



Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Slow proton transfer dynamics of a four member intramolecular hydrogen bonded isoindole fused imidazole system: A spectroscopic approach to photophysical properties



Debarati Ray, Animesh Pramanik, Nikhil Guchhait*

Department of Chemistry, University of Calcutta, 92 A. P. C. Road, Calcutta 700009, India

ARTICLE INFO

Article history:

Received 20 September 2014

Received in revised form 24 November 2014

Accepted 16 December 2014

Available online 17 December 2014

Keywords:

1-(2-Hydroxy-5-chloro-phenyl)-3,5-dioxo-1H-imidazo-[3,4-b] isoindol

Irreversible ESIPT

Dynamics

Emission spectroscopy

ABSTRACT

Spectral studies of 1-(2-hydroxy-5-chloro-phenyl)-3,5-dioxo-1H-imidazo-[3,4-b] isoindol (ADCL) in various solvents reveal the occurrence of excited state intramolecular proton transfer (ESIPT) process. Excitation at the shorter wavelengths preferentially leads to dual emission from an equilibrium mixture of excited state normal (N^* , lactim form) and tautomeric (T^* , lactam form) form due to the operation of proton transfer process. The proton transfer dynamics is found to be very slow in various organic solvents and it occurs in the nano-second time scale. This may be due to high energy barrier along the proton transfer coordinate through a strained four member hydrogen bonded network compared to the usual six member hydrogen bonded ring.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Tautomerism by transfer of a proton or a hydrogen atom from donor (OH, –NH) to the acceptor (C=O, –N=) group has been referred to as the most general and important reaction in chemistry and biology [1,2]. Since the first ever report of dual emission in salicylic acid due to operation of excited-state intramolecular proton transfer (ESIPT) reaction by Weller in 1950s, this phenomenon has been the focus of attention to a large number of experimental and theoretical groups till date. In some important biological processes such as DNA mutation and repair [3], photosynthesis [4], and respiration [5] etc. tautomerism by proton transfer process plays a very crucial role. In the nucleic acids and nucleotides the tautomerism of DNA base pairs purine and pyrimidine occurs naturally which is the actual reason behind the mutagenesis process. Because of the similarity to the DNA bases, 2-pyridone has drawn considerable interest to the chemists to study lactam–lactim tautomerization process. 2-Hydroxypyridine exhibits two stable tautomeric forms: the enol form (2HP, lactim form) and the keto form (2PY, lactam form). The keto – enol or lactim – lactam tautomerization process between 2HP and 2PY has been extensively studied experimentally in various phases, in matrixes, and also theoretically as one of the simplest systems of

intramolecular and intermolecular proton-transfer reactions. To characterize the tautomeric equilibria, researchers have used several techniques such as X-ray crystallography [6], UV–vis absorption [7], circular dichroism [8], NMR [9], Raman [10], and IR absorption spectroscopy [11] to get an in-depth understanding of the process involved.

Most of the ESIPT molecules possess six-member intramolecular hydrogen bonding (HB) unit between O–H (or N–H) and C=O (or pyridyl nitrogen) groups which leads to essentially barrierless or rather small barrier for the conversion from reactant to the product (the proton-transfer tautomer) [12–14]. As a result, ESIPT may take place during the period of low frequency vibrational motions associated with the hydrogen bond. In general, ESIPT reactions are believed to occur in the femtosecond time scale [15–18], however, in some cases slower ESIPT has been reported [19]. It is well known that under similar strength of proton donor/acceptor moieties, the strength of intramolecular hydrogen bonding follows the following order six member ring > five member ring > four member ring due to the combined effects of steric and orientation of hydrogen bond donor or acceptor groups. Therefore the ESIPT dynamics of four member intramolecular hydrogen bonding unit is expected to be much slower than the six or five member ring due to the very high energy barrier.

In our previous report we have shown ground and excited state proton transfer process through a four member intramolecular hydrogen bonding system, namely 1-(2-hydroxy-5methyl-phenyl)-3,5-dioxo-1H-imidazo-[3,4-b] isoindol (ADII) in various

* Corresponding author. Tel.: +91 33 2350 8386; fax: +91 33 2351 9755.
E-mail address: nguchhait@yahoo.com (N. Guchhait).

organic solvents [20]. Our present work demonstrates the photo-physical characterization of a system, very much similar to the ADII molecule, namely 1-(2-hydroxy-5-chloro-phenyl)-3,5-dioxo-1*H*-imidazo-[3,4-*b*] isoindol (ADCL, Scheme 1) in various organic solvents with main focus is to cast light on the dynamics of the ES IPT process. To our knowledge the observed slow excited state photo-tautomerization for this system was not noticed earlier.

