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Photoinduced proton transfer in the excited singlet state of 3, 7-dihydroxynaphthoic acid and solvent effect

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Abstract

The photophysics of 3, 7-dihydroxynaphthoic acid (DHNA) has been studied in different aprotic and protic solvents by steady-state and nanosecond transient emission spectroscopy. Both the monomer and the dimer of DHNA have been detected in the ground as well as in excited state in dilute solution ($\sim 10^{-5}$ mol dm^{-3}). A large Stokes shifted emission (~ 6500 cm^{-1}) indicates that DHNA undergoes thermodynamically favourable proton transfer in the excited state. It is proposed that the added base promotes the proton transfer only in polar protic solvents. The mechanism of the static processes has been investigated by making steady-state fluorescence quenching measurements and that of the dynamic processes by nanosecond fluorescence lifetime techniques.

1. Introduction

Although proton transfer (PT) reaction of salicylic acid (SA) was known four decades ago [1], not many studies have been done on this system. This is due to the fact that *o*-hydroxy carboxylic compounds such as SA dimerize readily even in dilute solution and get ionised in polar solvents. Two types of emission are generally observed in the case of SA and its derivatives. Large Stokes shifted emission (red band) is generally observed in hydrocarbon and nonpolar solvents. Another type of emission with relatively shorter Stokes shift (blue band) is observed in polar solvents. Pant et al. [2,3] suggested that the larger Stokes shifted 'red' band is due to the excited state PT to give rise to the tautomer. On the other hand, the normal form emits to give the blue band. However, in the case of 3, 5-*t*-butyl salicylic acid, Law et al. [4] showed that the carboxylate anion is the only precursor to tautomerisation.

It has been shown earlier that in the case of salicylic acid the most stable form in the ground state is the normal primary form and that in the excited state is the tautomeric form [5]. It has also been suggested that both the primary and tautomeric forms are intramolecularly hydrogen bonded. The tautomeric form results due to a PT in the primary form. Salicylic acid exists as a dimer in the solid state and in nonpolar solvents at higher concentration [2,3,6,7]. It exists as a monomer in polar solvents and gets protonated and deproto-

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nated in acidic and basic media, respectively [8]. SA is known to exist as a rotamer of the primary form with relatively weak intramolecular bond. Bisht et al. [7] assigned the primary and rotameric forms to π–π^* and n–π^* transitions, respectively. They attributed the large Stokes shift in emission spectra to the signature of tautomerisation. They observed intramolecular PT in dilute alkane solution. However, in concentrated solution and in solid state, the SA dimer showed dual emission. They suggested double PT and tunnelling mechanisms for the observed photophysical behaviour. Ware et al. [9] studied 3-hydroxy-2-naphthoic acid (HNA) in detail. They described a fluorescence quenching reaction via an intramolecular proton transfer for HNA. It has been shown that bases which promote the proton transfer function parallely by static and dynamic quenching mechanisms. Catalan et al. [10] studied some esters of *o*-hydroxynaphthoic acids. They suggested that the photostability of such compounds does not rely on the photophysics of their proton-transferred tautomer but on the nonradiative dynamics of their respective normal tautomers. All the molecules studied exhibit a great photostability to UV radiation compared to those of methyl salicylate and Tinuvin P. In molecules where both inter- and intramolecular PT are possible, it can represent an important nonradiative channel either to products or to the ground state. This type of PT processes could be important in the excited state if the transfer is via a hydrogen bond already formed in the ground state. The rate could be high enough to make the transfer competitive with intersystem crossing and lead to photochemical products.

For the last few years, we are engaged in studying the dynamics of PT in 4-methyl-2,6-diformyl phenol (MFOH) and its derivatives in solution [11–14]. In the case of 3-methyl-6-hydroxy-*m*-phthalic acid (HmPA) we have shown that the variations in steady-state spectra depend mainly on the solvent properties. A large Stokes shifted form of this acid (HmPA) undergoes intramolecular proton transfer (ESIPT) leading to tautomerisation in the excited singlet state in nonpolar solvents. In the present work we would like to report our findings on 3,7-dihydroxynaphthoic acid (DHNA) with a special emphasis on the elucidation of the mechanism of PT reaction by absorption, emission and nanosecond spectroscopy. We have discussed the photophysical properties of DHNA in comparison with those of salicylic acid (SA) and 3-hydroxy-2-naphthoic acid (HNA). Fluorescence quenching by the added base and excited state PT in protic solvents has also been described in this study.

