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Intermolecular Interaction in 2-Aminopyridine: A Density Functional Study

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Abstract: The absorption and fluorescence property of 2-amino pyridine (2-AP) and its dimer $(2AP)_2$ have been investigated using dispersion corrected density functional theory (DFT-D) method using B3LYP-D functional along with triple-ζ TZ2P basis in ADF suite of program. For the equilibrium geometries of the dimer, the ETS-NOCV calculations are performed. The formation of H-bond has been confirmed by the calculation of synergy (ΔE_{syn}) as well as from the spectral shift. A close agreement of the calculated spectra with that of experimental results has been found suggesting the dimers to be the preferable states of 2-AP in water medium.

AMS subject classifications: 74E40, 78M50

Key words: Density functional theory, 2-amino pyridine, absorption, fluorescence, H-bond

The excited state relaxation is of paramount importance in the photochemical process. Recently it has been noticed that the excited state relaxation can be induced through intermolecular Hydrogen bonding [1-4]. Photo induced proton-coupled electron transfers, where the proton donor and acceptor are held together by hydrogen bond (H-bond), have attracted considerable interest in recent years [5]. A number of studies by Han and co-workers [6-12] have shown that the gradual strengthening of the H-bond brings about the stabilization of the electronically excited state. H-bonded systems are ubiquitous within the

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biological macromolecules and hence the H-bond induced relaxation of excited state is deemed to be important in biological systems as well (13-15, 16). Pyridine and its derivatives are currently finding immense interest in the scientific community due to their luminescence property. Some of amino pyridine derivatives show anaesthetic properties and are used as drugs for certain brain disease [17-19]. 2-amino pyridine (2-AP) is used in the preparation of cytidine which is used as drug [20]. In spite of this biomedical application the photochemistry of this molecule has not been thoroughly investigated.

In this study we report a systematic density functional investigation of the absorption and fluorescence property of 2-amino pyridine (2-AP) and its dimer $(2AP)_2$. As the dimerization of 2-AP occurs through hydrogen bonding (H-bonding), is becomes essential to unveil the effect of intermolecular H-bonding interactions in the photochemical behaviour of 2-AP. It has been reported earlier that H-bonding plays a pivotal role in the photochemical description of a molecule. Moreover, the simple electronic structure of this compound offers simplicity and encourages studying the effect of H-bonding interaction in the photochemistry of this compound as a benchmark.

For the computation of weak interactions like H-bond, the correlated ab initio techniques such as second-order Møller-Plesset perturbation theory (MP2) are in wide use [21]. In recent years *ab initio* and density functional theory (DFT) based methods have become popular tool in the investigations of structure and electronic properties of molecules. DFT offers a cost effective way for the quantum chemical investigation of the molecular properties and has been proved to be efficient in producing accurate results [22]. Although the density functional methods, like the popular B3LYP functional, are reported to be incompetent for the accurate description of H-bonding [23], the inclusion of correction due to dispersion interactions in the scenario has been proved to be effective. In the present work, we opted for the dispersion corrected DFT (DFT-D) method for the computation of absorption and fluorescence spectra. All the DFT and time dependent DFT (TDDFT) calculations are performed using ADF suit of program [24]. The B3LYP functional has been used, augmented with dispersion correction developed by Grimme (B3LYP-D) [25], along with triple-ζ TZ2P basis. The solvent effects have been estimated using the conductor-like screening model (COSMO) implemented in ADF [26].

Structures of the monomer and the dimer are optimized at the B3LYP-D/TZ2P level. The optimized ground state structures of the monomer and the dimer are represented in Figures 1 and 2. The dimer is found to prefer a non-planar geometry at ground and excited states (Figure 2).