

REGULAR ARTICLE

Cooperative Excited-state Hydrogen Bond Strengthening and Weakening and Concerted Excited-State Proton Transfer and Twisted Intramolecular Charge Transfer of Thiazolidinedione Derivatives in Solution

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Abstract: The time-dependent density functional theory (TDDFT) method has been performed to investigate the photochemical properties of the hydrogen-bonded complexes of thiazolidinedione derivatives with dimethylformamide (DMF), water and methanol solvents. A cooperative mechanism of the excited-state intermolecular hydrogen bond strengthening and weakening upon photoexcitation has been proposed for the TZD-A-2DMF trimer. Moreover, we have also first demonstrated that the excited-state proton transfer (ESPT) and twisted intramolecular charge transfer (TICT) are coupled together in TZD-A-DMF dimer and significantly facilitated by the excited-state intermolecular hydrogen bonding. When TZD-C is dissolved in protic solvents, e.g. water and methanol, the hydrogen bond is further assessed for its specific role in understanding the photochemistry properties of TZD-C.

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

Key words: Hydrogen bonding dynamics, excited-state proton transfer, twisted intramolecular charge transfer, hydrogen bond strengthening and weakening, fluorescence quenching

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1 Introduction

Intermolecular hydrogen bonding interaction has been stated to be the important and indispensable site-specific interaction in the investigation of the photochemical and photophysics processes [1-5]. The intermolecular hydrogen bond strengthening mechanism between Coumarin 102 chromophore and solvent upon photoexcitation has been demonstrated for the first time by Han and coworkers [6], which is in contrast to the mechanism of excited-state intermolecular hydrogen bond cleavage proposed by Nibbering and coworkers [7]. Then, as reconsidered and verified by many other groups [8-10], Nibbering and coworkers also accepted the excited-state intermolecular hydrogen bond strengthening mechanism in 2012, and with the help of the mechanism, they have clarified the photoinduced electron-transfer dynamics of 9-fluorenone in amine solvents [11]. Interestingly, an investigation of thiocarbonyl chromophores in solutions indicates an electronic excited-state intermolecular hydrogen bond weakening phenomenon [12]. What's more, it has been demonstrated that both the excited-state hydrogen bond strengthening and weakening play very significant roles in the processes of internal conversion (IC) [13], electronic spectral shifts (ESS) [12], photoinduced electron transfer (PET) [14], intramolecular charge transfer (ICT) [15,16], and metal-to-ligand charge transfer (MLCT) [17,18], and so on. It is important to mention that an effective rule, illustrating and inferring excited-state hydrogen bonding strengthening or weakening via an electronic spectral red-shift or blue-shift, have been presented recently [12,19], and the effective rule has been taken into account to explain the experiment by other groups [20-26]. A great deal of the studies have been focused on the hydrogen bonding dynamics, however, it is still desirable to carry out further works dealing with the effect of the excited-state hydrogen bonding dynamics on the photochemistry, photophysics and photobiology.

The new-synthesized thiazolidinedione derivatives (TZDs) have been proved to be sensitive to trace the quantities of diverse hydrogen bonding interactions [27]. As a result of the presences of electron rich carbonyl groups around -NH group in the thiazolidinedione moiety, the -OH group in the aryl moiety, and the keto groups on both sides of the thiazolidinedione moiety, the TZDs are host-guest of hydrogen bond series. Most importantly, the TZD-A of electronic donor (D) and acceptor (A) linked by a single bond, without the bulk steric effect, may induce a twisted configuration form. Thus, it is expected that the configuration twist may take place in the excited states, and then confirmed by our

accurate calculations that an excited-state proton transfer process occurs simultaneously upon photoexcitation.

For many molecules in chemistry and biology, they can undergo an excited-state proton transfer (ESPT) assisted by species with hydrogen bond accepting and donating abilities [28]. It has been demonstrated that the excited-state proton transfer (ESPT) process, in which hydrogen bond acts as a channel, is often responsible for the colorimetric and fluorescent signaling of chemosensors [29, 30]. Additionally, upon photoexcitation, conformational twisting can enhance the charge transfer process. These special properties in the excited states have attracted unabated attentions. It has been found that, for a photoinduced charge transfer process, occurred within one molecule of electronic donor and acceptor linked by a single bond or a bridge subunit, a twist intramolecular charge transfer (TICT) mechanism was proposed in the excited states [31-33]. However, few works have been intrigued on the ultrafast excited-state proton transfer coupled by a large amplitude twisting relaxation in the excited state [32]. In this work, we will shed light on this issue.

