

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.

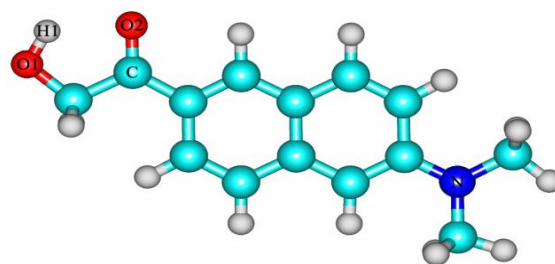


Figure 1. The geometric structures of the PRODAN derivative (1a).

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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°.

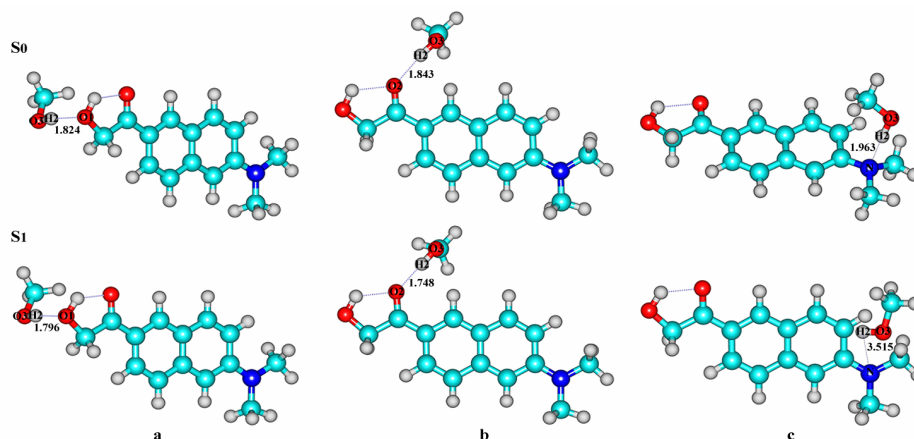


Figure 2. The geometric structures of three PRODAN-1a-MeOH hydrogen bonding complexes are optimized at cam-B3LYP/6-31G** level on the ground state and excited state.

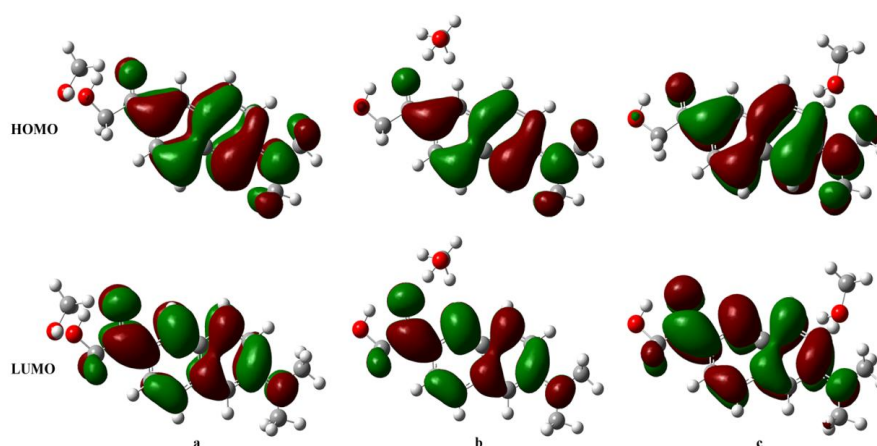


Figure 3. Frontier MOs of the PRODAN-1a-MeOH (a, b, c) complex

Thus, it can be seen the intermolecular hydrogen bonds of complexness (a) and (b) are enhanced on the excited state, while complexness (c) is weakened.

In order to further understand the nature of the hydrogen bonding effect on the excited state, we explored the details in the six low-lying excited states. The excitation energy and oscillation intensity of the hydrogen bond complex were calculated. The corresponding results have been listed in **Table 2**. The S_1 state of the dimers has the largest oscillator strength. Thus, the hydrogen-bonded PRODAN derivative (1a) dimers can be initially photo-excited to the S_1 state. It can be found the electronic excitation energies of three complexes on S_1 state are the lowest and corresponding oscillator strengths are largest in all six low-lying excited states. It could manifest the excited spectra from S_1 excited are most visible. Furthermore, the contribution of orbital transition demonstrates that the most transition probability proceeds from HOMO to LUMO.

