

## COMMUNICATION

### A theoretical study on ESPT mechanism of DALL-AcOH complex

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**Abstract:** In the present work, the excited-state intermolecular proton transfer (ESIPT) process of DALL-AcOH complex in AcOH solvent has been investigated theoretically using DFT/TDDFT methods. Based on comparing bond lengths, bond angles and infrared vibrational spectra involved in the two intermolecular hydrogen bonds ( $N_1-H_2\cdots O_3$  and  $O_5-H_6\cdots N_7$ ), we find that the photoexcitation has insignificant on intermolecular hydrogen bond ( $O_5-H_6\cdots N_7$ ). Oppositely, the intermolecular hydrogen bond  $N_1-H_2\cdots O_3$  was testified to be strengthened in the  $S_1$  state. In addition, intramolecular charge transfer occurring in DALL part, which facilitates ESIPT process. In the end, our constructed PESs provided the reasonable ESIPT mechanism that only excited-state single proton transfer exists in DALL-AcOH complex.

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

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

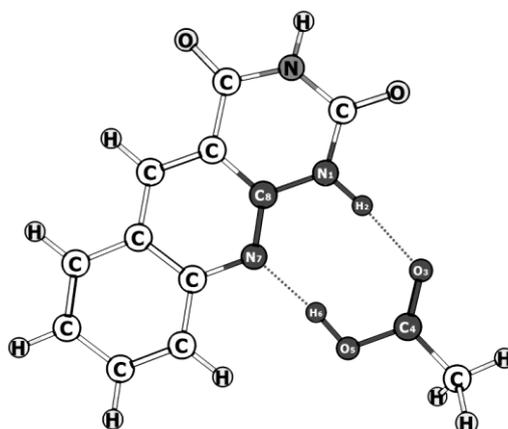
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Lumichrome, the main product of the photodecomposition and biodegradation of riboflavin, has been extensively studied because its alloxazine scaffold undergoes photoinduced tautomerization, changing its lumichrome-like emission into isoalloxazine-like mission [1-3].  $F_0$  and  $F_{420}$  are unique 5-deazaflavin-containing coenzyme and methanogenic signature molecules, essential for a variety of biochemical transformations associated with methane biosynthesis and light-dependent DNA repair [4]. 5-Deazaflavins (5-deazaalloxazine) are potential riboflavin antagonists with their own redox system, different from that of riboflavin [5]. 5-Deazaflavin and its homologues with the 5-deazaalloxazine (5-DALL) structure were also reported having in vitro antitumor activity [6-9]. Dezaalloxazines (DALL) are analogues of 5-deazaflavins, compounds that are cofactors in yellow chromophores [10]. There is an increasing interest in their photochemical properties since their discovery as chromophores in

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blue-light-sensing photoreceptors [11]. Particularly, recent years, lumichrome photophysical properties have changed to be hot [12-15], the investigations about DALL also changed to be high-profile. Peculiarly, the properties of excited-state proton transfer (ESPT) about 5-DALL sensor in acetic acid solution was provided by Sikorshi *et al.* [15, 16], the in-depth study about lumichrome has become more and more valuable. In fact, the ESPT mechanism of DALL is ambiguous theoretically. In addition, it is worth mentioning that ESPT processes are important in chemical and biological systems including photosynthesis and DNA based-pair tautomerization [17-20]. As far as we know, its optoelectronic applications attract extensive researchers such as fluorescence sensor, molecular switches, UV filters and so forth [21-23]. Therefore, in this present work, it is necessary to provide an in-detail theoretical investigation about excited-state dynamics of DALL in acetic acid solvent.



**Figure 1:** The optimized structures of DALL-AcOH.

Based on density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods, DALL couple with acetic acid molecule (DALL-AcOH) have been optimized to clarify the fundamental aspects concerning the structures occurring in both  $S_0$  and  $S_1$  state (seen in **Figure 1**). 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- $\zeta$  valence quality with one set of polarisation functions (TZVP) [26] have been selected after testing other basis sets. In addition, in all our calculations, the solvent effect (acetic acid (AcOH)) has been selected based on the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM) [27, 28]. **Table 1** lists the primary bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) of DALL-AcOH in  $S_0$  and  $S_1$  states based on the DFT/TDDFT methods in AcOH solvent, respectively. One should be noticed that  $N_1$ - $H_2$  bond is lengthened from 1.029  $\text{\AA}$  in the  $S_0$  state to 1.036  $\text{\AA}$  in the  $S_1$  state, and the  $H_2 \cdots O_3$  bond is shortened from 1.836  $\text{\AA}$  to 1.790  $\text{\AA}$ . Furthermore, the  $N_1$ - $H_2 \cdots O_3$  angle is also enlarged from 173.7 $^\circ$  to 177.6 $^\circ$ .