Available online at www.sciencedirect.com

Journal of Photochemistry and Photobiology A: Chemistry 170 (2005) 131–141

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Prototropism in 2-acetyl benzimidazole and 2-benzoyl benzimidazole

Papia Chowdhury[a], Subhasis Panja[a], Amrita Chatterjee[b],
Pranab Bhattacharya[b], Sankar Chakravorti[a,*]

[a] *Department of Spectroscopy, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India*
[b] *Medicinal Chemistry Division, Indian Institute of Chemical Biology, Jadavpur, Kolkata 700032, India*

Received 15 May 2004; received in revised form 5 August 2004; accepted 12 August 2004

Abstract

2-Acetyl benzimidazole (2ABI) and 2-benzoyl benzimidazole (2BBI) are found to show excited state prototropic activities in different solvents of varying pH. The absorption, steady state and time-resolved emission studies were made on the basis of a theoretical possibility study of proton transfer in the excited state. The existence of closed ring conformers for both the molecules in the ground state give rise to different emission bands upon excitation in hydroxylic, water and hydrocarbon solvents. Ground state hydrogen abstraction was found with addition of base. Excitation of the closed conformer leads to a band due to excited state intramolecular proton transfer (excited state Zwitterion) across the preexisting intramolecular hydrogen bond in hydrocarbon solvents and an additional intermolecular anionic band only in the hydroxylic solvents. On comparison, the intermolecular proton transfer is more active in 2BBI than 2ABI. An increase or decrease in basicity results in enhancement of emission from ionic conformer with parallel shrinking of the intramolecular proton transfer species.

Keywords: Proton transfer; Zwitterions; Time-resolved emission; Hydrogen abstraction; Anion band

1. Introduction

It is well-known fact [1,3–8] that the molecules having acidic and basic groups can undergo photo induced proton transfer process as a result of the change in acidity and basicity experienced by these groups in the excited state. If a molecule possesses both an acidic and a basic group in close proximity and with an appropriate geometry for an intramolecular hydrogen bond to be formed, an excited state intramolecular proton transfer process (ESIPT) may take place from acidic to basic part, the signature of that process is emission of strongly Stokes-shifted fluorescence [2] following absorption of a UV photon. These ESIPT processes take place through an intramolecular hydrogen bond, which forms usually part of a six- or five- membered ring. In 1955, Weller [1] noticed that methyl salycilate exhibited fluorescence with an unusually large Stokes shift, which corresponds to an excited state isomer formation via proton transfer. The classic paper of Weller [2] on excited state intramolecular proton transfer (ESIPT) of methyl salycilate (MS) spurred intense research on this subject in many laboratories [3–8]. Kasha [9] first showed that an intramolecular PT is facilitated in the excited state in those molecules where there is a hydrogen bond between the H atom of the donor group and the acceptor of that molecule in the ground state. Transfer of proton between two groups of an aromatic molecule causes a large electronic and structural rearrangement, which is associated with significant changes in dipole moments, molecular geometry and quite large ($\geq 1000\,\mathrm{cm}^{-1}$) fluorescence shift.

The proton transfer spectroscopy, ground and excited state reaction dynamics of N-heterocyclic is an interesting and developing subject area of research especially for the molecules containing more than one functional group [10–20]. The presence of either intramolecular or intermolecular hydrogen bonding in this type of molecule gives rise to many further new features in both the absorption and fluorescence

---

* Corresponding author. Tel.: +91 33 24734971; fax: +91 33 24732805.
E-mail address: spsc@iacs.res.in (S. Chakravorti).

1010-6030/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2004.08.009

spectra. More often than not, these bonding can alter the chemical and physical behavior of the molecule depending upon the nature of the solvent or adding acid and base. In molecules, which contain hydrogen atom donor (e.g. −OH, =NH, −NH2, etc.) and acceptor (=N–, >C=O, etc.) in close proximity, an intramolecular hydrogen bond is generally formed in the ground state. The intramolecular redistribution of electronic charge due to photonic excitation induces the ESIPT process, which is ultrafast in nature. In the recent years there has been engaging interest in the ESIPT process of these types of heterocyclic molecules. Among them, 2-(2′-pyridyl)-benzimidazole [10–12], 7-azaindole [13–15], 2-(2′-hydroxyphenyl)-benzimidazole [16–18], 2-(2′-hydroxyphenyl)-benzoxazole [19–21] has been well studied as prototypes of the molecules showing the ESIPT processes.

The dynamics of the proton transfer (PT) process could strongly be dependent on the nature of the solvent, namely with respect to the formation of a hydrogen bond. One of the prime features of most excited state proton transfers is their rapidity, on the femtosecond to picosecond time scale [22,23]. These rapid transfers are commonly attributed to a barierless process. Also a number of systems containing more than one H-bond exhibit multiple PTs [9]. There has been a growing interest in these kind of process (ESIPT) in the last years [24,25], owing to both the importance of understanding this ultrafast reaction at a molecular level [26,27] and the applications of the molecules that undergo those kind of processes, ranging from photochromic material [28] and laser dyes [29–31] to polymer UV stabilizers [28,32]. These also include energy/data storage devise and optical switching [33], Raman filters and hard scintillation counters [34] and triplet quenchers [34]. Other applications center on electroluminescent materials with photochemical stability, resistance to thermal degradation, and low self-absorption and light emitting diode materials [34]. It has been suggested that ESIPTs have the potential for understanding the binding properties of protein [35], as well as optical probes for biomolecules [36]. Because of all of the interesting and useful applications, different groups throughout the world are working with a wide variety of fluorescing acid-base containing molecules in order to systematize and control their emissive properties.

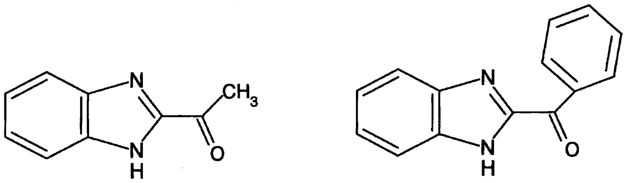
For the past few years our laboratory has largely been involved in characterising new heterocyclic type molecular system showing ESIPT and in elucidating their mechanism. Recently 2-acetyl benzimidazole (2ABI) and 2-benzoyl benzimidazole (2BBI) molecules have been synthesized by the substitution of acetyl and benzoyl group at 2 position of benzimidazole (BI) molecule to observe the change in the reaction dynamics of proton transfer process. Absorption and emission properties of BI were reported earlier [36-38] in detail. 2ABI and 2BBI are distinguished by their difference in substitution at 2 position of benzimidazole. Different substituents of benzimidazole have different conjugation with benzimidazole ring. Due to this difference in conjugation there may be some effects in the reaction dynamics of proton transfer characteristics of substituted benzimidazoles. In order to observe these in the present work we will first perform quantum chemical semi empirical calculations on the feasibility of excited state intramolecular proton transfer with respect to the dipole moment change and charge density distribution from the ground to excited state. On the basis of prediction, a detailed investigation of absorption and fluorescence properties of 2ABI and 2BBI in different environments will be carried out. In this paper we plan to try to identify the species those are responsible for different emissions with a view to understand different aspects of ESIraPT.

2. Materials and methods

2.1. Materials

2-Acetyl-benzimidazole or 2-(1-hydroxyethyl)-1-H-benzimidazole (2ABI) [39] was oxidized with pyridinium chloro chromate (PCC) as before and purified by column chromatography (on silica gel 60–120; 5% ethyl acetate in petrolium ether). It was crystallized from benzene [40]. The color of 2ABI crystal is white, mp 189 °C.

^{1}H NMR (CDCl3, 300 MHz) δ 2.84 (3H, s), 7.34–7.46 (2H, m), 7.6 (1H, d, J =7.8 Hz), 7.9 (1H, d, J = 7.8 Hz); ^{13}C NMR (CDCl3, 125 MHz) δ 26.3, 112.6, 122.3, 134.0, 143.8, 192.5.



