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The Effect of Acetonitrile Solvent on Excited-State Dynamics for N,N-dimethylanilino-1,3-diketone

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Abstract: N,N-dimethylanilino-1,3-diketone (DMADK) [R. Ghosh and D. K. Palit, Photochem. Photobiol. Sci. 12 (2013), 987-995.], a new chromophore of the unsymmetrically substituted 1,3-diketone, has been selected to investigate the excited state intramolecular proton transfer (ESIPT) and twisted intermolecular charge transfer (TICT) processes based on the time-dependent density functional theory (TDDFT) method. Two kinds of structures have been found in the S1 state: Enol-A* and Enol-B*. The comparation between primary bond lengths and bond angles demonstrates that intramolecular hydrogen bond is strengthening in the S1 state. Infrared spectra (IR) has been also applied to demonstrate the phenomenon of hydrogen bond strengthening. Further, intramolecular charge transfer was found based on frontier molecular orbitals (MOs), which implys the tendency of ESIPT process. Based on the constructed two dimensional plots of S0 and S1 states, we found that the ESIPT process and TICT process seem to be synergetic process rather than the sequential process reported in previous work.

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

Keywords: Infrared spectra, ESIPT, TICT, Frontier molecular orbitals

Proton transfer (PT) and charge transfer (CT), as the most significant processes in the field of photophysics and photochemistry, play important roles in many organic and stabilization of the secondary structure of biomolecules like proteins, nucleic acids and so on. Particularly,

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excited state intra- and inter- molecular proton transfer (ESIPT) reactions are more important in chemical and biological systems containing DNA based-pair tautomerization and photosynthesis [1-8]. In fact, the ESIPT process was firstly reported more than semicentury ago by Weller and co-workers [9, 10], since then, more and more researchers focused on it due to its optoelectronic applications such as fluorescence sensor, molecular switches, UV filters and so forth [11-15]. In addition, among various kinds of ICT process, the twisted ICT (TICT) process is an improtant one. With regard to the TICT model, the twisted geometry is favored where the donor moiety remains out of plane relative to the acceptor moiety [16]. As far as we know, the factors responsible for the formation and stabilization of the TICT state are polarity, viscosity and hydrogen bond [16-18]. The effects of polarity and viscosity of the medium on the TICT process have been well established [16], whereas the role of hydrogen bond in the formation and stabilization of the TICT state is still not unambiguously. Particularly, investigations on systems with both ESIPT and TICT processes are very limited [19-21].

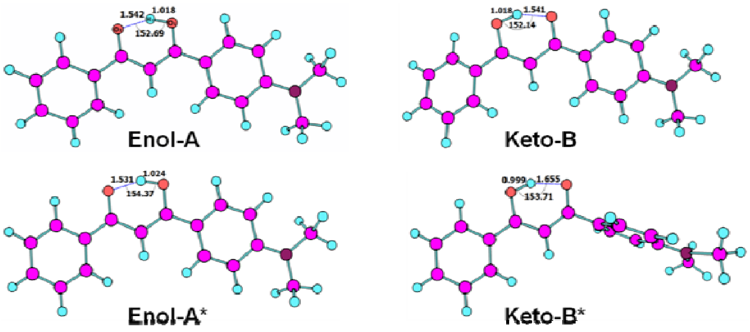

Figure 1: The optimized structures of DMADK. Enol-A: S0-state DMADK form; Enol-A*: S1-state DMADK form; Keto-B: proton-transfer S0-state DMADK form; Keto-B*: S1-state DMADK form.

N,N-dimethylanilino-1,3-diketone (DMADK), a new chromophore of the unsymmetrically substituted 1,3-diketone, was reported by Ghosh et al. [22, 23]. The sturctures of DMADK tautomeric forms with primary bond lengths and bond angles involved in intramolecular O1-H2···O3 based on our calculation have been shown in **Figure 1**. Based on steady state and ultrafast transitory absorption and fluorescence spectroscopic techniques, Ghosh et al. reported the relevant relaxation dynamics process in low polarity, medium polarity and high polarity solvents [23]. They believed that the excited-state dynamics for DMADK system may be dependent on different polarities. In high polarity solvent, Enol-A* undergos ultrafast ESIPT and then occurs TICT process [23]. However, one thing interests us is that whether the TICT process occurs later than ESIPT reaction in the S1 state? Moreover, spectroscopic techniques, such as steady state absorption and fluorescence spectra, time-resolved fluorescence spectroscopy, and so forth, provide only indirect information about some photo-chemical and photo-physical properties rather than mechamisms about excited-state dynamics.

