COMMUNICATION

Excited-state Intramolecular Proton Transfer of HDI and HBF: Excited-state Hydrogen-bonding Dynamics and Electronic Structures

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Abstract: Employing Density Functional Theory (DFT) and Time-dependent Density Functional Theory (TDDFT) methods, the theoretical study on two ESIPT molecules, HDI and HHF, was performed. The optimized structures and infra spectra (IR) results show that, upon photoexcitation, the intramolecular hydrogen bond of HDI is weakened while that of HHF is strengthened. These results further imply that the strengthening of the intramolecular hydrogen bond is not the indispensable condition for the occurrence of ESIPT. Meanwhile, by the results of frontier molecular orbitals, the observed differences of the electron density redistribution between HDI and HHF in K* show us why HDI only shows the forward ESIPT while HHF undergoes the ESIPT equilibrium. Finally, the energy curves of HDI and HHF reveal the preferred forward ESIPT for HDI and the easily occurred backward ESIPT for HHF, further supporting the results of frontier molecular orbitals.

Excited-state Intramolecular Proton Transfer (ESIPT), a common phenomenon in nature, is

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of great significance in the fields of the biosensors, lighting materials, enzyme catalysis and so forth [1-4]. A large number of works employing both the theoretical and experimental methods have been performed to investigate its physical and chemical properties [5-10]. It is well known that most of the ESIPT reactions involve the proton transfer through the intramolecular hydrogen bond in the excited state, giving rise to a structural change from Enol form (E* form) to Keto form (K* form). Due to the dramatic structural alternation, the ESIPT molecule in K form usually possesses a totally diverse photochemical property with respect to the original species (E form). In this way, the ESIPT dyes usually present a large Stockes shift, which is considered as the remarkable merit of the ESIPT molecule [11-12].

Intramolecular hydrogen bond plays an important role in ESIPT process. The dynamics of the intramolecular hydrogen bond in the excited state is always regarded as the key of the ESIPT[13-17]. Considerable works have demonstrated that the strengthening of the intramolecular hydrogen bond can facilitate the occurrence of ESIPT [17]. However, whether the strengthening of the intramolecular hydrogen bond is the necessary condition for ESIPT is not yet completely confirmed. In recent years, Zhao and Han put forward for the first time that IR spectra can provide a clear-cut signature of excited-state hydrogen-bonding dynamics which can help us understand the relationship between the intramolecular hydrogen-bonding dynamics and ESIPT reaction [13-14]. In detail, hydrogen-bonding dynamics can be monitored by the blueshift or redshift of the vibrational frequencies of the stretching vibrations involved in the hydrogen bond. The strengthening of the hydrogen bond can induce the redshift of the vibrational frequencies of hydrogen-bond-involved stretching vibrations, while the weakening of the hydrogen bond gives rise to the blueshift.

These days, the field of luminescent materials, especially the white lighting materials, has witnessed a great improvement [18-21]. A lot of molecules have been designed and synthesized, aiming to produce the more advanced materials. As it well known that the white lighting material is unusual because the natural luminophore cannot give the emission covering a wide range of the visible spectra [18]. In this case, the researchers all over the world made a great effort to develop the ESIPT molecule as the white lighting materials. In 2010, Chou and co-workers synthesized three ESIPT dyes, that is, 7-hydroxy-2,3-dihydro-1H-inden-1-one (HDI shown in **Figure 1**), 1-hydroxy-9H-fluoren-9-one (HHF shown in **Figure 1**) and 1-hydroxy-11H-benzo[b]fluoren-11-one (HHBF), respectively[18,22]. HHF and HHBF are the chemical modification of HDI. According to Chou's experimental results, HDI undergoes an ultrafast rate of forward ESIPT, giving rise to a unique K* emission, whereas the excited-state equilibrium is established for both HHF and HHBF. Our previous theoretical works have shown the mechanism of the excited-state equilibrium for HHBF[23]. The electron density swing is demonstrated to be the basic reason for the excited-state

equilibrium for HHBF. However, the theoretical study on HDI and HHF is relatively limited. In this work, employing DFT and TDDFT methods, the intramolecular hydrogen-bonding dynamics, frontier molecular orbitals and the potential-energy curves of HDI and HHF were calculated and investigated.

