due to the competitive interaction between intra- and intermolecular hydrogen bonding with solvent molecules.

Sinha and Dogra [11] investigated the ground and excited state prototropism of HBI molecule in various solvents. They suggested the formation of a zwitterionic species of HBI in water through electronic reorganization in the excited state. Chou et al. [20] have provided evidences for the formation of zwitterionic species for (hydroxyphenyl)benzazoles (HBAs). It is suggested that the proton transfer tautomers may be depicted by the zwitterionic or π-electron conjugated *cis*-keto tautomer. The photophysical behaviour of HBAs is shown to be quite different in protic solvents as compared to that observed in aprotic and nonpolar solvents [1]. Thus, it is of considerable interest to study and identify different spectroscopic species of related molecules in polar protic solvents, as the solvent polarity may affect their structures.

In our earlier study we have reported some results on a newly synthesized Schiff base, 7-ethylsalicylidene benzylamine (ESBA) in some nonpolar solvents [21]. We are unable to detect ESIPT in solution at room temperature, although the emission spectra show the presence of more than one species in the excited state. For the present work we have synthesized two more new orthohydroxy Schiff bases namely 7-phenylsalicylidene benzylamine (PSBA) and 7-ethylsalicylidene aniline (ESA). We have undertaken the study of ground and excited state proton transfer processes

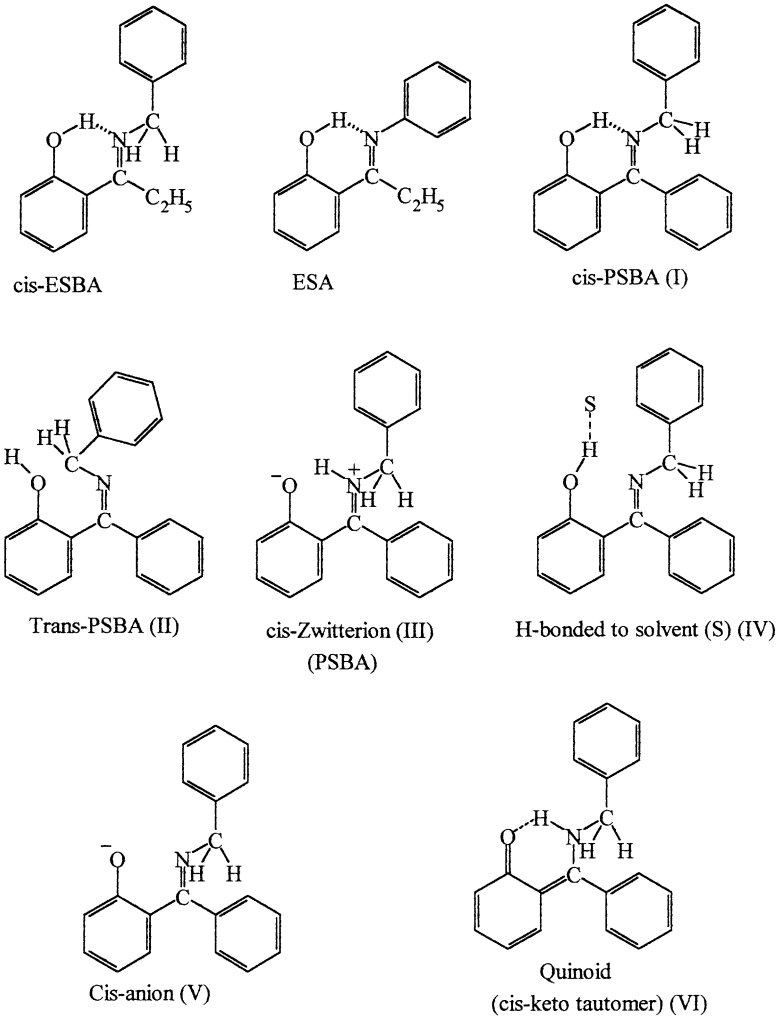


Fig. 1. Possible configurations of PSBA and structural formulae of ESA and ESBA.

of both PSBA and ESA in water, methanol, ethanol and ethylene glycol. The experimental study of this problem was done by means of absorption, emission and time-resolved fluorescence spectroscopy. It is anticipated that the high polarity and ability to form hydrogen bonds are special properties of water that could cause different behaviour compared to alcoholic solvents. The purpose of this investigation is to identify the nature of the species present both in the ground and excited state in these protic solvents. We have compared the results obtained with those found in the case of ESBA. The molecular structures of ESA and ESBA and possible configurations of PSBA are shown in Fig. 1.

