3-Phenylpyridinium hydrogen squarate: Experimental and computational study of a nonlinear optical material
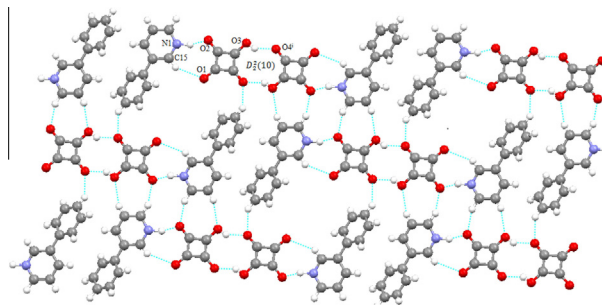
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HIGHLIGHTS

- Non-linear optical material.
- Supramolecular architectures.
- IR, UV spectroscopy and single crystal XRD.
- *Ab initio* calculations.
- Squaric acid and hydrogen squarate anions form α-dimer.

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···O interactions. The hydrogen squarate anions form α-dimer, while 3-phenylpyridinium molecule interacts through N—H···O and C—H···O with the hydrogen squarate anion.

ARTICLE INFO

ABSTRACT

The detailed investigation of an organic nonlinear optical (NLO) squarate salt of 3-phenylpyridinium hydrogen squarate (**1**), $C_{11}H_{10}N^+ \cdot C_4HO_4^-$, was reported in this study. The XRD data indicates that the crystal structure of the title compound is in the triclinic *P-1* space group. In the asymmetric unit, the 3-phenylpyridine molecule is protonated by one hydrogen atom donation of squaric acid molecule, forming the salt (**1**). The X-ray analysis shows that the crystal packing has hydrogen bonding ring pattern of $D_2^2(10)$ (α-dimer) through N—H···O interactions. The structural and vibrational properties of the compound were also studied by computational methods of *ab initio* at DFT/B3LYP/6-31++G(d,p) (**2**) and HF/6-31++G(d,p) (**3**) levels of theory. The calculation results on the basis of two models for both the optimized molecular structure and vibrational properties for the **1** are presented and compared with the experimental results. Non-linear optical properties (NLO) of the title compound together with the molecular electrostatic potential (MEP), electronic absorption spectrum, frontier molecular orbitals (FMOs) and conformational flexibility were also studied at the **2** level and the results were 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

Intermolecular interaction analyses in crystalline systems are important not only in supramolecular chemistry but also in many

disciplines of science. The work on these interactions can be defined as the study of the chemistry beyond the molecules. Among the intermolecular interactions the hydrogen bond is the most important in terms of both the energy and the crystal orientation [1–5]. Identifying hydrogen-bond motifs or supramolecular synthons is clearly very important for crystal engineering. The stability as well as supramolecular structure in crystal engineering is determined by the type of the hydrogen bonding interaction [5–8]. By choosing appropriate H-atom acceptors and donors, stable intermolecular hydrogen bonds can be formed, thereby providing novel organic systems with unique chemical and physical (optical, magnetic and electronic) properties [9–11]. Hydrogen-bonded systems generated from organic cations and anions are of special interest because they are expected to show stronger hydrogen bonds than neutral molecules [12–16]. Especially, the proton-transfer in the structure significantly affects the hydrogen bonding features in the crystal structure [16–19]. This strong interaction also promotes the nonlinear optical and electro-optical properties of the material. Therefore, many scientists in this context synthesize these type materials and study their potential in optical applications such as optical computing, optical information processing, optical disk data storage, laser remote sensing, etc. [20–31].

In the present work, we have selected squaric acid and its anions because of their potential in forming strong hydrogen bond structures with amine involved molecules, and this promotes supramolecular and nonlinear optical properties of the material [16–32]. Squaric acid (H_2SQ) can be found in three forms; uncharged H_2SQ, the HSQ^- monoanion and SQ^{2-} dianions on deprotonating by amines. H_2SQ and its anions are almost planar molecules due to the π-conjugation of their C—C and C—O bonds. Their four oxygen atoms behave as (sp^2) electron donors of one or two lone pair [14–19]. In the squarate anion form, the anions are generally linked to amines by N—H···O hydrogen bonds [24–42]. In the supramolecular architectures the monoanion HSQ^- displays a number of polyanionic forms classified as α-chains, β-chains, α-dimers, α-tetramers [32–35] and cyclic dimer [41].