All the geometry optimizations of HDI and HHF both in the ground and the excited state were carried out by means of density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods. The basis set 6-311+(2d,2p) and Becke's three-parameter hybrid exchange function with Lee-Yang-Parr gradient-corrected correlation functional (B3LYP) were used for all the calculations. Taking the solvent effect in to the consideration, the cyclohexane was chose as the solvent in SCRF calculation employing PCM. No constrains of symmetry, bonds, angles and dihedral angles were used in all the calculations. All the local minima were confirmed by the absence of the imaginary mode in the vibrational calculations. The potential-energy curves of HDI and HHF in the ground and excited states were qualitatively scanned by the constrained optimizations, by freezing the intramolecular hydrogen bond distance at a serious of values.
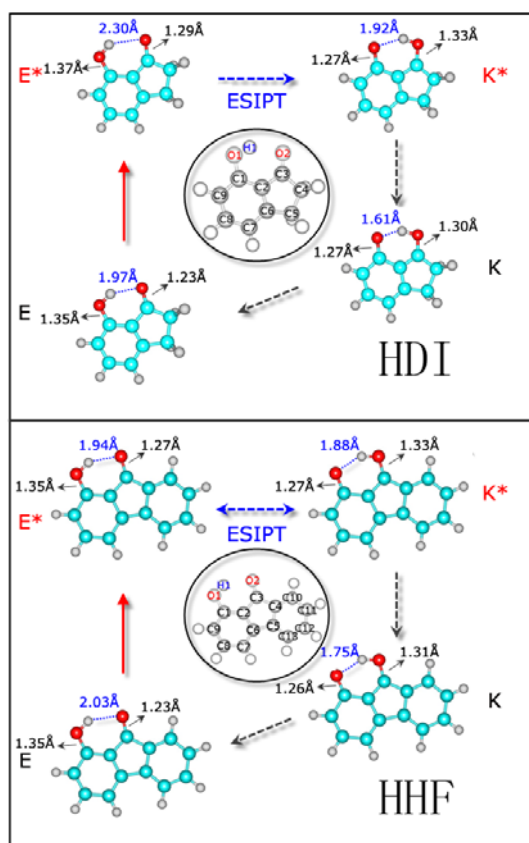

Figure 1: The fully optimized structures, atom numbers (in the circle) and

hydrogen-bond-related bond lengths of HDI and HHF in E, E*, K and K* state.

The fully optimized structures and the hydrogen-bond-related bond lengths of HDI and HHF in E, E*, K and K* state are shown in **Figure 1**. To begin with, in terms of HDI, the length of the hydrogen bond (H1…O2), upon the photoexcitation, shows an apparent increase from 1.97 Å to 2.30 Å, implying that the intramolecular hydrogen bond is weakened from E to E*. After ESIPT, the intramolecular hydrogen bond changes to 1.92 Å in K* state （O1⋯H1）. Then the emission from K* to K state gives rise to a strong intramolecular hydrogen bond （O1⋯H1）, whose length is only 1.61 Å. As for HHF, the length change of the intramolecular hydrogen bond exist an opposite tendency. From E to E*, the length of intramolecular hydrogen bond （H1⋯O2）decreases from 2.03 Å to 1.94 Å, demonstrating the strengthening of the intramolecular hydrogen bond. Then, in K* and K states, the lengths of intramolecular hydrogen bond （O1⋯H1） change to 1.88 Å and 1.75 Å, respectively. Moreover, it should be noticed that the other hydrgen-bond-related bond lengths do not show the prominent changes in different states.
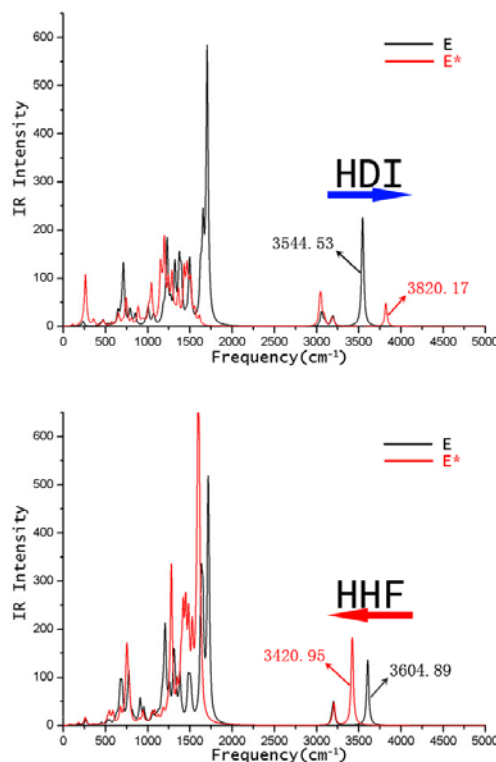

