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Synthesis, structure, spectral, thermal and first-order molecular hyperpolarizability of 4-benzoylpyridine isonicotinyl hydrazone monohydrate single crystals

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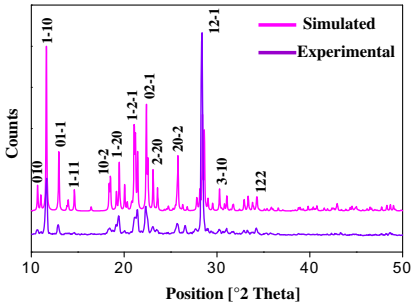
HIGHLIGHTS

- Synthesis and characterization of novel hydrazone derivative is reported.
- Product formation was confirmed by FT-IR and mass spectral studies.
- Structure is elucidated.
- First-order molecular hyperpolarizability is estimated.

GRAPHICAL ABSTRACT



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ABSTRACT

Single crystals of 4-benzoylpyridine isonicotinyl hydrazone monohydrate were grown by slow evaporation solution growth technique from ethanol at room temperature. It belongs to triclinic system with space group $P\bar{1}$ and the cell parameters are, $a = 8.9250(2)$ Å, $b = 9.1540(2)$ Å, $c = 10.87500(10)$ Å and $V = 797.88(3)$ Å^3. Powder XRD closely resembles with that of simulated pattern from single crystal XRD. The characteristic functional groups present in the molecule are confirmed by FT-IR and FT-Raman analyses. The crystal is transparent in the visible region having a lower optical cut-off at ~420 nm and the band gap energies are estimated by the application of Kubelka–Munk algorithm. Thermal analysis by TG/DTA indicates the stability of the material. The scanning electron microscopy studies reveal the surface morphology of the as-grown crystal. Mass spectrometry provides information pertaining to the structure and molecular weight of the compound. Theoretical calculations were performed using Hartree–Fock method with 6-31G(d,p) as the basis set for to derive the optimized geometry, dipole moment and first-order molecular hyperpolarizality (β) values.

1. Introduction

Hydrazone ligands create environment similar to biological systems by usually making coordination through oxygen and nitrogen atoms. Isonicotinoyl hydrazone analogs of isoniazid [1], an anti-tuberculosis drug is found to have superoxide scavenging activity [2]. 4-Benzoylpyridine as a mother compound forms complexes with transition metals [3–9] and co-crystallize with benzoic acids [10] and being derivatives with chlorine in the para position of the benzene ring [11]. Hydrazones and their metal compounds are of current interest for their physico-chemical properties and find applications in many important chemical processes that include sensors, nonlinear optics, medicine and others [12–17]. They are used as plasticizers, stabilizers for polymers and as polymerization initiators, antioxidants etc. Also, they act as herbicides, insecticides, nematocides, rodenticides and plant growth regulators. Many of the hydrazones find applications [18] in the treatment of diseases such as tuberculosis, leprosy and mental disorder [19,20]. Higher the charge transfer, larger is the

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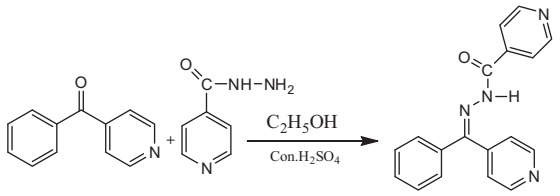
hyperpolarizability (β). These types of materials are chosen since they are very promising class due to large β values and the possibility of enhancing nonlinearity by molecular design. Extensive survey of literature reveals that the synthesis and growth of 4-benzoylpyridine isonicotinyl hydrazone monohydrate (BPIH) have not been reported so far to the best of our knowledge. In the present study, we report the synthesis, growth, structure, dipole moment and hyperpolarizability of BPIH. Further, the crystal is characterized by XRD, spectral and morphological studies.

