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Excited state proton transfer coupled with twisted intermolecular charge transfer for *N*,*N*-dimethylanilino-1,3-diketone in high polar acetonitrile solvent

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ABSTRACT

In the present work, *N*,*N*-dimethylanilino-1,3-diketone (DMADK), a new chromophore of the unsymmetrically substituted 1,3-diketone [R. Ghosh and D. K. Palit, Photochem. Photobiol. Sci. 12 (2013) 987–995], has been investigated about the excited state proton transfer (ESPT) based on the time-dependent density functional theory (TDDFT) method. The experimental UV/Vis and emission spectra are well reproduced by the calculated vertical excitation energies in the S_0 and S_1 states. For the optimized **Enol-B*** structure, the twisted intermolecular charge transfer (TICT) process can be confirmed in the S_1 state. Hydrogen bond strengthening has been testified in the S_1 state based on comparing primary bond lengths and bond angles involved in the intramolecular hydrogen bond between the S_0 state and the S_1 state. Furthermore, infrared spectra (IR) at the O—H stretching vibrational region and Molecular electrostatic potential surface (MEPS) based on our calculation also declare the phenomenon of hydrogen bond strengthening. The frontier molecular orbitals (MOs) analysis, MEPS, Mulliken's charge distribution analysis, Hirshfeld charge distribution analysis and Natural bond orbital (NBO) analysis methods manifest the intramolecular charge transfer, which reveals the tendency of excited state intramolecular proton transfer (ESIPT) process. The constructed PESs of both S_0 and S_1 states demonstrate that ground state intramolecular proton transfer (GSIPT) as well as reversed GSIPT processes exists in the S_0 state, and the ESIPT coupled with the TICT process can occur in the S_1 state rather than sequential ESIPT and TICT processes.

1. Introduction

Excited state inter- or intra- molecular hydrogen bond has drawn more and more attentions recently, which exerts its important actions such as intermolecular charge transfer (ICT), excited-state proton transfer (ESPT), fluorescence resonance energy transfer (FRET), fluorescence quenching, tuning effects on photochemistry and so forth [1–14]. In particular, in recent years, Han and co-workers have presented novel mechanisms about excited-state hydrogen bond [15–26]. They have successfully simulated the excited-state hydrogen-bonded dynamics and demonstrated that hydrogen bond could be strengthened significantly in the excited state theoretically, which has opened a new chapter for the field of excited-state dynamics.

Excited-state intramolecular Proton transfer (ESIPT), as one of the most fundamental and significant reactions involved in hydrogen bond, plays important roles in the field of photochemistry and photophysics. Since this phenomenon was firstly reported by Weller and co-workers in methyl salicylate molecule more than 50 years age [27,28], extensive investigations about ESIPT have been performed experimentally and theoretically. Till now, more and more people have focused on ESIPT process due to its unique photochemical properties, which facilitate novel optoelectronic applications such as molecular switches, fluorescence sensor, laser dyes and so on [29–42]. Generally, upon the photoexcitation, the normal (enol) form can be excited to the excited-state potential energy surface (PES) with ICT process. The driving force for transferring a proton in the excited state can be provided based on the energy gap between local excited state and relaxed excited state. Then, the photoexcited enol* form undergoes ESIPT to generate the excited tautomer form (keto*). The slope of the excited-state PES connecting these two stable points determines the relative kinetics. In general, the keto* form emits fluorescence with a longer wavelength than the emission of enol* form to the S_0 state [43].

In addition, among various kinds of ICT processes, the twisted ICT (TICT) process is a great area of interest. In the TICT model, the twisted geometry is favored where the donor moiety remains out of plane relative to the acceptor moiety [44]. To be specific, upon photo-excitation, the promoted state starts in a nontwisted conformation, then, in a radiationless process, it follows the hypersurface and transforms into a twisted structure, which is a local minimum on the PES along the rotation of the donor group. The factors primarily responsible for the formation and stabilization of the TICT state are polarity, viscosity and

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hydrogen bond [44–46]. The effects of polarity and viscosity of the medium on the TICT process have been well established in Ref. 44, however, the role of hydrogen bond in the formation and stabilization of the TICT state is still not unambiguously. Investigations of hydrogen bond effects on the TICT process have been a very active area of research [47–51]. In fact, as far as we know, investigations on systems with both ESIPT and TICT process are very limited [52–56].

