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Spectral characteristics of 2-(3′,5′-diaminophenyl)benzothiazole: effects of solvents and acid–base concentrations

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Abstract

Spectral characteristics of 2-(3′,5′-diaminophenyl)benzothiazole (3,5-DAPBT) have been studied in different solvents and H_0/pH/H range of −10 to 16. Increase in Stokes shifts observed with increase in polarity of solvents is due to increase in dipole moment (μ) on excitation to first excited singlet (S_1) state. Polarization also plays a major role in the increase of excited-state dipole moment (μ_e). Combining the results observed in absorption, fluorescence and fluorescence excitation spectra and lifetime studies, it is found that (i) MC1 is the only monocationic (MC) species in polar aprotic and polar protic solvents, whereas MC1 and MC3 (Scheme 1) are formed in cyclohexane + trifluoroacetic acid (TFA) medium in the ground (S_0) and S_1 states; (ii) DC2 is the only dicationic species present in polar protic solvents, whereas DC1 and DC2 (Scheme 1) are dicationic species in non-polar and polar aprotic solvents; (iii) only one kind of tricationic species is present in polar and protic solvents; (iv) monoanion (MA) formed by the deprotonation of any of the $-NH_2$ group, is non-fluorescent. Semi-empirical quantum mechanical calculations (AM1) and density functional calculations (DFT) have been performed on all kinds of ionic species. The spectral characteristics have been assigned to various prototropic species combining the experimental and theoretical results.

Keywords: 2-(3′,5′-Diaminophenyl)benzothiazole; Absorption spectrum; Fluorescence spectrum; pK_a values; Theoretical calculations

1. Introduction

Study of photophysical properties of heterocyclic organic molecules has achieved a considerable importance recently because many of these molecules form an integral part of intermediates [1], fine product for drugs [2–5] and pesticides [6,7], color industries [8], redox systems for solar energy [9], organized assemblies [10], laser dyes [11] and complex-forming agents [12,13].

Although substituted 2-aryl benzothiazoles are found to be useful from industrial point of view (for e.g., fluorescence whitening agents [14], and photoconducting materials [15] and as herbicides in agriculture), have not received much attention. The molecules belonging to benzothiozole series, which have been studied extensively are 2-(2′-hydroxyphenyl)benzothiazole (2-HPBT) [16], 2-(2′-aminophenyl), 2-(3′-amino phenyl) and 2-(4′-aminopheenyl)benzothiazoles (2-APBT, 3-APBT, 4-APBT) [17]. 2-HPBT has been studied extensively as this molecule gives rise to excited-state intramolecular proton transfer (ESIPT) [16], whereas the amino derivatives were studied from the following angles: (i) being strong electron donor in the excited-state, fluorescence spectrum of amino derivatives are more sensitive to the solvent polarity than the absorption spectrum. These molecules have been used as probe to study the various structural aspects of biological systems; (ii) molecules contain both electron-donating group ($-NH_2$) and electron-accepting group (=N–) without involving intramolecular hydrogen bonding (IHB) in S_0 state. Their monocations (MC) are formed by protonating $-NH_2$ group, which becomes strong acid in S_1 state [18] and may thus donate proton to =N– moiety in S_1 by second kind of ESIPT involving solvent molecules [19,20]. These studies have shown that 3-APBT is

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polar than 2-APBT or 4-APBT in S_1 state and thus is better probe molecule. It has also been observed that dipole moment of diamino aromatic system is the maximum if two substituents are present meta to each other than at any other positions. In other words, aromatic molecules containing two amino groups meta to each other can prove to be a very good probe system.

Present study on 3,5-DAPBT is a continuation of our earlier work on aromatic diamino compounds [21–25]. In this molecule, two amino groups are present meta to each other in the phenyl ring containing benzothiazole (BT) as an electron-acceptor moiety. Based on earlier studies, this molecule should be quite polar and can lead to greater interactions with the polar aprotic and polar protic solvents. In order to confirm the above-mentioned facts, absorption, fluorescence excitation and fluorescence spectroscopy, as well as, time-dependent spectrofluorimetry have been used. Effect of acid–base concentrations on the spectral characteristics have also been investigated and pK_a values for different prototropic reactions have been determined in S_0 and S_1 states. Characterization of various ionic species has been carried out by doing electronic structural calculations using semi-empirical AM1 method and DFT procedure using Gaussian 98 program.

