

CHAPTER 6

Photochemical study of 2-aminopyridine: A density functional investigation

Abstract

The sixth chapter provides a comprehensive study of molecular mechanism of excited state relaxation induced by intermolecular hydrogen-bond formation. The absorption and fluorescence property of 2-amino pyridine (2-AP) and its dimer (2AP)₂ are analyzed theoretically in order to unveil the effect of intermolecular H-bonding interaction in the photochemical behavior of 2-AP. All the calculations (DFT and TDDFT) are performed using ADF suit of program with dispersion corrected methods (DFT-D). To reveal the cooperativity due to H-bonding, a decomposition analysis (EDA) in the framework of the Kohn-Sham molecular orbital (MO) model is performed. The ETS-NOCV calculations are performed for the equilibrium geometries of the ground and excited states of the dimer. The formation of H-bond has been confirmed by the calculation of synergy (ΔE_{syn}) from the difference of interaction energy (ΔE_{int}) with and without H-bond interactions. H-bond interaction stabilizes the electronic excited state of the dimer resulting red-shift in the emission spectrum.

The molecular mechanism of the excited state relaxation induced by intermolecular hydrogen-bond formation is of great interest because it belongs to the most fundamental processes of photochemistry. The process of fluorescence quenching, occurring as a result of intermolecular hydrogen bonding, is a well-known phenomenon.²⁷²⁻²⁷⁵ Photo induced proton-coupled electron transfers, wherein the proton donor and acceptor are assembled by hydrogen bond interaction, have attracted considerable interest in recent years.²⁷⁶ Numerous studies by Mataga and co-workers^{277, 278} have been devoted to the case when both the proton donor and acceptor atoms belong to π -electronic systems. Moreover, excited state hydrogen bond interactions have also earned potential interest due to its connection with reversible or irreversible proton displacements or H-atom transfer reactions.^{278, 279} These reactions play a vital role in a wide range of chemical and biological processes.

Pyridine and its derivatives are currently finding immense interest in the scientific community due to their wide variety of application in various fields. They find use in the chemical industry as reagent and also play a central role in the structure and properties of nucleic acid.²⁸⁰ Some of amino pyridine derivatives show anaesthetic properties and are used as drugs for certain brain disease. 2-amino pyridine (2-AP) is used in the preparation of cytidine which is used as drug. In spite of this biomedical application, the photochemistry of this molecule has not been thoroughly investigated. In recent years *ab initio* and density functional theory (DFT) based methods have become a popular tool in the investigations of molecular structure and electronic properties. 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.²⁸¹

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 (2-AP)₂. As the dimerization of 2-AP occurs through hydrogen-bonding (H-bonding), it 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.^{282, 283} Although the density functional methods, like the popular B3LYP functional, are reported to be

incompetent for the accurate description of H-bonding,²⁸³ 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. All the DFT and time dependent DFT (TDDFT) calculations are performed using ADF suit of program. The B3LYP functional has been used, augmented with dispersion correction developed by Grimme (B3LYP-D), along with triple- ζ TZ2P basis. The solvent effects have been estimated using the conductor-like screening model (COSMO) implemented in ADF.

Structures of the monomer and the dimer are fully 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).

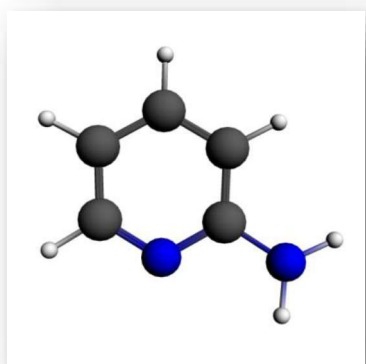


Figure 6.1. B3LYP-D/TZ2P optimized geometry of 2-aminopyridine at its ground state.

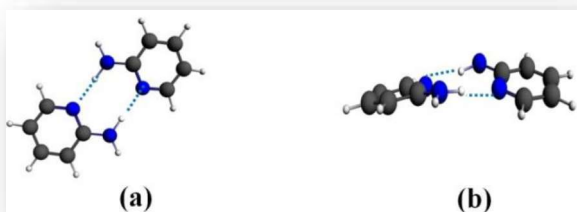


Figure 6.2. The H-bonded dimer (a) front view and (b) side view.