In the work of Sarkar et al. [27], the probes TZDs behave differently in the solvent DMF, the TZDs show a higher lifetime value in the DMF in contrast to other protic solvents. In addition, in protic solvents, e.g. water and methanol, TZDs shows minute changes in the absorption spectra between them, while show considerable different fluorescence spectra. We predict that the intermolecular hydrogen bonding is an essential factor to understand the photochemistry properties of them. Subject to the experimental scrutiny, more accurate quantum chemistry calculations are needed to be conducted on this issue. Therefore, in this paper, we exhibit a deep investigation of the cooperation between the excited-state hydrogen bond strengthening and weakening of the hydrogen-bonded trimer TZD-A-2DMF. At the same time, we established a rational model to illustrate the correlation between TICT and ESPT processes, which take place simultaneously in hydrogen-bonded TZD-A-DMF dimer. The effect of the hydrogen bonding interactions on tuning the properties of photoinduced TZDs in water and methanol is also shown.

2 Discussion

2.1 A cooperative mechanism of excited-state hydrogen bond strengthening and weakening of hydrogen-bonded trimer TZD-A-2DMF

The configurations of the TZDs are shown in **Figure 1**. Through the calculations of

B3LYP/6-311G+(d,p) method with Gassian 09 program package, we gained the equilibrium geometries of the hydrogen-bonded dimers as well as the corresponding trimer for TZD-A in DMF. The mainly results are shown in **Figure 2**.

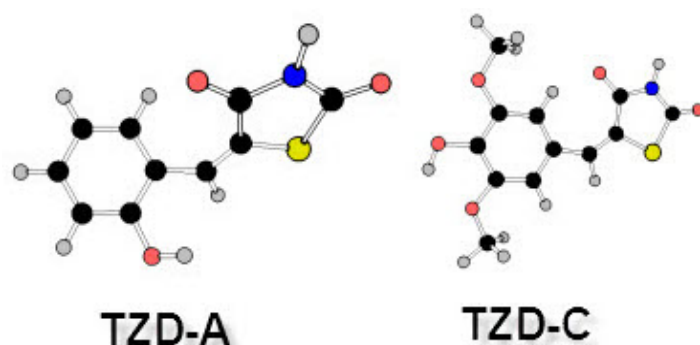


Figure 1: The configurations of the thiazolidinedione derivatives, TZD-A and TZD-C. black: C, gray: H, red: O, blue: N, yellow: S.

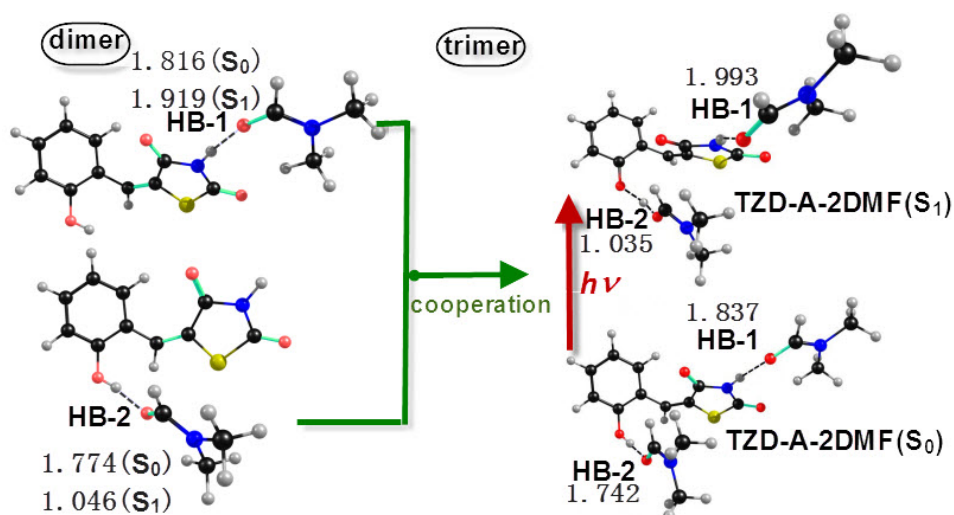


Figure 2: The configurations of hydrogen-bonded dimers TZD-A-DMF and hydrogen-bonded trimer TZD-A-2DMF. The important structural parameters are labeled in the picture.

From **Figure 2**, one can find that, in the ground state, for the hydrogen-bonded trimer TZD-A-2DMF, the added hydrogen bond HB-2 induces a weakening of the hydrogen bond HB-1. However, the addition of the hydrogen bond HB-1 induces a strengthening of the hydrogen bond HB-2. The hydrogen bond HB-1, which is calculated to be distinctly

weakened in the S_1 state in the dimer, continues to be lengthened due to photoexcitation of the trimer to the S_1 state. Similarly, the hydrogen bond HB-2, which is the tunnel of the excited-state proton transfer process, continues to be shortened drastically induced by photoexcitation of the trimer. In addition, the calculated electronic spectra blue-shift should arise from the cooperation of the hydrogen bonds HB-1 and HB-2, and the solvent-moderated shift of the energy levels should contribute to the special fluorescence spectra of TZD-A in DMF in the experiment [27].

