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Lactim–lactam tautomerism through four member hydrogen bonded network in isoindole fused imidazole system: A combined spectroscopic and theoretical approach to photophysical properties

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ABSTRACT

This article presents the photophysical study of a pharmaceutically important isoindole fused imidazole derivative, namely 1-(2-hydroxy-5methyl-phenyl)-3,5-dioxo-1*H*-imidazo-[3,4-*b*] isoindole (ADII) using steady state absorption, emission and time resolved emission spectroscopy. The molecule possesses a four member intramolecular hydrogen bonded ring composed of O—H and N atom suitable for intramolecular proton transfer process. Absorption study of ADII suggests the existence of its lactim and lactam tautomeric form in the ground state. The appearance of large Stokes shifted emission signifies lactim–lactam isomerization by excited state proton transfer reaction. Quantum chemical calculations at Density Functional Theory (DFT) (B3LYP/6-311+G**) and Hartree–Fock (6-311+G**) levels have also been performed in support of the experimental findings. Both the level of theory suggests the existence of two tautomeric forms in the ground electronic state and the calculated potential energy surfaces along the proton transfer coordinate suggest the preference of excited state proton transfer reaction than the ground state with respect to activation barrier. The pH variance experiment is also carried out for investigating different absorbing and emitting species of ADII in aqueous and ACN medium.

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1. Introduction

Among the various photoinduced intramolecular processes excited-state intramolecular proton transfer (ESIPT) process has been drawing great attention due to their ubiquitous application in various chemical and biological processes [1]. Numerous ESIPT molecules have been strategically designed and synthesized with an aim to understand the fundamental of proton transfer mechanism and/or to explore their potential applications in different directions [2–5]. Generally most of the ESIPT molecules possess a strong intramolecular hydrogen bonded six member ring between the donor O—H (or, N—H) and acceptor C=O (or, pyridinic N) groups. The close proximate acidic and basic moieties rearrange in an extremely fast period of time (within picoseconds) in the excited electronic state via a transfer of hydrogen or proton. ESIPT molecules are often characterized by dual emission: one corresponding to the normal emission, i.e., emission comes from the local excited (LE) state and the other large Stoke's shifted emission from the tautomeric species produced in the excited state.

This unique behavior of ESIPT phenomenon is widely applied in various fields such as: developments of ultraviolet stabilizers [6], laser dyes [7,8], radiation hard scintillators [9], LEDs [10], molecular energy storage [11], molecular switches [12] and molecular sensors [13], etc. Furthermore, the ESIPT phenomenon has been widely used as optical probes for the investigation of various biomimicking, biological and supramolecular microenvironments [14,15].

Structurally it is well known that under similar strength of proton donor/acceptor moieties, the strength of intramolecular hydrogen bonding is highest in case of six member system than five member system and least in case of four member one. For this reason intramolecular proton transfer (IPT) process in four member intramolecular hydrogen bonding system is very rare. The most popular and well studied molecule belonging to this class (i.e., four member intramolecular hydrogen bonding system) is 2-hydroxy pyridine (2HP) which remains in equilibrium between the two tautomeric forms: lactim form (i.e., the enol form 2-hydroxy pyridine (2HP)) and lactam form (i.e., the keto form 2-pyridone (2PY)) in the ground state. This two tautomeric pair present in substantial concentration at room temperature and the enthalpy change between the two forms (2HP and 2PY) is 2–3 kJ/mol in favor of the lactam form. A number of theoretical [16–19] and experimental [20–22] works have been done in order to explain the existence of two ground state tautomeric forms and the process of their interconversion. The most expected pathway related to this phenomenon is the direct proton transfer in the bare monomer. Theoretical calculation using DFT//B3LYP/6-311+G** method by considering IPT

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approach reveals a high energy barrier (~2 eV) for lactim to lactam conversion in the ground state [23,24]. Hence, the reaction is thought to be mediated by the assistance of protic solvents through intermolecular hydrogen bonding which might lead to reduction of energy barrier compared to the monomer. A large volume of theoretical and experimental works have been done in order to investigate the role of various proton donor/acceptor solvents for the tautomerization reaction in 2HP system [25–28]. The ground state intramolecular proton transfer (GSIPT) phenomenon in 2HP was also explained by considering tunneling process as light hydrogen atom is involved in it. Borst et al. experimentally showed the contribution of tunneling process in the first excited singlet state of 2HP system [29]. Latter, Tautermann et al. have developed a reliable theoretical method for the determination of the ground state tunneling splitting in 2HP and generalized the method to molecular systems having symmetric double well type of potential [30]. Tunneling process has been successfully applied to various systems to explain the intrinsic intramolecular proton transfer behavior [5,31]. Double proton transfer model has also been proposed by many researchers to explain the tautomerization process of 2HP system [32]. Although DFT//B3LYP method fails to explain the experimental results of 2HP-2PY system, but this method has been quite appreciably used by several researchers to generate the potential energy surfaces (PES), barrier height etc. with commendable efficiency.