Figure 2: Calculated IR spectra of HDI and HHF in ground state (black) and first excited state (red).
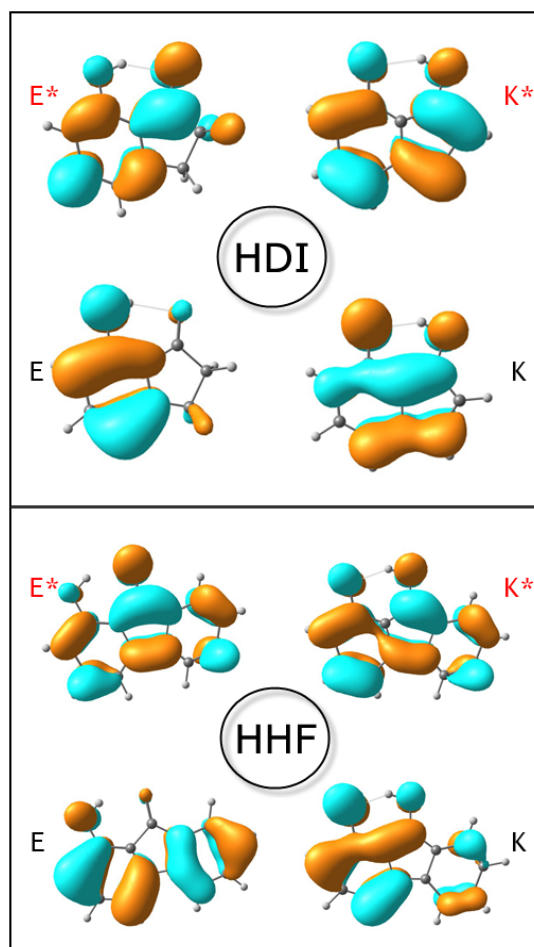
Figure 3: Frontier molecular orbitals of HDI and HHF in E (HOMO), E*(LUMO), K(HOMO)and K*(LUMO).

The excited-state dynamics of intramolecular hydrogen bond is of great importance for ESIPT reaction. The IR spectra of HDI and HHF in both E and E* were calculated to investigate the excited-state dynamics of intramolecular hydrogen bond. As is shown in **Figure 2**, for HDI, the vibrational frequency of the stretching vibration of O1-H1 appears at 3544.53cm-1 in the ground state (E). Upon the photoexcitation, this vibrational frequency moves to 3820.17cm-1. According to Zhao and Han's conclusion, from E to E*, the blueshift of the vibrational frequency of stretching vibration of O1-H1 clearly demonstrates the weakening of the intramolecular hydrogen bond for HDI. It should be noticed that, although the intramolecular hydrogen bond is weakened, HDI can also undergo an ultra-fast rate of forward ESIPT in the experiment. As a result, we can easily put forward the conclusion that the strengthening of the intramolecular hydrogen bond is not the necessary condition for ESIPT reaction. Then, as for HHF, the vibrational frequency of stretching vibration of O1-H1

shows the obvious distinctions with respect to HDI, which shifts from 3604.98cm-1 to 3420.95cm-1 by means of the photoexcitation. From E to E*, the redshift of vibrational frequency of stretching vibration of O1-H1 clearly indicates the strengthening of the intramolecular hydrogen bond.

The frontier molecular orbitals are capable to provide the insights into the nature of the electronic structures in the ground and excited state. In this work, the frontier molecular orbitals of HDI and HHF both in ground and excited state in two forms, E and K, were calculated and shown in **Figure 3**. From the TDDFT results, it is found that the first excited states of HDI and HHF for both E and K form are a dominant $\pi\pi^*$-type transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The results of frontier molecular orbitals simultaneously show that the processes of ESIPT reactions are all accompanied by the electron density transfer. As is well known that the diverse chemical groups in the conjugated system exhibit the different electronic properties, namely, the hydroxyl is the electron donating group and the carbonyl is the electron accepting group. As a consequence, for both HDI and HHF, the charge transfer from the O1 to O2 is observed upon the photoexcitation. For the proton, there exists the competitive relation between O1 and O2. So the charge transfer from O1 to O2, making the proton acceptor (O2) more basic and proton donor (O1) more acid, can be expected to provide the driving force for forward ESIPT (from E* to K*). After forward ESIPT, the electron density is redistributed again. Particularly, in terms of HDI from E* to K*, the electron density located on atom C2 disappears and that on atom O2 slightly decreases. Meanwhile, the electron density on C5 greatly increases while that on O1 only shows the slight rise, indicating the charge transfer from C2 and O2 to O1 and C5. This charge transfer obviously increases the electron density on proton accepter (O1), which, however, is not strong enough to trigger the backward ESIPT for HDI. On the contrary, for HHF, the direction of the charge transfer shows the differences, which is similar as HHBF[22], mainly from proton donor (O2) to accepter (O1). This electron density redistribution of HHF, driving the much more weaker proton attraction of the proton donor (O2) and the stronger proton attraction of proton accepter (O1), to a large extent, facilitates the occurrence of the backward ESIPT (from K* to E*).

