



# Effects of hydrogen bonding between pyrrole-2-carboxaldehyde and nearest polar and nonpolar environment

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## ABSTRACT

The present paper represents dominant effects of hydrogen bonding on the existence of different molecular aggregates in one of the heterocyclic pyrrole system: pyrrole-2-carboxaldehyde (PCL). Theoretical and experimental Raman spectral evidence verifies the existence of different molecular aggregates like dimeric, monomeric, hydrated complex states in PCL. Atoms in molecules (AIMs) analysis and fluorescence decay profile provide a strong signature of intermolecular hydrogen bonding ( $I_{er}HB$ ) as the possible reason for the existence of cis form of dimeric (X) molecular aggregates. The high remnant polarization of  $3.13 \mu\text{Ccm}^{-2}$  and smaller dielectric loss in solid form of PCL arise due to in X by ordering of dipoles as a result of  $I_{er}HB$ . A remarkable high ferroelectric response in solid phase makes PCL a desirable candidate to be used as raw material for energy storage devices. For solution phase, in presence of external hydroxylic environment, PCL reacts with external water molecules through weak  $I_{er}HB$  and creates different hydrated  $\text{PCL}/(\text{H}_2\text{O})_n$  complexes by creating water bridge with number of water molecules from 1 to n. An increasing number of water molecules helps to form stronger hydrated complex by separation of charges by lowering the transferring energy barrier.

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## 1. Introduction

Hydrogen bonded interactions dominate the physical properties of molecular systems from biological building blocks to nanoscale self-assembled structures [1–5]. It is perhaps the most extensively investigated class of weak interactions due to its contribution in the physical and chemical properties of water. It is prevalent in nature and shows its impact on structures and functions of most important biomolecules including amino acids, nucleotides etc. [6]. Hydrogen bond plays an active role in the formation of organic molecular crystal network [1,7,8]. It also plays a dominant role in reaction dynamics in liquids, ferroelectric and nonlinear optical responses in solid state materials etc. [9,10]. Molecular systems with intermolecular and intramolecular hydrogen bonding ( $I_{er}HB/I_{ra}HB$ ) can form dimeric, monomeric or complex structures in their different phases (solid, liquid, solution) [11]. Most organic systems having  $I_{ra}HB/I_{er}HB$  can form different cyclic dimeric/monomeric structures [11,12]. Five membered heterocyclic molecules are most important and largely available hydrogen bonded organic system where the carbonyl or carboxyl groups are responsible for the molecular arrangement [9,13]. Pyrrole group molecules are one of such heterocyclic system. Pyrroles and their derivatives are present in almost all possible natural products, pharmaceuticals, meta-materials and chlorophylls etc. [10,14,15]. Pyrrole-2-carboxylaldehyde (PCL) is one of the

pyrrole derivatives which is also a part of one of the bases of DNA. It is used as the flavor in commercial industry [16]. PCL is a heterocyclic molecule which contain amine group N—H as proton donor and carbonyl group C=O as proton acceptor. Both N—H and C=O moieties of PCL actively participate in the formation of  $I_{er}HB$  and  $I_{ra}HB$ . PCL is capable of establishing an  $I_{ra}HB$  within itself [16] and  $I_{er}HB$  with its neighboring environment. PCL can form cyclic dimeric structure by making  $I_{er}HB$  [12] between two monomers and can form complex due to interaction with the environment. Vibrational spectroscopy helps elucidate the structures of interactions in a specific molecular system. Vibrational Raman spectroscopy is a powerful tool for the study of the effects of weak hydrogen bonded interactions by changes in the spectral wavenumber. In terms of spectral shift and changes in intensity allow us to ascertain exactly which atoms and bonds are affected due to hydrogen bonding and up to what extent. In the present work Raman spectroscopy of hydrated PCL water clusters were used to study the effects of water through the shifting of the normal modes. Here we present a detail theoretical and experimental Raman spectroscopic study of hydrogen bonding between PCL molecules in solid phase and between PCL and water molecules in solution phase, in view of their probable applications in industry.