2-Acetyl-benzimidazole (I) 2-Benzoyl benzimidazole

2-Benzoyl benzimidazole or 2-(α-Hydroxybenzyl) benzimidazole (2BBI) was prepared by heating for 2 h, o-phenylene diamine with mandelic acid (1:1.2), in ethanol:conc. HCl: o-phosphoric acid (4:1:1). The mixture was basified with Na2CO3 and crystallized from ether, mp 85 °C.

The said benzimidazole was oxidized with pyridinium chlorochromate (PCC) [41]. In dry dichloro methane, activated molecular sieves (4 A°), benzimidazole, and PCC (5 equiv.) was stirred at room temperature for 4 h, monitored by TLC (dichloromethane).

The mixture was diluted with ether and filtered through celite. The celite was washed with ether and dichloromethane. The filtrate was evaporated at reduced pressure. The solid was crystallized from methanol water mixture. 2BBI is pale Yellow crystal of mp 210 °C.

^{1}H NMR (CD3OD, 300 MHz) δ 7.3–7.9 (9H, m); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 112.4, 122.7, 124.1, 128.9, 131.7, 134.3, 135.8, 184.4.

Methyl cyclohexane (MCH) (Fluka) was purified by nitration and sulfonation, dried over anhydrous sodium sulfate, and distilled at 101 °C. Ethanol (EtOH), methanol (MeOH), chloroform ($CHCl_3$), acetonitrile (ACN), ethyl ether (DEE), triethylamine (TEA) (E Merck, spectroscopic grade), pyridine (spectroscopic grade) were used as supplied but only after checking the purity fluorimetrically in the wavelength range of interest. Sodium ethoxide (NaEtH) was prepared in lab. For aqueous solution, we used deionized millipore water.

2.2. Absorption and emission spectra

The absorption spectra were taken with a Shimadzu UV–vis absorption spectrophotometer model UV-2401PC. The fluorescence spectra were obtained with a Hitachi F-4500 fluorescence spectrophotometer. For emission measurements, the sample concentration was maintained at $\sim 10^{-5}$ M in each case in order to avoid aggregation. The quantum yields were determined by using a secondary standard method with recrystallized β-naphthol in MCH ($\varphi_f = 0.23$). The fluorescence lifetime measurement was performed by time-correlated single photon counting coupled to a micro-channel plate photomultiplier (model 28090, Hamamatsu, Edinburgh Instrument).

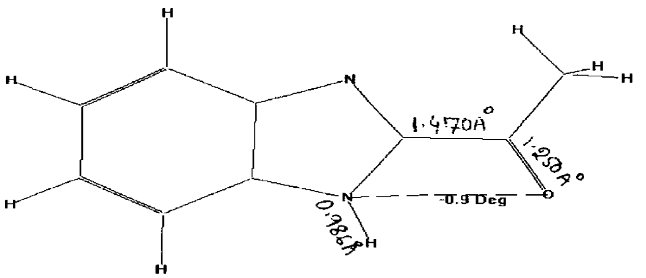
2.3. Quantum chemical calculations

Quantum chemical calculations with AM1 Hamiltonian were done on this molecule using MOPAC, version 7 software to know the ground and excited state geometry and other parameters like dipole moment, heat of formation, charge distribution etc.

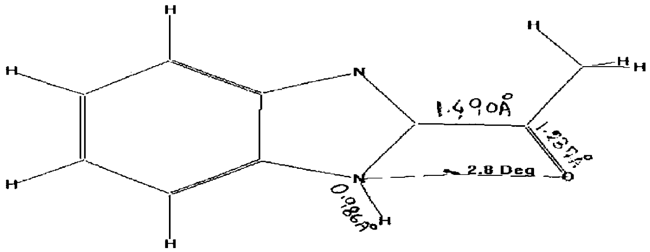
3. Results and discussion

3.1. Quantum chemical calculation

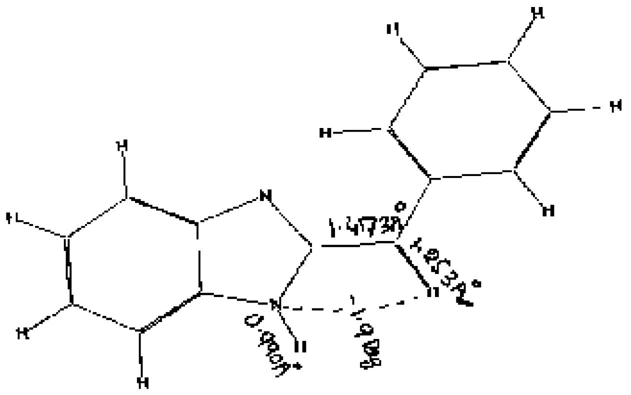
In order to have some better idea about the different excited state properties as well as the proton transfer feasibility study and to predict the nature and mechanism of proton transfer of 2ABI and 2BBI in ground and excited states, we have calculated the energies of different electronic transitions, heat of formation (enthalpy), charge distribution and the dipole moments using the MOPAC version 7 package with the AM1 Hamiltonian for both the molecules 2ABI and 2BBI in the ground and excited electronic states. Geometry optimization of the molecules was obtained by MOPAC's NLLSQ gradient minimization routine. Excited state calculation was done with the help of CI (6 × 6) calculation. CI calculation also provides a possible approach to calculate both the ground and excited state energies as a function of molecular geometry. Chart 1(a,b) depicts the calculated equilibrium geometry of 2ABI and 2BBI in the ground state as well as in the excited state. In the ground state, the C=O bond length is 1.237 Å but in the optimized excited state the C=O bond length increases to 1.250 Å for 2ABI and that for 2BBI in the ground and excited states are 1.236 and 1.253 Å. Again the angle



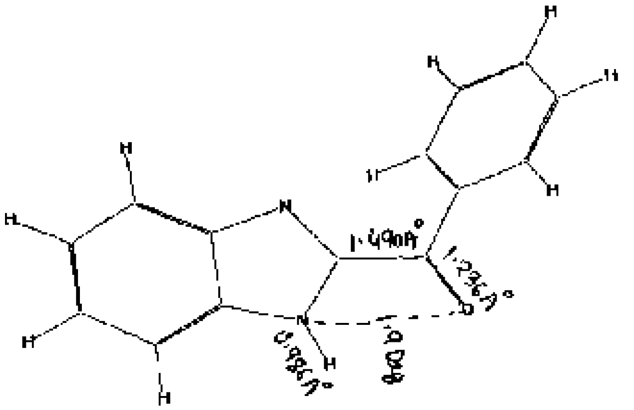
Excited state optimized geometry of 2ABI



(a) Ground state optimized geometry of 2ABI



Optimized geometry of 2BBI in excited state



(b) Optimized geometry of 2BBI in ground state

Chart 1.