2. Experimental

Both PSBA and ESA were synthesized from stoichiometric mixture of a particular salicylaldehyde and benzylamine in methanol by standard procedure [21]. The methoxy (–OCH_3) derivative of ESA, 7-ethylanicylidene aniline (EAA) was obtained by the same method using anisaldehyde. The solid products were recrystallized from methanol and dried. All the solvents used were of spectroscopic grade and freshly distilled before use. Triply distilled water was used throughout. Room temperature absorption and emission spectra were recorded in JASCO 7850 and Perkin Elmer luminescence spectrometer LS50B respectively. The fluorescence emission and excitation spectra at 77 K were recorded on a Hitachi F-4500 fluorescence spectrophotometer. The concentrations of both PSBA and ESA were maintained at (3–6) $\times 10^{-5}$ mol dm^{-3}. All the aqueous solution contained 2% (v/v) of ethanol, because all the compounds are poorly soluble in water.

The transient fluorescence lifetimes (τ_1 and τ_2) were recorded with an NF-900 nanosecond spectrophotometer (Edinburgh Instruments Ltd., UK) using a pulsed nitrogen lamp based on the time-correlated single photon counting technique. The quality of the fits over the fluorescence decay curves was assessed by reduced chi-square, $\chi^2_R = 1.1 \pm 0.2$.

3. Results and discussion

3.1. Absorption, emission and excitation spectra of PSBA

The colourless aqueous solution of PSBA shows a single absorption band at 390 nm. The intensity of this band increases without any change in position of the band by the gradual addition of NaOH (4.5×10^{-3} mol dm^{-3}). Hence, the 390 nm band is due to the transfer of a proton in aqueous media and responsible for the formation of an anion of PSBA (Fig. 1). The yellowish coloured solutions in neutral methanol and ethanol show two absorption bands at 322 and 410 nm. On the other hand, a single absorption band appeared at 322 nm both in ethylene glycol and cyclohexane. Some typical absorption spectra are depicted in Fig. 2.

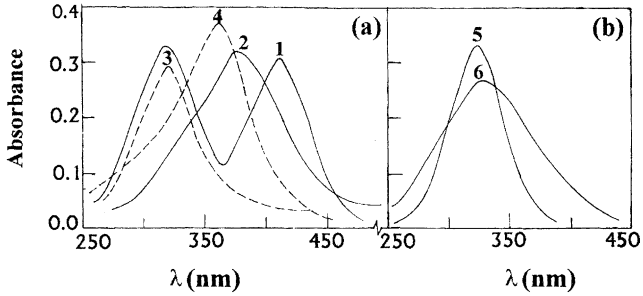


Fig. 2. Absorption spectra of PSBA and ESA: (a) PSBA (solid line) in ethanol (1) and water (2), ESA (dashed line) in water (3) and in presence of aqueous NaOH (4); (b) ESA in ethanol (5) and in presence of NaOH (6), [NaOH] = 5.1×10^{-3} mol dm^{-3}.

A good number of earlier works on SA derivatives have suggested predominant existence of an intramolecularly hydrogen bonded enol isomer in the ground state in nonpolar environment [13–16,22]. The 322 nm band can safely be assigned as due to the intramolecularly hydrogen bonded closed conformer (enol isomer) of PSBA (Fig. 1). The absorption spectra of SA exhibit a band around 400 nm region in polar hydrogen bonding solvents. It is suggested that this band is due to a form which is intermolecularly hydrogen bonded to the polar solvents [23,24]. On addition of NaOH, the 410 nm band is shifted to 390 nm due to the formation of anion. Accordingly, 410 nm band is not due to an anion. On the other hand, due to the presence of electron donating alkyl group both methanol and ethanol can accept proton from PSBA. We therefore, believe that the 410 nm band is due to an intermolecularly hydrogen bonded complex formed by the interaction between PSBA and alcohols which is converted to anion by the added base. Both the proton acceptor, methanol and ethanol can stabilize this complex. It is noted that by the addition of base the yellow colour gradually disappeared. It has long been recognised that SA in polar hydrogen bonding solvents gives rise to a broad visible absorption band located between 400 and 440 nm. Different explanations for the source of this band include an enolic form with intermolecular hydrogen bond to solvent, *cis-o*-quinone form and a protonated species. Lewis and Sandorfy [25] proposed that the coloured form of anil in polar solution is the zwitterionic form with its *cis* configuration. Becker et al. [26] from their study on SA suggested more than one configurations for the coloured form. Separation of charge is usually facilitated by a medium of high dielectric constant, and thus the yellow variety of PSBA can be assigned as the '*cis*' configuration with the ionic form predominating. The possible existence of the positive and negative charges in the '*cis*' zwitterionic form is the stabilising factor for the yellow modification. Williams and Heller [27] proposed in the case of azole derivatives that the yellow modification is mainly the *cis* ionic configuration. However, we believe that since the band (410 nm) is broad presence of more than one species cannot be ruled out. That is, one can say that zwitterion can also be present at this region in