To reveal the cooperativity due to H-bonding, an energy decomposition analysis (EDA) in the framework of the Kohn-Sham molecular orbital (MO) model is performed. In this approach, the interaction energy (ΔE_{int}) is partitioned into electrostatic interaction (ΔV_{elstat}), Pauli repulsive orbital interaction (ΔE_{pauli}), attractive orbital interaction (ΔE_{oi}) and dispersion interactions (ΔE_{disp}) as shown in the following,

$$\Delta E_{\text{int}} = \Delta V_{\text{elstat}} + \Delta E_{\text{pauli}} + \Delta E_{\text{oi}} + \Delta E_{\text{disp}} \quad (6.1)$$

This method combines the extended transition state (ETS) energy decomposition approach²⁸⁴ with the natural orbitals for chemical valence (NOCV) density analysis method.²⁸⁵ The ETS-NOCV calculations are performed for the equilibrium geometries of the ground and excited states of the dimer. The formation of H-bond has been confirmed by the calculation of synergy (ΔE_{syn}) from the difference of interaction energy (ΔE_{int}) with and without H-bond interactions.

$$\Delta E_{\text{syn}} = \Delta E_{\text{int-eq}} - \Delta E_{\text{int-noneq}} \quad (6.2)$$

Here, $\Delta E_{\text{int-eq}}$ corresponds to the interaction energy of the dimer in its equilibrium geometry. Next, the equilibrium geometry is distorted by moving the monomer units far from each other, so that no H-bond formation is possible, and the interaction energy ($\Delta E_{\text{int-noneq}}$) is estimated. A negative value of synergy indicates stabilization through the formation of H-bonding. ΔE_{int} is the energy change in systems due to formation of the association from individual units. This is interpreted as the amount of energy required to promote the separated fragments to form the dimeric structure. The synergy due to H-bonding is estimated through Equation 2 and the results are given in Table 6.1.

Table 6.1. Bonding energy decomposition of ground and excited states of the dimer.

Dimer	ΔV_{elstat} (kcal/mol)	ΔE_{pauli} (kcal/mol)	ΔE_{oi} (kcal/mol)	ΔE_{disp} (kcal/mol)	ΔE_{int} (kcal/mol)	ΔE_{syn} (kcal/mol)
Distorted Geometry	-0.30	-0.12	-0.03	-0.07	-0.52	--
Excited State	-25.93	29.92	-14.64	-4.30	-14.94	-14.42
Ground State	-26.24	30.31	-14.85	-4.26	-15.05	-14.53

From Table 6.1, it is clear that the hydrogen-bond formation is possible at both the ground and excited states. From the comparison of ΔE_{syn} values in Table 6.1, one can infer a greater stabilization of the H-bonded dimer at its ground state than the corresponding excited

state. However, from the components of ΔE_{int} it is observed that the dispersion energy change, which corresponds to the H-bonding interaction, is greater in the excited state than the ground state. Hence, it can be concluded that the H-bonding interaction is more pronounced at the excited state.

The absorption and fluorescence spectra are shown in Figures 6.3 and 6.4. It becomes prominent from the figures that there occurs a red-shift of the absorption and fluorescence peaks in the dimeric state compared to the monomer (Table 6.2). This red-shift can be attributed to the lowering in the HOMO-LUMO gap (ΔE_{HL}) due to H-bond formation. Table 6.3 accumulates the HOMOs and the LUMOs of the species in its different states and a lowering of the ΔE_{HL} is clearly visible. From the previous studies on H-bonded systems it becomes evident that polarization effects promote H-bonding interaction. It has also been seen that there occurs a mixing of the empty/occupied orbital on one fragment in the presence of another fragment due to polarization effect. From the nature of the HOMO and LUMO orbitals in Table 6.3, the mixing of two fragments is critically exposed. Hence, the diminished HOMO-LUMO gap can be explained as an outcome of the H-bonding interaction.

The red-shift in the fluorescence spectra can be explained from the stabilization of the S_1 electronic state of the dimer due to the formation of the H-bonding. The quenching of the energy gap for the $S_0 \leftarrow S_1$ leads to a red shift of the fluorescence λ_{max} value.

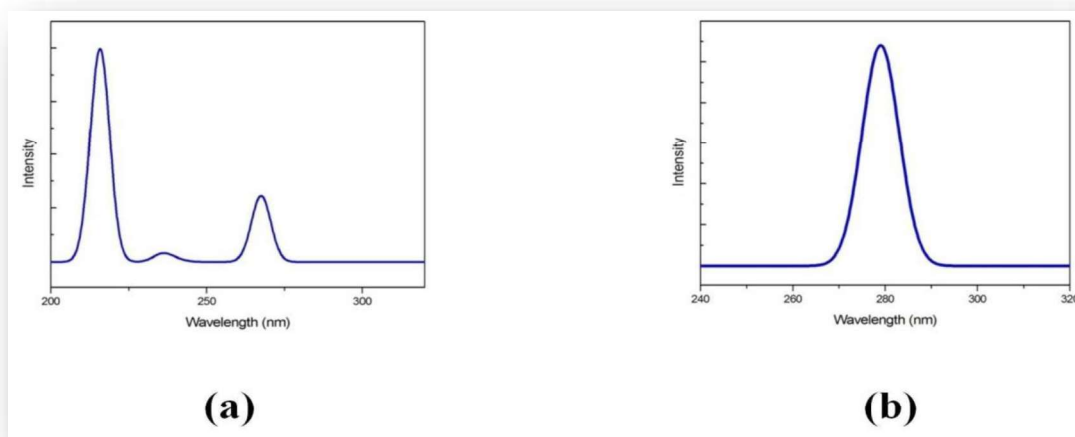


Figure 6.3. Absorption Spectra of (a) monomer unit and (b) hydrogen bonded dimer.