Frontier molecular orbital analysis can provide a perspective to understanding of the photoexcitation process. **Figure 3** shows the frontier molecular orbital of PRODAN-1a-MeOH (a, b, c) complexes. We can clearly see that the HOMO and LUMO orbitals of (a), (b) and (c) are nearly the same. It should be noted that the electron densities of HOMO and LUMO orbitals are completely localized over the PRODAN derivative (1a) molecule. From the TDDFT calculations of all the geometric conformations, the S_1 state with the largest oscillator strength of the hydrogen-bonded complex corresponds to the orbital transition from HOMO to LUMO.

Table 1. Calculated bond lengths L (Å) and bond angles ($^\circ$) of three hydrogen-bonded PRODAN-1a-MeOH complex on the ground state and excited state.

Electronic state	a		b		c	
	S_0	S_1	S_0	S_1	S_0	S_1
L_{O1-H2}	1.824	1.796				
L_{O2-H2}			1.843	1.748		
L_{N-H2}					1.963	3.515
$A_{O1-H2-O3}$	158.5	160.4				
$A_{O2-H2-O3}$	4	1	169.66	172.66		
$A_{N-H2-O3}$					164.02	103.14

Table 2. Electronic excitation energies (eV) and corresponding oscillator strengths (in parentheses) of the PRODAN-1a-MeOH low-lying electronically excited states. The contributions of the orbital transitions for the S_1 state are also listed.

	a		b		c	
	Energy (eV)	Oscillator strength	Energy (eV)	Oscillator strength	Energy (eV)	Oscillator strength
S_1	3.1931(0.9082)	3.1497 (0.9266)	3.2208(0.8533)			
	H→L 95.8%	H→L 95.7%	H→L 95.8%			
S_2	3.9731(0.0261)	3.9638 (0.0101)	3.9501(0.0793)			
	H→L+161.3%	H→L+156.7%	H→L+1 69.7%			
S_3	4.4525(0.0001)	4.5388 (0.0241)	4.3797(0.0001)			
	H-4→L82.0%	H-5→L 76.1%	H-3→L79.4%			
S_4	4.5966(0.8181)	4.5451 (0.7182)	4.6362(0.8209)			
	H-1→L 59.8%	H-1→L53.0%	H-1→L67.4%			
S_5	5.4332(0.4771)	5.3188 (0.0204)	5.3977(0.1498)			
	H-1→L+171.8%	H-3→L 73.7%	H-2→L48.4%			
S_6	5.4379(0.0256)	5.4174 (0.5109)	5.4399(0.3305)			
	H-3→L 67.7%	H-1→L+1 72.7%	H-1→L+1 51.6%			

Thus, the S_1 state of the PRODAN-1a-MeOH (a, b, c) complex should be the locally excited (LE) state on derivatives. In addition, the electron density at the site of the carbonyl group is evidently increased in LUMO in comparison with that in HOMO. This also indicates that the intermolecular hydrogen bond would be obviously strengthened in the S_1 state of the hydrogen-bonded PRODAN-1a-MeOH (b) complex. Herein, it is evident that the S_1 state is of the $\pi-\pi^*$ character.

