



Effects of solvent polarity and hydrogen bonding on coumarin 500



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ABSTRACT

The time-dependent density functional theory (TDDFT) is used to investigate the effects of solvent polarity and hydrogen bond on coumarin 500 (C500). Both the absorption maximum and the hydrogen bond strength of C500 hydrogen bonded complex are confirmed to have a linear relationship with the solvent polarity function Δf . The type B (at carbonyl group position) complex whose absorption spectrum is extremely agreement with the experimental results is demonstrated to be preponderant among all the hydrogen bonded complexes. The investigation of C500-phenol complex (type B) shows that the strengthening of hydrogen bond in the S_1 state induces the fluorescence intensity of C500 weakened. The solvent polarity is the key influencing factor on intermolecular hydrogen bond by comprising the influence of solvent polarity and substituent on C500.

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1. Introduction

The 7-aminocoumarins (with differently substituted amino groups at the 7-position) are extensively used in the study of solvatochromic properties because of its high fluorescence quantum yield and large solvatochromism. [1–3] Many theoretical and experimental studies have been performed to explore the nature of 7-aminocoumarins [4–16]. The hydrogen bonds between 7-aminocoumarins and solvent molecule are shared because the 7-aminocoumarins can be used both as a hydrogen donor and as a hydrogen acceptor. In the past few years, the intermolecular hydrogen bonds have been investigated because of its important role in many molecular systems [17–33]. As a site-specific solute–solvent interaction, the intermolecular hydrogen bonds between hydrogen donor and acceptor have considerable influence on the photophysics and photochemistry of chromophores in the hydrogen-bonding surroundings [34–38]. The intermolecular hydrogen bonds are also associated with such processes as fluorescence quenching (FQ), internal conversion (IC) and intramolecular charge transfer (ICT) [33]. Therefore, the influence of hydrogen bonds and solvent polarity on the spectra of 7-aminocoumarins in solution has also been widely studied [39,40]. However, C500, as one of the classical 7-aminocoumarins, is seldom studied. In order to better understand the behaviors of C500 in solvents, the TDDFT study of C500 has been performed.

The coumarin-phenol complex has been proved to be a good model to study solvent effects [34,41,42]. Therefore, in this work, the theoretical study of the geometries, emission spectra and the transition

mechanism of the hydrogen bonded C500-phenol complex in the excited states have been investigated to provide insight into the influence of hydrogen bond interactions on C500 upon photoexcitation. As shown in Fig. 1 (b), three types of hydrogen bonds can be formed between C500 and solvent molecule. Type A hydrogen bond is formed between the amino nitrogen and hydrogen atom of polar solvent molecule. Type B hydrogen bond is formed between the carbonyl oxygen and hydrogen atom of polar solvent molecule. And type C hydrogen bond is formed between the amino hydrogen and the electron lone pairs of polar solvent molecule. The Kamlet–Taft analysis of C500 performed by K. Das et al. demonstrated that the contribution of the b coefficient is only 12%, which predicts the contribution of hydrogen bond acceptor properties of the solvent on the spectral properties of the solute [40]. That is to say, type C hydrogen bond has little influence on C500. Therefore, we focus on type A and B hydrogen bonds in this work.

The functional test has been performed to select a suitable functional for C500 molecular. The geometry structures of C500 (shown in Fig. 1 a) and C500-phenol complex (shown in Fig. 1 c) have been optimized in both ground and excited states. The electronic excitation energies and oscillation strengths of the electronically excited states were investigated to analyze the nature of hydrogen bond. The detailed theoretical investigations of the molecular structure, spectral properties and frontier molecular orbital of C500-phenol complex were also performed. In addition, the AIM (atoms in molecules) analysis has been performed to investigate the influences of the substituent on hydrogen bonds.

2. Computational methods

The ground state and electronically excited state geometric optimizations of the free monomer and the C500-phenol complex

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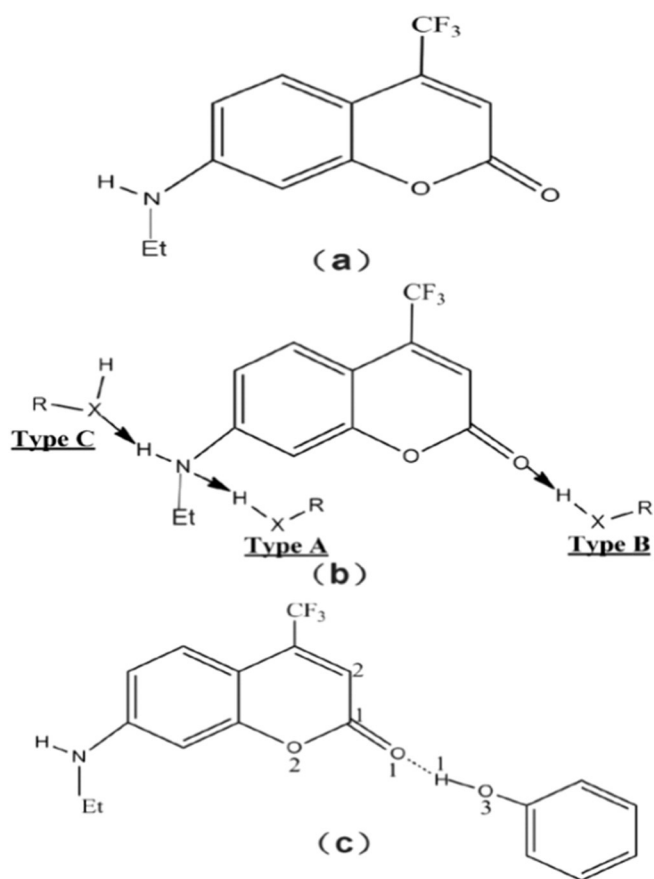


