

REGULAR ARTICLE

A DFT/TDDFT Investigation of Excited-State Intramolecular Proton Transfer Mechanism of New Chromophore

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Abstract: Based on the time-dependent density functional theory (TDDFT), the excited state intramolecular proton transfer (ESIPT) mechanism of a new compound **3** chromophore synthesized and designed by Mukherjee *et al.* [Sensors and Actuators B: Chemical, 202 (2014), 1190-1199] has been investigated theoretically. The calculations of primary bond lengths, angles, the IR vibrational spectra and hydrogen bond energies between the S_0 state and the S_1 state verified the intramolecular hydrogen bond was strengthened. The fact that reproduced the experimental absorbance and fluorescence emission spectra well theoretically demonstrates that the TDDFT theory we adopted is reasonable and effective. In addition, intramolecular charge transfer based on the frontier molecular orbitals demonstrated the indication of the ESIPT reaction. The constructed potential energy curves of ground state and the first excited state based on keeping the O-H distance fixed at a series of values have been used to illustrate the ESIPT process. A little barrier of 3.934 kcal/mol in the S_1 state potential energy curve (lower than that of 8.254 kcal/mol in the S_0 state) provided the transfer mechanism.

AMS subject classifications: 78M50, 74E40, 65D18

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1. Introduction

The hydrogen bond, as one of the most significant weak interactions, is omnipresent in nature, based on which life-cycle can be sustained in the world [1-5]. It plays important roles in crystal packing of many organic and organometallic molecules, stabilization of the secondary structure of biomolecules like proteins, nucleic acids and so forth [1-5]. In addition, a dual effect has been found in biological systems: on one hand, in the form of a collectively strong directional interaction it leads to stable supramolecular architectures which are inevitable for the construction of fundamental building blocks of life, and on the other hand, by virtue of its dynamic features, it serves as an active site for the occurrence of a vista of interactions [6]. Therefore, a thorough investigation of the interaction will be vital to delve into the critical evaluation of many phenomenon taking place not only in the crystal state, but also in solutions and living organisms [7-9]. Particularly, Han and co-workers have determined that intermolecular hydrogen bonds between solute and solvent molecules should be significantly strengthened in the electronic excited states after photo-excitation theoretically [10-18], since then, many investigations of mechanism respecting excited state hydrogen bonding need to be revisited in physics, chemistry and biology. Proton transfer (PT), as one fundamental class of photochemistry, has attracted more and more attentions along hydrogen bonding in recent years [15-33]. Especially, the excited state intramolecular proton transfer (ESIPT) reactions have been drawing great attention due to their unique photophysical and photochemical properties which facilitate novel optoelectronic applications such as fluorescence sensors, laser dyes and LEDs, UV filters, molecular switches and so forth [34-46]. 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.

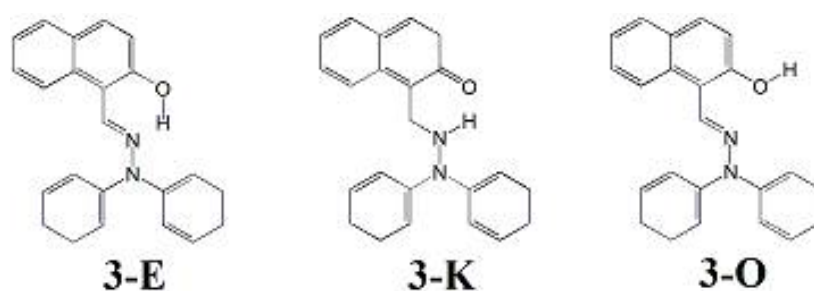


Figure 1: The structures of 3-E, 3-K and 3-O at B3LYP/ TZVP theoretical level.