between the two planes of the donor and acceptor moieties for 2ABI changes from ∼2.8° to ∼∼−0.9° for ground state to excited state. Similarly in the case of 2BBI the dihedral angle between the donor moiety plane and acceptor moiety plane in the optimized ground state geometry is ∼1.9° but in the optimized excited state it decreases to ∼∼−1.9°. This structural change, both the elongation of C=O bond and also the dihedral angle indicates nearness of proton to the acceptor and the possibility of proton transfer in the excited states of 2ABI and 2BBI molecules. For both the molecules 2ABI and 2BBI there are increments of the dipole moments from ground state to excited state. This large change in dipole moment is only accounted for by charge redistribution in excited state and that only possible in the case of intramolecular proton transfer from the acid moiety to the base moiety of 2ABI and 2BBI molecules. It was observed that in case of 2ABI with the variation of the dihedral angle the negative charge distribution over the proton donor nitrogen atom decreases from −0.2055 to −0.2044 whereas the negative charge distribution over the oxygen atom (proton acceptor) increases from −0.2987 to −0.2991 and in case of 2BBI the negative charge distribution over nitrogen atom decreases from −0.2048 to −0.2033 whereas the negative charge distribution over the oxygen atom increases from −0.2867 to −0.2883 which means in these configuration the proton donor part becomes more acidic and the acceptor part becomes more basic. This condition makes the proton transfer process more favorable in the excited state for both the molecules. Dependence of the ground and excited singlet states (S_0 and S_1) and triplet state (T_1) with the angle between the planes of the donor and acceptor moiety for 2ABI and 2BBI has been calculated (CI = 6 × 6) and has been plotted in Fig. 1. The ground state (S_0) shows a minimum value for a particular (∼>03°) angle between the two planes and then it increases with the increases of the change in the angle. So, in the ground state the structure is more stable and the ground state intramolecular proton transfer is no longer possible, whereas the first excited singlet state S_1 does not show such a variation but it shows an initial decrease with decrease of angle between the donor and acceptor planes. The first triplet state (T_1) also shows the similar type of variation of the first singlet state S_1. Fig. 2a shows that the heat of formation increases with decrease of angle between the donor and acceptor planes. Variation of dipole moment with the angle between the donor and acceptor planes shows the same type of results for both the molecules (Fig. 2b). This change in heat of formation and dipole moment confirms the proton transfer affinity of both the molecules. Almost same type of results obtained for both of the molecules 2ABI and 2BBI. The increased nature of heat of formation with the decrease of angle between the planes of the donor and acceptor moieties indicates that some external energy is required for transfer a proton from (N–H) group to C=O group of the molecules that is excited state intramolecular proton transfer (ESIPT), which is only possible by exciting the molecule. After examination of the computed charge distribution using the Mulliken scheme, it is evinced that there is an increase of charge distribution on the oxygen atom of the C=O group (basic moiety) and a simultaneous decrease in charge on the nitrogen atom of the N–H group (acid moiety) in going from ground state to excited state, which indicates a possible proton translocation in the excited state for both the molecules. So from the quantum chemical calculation we get an indication about the intramolecular relaxation of 2ABI and 2BBI in their excited state. It is probable that excitation of 2ABI and 2BBI will achieve a delocalized excited state and then relaxes to the proton transfer configuration by transferring the proton from the acid moiety to the basic moiety. With all these information we move to the steady state absorption and emission and also time resolved emission spectroscopy to get the total mechanism of excited state proton transfer, if any.

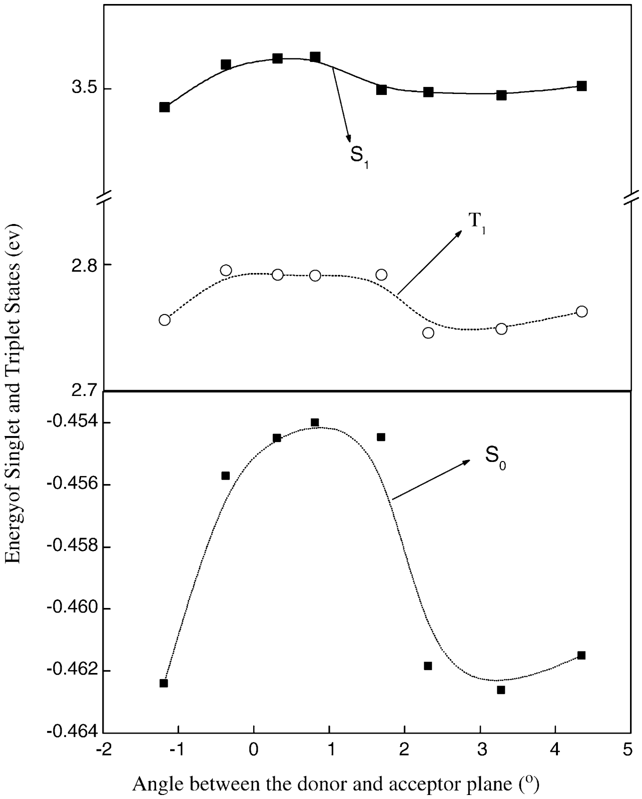


Fig. 1. Variation of S_0, S_1 and T_1 energy with change in dihedral angle between acidic and basic moiety planes of 2ABI.

3.2. Absorption spectra

The absorption spectra of 2-acetyl benzimidazole (2ABI) and 2-benzoyl benzimidazole (2BBI) were recorded at 300 K in various solvents. The absorption spectra of 2BBI in all the solvents were red shifted compared to that of 2ABI. The absorption spectra of both 2ABI and 2BBI show broad structureless bands in different organic hydrocarbon, polar, non-polar and hydroxylic solution, Fig. 3a and b. Tables 1 and 2 for 2ABI and 2BBI list the λ_{max} (abs) and ε_{max} of 2ABI and 2BBI in different solvents. The data in

Table 1
Absorption and Emission data of 2ABI

Solvent	Absorption data		Fluorescence data		
	Abs. maxima (nm)	ε_{max} at lower energy band ($dm^3\ mol^{-1}\ s^{-1}$)	Fluorescence peak		
			λ_f^1 (nm)	λ_f^2 (nm)	Quantum yield φ
MCH	299	23139	339.9	–	0.098
MCH + base	299.1	24815	340.5	–	0.098
ACN	299.7	27136	348.9	–	0.102
$CHCl_3$	303.4	26818	363.5	–	0.104
DEE	303.4	26560	362.6	–	0.099
MeOH	302.5	27428	324	438.5	0.108
EtOH	303.7	27756	325.8	424.9	0.112
Water	304.3	28770	342.1	469.4	0.311
Water + base	320.5	28795	–	470	0.320

Table 2
Absorption and emission data of 2BBI

Solvent	Absorption data		Fluorescence data		
	Abs. maxima (nm)	ε_{max} at lower energy band ($dm^3\ mol^{-1}\ s^{-1}$)	Fluorescence peak		
			λ_f^1 (nm)	λ_f^2 (nm)	Quantum yield φ
MCH	325	22113	351.04	–	0.017
MCH + base	325.5	23546	351.6	–	0.017
ACN	322	22332	361.2	–	0.016
$CHCl_3$	322.2	22350	358.5	–	0.018
DEE	322.2	22340	358	–	0.016
MeOH	322	22450	368	470	0.043
EtOH	321.8	22486	369.5	473.6	0.049
Water	321.5	22500	371.5	497.6	0.051
Water + base	338.2	23488	–	497.3	0.033

the figures and tables clearly indicate that the absorption spectra of 2ABI and 2BBI may be divided into three band systems in hydrocarbon solvents. For 2ABI the absorption spectrum exhibits a band at ∼235 nm, second band in the region 290–310 nm and a shoulder at 327 nm. In polar protic and hydroxylic solvents 2ABI shows only two bands: one at 225 nm and the last one at 290–310 nm region. The structure of this shoulder at 327 nm in hydrocarbon solvents vanishes with increasing polarity and hydrogen bonding capacity of the solvents. So the spectral change and presence of lower energy shoulder in hydrocarbon solvents are due to ketomethyl (acetyl) substitution as well as intramolecular hydrogen bonding between acid and base groups of molecule (2ABI) [42,43]. Also it is important to note here that the red shifted shoulder in hydrocarbon solvent and structureless tail possibly account for ground state closed conformeric form (I) (Scheme 1). The disappearance of the lower energy shoulder in polar or hydroxylic solvent is due to an increase in the solute-solvent interaction causing mainly a loss of structure (Scheme 2). Similar to 2ABI, 2BBI also shows three band systems: one at 270 nm, another around 320–330 nm, and the shoulder at 370 nm. It was observed that in the case of 2ABI the position of the absorption maximum of the lower energy band shifts to higher wavelength side in going from nonpolar to polar and hydroxylic solvents. The longest wavelength transition in pyrazole, imidazole, benzimidazole and their substituted derivatives [10–18,44,45] is $\pi \rightarrow \pi^*$ in character. It is generally followed by the increase in dipole moment and the dispersive interactions will be more in excited state as compared to that in the ground state and thus a red shift in absorption should be observed with increasing solvent polarity and hydrogen bonding ability [44]. A relatively high molar extinction coefficient (ε_{max} ∼20,000) of the first absorption maximum (∼327 nm at 2BBI and ∼293 nm in 2ABI) in all solvents and the band shift with solvent polarity indicate that the lower energy transition in these molecules like other benzothiazoles and benzimidazoles are of $\pi \rightarrow \pi^*$ character [10–18,44,45]. Again the shift observed in the absorption spectra, obtained in the hydrogen bonding solvents relative to the spectra obtained in non polar solvents show that, the solvents which form hydrogen bonds prevents the lone pair of >N–H group from taking part in the charge transfer interaction as $\pi \rightarrow \pi^*$ is the lowest energy transition. In the case of 2BBI a different behavior of band positions were observed in nonpolar and polar solvents in the absorption spectrum. In 2BBI the long wavelength absorption band system is slightly blue shifted with increasing polarity or tendency to form hydrogen bonds with the solvents. This opposite behavior of the $\pi \rightarrow \pi^*$ transition in absorption spectrum with increase of solvent polarity can be explained with the help of conjugation formed between benzimidazole group and the substituents ($-CH_3$, $-C_6H_6$). We know that solvent interaction is a kind of partial bond formation. Due to this, the phenyl ring rotates around the single bond and

