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Excited-State Intramolecular Proton Transfer in 2-(2'-Hydroxyphenyl)benzimidazole and -benzoxazole: Effect of Rotamerism and Hydrogen Bonding

Kaustuv Das, Nilmoni Sarkar, Ajit Kumar Ghosh,[†] Devashis Majumdar, Deb Narayan Nath, and Kankan Bhattacharyya*

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700032, India

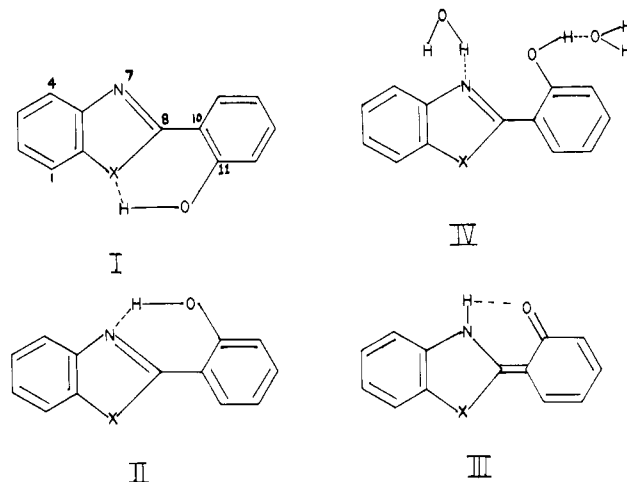
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An excited-state intramolecular proton transfer (ESIPT) process in 2-(2'-hydroxyphenyl)benzimidazole and -benzoxazole (HPBI and HBO, respectively) has been studied using steady-state and time-resolved emission spectroscopy at various temperatures and by semiempirical quantum chemical methods. For both of them two distinct ground-state rotamers I and II respectively responsible for the "normal" and the "tautomer" emission have been detected. In hydrocarbon solvents at room temperature and at 77 K the tautomer emission predominates over the normal emission for both HPBI and HBO. This indicates that rotamer II, responsible for the tautomer emission, is intrinsically stabler than rotamer I, which causes the normal emission. In alcoholic glass at 77 K for HPBI a dramatic enhancement of the normal emission is observed. It is suggested that due to the increased solvation, the more polar rotamer I becomes stabler than II for HPBI in alcohol and the substantial temperature variation is due to the change in the population of the two rotamers with temperature. From the detailed temperature variation in alcoholic medium the ground-state energy difference between rotamers I and II is determined. In dioxane–water mixtures it is observed that with the addition of water the quantum yield of the normal emission increases, which is ascribed to the inhibition of the ESIPT process due to the formation of an intermolecular hydrogen bond involving water. CNDO/S-CI calculations were performed optimizing the ground-state geometry by the AM1 method. Details of the energy, dipole moment, and charge distribution of the rotamers in the ground state (S_0) and the first excited singlet state (S_1) and the barrier for the interconversion of I and II in S_0 , S_1 , and first excited triplet state are discussed. The calculation indicates that the barrier for the interconversion of the two rotamers is too high in the excited state (S_1 and T_1) for free interconversion.

1. Introduction

In recent years the excited-state intramolecular proton transfer (ESIPT) phenomena has generated a lot of interest^{1–30} because of its widespread implications in the action of many lasing dyes⁵ and photostabilizers^{28,29} and in biology.³⁰ In the case of the adiabatic, barrierless ESIPT processes a proton (hydroxyl or amino) which is attached covalently to an atom A in the ground state of the molecule, in the excited electronic state, migrates to a neighboring hydrogen-bonded atom B at a distance of <2 Å to produce a "phototautomer" III (Scheme 1). Thus, the process can be depicted as a transition from $A-H\cdots B$ to $A\cdots H-B$. This process is extremely fast and occurs in the subpicosecond time scale even in rigid media and at temperatures down to 4 K. The recent subpicosecond IR and stimulated gain experiments indicate that the phototautomer is formed in about 100 fs at ambient temperatures.^{1,3,6,24,25} The extreme speed is presumably due to the fact that the process involves very slight (≈ 1 Å) movement of a light hydrogen atom. The lack of the observable temperature dependence of the rate of the ESIPT process indicates that the adiabatic ESIPT processes do not involve an Arrhenius type barrier crossing. However, many other excited-state proton-transfer processes with a barrier are also known.¹⁵ Since the time scale of the formation of the phototautomer is on the order of the vibrational period of low-frequency vibrations, it has been proposed that the Franck–Condon excited state of the molecule is very close to the intersection with the potential energy surfaces of the phototautomer, so that the molecule on excitation almost instantaneously crosses into the potential well of the latter and then relaxes vibrationally.^{1,3,6,24,25} The role of the vibrational mode responsible for this process is elucidated recently by

SCHEME 1



resonance Raman studies. Surprisingly, when the migrating proton belongs to a hydroxyl group, the ESIPT involves the skeletal vibrations instead of the O–H stretching vibrations.² The extreme speed of the process precludes any large scale geometry change to accompany the ESIPT process. In other words, the conformational requirement for the ESIPT process is rather stringent. In the general family of 2-(2'-hydroxyphenyl)benzimidazole (HPBI), -benzoxazole (HBO), -benzthiazole, and -benztriazole there are two possible intramolecularly hydrogen bonded rotamers, I and II (Scheme 1). It has been demonstrated^{13,18} that only II on excitation undergoes ESIPT to form the tautomer III, which gives rise to an emission with large Stokes shift. Rotamer I does not undergo ESIPT and is responsible for the short wavelength normal emission, which exhibits a mirror-image relation with the absorption. The major evidence in favor

[†] Department of Organic Chemistry, Indian Association for the Cultivation of Science.