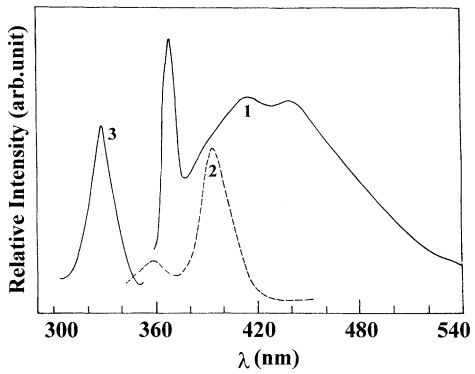


Fig. 3. Emission (1) and excitation (2, 3) spectra of PSBA in water, excitation wavelength = 330 nm (1), monitoring wavelength = 440 nm (2) and 370 nm (3).

addition to the hydrogen bonded species. We are unable to detect this 410 nm band in ethylene glycol. This suggests that the hydrogen bonding ability of the solvent plays an important role in the formation of intermolecular complex or zwitterion. The similarity in the absorption spectra of PSBA in basic solutions does not hold in neutral solutions. The 390 nm band exists in water only and the 410 nm absorption band is observed only in neutral methanol and ethanol. In ethylene glycol only the normal closed conformer absorption band (322 nm) is observed both in neutral and basic medium (triethylamine, TEA).

The emission spectra of PSBA show more than one band, one sharp band at 370 nm and another broad band peaking around 420–440 nm region in methanol and ethanol and two bands at 420 and 440 nm in water (Fig. 3). The 370 nm emission band being excitation wavelength dependent is shifted to 380 nm when excited with 340 nm light and is similarly shifted to 390 nm emission band when the excitation wavelength is 350 nm as shown in Fig. 4. Such systematic shifts of the emission band on increasing λ_{exc} hold good energetically for both the excitation wavelength as well as the emission wavelength. The energy differences found between the

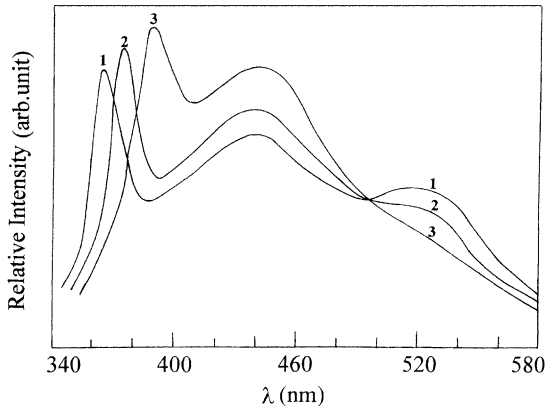


Fig. 4. Emission spectra of PSBA in ethylene glycol at different excitation wavelengths: 330 nm (1), 340 nm (2) and 350 nm (3).

emission and excitation bands are about 2900 cm^{-1}. This is in good agreement with the value expected for Raman signal due to CH stretching modes. Moreover, the excitation spectra of 390 nm emission do not agree with the absorption spectra of *cis*-enol form. All these experimental observations point to the fact that the existence of a sharp fluorescence emission band centred at 390 nm is due to Raman signal from the solvent. By the addition of NaOH ($\sim 10^{-3}$ mol dm^{-3}) the intensity of the broad band (420–440 nm) increases, without any change in position of the band. The excitation spectra of this broad band show two bands at 360 and 400 nm both in presence and absence of base. The emission spectra of PSBA in ethylene glycol show two bands at 370 and 450 nm, and a weak large Stokes shifted band at 530 nm (λ_{exc} = 330 nm). This large Stokes shifted ($\sim$12 000 cm^{-1}) band can be assigned to the ESIPT and formation of keto tautomer of PSBA (Fig. 1). It should be mentioned here that we observed the large Stokes shifted emission due to ESIPT also in solid samples of PSBA at 530 nm. Although we are unable to detect ESIPT in water, methanol and ethanol, ESIPT is seen to occur in a highly viscous liquid like ethylene glycol and in solid sample of PSBA. The keto tautomer is expected to originate from ground state enol form of PSBA. The SA molecule is also known to exist in the enol form in the solid state [28]. On increasing the λ_{exc} to 350 nm, the ESIPT band (530 nm) gradually disappeared as shown in Fig. 4. It can be seen from Fig. 1 that the ESIPT cannot take place from the *trans* form. However, ESIPT can take place from *cis* zwitterion of PSBA.

Agmon et al. [29] in the case of 8-hydroxypyrene-1,3,6-trisulfonate suggested that proton transfer to the solvent is far more efficient in water than in alcohol. This is established in the case of 2-(2′-hydroxyphenyl)benzimidazole by a number of subsequent recent studies [18,30]. From our results it may be suggested that a number of species of different structural configuration may be present in the excited state in polar protic solvents. In the case of ESBA we have detected as many as three different isomeric species even in nonpolar solvents [21]. Williams and Heller [27] investigated the spectroscopy of a series of substituted benzothiazole derivatives. They suggested the presence of as many as four different isomeric intermediates in the photochemistry, but there is no evidence of ESIPT. Lewis and Sandorfy [25] suggested a zwitterionic form for the coloured species in the excited state in which an intramolecular electron transfer occurs from the oxygen atom to the nitrogen atom.

