Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 145 (2015) 394–409

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Structural and vibrational spectroscopic studies on charge transfer and ionic hydrogen bonding interactions of melaminium benzoate dihydrate

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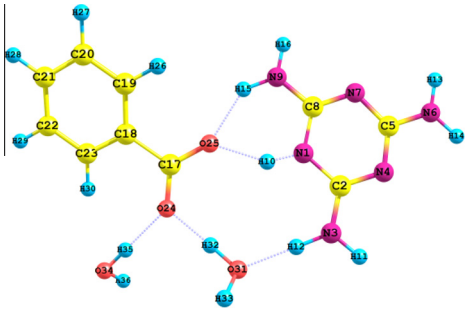
HIGHLIGHTS

- Synthesized by the slow solvent evaporation method.
- The experimental and theoretical study on the vibrations of MBDH is presented.
- The optimized geometrical parameters are in agreement with experimental values.
- HOMO–LUMO energy levels and MEP were constructed.
- ^{1}H and ^{13}C NMR reveals the structure of the compound.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 September 2014
Received in revised form 21 February 2015
Accepted 1 March 2015
Available online 10 March 2015

Keywords:
FT-IR spectroscopy
FT-Raman spectroscopy
Hydrogen bonded molecular crystal

ABSTRACT

Single crystals of melaminium benzoate dihydrate (MBDH) have been grown from aqueous solution by the slow solvent evaporation method at room temperature. Crystalline nature of the grown crystal has been confirmed by X-ray powder diffraction studies. The optimized geometry, frequency and intensity of the vibrational bands of MBDH were obtained by the Hartree–Fock and density functional theory using B3LYP/cam-B3LYP with 6-311++G(d,p) basis set. The harmonic vibrational frequencies were calculated and the scaled values have been compared with the experimental FT-IR and FT-Raman spectral values. The obtained vibrational wavenumbers and optimized geometric parameters are found to be in good agreement with the experimental data. UV–Visible spectrum was recorded in the region 200–400 nm and the electronic properties, HOMO–LUMO energies and other related electronic parameters are calculated. The isotropic chemical shifts computed by ^{1}H and ^{13}C NMR analysis also show good agreement with experimental observation. Natural bond orbital (NBO) analysis has been performed on MBDH compound to analyze the stability of the molecule arising from hyperconjugative interactions and charge delocalization. Molecular electrostatic potential surface (MEP) has also been performed by DFT/cam-B3LYP method with 6-311++G(d,p) basis set. Differential scanning calorimetric measurements performed on the powder sample indicate the phase transition point approximately at 368 and 358 K for heating and cooling, respectively.

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http://dx.doi.org/10.1016/j.saa.2015.03.002
1386-1425/