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TABLE 1: Room Temperature Emission Properties of HPBI and HBO ($\lambda_{\text{ex}} = 320 \text{ nm}$ for ϕ^f Measurement)

sample	solvent	normal emission					tautomer emission				
		ϕ_N^f	τ_1 (ns)	a_1	τ_2 (ns)	a_2	ϕ_T^f	τ_1 (ns)	a_1	τ_2 (ns)	a_2
HPBI	alcohol	0.08	1.5				0.44	4.0			
HPBI	dioxane	0.01	1.5				0.34	3.9			
HPBI	water	0.05	1.5	0.11	0.29	0.89	0.22	1.8			
HPBI	1:1 water-dioxane	0.13	1.0				0.51	4.0			
HBO	alcohol	0.004	0.9				0.006	0.13			
HBO	dioxane	0.0015	1.3				0.007	0.172			
HBO	18% water in dioxane	0.005	1.5				0.008	0.166			
HBO	72% water in dioxane	0.004	0.15	0.94	0.89	0.06	0.035	0.2	0.5	2.5	0.5
HBO	water	0.001	1.4	0.35	0.21	0.65	0.015	2.2	0.5	0.34	0.5

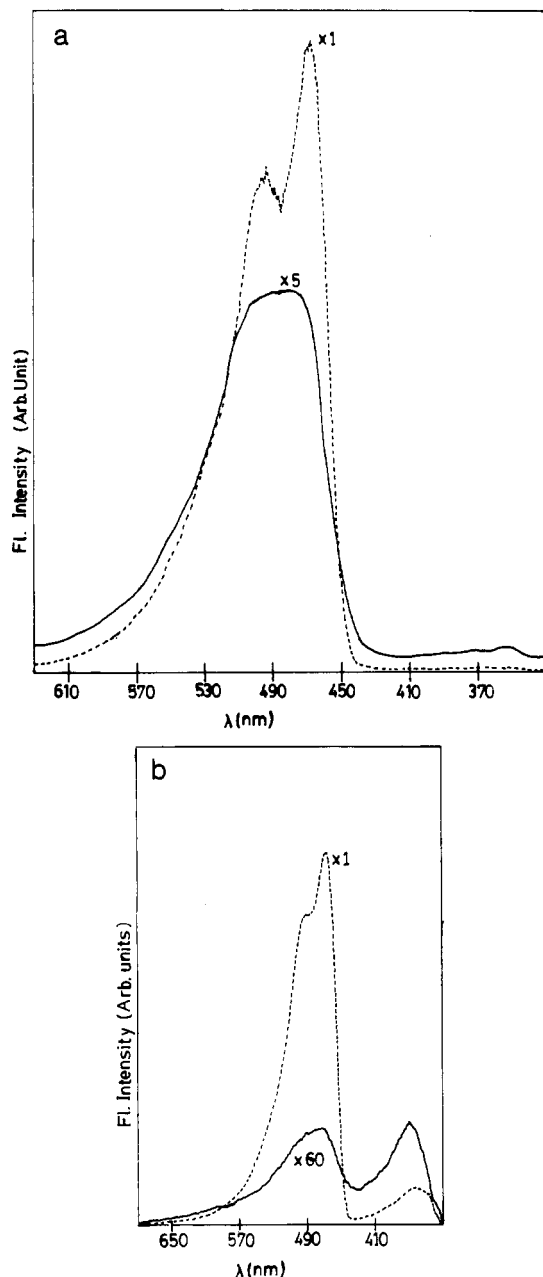


Figure 1. Emission spectra of HBO in (a) 3-methylpentane and (b) alcohol excited at 320 nm at room temperature (—) and at 77 K (---).

of this assignment is the differences in the excitation spectra of the normal and the tautomer emission, the large change of the relative intensities of the two kinds of emission with change in the temperature, and the differences in the temporal form of the decay of the normal emission and the formation of the tautomer emission.^{3,4,13,18} Another important issue is the competition between the *intramolecular* hydrogen bond (A—H...B) and the *intermolecular* hydrogen bonds involving protic solvents (S—H),

e.g. A—H...S—H...B (IV). Evidently, in structure IV it is difficult for the proton to go from A to B. Such an intermolecularly hydrogen bonded species does not undergo ESIPT. Thus, intermolecular hydrogen bonding inhibits the ESIPT process and favors the normal emission at the expense of the tautomer emission. It has been demonstrated that the intermolecular hydrogen bonds impede the intramolecular proton transfer process in the azaindole dimer.²³ In the present work we will shed further light on the effect of rotamerism and hydrogen bonding involving solvents on the ESIPT process by comparing the photophysical properties of HPBI and HBO. Further, we will present detailed semiempirical quantum chemical calculations on the energies and dipole moments of various species and the barrier for the interconversion of the two rotamers, I and II.

2. Experimental Section

HPBI and HBO were synthesized following literature procedures.^{31,32} The compounds are purified by vacuum sublimation, recrystallization, and column chromatography. Purified compounds exhibit a single TLC spot, and the spectra are similar to the reported ones.^{18,19} The solvents were purified by standard methods,³⁸ and in all experiments freshly distilled solvents were used. Temperature variation was done by passing precooled nitrogen vapor, and the temperature was measured using a copper-constantan thermocouple. Absorption and emission spectra were recorded in Jasco 7850 and Perkin-Elmer MPF 44B spectrophotometers, respectively. The quantum yields are determined with respect to that of quinine sulfate in 1 N H₂SO₄ as 0.55. The fluorescence decays were recorded in a picosecond setup in which the sample is excited by the second harmonic of a Coherent cavity-dumped rhodamine 6G dye laser (702) synchronously pumped by a Coherent CW mode-locked Antares Nd:YAG laser (76 S). The emissions are collected at magic angle (54.7°) polarization by a Hamamatsu MCP PM tube (2809U). The time resolution of this setup is about 50 ps. Deconvolutions of the fluorescence decays were done using global lifetime analysis software.³⁹ All calculations were done in a Sirius-32 minicomputer.