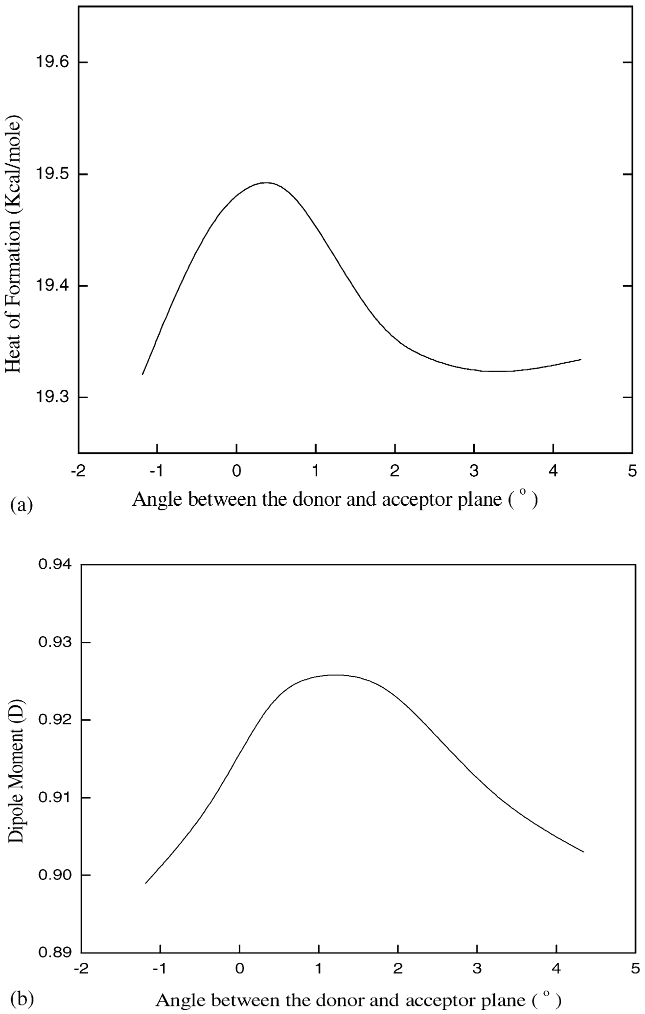


Fig. 2. Variation of (a) heat of formation and (b) dipole moment as a function of dihedral angle change between acidic and basic moiety plane keeping the ground state geometry fixed for 2ABI.

thus it is no longer in the plane of benzimidazole ring and the conjugation with the benzimidazole ring possibly decreases in case of 2BBI compared to 2ABI. This is reflected in the blue shift with increase in the polarity or hydrogen bonding ability of the solvents [46]. Hence the blue shift observed in only due to the steric effect.

3.3. *Effect of base on absorption spectra*

The absorption spectra of 2BBI in water over the wide range of basicity are shown in Fig. 4. With the increase of base concentration (NaEth) the low energy absorption band of 2BBI shifted considerably towards smaller wave numbers. The broad structureless red shifted band system, which appears at higher base concentration, may probably be due to anion formation. Since the normal benzimidazole is quite basic and thus it becomes more basic if electron donating groups are present in the molecule [47]. The red shift in the lower energy band confirms that protonation takes place at the pyridinic nitrogen atom and this band is of $\pi \rightarrow \pi^*$ in character (Scheme 2). This red shift is due to removal of hydrogen atom from nitrogen, which reduces the steric effect by making the molecule more planer.

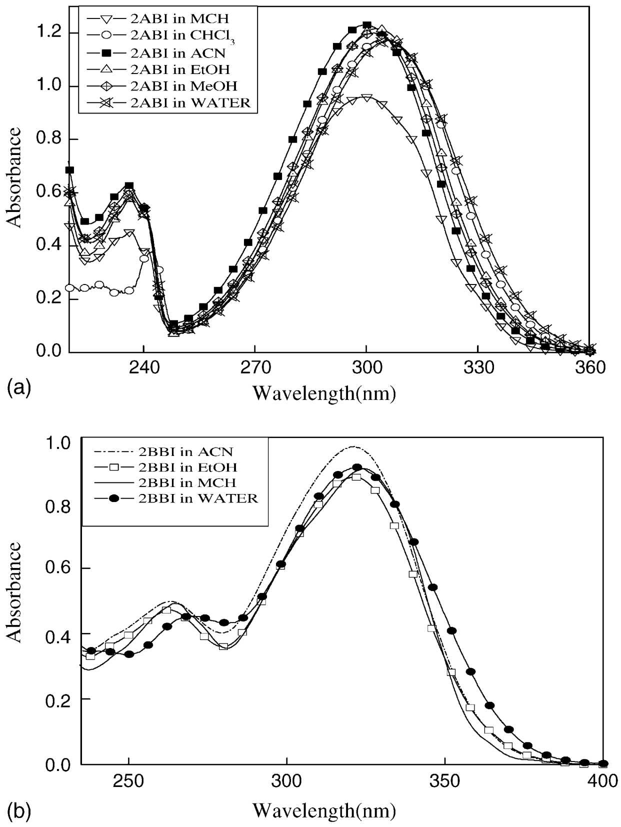
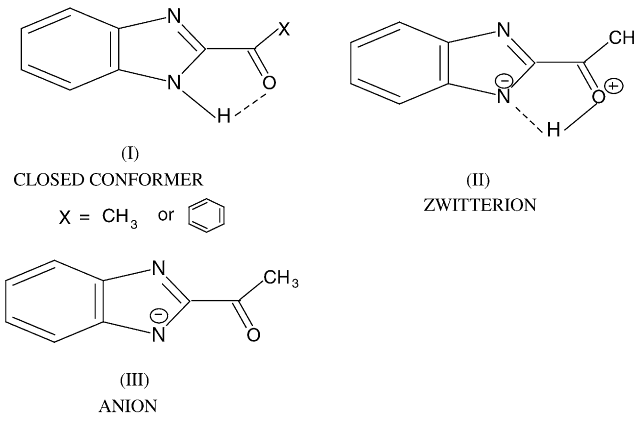
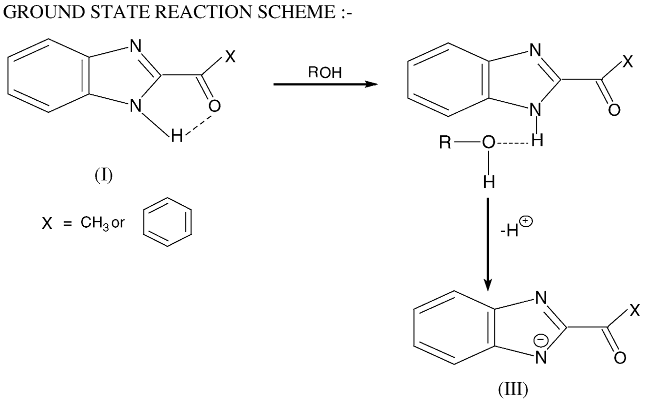


Fig. 3. Electronic absorption spectra of (a) 2ABI in different solvents. 2ABI = 5 × 10^{-5} mol dm^{-3} and (b) Electronic absorption spectra of 2BBI in different solvents. 2BBI = 5 × 10^{-5} mol dm^{-3}.