This study reports the synthesis, spectroscopic, structural and optical characterization of **1** $C_{11}H_{10}N^+ \cdot C_4HO_4^-$ molecule (Fig. 1). This research aims at two goals. 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. These properties were obtained by quantum mechanical calculations based on *ab initio* and DFT

methods. A comparison of the experimental and theoretical results has been given to make correct assignments in physico-chemical properties of the molecular structure. Therefore, molecular electrostatic potential (MEP), electronic absorption spectrum, frontier molecular orbitals (FMOs) and conformational flexibility of the title compound were studied at the **2** level. The nonlinearity together with physico-chemical stability of the title compound was also studied at the same level.

Experimental and calculational methods

General methods

A Vertex 80v Bruker FT-IR spectrometer was used to obtain IR spectrum in the 4000–400 cm^{-1} range. Electronic absorption spectrum was obtained for aqueous solutions of the compound (10^{-3} M) with an Agilent Technologies Cary 60 UV–Vis spectrometer in the range 800–200 nm. Simultaneous TG, DTG, and DTA curves of the compound were obtained using Shimadzu DTG-60 TG/DTA analyzer. The experiment was carried out in a dynamic air atmosphere with a flow rate of 20 mL min^{-1} in the range 20–1000 °C, using platinum crucible. Sample mass of 5–10 mg and a heating rate of 10 °C min^{-1} were used. Sintered α-alumina was used as the reference material.

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 3-phenylpyridine (0.36 g; 2 mmol) were dissolved in water (25 cm^3) mixture in the molar ratio 1:1 and the solution was heated to 50 °C in a temperature-controlled bath and stirred for 1 h. 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**, (white, yield 61%) $C_{15}H_{11}NO_4$: calc.: C, 66.49%; H, 4.29%; N, 5.14%. Found: C, 66.91%; H, 4.12%; N, 5.20%. M.p.: 194 °C.

X-ray crystallography

The diffraction data were collected on a STOE IPDSII image plate detector using Mo Kα radiation (λ = 0.71073 Å, *T* = 293 K). The technique used was $w - 2\theta$ scan mode with limits 1.5–25.8°. A summary of the key crystallographic information is given in Table 1. Data collection: Stoe X-AREA [43]. Cell refinement: Stoe X-AREA [43]. Data reduction: Stoe X-RED [43]. The structure was solved by direct-methods using SHELXS-97 [44] and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using ShellXL-97 [44]. All H atoms attached to carbon atoms were positioned geometrically and refined by a riding model with U_{iso} 1.2 times that of attached atoms and remaining H atoms were located from the Fourier difference map. Molecular drawings were obtained using Diamond 3.0 (demonstrated version) [45] and Mercury 2.3 [46].

Calculational methods

The crystal structure was used as an initial molecular geometry. Quantum chemical calculations were performed with Gaussian 03 program packages [47]. The output files were visualized by means of Gaussian View 03 software [48]. The geometry of neutral form of title compound was optimized at two levels of theory: Density
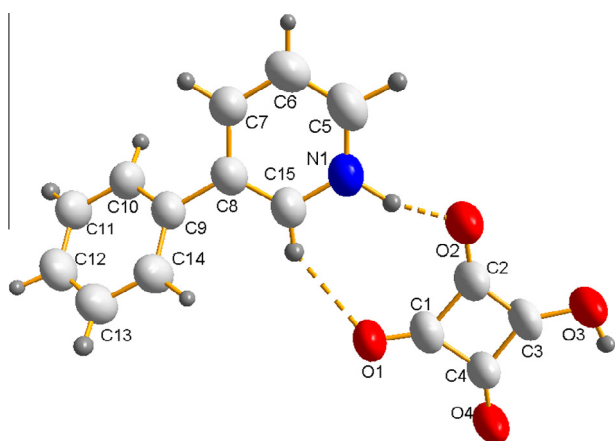

Fig. 1. The molecular structure of compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. The hydrogen bonds are shown as the dotted lines.