2. Experimental

3,7-Dihydroxynaphthoic acid (DHNA) 98% was used as received from Aldrich. The spectroscopic grade solvents, namely methanol, ethanol, *n*-heptane, 1,4-dioxane, acetone, acetonitrile (ACN) and ethylene glycol were dried and distilled before use as reported earlier [14]. NaOH used was of A.R. grade. Triply distilled water was used throughout. Absorption, emission and excitation spectra were recorded on a JASCO 7850 and a Perkin–Elmer MPF 44B spectrophotometer. The transient fluorescent lifetime (τ_f) was measured with an SP-70 nanosecond spectrometer (Applied Photophysics, UK) using a pulsed nitrogen lamp based on the time correlated single photon counting technique. The concentration of the dilute solution of DHNA was maintained at $4–6 \times 10^{-5}$ mol dm^{-3}. The relative fluorescence quantum yields (ϕ_f) and all other experimental details were the same as reported earlier [15–17].

3. Results and discussion

The absorption spectra of DHNA show a single broad band peaking around 360–370 nm (blue band 1) in pure water. However, in methanol, ethanol, ACN, acetone, dioxane, *n*-heptane and ethylene glycol, the absorption spectra appeared around 380–390 nm region (red band 1). Both the blue band 1 in water and the red band 1 in methanol and ethanol are shifted to 400 nm (Fig. 1) on addition of NaOH ($\sim 10^{-3}$ mol dm^{-3}) alongwith an increase in the intensity of the band. On the addition of triethylamine (TEA), the red band in ACN and ethylene glycol is shifted to 360 nm (Fig. 1). In acetone and dioxane, both the bands (blue

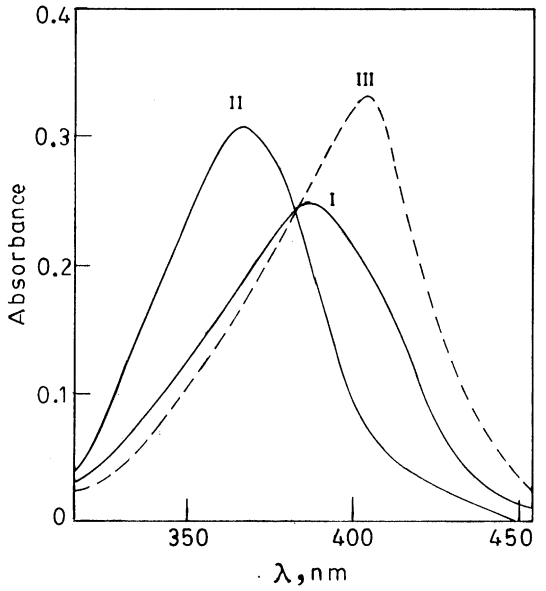


Fig. 1. Absorption spectra of DHNA in pure ethanol (I), water (II) and water + NaOH (III).

and red) appear on addition of TEA. In *n*-heptane, the absorption band does not show any spectral change by the added TEA ($\sim 10^{-3}$ mol dm^{-3}). It is pertinent to mention here that the colourless solution of DHNA becomes yellow in colour in presence of NaOH in protic solvents. The probability of dimer formation in water at this low concentration of DHNA ($\sim 10^{-5}$ mol dm^{-3}) is unlikely. Hence, we believe that the red band 1 is due to the dimer of DHNA. However, since the band is broad hence the presence of small amount of dimer even in water in the ground state cannot be ruled out. The red band, blue band and 400 nm absorption band can safely be assigned to the dimer, monomer and anion of DHNA, respectively. Similar observation was made by Tripathi and co-workers [2] in the case of salicylic acid (SA). It has been shown that on addition of ether the dimers break down into monomers and the solution now gives the lower wavelength band only corresponding to hydrogen bonded monomers.

