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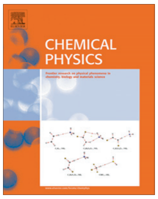

Deciphering the role of multiple hydrogen bonding sites on the microsolvation of 3-(phenylamino)-2-cyclohexen-1-one with water in the excited states

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ABSTRACT

We report here our investigations on the H-bonding modifications of molecular electronic structures and properties of 3-(phenylamino)-2-cyclohexen-1-one (PACO) and its 1:3 microhydrated cluster in the ground (S_0) and first two excited states (S_1 and S_2). The changes in bond lengths, atomic charges, natural bond order and aromaticity in the S_0, S_1 and S_2 states have been analysed. The electronic state dependence of the hydrogen bonding strengths at different H-bonding sites of PACO has been looked into. The hydrogen bonds formed through the H-bond accepting carbonyl moiety in PACO.3H_2O cluster appears to get weaker in the excited states while that formed through the H-bond donating amino moiety gets much stronger, compared to their ground state counterpart. The simultaneous strengthening of H-bonds at one site and weakening at another in the S_1 and S_2 states may have link to the overall stabilization of the clusters in the excited states relative to the ground state as observed experimentally.

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1. Introduction

Hydrogen bonding in molecular systems is of fundamental importance in chemistry and biology [1–8]. Investigations of hydrogen bonding through studies on structure and dynamical properties molecular clusters provide deep insight into the microscopic as well as macroscopic behavior of molecules [9–13]. These studies provide an opportunity to study a particular behavior of a molecule in a tailored environment [9] and also facilitate investigations of the effects of bulk solvation on a molecule in a systematic way. The bulk of the studies on H-bonding have so far been devoted to the ground state of a molecule. Of late, hydrogen bonding in the electronically excited states have been receiving increasing attention since the advent of many state-of-the-art time-resolved spectroscopic techniques, such as femtosecond transient absorption spectroscopy, femtosecond time-resolved fluorescence spectroscopy, time-resolved vibrational spectroscopy, etc. [14–19]. Quantum chemical calculations [20–29] have been used fruitfully to explore different facets of excited state hydrogen bonding in the recent years. Configuration interaction (CI), CI Singles (CIS), CI singles and doubles (CISD), time-dependent density functional theory (TDDFT) and complete active space self-consistent field (CASSCF) methods have been widely used for this purpose. [20–29]. As optimization of the excited states of large organic molecules using multi-configuration self-consistent field (MCSCF) methods are costly, calculations at the TDDFT level of theory for this purpose has become a popular choice now-a-days [26–29]. Molecules that undergo intramolecular charge transfer (ICT) in the excited state are specially interesting for studying hydrogen bonding in excited states [2,30] as the electronic charge distribution of these molecules can be quite different in the excited states compared to their ground state counterparts. The hydrogen bond donor and acceptor sites present in these molecule may either be activated or deactivated in the excited state [23,24,30], resulting in stabilization or destabilization relative to the ground state which can affect their spectroscopic properties.

The molecule under investigation, 3-(phenylamino)-2-cyclohexen-1-one (PACO, Scheme 1) is a member of the well-known β-enaminone molecular family, which is used as precursors to many bio-active natural products [31–33]. These molecules have been reported to take part in many electrophilic, neocleophilic, cycloaddition and photochemical reactions (for review, see [33]). We have shown [34] that PACO is an intramolecular charge transfer (ICT) probe that shows dual emission in the excited state, presumably coming from a locally excited (S_1-LE, $n\pi^*$) state and an ICT state (S_1-ICT, $n\pi^*$) formed upon excitation by light. The mechanism of the ICT in this molecule has been studied using steady state as well as time resolved spectroscopic techniques in conjunction with

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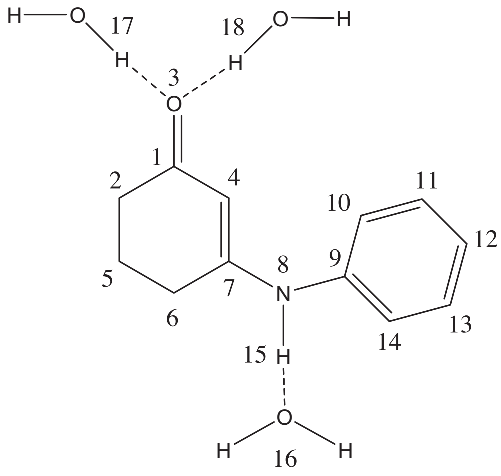

Scheme 1. The structure of 3-(phenylamino)-2-cyclohexen-1-one (PACO). The numbering of some of the atoms are done for reference.

