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Synthesis, crystal growth and physiochemical characterization of organic NLO crystal: L-ornithinium dipicrate (LODP)

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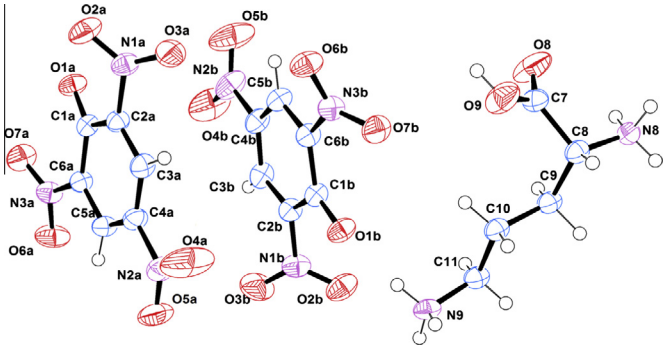
HIGHLIGHTS

- Organic NLO crystals of L-ornithinium dipicrate were grown by slow evaporation.
- Thermal studies show the compound is stable up to 210 °C.
- Powder SHG efficiency was 14.57 greater than that of standard KDP.

GRAPHICAL ABSTRACT



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ABSTRACT

L-ornithinium dipicrate (LODP) has been synthesized and good quality single crystals were grown by slow evaporation method at room temperature. Single crystal XRD confirms that the grown crystal belongs to the monoclinic system with the noncentrosymmetric space group $P2_1$. Powder X-ray diffraction study confirms the crystalline nature of the compound. FTIR spectral analysis confirms the functional group in the synthesized compound. Thermogravimetric and differential thermal analyses reveal the thermal stability of the crystal. The optical absorption spectrum shows the absence of absorption between 475 nm and 800 nm. The dielectric measurements were carried out to estimate the dielectric parameters of the grown crystal in the frequency range from 50 Hz to 5 MHz at various temperatures. The second harmonic property has been investigated by Kurtz–Perry powder technique. The relative SHG efficiency of LODP is found to be 14.57 times greater than that of the reference material KDP.

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Introduction

In recent years, the various classes of organic nonlinear optical materials have been investigated worldwide and also it is preferred in many applications such as optical communications, optical switching and information storage and photonics technology [1,2]. Due to their low cost, high nonlinearity, low dielectric constant, high flexibility, high optical damage threshold and ultrafast response. Organic crystals are of special interest compared to inorganic crystals [3–8]. Amino acids are popularly referred as the building blocks of protein. Amino acid family crystals are of great interest due to their rich nonlinear optical properties. Its specific features such as Zwitterionic nature, weak Vander Waals, hydrogen bonds and wide transmittance in the visible and UV-spectral region make them an ideal candidate for NLO applications [9,10]. Amino acids contain protonated amino group (NH^+) and deprotonated carboxylic acid group (COO^-); owing to its

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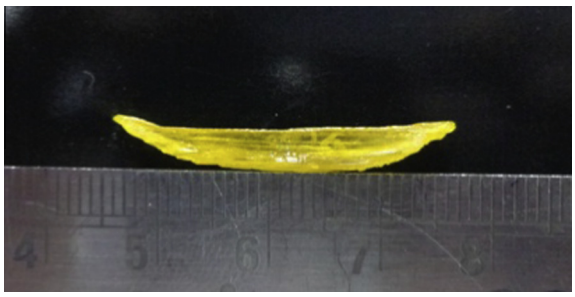

Fig. 1. As grown crystals of L-ornithinium dipicrate.

asymmetric carbon atom most of the amino acids crystallize in a noncentrosymmetric space group [11]. The picrates are convenient for identification and quantitative analysis of organic compounds. Also it is used in human therapy such as treatment of burns, antiseptic and astringent agent. The bonding of these picrate complexes depends on the nature of the donor–acceptor system. Due to its Zwitterionic nature, an amino acid nonlinear optical property is increased when mixed with organic acids. Picrates are attractive candidates for the formation of salts with various organic bases. Due to this formation of the conjugated base, picrate, the value of molecular hyperpolarizability improved because of the proton transfer. Previously some of the picrate of amino acids such as L-threoninium picrate, L-prolinium picrate, L-alanine L-alaninium picrate, L-isoleucinium picrate, L-leucine L-leucinium picrate, DL-phenylalanine DL-phenylalaninium picrate and DL-methionine DL-methioninium picrate, L-asparaginium picrate, L-histidinium dipicrate dihydrate, L-tryptophanium picrate and L-valinium Picrate were reported [12–27]. On the basis of these facts, in the present communication we describe the synthesis and characterization of the L-ornithinium dipicrate crystal. The grown crystals were characterized by various characterization techniques such as single crystal XRD, powder XRD, FTIR, UV, Dielectric, photoconductivity, TG/DTA and powder SHG studies and the results were discussed.