3. Results and Discussions

3.1. Emission Properties at Room Temperature. Origin of Normal and Tautomer Emission. At room temperature for both HPBI and HBO the quantum yield of the long wavelength tautomer emission (ϕ_T^f) is quite large and that of the short wavelength normal emission (ϕ_N^f) is weak in many solvents.^{13,18,19} At room temperature the normal emission is extremely weak ($\phi_N^f < 0.01$) in nonpolar solvents (e.g. dioxane, hydrocarbon, etc.). In polar solvents, particularly protic solvents, ϕ_N^f increases (Figure 1). The room temperature emission characteristics of HBO and HPBI are summarized in Table 1. The excitation spectrum of the very weak normal emission differs considerably from that of the tautomer emission in many solvents ranging from the polar hydrogen-bonding solvents (water, alcohol, etc.) to nitriles and even in scrupulously dry hydrocarbon solvent.^{13,18} This difference suggests that the normal and tautomer emissions originate from two distinctly different species. Since the highly

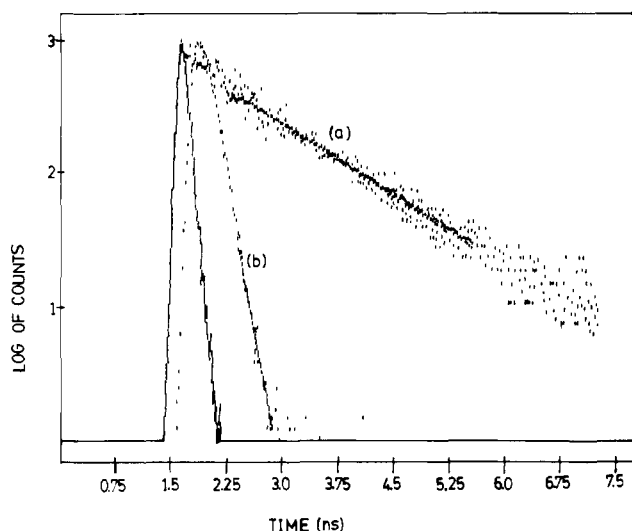


Figure 2. Fluorescence decay of HBO in dioxane at room temperature (a) at 360 nm and (b) at 495 nm.

polar solvents (alcohol, water, etc.) are also strongly hydrogen bonding, many workers^{1,3-11,14,15,24,25} attributed the normal emission to the solvated intermolecularly hydrogen bonded species (e.g. IV) and the tautomer emission to the unsolvated intramolecularly hydrogen bonded species. However, the fact that the difference in the excitation spectra persists even in the scrupulously dry hydrocarbon solvent, where no intermolecular hydrogen bonding involving the solvent is possible, suggests that the dual emission is not due to the solvated and the unsolvated species.

The time-resolved studies also suggest the existence of two distinct species. In the case of both HBO and HPBI in a variety of solvents (Table 1 and Figure 2) the lifetime of the normal emission is considerably different from that of the tautomer emission, which indicates that the two kinds of emission arise from two different species. Further, the rate of decay of the normal emission does not correspond to the rise of the tautomer emission, which is faster than the time resolution of our setup (50 ps) even at 77 K (Figure 3). This demonstrates that the tautomer is not formed as a result of the decay of the species giving the normal emission. In other words the two species giving rise to the normal and the tautomer emission are distinctly different. One of them does not undergo ESIPT at all, while the other exclusively undergoes ESIPT in the subpicosecond time scale to produce the tautomer emission. Even in nonpolar solvents (dioxane or hydrocarbon), the decay of the normal emission does not correspond to the growth of the tautomer emission. We assign the normal and the tautomer emission, respectively, to the two distinctly different rotamers, I and II. The energies of the two rotamers vary with the solvent dielectric constant because of the differences in their dipole moments (section 3.4). Thus, with the variation in polarity the relative energies and consequently the relative population of the two rotamers change. In hydrocarbon or dioxane ($\epsilon \approx 2$) the solvation energy is very small. The predominance of the tautomer emission in such nonpolar solvents indicates that rotamer II, responsible for the tautomer emission, is stabler than I, which produces the normal emission. However, since semiempirical calculations show (section 3.4) that I has a dipole moment slightly higher than that of II in the polar solvents (alcohol, etc.), I is stabilized more than II. In the case of HPBI rotamer I becomes stabler than II in alcohol. Thus, in the polar solvents the population of I increases, and hence the normal emission of HPBI is enhanced in the polar solvents. In protic solvents there is a possibility of formation of intermolecularly hydrogen bonded species like IV, which gives rise to the normal emission at the expense of tautomer emission. Evidence in favor of this is known in the presence of water for azaindole.²³ We will

