



Investigations on spectroscopic, dielectric and optical studies in 3-hydroxypyridinium 4-nitrobenzoate crystals

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ABSTRACT

An organic crystal of 3-Hydroxypyridinium 4-nitrobenzoate (3HPNB) of size $3 \times 9 \times 3 \text{ mm}^3$ has been grown by the slow evaporation technique at room temperature. The cell parameters for the grown crystal were confirmed using X-ray diffraction method. FTIR, FTRaman and ^1H NMR spectral studies were carried out to confirm the functional groups present in 3HPNB. The theoretical factor group analysis of 3HPNB predicts the total number of the vibrational mode exhibited by the molecule. Thermogravimetric analysis reveals the melting point of 3HPNB. The observed UV cut-off wavelength 387 nm of the grown crystal confirms the suitability of this material for optical applications. The dielectric constant and dielectric loss of 3HPNB establishes the normal dielectric behaviour. The mechanical study for the sample was carried out. The first order hyperpolarizability and energies of HOMO-LUMO are also reported. Emission of green light and low value of second harmonic conversion efficiency of the sample of 3HPNB in Kurtz and Perry method reveals the suitability of the crystal for NLO applications.

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1. Introduction

Currently NLO materials have high potential applications in the field of optical computing, optical signal processing, optical communication and dynamic image processing [1,2]. Based on the need of high second order optical non linearity, stable physico-chemical property and stable transparency cut off, high quality NLO crystal has grown in past few decades. A Different variety of organic, inorganic and semiorganic materials and their molecular systems have been investigated for NLO activity. Due to high order electronic susceptibility structure modification through standard synthetic method, fast response time, organic NLO materials are attracting a great deal of attention over inorganic NLO materials [3]. Extended π -conjugated systems, as well as the presence of asymmetrical charge transfer, organic compounds have a high order of non linearity. Electron donating and electron accepting property of aromatic ring substituent are the reasons for charge transfer [4].

The electron donor-acceptor (EDA) or charge transfer (CT) complexes intrigued the crystal engineers due to their early interaction

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with the substrates [5]. This property of CT was recognized as possible tool for promoting crystallization. Pyridine is a good hydrogen bond acceptor and a strong organic base. Several pyridinium compounds like 4-methylpyridinium 4-hydroxybenzoate [6], Dimethyl amino pyridinium 4-nitrophenolate 4-nitrophenol [7], 2 aminopyridinium 4-methylbenzoate [8], Bis (2-aminopyridinium) maleate [9], 2 amino-5-nitro pyridinium L-tartrate [10] have interesting physical properties such as dielectric, hardness and non-linear optical properties. 3-Hydroxypyridine (3-HP) has a hydrogen bond donating hydroxy group and one hydrogen bond accepting heterocyclic nitrogen. It is also the active unit in pyridoxine with pKa value 8.65.

A Crystalline molecular complex of 3-hydroxy pyridine is formed with carboxylic acid by proton transfer through the hydrogen-bonding network. Proton transfer occurs when pKa value difference between acid and base exceed 3.75. Benzoic acid with an electron withdrawing group (NO_2) is more acidic in nature with lower pKa value. 4-nitro benzoic acid has pKa value of 3.44. The titled compound 3HPNB has a three dimensional framework. A polymeric structure is formed between 3-hydroxypyridine and 4-nitrobenzoic acid that are linked into a three dimensional supra-molecular framework by $\text{N-H}\cdots\text{O}$, $\text{O-H}\cdots\text{O}$ hydrogen bonds and $\text{C-H}\cdots\text{O}$ interactions with nitro oxygen. 3 hydroxypyridinium 4-nitrobenzoate (3HPNB) is also a member of pyridinium family

and forms organic salt complex of 3-hydroxypyridine with nitro substituted aromatic carboxylic compound. In this article the details of the synthesis, crystal growth, spectroscopic studies, optical properties, hardness and SHG efficiency of 3HPNB are reported.

2. Synthesis and crystal growth

3HPNB was synthesized from 3-hydroxypyridine and 4-nitro benzoic acid of analytic grade taken in stoichiometric amounts of equimolar ratio. The saturated solution was prepared separately by dissolving 3-hydroxy pyridine and 4-nitro benzoic acid in ethanol. The solution was mixed together and stirred continuously about 4 h in an airtight container maintained at a constant temperature to yield a homogenous mixture of the solution and the pH value was 4. The homogeneous solution was filtered by grade one Whatman filter paper and kept in air tight container. The reaction scheme of 3HPNB is given in Fig. 1. Selecting of solvent is very important for the growth of good quality crystal. Solubility curve for this crystal is shown in Fig. 2. Different organic solvents viz ethanol, methanol and acetone were used for the growth of 3HPNB and investigated. Properties of solvent like molecular weight, polarity, hydrogen bond interactions and dipole moments are the major factors that influence crystals habits and crystal growth on nuclei. Crystallizing of 3HPNB using acetone crystals were obtained after span of 10 days in spurious form while crystallizing in methanol, crystals were harvested after span of 5 weeks in nontransparent, platelet form. Transparent with good morphology crystals were harvested after a period of 20 days with $3 \times 9 \times 3 \text{ mm}^3$ dimension with ethanol and it was used for various characterizational studies. Grown crystals from ethanol and methanol are shown in Fig. 3a and b. Morphology of 3HPNB was stimulated using Win X morph software [11]. The morphology of the titled compound is shown in Fig. 4.