In this work we will report the molecular structure, characteristics of  $I_{er}HB/I_{ra}HB$  and different properties of hydrogen bonded compound PCL and its solvent effects by using density functional theory (DFT). This work is a part of a systematic theoretical and experimental investigation of the different dimeric, monomeric structures of PCL in solid and liquid phases and different solvents. PCL behaves differently in solid and liquid

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phases because of  $I_{\text{er}}\text{HB}/I_{\text{ra}}\text{HB}$ . PCL shows good performance in terms of reversibility and stability as a charge storage device, which may have a useful implication in designing memory devices. To study the existence of different species we have used time correlated single photon counting technique. We have also used impedance spectroscopy, to study charge polarization on PCL. To uncover the mechanism of PCL's different optical behavior in its different phases we have used AIMs (atom in molecules) analysis to explain how low energy structure of PCL hydrogen bonded to another PCL or water to make hydrated complex by  $\text{N}-\text{H}\cdots\text{O}$ , and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonding bridge. AIM analysis is used to elucidate the transfer of charge from acceptor to donor in a hydrogen bonded complex. We have analyzed the changes in the electron density in the nitrogen atom of amine group and carbon atom of carbonyl group as well as in the carbon-carbon and carbon-nitrogen bonds in the dimeric/monomeric and in hydrogen bonded hydrated complex of PCL. Changes in electron densities and Laplacians can demonstrate whether a molecule's  $I_{\text{er}}\text{HB}/I_{\text{ra}}\text{HB}$  are strengthened or weakened in various hydrogen bonded complexes.