So the changes occur in the absorption spectra of 2ABI and 2BBI are due to the benzoyl and acetyl substitution in the 2 position of benzimidazole group. There is a red shift in the lower energy absorption band of 2BBI compared to that of 2ABI. Thus the introduction of $-C_6H_6$ group instead of $-CH_3$ group gives rise to a red shift of absorption band. This is due to electronic delocalization produced by the phenyl



Scheme 1. Different structures of the molecules.



Scheme 2.

group at position 2 and to a lesser extent to the intramolecular hydrogen–bonding interaction. This red shift is consistent with a planar ground state configuration. This phenyl group may give rise to a loss of vibrational structure of the benzimidazole and thus the red shift may be produced.

3.4. Emission studies

The room temperature emission spectra of 2ABI and 2BBI in different hydrocarbon, polar, nonpolar and hydroxylic solvents are shown in Fig. 5a and b. Benzimidazole is a highly fluorescent agent, which shows only one emission band [48] at about 34,500 cm^{-1}. Here we report on the fluorescence properties of two benzimidazole derivatives where in 2 position of benzimidazole moiety acetyl and benzoyl groups have been substituted. 2-Acetyl benzimidazole (2ABI) exhibits a Stokes shifted fluorescence band at 340 nm with moderately high intensity in almost all polar and non polar hydrocarbon solvents, having a bathochromic shift of fluorescence maximum with increasing solvent polarity at room temperature with excitation wavelength 290 nm. Position of this band remains unaffected with varying the excitation wavelength. If we excite the molecule at 240 nm we get another fluorescence band at 290 nm apart from this (340 nm) Stokes shifted fluorescence band in all the solvents (nonpolar, polar, hydroxylic). According to Kondo and Kuwano [48] this higher energy fluorescence band of 2ABI at ~290 nm is due to neutral benzimidazole molecule. In all polar protic and hydroxylic solvents 2ABI exhibits two distinct fluorescence bands with a bathochromic shift with solvent polarity. It has been shown by Tway and Love [49] that the transition in BI (Benzimidazole) is of $\pi \rightarrow \pi^*$ character and the absorption and fluorescence spectra are only slightly affected by the polarity or hydrogen bonding ability of the solvents. So the effects of solvents on the spectra of 2ABI and 2BBI would be mainly due to their interaction with Acetyl or Benzoyl group. In nonpolar hydrocarbon solvent the fluorescence spectra of 2ABI show one distinct band peaking at around 340 nm. But with increasing polarity a shift was observed in the higher wavelength band. Excitation spectra monitoring at 340 nm agree reasonably with the absorption a spectrum showing that large

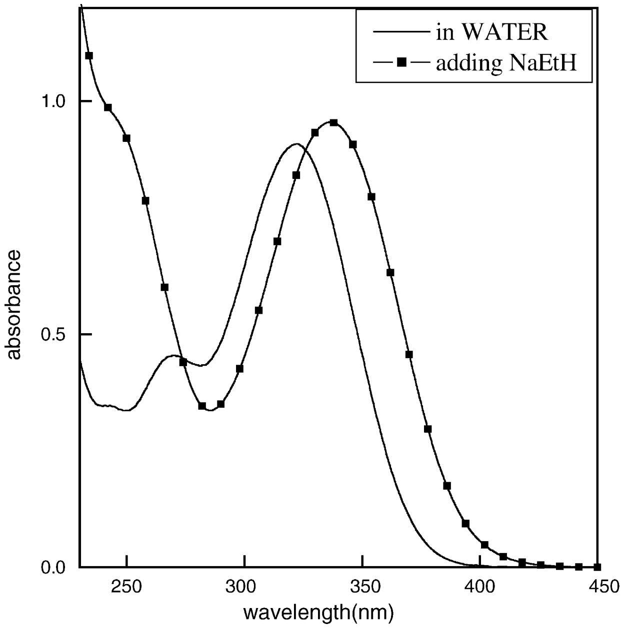


Fig. 4. Electronic absorption spectra of 2BBI in water and in the presence of base (NaEtH).

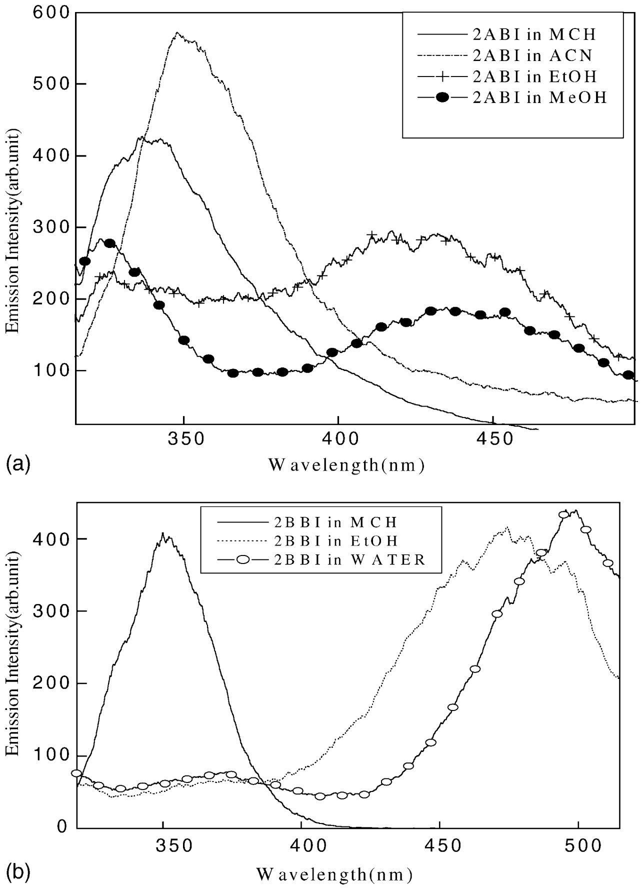
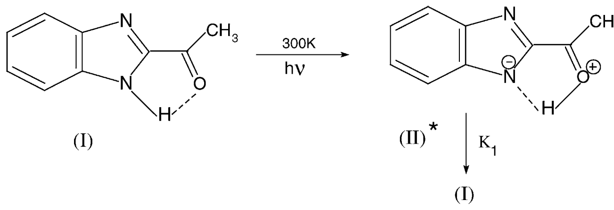


Fig. 5. Fluorescence emission spectra of (a) 2ABI and (b) 2BBI, in different solvents. excitation wavelength (λ_{exc}) = 290 nm.

EXCITED STATE REACTION SCHEME IN HYDROCARBON SOLVENT



Scheme 3.

Stokes shifted fluorescence at 340 nm originating from the main absorbing species in the ground state. In ACN the higher wavelength band position is 350 nm. The band position and shape are found to be independent of excitation wavelength (λ_{exe} = 290 nm) in almost all solvents and independent of concentration in the range of 10^{-4}–10^{-5} mol dm^{-3}. The red shift observed in fluorescence band maximum with increasing solvent polarity can be explained as, besides the vibrational relaxation in the upper state the excited Frank–Condon state is further equilibrated in excited state due to solvent relaxation, which is more in the solvent of higher polarity. Due to this the red shift observed in the fluorescence maximum from nonpolar to polar solvent. The main species existing in nonpolar solvents is considered to be the intramolecularly hydrogen bonded species (closed conformer). So in analogy with the fluorescence of 2-(2′-hydroxyphenyl) benzimidazole (HPBI) [50], 2-(2′-benzamidophenyl) benzimidazole (2BAPBI) [51] the large stokes shifted lower energy band (340 nm) (II of Scheme 1) may be considered to originate from the excited state intramolecular proton transfer (ESIPT) form of 2ABI (Scheme 1 and Scheme 3).