The intensity change of intermolecular hydrogen bonds during photoexcitation can be observed directly by detecting the infrared stretching vibration frequency of the ground state involved in the formation of hydrogen bonds [22-23,35]. Therefore, we calculated the infrared vibration spectra in the S_1 state and compared with that in the ground state. For the sake of convenience, the infrared spectra of the ground and excited states of the PRODAN-MeOH (a, b, c) hydrogen bond complexes are showed in **Figure 4**. Generally, when the stretching vibration moves toward the low frequency, a red shift occurs, and the strength is remarkably enhanced [36]. Thus, we focused on the group which is closely connected with hydrogen bonding. In the IR spectrum, it can be seen the detailed changes of hydrogen bond in the excited state. It should be noted that the calculated O3-H2 stretching vibrational frequency of PRODAN-1a-MeOH (a) and (b) complexes in the S_0 state are located at 3652 cm^{-1} and 3688 cm^{-1} . However, it is located at 3601 cm^{-1} and 3536 cm^{-1} in the S_1 state. The redshift of PRODAN-1a-MeOH (b) complex is more than 150 cm^{-1} . Moreover, the stretching vibrational intensity of hydroxyl group in (b) complex is rather strong on excited state. Since the peak of stretching vibration peak of the C1=O2 group of hydrogen bonded complex PRODAN-1a-MeOH (a) and (b) complex in the S_1 state is located at 1635 cm^{-1} and 1617 cm^{-1} , with red shift about 133 cm^{-1} and 135 cm^{-1} . Thus, it is confirmed that the intermolecular hydrogen bonding of C=O...H-O between PRODAN derivative (1a) and methanol

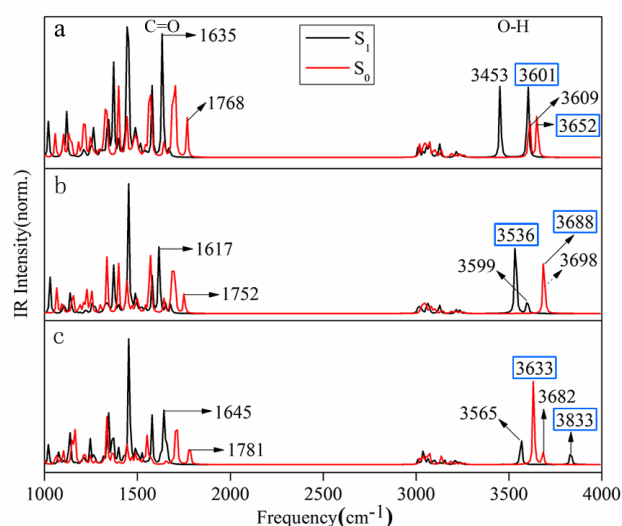


Figure 4. Calculated infrared spectra of PRODAN-1a-MeOH (a), (b), (c) complexes in different electronic states. The vibration frequencies of the C=O2, O1-H1 and O3-H2 (blueness square frame) groups' stretching modes in different electronic states are shown.

solvent can be significantly strengthened in the S_1 state. On the other hand, the calculated the stretching vibration for PRODAN-1a-MeOH (c) in the S_1 state, the peak of the O3-H2 stretching vibration occurs at 3833 cm^{-1} . It means a large blue shift relative to the S_0 state about 200 cm^{-1} . At the same time, the strength of hydroxyl group in PRODAN derivative (1a) is down. It suggests that the intramolecular hydrogen bond C=O...H1-O1 of the hydrogen bond complex PRODAN-1a-MeOH (c) is strengthened, while the strength of the intermolecular hydrogen bond O3-H2...N is weakened. It can be conclude that the hydrogen bonds of PRODAN-1a-MeOH (a) and (b) complexes are more stable in the S_1 state than those in the S_0 state, whereas the intermolecular hydrogen bond of PRODAN-1a-MeOH (c) is relatively weak in the excited state.

CONCLUSIONS

In summary, we optimized the structures of the hydrogen bond complexes of PRODAN derivative 1a and methanol solvent by DFT/TDDFT method using cam-B3LYP functional with 6-31G** basic set, methanol solvent described by SMD. The excitation energy and the electronic spectra were also calculated based on the most stable geometries. The structures and the excitation energy of PRODAN-1a-MeOH (a), (b) and (c) complexes can be markedly changed by hydrogen bonding interactions in the excited state. In addition, hydrogen bonds can also significantly influence stretching vibration. The IR vibrational spectra of PRODAN-1a-MeOH (a) and (b) complex shifted to the red, while that of PRODAN-1a-MeOH (c) complex shifted to the blue in the excited state. By analyzing the results, we have theoretically demonstrated that H-O...H-O and C=O...H-O hydrogen bonding of PRODAN derivative in methanol solvent were strengthened in S_1 state. We hope that this study will help understand the dynamic mechanism of PRODAN derivative.

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