2. Experimental

2.1. Synthesis and crystal growth

4-Benzoylpyridine isonicotinyl hydrazone monohydrate was synthesized by mixing stoichiometric amounts of 4-benzoylpyridine and isonicotinohydrazide in the molar ratio of 1:1. The reactants were dissolved in ethanolic medium with catalytic amount of concentrated sulphuric acid and refluxed for 3–5 h to form aryl acid hydrazone. The completion of the reaction was confirmed by thin layer chromatography. The reaction mixture was then poured in ice cold water and the precipitate obtained was filtered and dried. Purity of the compound was improved by recrystallization process using ethanol as a solvent.



BPIH single crystals were grown using slow evaporation solution growth technique at room temperature. A saturated solution in ethanol was prepared and the solution was stirred for 2–3 h at room temperature to obtain a homogenous solution. A beaker containing BPIH solution was tightly covered with a thin polythene sheet to control the evaporation rate of the solvent and kept undisturbed in a dust free environment. Numerous tiny crystals were formed at the bottom of the container due to spontaneous nucleation. Tiny crystals of BPIH were harvested after 3–4 days and the photographs of as-grown crystals are shown in Fig. S1 (see Supplementary data).

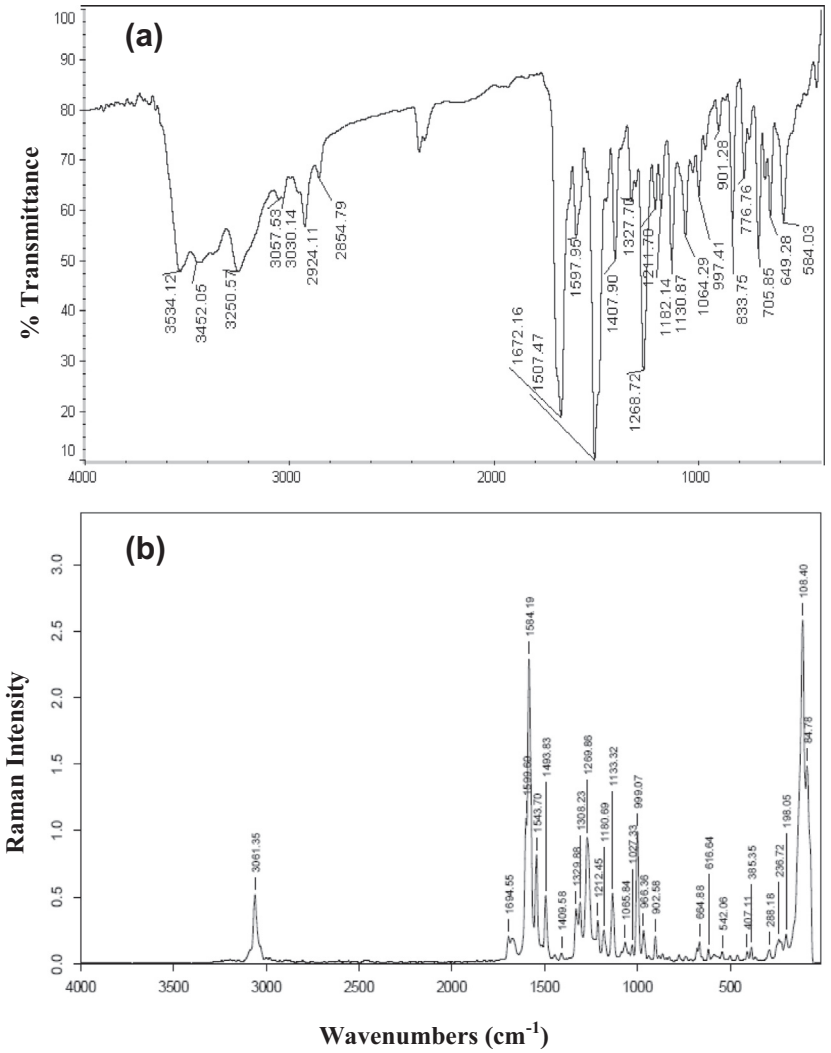


Fig. 1. (a) FT-IR and (b) FT-Raman spectra of BPIH.