The fluorescence spectrum of 2ABI in EtOH with excitation at 290 nm shows two distinct fluorescence bands, one lower energy bands at ~324 nm and another large Stokes shifted band at ~445 nm (Fig. 5a). The fluorescence excitation spectrum in EtOH obtained by monitoring the emission at 440 nm clearly reflects the absorption spectrum (Fig. 6). On changing hydrocarbon solvent by polar hydroxylic solvents we observe that the higher energy fluorescence band intensity reduces and the lower energy band intensity increases, resulting in red-shifted emission spectra. This change in fluorescence spectrum in higher energy side has been attributed to the fluorescence of the zwitterionic form resulting from excited state proton transfer and not from the enol tautomer in the intramolecularly proton transferred conformer. In the case of tautomer formation in the excited state the intensity of the two bands would not change in that fashion with increase in polarity of solvents. These observations clearly indicate that there are two fluorescing species in the excited state, one is the zwitterionic form of the molecule which occurs due to intramolecular proton transfer (band at ~324 nm, II) and the second one comes at lower energy side at ~445 nm due to formation of anion (III) which is due to the intermolecular proton transfer between solute and solvent in the excited state (Scheme 1 and Scheme 4). A similar result was obtained in solvent like MeOH and water. In polar protic and hydroxylic solvents 2ABI shows an increase in emission intensity of the lower energy band with a slight red shift. Hydroxy derivatives of aromatic compounds are generally acidic in the excited singlet state relative to the ground state [52], so there is a tendency for intermolecular proton transfer to the solvent. Because in water the proton activity is high, an intermolecular translocation of proton is observed. This is reflected in the increase of rate of excited state proton transfer in polar solvents.

It is pertinent to mention here that in ethanol 2ABI shows lower energy emission band at ~445 nm. Increasing the ACN concentration (from 1 to 70%) by addition of ACN in this solution shows the decrease of emission intensity of this band. At maximum concentration of ACN (70%) the band at 445 nm totally disappears showing only one band at the higher energy side. So in excited state the band at ~445 nm region is due to excited state intermolecular proton transfer between solute and solvent interaction (Fig. 7) (III of Scheme 4). Similar type of results were obtained replacing ethanol by water only with more pronounced effect of intermolecular proton transfer.

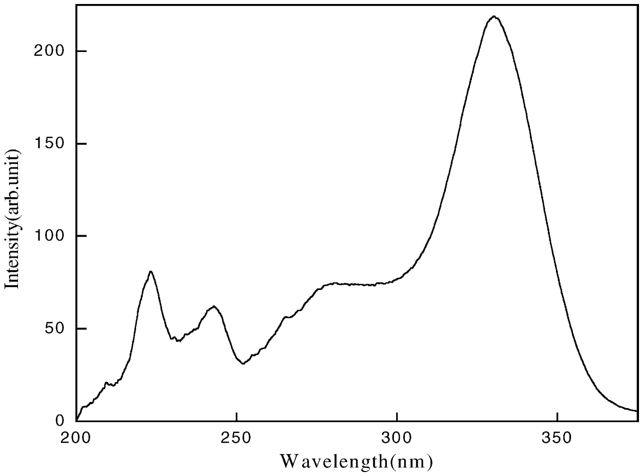
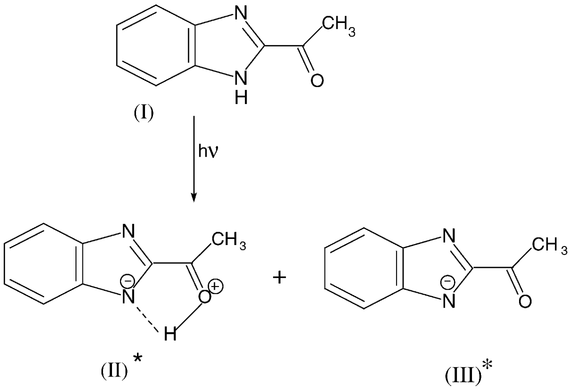


Fig. 6. Excitation spectra of 2ABI in ethanol (EtOH) monitoring wavelength 440 nm.

EXCITED STATE REACTION SCHEME IN HYDROXYLIC SOLVENT



Scheme 4.

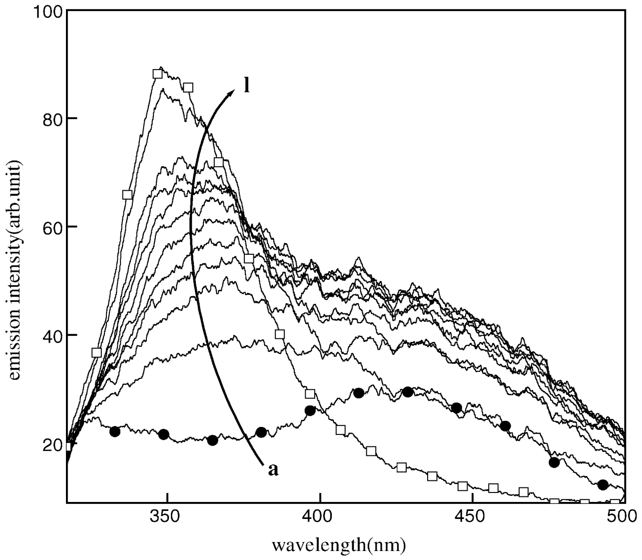


Fig. 7. Fluorescence emission spectra of 2ABI in (a) pure ethanol (b–l) increasing the percentage of ACN = 1.6–70%.

Fig. 5b shows the fluorescence spectra of 2BBI in different solvents at room temperature. The fluorescence spectra of 2BBI also show strong solvent dependent properties. In hydrocarbon medium 2BBI exhibits a single fluorescence band at 350 nm on excitation by different λ_{exe} in the wide range of absorption band keeping the fluorescence intensity and quantum yield as well as band shape unaltered. The fluorescence lifetimes in MCH and water for 2ABI were measured to be 3.03 and 3.47 ns, respectively, and that for 2BBI were 3.17 and 3.27 ns, respectively while monitoring at 350 nm (Fig. 8). The lifetime in other solvents is below the measuring limit of the instrument. The excitation spectra corresponding to the two peaks are identical to each other and closely resemble the absorption spectrum. In comparison to benzimidazole [48] the lower energy band (~350 nm) is due to excited state intramolecular proton transfer (Scheme 3). On placing 2BBI in polar protic and hydroxylic solvents this peak decreases heavily and a new high intense peak arise at ~500 nm. This observation indicates that the rate of excited state intermolecular proton transfer increases in 2BBI in hydroxylic solvents than 2ABI (Scheme 4).

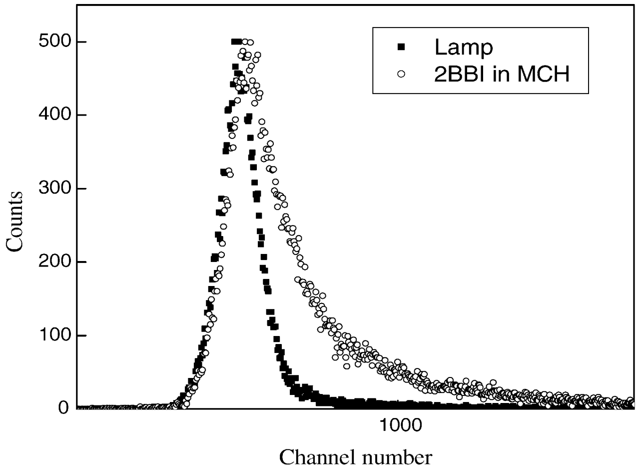


Fig. 8. Typical decay profile of 2BBI (emission wavelength monitored at 316 nm) in MCH. The decay curve represents the best computer fit of the experimental points to a single exponential decay: excitation wavelength is 350 nm. The lamp profile is denoted by the dark circles.

