



# Structural and spectroscopic properties of piperidinium-4-carboxylic acid hydrogen squarate



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## ABSTRACT

The 1:1 complex of protonated piperidine-4-carboxylic acid (P4C<sup>+</sup>H) with hydrogen squarate anion (HSQ<sup>-</sup>) was prepared and characterized by a single-crystal X-ray diffraction, B3LYP/6-311++G(d,p) calculations, FTIR and NMR spectroscopies. The crystals are orthorhombic, *Pbcn* space group. The molecules are linked through the O—H...O hydrogen bonds of 2.723(1) and 2.574(1) Å formed between P4C<sup>+</sup>H and HSQ<sup>-</sup>, and between HSQ<sup>-</sup> anions linked into a  $\beta$ -chain, respectively. The hydrogen squarate anion is surrounded by four P4C<sup>+</sup>H cations which are involved in the N<sup>+</sup>H...O hydrogen bonds of the lengths from 2.815(1) to 3.183(2) Å. The potential energy distributions (PED), calculated for the optimized structure of the title complex at B3LYP/6-311++G(d,p) level of theory, were used for the assignments of IR bands in the experimental and calculated spectra. The FTIR spectrum was consistent with the X-ray results. The theoretical and experimental IR spectra have been compared. The NMR spectra in an aqueous solution and in the solid-state have been studied.

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## 1. Introduction

Compounds with both amino and carboxylic groups, like amino acids, can exist as zwitterions in the crystalline state, as well as in an aqueous solution, however in the gas phase they are present in the neutral form. In a zwitterion, both charged groups, COO<sup>-</sup> and N<sup>+</sup>H<sub>3</sub> (or N<sup>+</sup>H<sub>2</sub>, N<sup>+</sup>H) interact with each other or with other proton-donors or proton-acceptors, by means of electrostatic, polarization and hydrogen-bonding interactions. These interactions affect their structural conformation, functionality and biological activity [1]. Interesting are the structural isomers of piperidine-carboxylic acid with the COO<sup>-</sup> group at 2-position (pipecolic acid or homoproline) [2], at 3-position (nipecotic acid) [3] and at 4-position (isonipecotic acid) [4,5]. These compounds have a piperidinium ring, which enables the charge separation between the ammonium and carboxylate groups.

Piperidine-4-carboxylic acid (P4C) can be treated as  $\gamma$ -amino acid, in which the amino group is incorporated in the ring. The two interacting centers, the proton-donor N<sup>+</sup>H<sub>2</sub> group and the proton-acceptor COO<sup>-</sup> group are characterized by the dissociation constants of 10.33 and 3.86, respectively [6]. Recently, the hydrogen-bonded complexes of P4C with hydrochloric acid [5,7], chloroacetic acid [8] and L-tartaric acid [9] have been studied.

In this work we focused our attention on the 1:1 complex of P4C with squaric acid (3,4-dihydroxy-3-cyclobuten-1,2-dione, H<sub>2</sub>SQ), which can play a role as a proton-donor and a proton-acceptor [10,11]. Squaric acid by transfer of one proton generates a hydrogen squarate anion, HSQ<sup>-</sup>, or by transferring two protons can generate a squarate dianion, SQ<sup>2-</sup>. H<sub>2</sub>SQ and its anions, HSQ<sup>-</sup> and SQ<sup>2-</sup>, are almost flat molecules, because of the  $\pi$ -conjugation of their C—C and C—O bonds, and therefore their four oxygen atoms behave as planar (sp<sup>2</sup>) electron donors of one or two lone pairs [10–12]. The hydrogen squarate anion can assume a number of polyanionic supramolecular architectures, which are classified as  $\alpha$ -chain,  $\beta$ -chain,  $\alpha$ -dimer and  $\alpha$ -tetramer [10–13]. In  $\alpha$ -chain the neighboring oxygen atoms, OH and O, (at 1 and 2 positions) are incorporated in the short H—bond system with the O...O distance between 2.47 and 2.55 Å, whereas in  $\beta$ -chain the oxygen O—H atom at position 1 and the oxygen atom C=O at position 3 of the neighboring anion are involved in the medium-strong O—H...O hydrogen bonds with the O...O distance between 2.55 and 2.62 Å [10]. Squaric acid and its anions have been frequently used as counter anions in the preparation of a number of molecular crystals. The interactions of H<sub>2</sub>SQ with nitrogen bases results in a variety of hydrogen-bonding complexes and their structures are stored in the Cambridge Crystallographic Database Center [14]. The zwitterionic compounds, being both the proton-donors and proton-acceptors, are an ideal model for investigation of a proton-transfer reaction and electrostatic attraction between themselves and squaric acid. Several earlier papers of the research