In the present work we have carried out detailed photophysical study of a synthesized heterocycles of isoindole fused imidazole bearing phenolic subunit, namely 1-(2-hydroxy-5methyl-phenyl)-3,5-dioxo-1*H*-imidazo-[3,4-*b*] isoindole (ADII) in order to understand its dual emissive behavior using simple spectroscopic technique. In medicinal chemistry, this type of heterocyclic compound is widely used as templates to design a variety of biologically active agents [33]. Generally imidazole-based heterocyclic molecules play an important role in various biochemical processes too [34–36]. It is important to note that the present compound ADII can be used successfully to stain human squamous epithelium cells particularly the nuclei [37]. Structurally the molecule having a four member intramolecular hydrogen bonding unit may be responsible for intramolecular proton transfer behavior. The spectral study of ADII is also interesting from the fundamental aspect of lactam–lactim tautomerisation process. Along with spectroscopic technique, quantum chemical calculations have also been performed in order to get a knowledge related to the stability of different conformers of ADII and viability of ground and excited state proton transfer process. The ground state structures of different conformers of ADII have been optimized using Density Functional Theory (DFT) and Hartree–Fock (HF) levels of theory and the excited state optimization has been performed only at Hartree–Fock (HF) level of theory. The ground and excited state potential energy curve (PEC) along the PT coordinate have been constructed to follow the possibility of the IPT process.

2. Experimental

2.1. Synthesis of ADII

A 1:3 mixture of ninhydrin (1.4 mmol) and p-cresol (4.2 mmol) was refluxed in AcOH until the adduct 2-hydroxy-2-(2¢-hydroxy-aryl)-1,3-indanediones (where aryl = 2-hydroxy-5-methyl-phenyl) was completely formed. The complete formation of the desired adduct was checked by TLC. Then urea (16.6 mmol) was added to the above reaction mixture and the mixture was refluxed for further 2.5 h. The reaction mixture turned into red color. Then the cold reaction mixture was poured into ice-cold water. A yellow solid product was filtered and purified by column chromatography over silica gel (petroleum ether/ethyl acetate, 70/30, v/v) to give our desired compound 1-(2-hydroxy-5methyl-phenyl)-3,5-dioxo-1*H*-imidazo-[3,4-*b*] isoindole. The compound was characterized by both ^{1}H and ^{13}C NMR spectroscopy and was crystallized from acetone. ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.64 (bs, —NH), 7.80 (d, J = 7.8 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.41–7.32 (m, 3H), 7.05 (d, J = 8.2 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 157.4, 152.3, 144.5, 131.3, 129.1, 128.3, 127.8, 126.6, 124.2, 122.4, 119.0, 117.6, 116.4, 113.8, 113.4, 111.8.

2.2. Materials

Spectroscopic grade solvents such as acetonitrile (ACN), dioxane (DOX), methanol (MeOH), chloroform ($CHCl_3$) and methyl cyclohexane (MCH) were purchased from Spectrochem (India) and were used after proper distillation whenever required. Triply distilled water was used for the preparation of solutions. Trifluoroacetic acid (TFA) and triethyl amine (TEA) from Spectrochem were used as supplied. Sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) were obtained from E-Merck and were used as received.

2.3. Instrumentation and procedure

2.3.1. Steady-state spectral measurements

The absorption and emission measurements were performed on a Hitachi UV-Vis U-3501 spectrophotometer and Perkin-Elmer LS-55 fluorimeter, respectively. All the collected spectra were with appropriate background correction. Only freshly prepared solutions were used for spectroscopic study and all experiments were carried out at room temperature (300 K).

Fluorescence quantum yield (Φ_f) was determined using the following equation where β-naphthol (Φ_R = 0.23) in MCH is used as the secondary standard.

$$\Phi_S = \Phi_R \cdot \frac{A_S \cdot OD_R \cdot n_S^2}{A_R \cdot OD_S \cdot n_R^2} \quad (1)$$

Where, Φ_S and Φ_R are the quantum yields, A_S and A_R are the integrated fluorescence areas, OD_S and OD_R are the absorbance values and n_S and n_R are the refractive indices of sample and reference molecule, respectively.

2.3.2. Time-resolved fluorescence decay

Fluorescence lifetimes were obtained by the method of Time Correlated Single-Photon counting (TCSPC) on FluoroCube-01-NL spectrometer (Horiba Jobin Yovon) using light source of nano LED at 336 nm, 291 nm and laser source at 450 nm. The signals were collected at the magic angle of 54.7^o to eliminate any considerable contribution from fluorescence anisotropy decay. The decays were deconvoluted using DAS-6 decay analysis software and the acceptability of the fits was judged by χ^2 criteria and visual inspection of the residuals of the fitted function to the data. The time-resolved fluorescence decay ($I(t)$) is described by the following expression:

$$I(t) = \sum_i \alpha_i \tau_i \quad (2)$$

and the mean (average) fluorescence lifetimes are calculated using the following equation [38]:

$$\langle \tau_{i0} \rangle = \frac{\sum_i \alpha_i \tau_i^2}{\sum_i \alpha_i \tau_i} \quad (3)$$

in which α_i is the pre-exponential factor corresponding to the ith decay time constant, τ_i.

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