The emission spectra of DHNA show a broad band peaking around 420–460 nm (blue band 2) in *n*-heptane, dioxane, ACN, acetone and benzene. The excitation spectra of this emission (blue band 2) appeared at 390 nm with a shoulder at 360 nm. Hence, both the excitation spectra and shoulder agree reasonably well with their absorption spectra of dimer (390 nm) and monomer (360 nm) of DHNA. The broad 420–460 nm emission can be assigned mainly to the dimer of DHNA. However, the presence of small amount of monomer cannot be ruled out (since the band is broad). In presence of a base like TEA, another relatively weak band occurred around 500–520 nm (red band 2) in *n*-heptane, benzene, ACN and dioxane (Fig. 2) and can be assigned to the monomer of DHNA. The excitation spectra of red band 2 emission are almost similar to those observed in the case of blue band 2. On gradual addition of TEA ($\sim 10^{-3}$ mol dm^{-3}), the intensity of blue band 2 decreases considerably in *n*-heptane, dioxane and benzene. However, in ACN and acetone, the blue band 2 completely disappears due to the added TEA. It is also noted that the red band 2 remains independent in position of any λ_{exc} in all the aprotic solvents with a small decrease in intensity only. This fluorescence quenching behaviour can be explained by simple Stern–Volmer (S–V) mechanism:

$$I_0/I = 1 + k_q\tau_0[\mathrm{TEA}],$$

where I_0/I is the intensity ratio without and with quencher, k_q is the bimolecular rate constant. The lifetime of DHNA ($\tau_0 = 12.5$ ns) is obtained from transient measurement when [TEA] = 0.

The bimolecular quenching constants (k_q) obtained from steady-state S–V plots are 1.8×10^{10} s^{-1} and 4.3×10^{10} s^{-1} in dioxane and ACN, respectively. The magnitude of the bimolecular rate constants is similar to the diffusion-controlled reaction rate. The S–V plots are linear (not shown) suggesting that a simple quenching mechanism is operating. It can be said from the steady-state measurements that the experimental results are consistent with the S–V quenching mechanism.

Our observation shows that the intensity of blue band 2 decreases or disappears both by the added base and in aprotic nonpolar and polar solvents. This is at the expense of the state responsible for the blue band 2. These spectral changes are observed both in the ground as well as in the excited state by the added base (B). It can be said now that there is interaction between DHNA and base both

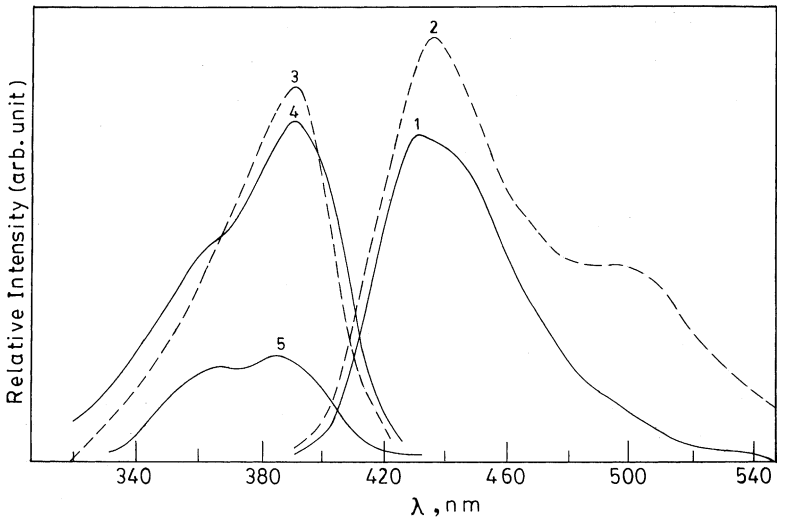


Fig. 2. Emission (1,2) and excitation (3–5) spectra of DHNA in: pure *n*-heptane (1), heptane + TEA (2), heptane (3) at $\lambda_{mon} = 440$ nm, heptane + TEA (4) at $\lambda_{mon} = 440$ nm and heptane + TEA (5) at $\lambda_{mon} = 510$ nm.

