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Structure, growth and characterization of picolinium perchlorate single crystals

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ABSTRACT

Picolinium perchlorate organic single crystals were grown using slow evaporation solution growth technique at room temperature using water as a solvent. The structure of the title compound was supported by proton NMR analysis and the single crystal X-ray diffraction data. Crystallographic studies revealed that the compound crystallized in monoclinic system with space group *C*2/*c*. The HRXRD rocking curve measurements revealed the crystalline perfection of grown crystal. First order hyperpolarizability, HOMO and LUMO energies are calculated using Density Functional Theory (DFT) with a hybrid functional B3LYP and the 6-311++G(d,p) basis set. Global reactivity indices are calculated. Thermal studies were carried out on the title compound. The UV–vis–NIR spectrum was recorded to study the optical transparency of the grown crystals. The mechanical stability of the crystal was analyzed by Vicker's microhardness studies.

1. Introduction

Organic crystals in terms of nonlinear optical property possess advantages, when compared to their inorganic counterparts. One of the intensely studied fields in chemistry and physics are the optical properties of molecular crystals. The importance of those materials has been demonstrated in the recent years by the increased number of applications in nonlinear optics and in electronics. Optical nonlinearities of conjugated organic systems have been widely studied in view of their potential in photonic and electro-optic devices [1,2]. Nonlinear optical materials are expected to be active elements for optical communications and optoelectronics. Organic crystals are highly recognized as the materials of the future because their molecular nature combined with versatility of synthetic chemistry can be used to alter their structure in order to maximize the nonlinear properties [3–5]. The most important applications of NLO materials is their use for fast data transfer combined with a very high Signal-to-Noise ratio, even over long distances. In recent years, different applications of NLO and photorefractive materials have been developed, for example, optical frequency conversion, electro-optical modulation, dynamic holography, optical writing and optical guiding of laser beams [6].

In order to satisfy the day-to-day technological requirements, many scientists focused their attention on the growth of materials which have a good nonlinear optical behavior and be optically transparent in the visible and near IR regions. To study the hydrogen-bonding pattern in pharmacologically important picolinic acid was treated with different inorganic acids and the structure of a complex with perchloric acid is reported in the present investigation. Its hyperpolarizability was estimated by using DFT theory. Its highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) Energies were calculated.

2. Experimental

The starting material was synthesized by taking 2-picolinic acid and perchloric acid in a 1:1 stoichiometric ratio. The reaction scheme is depicted in Fig. 1.

A calculated amount of the 2-picolinic acid is dissolved thoroughly in the deionized water. Then perchloric acid was added to the aqueous solution. The solution is stirred well using a magnetic stirrer to yield a saturated homogenous solution for six hours. The solution was then filtered twice to remove the suspended impurity and allowed to crystallize by slow evaporation. After growth period of three weeks, best quality and highly transparent single crystal was harvested and is shown in Fig. 2.

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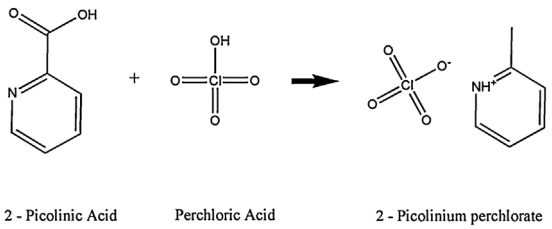

Fig. 1. Reaction scheme of PP.

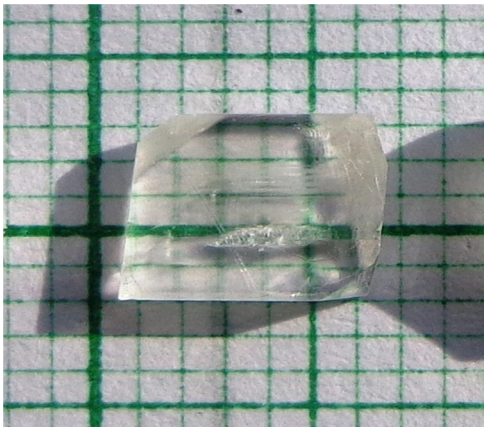

Fig. 2. Photograph of as grown PP single crystals.

3. Single crystal X-ray diffraction studies

Intensity data for picolinium perchlorate was collected using a Bruker AXS Kappa APEX II single crystal CCD diffractometer equipped with graphite-monochromated Mo*K*α radiation (λ = 0.71073 Å) at room temperature with a crystal dimension of 0.35 × 0.25 × 0.2 mm^3. Accurate unit cell parameters were determined from the reflections of 36 frames measured in three different crystallographic zones. The data collection, data reduction and absorption correction were performed by APEX2, SAINT-plus and SADABS program [7]. The structures was solved by direct methods procedure and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using SHELXL-97 program [8]. The positions of all the hydrogen atoms were identified from difference electron density map, and they were constrained to ride on the corresponding non-hydrogen atoms. The hydrogen atom bound to carbon atoms is constrained to a distance of C—H = 0.93–0.97 Å and U_{iso}(H) = 1.2U_{eq}(C) and 1.5U_{eq}(C). The crystallographic data and the structure refinement parameters of PP are presented in Table 1.

