

TDDFT assessment of excited state intramolecular proton transfer in a panel of chromophore 2-hydroxypyrene-1-carbaldehyde

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Abstract. Time dependent density functional theory method at the def-TZVP/B3LYP level was employed to investigate excited state intramolecular proton transfer (ESIPT) properties of 2-hydroxypyrene-1-carbaldehyde (HC). Our calculated results of the primary bond lengths and infrared vibrational spectroscopic information show that, upon photoexcitation, the intramolecular hydrogen bond is significantly strengthened in S_1 state, which facilitates the proton transfer process effectively. Furthermore, the electron density distributions of frontier molecular orbitals were demonstrated to be a positive factor for the ESIPT. By the monitor of the characteristic peaks stretching vibration of O-H group in the IR spectra, we have further confirmed the occurrence of ESIPT. The constructed potential energy surface of the S_1 state has also been used to explain the proton transfer process and evaluate the radiationless pathway, indicating that the ESIPT process occurs most easily in HC molecule.

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Key words: Time dependent density functional theory; excited state intramolecular proton transfer; hydrogen bonding

1 Introduction

Ever since the seminal experimental observation of the excited-state intramolecular proton transfer (ESIPT) reaction of methyl salicylate (MS) by Weller et al. in the middle of the last century [1], the phenomenon of photoinduced proton transfer process has attracted countless works in many fields of chemistry and molecular biology [2-15]. A very fascinating feature of molecules undergoing ESIPT is the presence of a strong intramolecular

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hydrogen bond, in which the acidity and basicity relations can be controllable by photoexcitation. As a consequence, the electronic excitation of such molecules represent large Stokes shift due to the characteristic conversion from an excited enol (E^* form) to an excited keto (K^* form) tautomer along a preformed hydrogen bond. It is worth mentioning that the ESIPT process was found to proceed exceptionally fast at a subpicosecond time scale because it involves a negligible activation barrier [16-22]. This ultrafast nature of ESIPT molecules attracts highest scientific interest whereby paving potential avenues for prospective applications, such as luminescent materials [23, 24], fluorescent chemosensors [25], photostabilizers [26, 27], molecular probes [28], metal ion sensors [29-31], and organic light emitting devices (OLEDs) [32, 33].

2-hydroxypyrene-1-carbaldehyde, hereafter also HC, possessing exclusively an intramolecular $O_2-H_{10}\cdots O_1$ hydrogen bond to form a strong quasi-aromatic chelating ring, is a typical panel of chromophore exhibiting the phenomenon of ESIPT (Fig. 1). In the year of 1988, Einhorn and coworkers first provided a new methodology, for ortho-hydroxylation of aromatic aldehydes via ortho-lithiated aromatic amino alkoxides, to synthesize HC. They reported that HC molecule is a starting material for the synthesis of pyrenofurans, which showing exceptional mutagenic activities [34]. Until now, however, the complete picture of photophysical and photochemical characteristics for HC has remained poorly understand. Moreover, we are yet to elucidate the finer details of ESIPT process of the intramolecular hydrogen bonding ring system. Thus, theoretical investigations to get thoroughly insights into the inner intricacies involved in the ESIPT process of HC are needed.

In present work, we concentrated our efforts on unraveling the dynamics and mechanisms of the ESIPT process of HC. We investigated the structural and electronic properties in the ground (S_0) and first excited (S_1) states, using the density functional theory (DFT) and time-dependent density functional theory (TDDFT) method, respectively. Furthermore, its proton-transfer tautomer have been globally optimized and found stable. Simultaneously, the vertical single state excitation energy, corresponding to the oscillator strengths in different electronic states, and the frontier molecular orbitals (MOs) were presented. Further verification of the occurrence of proton transfer reaction was also implemented via IR spectra analysis. In addition, the potential energy curve as a function of the proton-transfer coordinate was calculated, which provide us a very effective way to ensure the occurrence of ESIPT.