Experimental

Crystal growth

LODP was synthesized by taking L-ornithine and picric acid in an equimolar ratio of 1:2. L-ornithine and picric acid were dissolved separately in water and acetone, stirred well for about 20 min using a magnetic stirrer. Then, these solutions were mixed together and stirred for about one hour. The saturated solution was filtered twice using whatman filter paper and transferred to crystallizing vessel. Top of the vessel was covered with thin plastic sheet and to facilitate the slow evaporation, a few holes were made on it. For the slow evaporation of the solvent, the beaker was kept undisturbed at room temperature. Well defined yellow colored crystals with good transparency appeared in the growth period of 15 days. The photograph of the grown crystal is shown in[1] Fig. 1.

Results and discussion

X-ray diffraction analysis

The single crystal X-ray diffraction data of the title compound were collected at 293 K with graphite-monochromated Mo Kα radiation (λ = 0.071073 nm), and used Enraf–Nonius CAD-4 diffractometer with the ω–2θ scan mode. A suitable sample of size 0.26 mm × 0.21 mm × 0.18 mm was chosen and mounted on the goniometer. Lattice parameters were collected from least-squares fit of 25 reflections. A total of 11,500 (5188 independent R_{int} = 0.0320) reflections were measured. Cell refinement and data reduction were carried out using CAD-4 EXPRESS [28] and XCAD4 [29]. The structures were solved by direct methods procedure using SHELXS-97 [30] and refined by full-matrix least-squares on F^2 using SHELXL-97 program [30]. All non-hydrogen atoms were anisotropically refined. The hydrogen atom positions were fixed at geometrically calculated distances to allow riding on the parent atoms to which they are attached. ORTEP diagram of LODP crystal is depicted in Fig. 2. The crystal data and details pertaining to data collection and the structure refinement are given in Table 1. The relevant bond lengths, bond angles and torsion angles are listed in Table 2. The selected hydrogen bond geometries are given in Table 3. The molecular graphics were prepared by using the ORTEP [31]. The X-ray diffraction study reveals that the grown LODP crystal belongs to the monoclinic system with the noncentrosymmetric space group $P2_1$. The lattice parameter values are found to be a = 9.67 (1) Å, b = 5.26 (2) Å, and c = 12.07(3) Å, which are in good agreement with the earlier reported values [32]. Crystallographic data for the title compound is given in Table 1. The L-ornithinium dipicrate crystal structure comprises of crystallographically independent two picrate anions and one ornithinedication. Protonation occurs at the two possible amine sites in the ornithine molecule at atom N8 and N9 respectively which leads to the formation of cation and the two picrate anions have been formed by loss of one H atom at the hydroxyl group in the picric acid at atom O1A and O1B respectively, it is confirmed by the variations of the hydroxyl C—O bond distances (d (C1A—O1A) = 1.256(6) Å, d (C1B—O1B) = 1.256(6) Å). The ornithine residue consists of two planar groups, viz. the carboxyl group and the aliphatic side chain. The plane of the aliphatic chain forms a dihedral angle of 72.17(3)° with the carboxyl plane. The backbone conformation angle (O8—C7—C8—N8) indicates a gauge conformation [30.73°]. The other angles, (N8—C8—C9—C10), (C8—C9—C10—C11) and (C9—C10—C11—N9) have fully extended trans–trans conformations [177.32 (2)°, −179.35(5)° and 176.23(3)°] respectively. During the crystallization process, the removal of phenolic H atom from the picric acid leads to a shortening of the C1A—O1A = 1.256(6) Å and C2B—O2B = 1.256(6) Å bond lengths. These bond length values are intermediate between the typical single-bond and double-bond values, implying that the negative charge located on the phenolate O atom is delocalized. Both aromatic rings in picrate anions are good approximation with planar, maximum deviation from the least-square plane calculated by the six ring atoms is 0.008(1) Å in the anion A and 0.018(2) Å in anion B. The three nitro groups of the picrate anion A deviate from the benzene plane by 36.00(3)° (N1A), 2.88(3)° (N2A) and 12.42(3)° (N3A) and in anion B the twist angles are 44.22(3)° (N1B), 7.44(3)° (N2B) and 27.35(3)° (N3B) respectively. The hydrogen atoms H1 of N9 and H12 of N8 in the amine groups of the ornithinium cation forms a strong N—H...O hydrogen bonds with hydroxyl group O1A and O1B atoms of the picrate A and B anions respectively. The hydrogen atom H13 of O9 in the carboxyl group of the ornithinium cation forms a strong O—H...O intermolecular hydrogen bonds with the nitro group of O7A and O7B atoms of the picrate A and B anions respectively. Cation is linked to anion through N9—H1...O1B and O9—H13...O7B intermolecular hydrogen bonds, which leads to the formation of ring $R_2^2(14)$. The crystal structure is stabilized by the strong N—H...O, O—H...O and weak intermolecular hydrogen bonds and also the O—H...O intramolecular hydrogen bonds. Powder X-ray diffraction study was carried out by employing JEOL-JDX 8030 X-ray diffractometer with Nickel filtered Cu Kα (λ = 1.5405 Å) radiation. The grown LODP crystal was finely powdered and it has been subjected to powder XRD analysis. Narrow

[1] For interpretation of color in Fig. 1, the reader is referred to the web version of this article.

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