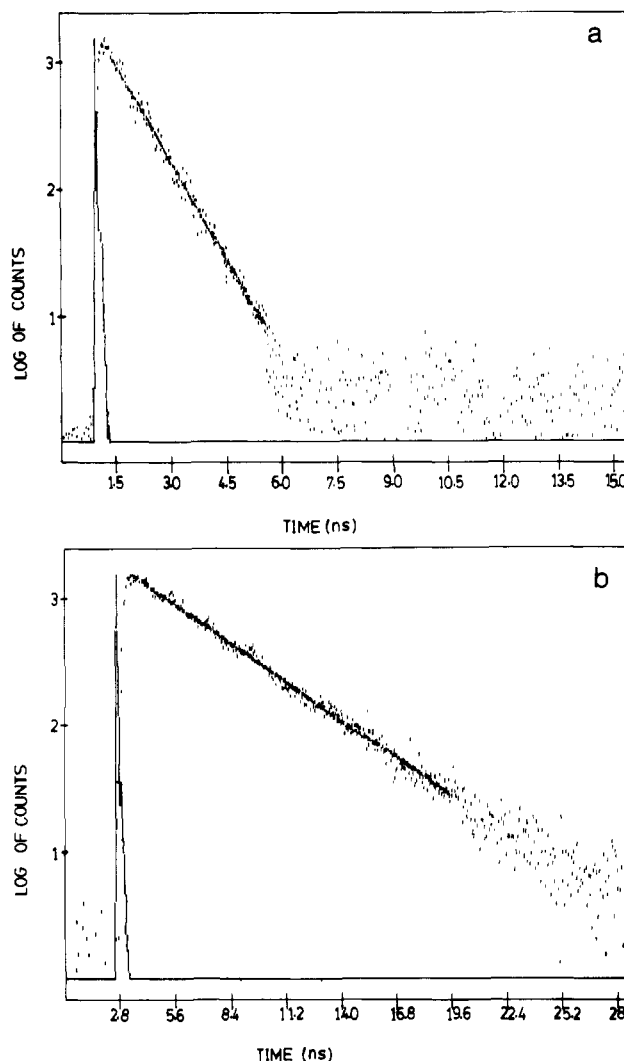


Figure 3. Fluorescence decay of HBO in alcohol at (a) 370 nm at 77 K and (b) 470 nm at 77 K.

discuss the effect of water on HBO and HPBI in considerable detail in section 3.3. In alcoholic medium at room temperature both for HPBI and HBO the quantum yield of the tautomer emission is higher than that of the normal emission. Thus, we conclude that the intermolecular hydrogen bond involving alcohol is not strong enough to compete with the intramolecular hydrogen bonds for both HBO and HPBI and the contribution of the solvated species IV is minor in alcohol.

3.2. Temperature Dependence of the Emission Properties of HPBI and HBO. In hydrocarbon glasses (e.g. 3-methylenepentane) at 77 K both HPBI and HBO exhibit intense tautomer emission and very weak normal emission (Figure 1a). Since the hydrocarbon solvents impart very little solvation energy, it may be concluded that rotamer II, responsible for the tautomer emission, is intrinsically stabler than rotamer I for both HBO and HPBI. However, in polar alcoholic glass at 77 K for HPBI the quantum yield of the normal emission becomes more than 2 times larger than that of the tautomer emission (Table 2). The corresponding lifetime, however, remains almost unchanged for HPBI. Thus, the rather dramatic change in the emission yields of HPBI is not due to any temperature dependent change in the nonradiative rates. The large change in the relative emission yields may be attributed to the change in the ground-state populations of the two rotamers (I and II) with temperature. The dramatic enhancement of the normal emission indicates that in the case of HPBI in alcohol rotamer I is stabler than II, and since at low temperature the population of the stabler rotamer I increases, the normal emission dominates over the tautomer emission at low temperature.

TABLE 2: Low Temperature (77 K) Emission Properties of HPBI and HBO in Alcohol ($\lambda_{\text{ex}} = 320$ nm for ϕ^f Measurement)

sample	normal emission		tautomer emission	
	ϕ_N^f	τ (ns)	ϕ_T^f	τ (ns)
HPBI	0.47	1.7	0.2	4.0
HBO	0.038	1.1	0.372	5.7

The observed ratio of quantum yields of the normal and the tautomer emission is given by

$$\phi_N^f / \phi_T^f = (N_I / N_{II})(\epsilon_I / \epsilon_{II})(\phi_N^0 / \phi_T^0) \quad (1)$$

where N_i and ϵ_i denote number and extinction coefficients of the i th species and ϕ_N^0 , ϕ_T^0 the quantum yield of the normal and tautomer emission, respectively. The ratio of the extinction coefficients may be safely assumed to be independent of temperature. In general, the quantum yields of the emission vary with the temperature due to the variation in the nonradiative rates. For HPBI the lifetimes of the normal and the tautomer emission do not change much between room temperature (299 K) and 77 K, indicating that the rate of the nonradiative processes of HPBI are more or less independent of the temperature. Thus, the individual quantum yields (ϕ_N^0 and ϕ_T^0) may be assumed to be constant over this range of temperature. Thus, eq 1 reduces to

$$\phi_N^f / \phi_T^f = \text{constant} \times \exp[-(E_I^g - E_{II}^g) / RT] \quad (2)$$

where E_I^g , E_{II}^g are the ground-state energies of rotamers I and II. Hence, the plot of $\ln(\phi_N^f / \phi_T^f)$ vs $1/T$ should be a straight line from the slope of which one can calculate the difference in the ground-state energies ($E_I^g - E_{II}^g$) of the two species responsible for the normal and the tautomer emission, respectively. Figure 4a gives such a linear plot for HPBI. This plot indicates that for HPBI in the ground state rotamer I, giving the normal emission, is stabler than rotamer II by 1.2 kcal/mol in alcohol.