It is generally agreed that upon photoexcitation of solid SAs, the absorption of a photon causes a fast proton transfer. It is proposed that subsequent to proton transfer, either rotation takes place around the ring carbon–imine carbon bonds to form a quinoid structure (Fig. 1) or around the C=N bond to form a *cis* zwitterion. Becker et al. [26] from their study on trifluoroethanol (TFE) proposed that proton transfer was not occurring upon excitation, rather the anil was undergoing an *anti–syn* isomerization around the C=N bond. Orthohydroxy Schiff bases could undergo ESIPT only

under *anti–syn* isomerization around C=N bond if the barrier height is low. In the case of benzylidene aniline and SA they suggested that *anti–syn* isomerization should take place in a singlet excited state. In the case of PSBA the movement around C=N bond is restricted and barrier height around C=N bond should be large.

3.2. Absorption, emission and excitation spectra of ESA

The absorption spectra show a single band at 322 nm in all the protic solvents studied. By the addition of NaOH ($\sim 10^{-3}$ mol dm^{-3}) a new band appeared at 360 nm in water at the expense of 322 nm band. The absorption spectra in methanol and ethanol become broad by the added alkali (Fig. 2b). In ethylene glycol the absorption spectra of ESA remain unaffected by the addition of a strong base like TEA. On gradual addition of NaOH, the intensity of 360 nm band in water continues to increase without any change in position of the band. The 322 and 360 nm bands are assigned to intramolecularly hydrogen bonded closed conformer and anion of ESA, respectively.

The emission spectra of ESA in water and ethylene glycol show three bands: (i) a sharp band at 370 nm; (ii) a broad band around 420–460 nm region; (iii) a relatively weak large Stokes shifted band at 530 nm. In methanol and ethanol two emission bands occurred at 370 and 530 nm. Thus, it can be said that unlike PSBA, in the case of ESA, ESIPT and formation of keto tautomer are evidenced by a large Stokes shifted ($\sim 12\,000$ cm^{-1}) emission in all the protic solvents studied here. It should be mentioned here that like PSBA, the ESIPT band is observed also in solid media. In the case of solid ESA we observed only single emission band at 530 nm (Fig. 5). That is to say that ESIPT is almost complete in solid media and the population of the tautomer is largest in solid sample compared to that observed in solution. The ESIPT band in water is relatively weak compared to those observed in other protic solvents. The appearance of both the normal and tautomer emission of ESA seems to be dictated by the competition between intra- and intermolecularly hydrogen bonding with solvent molecules. The electron donating alkyl group present near nitrogen atom can enhance the proton accepting property of the nitrogen atom to form the hydrogen bond. This will decrease the proton transfer barrier height in ESA. We observed ESIPT in all the protic solvents even at room temperature in the case of ESA. By the gradual addition of aqueous NaOH ($\sim 10^{-3}$ mol dm^{-3}) the intensity of 420–460 nm broad band in water increases in intensity at the expense of 530 nm band. On the other hand, in methanol, ethanol and ethylene glycol a new broad band appeared around 420–460 nm region at the expense of 530 nm band by the added base. The excitation spectra obtained by monitoring the broad 430–460 nm emission show two bands at 360 and 400 nm both in presence and absence of base. The 360 nm band is indeed identical to the anion absorption band. The methoxy derivative of ESA, EAA shows a single emission band at 370 nm (normal Stokes shift) in water and ethanol. It can be said therefore that methylation perturbed the excited state reaction of ESA. This indicates the existence of anion or zwitterion in the 420–440 nm broad band. Moreover, the normal closed conformer is not responsible for the emission of 420–440 nm broad band. The fluorescence excitation spectra of EAA emission appeared at 325 nm and agree well with its absorption counterpart. All these observations suggest that the species responsible for higher energy emission has an enol type structure, may be *trans* or *cis* in the case of ESA and probably in a *trans* configuration in the case of PSBA.

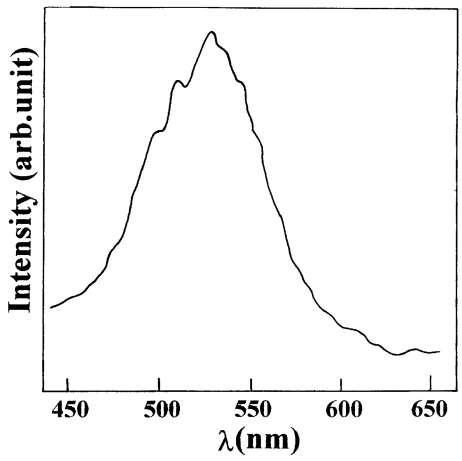


Fig. 5. Emission spectra of solid ESA, excitation wavelength = 330 nm.