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group of Kolev have concerned complexes of amino acids and their derivatives with H<sub>2</sub>SQ [15–24]. Recently, we have studied the O—H···O and N—H···O interactions of glycine derivatives with H<sub>2</sub>SQ [25] and nipecotic acid (piperidine-3-carboxylic acid, P3C) with H<sub>2</sub>SQ [26]. From the point of view of material science the new information on the interactions between the zwitterionic compound, like piperidine-4-carboxylic acid, P4C, and squaric acid, H<sub>2</sub>SQ, (**1**) and detail interpretation the vibrational spectra, both for the crystal compound and for the isolated molecule could be better understand the activity of P4C. The structure of the crystalline complex was determined by the single-crystal X-ray analysis and the compound was characterized by FTIR and NMR spectroscopies. The structure of the title complex was optimized by the B3LYP/6-311++G(d,p) approach.

## 2. Experimental

### 2.1. Synthesis

To 0.565 g (0.004 M) of piperidine 4-carboxylic acid in the methanol–water (2:1) solution (3 ml), 0.499 g (0.004 M) of squaric acid dissolved in 2 ml water was added and the reaction mixture was heated for 5 min. After cooling to the room temperature the crystals of the 1:1 complex of piperidine-4-carboxylic acid with squaric acid precipitated (0.802 g, 75%). The crude product of piperidinium-4-carboxylic acid hydrogen squarate (**1**) was recrystallized from H<sub>2</sub>O, m.p. 232–233 °C. Elemental analysis for C<sub>10</sub>H<sub>13</sub>NO<sub>6</sub>; calc.: %C, 49.38; %H, 5.39; %N, 5.76; found: %C, 49.31; %H, 5.56; %N, 5.78.

### 2.2. Measurements

X-ray diffraction data of the complex **1** were collected on a Super Nova Diffractometer. The structure was solved by direct methods using SHELXS-97 and refined on F<sup>2</sup> by the full-matrix least-squares with SHELXL-97 [27]. The crystal data, details of data collection and structure refinement are given in Table 1 and the final atomic coordinates in Table S1 (Supplementary material). The

**Table 1**  
Crystal data and structure refinement for piperidinium-4-carboxylic acid hydrogen squarate (**1**).

Empirical formula	C <sub>10</sub> H <sub>13</sub> NO <sub>6</sub>
Formula weight	243.21
Temperature	130(2) K
Wavelength	1.54184 Å
Crystal system	Orthorhombic
Space group	<i>Pbcn</i>
Unit cell dimensions	<i>a</i> = 6.3511(2) Å <i>b</i> = 12.0902(4) Å <i>c</i> = 26.7044(9) Å
Volume	2050.51(12) Å <sup>3</sup>
Z	8
Calculated density	1.576 g/cm <sup>3</sup>
Absorption coefficient	1.133 mm <sup>-1</sup>
F(000)	1024
Crystal size	0.30 × 0.24 × 0.03 mm
θ range for data collection	9.33–74.50°
Limiting indices	−6 ≤ <i>h</i> ≤ 7 −14 ≤ <i>k</i> ≤ 14 −33 ≤ <i>l</i> ≤ 28
Reflections collected/ unique	4466/2046 [R(int) = 0.0236]
Completeness to θ = 74.50°	97.9%
Max. and min. transmission	0.9668 and 0.7274
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	2046/0/206
Goodness-of-fit on F <sup>2</sup>	1.056
Final R indices [I > 2σ(I)]	R1 = 0.0394, wR2 = 0.1050
R indices (all data)	R1 = 0.0429, wR2 = 0.1096
Largest diff. peak and hole	0.394 and −0.214 e Å <sup>-3</sup>

crystallographic and structural data in CIF format are available from the Cambridge Crystallographic Database Centre (CCDC 1403620).