For HBO the lifetime of the tautomer emission, however, increases from 130 ps at 299 K to 5.7 ns at 77 K (Table 2). Mordzinski and Grellmann²¹ have studied in detail the temperature variation of the lifetime (τ_T^f) and the quantum yield of the tautomer emission (ϕ_T^f) and the triplet-triplet absorption. They have shown the existence of a thermally activated nonradiative process, $k_{\text{NR}} = k_{\text{NR}}^0 \exp(-E_a/RT)$, as a result of which τ_T^f , ϕ_T^f , and triplet yield increase with the decrease in temperature and become constant below ≈ 170 K. Thus, it appears that the approximation that ϕ_N^0 and ϕ_T^0 are constant is valid for HBO at temperatures below 170 K. For HBO the plot of $\ln(\phi_N^f / \phi_T^f)$ vs $1000/T$ indicates that the ratio ϕ_N^f / ϕ_T^f becomes almost constant below 170 K. This suggests that the two rotamers, I and II, have almost equal energy in the case of HBO in alcohol and the temperature variation arises from the temperature dependence of the nonradiative process in the excited state of tautomer III.²¹

3.3. Competition of Intra- and Intermolecular Hydrogen Bonding: Water-Dioxane Mixtures. It is observed that in general with the increase in the hydrogen-bonding ability of the solvent the yield of the normal emission, ϕ_N^f , increases quite appreciably and ϕ_T^f either increases slowly or decreases.^{19,23} The emission quantum yield of HPBI, relative to the yield in pure dioxane, in a series of dioxane-water mixtures exhibits similar trends (Figures 5 and 6). In pure dioxane, a nonpolar and weakly hydrogen bonding solvent, the normal emission is very weak. With the addition of water, intensity of the tautomer emission increases only slightly, while intensity of the normal emission increases up to 14 times (at 50%–75% water, v/v) and decreases slightly at higher percentages of water (Figure 6a). In pure water ϕ_N^f of HPBI is 5 times that in pure dioxane. On going from dioxane

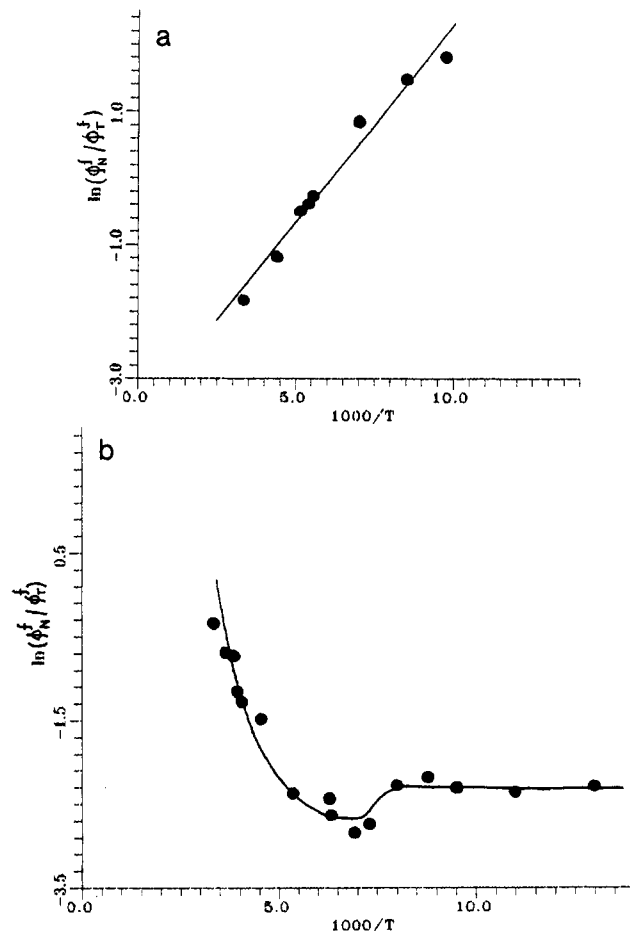


Figure 4. Temperature dependence of the relative emission quantum yields of (a) HPBI and (b) HBO in alcohol.

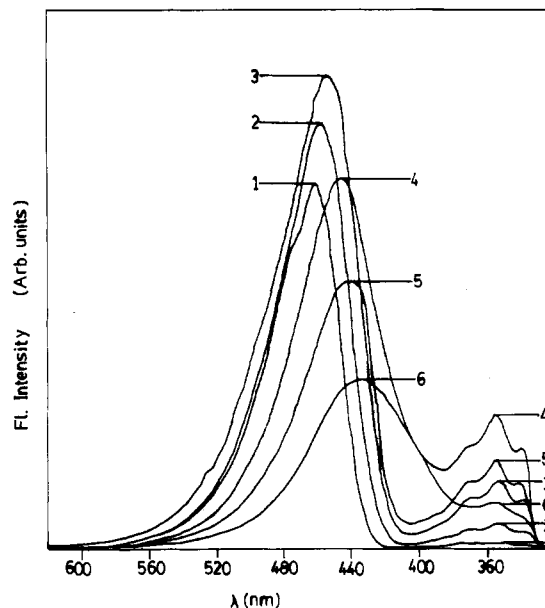


Figure 5. Emission of HPBI in water-dioxane mixture: (1) dioxane; (2–5) 5%, 10%, 70%, and 90% water v/v in dioxane, respectively; (6) pure water.

to 75% water as ϕ_N^f changes by a factor of 14, the lifetime of the normal emission actually decreases slightly from 1.5 ns in pure dioxane to 1.0 ns at 50% dioxane and becomes biexponential with components 290 ps and 1.5 ns in pure water (Table 1). The 14-fold increase in the quantum yield of the normal emission ϕ_N^f in spite of the decrease in lifetime of the normal emission indicates that the increase in the emission intensity is not due to any change in the nonradiative rates from the normal excited