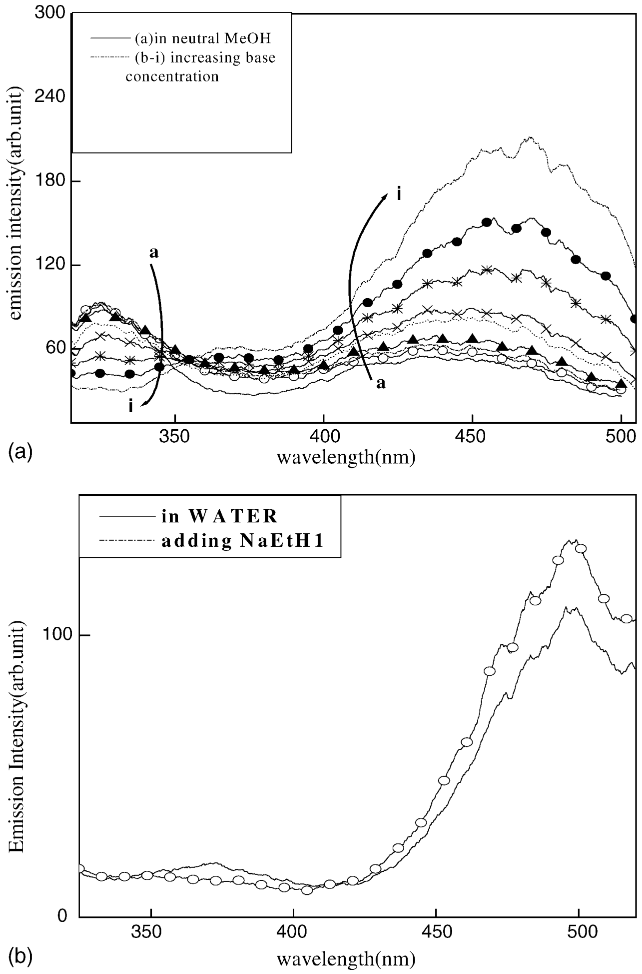


Fig. 9. Fluorescence emission spectra of (a) 2ABI in (a) neutral MeOH and (b–i) with increasing the concentration of base and (b) 2BBI in water with the presence of base sodium ethoxide (NaEtH).

3.5. *Effect of base on emission spectra*

The spectral behavior of 2ABI in methanol (MeOH) with addition of electron donor concentration as base (NaEtH) is depicted in Fig. 9a. In aqueous MeOH with the addition of NaEtH, a high intense emission peak is observed at ~475 nm with a simultaneous decrease in intensity of higher energy emission peak. The electron-donating alkyl group is present in polar solvents (MeOH, EtOH) and is able to release an electron towards the oxygen atom of the hydroxyl group (due to +I effect). That is, when the dipole moment of the probe molecule is larger in more polar environments, they act as strong proton acceptors, partially in the excited state. These indicate that 2ABI has been deprotonated to its anion in various polar solvents. The intensity of lower energy band seems to increase with a red shift with addition of base. An isoemissive point occurs at 355 nm between the 324 and 455 nm peak as the base concentration is increased. This spectral behavior in basic solution indicates that there is equilibrium between the zwitterionic form and anionic form of the molecule. In tautomer, like zwitterion, there is no positive and negative charge, so the tautomer structure is a stable structure and there is no possibility of its conversion to open conformer and anion. So we may conclude that the band at 324 nm is due to zwitterionic form of the molecule.

In the case of 2BBI, with addition of small amount of NaEtH in polar protic and hydroxylic solvent the higher energy peak position and intensity remain unchanged but a simultaneous decrease of 375 nm peak intensity and increase of 500 nm peak intensity could be observed (Fig. 9b). Again an isoemissive point was observed at 420 nm. This spectrum also confirms the existence of anionic form of 2BBI. But the rate of production of anion in case of 2BBI is smaller than that of 2ABI. All the experimental data in absorption and emission spectra for both the molecule show that pyridinium type nitrogen atom in 2ABI and 2BBI becomes less basic that is more acidic in its first electronically excited state due to charge density decrement at this nitrogen, whereas the charge density increases in pyrrole type nitrogen, thereby rendering it more basic in its first electronically excited singlet state.

Our forgoing results can most plausibly be explained by postulating the existence of two distinct excited state species in both the molecules 2ABI and 2BBI. The first of these is zwitterion 2ABI (II of Scheme 1), which is responsible for the emission band at ∼324 nm; formed by excited state intramolecular proton transfer; and the other one at extreme red at ∼455 nm is the phenolate anion (III of Scheme 1), resulting from excited state intermolecular proton transfer to the solvent (Schemes 3 and 4). A panoply of evidence [42,50,51] favor the assignments that the excited phenolate anion is responsible for an emission band with a maximum at ∼475 nm, while the zwitterion fluorescence maximum is at ∼324 nm. Both the zwitterion and the phenolate anion are capable of considerable resonance stabilization by delocalization of their formal charges. It is therefore expected that their fluorescence will exhibit unusually large Stokes shifts [42]. So the change in large Stokes shifted fluorescence intensity could be attributed to fluorescence of the zwitterionic form due to excited state proton transfer and formation of anion due to intermolecular reaction with solvent. By adding base the intermolecular hydrogen bond is ruptured due to creation of anion and this decreases the normal fluorescence intensity.

Comparing the emission spectrum of benzimidazole [48,49] with that of 2ABI, the peak at ∼475 nm of 2ABI may be assigned due to the fluorescence from the phenolate anion, the 324 nm peak may be assigned due to the fluorescence from zwitterion 2ABI (Scheme 3 and Scheme 4). Analysis of the alteration in peak intensity for both of the species as a function base variation indicates that the change occurs solely as a consequence of the change in the excited state. We could not observe any spectral change in non-polar solvents with addition of acid or base. This confirms that the intramolecular hydrogen bond is much stronger in 2ABI in the excited state.

We have also done some low temperature studies to observe the existence of open conformer in the molecules, which will be described, in the next communication.

4. Conclusion

The quantum chemical calculations suggest from the interplaner angle decrease and C=O bond increasing tendency in the excited state that intramolecular proton transfer is only possible in the excited state. The absorption spectra of 2ABI and 2BBI in different solvents point to the presence of an intramolecularly hydrogen-bonded closed conformer in the form of a shoulder in a nonpolar hydrocarbon solvent at ∼327 nm for 2ABI and at ∼370 nm for 2BBI. From Tables of 2ABI and 2BBI we find that the long wavelength transition in both the molecules are $\pi \rightarrow \pi^*$. In the case of 2ABI in ground state a red shift in $\nu_{\max}$ (abs) was observed which increases with solvent polarity. Similar results were also observed in solvents of increasing hydrogen-bonding ability. This is generally followed by the increase in the dipole moment and the dispersive interaction, which are more in the excited state as compared to these in ground state. As a result the red shift occurs in the absorption spectra. However, in case of 2BBI opposite results were observed. Instead of the red shift a blue shift is observed in $\nu_{\max}$ (absorption) with increase in solvent polarity. Dipole–dipole interaction or hydrogen bond formation between the solute and solvent occurs due to the addition of different substituents at 2 position of benzimidazole (BI). The phenyl group rotates and it is no longer in the plane of the BI ring and so the conjugation decreases. This is reflected in the absorption spectra as the blue shift increases with increase in the polarity or hydrogen bonding ability of the solvents. However, the red shift in $\nu_{\max}$ (absorption) of $2BBI^-$ is due to the removal of hydrogen atom from nitrogen, which reduces the steric effect. The red shift observed in fluorescence maximum with increase in the polarity of the solvents in 2BBI compared to 2ABI may be explained in the similar way. In the excited state for both the molecules red shifted fluorescence bands observed in hydrocarbon (small red shift) and hydroxylic (large red shift) solvents. Besides the vibrational relaxation in the upper state, the excited Franck–Condon state is further stabilized to the equilibrium excited state due to solvent relaxation, which is more for the solvents of increased polarity. Due to this the red shift in fluorescence band maxima were noticed. In the case of 2ABI a large Stokes shifted fluorescence band at 340 nm in hydrocarbon solvents has been identified to be due to a possible excited state intramolecular proton transfer (ESIPT). The excitation spectra confirm that the appearance of this 340 nm band is due to excitation of ground state closed conformer. In hydroxylic solvents the two bands, one at ∼324 nm and second at ∼445 nm were analyzed and found to be due to zwitterionic intramolecular proton transfer and the second one due to intermolecular proton transfer between solute and solvent. In basic alcoholic medium the lower energy band intensifies with a red shift (band at ∼475 nm) due to anion formation with a parallel decrease in 324 nm band. For 2BBI almost same type of results were obtained in the excited state at room temperature, total red shifted fluorescence band system occurs. For 2BBI intensity of intermolecular proton transfer was very much higher than that of intramolecular proton transfer band compared to 2ABI.

