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REGULAR ARTICLE

A DFT/TDDFT investigation on the ESIPT mechanism of a novel sensor BIP

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Abstract: In the present work, (E)-2-(((1H-benzo[d]imidazol-2-yl)-imino)methyl)-5-(dimethylamino)-phenol (BIP), as one kind of the novel and few studied sensors containing both NH and OH binding sites, has been selected to investigate the excited state dynamic properties based on the time-dependent density functional theory (TDDFT) method. Our calculated absorption and fluorescence spectra based on the TDDFT method are in agreement with the experimental results. Two kinds of structures of BIP chromophore (BIP-enol and BIP-keto) are found in the first excited (S_1) state, which should be resulted from the excited state proton transfer reaction. The phenomenon of hydrogen-bond strengthening has been found in the S_1 state, which was based on comparing staple bond lengths and bond angles involved in hydrogen bond between the S_0 state and the S_1 state. In addition, the calculated infrared spectra at the O-H stretching vibrational region and calculated hydrogen bond energy also declare the phenomenon of hydrogen bond strengthening. The frontier molecular orbitals (MOs) analysis and Natural bond orbital (NBO) manifest the intramolecular charge transfer of BIP chromophore, which reveals the tendency of proton transfer. The potential energy surfaces of the S_0 and S_1 states are constructed to explain the mechanism of the proton transfer in excited state in detail.

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

Keywords: Hydrogen bond; ESIPT; Frontier molecular orbitals; Electronic spectra; Potential

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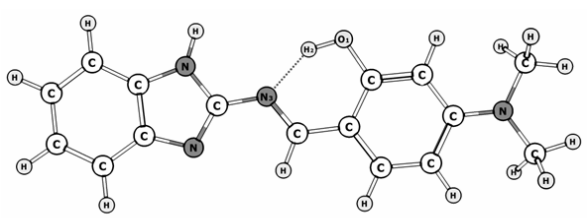
energy curves.

1. Introduction

As one of the most important weak interactions, hydrogen bond (no matter whether it is inter- or intra- molecular hydrogen bond) is omnipresent in nature, based on which life-cycle can be sustained in the world [1-5]. Hydrogen bond 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 [1-5]. Peculiarly, in biological systems, the dual effect has been found: on one hand, hydrogen bond can be used to establish supramolecular architectures in the form of a conjointly strong directional interaction, which are unescapable for the construction of fundamental building blocks of life [6]. On the other hand, it acts as an active site for the occurrence of a vista of interactions based on its dynamic features [6]. Its significance is conspicuous in various real life examples and a thorough investigation of hydrogen bond 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 [7-9]. Zhao and Han have determined that intermolecular hydrogen bond between solute and solvent molecules should be significantly strengthened in the corresponding electronic excited states after photo-excitation theoretically [10-18], since then, many investigations of mechanism involved in exited state hydrogen bond need to be revisited in physics, chemistry and biology.



BIP-enol

BIP-keto

Figure 1: Views of optimized structures for BIP-enol and BIP-keto based on B3LYP/TZVP theoretical level. (BIP-enol: normal BIP structure; BIP-keto: proton transfer BIP structure).