2 Theoretical methods

In our work, all the electronic structure calculations were carried out using the TURBO-MOLE program suite [35-40]. The ground-state geometry optimization was performed using density functional theory (DFT). Vertical singlet state excitation energy calculations and excited state geometry were optimized by means of the time dependent density functional (TDDFT) method. We employed the B3-LYP (Becke's three-parameter hybrid

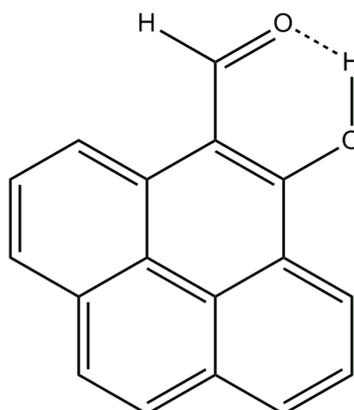


Figure 1: The schematic chemical structure of HC molecule. For clarity, all the hydrogen atoms are not shown.

exchange function with Lee-Yang-Parr gradient-corrected correlation) functional in both DFT and TDDFT calculations [35, 37]. The triple- ζ valence quality with one set of polarization functions (TZVP) was chosen as basis sets throughout [38, 39]. Fine quadrature grids 4 were employed. The convergence thresholds both the ground state and excited state optimization were set to be 10^{-6} . The IR intensities were determined from the gradients of the dipole moment.

3 Results and discussion

3.1 Optimized structures

The equilibrium structures of the stationary points provided us more detailed insights into the changes of transformed structure upon photoexcitation. Figs. 2 and 3 depict the optimized geometries of the HC molecule with numbering of the atoms obtained using the B3LYP function with the TZVP basis set in the ground state S_0 and the electronic excited state S_1 , respectively. And its tautomer (K^* form) in the first excited state was also calculated with the same method. The results showed that in the S_1 state HC exhibited a similar structure to that in the ground state. There both exists an intramolecular hydrogen bond $O_2-H_{10}\cdots O_1$ between the H_{10} atom and the O_1 atom. Whereas one can find that intramolecular hydrogen bond $O_1-H_{10}\cdots O_2$ can be formed in the S_1 state proton-transferred tautomer. The most primary structure parameters involved in the proton transfer were listed in Table 1. Based on the results of our calculations, it should be noticed that the calculated hydrogen bond length of $O_1\cdots H_{10}-O_2$ is shortened from 1.609 Å in the ground state to 1.550 Å in the excited state E^* form. Meanwhile, the O_2-H_{10} bond length changes from 1.002 Å in the S_0 state to 1.022 Å in the S_1 state, and the $C_{17}=O_1$ bond length elongates from 1.239 Å to 1.267 Å. This phenomenon indicates that the intramolecular hydrogen bond is significantly strengthened in the S_1 state, which keeps high degree with the previous finding drawn by Zhao and co-workers [41-43].

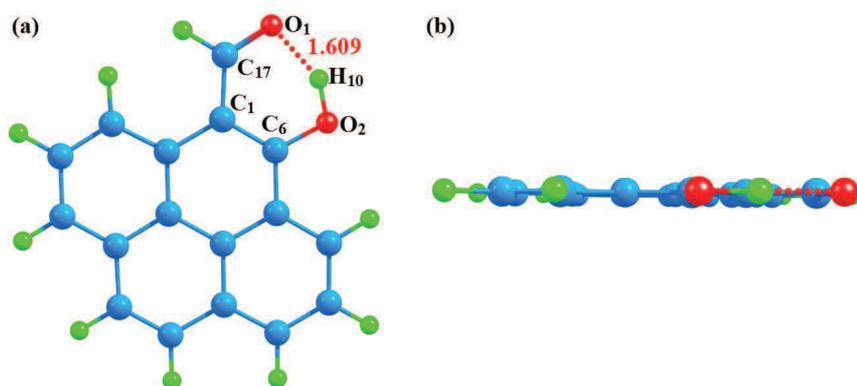


Figure 2: Optimized most stable geometric structure of HC molecule in the ground state S_0 (a) and its planar construction (b). The main geometrical parameters (bond lengths in Å) are also presented.

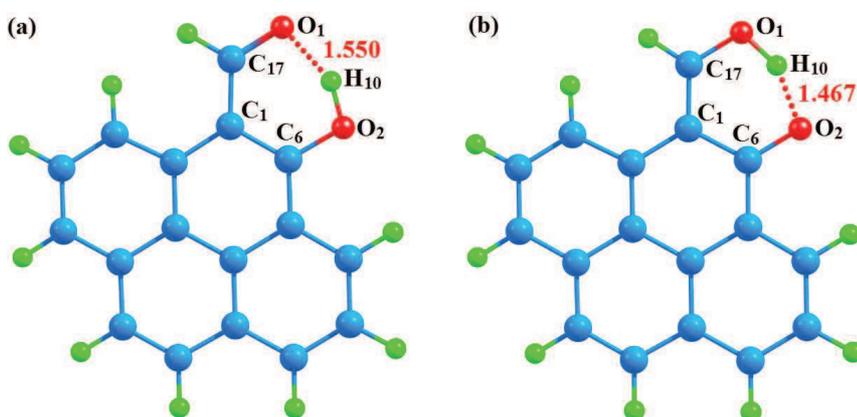


Figure 3: Optimized geometric structure of HC molecule in the electronic excited state S_1 (E^* form and K^* form).

