Journal of Molecular Structure 1074 (2014) 107–117

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Synthesis, structure, spectral, thermal analyses and DFT calculation of a hydrogen bonded crystal: 2-Aminopyrimidinium dihydrogenphosphate monohydrate

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HIGHLIGHTS

- 2APDHP have been grown by the slow evaporation technique.
- Theoretical study was attempted by the Density Functional Theory.
- Spectroscopic properties were observed by FT-IR and Raman techniques.
- NBO analysis of the title molecule were studied.
- Thermal studies of the title compound was analyzed by TGA/DSC.

ARTICLE INFO

Article history:
Received 14 March 2014
Received in revised form 21 May 2014
Accepted 23 May 2014
Available online 4 June 2014

Keywords:
Crystal growth
Hydrogen bonding
FT-IR and Laser Raman spectra
TGA/DTA/DSC studies
Factor group analysis
DFT

ABSTRACT

A proton transfer complex of 2-aminopyrimidine with phosphoric acid was synthesized and crystallized. Single crystal X-ray studies, the vibrational spectral analysis using Laser Raman and FT-IR spectroscopy in the range of 4000–400 cm^{-1}, UV–Vis-NIR studies and thermogravimetric analyses were carried out in the solid crystalline form. The single crystal X-ray studies shows that the crystal packing is dominated by N—H···O and O—H···O hydrogen bonds leading to a hydrogen bonded ensemble. The two dimensional cationic layers, connected through the centrosymmetric anionic dimer of $R_2^2(8)$ motif, is extending along *ab* plane of the crystal leading to zig-zag infinite chain $C_2^1(6)$ and $C_2^2(6)$ motifs. To investigate the strength of the hydrogen bonds, vibrational spectral studies were adopted and the shifting of bands due to the intermolecular interactions were analyzed. Density Functional Theory (DFT) using the B3LYP function with the 6-311++G(d,p) basis set was applied to the solid state molecular geometry obtained from single crystal X-ray studies. The optimized molecular geometry and computed vibrational spectra are compared with experimental results which shows appreciable agreement. NBO analysis has been carried out by DFT level. In this study explains charge delocalization of the present molecule which shows the possible biological/pharmaceutical activity of the molecule. The number of normal modes were also attempted by the factor group analysis method. It is evident that the influence of extensive intermolecular hydrogen bonds reduces the T_d symmetry of the phosphate anion to the lower C_{2v} symmetry. The existence of exothermic peaks in DTA iterate the breaking of intermolecular hydrogen bonds and the phase change of the crystal. The presence of water molecule is also confirmed in the thermal analyses.

Introduction

Derivatives of pyrimidine play an essential role in many biological and pharmacological processes. Pyrimidines occur widely in the DNA and RNA in many forms. The large number of amino substituted pyrimidines as antagonists of folic acid [1] was observed in the 1948. The enzyme of dihydrofolate reductase (DHFR) is amino substituted pyrimidine drug, which act as a inhibitor of malarial plasmodia [2,3]. Many of the pyrimidine derivatives are found with the activities such as antibacterial, antineoplastic, antiviral, antifungal and anti-cancer agent [4–8].

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http://dx.doi.org/10.1016/j.molstruc.2014.05.054
0022-2860/

The biological properties of pyrimidines arise due to their tendency of making extensive intermolecular contacts, which are playing essential role in molecular recognition and crystal engineering [9,10]. Because of their strength as well directional nature compared with other intermolecular non-covalent interactions, hydrogen bonds are normally used as a tool in designing the structure of the organic crystals [11]. Crystal engineering or the design of organic crystals with the specific physical and chemical properties continues to elicit intense interest. This new subject encompasses a wide variety of research activity ranging from the understanding of crystal packing in organic and semi organic crystals to the design of open network structures. This structure extension property through non-covalent interactions was recognized as a possible tool for promoting cocrystallization [12]. As it is known that co-crystals are crucial for the production of pharmaceutical compounds. The most widely used application is in drug development and more specifically, the formation, design and implementation of active pharmaceutical ingredients (API's) [13].

