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Excited state intramolecular proton transfer in anionic and cationic species of 2-(2′-amino-3-pyridyl)benzimidazole

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Abstract

Excited state intramolecular proton transfer (ESIPT) process has been studied in the monoanionic and monocationic species of 2-(2′-amino-3-pyridyl)benzimidazole (2-A3PyBI) in aqueous and organic solvents. Dual fluorescence is observed from monocationic (aqueous and alcoholic solvents, partly from non-polar and polar aprotic ones) and monoanionic species in aqueous media. Presence of different species has been characterized with the help of absorption, fluorescence excitation and fluorescence spectroscopy, as well as, time resolved fluorimetry. The electronic structure calculations were performed on each species using semi-empirical quantum mechanical AM1 method and density functional theory B3LYP with 6-31G** basis set using Gaussian 98 program to characterize the particular ionic species. Presence of electron withdrawing pyridine =N– atom and negative charge on the benzimidazole moiety plays the vital role in increasing the rate of ESIPT process.

Keywords: 2-(2′-Amino-3′-pyridyl)benzimidazole; Absorption spectrum; Fluorescence spectrum; ESIPT; Prototropic equilibrium; Theoretical calculations

1. Introduction

Intramolecular hydrogen bonding (IHB) is known to have considerable effect on the geometric, electronic, vibrational and radiationless transitional properties of the substituted aromatic molecules [1–3]. Besides its relevance in understanding the conformation in bio-molecules [4,5], the above mentioned properties have many practical utilities worthy of considerations, e.g., dye lasers [6,7], high energy radiation detectors [8], development of UV photo-stabilizers [9], molecular energy storage devices [10], fluorescent probes [11,12], etc.

Basic requirements for ESIPT reactions to take place are: (i) IHB between the acidic centers (–NH_2, –OH groups) and the basic centers (>COOH, =N– moieties) in the ground (S_0) state [13], (ii) increase in acidic and basic character of these groups on excitation to first singlet excited (S_1) state [14], (iii) ESIPT process in S_1 state should be exothermic, i.e., energy of tautomer formed by ESIPT from enol form should be lower than that of enol form [15–18], (iv) S_1 state of enol form should be of (π, π*) in character, because the activation barrier for the conversion of enol to tautomer is the smallest for S_1 state of (π, π*) in nature and largest for (^{3}n, π*) triplet state [19]. Presence of first two criteria does not guarantee that ESIPT will occur and Gillespie et al. [13,16] were the first to show the absence of large Stokes shifted tautomer emission in 1-aminoanthraquinone (1-AA) and 1,4-dihydroxyanthroquinone (1,4-DHA).

In our recent studies on ESIPT process in 2-(2′-aminophenyl)benzimidazole (2-APBI) [20,21], (Scheme 1) though we observed the presence of ESIPT reaction from the acidic –NH_2 group to benzimidazole (BI) =N– atom, fluorescence quantum yield of the tautomer band (Φ_f^T) was very small as compared to that of small Stokes shifted normal emission (Φ_f^N). Ratio (Φ_f^T/Φ_f^N) in cyclohexane is 0.42 and decreases to 0.0 with increase in the polarity and protic nature of solvents. Small Φ_f^T of tautomer could be due to smaller rate of ESIPT in S_1 state as the pK_a and pK_a* values of the deprotonation reaction of –NH_2 group are >16 and 11–12, respectively. Smith et al. [22] and our group [23–25]

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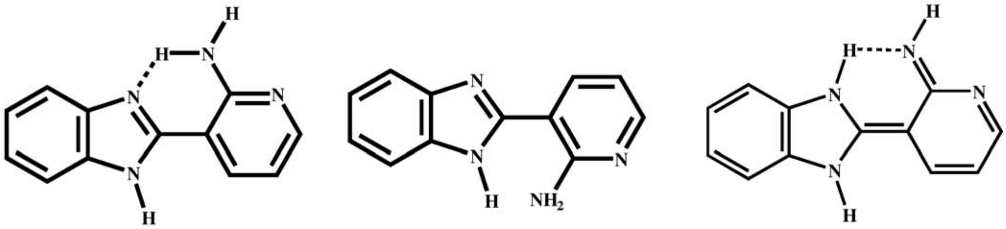

a-1 **a-2** **T**

Scheme 1.

have shown that the rate of ESIPT process from the $-NH_2$ group can be increased either by increasing the acidity of $-NH_2$ group by replacing one of the $-NH_2$ proton by electron withdrawing group ($-COCH_3$, $-COC_6H_5$) or increasing the basicity of electron withdrawing group.

