

## ESIPT of 1-[N-(2-pyridyl) aminomethylidene]-2(1H)-Naphthalenone: A TDDFT study

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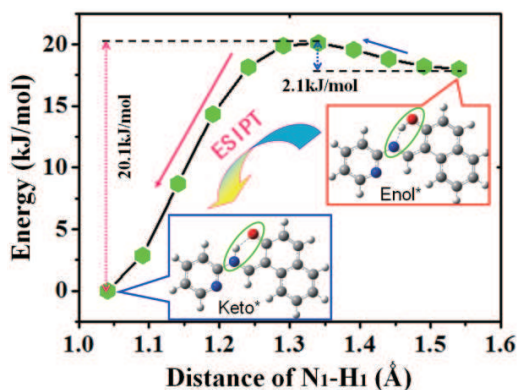
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**Abstract.** In the present work, the excited state intramolecular proton transfer (ESIPT) process between the Enol and Keto forms of the title compound has been investigated with the time-dependent density functional theory (TDDFT) method. The geometric structures, frontier molecular orbitals, electrostatic potential (ESP) maps as well as the absorption and fluorescence spectra of the two forms of the title compound have been investigated. The calculated absorption spectra of the Keto form are more in agreement with the experimental results. Moreover, the potential energy curves of the intramolecular proton transfer (IPT) within the title compound have been scanned in both ground state  $S_0$  and the first excited state  $S_1$ . We found that the intramolecular proton transfer from Enol form to Keto form in excited state is almost barrierless with an energy barrier 2.1 kJ/mol whereas intramolecular proton transfer between the two forms of the title compound in ground state is forbidden with energy barrier as high as 10.5 kJ/mol.



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**Key words:** Intramolecular hydrogen bonding; ESIPT; Frontier molecular orbitals; Electronic spectra; Potential energy curves.

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## 1 Introduction

As one of the most important weak interactions, hydrogen bonding plays important roles in organometallic molecules, crystal packing of many organic, nucleic acids, stabilization of the secondary structure of biomolecules like proteins, and so forth [1-4]. Its significance is conspicuous in various real life examples and a thorough investigations of hydrogen bonding interactions will be vital to delve into the critical evaluation of many phenomenon coming up not only in the crystal state, but also in solutions and living organisms [5-6]. Zhao and Han have determined that intermolecular hydrogen bonding between solute and solvent molecules should be significantly strengthened in the corresponding electronic excited states after photo-excitation theoretically [7-12], since which many investigations of mechanism involved in excited state hydrogen bonding need to be revisited in physics, chemistry and biology. Up to now, many different sensing mechanisms, such as intramolecular charge transfer (ICT), photo-induced electron transfer (PET), fluorescence resonance energy transfer (FRET), and excited state proton transfer (ESPT) and so forth [13-21], are relevant with hydrogen bonding. Particularly, the excited state inter- and intra- molecular proton transfer (ESIPT) reactions have been drawing great attention due to their unique photo-physical and photo-chemical properties. Many novel optoelectronic applications, such as molecular switches, fluorescence sensors, UV filters, laser dyes and LEDs and so forth [22-29], are facilitated based on ESIPT reactions. Naturally, the attention focused on this phenomenon is both cognitive and applied, through which it crops up as a demanding subject of research even today.

1-[N-(2-pyridyl) aminomethylidene]-2(1H)-Naphtalenone, as one of the Schiff base compounds, displays interesting photochromic and thermochromic features [30-40]. Photochromism arise via H-atom transfer from the hydroxy O atom to the imine N atom [30, 31]. Such proton-exchanging materials can be utilized for the design of various molecular electronic devices [32-34]. In general, 2-hydroxy Schiff bases display two possible tautomeric forms, the enol-imine (OH) and the keto-amine (NH) forms. Depending on the tautomers, two types of intramolecular hydrogen bonds are observed in Schiff bases: O-H $\cdots$ N in enol-imine and N-H $\cdots$ O in keto-amine tautomers [34-38], as shown in Scheme 1. In previous publication, IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, UV-vis and the crystal structure of the title compound had been studied [39]. Also some physicochemical properties of the title compound had been investigated using the DFT method [40]. However, to the best of our knowledge, geometric optimizations of the excited-state structures as well as theoretical calculations of the emission spectra of the title compound have not been carried out yet.