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Crystal growth, spectral, optical and thermal properties of semiorganic nonlinear optical material: Picolinic acid hydrochloride

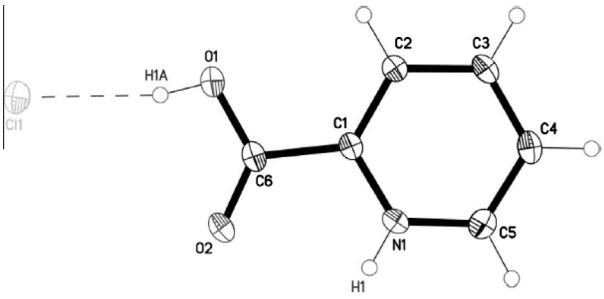
S. Gowri [a], T. Uma Devi [b,*], D. Sajan [c], C. Surendra Dilip [d], A. Chandramohan [e], N. Lawrence [f]

[a] Department of Physics, Cauvery College for Women, Tiruchirappalli 620 018, India
[b] Department of Physics, Government Arts College for Women (autonomous), Pudukottai, India
[c] Department of Physics, Bishop Moore College, Mavelikara, Alappuzha, 690 110 Kerala, India
[d] Department of Chemistry, BIT Campus, Anna University, Tiruchirappalli 620 024, India
[e] Department of Chemistry, SRMV College of Arts and Science, Coimbatore, Tamilnadu, India
[f] Department of Physics, St. Joseph's College (autonomous), Tiruchirappalli, 620 018, India

HIGHLIGHTS

- PHCL crystallizes in orthorhombic crystal system.
- Molecular structure was confirmed by NMR spectral analysis.
- The kinetic and thermodynamic parameters of thermal degradation process have been calculated.

GRAPHICAL ABSTRACT



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ABSTRACT

The bulk single crystal of 2-picolinic acid hydrochloride (PHCL) (a semi-organic nonlinear optical material of dimensions $25 \times 15 \times 10\ mm^3$) was successfully grown by slow solvent evaporation technique. The XRD results revealed the cell parameters and the centrosymmetric nature of the crystal structure. FT-IR spectral study identified the functional groups, nature of bonding and their bond strength. The UV–Vis–NIR studies recognized the optical transmittance window and the lower cut off wavelength of the PHCL crystal and thus it could be performed as a NLO material. ^1H NMR and ^{13}CNMR spectra were correlated with the XRD standard for the molecular structure reveals harmony of the materials. Thermal properties of the crystal were studied by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA); the derived kinetic parameter values support the intuitive association of picolinicacid and HCl leads to the spontaneous formation of PHCL with a first order reaction. The presence of a proton and a proton acceptor groups provide the necessary stability to induce charge asymmetry in the PHCL structure. The load dependent hardness values of the crystal were measured by microhardness testing.

Introduction

In the recent times the research activities are focussing on the design and development of highly efficient semi-organic nonlinear optical (NLO) materials [1]. Nonlinear optical (NLO) effect is the atomic level response in a dielectric material to the electric fields present in an intense light beam. The propagation of a light wave through a dielectric material produces changes in the spatial and temporal distribution of electrical charges as the electrons in the atoms interact with the electromagnetic fields of the light wave. The interaction between the laser beam and the delocalised π-electrons in the organic molecule (having a π-electron conjugated system) cause nonlinear polarization. The amount of nonlinear polarization of the organic molecule can be increased when an

* Corresponding author. Tel.: +91 9262411234.
E-mail address: kavin_shri@yahoo.co.in (T. Uma Devi).

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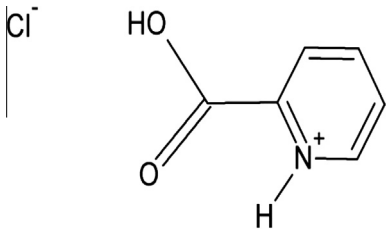

Fig. 1. Chemical structure of PHCL.

electron donating group (donor) or an electron withdrawing group (acceptor) is introduced (inorganic material) into the π-electron conjugated system [2,3]. The development of functional molecular materials with desirable physical properties such as ferroelectric, ferromagnetic, photo conducting and NLO properties for practical applications has become one of the fast growing multi-disciplinary thrust research areas. The semi-organic crystals possess attractive properties such as high damage threshold, wide transparent region and a high nonlinear coefficient [4]. Many applications using NLO materials require single crystals of these materials in bulk form that could be achieved only with semi-organic crystals, which exhibit wide transparency, large and bulky crystal morphologies. The picolinic acid (pyridine 2-carboxylic acid) is very often used in NLO studies as it has the ease of protonation in acid solution [5,6]. The compound picolinic acid hydrochloride (PHCL) crystallizes in centrosymmetric space group P_{nma} having four independent molecules in the asymmetric unit. In PHCL ($C_6H_6NO_2^+ \cdot Cl^-$) there are two strong hydrogen bonds namely OH···Cl and N—H···Cl are formed between the cations and anions as zigzag chains that are parallel to the '*a*' axis. The Chemical Structure of PHCL crystal is shown in Fig. 1.