in the ground and excited state. It can also be said that excited state intramolecular proton transfer (ESIPT) is not being observed since the intramolecular bond gets ruptured due to the interaction between DHNA and base to form the open conformer (IIa). Moreover, ESIPT cannot be observed due to the formation of dimer in aprotic solvents. Tripathi and co-workers [2] suggested double PT in the case of SA dimer. Our observation reveals that both static and dynamic

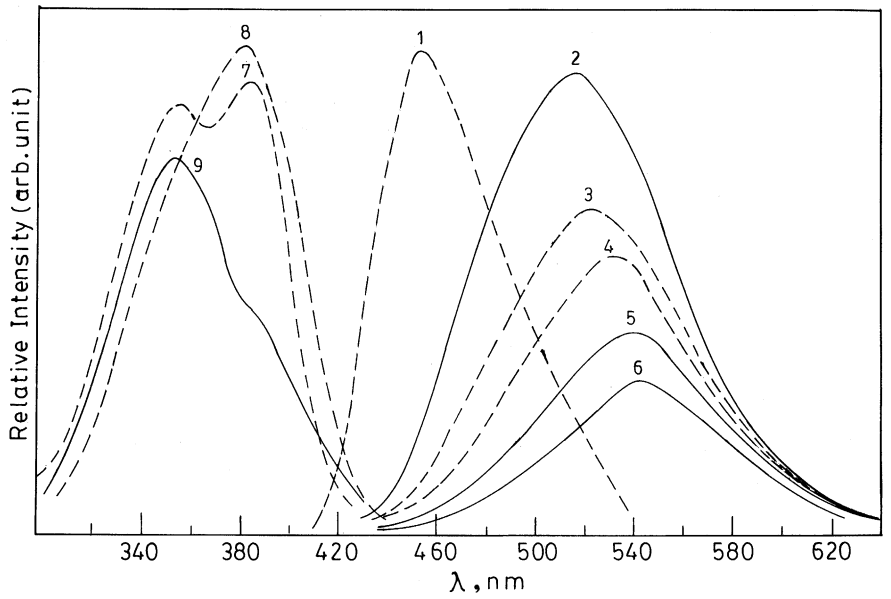
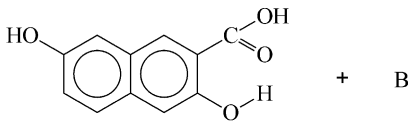
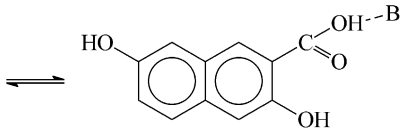


Fig. 3. Emission (1–6) and excitation (7–9) spectra of DHNA in: pure ethanol (1), ethanol + NaOH (2–6) at different λ_{exc} (nm): 370 (2), 380 (3), 390 (4), 400 (5) and 410 (6); pure water (7) at $\lambda_{mon} = 520$ nm, pure ethanol (8) at $\lambda_{mon} = 460$ nm and ethanol + NaOH (9) at $\lambda_{mon} = 540$ nm.

quenching are responsible for this observed decrease of emission intensity. It has been shown in the case of methoxy derivative of hydroxynaphthoic acid that static quenching can be neglected and the interaction is mainly between acid proton and base [9]. Accordingly, it can be said that the formation of intermolecular complex perturbs intramolecular PT. If this be the case, the ground state interaction pertains to the following:



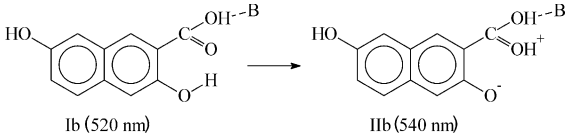
Ia



IIa

On the basis of steady-state measurements, Hirota [18] suggested that the equilibrium between orthohydroxynaphthoic acid (OHNA) in its two forms in the excited state is set up rapidly during the lifetimes of the two states. He showed that static quenching represents over 90% of the quenching in OHNA.