Based on the above facts, the synthesis of new semiorganic crystal, which contains the inorganic frame work was attempted here. The tendency of making extensive hydrogen bonding network was exploited here to obtain the hydrogen bonded crystal, namely 2-aminopyrimidinum dihydrogenphosphate monohydrate (2APDHP) single crystal. In the present study, 2APDHP was performed by combining the single crystal X-RD, thermal studies, experimental and theoretical vibrational spectral analysis using DFT to derive information about electronic effects and intermolecular charge transfer responsible for biological activity. Though the molecular structure already reported with single crystal X-ray studies [14], a detailed account on hydrogen bonding network attempted here.

Experimental details

Material preparation

The commercially available 2-aminopyrimidine (2AP) ($C_4H_5N_3$) (Alfa Acer, purity > 98%) is a weak Bronsted base and can acquire a proton in a strongly acidic aqueous medium at lower pH, leading to the formation of salts. The formation of 2APDHP on chemical reaction with orthophosphoric acid is indicated as molecular structures in Scheme 1. The 2APDHP crystal is obtained by slow evaporation method of dissolving 2AP in an orthophosphoric acid solution at room temperature in the molecular ratio 1:1. The good quality single crystals with the maximum dimensions of 9 × 4 × 2 mm were harvested after a distinctive growth within the period of two weeks. The grown single crystals with the sharp edges in developed faces, are shown in Fig. 1.

X-ray crystal structure determination

The unit cell parameters and the crystal structure were determined from single-crystal X-ray diffraction data obtained

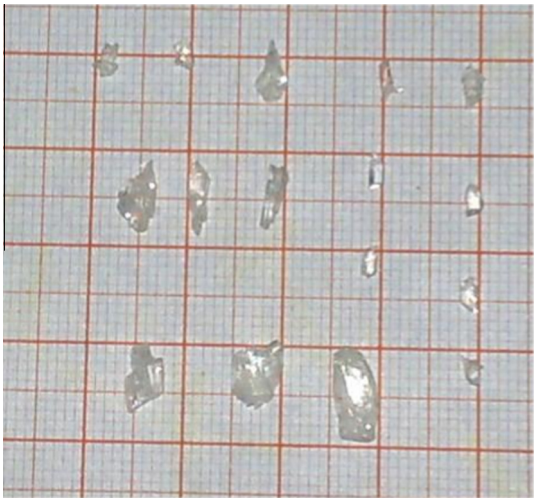
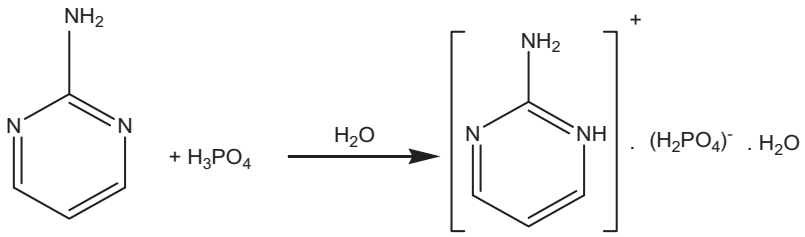


Fig. 1. As-grown single crystals of 2APDHP.

with a Bruker SMART APEX CCD area detector diffractometer (graphite-monochromated, Mo Kα = 0.71073 Å). The observed cell values were compared with reported structure [14]. The data collection, cell refinement and data reduction were made using SAINT program [15]. The structure solution, structure refinement and the related calculations were performed using SHELXTL/PC [16]. The structure was solved by direct methods, and full-matrix least-squares refinements were performed on F^2 using all unique reflections. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters and hydrogen atoms were refined isotropically. The H atoms participating in hydrogen bonds were located from difference Fourier map and all the other hydrogen atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å $U_{iso}(H) = 1.5U_{eq}$(parent). Drawings of the molecular structure and the packing diagram were obtained using Mercury [17] and PLATON [18] programs respectively. Further crystal data, experimental conditions, and structural refinement parameters are presented in Table 1.

Computational details

The entire theoretical calculations were performed at Density Functional Theory using Gaussian 03W [19] program package, invoking gradient geometry optimization [20]. The first task for the computational work was to determine the optimized geometry of the compound. The spatial coordinate positions of 2APDHP, as obtained from an X-ray structural analysis, were used as the initial coordinates for the theoretical calculations. At B3LYP level, initial geometry was minimized without any constraint in the potential energy using the 6-311++G(d,p) basis set. The optimized structural parameters were used to calculate vibrational frequencies. Then vibrationally averaged nuclear positions of 2APDHP were used



Scheme 1. Reaction of 2AP with Orthophosphoric acid.