

REGULAR ARTICLE

A DFT/TDDFT Investigation on Intramolecular Proton Transfer of Bis(imino)isoindole

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Abstract: The density functional theory (DFT) and time-dependent density functional theory (TDDFT) method were carried out to investigate intramolecular hydrogen bond and intramolecular proton transfer of Bis(imino)isoindole in the ground- and excited-state. From the analysis of IR spectra, electronic spectra and the corresponding frontier molecular orbitals, we found that the intramolecular hydrogen bond I is strengthened while the intramolecular hydrogen bond II is weakened in BII molecule in the S1 state. The potential energy curve shows that the proton cannot spontaneously transferred in the ground state because of the relative high potential energy barrier. After photo-excitation, the strengthening of intramolecular hydrogen bond I may lower the potential energy barrier and then promote the proton transfer.

AMS subject classifications: 74E40, 78M50

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1 Introduction

The photo-induced excited-state proton transfer (ESPT) has been extensively studied due to its important role in physical and biological systems. Weller and co-workers [1] firstly observed the excited-state proton transfer phenomenon of methyl salicylate in the characteristic experiment. Taylor and co-workers [2] found that the 7-azaindole dimer has different tautomer in ground and first excited states. Sengupta et al. [3] were used proton

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transfer theory to explained the dual fluorescence in 3-hydroxyflavone. Chou and co-workers [4] described a functioning photo-induced proton transfer of 3-hydroxyflavone in the excited-state occurs in less than 8ps. The hydrogen bond is found to be very important in excited-state proton transfer process [5-9] for its good directional character. Recently, Han and co-workers have presented a new mechanism that the intermolecular hydrogen bond is significantly strengthened upon photo-excitation [10-14]. On the basis of the great success of hydrogen bond strengthened theory, many phenomena such as excited-state hydrogen bond dynamic and proton transfer (PT) reaction should be revisited.

The spectroscopic techniques can only give indirect information about the excited-state intramolecular proton transfer, so there are still some unsolved problem about the specific role of intra- and intermolecular hydrogen-bond interactions in the ESPT process. And the wide use and reliable accuracy of the density functional theory (DFT) and time-dependent density functional theory (TD-DFT) give us a new way to study the excited state proton transfer. In the present work, the Bis(imino)isoindole (BII) and its isomer are optimized in the ground and excited states using the DFT and TDDFT methods at B3LYP/6-31++g(d) level based on CPCM model in methanol. The configurations of the molecules are shown in the Figure1. The IR spectral shifts of O-H and N-H vibrational modes in the molecules are monitored to predict the changes of intramolecular hydrogen bond. Moreover, the electronic spectra, frontier molecular orbitals and potential energy curves are also calculated to investigate the intramolecular proton transfer mechanisms.

2 Computational details

All the computations were performed using the Gaussian09 program package[15] at the popular Becke's three-parameter hybrid exchange functional with Lee-Yang-Parr gradient-corrected correlation (B3LYP) [16] with the standard 6-31++G(d) level. The 6-31++G(d) basis set has sufficient flexibility to describe the system and chosen as the basis set throughout. The geometric optimizations were performed by DFT method in the S_0 state and TDDFT method in the S_1 state. The TD-DFT method has been proved to be very useful to describe the hydrogen bond system in the excited states. The methanol was selected as the solvent in the calculations and the continuum polarizable continuum model (CPCM) [17, 18] was chosen to evaluate solvent effects. These computations were performed on BII and its isomer without any constraint of bonds, angles, dihedral angles or symmetry. All the local minima geometries are confirmed by the absence of an imaginary mode in vibrational analysis and calculations.