2.2 The coupled ESPT and TICT in the TZD-A-DMF dimer

The equilibrium geometric structures of the ground and the first excited states of the hydrogen-bonded dimer of TZD-A with DMF have been calculated using DFT and TDDFT methods with Gaussian 09 program package. It has been demonstrated that ESPT process takes place, assisted by the intermolecular hydrogen bond $O-H\cdots O=C$. At the same time, the thiazolidinedione ring is almost perpendicular to the aryl ring in the S_1 state. In the **Figure 3(D)**, from the electron density redistribution in the S_1 state HOMO-LUMO transition, it is clear that the S_1 state of the dimer has the strong intramolecular charge transfer (ICT) properties. Considering the planar configuration in the ground state and the properties of orbital transitions, the excited-state twisted intramolecular charge transfer (TICT) process is proposed. The excited state charge redistribution should be responsible for the excited-state configuration twist.

In **Figure 3(A)**, the two possible first excited-state proton transfer (ESPT) potential energy curves of TZD-A-DMF as a function of $O-H$ distance are shown, the red curve is the one without configuration twisting, while the black one exhibit the configuration twisted ESPT potential energy curve. There is a relative high energy barrier along the potential energy curve of the S_1 state with the dihedral angle 26.92° . A hinder is encountered in the ESPT process with the absence of the TICT process. In **Figure 3(B)**, we show the two possible first excited-state twisted intramolecular charge transfer (TICT) potential energy curves of TZD-A-DMF as a function of DA, and in the red one, no ESPT takes place, while in the black, both the TICT and ESPT take place. We can gain the indication that the sole TICT state is much more favorable in the S_1 state than the sole ESPT state in the S_1 state. From the relative energies at the beginning of the curves, we predicted that the ESPT tends to occur in the S_1 state primarily, then the TICT relaxation process is activated by ESPT the process. **Figure 3(C)** shows the local minima geometries obtained from the potential energy curves above, one can find that the concerted ESPT and TICT process of the hydrogen-bonded TZD-A-DMF dimer is energetically preferable.