Introduction

Crystal Engineering is now a rapidly developing interdisciplinary field with a wide scope for basic research and promising industrial applications. Crystal Engineering of organic solids, especially with respect to understanding the nature of various intermolecular interactions, has influenced the concepts of supramolecular chemistry. Supramolecular chemistry is the chemistry of molecular aggregates assembled via non-covalent interactions [1,2]. Hydrogen bonding and π–π interactions are frequently employed as driving forces to give well defined supramolecular architectures [3]. Melamine is an interesting molecule in the field of crystal engineering [4] and supramolecular chemistry [5]. Melamine and its salts are well known fire retardant additive systems for many polymeric materials. It has been used in the production of melamine–formaldehyde resins for surface coatings, laminates and adhesives. This melamine molecule is of great interest in recent years because of the tautomerization it undergoes with the substitution of an OH or SH group in the carbon adjacent to the ring nitrogen. This tautomerization results in the formation of C═O or S═O functional group. Furthermore, the protonation of melamine occurs in the ring nitrogen atom results in tautomerization to form an exogenous = NH_2^+ group and has unique identifying IR bands [6,7]. This behavior enables melamine to be both an excellent hydrogen bond donor and acceptor. Melamine and its organic/inorganic complexes can develop well defined supramolecular structures via multiple hydrogen bonded system. Thus the molecule is also prone to the formation of hydrogen bonded dimmers, which have been utilized to study self assembling systems. Benzoic acid is the simplest aromatic acid, which is used as a building block for the synthesis of alkyd resins and serves as an intermediate chemical in the biosynthesis of many secondary metabolites. It has many biomedical applications, especially they are good inhibitors for influenza viruses and it is also mainly used in industrial settings. The vibrational (both IR and Raman) spectroscopy of both melamine and benzoic acid have already been discussed [6–8]. Larkin et al. [9] have already reported the normal modes of s-triazine by infrared and Raman spectral analysis with *ab initio* force field calculations. Larkin [7] discussed the IR and Raman spectra of melamine in DMSO solution, in particular with regard to the NH_2 stretching (doublet) observed due to equal hydrogen bonding. Vibrational spectra and normal mode calculations of benzoic acid single crystals were reported by Klausberger et al. [10]. Melamine and benzoic acid were chosen as the subject of present study to know the molecular structure and the spectral features of their complexes. The COO^- group in benzoic acid is an excellent hydrogen acceptor whereas the amino group in melamine is an excellent hydrogen donor. It is interesting to note that the crystallization of melamine and benzoic acid in water solution gives rise to various hydrogen bonded patterns and forms a three dimensional network structure. The melamine molecule tautomerizes into iso form (melaminium cation) and forms a hydrogen bonded dimer with the carboxylic acid of benzoic acid. The crystal structure of MBDH was reported by Perpetuo et al. [11]. The asymmetric unit of MBDH ($C_3H_7N_6^+ \cdot C_6H_5COO^- .2H_2O$) consists of singly protonated melaminium cations, benzoate anions and water molecules. In the present study, the structure has been determined by X-ray powder diffraction study. Also in this communication, a detailed interpretation of spectral studies, like IR, Raman, UV–Visible and NMR are reported along with quantum chemical studies for the first time.

Experimental

Preparation of MBDH

MBDH was synthesized from melamine and benzoic acid in the stoichiometric ratio 1:1. To the hot solution of melamine, the dissolved benzoic acid solution was added gently, and stirred well continuously for 5 h to get the homogeneous solution. The resulting solution was filtered and allowed to evaporate at room temperature, which yielded needle shaped crystals within a period of 20–25 days. The reaction scheme and the photograph of as grown crystals are shown in Fig. 1.

Characterization

X-ray powder diffraction data of MBDH crystal were collected at room temperature using Rich Seifert X-ray powder Diffractometer with CuK_α radiation (λ = 1. 5406 Å) in the 2θ range from 10° to 70° at a scanning rate of 1° min^{-1}. From the X-ray data, the various planes of reflections were indexed using XRDA 3.1 program and the lattice parameters were evaluated.

The FT-IR spectrum was recorded using Perkin Elmer spectrum one FT-IR spectrometer in the region 4000–400 cm^{-1} at room temperature using KBr pellet technique and each IR spectrum was

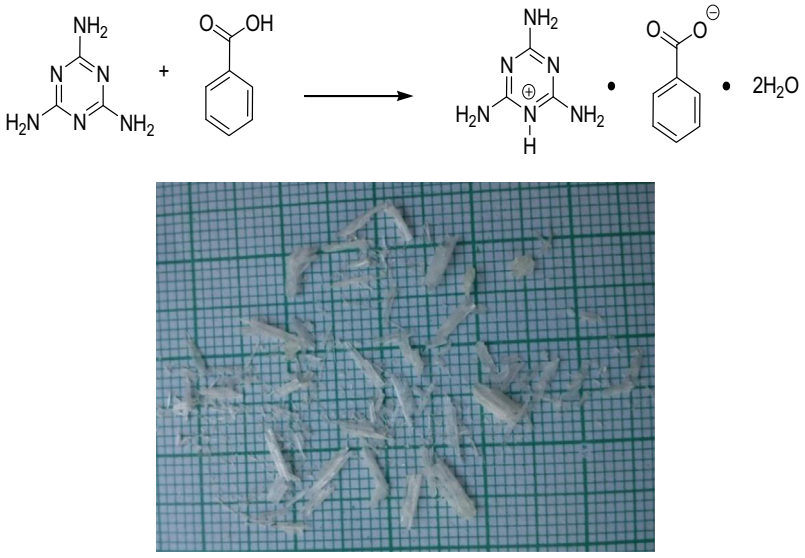

Fig. 1. Reaction scheme (top) and photograph (bottom) of as-grown MBDH crystals of MBDH.