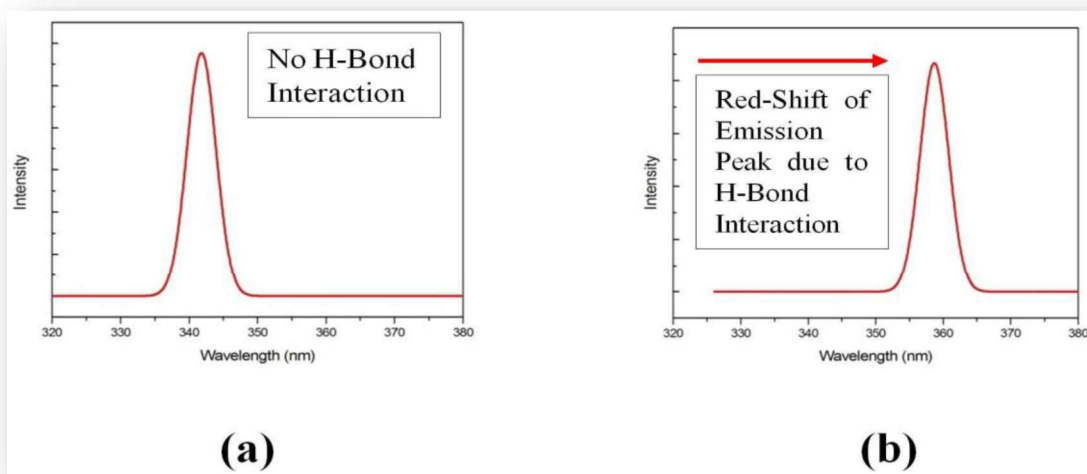


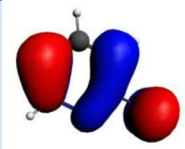
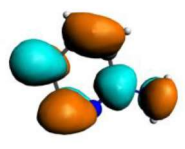
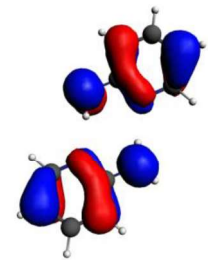
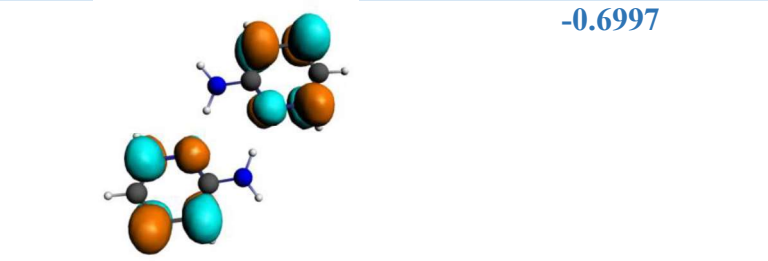
Figure 6.4. Fluorescence Spectra of (a) monomer unit and (b) hydrogen bonded dimer.

Table 6.2. Comparison of the calculated value λ_{max} of absorption and fluorescence with experimentally reported values.

System	λ_{max} of absorption in nm		λ_{max} of fluorescence in nm	
	Calculated	Experimental	Calculated	Experimental
2-AMP monomer	216	292 ^(a)	342	363 ^(a)
2-AMP Dimer	279		359	

^(a) Experimentally reported λ_{max} of absorption and fluorescence in water medium.²⁸⁶

Table 6.3. HOMO-LUMO gap of monomer unit and hydrogen bonded dimer.

System	Orbitals	Energy in eV	ΔE_{HL} in eV
2-AMP monomer		-5.8743	6.0044
		0.1257	
2-AMP dimer		-5.6443	4.9446
		-0.6997	

The calculated values of λ_{max} of both the absorption and fluorescence spectra of the 2-AP monomer and dimer are given in Table 6.2. The close agreement of the calculated values with the experimental results suggests that dimers are the most preferable states of 2-AP in water solution. This can also be inferred from the Table 6.1 as the high negative synergy of the dimer in both the ground and excited states indicates the formation of H-bonding. The formation or the change in the strength, of the intermolecular hydrogen bonds following excitation may simply lead to new vibronic dissipative modes that couple excited and ground states.^{274, 287, 288}