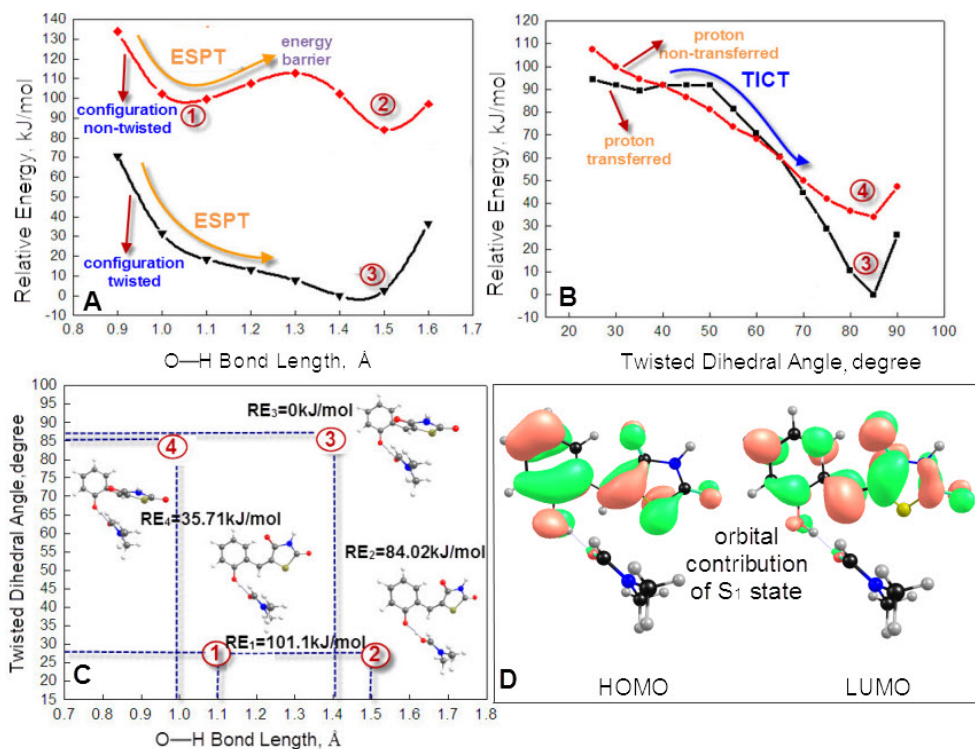


Figure 3: (A) The two possible excited-state proton transfer (ESPT) potential energy curves of TZD-A-DMF, as a function of O—H distance (involved in the hydrogen bond O—H···O=C) when keeping the dihedral angle between aryl ring and thiazolidinedione ring (DA) twisted (DA=85.91°, the black curve) and untwisted (DA=26.92°, the red curve), respectively; (B) The two possible excited-state twisted intramolecular charge transfer (TICT) potential energy curves of TZD-A-DMF, as a function of DA when keeping the proton transferred (O—H distance fixed at 1.442 Å, the black curve) and untransferred (O—H distance fixed at 0.983 Å, the red curve), respectively; (C) The local minima geometries obtained from the possible potential energy curves above. The serial numbers 1 and 2 in Figure 3(A) correspond to the excited-state twisted configurations with the proton transferred and untransferred, respectively. The serial number 3 in Figure 3(A) corresponds to the geometric structure with the twisted DA and proton transferred. The serial number 4 in figure 3(B) corresponds to the twisted configuration without proton transferred; (D) The frontier orbitals for TZD-A-DMF are shown, the orbital transition from HOMO to LUMO contributes to the S₁ state of TZD-A-DMF.

2.3 The effect of the hydrogen bonding on tuning the properties of photoinduced TZDs in water and methanol

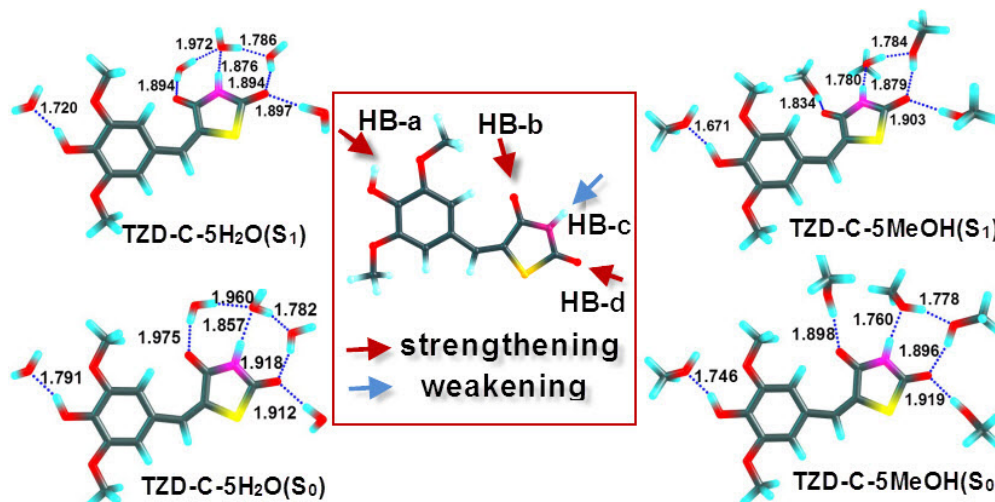


Figure 4: The geometries for the potential complexes with multi-hydrogen-bonds for TZD-C in water and methanol. The four possible hydrogen bonding sites are labeled.

In this section, all the calculations were taken on using the B3LYP/TZVP method together with the conductor-like polarizable continuum model (CPCM) being applied. We have established two rational models of the multi-hydrogen-bonded complexes for TZD-C in water and methanol, respectively. The optimized geometries in both ground and excited states are shown in **Figure 4**. One can find that, the hydrogen bonds formed at site HB-c are weakened after photoexcitation. However, in the other sites, the corresponding hydrogen bonds are undoubtedly strengthened by electronic excitation. Considering the different changes in hydrogen bonding in the electronic excited state for both the complexes of TZD-C in water and methanol, we conceive that the hydrogen bond plays a crucial role in understanding the distinct different fluorescence spectra between TZD-C in both water and methanol solvents.

3 Conclusion

A novel cooperative mechanism of the hydrogen bond strengthening and weakening in the electronic excited state of the hydrogen-bonded TZD-A-2DMF trimer is proposed. In the hydrogen-bonded TZD-A-DMF dimer, both the processes of TICT and ESPT occur

simultaneously upon photoexcitation. The concerted ESPT and TICT process for the hydrogen-bonded TZD-A-DMF dimer is barrierless. Moreover, the excited-state hydrogen bonding of the TZD-C in water and methanol solvents are also discussed. The considerable different excited-state hydrogen bonding may be ascribed to the different photochemical properties of TZD-C in water and methanol solvents.

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