We observe anion in pure water and in basic alcohols in the case of PSBA and in basic solution in the case of ESA. Becker et al. [26] showed the existence of the anion of HBT in absolute methanol and ethanol and observed only anion in basic alcohols. We believe the existence of anion both in the case of PSBA and ESA in the emission band around 420–460 nm region in alcohols and in water. The excitation spectra monitored at the two emission bands are different. Hence, the species responsible for different emission must have come from different species in the ground state. A strong normal emission along with a keto tautomer emission was reported for 2-(2′-hydroxyphenyl)benzimidazole in polar solvent [11]. This is explained by the existence of two intramolecularly hydrogen bonded rotamers in the ground state, the *cis*-enol and *trans*-enol form. It is suggested that the excited state tautomer can be obtained only by electronic excitation of the *cis*-enol form and the *trans*-enol form is responsible for the normal emission. The *trans*-enol form cannot undergo ESIPT.

Both PSBA and ESA are yellow coloured solid compounds. The coloured nature of the compounds indicates that their ground state most likely is a molecule with the proton bonded to nitrogen that is mainly a zwitterion. Lewis and Sandorfy [25] examined the coloured form in solution as well as the solid state by IR spectroscopy and suggested that the coloured form of an anil is in fact the zwitterion in its *cis* configuration. In the case of HBT, Becker et al. [6]

proposed that the coloured form is expected to exist in at least two different conformations. The presence of one or two conformers for the coloured form is dependent on the hydrogen bonding character of the solvent used. Itoh et al. [31] in a similar fluorescence study showed that both the anion and the zwitterion are produced in alcohols. We would like to propose that the broad band around 420–460 nm region must be responsible for at least two species, the anion and the zwitterion both in the case of PSBA and ESA which are generated from the intermolecularly hydrogen bonded complex. Becker et al. [6] believed that the anion and zwitterion of HBT are generated from the intermolecular hydrogen bonded HBT. The anion may also be generated from zwitterion. The intermolecular hydrogen bonded species cannot undergo proton transfer but can undergo anti–syn isomerization around the C=N bond.

In our earlier work with 4-methyl-2,6-diformylphenol, we have shown that ESIPT cannot be observed in polar hydrogen bonding solvents. This is due to the interaction with polar solvents and rupture of the intramolecular bond [32]. The ESIPT can be observed only as long as intramolecular bond exists. This indicates that intramolecular bond in ESA is so strong that polar solvent alone cannot rupture the hydrogen bond completely, and a promoter base is necessary for this purpose. Filarowski et al. [33] suggested that intramolecular bond length is the shortest in electron donating substituted Schiff bases compared to the other Schiff bases without alkyl substitution. They also proposed that both the steric and electronic interaction of such groups strengthens the intramolecular bond. The NMR spectra of hydroxyl proton appeared at 16.0 and 13.2 ppm in the case of ESA and PSBA, respectively. This further supports the fact that intramolecular bond in ESA is stronger than that in PSBA. All the protic solvents have hydrogen bonding properties that facilitate intermolecular hydrogen bonding with PSBA and ESA in solution. In presence of higher concentration of base the intermolecular complex can give rise to the formation of an anion. The increased concentration of base increases the population of the anion thereby decreasing the tautomer concentration.

The large change of energy (2871 cm^{-1}) must involve formation of some new species that seem to fluoresce at longer wavelengths relative to that of anionic species. Such a broad band around 420–460 nm region of the emission also supports the formation of another new species. We believe that this new species is a dipolar zwitterion (Fig. 1). Since the anion and zwitterion of PSBA and ESA fluoresce around 420–460 nm region, the zwitterion is expected to fluoresce at 440 nm and anion at 420 nm. The actual maxima of zwitterion would be slightly higher than 440 nm because of solvation effects. In the case of nitroderivatives of 2-(2′-hydroxy-5′-nitrophenyl) benzothiazole derivatives, Becker et al. [6] suggested that both the anion and the zwitterion are produced adiabatically from the enol form.

It can be seen from Fig. 1 that ESIPT can occur only from *cis* configuration in the case of PSBA. The *cis–trans* isomerization can take place both in the case of PSBA and ESA. If this process is fast enough ESIPT cannot be observed. However, ESIPT can be observed in the case of ESA even in presence of *cis–trans* isomerization. We believe that this must be due to the absence of $–CH_2$ in ESA (Fig. 1).

Table 1
Lifetimes (τ_1^f and τ_2^f) and decay rate constants at 298 K (k_1^f and k_2^f) of PSBA[a]

Solvent	τ_1 (ns)	τ_2 (ns)	$k_1 \times 10^{-8}$ (s^{-1})	$k_2 \times 10^{-8}$ (s^{-1})
Water	4.6 (22)	1.2 (78)	2.2	8.3
Methanol	4.1 (70)	0.9 (30)	2.4	11.1
Ethanol	3.7 (68)	1.0 (32)	2.7	10.0
Ethylene glycol	4.4 (65)	1.3 (35)	2.3	7.7

[a] Monitoring wavelength (λ_{mon}) = 460 nm. The percentages of the species present are given in parentheses.