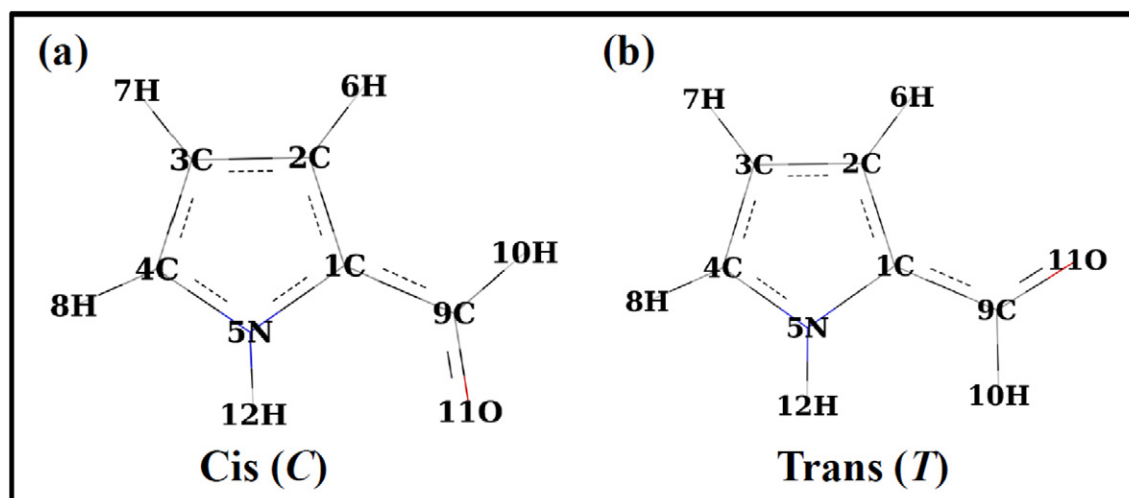
## 2. Materials and methods

PCL, tetrahydrofuran (THF), acetone, pentane and ethanol were purchased from Sigma-Aldrich and used after checking the purity fluorimetrically. Raman spectra were recorded by using a 532 nm excitation from a diode pumped frequency doubled Nd:YAG solid state laser (model GDLM-5015 L, 8 mW). Deionized water (Millipore) was used to measure the Raman spectra in solution form. The concentration of PCL used  $10^{-5}$  M in solution phase. P-E loop Tracer (Marine India) based on modified Sawyer-Tower circuit was used to measure the spontaneous polarization properties of molecules in the form of P-E loop. For P-E loop measurement sample was placed in P-E loop tracer in the form of a pellet of thickness approximately 10 mm. The dielectric constant ( $\epsilon_r$ ) and dielectric loss ( $\tan \delta$ ) of the PCL were measured in a wide frequency range (10 Hz–1 MHz) using LCR meter (Hioki 3522). The fluorescence decay profile [17] for PCL in solid phase was performed with a time resolved fluorescence spectroscopic systems on a time correlated single-photon counting (TCSPC) system, HORIBA Jobin Yvon. The probe molecule has been excited by NanoLED with 260 nm light. NanoLED is used to generate short optical pulses (70 ps) over a wide range of repetition rates and wavelengths. NanoLEDs have a unique structure that consists of 40-nm-thick nanodisks sandwiched between two layers of nanorods.

## 3. Computational details

All the theoretical calculations were carried out using the Gaussian 09 program [18]. We build molecular geometries of conformers of PCL

and other hydrated PCL for molecular calculations by using Gauss View 5 molecular visualization computational program [19]. The numbering of the probe molecules was provided randomly. All atoms were placed in order to adjust molecular geometry according to a predefined set of rules and then by imposing symmetry restriction on conformers of PCL we achieved the actual geometry. For the ground state geometry, we performed simulations in various phases of PCL like dimer and PCL with different external water molecules. The probe system was optimized with density functional theory (DFT) using B3 [20] exchange functional combined with the LYP [21] correlation functional resulting in the B3LYP exchange correlation functional, which combines the hybrid functional of Becke with the gradient-correlation functional of Lee et al., and the split-valence polarized B3LYP/6-311++G (d, p) basis set. In optimization calculation, with initial wave function the potential energy of a starting probe geometry has been computed and then searches a new geometry of a lower energy by varying different geometrical parameters like bond length, bond angles etc. This procedure is repeated until the lowest energy geometry is found. The stability of the molecule is checked by verifying the existence of imaginary (negative) frequencies. In our case no imaginary frequencies exist. Computed Raman modes are obtained by frequency calculation. Frequency calculations are valid only at stationary points on the potential energy surface. So the frequency calculations were performed on optimized structures. Frequencies are used to predict Raman modes and entropy of the system. Frequency job begins by computing the energy of the input structure. The entropy ( $S$ ) of the probe molecule is calculated using  $G = H - TS$ , where  $H$  is the enthalpy,  $G$  is the Gibbs free energy and  $T$  is the temperature for probe system. All the computations for the system are carried out at  $T = 298.15$  K and 1 atm pressure. To visualize the vibrational normal modes, Raman modes Gauss View 5 molecular visualization program [19] was used. We have used scaling factor 1 for frequency calculations. The solvent effects on molecular geometries were studied by using the polarized continuum model (PCM) [22]. In implicit solvation model the probe molecule placed inside a cavity in a continuous homogenous dielectric medium which represents the solvent. We have used water and acetone as solvents. The gas phase optimized geometries are used to study the solvent effects. To calculate atomic charges and its related properties we have used the theory of atoms in molecules (AIM). Theory of AIM uses electron density ( $\rho$ ), its gradient ( $\nabla\rho$ ) and Laplacian of electron density ( $\nabla^2\rho$ ) to define the chemical properties such as bonds between atoms and atomic charges within molecule [23]. AIM theory defines an atom as a region of three dimensional space bounded by a zero flux surface where the gradient of electron density has no perpendicular component. The nucleus within the atom is considered as local maximum in terms of electron density. So the



Scheme 1. Different structures of pyrrole-2-carboxaldehyde monomers: cis (C) and trans (T).

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