N,*N*-Dimethylanilino-1,3-diketone (DMADK), a new chromophore of the unsymmetrically substituted 1,3-diketone, was studied by Ghosh et al. [57,58]. The optimized structures of DMADK tautomeric forms have been shown in Fig. 1. Due to the low energy difference and low potential energy barrier between **Enol-A** and **Keto-B** forms in the S_0 state, both structures can coexist in the S_0 state through ground-state proton transfer (GSPT) and reversed GSPT processes [57]. Based on steady state and ultrafast transient absorption and fluorescence spectroscopic techniques, they reported the relevant relaxation dynamics process in low polarity, medium polarity and high polarity solvents [58]. They concluded that different polarities play different roles in the excited-state dynamics for DMADK system. Particularly, in high polarity solvent, in the S_1 state, **Enol-A*** undergoes ultrafast ESIPT and then occurs TICT process [58]. In fact, both the **Enol-A** and **Keto-B** forms exist in the S_0 state with GSIPT and reversed GSIPT processes, which is undisputed due to low potential barriers. We also provide the same conclusion below. However, one thing interests us is that whether the TICT process occurs later than ESIPT reaction in the S_1 state. In other words, whether TICT and ESIPT is sequential? 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. In order to comprehend the detailed mechanism, density functional theory (DFT) and time-dependent density functional theory (TDDFT) have been selected to clarify the fundamental aspects concerning the different electronic states and structures occurring in the PT and ESPT reactions. In effect, it can be found from previous work that the DMADK system may refer to more complicated excited-state dynamic processes such as ISC [58]. In the present work, however, we major in the mechanism of ESIPT and TICT processes in polar solvent, and we believe that much deeper research involved in the transformational process from single excited state to triplet excited state will be our future work. The configurations of S_0 state and S_1 state were optimized, further vertical excitation energies, Infrared (IR) vibration spectra, hydrogen bond energies, the frontier molecular orbitals (MOs), Mulliken's charge distribution analysis, Hirshfeld charge distribution analysis and Natural bond orbital (NBO) analysis, and homologous potential energy curves were calculated and analyzed to provide the clear and definite excited-state process.

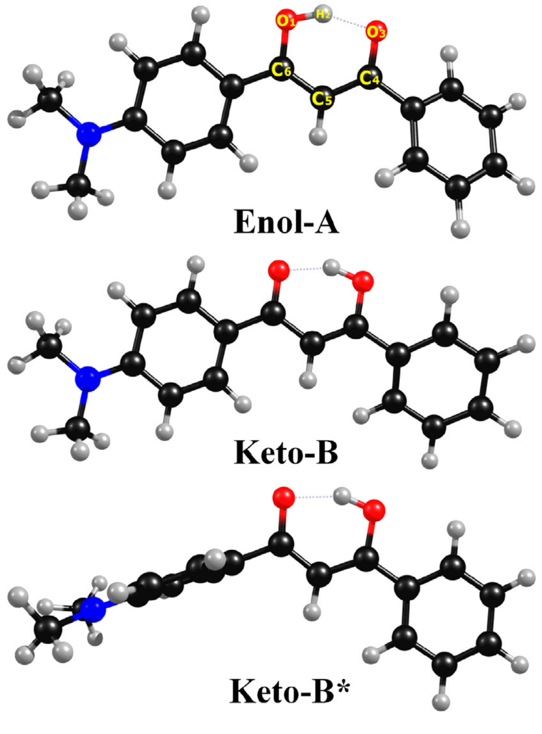

Fig. 1. The optimized structures of DMADK tautomeric forms. **Enol-A**: normal DMADK structure; **Keto-B**: proton-transfer form of DMADK; and **Keto-B***: the S_1-state structure of **Keto-B**.

2. Computational details

In the present work, all the theoretical calculations presented have been finished based on the DFT and TDDFT methods with Becke's three-parameter hybrid exchange function with the Lee–Yang–Parr gradient-corrected correlation functional (B3LYP) [59–64] as well as the triple-ζ valence quality with one set of polarisation functions (TZVP) [65] basis set by Gaussian 09 programs [66]. Since the experiment was conducted in acetonitrile (ACN) solvent [58], 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) [67–69]. The geometries of S_0 and S_1 states for the normal tautomer **Enol-A**, proton-transfer form in the S_0 state **Keto-B** and the S_1-state form **Keto-B*** were optimized without constrain of bonds, angles and dihedral angles. Vibrational frequency calculations have been used to analyze the optimized structures to confirm that these structures corresponded to the local minima on the S_0 and S_1 PESs (no imaginary frequency). The calculations of vertical excitation energies were also performed from the ground-optimized structures based on TDDFT method with IEF-PCM, and our theoretical calculations predicted the six low-lying absorbing transitions. All of the single-point calculations, namely, the energy corrections and NBO analysis have been calculated at the B3LYP/TZVP theoretical level. The contributions of individual atom to frontier molecular orbits are obtained based on the Ros-Schuit (SCPA) partition [70]. The S_0 and S_1 PESs have been scanned by constraining optimizations and frequency analyses to obtain the thermodynamic corrections in the corresponding electronic state, and keeping bond length O_3-H_2 of **Keto-B** form 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.

Fine quadrature grids of size 4 were employed. The self-consistent field (SCF) convergence thresholds of the energy for both the ground state and excited state optimization were set at 10^{-8} (default settings are 10^{-6}). Harmonic vibrational frequencies in the ground and excited state were determined by diagonalization of the Hessian. The excited-state Hessian was obtained by numerical differentiation of the analytical gradients using central differences and default displacements of 0.02 Bohr. The infrared intensities were determined from the gradients of the dipole moment [64].

3. Results and discussion

3.1. Optimized geometric structures

In order to confirm the stable structures of **DMADK** chromophore, the configurations of **Enol-A**, **Keto-B** and **Keto-B*** have been optimized based on the B3LYP function with TZVP basis set with ACN selected in the calculations according to the IEFPCM salvation model (shown in Fig. 1). It is worth mentioning that vibrational frequencies of these optimized structures have been analyzed to confirm they are at the minima. In addition, the most notable atoms involved in the intramolecular hydrogen bonding have been marked with serial numbers seen in Fig. 1. Primary bond lengths and bond angles of stable structures have been listed in Table 1. For **Enol-A** form, it should be noticed that the O_1—H_2 bond is lengthened from 1.018 Å in the S_0 state to 1.024 Å in the S_1