Experimental

Synthesis and growth of single crystal

The picolinic acid $C_6H_5NO_2$, and the hydrochloric acid HCl (both with AR grade purity) were obtained from Sigma. To the homogeneous solution of picolinic acid (dissolved in double distilled water), HCl is added slowly with continuous stirring until it is completely miscible and forms a homogeneous solution. The precipitates were then washed with distilled water until excess chloride ions (qualitative test with $AgNO_3/HNO_3$ solution) are eliminated and the remaining is maintained in an aqueous suspension.

The following reaction leads to the formation of PHCL

$$C_6H_5NO_2 + HCl \rightarrow C_6H_6NO_2^+Cl^-$$

The solutions and as well as the water employed for washing the precipitates were purged with nitrogen gas and the system was maintained in an isolated manner to avoid oxidation. The prepared solid-state compounds were maintained in aqueous suspension with 50 mL picolinic acid solution of 0.10 mol concentration, and the suspension was heated slowly to near ebullition, until the acid is totally neutralised. Any excess acid was removed by filtration and the crystals were evaporated to dryness in a water bath, subsequently dried in hot air and kept in a desiccator over anhydrous calcium chloride. Photograph of the grown PHCL single crystal is exhibited in Fig. 2.

Materials and methods

All chemicals used are of the analytical reagent grade (AR), and of the highest purity available. The solvents are obtained in spectroscopic pure form (BDH). Hydrochloric and Nitric acid (Merck) are used along with the de-ionized water collected from an all glass equipments were generally used in all preparations.

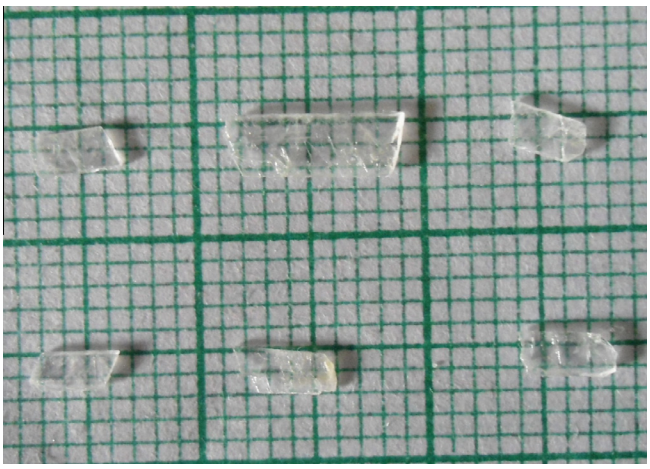

Fig. 2. Photograph of the as-grown single crystal of PHCL.

X-ray powder patterns were obtained using Siemens D-5000 X-ray diffractometer employing Mo Kα radiation of $\lambda = 1.5406$ Å. The attenuate total reflectance infrared spectra for picolinic acid and its PHCL crystal were run on a Perkin–Elmer FT-IR type 1650 spectrophotometer in the wave number region from 4000 to 500 cm^{-1}. The spectra were recorded using KBr pellets. The solid reflectance spectra were measured using a Shimadzu 3101 pc spectrophotometer. Simultaneous TG–DTA curves were obtained with two thermal analysis system, model SDT 2960 from TA Instruments. The air flow of 100 mL min^{-1} is purged for TG–DTA experiments. A heating rate of 20 °C min^{-1} was adopted and the sample (7 mg) were kept in a alumina and aluminum crucibles, the latter with perforated cover, were used for TG–DTA.

Results and discussion

X-ray diffraction studies

The compound crystallizes in orthorhombic system with space group P_{nma} possessing the lattice parameters of $a = 13.7876$ Å, $b = 6.5268$ Å, $c = 7.7517$ Å and the unit cell volume $V = 1232$ Å^3 which matches well with earlier reports [7].

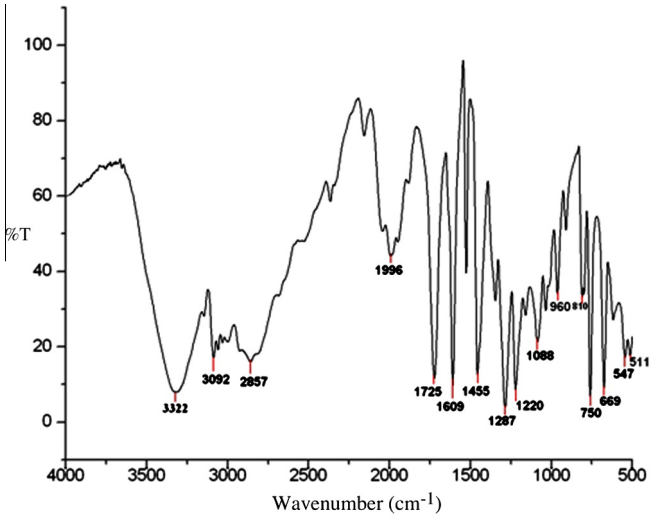

Fig. 3. FT-IR spectrum of PHCL.