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Synthesis, an experimental and quantum chemical computational study of a new nonlinear optical material: 2-Picolinium hydrogensquarate



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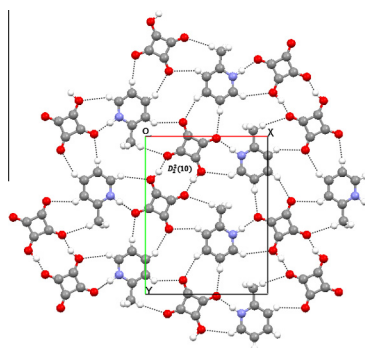
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HIGHLIGHTS

- 2-Picolinium hydrogensquarate.
- Non-linear optical material.
- Supramolecular architectures and α -dimer.
- IR, UV spectroscopy and single crystal XRD.
- *Ab initio* calculations.

GRAPHICAL ABSTRACT

The X-ray analysis clearly indicated that the crystal packing has shown the hydrogen bonding ring pattern of $D_2^2(10)$ (α -dimer) through N—H \cdots O interactions. The hydrogensquarate anions form α -dimer, while 2-Picolinium molecule interacts through N—H \cdots O and C—H \cdots O with the hydrogensquarate anion.



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ABSTRACT

The experimental and theoretical investigation results of a novel organic non-linear optical (NLO) organic squarate salt of 2-Picolinium hydrogensquarate (**1**), $C_6H_8N^+ \cdot C_4HO_4^-$, were reported in this study. The space group of the title compound was found in the monoclinic $C2/c$ space group. It was found that the asymmetric unit consists of one monohydrogen squarate anion together with mono protonated 2-Picolinium, forming the (**1**) salt. The X-ray analysis clearly indicated that the crystal packing has shown the hydrogen bonding ring pattern of $D_2^2(10)$ (α -dimer) through N—H \cdots O interactions. The hydrogensquarate anions form α -dimer, while 2-Picolinium molecule interacts through N—H \cdots O and C—H \cdots O with the hydrogensquarate anion. The structural and vibrational properties of the compound were also studied by computational methods of *ab initio* performed on the compound at DFT/B3LYP/6-31++G(d,p) (**2**) and HF/6-31++G(d,p) (**3**) level of theory. The calculation results on the basis of two models for both the optimized molecular structure and vibrational properties for the **1** obtained are presented and compared with the X-ray analysis result. On the other the molecular electrostatic potential (MEP), electronic absorption spectra, frontier molecular orbitals (FMOs), conformational flexibility and non-linear optical properties (NLO) of the title compound were also studied at the **2** level and the results are reported. In order to evaluate the suitability for NLO applications thermal analysis (TG, DTA and DTG) data of **1** were also obtained.

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Introduction

The hydrogen bonding is one of the most important forces among the interactions in crystal engineering especially considering the arrangement of molecules and ions as building blocks [1–4]. The stability as well as supramolecular structure in crystal engineering is determined by the type of the hydrogen bonding interaction [5–7]. Choosing proper donor and acceptor site, one can obtain a novel hydrogen bonding pattern that is unique and has a desired physical and chemical properties [8–10]. The hydrogen-bonded systems formed by organic cations and anions should also be mentioned here due to their strong interactions compare to neutral molecules [11–15]. It should be added here that the proton-transfer in the structure significantly affects the hydrogen bonding features in the crystal structure of a salt [15–17]. This strong interaction also promotes the nonlinear optical property of the material. Therefore many scientists in this context synthesize the novel materials showing nonlinear optical behavior and study their potential in optical applications such as optical computing, optical information processing, optical disk data storage, and laser remote sensing [18–20].

Ongoing study on squaric acid and its anions because of their potential in forming supramolecular structure as well as their nonlinear optical properties, the title compound has been synthesized. Squaric acid (H_2SQ) can be found in three forms uncharged H_2SQ , the HSQ^- monoanion and SQ^{2-} dianions on deprotonating by amines [13–17,21–23]. In the squarate anion form, the anions are generally linked to amines by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds [21–27]. In the supramolecular architectures the monoanion HSQ^- displays a number of polyanionic forms classified as α -chains, β -chains, α -dimers and α -tetramers [13,14,21,25,28]. This study reports the synthesis, spectroscopic, structural and optical characterization of **1** ($\text{C}_6\text{H}_8\text{N}^+\cdot\text{C}_4\text{HO}_4^-$) molecule (Fig. 1). The aim of this research is twofold. The first one is to determine the supramolecular architectures of title structure together with spectroscopic properties. The second is to obtain optical properties of **1** for possible use as optical material. In order to do further investigation on the properties of the title compound, *ab initio* calculations were carried out. A comparison of the experimental and theoretical results has been given which is useful in making correct assignments in physical and chemical properties of the molecular structure. In order to these, molecular electrostatic potential (MEP), electronic absorption spectra, frontier molecular orbitals (FMOs) and conformational flexibility of the title compound were studied at the **2** level. The nonlinear optical properties together with physicochemical stability of the title compound were also studied.

