

## COMMUNICATION

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

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Received 28 Oct 2015; Accepted (in revised version) Nov 15 2015

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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 comparison 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 implies 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

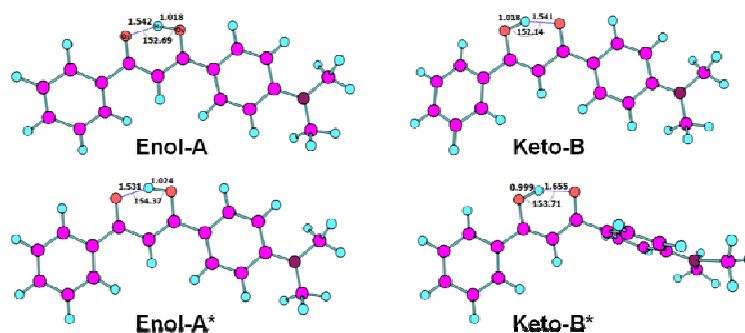
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Proton transfer (PT) and charge transfer (CT), as the most significant processes in the field of photophysics and photochemistry, play important roles in many organic and stabilization of the secondary structure of biomolecules like proteins, nucleic 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 important 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 structures 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\* undergoes 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