2. Experimental

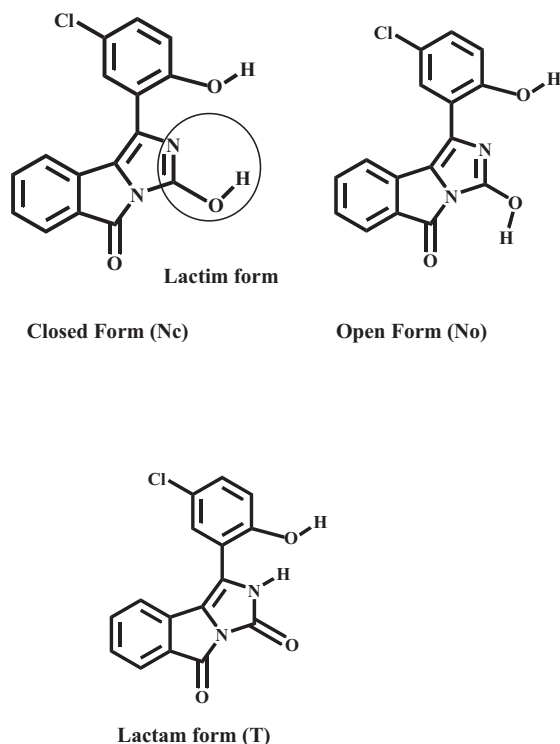
2.1. Materials

The title compound 1-(2-hydroxy-5-chloro-phenyl)-3,5-dioxo-1*H*-imidazo-[3,4-*b*] isoindole (ADCL) was synthesized as was reported recently in the literature [21]. Various spectroscopic grade solvents such as acetonitrile (ACN), dioxane (DOX), methanol (MeOH), chloroform (CHCl₃) 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 aqueous solutions. Trifluoroacetic acid (TFA) and triethyl amine (TEA) from Spectrochem were used as supplied. Sulfuric acid (H₂SO₄) and sodium hydroxide (NaOH) were obtained from E-Merck and were used as received.

2.2. Instrumentation and procedure

2.2.1. Steady-state spectral measurements

The absorption and emission spectral measurements were carried out using a Hitachi UV-vis U-3501 spectrophotometer and PerkinElmer LS-55 fluorimeter, respectively. All the collected spectra (absorption and emission) 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). In all measurement the sample concentration has been maintained within the range of 0.5–2 μM.



Scheme 1. Schematic presentation of ADCL molecule (both lactim and lactam form).

Fluorescence quantum yield (Φ_f) was determined using the following equation where β -naphthol in MCH ($\Phi_R = 0.23$) [20] and Coumarin 153 in cyclohexane ($\Phi_R = 0.9$) [22] were used as the secondary standard.

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

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.

2.2.2. 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 Yvon) using light source of nano LED at 340 nm and laser source at 450 nm. The signals were collected at the magic angle of 54.7°. The decays were deconvoluted using DAS-6 decay analysis software and the acceptability of the fits was judged by χ^2 criteria. The time-resolved fluorescence decay ($I(t)$) is described by the following expression:

$$I(t) = \sum_i \alpha_i \exp\left(\frac{-t}{\tau_i}\right) \quad (2)$$

where τ_i is the characteristic decay time constant of the *i*th component with relative amplitude of α_i .

3. Results and discussions

3.1. Absorption study

Fig. 1 shows the absorption spectra of ADCL in various solvents at room temperature (300 K). The absorption spectra of the studied compound ADCL are composed of two bands at ~315 nm and ~400 nm. By comparing these absorption bands with the previously studied similar compound ADII [20] or parent compound 2HP [23] we can assign these two bands to the lactim and lactam form, respectively, of the compound. From the previous studies it is noticed that for both ADII and 2HP system, the lactim absorption band (at room temperature 300 K) is found to be predominant over the lactam form. Interestingly in the present case of ADCL molecule, broad lactam absorption band is found to be dominated over the lactim form.

3.2. Fluorescence study

The steady state fluorescence spectra of ADCL were recorded in different nonpolar, polar protic and aprotic solvents by exciting at the respective absorption maxima of the lactim and lactam form and are

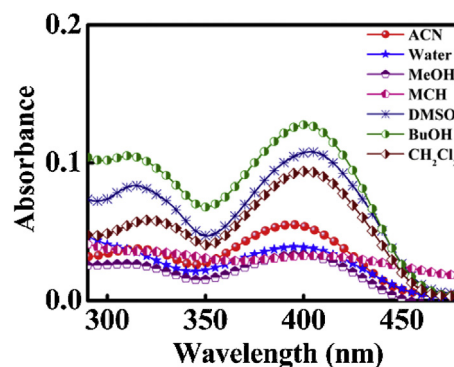


Fig. 1. Absorption spectra of ADCL in different solvents at room temperature.

Download English Version:

<https://daneshyari.com/en/article/25860>

Download Persian Version:

<https://daneshyari.com/article/25860>

[Daneshyari.com](https://daneshyari.com)