Therefore, in the present work, density functional theory (DFT) and time-dependent density functional theory (TDDFT) have been selected to clarify the fundamental aspects concerning the structures occurring in the S1 state. All the calculations about electronic structures were dependent on the Gaussian 09 program suite [24]. Becke's three-parameter hybrid exchange function with the Lee–Yang–Parr gradient-corrected correlation functional (B3LYP) [25] as well as the triple-ζ valence quality with one set of polarisation functions (TZVP) [26] have been selected after testing other basis sets. In addition, since the experiment was conducted in acetonitrile (ACN) solvent [23], in all our calculations, the solvent effect (ACN) has been selected based on the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEF-PCM) [27, 28]. For Enol-A and Enol-A* forms, it should be noticed that the O1-H2 bond is lengthened from 1.018 Å in the S0 state to 1.024 Å in the S1 state, and the H2···O3 bond is shortened from 1.542 Å to 1.531 Å (shown in **Figure 1**). Furthermore, the O1-H2···O3 angle is also enlarged from 152.7º to 154.4º after the photo-excitation. The decrease of H2···O3 bond length and the increase of δ(O1-H2···O3) bond angle indicate the formation of a relative stronger hydrogen bond in the S1 state. In addition, as to the Keto-B and Keto-B* configuration, it should be noted that O3-H2 bond length is decreased from 1.018 Å (S0) to 0.999 Å (S1) and O1···H2 bond length is increased from 1.541 Å (S0) to 1.655 Å (S1), which also demonstrates the strengthening of hydrogen bond O1···H2-O3 in the S1 state for Keto-B* structure. Further, the IR spectra of Enol-A were calculated in both S0 state and S1 state, particularly, the IR spectra in electronically excited states are difficult and time-consuming (shown in **Figure 2**). The one should be noticed that the calculated O1-H2 stretching vibrational frequency in S0 state is 2767.2 cm-1, upon the electronic excitation, it changes to be 2664.9 cm-1 in the S1 state. The apparent red-shift of O1-H2 stretching frequency further manifests the intramolecular hydrogen bonds O1-H2···O3 was strengthened in the S1 state [29-37].

The calculated frontier molecular orbitals (MOs) of the Enol-A was shown in **Figure 3** to explore the nature of the electronically excited state. The calculated electronic transition energies and relative oscillator strengths as well as compositions have been listed in Tabel 1. It is obvious that the first excited singlet has the ππ*-type character from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) with a large oscillator strength of 0.9412. For this reason, only the HOMO and LUMO orbitals have been shown in **Figure 3**. The one should be noticed that the HOMO and LUMO are localized on different parts. It is worth mentioning that the O1 and O3 make larger and less contribution to the HOMO, whereas these contributions are greatly decreased and increased in the LUMO oribital, respectively. That is to say, the first excited state involves the intramolecular charge transfer.

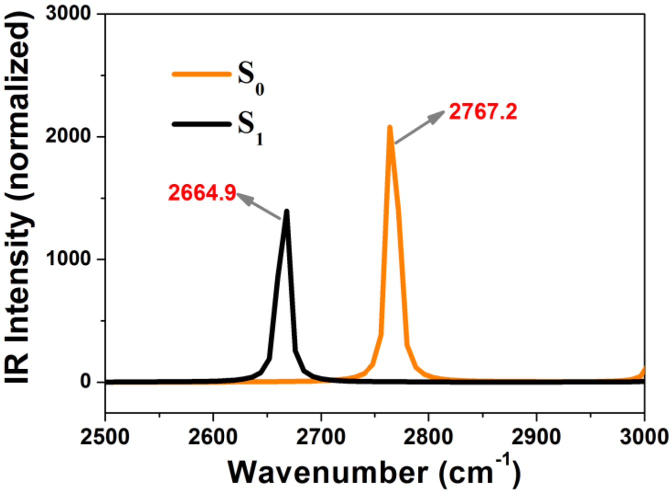

Figure 2: The calculated IR spectra of Enol-A structure in ACN solvent at the spectral region of O-H stretching band at B3LYP/TZVP theoretical level.