Upon photo-excitation, however, the PT reaction from the excited E^* form occurs to form the excited k^* tautomer. Concomitantly, the one new intramolecular hydrogen bond $O_1-H_{10}\cdots O_2$ is formed between new enol group and carbonyl group. It is noteworthy that the interatomic distances $H_{10}-O_2$ in hydrogen-bonded $O_1-H_{10}\cdots O_2$ part of the tautomer is considerably shorter compared to those in S_0 and S_1 state. When the proton is bound to O_2 (E^* form) the O_2-H_{10} bond length is shorter than when it is bound to O_1 (k^* form), reflecting the higher acidity of O_1 with respect to O_2 . In addition, the $C_{17}=O_1$ distance increases as expected when passing from E^* to the k^* tautomer, while the opposite is true for the distance between O_1 and O_2 in the proton-transfer tautomer, which are much shorter than the corresponding distance in the ground state and excited state E^* form. The most plausible explanation is that the hydrogen bonded quasi-aromatic chelating ring becomes smaller after exciting, and the interactions of involved atoms increase. Therefore, as evident from the data above, the ESIPT reaction should be significantly

Table 1: The calculated dominating bond lengths (Å) and angles (°) in the S_0 state and the S_1 state based on the DFT and TD-DFT methods, respectively.

	S_0	S_1 -E*	S_1 -K*
C ₁ -C ₁₇	1.444	1.436	1.405
C ₁₇ -O ₁	1.239	1.267	1.318
C ₆ -O ₂	1.329	1.336	1.284
O ₂ -H ₁₀	1.002	1.022	1.467
O ₁ -H ₁₀	1.609	1.550	1.051
O ₁ -O ₂	2.521	2.504	2.456
O ₂ C ₆ C ₁	121.93	119.86	120.25
C ₁₇ C ₁ C ₆	117.75	122.84	118.24

facilitated by the intramolecular hydrogen bond.

3.2 Absorption peak and frontier molecular orbitals

The electronic excitation energies as well as the corresponding oscillator strengths of the first six states were calculated using the TDDFT/B3LYP/TZVP method and listed in Table 2. We can find that the maximum absorption wavelength for HC molecule is 397 nm, which is mainly associated with the S_0 - S_1 transition with the largest oscillator strength values.

Table 2: The electronic excitation energy (E), corresponding oscillator strengths (OS) of the HC molecule in different excited states and dominant Orbital Transition (OT) contributions to the excited states with their percentage. Calculated fluorescence emission peak (Flu.) of HC molecule in E* and K* form. H: highest occupied molecular orbital (HOMO), L: lowest unoccupied molecular orbital (LUMO).

	E (nm)	OS	OT	
S_1	397	0.120	H→L (94.5%)	
Flu.	440(E*)	452(K*)		
S_2	343	0.010	H-1→L (71.9%)	H→L+2 (16.3%)
S_3	323	0.102	H→L+1 (63.3%)	H-3→L (13.3%)
S_4	323	0.019	H-3→L (74.3%)	H→L+1 (11.4%)
S_5	305	0.035	H→L+2 (45.6%)	H-1→L (18.4%)
S_6	292	0.080	H-2→L (75.6%)	

Frontier molecular orbitals (MOs) are widely used to understand the nature of the excited states [42-45]. Thus, the charge distribution of the frontier MOs in the electronic excited state for HC was depicted in Fig. 4. From the results listed in Table 2, we know that the S_1 state of the HC corresponds mainly to the molecular orbital transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Hence, in Fig. 3, we only show the schematic plots of HOMO and LUMO

orbital. It is to be noted that the HOMO and LUMO of the studied molecular system are respectively the π and π^* character. That is to say, the S_1 state is of $\pi\pi^*$ -type feature, which is believed to facilitate the proton transfer [43-45]. It can be seen clearly that, upon transition from the HOMO to the LUMO, the electron density on the carbonyl group increases, while that on the hydroxyl group decreases. Interestingly, after exciting to the S_1 state, the transition leads to more negative charge distributed on the O_1 atom and the enlarged interaction between O_1 and H_{10} . We suggest that the intramolecular charge redistribution and electronegativity change of O_1 in the S_1 state will facilitate ESIPT processes from O_2 atom to O_1 atom. Therefore, the ESIPT is expected to occur due to the intramolecular charge transfer.

