

New insight into the hydrogen bond effects in one of PRODAN derivatives (1a) on excited state in methanol solvent

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Abstract. PRODAN derivatives would be a potential probe molecules. The hydrogen bond effects in PRODAN derivatives on excited state in methanol solvent have some significance to explain their dynamic experiments. In this paper, we have presented a theoretical investigation into the influence of hydrogen bonding on the structural and spectral properties of PRODAN derivative (1a) and methanol complexes using time dependent density functional theory. The focused work is the structures and vibrational spectra of PRODAN derivative (1a) hydrogen bonding compounds in methanol solvent. It was observed that the distances of hydrogen bonding between derivative and methanol molecule in complexes shortened in the S_1 state. The results suggested that the behavior and effect of hydrogen bonds increased in the excited proceed. In addition, the IR vibrational spectra of PRODAN-1a-MeOH complex occurred shift in the S_1 state. As a consequence, the hydrogen bonding of PRODAN derivative (1a) could play a role in the geometries and electronic spectra in excited state.

Keywords: Hydrogen bond; TDDFT; Excited state; Infrared spectra

INTRODUCTION

Hydrogen bonding is a special weak electrostatic interaction, which is widely found in various systems, and it plays a crucial role in the nature of matter. Many experimental and theoretical methods are widely used to study the properties of intermolecular hydrogen bonds [1-4]. The existence of hydrogen bonds has a great advantage to the structure and stability of the molecule [5-18]. However, the kinetics of hydrogen bonding is rarely understood, so it is necessary to study the properties of hydrogen bonds in the excited state [19]. Due to the difference of the charge distribution between the different states of the hydrogen bonding system, the hydrogen donor and acceptor molecules must be reorganized in the electronic excited state [20]. This process is called the hydrogen bond dynamics of excited states [21-24]. The kinetic behavior of hydrogen bonds occurs in the ultra-fast time scale of hundreds of femtoseconds, and we can use femtosecond time resolved spectroscopy to monitor the ultrafast dynamics of hydrogen bond in the excited state.

Studies have shown that PRODAN (6-propionyl-2-dimethylaminonaphthalene) is a probe of micropolarity [25]. Isaac G. Alty et al. have studied the effect of intramolecular hydrogen bonding on the fluorescence of PRODAN derivatives [26]. It responds to influences an increase in solvent dipolarity with a red shift in its fluorescence maximum. This behavior was the result of the charge transfer from the amino group to the carbonyl group, which gave rise to a larger dipole moment

on the excited state. The results shown that the intramolecular hydrogen bonds in the PRODAN derivatives affect the excited state behavior in several ways. Due to the intermolecular hydrogen bond, it causes a slight quenching in the presence of low concentration of alcohol. The results confirmed the importance of carbonyl transformation in alcohol quenching. PRODAN compounds have hydroxyl groups on the alkyl chains of the ketones, PRODAN derivatives can undergo proton transfer in excited molecules. Recently, Han K.L and his collaborators on the excited state of intramolecular and intermolecular hydrogen bond dynamics research is more comprehensive [1,4,10, 22, 24-25,27-30]. Their studies showed that excited hydrogen bonds play an important role in photochemical reactions, such as torsional effects, fluorescence quenching, excited state proton transfer, etc.

In this paper, we mainly study the behavior of hydrogen bond between PRODAN derivative (1a) and methanol in excited state. The purpose is to explore the effect of hydrogen bonding on complexes dynamic in the excited state. First of all, we will optimize the structures of PRODAN derivative (1a) with methanol complexes in the ground state and the excited state.

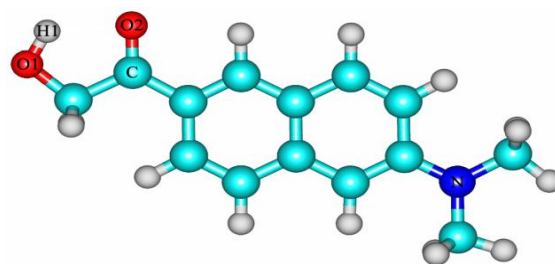


Figure 1. The geometric structures of the PRODAN derivative (1a).

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Then, electronic excitation energies and infrared spectrum will be studied. Furthermore, the frontier molecular orbitals (MOs) would be helpful for understanding the excited proceed and be discussed. A final section summarizes and gives the conclusions of this study.

THEORETICAL METHODS

All the calculations were carried out with the Gaussian 09 program [31]. The geometry optimizations of all structures considered here for the ground state were performed on cam-B3LYP functional [32-34] with 6-31G** basis sets. The excited state electronic structures were calculated by applying time-dependent density functional theory (TDDFT) method at the same level. The hydrogen bond effects of molecule in methanol solvent were calculated using SMD model.

