



Crystal growth, characterization and theoretical studies of 4-aminopyridinium picrate



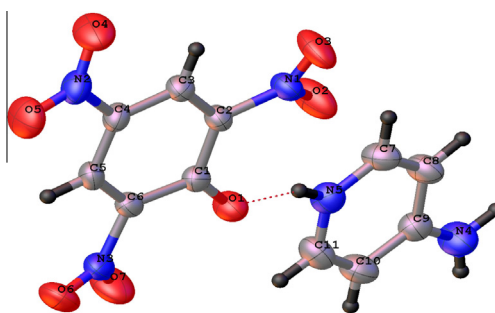
A. Aditya Prasad, K. Muthu, M. Rajasekar, V. Meenatchi, S.P. Meenakshisundaram*

Department of Chemistry, Annamalai University, Annamalinagar 608 002, India

HIGHLIGHTS

- The electron density mapping is interpreted.
- XRD closely resembles the simulated pattern.
- First-order molecular hyperpolarizability is estimated.
- Crystalline cohesion is achieved by N–H...O and C–H...O hydrogen bonds.

GRAPHICAL ABSTRACT



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ABSTRACT

Single crystals of 4-aminopyridinium picrate (APP) were grown by slow evaporation of a mixed solvent system methanol–acetone (1:1, v/v) containing equimolar quantities of 4-aminopyridine and picric acid. Structure is elucidated by single crystal XRD analysis and the crystal belongs to monoclinic system with four molecules in the unit cell (space group $P2_1/c$) and the cell parameter values are, $a = 8.513 \text{ \AA} (\pm 0.015)$, $b = 11.33 \text{ \AA} (\pm 0.02)$, $c = 14.33 \text{ \AA} (\pm 0.03)$ and $\beta = 104.15^\circ (\pm 0.019)$, $V = 1340 \text{ \AA}^3 (\pm 6)$ with refined R factors $R_1 = 0.0053$ and $wR_2 = 0.0126$. The electron density mapping is interpreted to find coordinates for each atom in the crystallized molecules. The various functional groups present in the molecule are confirmed by FT-IR analysis. UV–visible spectral analysis was used to determine the band gap energy of 4-aminopyridinium picrate. Powder X-ray diffraction pattern reveals the crystallinity of the as-grown crystal and it closely resembles the simulated XRD from the single crystal XRD analysis. Scanning electron microscopy reveals the surface morphology of the grown crystal. Optimized geometry is derived by Hartree–Fock theory calculations and the first-order molecular hyperpolarizability (β), theoretically calculated bond length, bond angles and excited state energy from theoretical UV–vis spectrum were estimated.

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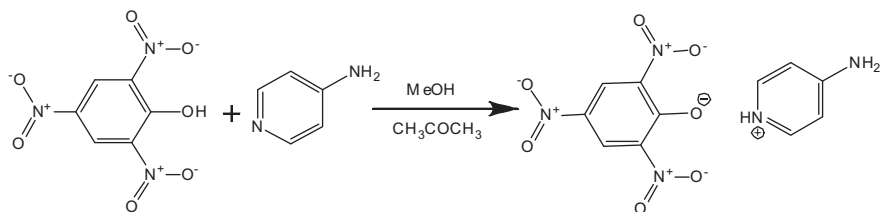
Introduction

Despite numerous theoretical and experimental studies, several fundamental questions concerning the geometries of charge transfer complexes remain unanswered. In particular, little is known about the relative importance of classical van der Waals interac-

tions and charge transfer forces in controlling the overall configuration and donor–acceptor contacts in charge-transfer interactions on the internal geometries. Pyridinium cations have been studied especially extensively [1–3] and particular attention has been given to the donor–acceptor properties. Several complexes of picric acid with organic molecules exhibit nonlinear optical applications [4]. During the past decade there has been considerable interest in the physical and structural properties of charge-transfer complexes [5–8].

* Corresponding author. Tel.: +91 4144221670.

E-mail address: aumats2009@gmail.com (S.P. Meenakshisundaram).



Scheme 1.



Fig. 1. Photograph of APP crystals.

The crystal structure of the 4-aminopyridinium picrate was reported earlier [9]. In the present work, we report the growth, characterization, electron density mapping and theoretical studies using Hartree–Fock and DFT method.

Experimental procedure

Synthesis and growth

4-Aminopyridinium picrate was synthesized by mixing stoichiometric amounts of 4-aminopyridine (Sigma–Aldrich) and picric acid (Sigma–Aldrich) in an equimolar ratio 1:1 using methanol as solvent (Scheme 1). The mixture was stirred at room temperature for 3 h and APP was obtained as yellow color precipitate. The product was purified by recrystallization using mixed solvent, methanol and acetone (1:1, v/v).

Recrystallized APP was dissolved in mixed solvent system (methanol:acetone, 1:1, v/v) and the solution warmed with con-

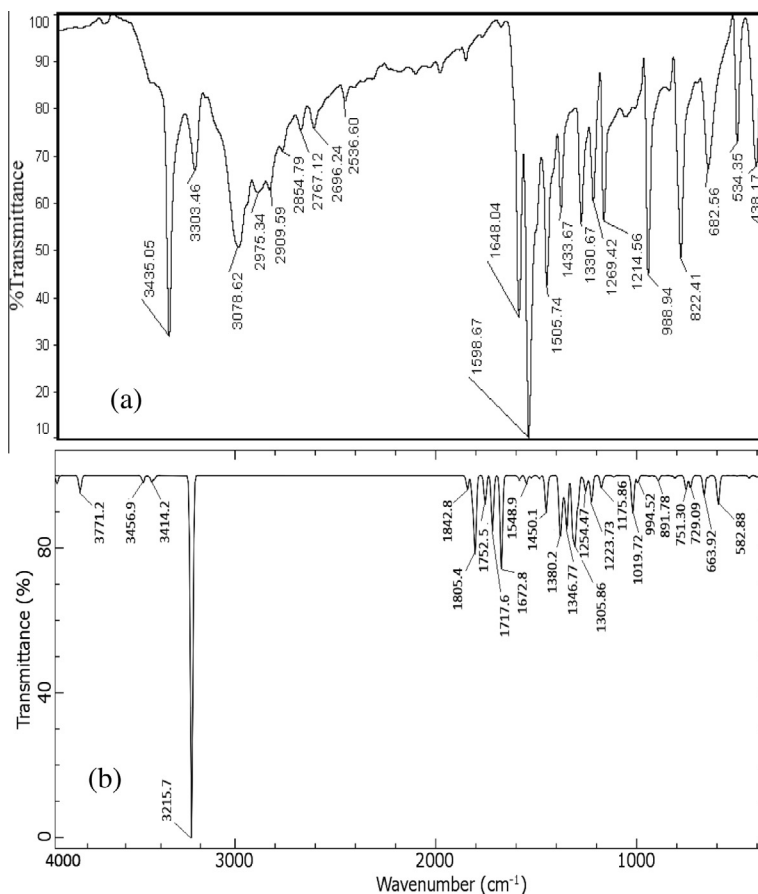


Fig. 2. FT-IR spectra of APP (a) experimental and (b) theoretical.

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