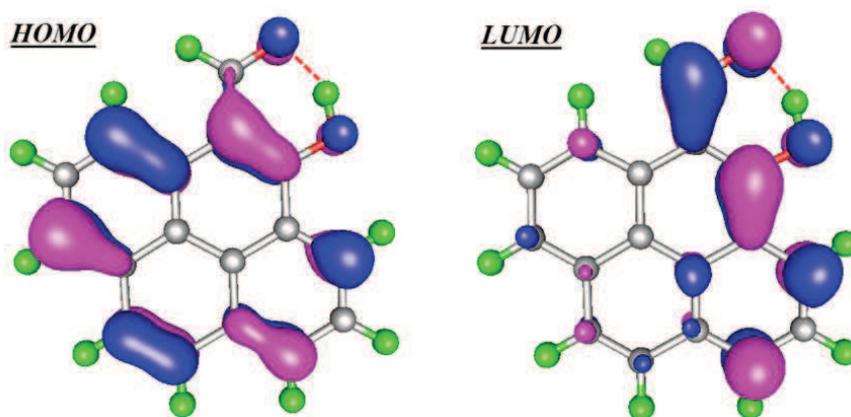


Figure 4: The calculated frontier molecular orbitals HOMO and LUMO for HC at the TDDFT/B3LYP/TZVP level.

3.3 Infrared (IR) spectrum

As is well known, the excited-state hydrogen bonding behavior can be investigated by monitoring the characteristic vibrational modes involved in the hydrogen bond formation [41, 42]. Here, the stretching modes of both the O_2-H_{10} groups of S_0 and S_1 E^* form, and O_1-H_{10} groups of S_1 K^* form are shown in Fig. 5. We can clearly see that there are three sharp peaks in the spectral range from 1500 to 3500 cm^{-1} . The characteristic peak centered at 2889 cm^{-1} and 2563 cm^{-1} are assigned to the O_2-H_{10} groups stretch mode. We can clearly find that the O_2-H_{10} group stretching band is drastically red-shifted by 326 cm^{-1} from the ground state to the S_1 state. But without ignorance, for S_1 tautomer form, the characteristic peaks of S_0 and S_1 are disappeared, whereas the new characteristic band around 2189 cm^{-1} which is assigned as O_1-H_{10} comes out.

From the calculated IR spectra, it can be demonstrated that the intramolecular hydrogen bond $O_1 \cdots H_{10} - O_2$ is significantly strengthened in S_1 state, since the red-shift of O_2-H_{10} vibrational frequencies provides an auxiliary evidence. Importantly, the remarkable shift of the characteristic peak in S_1 K^* form in comparison to the S_0 state and the

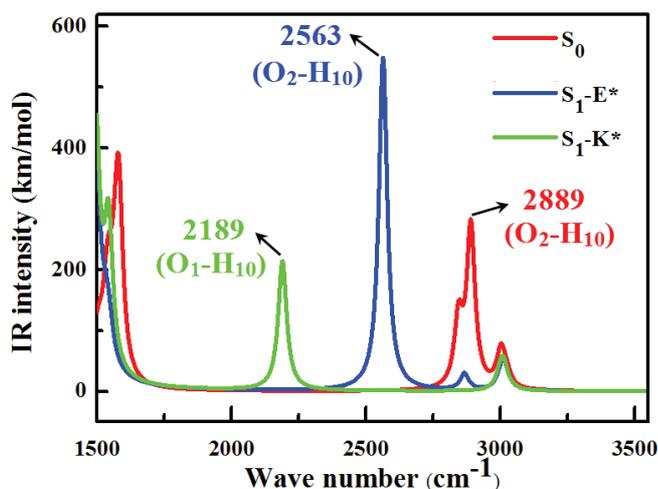


Figure 5: Calculated infrared absorption spectra of HC in the ground state S_0 and first singlet excited state S_1 at the spectral region of O-H stretching band.

S_1 state indicates that the bond of O_2-H_{10} breaks up and a new bond which should be O_1-H_{10} forms. Meanwhile, it is also consistent with the results drawn from the geometry optimizations. Consequently, the comparisons of the calculated IR spectrum in both the ground state and the excited state directly become another very effective way to ensure the occurrence of ESIPT.