The emission spectra of DHNA in pure water occurred at 520 nm and can be assigned to the monomer of DHNA. The intensity of this band is found to decrease without any change in position of the band on increasing the excitation wavelength ($\lambda_{exc} = 380$–420 nm). However, in presence of NaOH ($\sim 10^{-3}$ mol dm^{-3}) the 520 nm band is shifted to 540 nm on increasing the λ_{exc}. The excitation spectra of 520 nm emission show two bands, one strong band at 360 nm and another weak band at 380 nm indicating the existence of both monomer and dimer even in water however low the concentration of dimer may be in the ground state. The excitation spectra of 540 nm emission show a single band at 360 nm. On the other hand, the emission spectra of DHNA show a single band at 460 nm in methanol and ethanol. On addition of NaOH ($\sim 10^{-3}$ mol dm^{-3}) the 460 nm band is shifted to 520 nm due to the formation of monomer of DHNA. It is also noted that on increasing the λ_{exc} (370–410 nm), the 520 nm band is further red shifted to 540 nm as shown in Fig. 3 keeping the excitation spectra at 360 nm. It can be said now that this red-shifted emission (540 nm) is the state in which PT has taken place in alcohols and water in presence of NaOH as shown below:



Ib (520 nm) IIb (540 nm)

This observation indicates that once the acid proton is blocked due to the interaction with base, ESIPT can take place in DHNA. In pure alcohol or water, the intensity of the band (520 nm) decreases gradually on increasing λ_{exc} without any change in position of the band. In other words, population of the species decreases on increasing λ_{exc}. There is no evidence of ESIPT. The excitation spectra of both the emissions (blue band 2 and red band 2) show a single strong band at 360 nm with a shoulder at 380 nm in all the aprotic solvents studied here. The observations indicate the presence of both monomer and dimer in all the solvents studied even in the excited state except in water. The existence of monomer is predominant in presence of a base in protic solvents. Both dimer and monomer can be observed in nonpolar and weakly polar solvents even in presence of base. In the case of 3-hydroxy-2-naphthoic acid (HNA), Ware et al. [9] made similar type of observations in presence of pyridine. In ACN they observed dual emission even in absence of pyridine in the case of HNA and the 550 nm band was observed on lowering the temperature to −70 °C. From the spectra obtained in basic solution containing OHNA, Hirota [18] suggested the hypothesis that the red-shifted emitter is the state in which PT has taken place. In the case of DHNA, we would like to propose the same mechanism for the red-shifted emission band (540 nm) in presence of NaOH. The red-shifted band is more pronounced in water than in alcohols. We are unable to detect this red-shifted band (540 nm) in any aprotic solvents studied

here even in presence of base. The tendency for carbonyl and carboxyl aromatic compounds to become more basic in the excited singlet state relative to the ground state is well established [9,19]. It is reasonable to assume therefore, that excitation would enhance the tendency of PT in the excited DHNA. It is expected that due to the hydrogen bonding to the carboxyl proton, the added base would lower the potential energy of the transfer. It should be noted that there exist sufficient differences between SA and DHNA with regard to the base perturbation.

We have also studied the fluorescence decays in different neutral and basic solvent media. The fluorescence decay of DHNA has been measured on the nanosecond timescale and shows a single exponential decay both in presence and absence of base. A typical decay profile of DHNA is shown in Fig. 4. It can be seen from Table 1 that lifetime values are always relatively short in the case of monomer compared to that of dimer. Our kinetic studies reveal that the base acts on the excited state of DHNA and the decay rates are faster in the case of dimer. We have failed to observe a rise time in the decay profiles. This indicates that proton transfer has taken place from a photoexcited intermolecularly bonded complex (Ib), where Ib can be the intermediate involved in monomer formation:

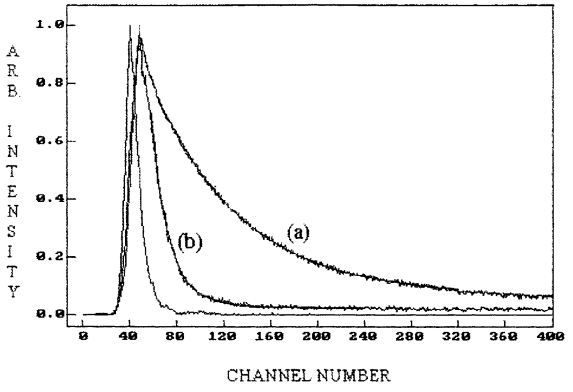


Fig. 4. Decay profile of DHNA ($\lambda_{mon} = 440$ nm) in pure dioxane (a) and dioxane + TEA (b). The solid curve represents the best computer fit of the experimental points to a single point decay. The lamp profile is denoted by a solid line (time resolution = 0.18 ns/channel). $\lambda_{exc} = 370$ nm.

