



Spectroscopic, optical, thermal, antimicrobial and density functional theory studies of 4-aminopyridinium 4-hydroxy benzoate hydrate crystal



P. Karthiga Devi ^{a,*}, K. Venkatachalam ^a, M. Poonkothai ^b

^a Department of Physics, Government Arts College, Coimbatore, Tamil Nadu, India

^b Department of Zoology, Avinashilingam Institute for Home Science & Higher Education for Women, Coimbatore, Tamil Nadu, India

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ABSTRACT

The organic crystal 4-aminopyridinium 4-hydroxy benzoate hydrate was grown using slow evaporation method. Various characterization techniques such as single crystal X-ray diffraction, powder X-ray diffraction, FTIR, UV–visible–NIR spectroscopy and thermal analysis (TG–DSC) were employed to assay the structure and properties of the grown crystal. The antimicrobial evaluation of 4-aminopyridinium 4-hydroxy benzoate hydrate crystal was also performed against some bacteria and fungi. The minimum inhibitory concentration (MIC) values of 4-aminopyridinium 4-hydroxy benzoate hydrate were determined for bacterial and fungal strains. The assessment of optimized structure of the molecule and vibrational frequencies were done using DFT/B3LYP method with 6-31 G (d, p) basis set. The stability of the molecule, hyperconjugative interactions, delocalization of charges and intermolecular hydrogen bond were studied by applying natural bond orbital (NBO) analysis. TD-DFT method employing polarizable continuum model (PCM) was used to examine the electronic absorption spectrum. Evaluation of molecular electrostatic potential (MEP), Mulliken population charges and nonlinear optical (NLO) properties were also carried out. In addition, from the optimized geometry, frontier molecular orbitals analysis was executed.

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1. Introduction

The assimilation of supramolecular synthons between common functional groups is the onset in crystal engineering [1]. S. K. Seth et al. reported different supramolecular structural diversities and interactions between molecules in acetophenone and chromone derivatives and naphthyridine co-crystals [2–4].

The co-crystallization of aminopyridine and carboxylic acids has been reported earlier. The structural study of the compound 4-aminopyridinium 4-nitrobenzoate 4-nitrobenzoic acid has been reported by C. K. Quah et al. [5]. The structure of 2-aminopyridinium maleate maleic acid has been reported [6]. Literature shows that 2-aminopyridinium benzoate (2-APB) crystal has been grown and studied through several characterization techniques [7]. A thorough investigation on the effective and particular identification of the acid-pyridine synthon [8–10] and

amine-phenol synthon [11–16] has been reported. An elaborate study of formation of supramolecular assemblies associated with lone pair- π interactions, π - π interactions and anion- π interactions have been done [17–21].

Acid-pyridine is a strong and popular synthon for designing crystals when it exists in different crystal structures, that is, two functional groups simultaneously [1]. Etter's [22] hydrogen bond rule proves that 1) in a crystal structure of a compound all hydrogen atoms of acid which are present in a molecule will be utilized for hydrogen bond formation. 2) For all hydrogen bond donors, all good proton acceptor will be expended in the formation of hydrogen bond. 3) Hydrogen bonds will be formed between the most excellent hydrogen bond donor and the most excellent hydrogen bond acceptor. At physiological pH 4-aminopyridine which is found to be biologically active exists in neutral/ionic form [23]. It is prominent that antioxidants are molecules strong enough to prevent the oxidation of other molecules by eliminating free radicals thereby suppressing the chain reactions, and hinder other oxidation reactions by being oxidized themselves. Hydroxy-benzoic acids are found to be excellent antioxidants and activate

* Corresponding author.

E-mail address: karthvi19@gmail.com (P. Karthiga Devi).

apoptosis which is caused by fragmentation of DNA [24].

Antibiotic activity is exhibited by a great number of quaternary ammonium and pyridinium salts by means of adsorption on the cell membrane and building up ensuing changes in the organization of cells of microbes such as bacteria, fungi, protozoa, etc. [25] Hence, the antimicrobial evaluation of the 4 aminopyridinium 4 hydroxy benzoate hydrate crystal was also carried out against some fungi and bacteria.

The nonlinear optical (NLO) characteristics of several large organic molecules and polymers have been investigated by theoretical and experimental methods for the past few years [26]. The unlimited architectural flexibility of the organic molecules allows them to be modified for designing and acquiring novel processible nonlinear optical (NLO) materials and their structures can be changed to acquire the preferred NLO properties [27]. The synthesis and characterization of NLO materials in the field of optoelectronics and photonics have been extensively used by many researchers for a long time [28].

In the present work, 4-aminopyridine and para hydroxy benzoic acid have been co-crystallized and is intended to achieve a dual approach (experimental and theoretical) on the investigation of FT-IR and UV–Vis spectra. The absorption spectrum of 4APPHBH was evaluated by using time-dependent density functional theory (TD-DFT) in the solution phase. In addition to, it is also intended to shed light on theoretical calculation of optimized geometry, HOMO–LUMO energy gap, molecular electrostatic potential map, NLO characteristics, Mulliken charges and NBO analysis of the title compound by using density functional theory (DFT) with B3LYP/6-31G(d,p) basis set.

