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Proton-Transfer and Photo-deamination Reactive Mechanisms Studies of Amines Compounds

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Abstract: The reference [J. Org. Chem. 2015, 80, 10817.10828] has reported that the Quinone Methides (QMs) that are of significant medicinal benefits in biological field can be generated *via* photo-deamination reaction. In this study, the density functional theory (DFT) and time-dependent DFT (TDDFT) methods have been carried out to investigate the reactive mechanisms of free amines compounds **1** and **3**. The excited state hydrogen bonding strengthening mechanism has been demonstrated by analyses of frontier molecular orbitals (MOs). Potential energy surfaces (PESs) calculations have been performed for illustrating excited state intramolecular proton transfer (ESIPT) and photo-deamination reactions of forms 1 and 3. The reactive sites of QM1 and QM3 molecules can be accurately predicted via analyses of ESP.

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

Keywords: Photo-deamination reaction; Excited state intramolecular proton transfer; Potential energy surfaces; Hydrogen bond

The Quinone methides (QMs) acted as reactive intermediates have great valuable bioactivities in biochemistry and photochemical fields, *etc* [1, 2]. Moreover, the QMs have played a pivotal role in antineoplastic antibiotics efficacy, when they react with biomacromolecules such as DNA, proteins, basic groups and so on [3]. In addition, the QMs

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can show antiproliferative activity by reacting with proteins [4]. The QMs can be produced within two reactions: thermochemical reaction and photochemical reaction [5, 6]. However, the photo-deamination reaction, serving as common photochemical method, is extremely advantageous to be performed [7]. Photo-deamination reactions are widely applied to researches of bioactivity and production modes of QMs, but the mechanisms and processes of photo-deamination reactions are rarely studied. Škalamera *et al.* have investigated qualitatively the reactive mechanism of photo-deamination reaction for amines compounds [8]. In this study, the free amines compounds **1** and **3** have been paid intriguing attentions, since the hydrogen bond interactions are crucial moieties in two compounds. The nonnegligible effects of ESIPT reactions along with corresponding orientations of hydrogen bonds should be taken into consideration on photo-deamination reaction. Upon photoexcitation process the compounds **1** and **3** can undergo the ESIPT reactions, and then the photo-deamination reactions will occur because of nitrogen protonation. For quantificationally and qualitatively accounting for the mechanisms of photo-deamination reactions, the theoretical computational methods have been performed in this study. The information of wave function has been calculated and analyzed for compounds **1** and **3** in different electronic states *via* DFT and TDDFT methods, respectively. Most of contemporary

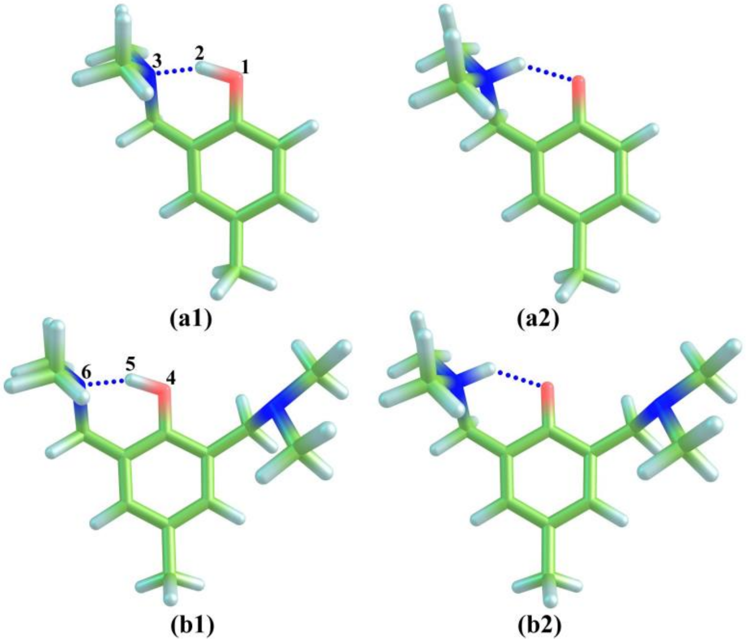

Figure 1: The optimized geometrical configurations of (a1) **1**, (a2) **1-T**, (b1) **3**, (b2) **3-T** in the S_1 state. Labeled symbol of elements and newly named serial number 1-8 of crucial atoms. The green sticks: C atoms. Red sticks: O atoms. Blue sticks: N atoms. Cyan sticks: H atoms.