Acknowledgement

The authors express deep sense of gratitude to Professor S. Basak, SINP for kindly allowing the fluorescence lifetime measurements in his laboratory.

References

[1] A. Weller, Naturewissenschaften 42 (1955) 175.
[2] A. Weller, Z. Electrochem. 60 (1956) 1144.
[3] M.H. Van Benthem, G.D. Gillispie, J. Pys. Chem. 88 (1984) 2954.
[4] K.P. Ghiggino, A.D. Scully, H.I. Leaver, J. Phys. Chem. 90 (1986) 5089.
[5] E.M. Kosower, D. Huppert, Annu. Rev. Phys. Chem. 37 (1986) 127.
[6] K.Y. Law, J. Shoham, J. Phys. Chem. 99 (1995) 12103.
[7] J. Goodman, L.E. Brus, J. Am. Chem. Soc. 100 (1978) 7472.
[8] J.L. Herek, S. Pederson, L. Banares, A.H. Zewail, J. Chem. Phys. 97 (1992) 9046.
[9] M. Kasha, J. Chem. Soc. Faraday Trans. II 82 (1986) 2379.
[10] M. Kondo, Bull. Chem. Soc. Jpn. 51 (1978) 3027.
[11] R.G. Brown, N. Entwistle, J.D. Hepworth, K.W. Hodgson, B. May, J. Phys. Chem. 86 (1982) 2418.
[12] M.F. Rodŕiguez-Prieto, M. Mosquera, M. Novo, J. Phys. Chem. 94 (1990) 8536.
[13] R.S. Moog, M. Maronecelli, J. Phys. Chem. 95 (1991) 10359.
[14] Y. Chen, F. Gai, J.W. Petrich, J. Am. Chem. Soc. 115 (1993) 10158.
[15] S. Manta, M. Maronecelli, J. Phys. Chem. A 102 (1998) 3860.
[16] K. Das, N. Sarkar, A.K. Ghosh, D. Majumder, D.N. Nath, K. Bhattacharya, J. Phys. Chem. 98 (1994) 9126.
[17] A. Douhal, F. Amat-Guerri, M.P. Lillo, A.U. Ačuna, J. Photochem. Photobiol. A: Chem. 78 (1994) 127.
[18] M. Mosquera, J.C. Penedo, M.C. Ríos, M.F. Rodríguez, Rodŕiguez-Prieto, J. Phys. Chem. 100 (1996) 5396.
[19] T. Arthen-Engel, T. Bultmann, N.P. Ernsting, Chem. Phys. 163 (1992) 43.
[20] G.J. Woolfe, M. Melzig, S. Schnider, F. Dörr, Chem. Phys. 77 (1983) 213.
[21] M.A. Ríos, M.C. Ríos, J. Phys. Chem. 99 (1995) 12456.
[22] C. Chudoba, E. Riedle, M. Pfeiffer, T. Elsaesser, Chem. Phys. Lett. 263 (1996) 622.
[23] D.W. Cho, Y.H. Kim, M. Yoon, S.C. Jeong, D. Kim, Chem. Phys. Lett. 226 (1994) 275.
[24] L.G. Arnaut, S.J. Formoshino, J. Photochem. Photobiol. A: Chem. 75 (1993) 1.
[25] S.M. Ormson, S.M. Brown, Prog. React. Kinet. 19 (1994) 45.
[26] S.-i. Nagaoka, U. Nagashima, Spectroscopy and dynamics of elementary proton transfer in polyatomic systems, Chem. Phys. (special issue) 136 (1989) 153.
[27] C. Chudoba, S. Lutgen, T. Jentzsch, E. Riedle, M. Woermer, T. Elsaesser, Chem. Phys. Lett. 240 (1995) 35.
[28] H. Durr, H. Bouas Laurnet (Eds.), Photochromism. Molecules and Systems., Elsevier, Amsterdam, 1990.
[29] P. Chou, D. McMorrow, T.J. Aartsma, M. Kasha, J. Phys. Chem. 88 (1984) 4596.
[30] D.A. Parthenopoulos, D. McMorrow, M. Kasha, J. Phys. Chem. 95 (1991) 2668.
[31] A.U. Ačuna, A. Costela, J.M. Muñoz, J. Phys. Chem. 90 (1986) 2807.
[32] J. Rieker, E. Lemmert-Schmitt, G. Geoker, M. Roesseler, G.J. Stueber, J.L. Birbaum, M. Stongo, G. Rytz, J. Phys. Chem. 96 (1992) 10225.
[33] K. Kuldova, A. Corval, H.P. Trommsdorff, J.M. Lehn, J. Phys. Chem. A 101 (1997) 6850.
[34] M.L. Martinez, W.C. Cooper, P.T. Chau, Chem. Phys. Lett. 193 (1992) 151.
[35] A. Sytnik, J.C. Del Valle, J. Phys. Chem 99 (1995) 13028.
[36] A. Sytnik, I. Litvinyul, Proc. Natl. Acad. Sci. USA 93 (1996) 12959.
[37] J.H. Longworth, R.O.R. Rahn, R.G. Schulman, J. Chem. Phys. 45 (1996) 2930.
[38] P. Svejda, R.R. Anderson, A.H. Maki, J. Am. Chem. Soc. 100 (1978) 7131.
[39] D.K. Maiti, P.K. Bhattacharya, Synth. Commun. 28 (1998) 99.
[40] G.W.H. Cheesemen, J. Chem. Soc. (1964) 4645.
[41] L.A. Paquette, Encyclopedia of Reagents for Organic Synthesis, vol. 6, Pergamon Press, New York, 1979, p. 4356 ;
D. Barton, W.D. Ollis, Comprehensive Organic Chemistry, The Synthesis and Reaction of Organic Compounds, vol. 1, Pergamon Press, New York, 1979, p. 645.
[42] P. Chowdhury, S. Panja, S. Chakravorti, J. Phys. Chem. 107 (2003) 83.
[43] P.R. Bangal, S. Chakravorti, J. Phys. Chem. A 103 (1999) 8585.
[44] J. Dey, S.K. Dogra, J. Phys. Chem. 98 (1994) 3638.
[45] M.H.M. Grimmet, Advances in Heterocyclic Chemistry, vol. 12, Academic Press, New York, 1970, p. 104.
[46] A.K. Mishra, S.K. Dogra, Spectrochim. Acta 39A (1983) 609.
[47] M. Swaminathan, S.K. Dogra, Ind. J. Chem. 22A (1983) 278.
[48] M. Kondo, H. Kuwano, Bull. Chem. Soc. Jpn. 42 (1969) 1433.
[49] P.C. Tway, L.J.C. Love, J. Phys. Chem. 86 (1982) 5223.
[50] K. Das, N. Sarkar, D. Majumder, K. Bhattacharya, Chem. Phys. Lett. 198 (1992) 443.
[51] S. Santra, G. Krishnamoorthy, S.K. Dogra, Chem. Phys. Lett. 311 (1999) 55.
[52] L.E. Cramer, K.G. Spears, J. Am. Chem. Soc. 100 (1978) 221.