The potential-energy curves of HDI and HHF as a function of the lengths of the intramolecular hydrogen bond (H1…O2) were fully scanned and shown in **Figure 4**, revealing the thermodynamic properties of two ESIPT molecules. To start with, for HDI in the first excited state, the potential energy of E* is 4.42kcal/mol higher than that of K*. And the forward ESIPT (from E* to K*) crosses an energy barrier of 1.80 kcal/mol while that for the backward ESIPT（from K* to E*）is 6.22 kcal/mol. As a result, for HDI, the forward ESIPT is obviously much more preferred. Additionally, in terms of HDI in ground state, the

potential energy of K is much higher than that of E, supporting the favored proton transfer from K to E. Then, in the case of HHF, the potential energy of E* is 5.83kcal/mol lower than that of K*. And the forward ESIPT needs to cross an energy barrier of 8.39 kcal/mol while that for backward ESIPT is only 2.56 kcal/mol. Consequently, the occurrence of backward ESIPT is much more easily for HHF compared to HDI. In the ground state of HHF, similar as HDI, the potential energy of K is also much higher than that of E. As a result, HHF will undergo the transfer from K to E with a high reaction rate in the ground state.
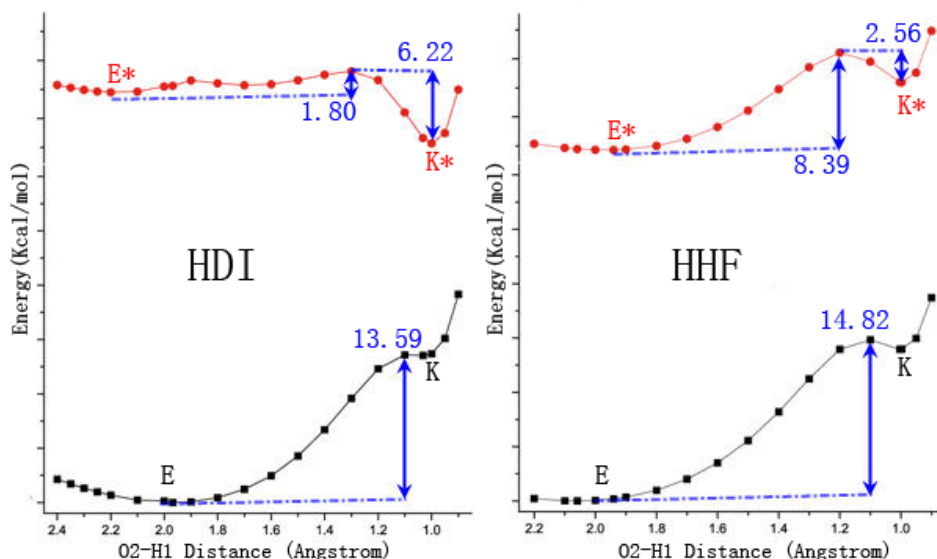

Figure 4: Calculated potential-energy curves of HDI and HHF as a function of H1…O2 bond length in the ground state (black) and the first excited state (red). The related energy barriers are shown in blue.

In summary, the calculation results show considerable differences of the photochemical properties between HDI and HHF. The intramolecular hydrogen bond dynamics suggests that, from the ground state to first excited state, the intramolecular hydrogen bond of HDI is weakened while that of HHF is strengthened. This result, from another perspective, implies that the strengthening of the intramolecular hydrogen bond upon photoexcitation is not the necessary condition for the occurrence of ESIPT. What's more, the results of frontier molecular orbitals reveal that the charge transfer involves in all the processes of ESIPT reaction. By means of the photoexcitation, the charge transfer from the proton donor to acceptor is observed for both HDI and HHF, providing the driving force for the forward ESIPT (E* to K*). After forward ESIPT, the electron density is redistributed. For HDI, the charge transfer from C2 and O2 to O1 and C5 is found while HHF presents the charge transfer directly from proton donor (O2) to proton acceptor (O1). These differences help us

to understand why HDI only presents the single-emission spectra while HHF exhibits the dual-emission spectra in the experiments. Meanwhile, the potential-energy curves demonstrate the preferred forward ESIPT for HDI and the easily occurred backward ESIPT for HHF, which further support the results of frontier molelcular orbitals.

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