quantum chemical calculations. Solvent, pH, excitation wavelength and temperature dependent studies on the spectral properties of the probe have been undertaken. Using a combined experimental and theoretical analysis we have surmised that the absorption excites the molecules to the second excited ($S_2, \pi\pi^*$) state that presumably has a conical intersection with the first excited ($S_1, n\pi^*$) state from which the emission occurs. Our further studies [35] revealed that both the polarity and hydrogen bonding abilities of the solvents plays their role in shaping the photophysics of PACO. The effect of microsolvation on the spectral properties of the probe has been investigated with the help of IR spectroscopy and quantum chemical calculations [36]. It has been seen that the 1:1 molecular clusters of the probe with the solvents do not represent the structure in the bulk. A combined experimental and theoretical analysis [34] undertaken earlier showed that PACO forms 1:3 hydrogen bonded microcluster with water in the ground state. The molecules of β-enaminone series possess high first hyperpolarizability (β).[37] The simple two-state model for the first hyperpolarizability proposed by Ouder [38] indicates that the value of β of a molecule depends on, among other factors, the difference in dipole moments between the ground and excited state of that molecule. So, detailed knowledge about the excited state properties of these molecules is necessary to understand the origin of high β values exhibited by these molecules. The excited state behavior of these molecules, however, remains to be fully understood yet.

In this contribution, we compare the microsolvation of PACO through hydrogen-bonding with water, both in the ground (S_0) and first two excited states (S_1 and S_2), as predicted by quantum chemical calculations and examine how far the predictions match with our experimental findings. The layout of the paper is as follows. In Section 2, the materials and methods used in the present study have been described briefly. Sections 3.1 and 3.2 deal with the results of our quantum chemical calculations on the ground (S_0) and first two excited (S_1 and S_2) states of PACO and its 1:3 molecular cluster with water, respectively. The experimental studies on the absorption and emission studies of PACO have been described in Section 3.3. The important inferences drawn from the present study have been summarized in Section 4.

2. Materials and methods

2.1. Experimental methods

The probe molecule, PACO has been synthesized using the procedure described elsewhere [32,34]. The structure of the molecule was confirmed through ^{1}H and ^{13}C NMR and IR spectra of the molecule, which have been reported in Ref. [34]. The steady state electronic absorption and emission spectra of PACO were recorded using a Shimadzu UV–VIS recording Spectrophotometer UV-2401 (PC) S220 V and Fluoro Max 3 (Jobin Yvon Horiba) fluorimeter, respectively. Cyclohexane was of spectroscopic grade (Spectrochem). Triply distilled water was used to prepare the aqueous solution and was checked for residual fluorescence, if any, before use. All the spectral data were recorded at an ambient temperature of 23 °C.

2.2. Quantum chemical calculations

The ground state equilibrium geometry of the isolated probe molecule, PACO in the gas phase has been optimized fully using density functional theory (DFT) and Dunning's correlation consistent valence double-ζ basis set (cc-pVDZ). A hybrid Becke's three parameter-Lee–Yang–Parr functional (B3LYP) was used. The geometries of first two excited (S_1 and S_2) states of PACO in the gas phase have been optimized using time dependent density functional theory (TDDFT) employing the same functional and basis set as used for calculation of the ground state structure.

The ground state equilibrium geometry of the 1:3 molecular cluster of PACO with water in the gas phase have been optimized fully using DFT, employing hybrid B3LYP functional. For the hydrogen bonded system correlation consistent valence double-ζ basis set augmented with a set of diffused functions (aug-cc-pVDZ) basis set was used. The gas phase excited (S_1 and S_2) state equilibrium structures of 1:3 molecular cluster of PACO with water have been optimized fully using time dependent density functional theory (TDDFT) and employing the same functional and basis set as used in the ground state calculation. All the calculations have been performed using the standard quantum chemical software, Gaussian 09 [39]. The visualization of the molecular structures has been done using the MOLDEN software [40].

3. Results and discussion

3.1. Electronic structure of PACO in the ground (S_0), first (S_1) and second (S_2) excited states

The ground state (S_0) equilibrium geometry of PACO in the gas phase has been optimized fully using density functional theory (DFT) employing B3LYP functional and cc-pVDZ basis set. The optimized geometry has been displayed in Fig. 1 and the key structural parameters have been reported in Table 1. The first two excited states (S_1 and S_2) of PACO have been optimized using TDDFT and same functional and basis set as their ground state counterpart. The excited state optimized structures have been shown in Fig. 2

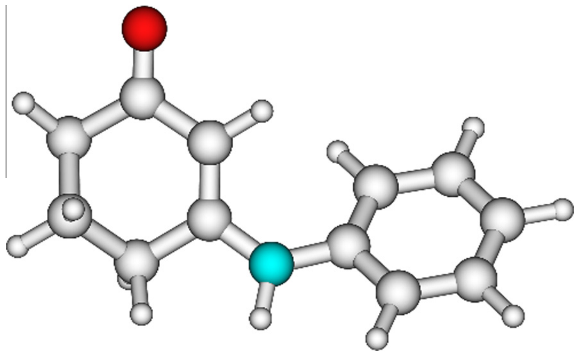

Fig. 1. The ground state (S_0) optimized structure of PACO as calculated using DFT, employing B3LYP functional and cc-pVDZ basis set.

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