Table 1
Lifetimes (τ_f, ns) and decay rates (k_f) of fluorescence at different emission wavelengths (λ_{em}, nm) in different solvent media at room temperature

System	λ_{em} (nm)	τ_f (ns)	k_f (s^{-1})
n-Heptane	420	10.0	1.0×10^{10}
Dioxane	420	14.5	6.9×10^{11}
Dioxane + TEA	510	2.8	3.6×10^{10}
ACN	440	10.4	9.6×10^{11}
ACN + TEA	510	6.0	1.2×10^{10}
$CHCl_3$	440	10.2	9.8×10^{11}
$CHCl_3$ + TEA	520	2.8	3.6×10^{10}
Methanol + NaOH	510	3.8	2.6×10^{10}
Ethanol + NaOH	520	4.5	2.1×10^{10}
Water	520	2.1	4.8×10^{10}
Water + NaOH	540	3.1	3.2×10^{10}

$$\mathrm{DHNA} + \mathrm{B} \rightarrow \mathrm{DHNA}\ldots.\mathrm{B} \rightarrow (\mathrm{DHNA}^{-}..\mathrm{HB}^{+})^{*}$$

Slower decay rates indicate stronger interaction with base compared to dimer formation. This difference in interaction rate is probably due to the difference in the acidic character of DHNA in the excited state. Once the molecule is excited, the interaction at any of the several sites may provide perturbation to cause the reaction. Hence, as the number of sites increase the transfer rate may decrease.

In relatively concentrated solution of DHNA in methanol ($\sim 6.5 \times 10^{-4}$ mol dm^{-3}), we observed a weak monomer band at 520 nm in addition to the 460 nm dimer band. Tripathi and co-workers [20] observed dual emission even in solid medium. In solid media where dimerisation is expected to be complete, they observed monomer band with comparable intensity to that of dimer band. They concluded that the higher wavelength band is due to monomer and the lower wavelength band is due to the dimer [6,21]. It has been shown that the equilibrium constant for monomer–dimer formation is difficult to establish in this system due to the coexistence of both monomer and dimer at all concentrations of SA. In benzoic acid, Itoh [22] assumed almost complete dimerisation at a concentration of 6.7×10^{-3} mol dm^{-3} and at a concentration of 10^{-5} mol dm^{-3} dimer present is $\sim$8%. In the case of SA, Bisht et al. [7] suggested that the dimer fraction at 10^{-5} mol dm^{-3} is $\sim$0.08 and at

$\sim 10^{-3}$ mol dm^{-3} it is $\sim$0.75. They pointed out that even in highly concentrated solutions ($>10^{-3}$ mol dm^{-3}) and in solid, the monomer band still shows up with considerable intensity. Our observations show that the tendency of dimer formation is higher in nonpolar and weakly polar solvents compared to that in polar solvents. However, dimer of DHNA is present in all the solvents even in dilute solution ($\sim 10^{-5}$ mol dm^{-3}). Formation of dimer in water is negligibly small. The broad band of dimer appears at different positions between 420 and 460 nm in the excited state depending upon the nature of the solvent used. This indicates that the ability of dimer formation is different in different solvents.

4. Conclusion

Studies of fluorescence quenching via intramolecular proton transfer are described for DHNA in several solvents. It has been found that base promotes proton transfer and functions by parallel static and dynamic quenching mechanisms. The mechanisms of both the static and the dynamic processes have been investigated by making steady-state fluorescence quenching measurements. Our studies suggest that DHNA forms a dimer even in dilute solution in all the protic, aprotic, polar and nonpolar solvents used in this study except in water. However, population of dimer is different in different solvents depending upon the nature of the solvent. ESIPT cannot be observed in DHNA in pure solvent due to the formation of dimer. Dimers are detected both in the ground and excited state. Anions are detected only in protic solvents. Monomers are formed by the addition of a strong base like TEA or NaOH due to the intermolecular interaction. The dimer is converted to monomer by the added base in all the solvents used except in *n*-heptane in the ground state.

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