Fig. 1. (a) The structure of C500; (b) Three positions to form hydrogen bonds in C500; (c) The structure of C500-phenol complex.

were performed using the DFT and TDDFT methods, respectively. All the local minima geometries are confirmed by the absence of an imaginary mode in vibration analysis and calculations. The popular Becke's three-parameter hybrid exchange functional with Lee–Yang–Parr gradient-corrected correlation (B3LYP) [43,44] and the 6-311++G(d,p) basis set are used throughout. The polarizable continuum model (PCM) [45] has been demonstrated to be suitable for the systems which have no solvent–solute hydrogen-bonding interactions, while the integral equation formalism version of polarizable continuum model (IEFPCM) [46] is suitable for hydrogen-bonding systems [47]. Therefore, the IEFPCM is employed for polar systems and the PCM is employed for nonpolar systems to account for the solvent effects. AIM [48] analysis and plots of reduced electron density gradient (RDG) [49] versus $\text{sign}(\lambda_2)\rho$ are performed at the B3LYP/6-311++G(d,p) level. All calculations in the present work were carried out using the Gaussian 09 program package [50], Multiwfn 3.3.5 [51] and VMD programs [52]. These computations were performed on C500 and its derivatives without the constraint of bonds, angles, dihedral angles or symmetry.

3. Results and discussion

3.1. The influence of solvent polarity on C500

The functional test has been performed to select a suitable functional. The calculated absorption wavelength of C500 in CCl_4 and hexane solvents using different functional (B3LYP, B3PW91, BP86, CAM-B3LYP and PBE0) and the experimental data are listed in

Table 1

The absorption wavelength (nm) of C500 calculated at 6-311++G(d,p) level with different functional. The experimental results are also listed for comparison.

	B3LYP	B3PW91	BP86	CAM-B3LYP	PBE0	EXPERIMENT
CCl_4	369	372	435	331	360	368.97
Hexane	368	373	430	328	357	366.07

Table 1. According to **Table 1**, the absorption wavelength of C500 in CCl_4 solvent (369 nm) calculated by the B3LYP functional is consistent with experiment data (368.97 nm) [40]. Therefore, the results calculated by the TD-B3LYP/6-311++G(d,p) method are focused on here.

The absorption spectra of C500 hydrogen bonded complex in several polar solvents are investigated to determine the structure C500 in polar solvent. As shown in **Table 2**, in MeOH solvent, the absorption wavelengths of C500 monomer, type A hydrogen bonded complex, type B hydrogen bonded complex and type A + B hydrogen bonded complex are located at 385.99, 366.91, 392.02 and 371.90 nm respectively. This result shows that the absorption maximum of type A hydrogen bonded complex (366.91 nm) and the experiment data (390.98 nm) vary considerably [40] and that the absorption maximum of type A + B hydrogen bonded complex and monomer also vary greatly (4.99 and 19.08 nm respectively) with experiment results [40]. However, the absorption maximum of type B hydrogen bonded complex is in good agreement with experiment data with a very small error (1.04 nm) [40]. The results in other polar solvents are the same as those in MeOH solvent. The absorption maximum of type B hydrogen bonded complex is in good agreement with experiment data whereas the other hydrogen bonded complexes vary greatly with experiment data [40]. Therefore, type B hydrogen bonded complex is considered to be preponderant among all hydrogen bonded complexes.

The absorption spectra of type B hydrogen bonded complexes in nine solvents have been studied to investigate the effect of solvent polarity on C500 hydrogen bonded complexes. Interestingly, a linear relationship (see **Fig. 2 A**) is found between the absorption maximum and solvent polarity function Δf [53]. That is to say, the polarity of solvent has a great impact on absorption wavelength. Similarly, the analysis of the hydrogen bond lengths of type B hydrogen bonded complexes indicates that there exists a linear relationship (see **Fig. 2 B**) between the hydrogen bond lengths and solvent polarity function Δf ($\Delta f = (\epsilon - 1) / (2\epsilon + 1) - (n^2 - 1) / (2n^2 + 1)$) [53]. The good linear relationship in **Fig. 2** demonstrates that the stronger the polarity of solvent is, the stronger the hydrogen bonds of C500 hydrogen bonded complexes are.

3.2. The influence of intermolecular hydrogen bond on C500

3.2.1. The optimized structures of C500-phenol complex both in the S_0 and S_1 states

The structure of C500-phenol complex has been optimized to delineate the detailed aspects of type B hydrogen bond. The optimized structures and some of important structural parameters of type B

Table 2

Absorption wavelengths of three type hydrogen bonded complexes of C500, C500 monomer and experimental data in various solvents.

Solvent	Type B/nm	Type A/nm	Type A + B/nm	Monomer/nm	Experimental/nm
MeOH	392.02	366.91	371.90	385.99	390.98
1-Butanol	389.09	367.87	372.91	386.27	393.07
2-Propanol	389.77	370.30	374.86	386.11	395.16
Water	392.69	366.19	371.60	383.85	388.08
EtOH	389.86	368.10	373.20	386.26	393.04

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