The title compound picolinium perchlorate crystallizes in monoclinic space group *C*2/*c* with eight set of anions and cations in the unit cell. Fig. 3 illustrates the molecular structure of PP. Crystal packing diagram is shown in Fig. 4. The bond lengths of the perchlorate anion Cl1—O3 = 1.401 Å, Cl1—O4 = 1.410 Å, C1—O3 = 1.416 Å agrees with the Cl=O value of the perchloric acid whereas Cl1—O5 = 1.439 Å value lies between Cl—O single and double bond reveal that the dissociation of hydrogen atom to the picolinic nitrogen atom. The picolinium N—H atom is clearly judged from the appearance of strong difference electron density peak near the N atom. The presence of donor and acceptor sites in the molecule form C3—H3···O4(2) [−*x* + 1/2,*y* + 1/2,−*z* + 1/2]. C4—H4···O2(3) [*x*,−*y*,*z* = 1/2]; C6—H6···O3(6) [*x* − 1/2,*y* − 1,*z* = 1/2]. The supramolecular networks in the crystal structure are stabilized by the presence of C—H···O and O—H···O hydrogen bonds. The alternate anion and cation along the *b*-axis through strong N1—H1A···O6(2) [−*x* + 1/2,*y* + 1/2,−*z* + 1/2] O1—H1A···O5(1)

Table 1
Crystal data and structure refinement for PP.

Empirical formula	$C_6H_6ClNO_6$
Formula weight	223.57
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *C*2/*c*
Unit cell dimensions	*a* = 13.98 (18) Å alpha = 90 deg. *b* = 8.37(10) Å beta = 100.20(7) deg. *c* = 15.26(18) Å gamma = 90 deg.
Volume	1758.1(4) A^3
Z, Calculated density	8, 1.689 Mg/m^3
Absorption coefficient	0.439 mm^{-1}
F(0 0 0)	912
Crystal size	0.30 × 0.25 × 0.25 mm
Theta range for data collection	2.71 to 28.35 deg.
Limiting indices	$-18 \le h \le 18$, $-10 \le k \le 11$, $-20 \le l \le 18$
Reflections collected/unique	8111/2552 [*R*(int) = 0.0229]
Completeness to theta = 25.00	99.5%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8981 and 0.8295
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2152/0/131
Goodness-of-fit on F^2	1.074
Final *R* indices [*I* > 2sigma (I)]	R1 = 0.0496, *w*R2 = 0.1445
R indices (all data)	R1 = 0.0565, *w*R2 = 0.1527
Largest diff. peak and hole	0.440 and −0.397 e. A^{-3}

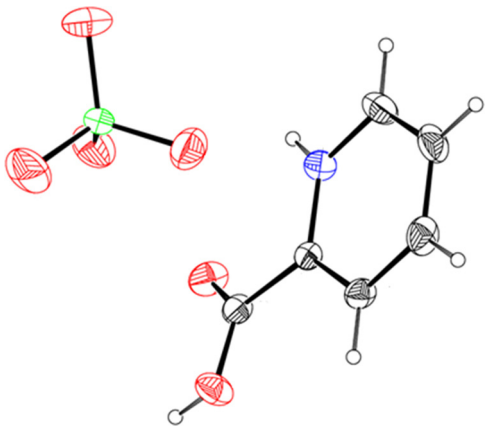

Fig. 3. Molecular structure of PP.

[−*x* + 1/2,*y* + 1/2,−*z* + 1/2] hydrogen bonds form a chain type of architecture, C3—H3···O4(2) [−*x* + 1/2,*y* + 1/2,−*z* + 1/2]. C4—H4···O2(3) [*x*,−*y*,*z* = 1/2] hydrogen bond interlinks these molecular chain to form an extended planar layer parallel to the (1 0 0) plane and is shown in Fig. 5. The C6—H6···O3 (6)

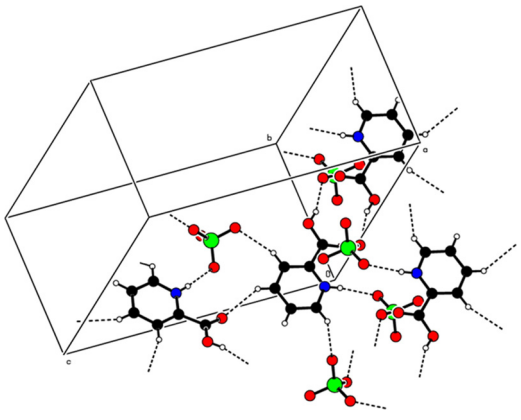

Fig. 4. Crystal packing diagram of PP.