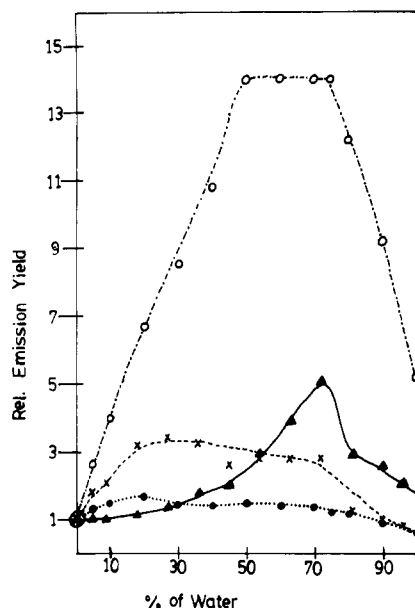


Figure 6. Variation of emission quantum yields of HPBI and HBO in a water-dioxane mixture. \circ and \bullet correspond to the relative emission quantum yields of the normal and tautomer emission for HPBI, respectively, and \times and \blacktriangle correspond to those for HBO, respectively.

state. The enhancement in the normal emission intensity is surely due to the increase in the population of the species giving rise to the normal emission in the highly polar aqueous medium. The solvation energy for I and II can be calculated in the Onsager model using the calculated dipole moment (section 3.4) of the rotamers, neglecting specific hydrogen bonding with the solvents. Such a calculation shows that on going from dioxane ($\epsilon = 2$) to water ($\epsilon = 80$) rotamer I gains a stability of 115 cal/mol over that of II. This additional stability of I should cause ϕ_N^f to increase by a factor $\exp(-115/RT)$, i.e. by about 20% at 299 K, which is too small to account for the observed 5-fold increase. Thus, it appears that the observed appreciable increase in the normal emission is not due to a simple increase in polarity and is rather due to the intermolecular hydrogen bonding effects. In the strongly hydrogen bonding solvent water, the intermolecular hydrogen bonds involving water disrupt the intramolecular hydrogen bonds of I and II. In the presence of the intermolecular hydrogen bond while rotamer I continues to give the normal emission, a second component of the normal emission arises from rotamer II through structures like IV. In IV the ESIPT process is inhibited, and the emission resulting from IV will be energetically very similar to the normal emission. Thus, the increase in ϕ_N^f with addition of water is attributed to the inhibition of ESIPT by the intermolecular hydrogen bonding and the corresponding increase in the quantum yield of normal emission through species like IV. Such a mechanism of enhancement of the normal emission is already proposed for other molecules.²³ With the increase in the relative proportion of water in dioxane the population of IV increases, and this accounts for the rather large increase in the quantum yield of the normal emission with increase in the water content.

That more than one species (I and IV) is involved in the normal emission of both HBO and HPBI in the presence of water is also indicated by the appearance of biexponential fluorescence decay of the normal emission in the presence of water (Table 1). However, the observed biexponential decay ($a_1 \exp[-t/\tau_1] + a_2 \exp[-t/\tau_2]$) does not necessarily imply the presence of just two species (e.g. I and IV). The different HBO or HPBI molecules forming hydrogen bonds with waters at different centers experience slightly different local environments and hence different lifetimes. The superposition of many such exponential decays might look like a biexponential decay.⁴⁰ The biexponential decay

TABLE 3: Relative Energies^{a,b} (in eV) and Dipole Moments (in D) of the Ground (S_0), First Excited (S_1), and Corresponding Triplet (T_1) State for Rotamers I, II, and III of HPBI and HBO in Isolated as Well as Solvated (in Ethanol) Conditions^c

molecule	species	ground state (S_0)		excited state (S_1)		excited state (T_1)	
		E	μ	E	μ	E	μ
HPBI	I	0.055 (0.0)	3.91	4.00 (3.73)	8.51	3.05 (2.86)	7.39
	II	0.075 (0.034)	3.36	4.14 (3.92)	7.78	3.22 (3.01)	7.35
	III	0.446 (0.34)	5.49	3.71 (3.65)	4.03	2.65 (2.61)	3.17
HBO	I	0.015 (0.013)	0.82	4.08 (3.89)	7.17	3.10 (2.96)	6.30
	II	0.016 (0.0)	1.76	3.93 (3.74)	7.21	2.95 (2.76)	7.28
	III	0.403 (0.338)	4.26	3.66 (3.60)	4.34	2.64 (2.60)	2.88

^a Relative energies are calculated with respect to the ground-state minimum energy form in ethanol. ^b Relative energies in ethanol are presented within parentheses. ^c The energies for the excited states were calculated using the CNDO/S-CI method using the ground-state-optimized geometries of the respective species.

for the tautomer emission is also attributed to the local inhomogeneity arising from the intermolecular hydrogen bonding with water.

In the case of HBO on addition of water to dioxane the ϕ_T^f of HBO increases up to 5 times and then decreases. In this case the increase in the quantum yield of the tautomer emission may be attributed to the suppression of nonradiative rates as the lifetime of HBO increases on addition of water. With addition of water the intensity of the normal emission of HBO also increases up to 2.5 times and then decreases (Figure 6). The increase in ϕ_N^f for HBO once again proves that intermolecular hydrogen bonding favors normal emission.