3.3. The decay behaviour of PSBA fluorescence

The fluorescence decay of PSBA in protic solvents has been measured on nanosecond time-scale. After deconvolution a biexponential decay curve is obtained, that is, the measured fluorescence decay can adequately be described by a double exponential function with two different lifetimes (τ_1 and τ_2). The weighted residue appeared to be better distributed when a double exponential is fitted. The lifetime values are displayed in Table 1. The biexponential decay with two different lifetimes indicates the presence of at least two species in the excited state. The biexponential decay and higher lifetimes in protic solvents compared to those in cyclohexane (0.8 and 1.6 ns) further support the presence of intermolecular interaction.

Two decay components suggest the existence of the potential barrier between the two excited species. In the potential surface with a barrier, the rate of proton transfer correlates with frequency of O–H stretching mode. The decay rate usually becomes smaller in the lower energy region of the fluorescence spectra. Hence, the decay rate of the short-wavelength fluorescence is larger. Accordingly, we would like to propose that decay rate of slow components corresponds to anion. When monitoring the decay of the emission we found a short-lived component and a long-lived component in all the protic solvents. The contribution to the emission decay of the long-lived component compared to the short-lived component is the smallest in ethanol and the largest in water. We would like to attribute the short-lived component to the zwitterionic form and the long-lived component to the anion. All the protic solvents have strong hydrogen bonding properties that facilitate intermolecular hydrogen bonding with PSBA and ESA in solution. We are unable to measure lifetime of ESA on our nanosecond instrument. Rate of proton transfer is relatively faster in the case of ESA.

We are unable to detect any significant change for decay rate in ethylene glycol compared to other protic solvents

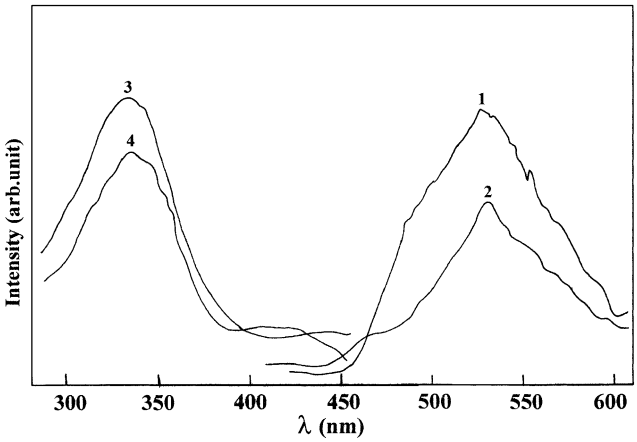


Fig. 6. Emission spectra of (1) ESA and (2); PSBA, excitation spectra of (3) ESA and (4) PSBA in ethanol at 77 K, excitation wavelength = 330 nm and monitoring wavelength = 530 nm.

used. Ding et al. [22] made similar observation in the case of HBT. We believe then that the anion is photochemically produced after excitation of the intermolecular hydrogen bonded enol or by the addition of base except in water. Itoh et al. [31] found that both anion and the zwitterion are produced after excitation in alcohols. Becker et al. [26] suggested that the anion or zwitterion of HBT are generated from two different species.

3.4. Emission spectra at 77 K

A strong single large Stokes shifted fluorescence band is observed at 530 nm in methanol and ethanol both in the case of PSBA and ESA at 77 K (Fig. 6). The observed fluorescence excitation spectra are almost identical with the absorption spectra of normal closed conformer both in the case of PSBA and ESA. Similar observation was made by Ding et al. [22] for HBT in low temperature glasses. Sekikawa et al. [24], in the case of SA, observed ESIPT even below 70 K. The single large Stokes shifted fluorescence shows that the excited enol form relaxes to the excited keto form, indicating that the photoexcitation causes the proton transfer. The ESIPT band is found to be independent of any excitation wavelength (λ_{exc}). However, intensity of the band was found to increase on lowering the temperature to 77 K.

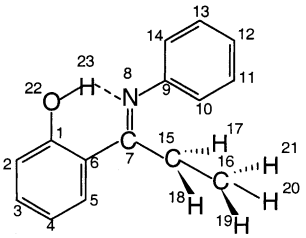
It is expected that at 77 K *cis–trans* isomerization cannot occur so easily, like room temperature. Hence, the *cis* form should be more populated and stable even in the excited state. Accordingly, ESIPT can take place at 77 K even in the case of PSBA. In the case of ESA, ESIPT can take place even from *trans* form due to the absence of CH_2 group (Fig. 1). We are unable to detect any evidence for phosphorescence at either room temperature or liquid nitrogen temperature. Our significant observation is that no anion or zwitterion is detected at 77 K. Only the ESIPT band due to keto tautomer is observed both in the case of PSBA and ESA. That is ESIPT is complete at this temperature. However, it is pertinent to mention that ESIPT can generate a resonance hybrid of the canonical forms, zwitterion and ketone. Williams and Heller [27] studied as many as 20 azole derivatives. They were unable to detect any evidence for phosphorescence at either room temperature or liquid nitrogen temperature.