RESULTS AND DISCUSSION

The geometric structures of the PRODAN derivative (1a) are shown in **Figure 1**. The three possible structures of hydrogen

bonding complexness on the ground state and the first excited state are optimized respectively in **Figure 2**. Several important parameters of geometries are included in **Table 1**. In order to facilitate the discussion below, we mark the number on atoms involved in hydrogen bonding. The calculated results show that the O1-H2 bond length of the PRODAN-1a-MeOH (a) structure on the ground state is 1.824 Å, the O2-H2 bond length of the PRODAN-1a-MeOH (b) structure in the ground state is 1.843 Å. The bond lengths of those on the S_1 state are 1.748 Å and 1.796 Å, respectively. It is clear that the bond lengths of the hydrogen bonding O1-H2-O3 and O2-H2-O3 become shorter; this suggests that intermolecular hydrogen bonds on the first excited state are enhanced. Moreover, the bond angles involved PRODAN-1a-MeOH (a) and (b) hydrogen bonding are stretched from 158.54° and 169.66° on the S_0 state to 160.41° and 172.66° on the S_1 state. Thus, the hydrogen bonding complex of PRODAN-1a-MeOH (a) and (b) are more stable on the S_1 state. The PRODAN-1a-MeOH (c) is another situation, here we consider the N of PRODAN derivative (1a) taken part in the hydrogen bonding. The bond length of N-H2 elongates from 1.963 Å on the S_0 state to 3.515 Å on the S_1 state, the bond angle of N-H2-O3 decreases from 164.02° to 103.14°.

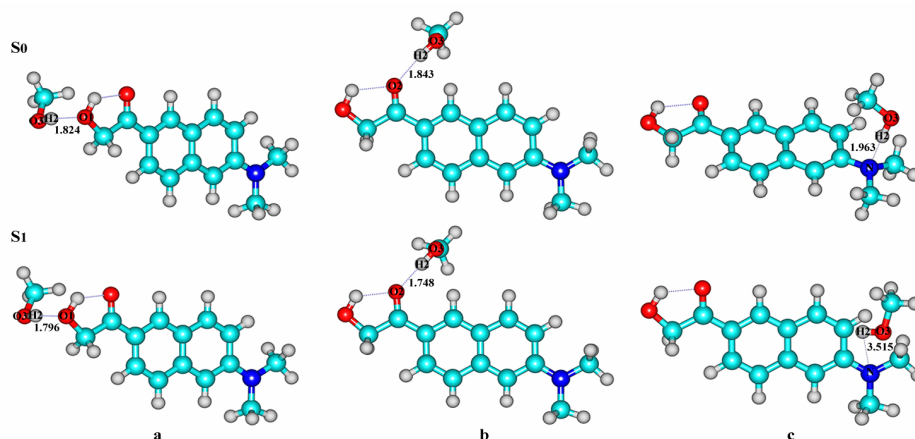


Figure 2. The geometric structures of three PRODAN-1a-MeOH hydrogen bonding complexes are optimized at cam-B3LYP/6-31G** level on the ground state and excited state.

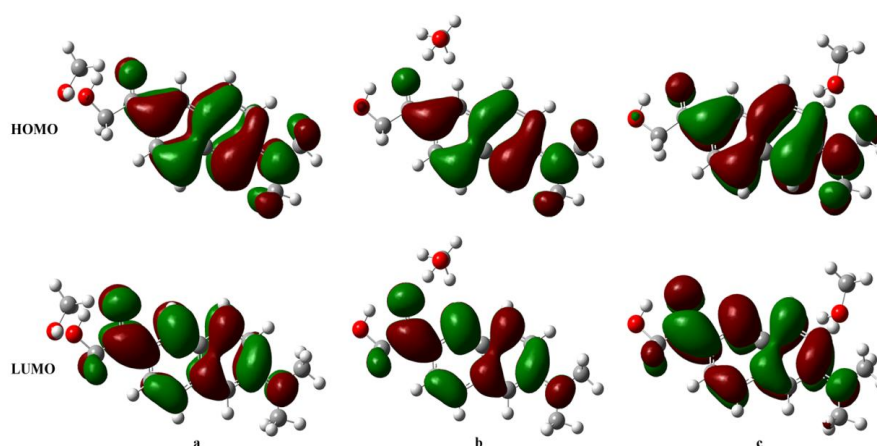


Figure 3. Frontier MOs of the PRODAN-1a-MeOH (a, b, c) complex