FTIR spectra were measured in Nujol and Fluorolube suspensions between KBr plates using a Bruker IFS 66 v/S instrument, with the resolution of 2 cm<sup>-1</sup>. Each spectrum was accumulated by acquisition of 64 scans.

The NMR spectra were recorded on a Varian VNMRS-400 spectrometer operating at 402.64 and 101.24 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively. The spectra were measured in D<sub>2</sub>O relative to an internal standard of 3-(trimethylsilyl) propionic-d<sub>4</sub> acid sodium salt. Solid state <sup>13</sup>C NMR data were recorded on a 400 MHz Varian NMR System equipped with a T3-NB-HX probe operating at a <sup>13</sup>C frequency of 101.24 MHz. The sample was packed in a 4 mm zirconium rotor with Teflon bottom and top spacers and Vespel drive tips. The cross polarization pulse sequence called tanpdx was used for normal proton decoupling. A typical parameter set was as follows: spectra width 34,722.2 Hz, pulse width 3.5 μs for the 90° pulse for <sup>13</sup>C, recycle delay time 5 s, a Hartmann–Hahn contact time milliseconds (ms), acquisition time 40 ms, and total scan number 12,000. The magic angle spinning rate was set to 5000 Hz. Spectrum was referenced to an external adamantane peak at 38.3 ppm and was converted to tetramethylsilane at 0.0 ppm. Data were collected and processed with software Vnmrj 2.3 A.

Elemental analysis was made using an Elemental Model Vario EL III.

### 2.3. Computational details

The DFT calculations were performed with the GAUSSIAN 09 program package [28]. The calculations employed the B3LYP exchange-correlation functional, which combines the hybrid exchange functional of Becke [29,30] with the gradient-correlation functional of Lee et al. [31] and the split-valence polarized 6-311++G(d,p) basis set [32]. All calculated IR frequencies are positive and confirm that the optimized structure corresponds to a minimum energy.

The Potential Energy Distribution (PED) of the vibrational modes of the optimized molecule (**2**) was determined using VEDA 4 program [33] made available by Jamroz [34]. Only the PED greater than 10% were considered.

## 3. Results and discussion

### 3.1. Crystal structure

Piperidine-4-carboxylic acid (P4C) forms a stable crystalline complex at the 1:1 ratio with squaric acid (3,4-dihydroxy-3-cyclobuten-1,2-dione, H<sub>2</sub>SQ), **1**. Compound **1** crystallizes in orthorhombic *Pbcn* space group with eight molecules per unit cell. Labeling of atoms is shown in Fig. 1a. The bond lengths, bond and torsion angles are given in Table 2. Squaric acid transfers one proton, H(4), to the carboxylate O(1) atom of P4C, generating the hydrogen squarate anion, HSQ<sup>-</sup>, and piperidinium-4-carboxylic acid cation, P4C<sup>+</sup>H. The C(7)—O(1) and C(7)—O(2) bond lengths of 1.338(2) and 1.208(2) Å, respectively, suggest the protonation site at the O(1) atom. A similar bond length of C(7)—O(1) was observed in piperidinium-4-carboxylic acid chloroacetate [8]. The piperidinium ring has a chair conformation with the carboxylic group in the equatorial position, similarly as in the piperidine-4-carboxylic acid derivatives studied earlier [4,5,7–9].

P4C<sup>+</sup>H and HSQ<sup>-</sup> are linked through the O(1)—H(4)···O(4) medium strong hydrogen bond, with the O(1)···O(4) distance of 2.723(1) Å (Table 3). The geometrical parameters (Table 2) show that the C(8)—O(3)H bond length of 1.306(2) Å is longer than the three other C—O bonds, whose lengths vary from 1.234(2) to 1.252

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