3.5. Theoretical work

AM1 is a method, which is claimed to describe energetics, and topographies of hydrogen bonded systems fairly accurately [34]. The semiempirical molecular orbital AM1 method provides good estimates of geometries and heats of formation of organic molecules and gives an insight relating to reaction paths of chemical changes that they undergo [35]. A number of workers have used the semiempirical calculations at the MNDO [36] and AM1 [37] levels of approximation to describe excited state proton transfer reactions. In our earlier work we have optimized the ground state geometrical parameters of 4-methyl-2,6-diformyl phenol at the AM1 level [38]. Our results show a fair agreement with the ab initio data and the results obtained experimentally. In the present paper we have conducted some theoretical investigation on the proton transfer reaction of ESA in a semiempirical framework at the AM1 level of approximation. The geometrical parameters of ESA have been optimized within the limitations of AM1 method. The optimized parameters together with the atomic labelling used are reported in Table 2. The calculated activation barrier is quite high in the S_0 state and therefore, the proton transfer rate is expected to be very low in this state. This corroborates our experimental observation that intramolecular proton transfer does not take place at all in the S_0 state. The optimized parameters are reported in Table 2. The electron donating group in ESA has expectedly increased the C=N bond lengths and the increase in electron density of the nitrogen atom has resulted in a shorter equilibrium N(8)–H(23) distance. To construct the reaction path representing the proton transfer in ESA, the N(8)–H(23) distance (R, 2.2806 Å) has been chosen as the co-ordinate. As the proton translocation distance of the mobile hydrogen atom is considered to be the key parameter for the construction of the excited state proton transfer potential, the N(8)–H(23) distance is varied between what is normal for the primary and what is known to be the equilibrium tautomeric N(8)–H(23) distance.

The maxima in the S_0 state is a true saddle point on the potential energy surface (PES) and occurs at a proton transfer distance of 1.3 Å (Fig. 7). Table 2 shows the exo(endo)thermicities and activation energies for the tautomerization process of ESA in S_0, S_1 and T_1 states. It turns out that the reaction is appreciably endothermic in the S_0 state and the activation energy (ΔE_{Act}) for the transfer is also quite high. Thus, proton transfer in the S_0 state is unlikely to occur. On the other hand, the tautomeric form in the excited state (S_1) is predicted to be relatively more stable than the primary closed form. Thus, the endothermic proton transfer process in the ground state (S_0) is predicted

Table 2
Energetics of ESA: activation (ΔE_{Act}) and tautomerization (ΔE_{PT}) energy in S_0, T_1 and S_1 states and physical parameters of ESA in the S_0 state



ESA

	Initial	TS	Final	Tautomer
Charge density (q) on				
H(23)	0.2423	0.3461	0.2706	0.2831
N(8)	−0.2020	−0.3028	−0.2747	−0.2819
O(22)	−0.2549	−0.4265	−0.4003	−0.4037
C(7)	0.0847	0.2372	0.2249	0.2280
C(1)	0.1294	0.3106	0.3063	0.3057
Distance between (Å)				
O(22)–H(23)	0.9684	1.8188	2.0117	2.0229
H(23)–N(8)	2.2806	1.2295	1.0019	1.0054
N(8)–C(7)	1.2913	1.3479	1.3622	1.356
C(7)–C(6)	1.4826	1.4093	1.4003	1.4017
C(6)–C(1)	1.4069	1.4580	1.4651	1.4636
C(1)–O(22)	1.3704	1.2613	1.2533	1.2538
Angle between (°)				
C(1)–C(6)–C(7)	123.39	122.76	123.07	122.94
N(8)–C(7)–C(6)	120.03	123.09	123.47	123.70
C(6)–C(1)–O (22)	125.32	123.68	123.58	123.52
C(1)–C(22)–H(23)	109.70	106.87	102.71	
Dihedral angle (°)				
C(6)–C(1)–O(22)–H(23)	−7.12	2.03	−1.74	
N(8)–C(7)–C(6)–C(1)	43.87	9.47	7.71	−2.35
C(7)–C(6)–C(1)–O(22)	1.12	−4.24	−2.00	−0.51
Energetics (kcal/M)				
S_0	−4421.61	−4398.96	−4415.97	22.65[a], 05.64[b]
T_1	−4358.02	−4345.00	−4379.84	11.02[a], −21.82[b]
S_1	−4334.37	−4323.09	−4343.88	09.28[a], −9.51[b]

[a] ΔE_{act} values.
[b] ΔE_{PT} values.

to become an exothermic one in the S_1 state. A relatively low proton transfer barrier in the S_1 state is indicative of a rather shallow well characterising the primary form. It is not deep enough to contain an appreciable number of bound vibrational levels, so that the potential is effectively of the anharmonic single well type.