3. Single crystal XRD analysis

X-ray diffraction intensity data of 3HPNB were collected on Bruker axis SMART APEXII single crystal X-ray diffractometer. The crystal structure of 3HPNB belongs to the triclinic system to space group of P1 and the number of molecules per unit cell is $Z = 4$. The unit cell dimensions of grown crystal obtained by X-ray diffraction are $a = 7.2006 (7) \text{ \AA}$, $b = 10.7782 (10) \text{ \AA}$, $c = 25.215 (2) \text{ \AA}$, $\alpha = 97.978 (2)^\circ$, $\beta = 94.526 (2)^\circ$, $\gamma = 103.135 (2)^\circ$. The obtained lattice parameters from the single crystal X-ray diffraction were well suited with the literature [12] values. The comparative values of cell parameters are tabulated in Table 1.

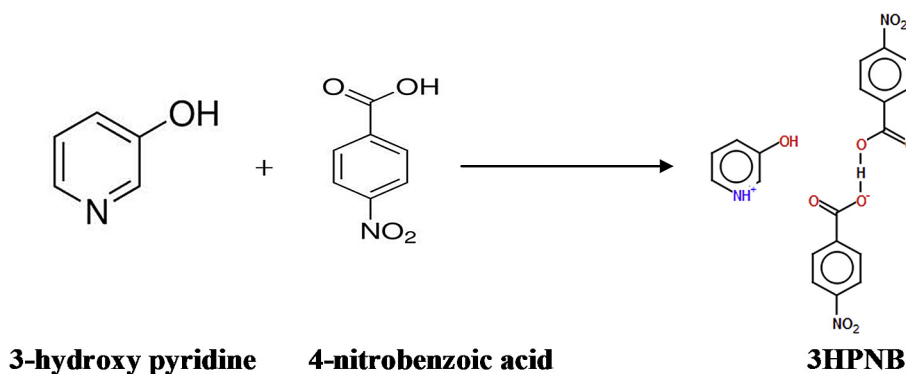


Fig. 1. Reaction scheme of 3HPNB.

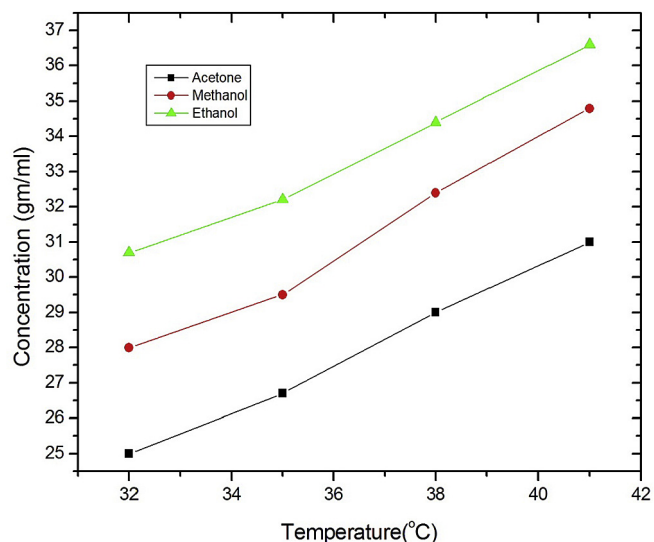


Fig. 2. Solubility curve of 3HPNB.

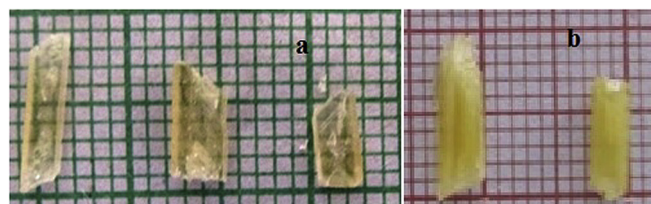


Fig. 3. Grown crystal of 3HPNB in (a)Ethanol and (b)Methanol.

4. Vibrational analysis

4.1. Factor group analysis

The 3HPNB crystal crystallizes in the monoclinic system, $P\bar{1}$ space group, C_1 point group and molecule has 46 atoms ($Z = 4$). The total vibrational mode of 3HPNB crystal is 552, it is determined by using Factor group analysis method., which can be decomposed according to the irreducible representation of the point group as 549 optical modes ($274A_g + 275A_u$) along with three acoustic modes ($2A_g + A_u$). The acoustic modes correspond to the translations of free molecule, which lead to inactive Infrared (IR) and Raman mode in the crystal. The total vibration modes predict 528 internal vibrations which can be distributed as ($264A_g + 264A_u$) and 24

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