In continuation to our study on 2-APBI, we have synthesized 2-(2′-amino-3-pyridyl) benzimidazole (2-A3PyBI, Scheme 1) molecule which contain an electron withdrawing pyridine =N– atom ortho to $-NH_2$ group. Photophysics of this molecule has shown that ratio of (Φ_f^T/Φ_f^N) in 2-A3PyBI in cyclohexane increases and is much larger than that observed in 2-APBI in cyclohexane [26]. Acidity of $-NH_2$ group can be increased by protonating pyridine =N– atom or by increasing the basicity of BI moiety. Present study involves the effect of acid-base concentration on the photophysics of 2-A3PyBI, as well as, on the ESIPT reaction. Absorption, fluorescence excitation and fluorescence spectroscopy and time correlated single photon counting spectrofluorimetry has been used. Both semi-empirical (AM1) quantum mechanical and DFT-B3LYP calculations using 6-31G** as basis set, employing Gaussian 98 program were also carried out on the ionic species to supplement the experimental results.

2. Materials and methods

2-A3PyBI was synthesized by refluxing equivalent amount of 1,2-diaminobenzene and 2-aminonicotinic acid (both procured from Aldrich Chemical Company, UK) in polyphosphoric acid medium as described in literature [27]. 2-A3PyBI was purified by repeated crystallization from methanol. Purity was checked by the desired spectroscopic techniques, as well as, getting similar fluorescence and fluorescence excitation spectra using different excitation (λ_{ex}) and emission (λ_{em}) wavelengths respectively. All the solvents used were either of spectroscopic or HPLC grade from E. Merck and were used as received. Spurious emission was checked for each solvent by excitation at the same wavelength as used for each solution of 2-A3PyBI in different solvents and containing different acid-base concentrations. Triply distilled water was used for the preparation aqueous solutions.

Procedure used to prepare solutions and adjustment of pH was the same as described in our recent papers [28,29]. Hammett's acidity scale [30] was used for H_2SO_4–H_2O mixture for pH < 1 and Yagil's basicity scale [31] was used for NaOH–H_2O mixtures for pH > 13. These Hammett's and Yagil's functions represent the actual (or free) amount of protons or hydroxyl ions available in the desired solution to react with weak base or acid, respectively. Acid concentration in cyclohexane was controlled by trifluoroacetic acid (TFA), whereas in acetonitrile and methanol, it was controlled by H_2SO_4. Details of instruments used for recording absorption, fluorescence, fluorescence excitation spectra and excited state lifetimes are the same as described in our recent papers [28,29]. Fluorescence quantum yield (Φ_f) was measured from solutions having absorbance less that 0.1 using quinine sulphate in 1N H_2SO_4 as reference ($\Phi_f = 0.55$) [32]. Concentration of 2-A3PyBI was kept at 1.03×10^{-5} M to avoid self-absorption.

3. Theoretical calculations

Schemes 2–4 consider different monocations (MCs, MC-1, MC-2, MC-3 and MC2-T), dications (DCs, DC-1, DC-2 and DC-3) and monoanions (MAs, MA-1, MA-2 and MA-T), respectively for theoretical calculations. Geometry of all the species were fully optimized using AM1 method (QCMP 137, MOPAC 6/PC) [33] and using the coordinates obtained from PCMODEL [34] in S_0 and S_1 states after taking into account the configuration interactions (CI = 5 in MOPAC, 100 configurations). Total energy (E), dipole moment (μ), and dihedral angle (φ, N_8–C_9–C_{10}–C_{11}) have been compiled in Tables 1–3 for monocations, dications and monoanions, respectively. Standard single point calculations were performed on each species by taking the same geometries in S_0 and S_1 states to get the Franck–Condon absorption and fluorescence transition energies respectively. Transition energies (ΔE_{ij}) for each species were also calculated using CNDO/S-CI method [35] as described in our recent paper [28]. Total energy (E_j) was obtained by the expression ($E_j = E_i + \Delta E_{ij}$). First two transitions are compiled in the respective tables.