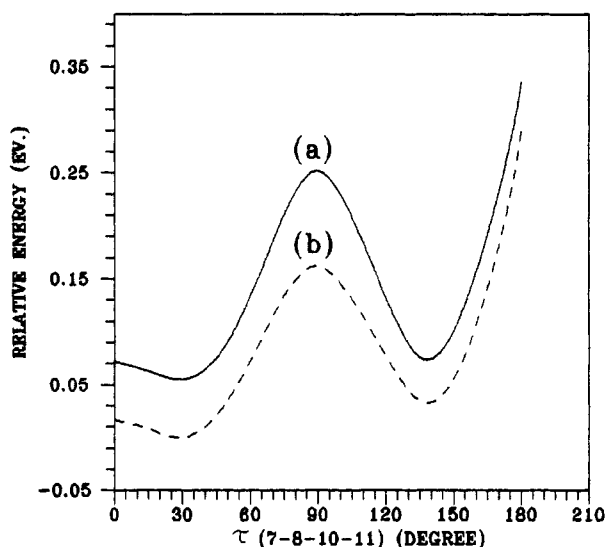
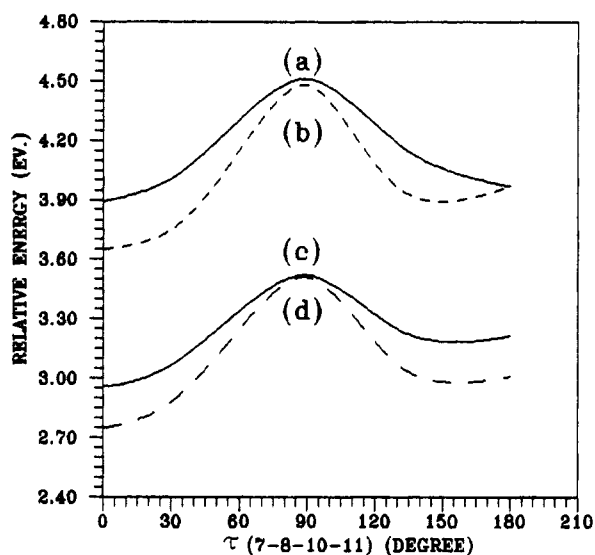
3.4. Quantum Chemical Calculation. The ESIPT phenomenon has inspired a large number of theoretical calculations.^{12–18} Unfortunately, many of them^{14,18} did not make use of geometry optimization and did not deal with two rotamers. Recently, using ab initio methods in the STO-3G basis set, Nagaoka et al.^{11a} calculated the barrier for interconversion of the rotamers in the ground state of HBO and HBT. However, they did not calculate the barrier for interconversion and the change in the π -electron densities in the excited singlet state (S_1). Further, they did not calculate the geometry of the tautomer in either the ground or the excited state, nor did they discuss anything about HPBI. In the present work we have calculated all these quantities for both HBO and HPBI.

The ground-state geometries of the three species, I, II, and III, for both HBO and HPBI were optimized using the AM1 method.³³ Complete optimization of all the geometrical parameters gives the ground-state energy (E_g) of each species. The energy of the excited states are calculated using the standard CNDO/S-CI method.^{34–37} Table 3 gives the energy and dipole moment of the species I, II, and III in the ground and the first excited singlet and triplet states. Table 4 gives the emission assignments for HBO. The emission assignments for HPBI have been discussed already.¹³ It is easy to see that the calculated energies are in good agreement with the experiment.

The calculated charge densities indicate that in the first excited singlet of both HBO and HPBI the π -electron densities at the nitrogen atom of the five-membered ring increase significantly (from -0.16 to -0.32 eu for HPBI and from -0.18 to -0.32 eu for HBO), while the π -electron density increases slightly at the hydroxylic oxygen atom (from -0.25 to -0.28 eu for HPBI and from -0.25 to -0.279 eu for HBO). In fact, in the first excited singlet the nitrogen atom becomes richer in electrons than the

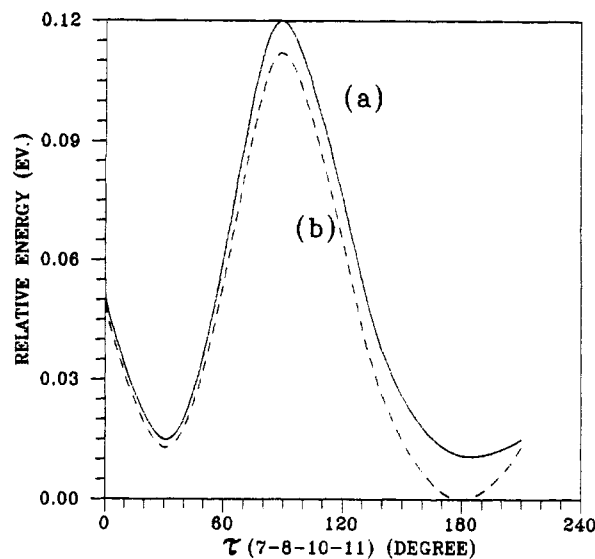
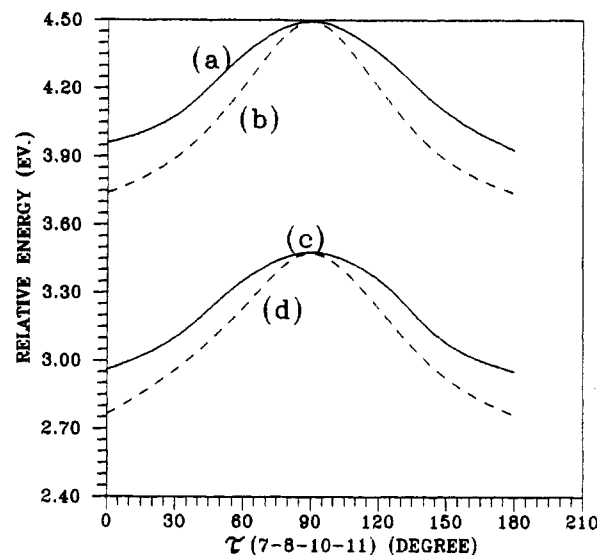
TABLE 4: Assignments of Photoprocesses of HBO

fluorescence (eV)				phosphorescence (eV) ^a			
normal		tautomer		normal		tautomer	
expt	calc	expt	calc	expt	calc	expt	calc
3.8	3.71	3.20	3.26	2.8	2.76	2.3	2.26