3.4 The potential energy curves and the sensing mechanism

To further obtain the nature of the ESIPT process in the sensing mechanism, potential energy curves of the excited state along the proton transfer coordinates were calculated and shown in Fig. 6. Each point in the potential energy profile is sufficiently optimized by fixing the distance between O_2 and H_{10} atoms by 0.1\AA in each step at the TDDFT level. The potential energy curves were scanned and constructed in the range from 0.9\AA to 1.7\AA . Firstly, we can see that, upon the vertical transition at the geometry of the minimum in the ground state, there are two stable points in the excited state S_1 , corresponding to two stable equilibrium geometries, which is associated with E^* and K^* form. It can be obviously find that the S_1 -state potential energy curve exhibits a barrier of 2.28 kcal/mol between the two forms at the coordinate 1.02\AA and 1.47\AA . While after crossing the potential barrier, the energy of the S_1 state decreases along with the lengthening of O_2-H_{10} bond until reaches a stable energy point, which corresponds to the stable optimized geometry of the HC tautomer. Consequently, the proton H_{10} overcomes the low barrier, and O_1 atom captures it to form a new intramolecular hydrogen bond $O_1-H_{10}\cdots O_2$. This directly proved that ESIPT process is indeed very likely to proceed upon photoexcitation to the S_1 state.

It is clear from the above overview that after Frank-Condon transition to the S_1 state,

HC molecule exhibits the mechanism of dual-fluorescence. In detail, a locally excited (LE) state is formed after excitation, and then it is transformed into an ESIPT state. Subsequently, we computed the emission peak of HC molecule to get mechanistic insights into the ESIPT reaction. From our calculations (Table 2), we come to a conclusion that the E* form of HC molecule in LE state releases a fluorescence wavelength 440 nm, after crossing the potential barrier, the K* form in ESIPT state returns to the ground state with a fluorescence emission maximum at 452 nm.

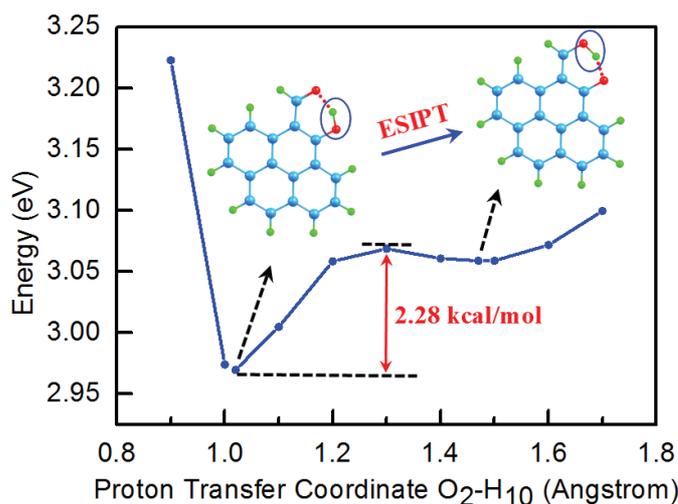


Figure 6: Potential energy curves of the first excited state for HC chromophore along with O_2-H_{10} bond length.

4 Conclusions

Systematic investigations on the ESIPT reaction in HC molecular presenting an intramolecular hydrogen bond have been performed using both DFT and TDDFT methods. The geometric structures of HC system and its tautomer in both the ground state S_0 and the lowest singlet excited state S_1 were unveiled in detail at B3LYP/TZVP theoretical level. The calculation results indicate that one intramolecular hydrogen bond $O_1 \cdots H_{10}-O_2$ could be formed in HC molecular, which is demonstrated to be significantly strengthened in the electronically excited state based on changes in bond length and the IR vibrational spectra. Consequently, the hydrogen bond strengthening would further provide a driving force in facilitates the ESIPT reaction. The calculated MOs depicted that the S_1 state of the HC system is the $\pi\pi^*$ character, and the increasing of electron density on the carbonyl group is strongly conducive to the occurrence of ESIPT. Furthermore, the formation and disappearance of the characteristic peaks involved in the formation of hydrogen bonds in the calculated IR spectra are demonstrated to become a typical feature of ESIPT. In addition, potential energy curves of the S_0 and S_1 states were constructed based on keeping the O_2-H_{10} distance fixed at a series of values. The results correlate well with the

phenomenon that the H_{10} atom transfers from O_2 to O_1 , which provide a direct evidence of an ESIPT process occurs upon photoexcitation to the S_1 state. Finally, by monitoring the fluorescence emission spectra, we successfully achieved the reasonable deactivation mechanism for the excited state of HC system, making us comprehend the phenomenon proton transfer.

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