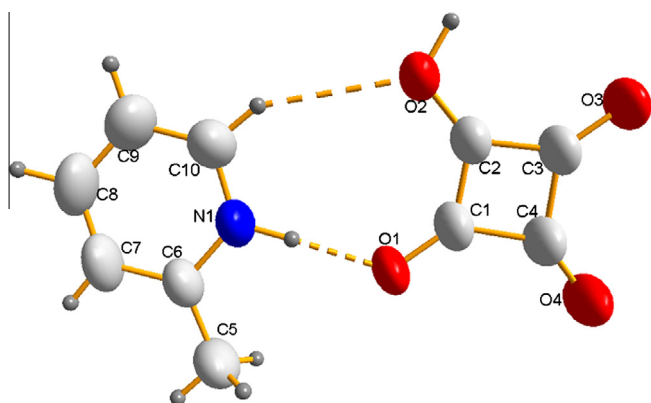


Fig. 1. The molecular structure of compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. The hydrogen bonds are shown as the dotted lines.

Experimental and theoretical methods

General method

The IR spectra were recorded on a Vertex 80v Bruker FTIR spectrometer using KBr pellets and operating in the $4000\text{--}400\text{ cm}^{-1}$ range. Electronic absorption spectra were obtained for aqueous solutions of the compound (10^{-3} M) with an Agilent Technologies Cary 60 UV–Vis spectrometer in the range $800\text{--}200\text{ nm}$. Thermal analysis curves (TG, DTA and DTG) were recorded simultaneously on a Shimadzu DTG-60 thermal analyzer in N_2 atmosphere at a heating rate of $10\text{ }^\circ\text{C}\times\text{min}^{-1}$ in the temperature range $50\text{--}600\text{ }^\circ\text{C}$ using platinum crucibles.

Synthesis

All chemical reagents were analytical grade commercial products. Solvent was purified by conventional methods. Squaric acid (H_2SQ ; 0.23 g, 2 mmol) and 2-Picoline (0.19 g; 2 mmol) were dissolved in water (25 cm^3) mixture in the molar ratio 1:1 and the solution was heated to $50\text{ }^\circ\text{C}$ in a temperature-controlled bath and stirred for one hour. The reaction mixture was then slowly cooled to room temperature. The crystals formed were filtered and washed with 10 cm^3 of water and methanol and dried in air. A few days later, well-formed crystals were selected for X-ray studies. Elemental analysis for **1**, (colorless, yield 43%) $\text{C}_{10}\text{H}_9\text{NO}_4$: Calc.: C, 57.97; H, 4.38; N, 6.76%. Found: C, 57.83; H, 4.32; N, 6.38%. M.p.: $214\text{ }^\circ\text{C}$.

X-ray crystallography

The diffraction data were collected on a STOE IPDSII image plate detector using Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$, $T = 293\text{ K}$). The technique used was $w\text{-}2\theta$ scan mode with limits $1.9\text{--}27.6^\circ$. A summary of the key crystallographic information is given in Table 1. Data collection: Stoe X-AREA [29]. Cell refinement: Stoe X-AREA [29]. Data reduction: Stoe X-RED [29]. The structure was solved by direct-methods using SHELXS-97 [30] and anisotropic displacement parameters were applied to non-hydrogen atoms in a

Table 1
Crystal data and structure refinement for compound.

Formula	$\text{C}_6\text{H}_8\text{N}^+\text{C}_4\text{HO}_4^-$
Formula weight (g)	207.18
Temperature (K)	293
Wavelength (\AA) (Mo $\text{K}\alpha$)	0.71069
Crystal system	Monoclinic
Space group	$\text{C}2/c$
Unit cell dimensions	
a, b, c (\AA)	11.715 (5), 13.684 (5), 13.200 (5)
β ($^\circ$)	115.061 (5)
Volume (\AA^3)	1916.9 (13)
Z	8
Absorption coefficient (mm^{-1})	0.11
Calculated density (g cm^{-3})	1.436
Crystal size (mm)	$0.52 \times 0.36 \times 0.13$
$F(000)$	864
θ range ($^\circ$)	$1.7\text{--}27.2$
Index ranges	$-14 \leq h \leq 13$; $-17 \leq k \leq 17$; $-16 \leq l \leq 16$
Measured reflections	7461
Independent reflections	2024
Reflections observed [$I > 2\sigma(I)$]	1005
Absorption correction	Integration
Refinement method	Full-matrix least-squares on F^2
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0397$ $wR_2 = 0.098$
Goodness-of-fit on F^2	0.87
Largest diff. peak and hole (e \AA^{-3})	0.11, -0.12

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