The PES for the proton transfer reaction has been generated through the calculation of the energies of the configurations with varying N(8)–H(23) (2.2806 Å) distance. At each such point all other geometrical parameters have been optimized. This distance has been restrained to a particular value for a single configuration. Fig. 7 represents the simulated PES for the ESIPT process of an isolated ESA molecule in the three different states. The figures reflect that the ESIPT process is endothermic in the S_0 state and exothermic both in the S_1 and T_1 states. Accordingly, the reaction is thermodynamically unfavourable in the S_0 state but is favourable both in the S_1 and T_1 states if the barrier height is low. The barrier height is relatively low both in the S_1 and T_1 states compared to the S_0 state. We observed ESIPT both in the S_1 and T_1 states in the case of ESA. Solvent stabilization of the electronic states in alcoholic solvents with different polarities has been estimated assuming Onsagar's continuum model. The general PES corresponds to the solvent stabilised species in all the states and gives a theoretical estimate of the activation energy as well as the energy change for the process in the solution phase.

The basic nature of PES does not change remarkably from that in the isolated condition. It is worth mentioning here that significant changes occur in the hydrogen bonded chelate ring. The O(22)–C(1) single bond in the primary form has been converted into a double bond similar to

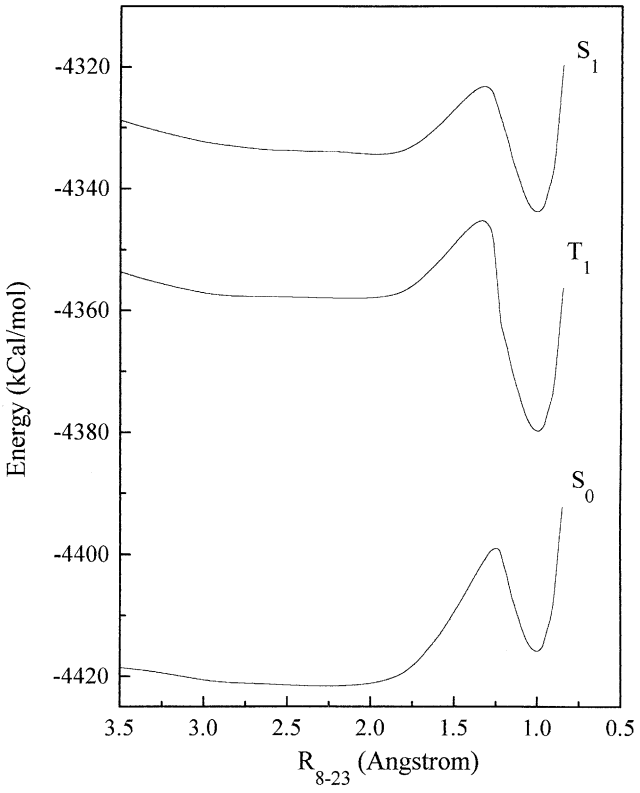


Fig. 7. Variation of potential energy during proton transfer in ESA molecule in S_0, S_1 and T_1 states.

the C(6)–C(7) bond, and the C(7)–N(8) double bond has changed to a single bond. Hence, the phenolic (enolic) structure in the ground state is converted to a keto like structure upon excitation. This is consistent with our experimental results. The computed electron densities on the O22 and N8 are considerably different from each other (Table 2). Thus the fluorescing state of ESA can be regarded as ionic and the transfer process appears to be like a proton transfer rather than hydrogen transfer process. This seems to indicate that ESIPT is from a zwitterionic species.

4. Conclusions

In solution among all the three compounds, ESBA, PSBA and ESA we observed ESIPT only in the case of ESA at room temperature. In the case of ESA, ESIPT can be observed even from *trans*-isomer and in presence of *cis–trans* isomerization. This is due to the absence of $–CH_2–$ group in ESA. The presence of $–CH_2–$ group in PSBA prevents the ESIPT. The keto tautomer is the predominant species at 77 K and in solid sample both in the case of ESBA, PSBA and ESA. The *cis*-enol form is the most stable form in the ground state and intramolecular proton transfer is improbable in S_0 state because of thermodynamic and kinetic considerations. We believe that all the three species, the anion, zwitterion and intermolecularly bonded complex exist in 420–460 nm emission region in the case of both the compounds, PSBA and ESA.

Acknowledgements

This work is supported by INSA—Polish Academy of Science Exchange Programme (Polish Grant #KBN 3T09A03716). Authors are grateful to the Department of Spectroscopy of this institute (IACS) for low temperature measurements and Saha Institute of Nuclear Physics, India for nanosecond lifetime measurements. Samaresh Mukherjee would like to thank the Department of Chemistry, University College Dublin for provision of financial support and laboratory facilities. Thanks also to IACS for granting leave to S. Mukherjee and to Ms. Sarbani Saha and Debi Banerjee for preparing the manuscript.

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