2. Experimental and theoretical methods

The lattice parameter values of 4APPHBH single crystal were estimated using ERNAF NONIUS CAD4 single crystal X-ray diffractometer. The FTIR spectrum of 4APPHBH was recorded in the range of 4000–400 cm^{-1} on Bruker FTIR spectrometer using KBr pellet technique. UV–Vis analysis of the grown crystal was made between 200 and 1500 nm using JASCO UV–Vis–NIR spectrometer in water solvent. TG-DSC assay was done in the temperature range of 30 °C to 500 °C using the NETZSCH STA 449F3 thermal analyzer under nitrogen atmosphere to study the thermal properties of the grown crystal.

4-Aminopyridinium para hydroxy benzoate hydrate was prepared from a solution containing equimolar amounts of para hydroxy benzoic acid (1.38 g, 10.0 mmol) and 4-aminopyridine (0.94 g, 10.0 mmol) in water. The solution was stirred in a magnetic stirrer for 3 h and filtered through Whatmann filter paper to remove any impurities present in the solution. The solution was allowed to evaporate slowly and single crystals were harvested after a time span of 15 days. Crystals appropriate for X-ray study were obtained by recrystallizing the compound repeatedly. Single crystal grown from the saturated solution of 4APPHBH is shown in Fig. S1. (supporting information).

2.1. Computational details

The molecular structure of 4APPHBH has been elucidated theoretically with Gaussian09 program using the DFT (B3LYP) level of theory at 6-31 G (d, p) basis set and vibrational wave numbers have been estimated. The nonexistence of imaginary wave numbers of the theoretically calculated vibrational spectrum affirms that the structure that has been deduced corresponds to minimum energy. In order to correct anharmonicity in the vibrational modes, a scaling factor of 0.967 has been used to scale the wave numbers and the assignments were aided by VEDA program.

3. Result and discussion

3.1. Optimized geometry

The optimized structure of 4APPHBH is shown in Fig. 1. The bond lengths and bond angles for the optimized structure corresponding to the experimental values obtained by x-ray diffraction method [1] are listed in Table 1. Generally strong bonds are formed due to large overlap which tends to reduce the bond length. Hence a strong bond will have a short bond length [29]. Strong bonds are formed between N18–C19, N18–C25, C14–O3, O1–H15 and O3–H31 for 4APPHBH because they have shorter bond lengths than others. For the title compound, the C=O bond length is elongated to 1.34 Å and C–O bond length is shortened to 1.36 Å. The calculated C–H bond lengths are found to be around 1.08 Å while the experimental values are around 0.93 Å. It is observed that there is a slight variation in the calculated geometrical parameters and the experimental ones because the experimental parameters are calculated in solid phase whereas the theoretical parameters are calculated in gas phase (see Table 2).

The deviation of the calculated structure from the structure determined by X-ray diffraction is illustrated with a RMSD error value of 0.64 Å. This value of error may be attributed to the aspect that X-ray structure was solved in a crystalline form whereas the optimized structure was calculated for isolated molecule. The optimized structure of 4APPHBH is superimposed on the crystal structure and is presented in Fig. 2.

3.2. X ray diffraction analysis

The lattice parameter values of 4APPHBH single crystal were estimated using ERNAF NONIUS CAD4 single crystal X-ray diffractometer. 4APPHBH crystal appertains to triclinic crystallographic system with space group $P\bar{1}$. The unit cell parameters are $a = 7.481 \text{ \AA}$ $b = 11.74 \text{ \AA}$ $c = 14.31 \text{ \AA}$ and $\alpha = 87.59^\circ$ $\beta = 77.95^\circ$ $\gamma = 83.63^\circ$. It has been found that the values match well with the reported values [1]. The asymmetric unit contains two 4-aminopyridinium, two 4-hydroxy benzoate and two water molecules. Structures of materials can be elucidated using powder diffraction method which is based on the principle of X-ray, electron or neutron diffraction [30]. The recorded powder X-ray diffraction pattern of 4APPHBH sample is displayed in Fig. 3. The crystalline character of the material is established by the sharp and apparent Bragg peaks at particular angles.

3.3. FTIR analysis

The FTIR spectrum of 4APPHBH was recorded in the range of 4000–400 cm^{-1} on a Bruker FTIR spectrometer using KBr pellet method and the observed spectrum is shown in Fig. 4. The spectral assignments are specified in Table 2. In the experimental FTIR spectrum the absorption band at 3372 cm^{-1} is due to NH asymmetric stretching whereas it corresponds to 3371 cm^{-1} in the calculated FTIR spectrum. C–H vibration gives a band at 3154 cm^{-1} in the experimental IR spectrum and at 3154 cm^{-1} in the calculated IR spectrum. The absorption bands at 2872 cm^{-1} and 2786 cm^{-1} are assigned to C–H symmetric and asymmetric stretching in the experimental IR spectrum and the C–C stretching band appears at 1596 cm^{-1} . A strong asymmetrical stretching band around 1638 cm^{-1} and a weaker symmetric stretch at 1442 cm^{-1} are displayed by the carboxylate ion in the experimental FTIR spectrum and these two vibrations are indicated by the absorption bands at 1640 cm^{-1} and 1439 cm^{-1} in the calculated IR spectrum of the title compound. The results directly associates with the transfer of proton from acid to nitrogen atom of pyridine. The absorption band

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