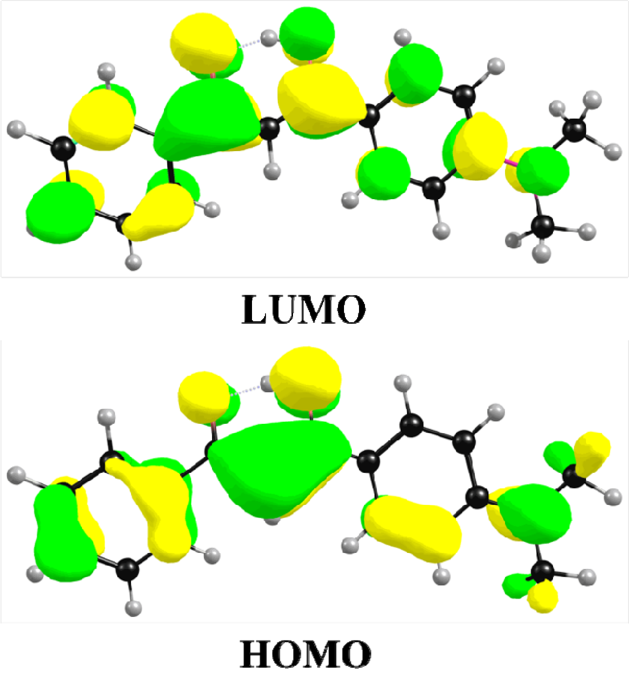

Figure 3: Frontier molecular orbitals (HOMO and LUMO) of Enol-A chromophore.

Table 1 Electronic excitation energy (nm), corresponding oscillator strengths and the corresponding compositions for the Enol-A chemosensor based on the TDDFT method.

	Transition	λ (nm)	*f*	Composition	CI (%)
Enol-A	S_0-S_1	411.8	0.9412	H→L	99.08%
	S_0-S_2	316.8	0.0039	H-5→L	50.82%
	S_0-S_3	301.4	0.2596	H-1→L	74.91%

In order to reveal the detailed process in the S1 state, the two dimensional plots have been scanned based on scanning both dimethylanilino twisting dihedral angle and proton transfer bond length (shown in **Figure 4**). All the geometrical structures of S0 and S1 states have been optimized among the Keto-B geometries based on fixing bond length O3-H2 and dimethylanilino twisting angle ranging from 0.918 Å to 1.718 Å in step of 0.1 Å and -2.49° to 177.51° in step of 10°, respectively. It can be seen clearly that both the two dimensional plots of S1 state is symmetrical along about 90° of dimethylanilino twisting angle. Therefore, A point is equal to B point seen in Figure 4. The coordinates of the primary stable structures have been displayed as follow: A (-2.49°, 1.518 Å) and C (87.51°, 1.018 Å). The potential energy barrier from A point to C point is calculated to be 1.198 kcal/mol. It can be found obviously in **Figure 4** that it is the corporate action of ESIPT process and dimethylanilino twisting process rather than the one reported in previous work that ESIPT process firstly populates Keto-B*, then it undergoes a twisted intramolecular charge transfer process via twisting of the N,N-dimethylanilino group.

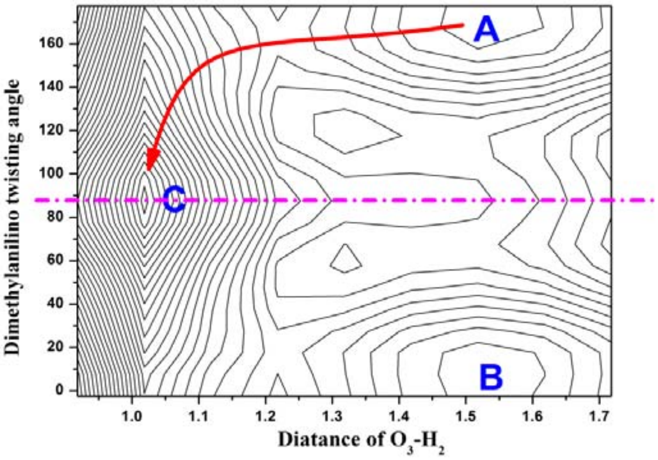

Figure 4: Optimized S1-state two dimensional plots based on scanning both dimethylanilino twisting dihedral angle and proton transfer bond length.

In summary, the ESIPT coupled with TICT process in ACN solvent has been performed based on TDDFT calculations. Hydrogen bond strengthening has been testified in the S1 state based on comparing primary bond lengths and bond angles involved in the intramolecular hydrogen bond between the S0 state and S1 state. IR at the O1-H2 stretching vibrational region also declare the phenomenon of hydrogen bond strengthening in the S1 state. The frontier molecular orbitals implys the tendency of ESIPT. The constructed S1-state two dimensional plots indicate that ESIPT coupled with TICT process can occur in the S1 state rather than sequential ESIPT and TICT processes.

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