^a Experimental values from ref 8.Figure 7. Potential energy surface for the ground state (S_0) of HPBI in the (a) isolated and (b) solvated (ethanol) condition.Figure 8. Potential energy surface for the excited S_1 and T_1 states of HPBI in the isolated as well as solvated (ethanol) condition. a, b, c, and d are respectively the potential energy surfaces for the isolated S_1 , solvated S_1 , isolated T_1 , and solvated T_1 states.

hydroxylic oxygen atom. This redistribution of the π -electron densities in the excited electronic state is the driving force for the intramolecular proton transfer from the hydroxylic group to the nitrogen atom. For the imino (NH) nitrogen of the imidazole ring in HPBI or the oxygen atom of the oxazole ring of HBO there is hardly any change in π -electron densities. This explains why rotamer I does not undergo ESIPT. For tautomer III the bond joining the 2-hydroxyphenyl group to the rest of the molecule is quite short (1.38 Å for HBO and 1.41 Å for HPBI, which is consistent with the proposed structure of III containing a double bond at this place.

In the ground state of the isolated molecules for both HPBI and HBO tautomer III is the most energetic species (Table 3). However, in the first excited singlet III is the stablest species,

Figure 9. Potential energy surface for the ground state (S_0) of HBO in the (a) isolated and (b) solvated (ethanol) condition.Figure 10. Potential energy surface for the excited S_1 and T_1 states of HBO in the isolated as well as solvated (ethanol) condition. a, b, c, and d are respectively the potential energy surfaces for the isolated S_1 , solvated S_1 , isolated T_1 , and solvated T_1 states.

which is consistent with the low-energy tautomer emission band. Since I has a slightly higher dipole moment than II in polar solvents, I is solvated more than II. When the solvation energy is added,³⁴ in ethanol I becomes stabler than II by 780 cal/mol for HPBI.

Figures 7 and 8 give the potential energy (PE) curves for the interconversion of I and II for HPBI in the ground and the excited state, respectively. Figures 9 and 10 give the ground- and excited-state PE curves for HBO. For isolated HPBI in the ground state the barrier for interconversion is 4.6 kcal/mol for the isolated molecule and 3.7 kcal/mol in alcohol (Table 5). For HBO the numbers are 2.51 and 2.58 kcal/mol, respectively. This indicates that in the ground state the two rotamers are interconvertible. The ground-state barrier of HBO calculated by Nagaoka et al. (10 kcal/mol) is higher than that calculated by us. In the first singlet state the barriers for HPBI in the isolated molecule and in the alcohol medium are 13.8 and 19 kcal/mol, respectively, and for HBO, 13.09 and 17.42 kcal/mol, respectively. In both cases the barrier is much higher than those in the ground state. Due to this high barrier, the interconversion of rotamers I and II is too slow to occur within the singlet lifetime for both HPBI

TABLE 5: Barrier for Interconversion (in kcal/mol) between Rotamers I and II^a

molecule	state	barrier	molecule	state	barrier
HPBI	S ₀	4.6 (3.78)	HBO	S ₀	2.51 (2.58)
	S ₁	13.8 (19.0)		S ₁	13.09 (17.42)
	T ₁	12.4 (17.3)		T ₁	12.11 (16.38)

^a Figures in parentheses denote barriers in ethanol including solvation.

and HBO. The barriers for interconversion in the triplet states are also much higher than those in the ground state (Table 5).

4. Conclusion

The major findings of this work are as follows:

(1) Intermolecular hydrogen bonds involving water giving rise to IV impede the ESIPT process, resulting in an increase in the quantum yield of normal emission at the expense of the tautomer emission. However, in alcohol the intermolecular hydrogen bonding with alcohols is not strong enough to compete with the intramolecular hydrogen bonding for both HPBI and HBO. Hence, tautomer emission dominates over normal emission in alcohol at room temperature for both of them.

(2) From the temperature variation the energy difference between the two rotamers, I and II, responsible for the normal and tautomer fluorescence is determined for HPBI in alcohol. For HBO the temperature variation study suggests that the two rotamers have almost equal energy in alcohol.

(3) The time-resolved studies indicate that the species giving rise to the normal and the tautomer emission (rotamers I and II) are independent of each other. I (and IV) on excitation gives normal emission, while II on electronic excitation produces the tautomer in the ultrafast time scale.

(4) The quantum chemical calculations indicate that the barrier for the interconversion between I and II increases in the excited electronic state, and hence I and II are not freely interconvertible in the excited singlet state. Further, the calculations indicate that in the S₁ state the nitrogen atom becomes richer in π -electrons than the oxygen atom of the hydroxyl group, and this is the driving force of the proton transfer. The energy and the geometries of the tautomer in the ground and excited states are also calculated. This calculation shows that, in the ground state, the tautomer has a higher energy than both I and II. In the S₁ state, however, III is stabler than I and II.

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