2. Materials and methods

3,5-DAPBT was synthesized by refluxing equivalent amounts of 1-amino phenylthiol and 3,5-diaminobenzoic acid in polyphosphoric acid, as described in Ref. [26]. 3,5-DAPBT was purified by repeated crystallization from methanol. Purity of the compound was checked by chemical analysis, single point on TLC, NMR data and resemblance of fluorescence excitation spectra recorded at different emission wavelengths (λ_{em}). All the solvents used were either of spectroscopic grade or HPLC grade from Merck and thus were used as such. Spurious emission was checked for each solvent by exciting at the same wavelength as used for each solution of 3,5-DAPBT in different solvents. Triply distilled water was used for the preparation of aqueous solutions.

Procedure used to prepare the solutions and adjustment of pH was the same as described in our recent papers [20,27]. Hammett's acidity scale [28] was used for $H_2SO_4{\cdot}H_2O$ mixtures for $pH < 1$ and Yagil's basicity scale [29] was used for $NaOH{\cdot}H_2O$ mixtures for $pH > 13$. Details of instruments used for recording absorption, fluorescence excitation and fluorescence spectra and measuring lifetimes are the same as described in our recent papers [20,27]. Fluorescence quantum yield (Φ_f) was measured from solutions having absorbance less than 0.1 using quinine sulphate in 1N H_2SO_4 as reference ($\Phi_f = 0.55$) [30]. Concentration of 3,5-DAPBT was kept at 7×10^{-6} M. Prototropic reactions were studied in aqueous medium containing 1% (v/v) methanol.

3. Theoretical calculations

Theoretical parameters (e.g. total energy, E, relative to the most stable species; dipole moment, μ, etc.) of 3,5-DAPBT in S_0 and S_1 states were obtained by optimizing the geometry in the respective state using AM1 method (QCMP137, MOPAC 6/PC) [31,32]. In S_1 state, configuration interactions (CI = 5 in MOPAC, 100 configurations) were considered to optimize the geometry. Transition energies for absorption and emission processes were obtained by carrying out single point calculations in AM1 method and employing S_0 and S_1 state geometries, respectively. The respective data are compiled in Table 1.

Dipolar solvation energies for different species in different states have been calculated using the following expression based on Onsager's theory [33]:

$$\Delta E = -\left(\frac{\mu^2}{a^3}\right) f(D)$$

where $f(D) = (D - 1)/(2D + 1)$, D the dielectric constant of the medium, μ the dipole moment in the respective state and a the Onsagar cavity radius. For non-spherical molecules like 3,5-DAPBT, value of a has been obtained by taking 40% of the maximum length of the molecule [34]. It is found to be 0.49 nm.

Theoretical parameters for different cationic species (three monocations, MCs and three dications DCs, Scheme 1) were also obtained using the above-mentioned theoretical procedures and the relevant data are compiled in Tables 1 and 2, respectively. The electronic structure calculations were also performed on each species, as mentioned in Scheme 1, using Gaussian 98 program [35]. The geometry optimization was performed on each species of 3,5-DAPBT in S_0 state using hybrid density functional theories (DFT) [36,37] B3LYP with 6-31 G^{**} basis set [35,38]. The geometry of these stationary points on S_1 state (π, π^*) was calculated using configurations interaction singles (CIS) [35,39] theory with 6-31G^{**} basis sets. Time-dependent (TD) [40,41] DFT B3LYP was also used to calculate the excited-state energies at calculated stationary point geometry in S_0 and S_1 states. Relevant data are complied in Tables 1 and 2, respectively.

4. Results and discussion

4.1. Effect of solvents

4.1.1. Absorption spectrum

Table 3 depicts the absorption band maxima (λ_{max}^{ab}) and molecular extinction coefficient ($\log \varepsilon_{max}$) in all the solvents except cyclohexane because 3,5-DAPBT is partially soluble in this solvent. Besides a broad shoulder around ∼360 nm, a structured band appears at ∼313 nm with vibrational frequency of $910 \pm 60\ cm^{-1}$ in non-polar solvents. Structure is lost as polarity and hydrogen bonding capacity of the solvents increase. As compared to 1,3-diaminobenzene (1,3-