

## Structural, spectroscopic and theoretical studies of the 1:1 complex of *N*-methylpiperidine betaine with squaric acid

Z. Dega-Szafran\*, G. Dutkiewicz, Z. Kosturkiewicz, M. Szafran

Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

### ARTICLE INFO

#### Article history:

Received 12 January 2012

Received in revised form 8 February 2012

Accepted 8 February 2012

Available online 16 February 2012

#### Keywords:

*N*-methylpiperidine betaine

Squaric acid

Hydrogen bonds

X-ray diffraction

FTIR and NMR spectroscopies

DFT calculations

### ABSTRACT

The 1:1 complex of *N*-methylpiperidine betaine, MPB, with squaric acid, H<sub>2</sub>SQ, has been characterized by single-crystal X-ray analysis, FTIR and NMR spectroscopies, and by DFT calculations. The crystals are orthorhombic, space group *Pbca*. Two non-equivalent O—H...O hydrogen bonds of 2.472(1) and 2.508(2) Å link H<sub>2</sub>SQ with MPB. The piperidinium ring has a chair conformation with the methyl group in the equatorial position and the CH<sub>2</sub>COO<sup>−</sup> substituent in the axial one. The geometry of the optimized structures of the MPB-H<sub>2</sub>SQ complex at the B3LYP/6-31G(d,p) level of theory, in a vacuum and solvated by water, have been used to calculate harmonic IR frequencies and to predict the chemical shifts in H<sub>2</sub>O.

© 2012 Elsevier B.V. All rights reserved.

### 1. Introduction

The piperidine ring in *N*-methylpiperidine betaine (1-carboxymethyl-1-methylpiperidinium inner salt, MPB) as well as in its complexes with acids, has a chair conformation. In *N*-methylpiperidine betaine two groups are attached to the nitrogen atom, the methyl group is in the axial position and the carboxymethyl substituent is in the equatorial position [1]. MPB is a weak base, its  $pK_a = 2.01$  [2]. In the series of 1:1 complexes, studied by X-ray diffraction, the bulky CH<sub>2</sub>COO group in MPB-HF is in the equatorial position [3], while in MPB-HCl [4], MPB-HBr [5], MPB-2,4-dinitrophenol [6] and MPB-4-hydroxybenzoic acid [7] it is in the axial position. In all investigated 2:1 complexes of MPB with mineral acids the CH<sub>2</sub>COO group is in the equatorial positions [8–10]. However, in the complexes of (MPB)<sub>2</sub>H<sub>2</sub>SiF<sub>6</sub> [11] and [(MPB)<sub>2</sub>(l-tartaric acid)]<sub>2</sub> [12], and in  $\alpha$  and  $\beta$  4-OH-MPB inner salts [13], in one MPB molecule the CH<sub>2</sub>COO group is found to be equatorial while in the other is axial. The orientation of the substituent around the quaternary nitrogen atom in six-membered saturated heterocycles depends on the interconversion process such (i) rotation about the single bonds of the ring substituents, (ii) pyramidal nitrogen inversion and (iii) ring inversion [14]. However, piperidinium salts in which the nitrogen atom is substituted by two alkyl groups can be converted only by the ring inversion [15]. Comparison of the conformations between the 1:1 complexes of MPB-HX

with the axial CH<sub>2</sub>COO group [4,5] and the 2:1 complexes (MPB)<sub>2</sub>HX with the equatorial CH<sub>2</sub>COO group [8–10] can suggest that the arrangement of the molecules in crystal packing plays a crucial role on the orientation of the more bulky CH<sub>2</sub>COO group at the piperidinium ring.

In this work we extended our study on the complex of *N*-methylpiperidine betaine with squaric acid (3,4-dihydroxy-3-cyclobuten-1,2-dion, H<sub>2</sub>SQ). Squaric acid is a strong diprotic acid characterized by two dissociation constants,  $pK_1 = 1.2$ – $1.7$  and  $pK_2 = 3.2$ – $3.5$  [16–18]. The  $pK_a$  difference between H-bond donor and H-bond acceptor group [ $\Delta pK_a = pK_{AH} - pK_B$ ] can be used to predict the H-bond strength [19,20]. Thus taken the values of  $pK_1$  and  $pK_2$  of squaric acid equal 1.2 and 3.5, respectively, from Ref. [17], the  $\Delta pK_a$  values described the complex of H<sub>2</sub>SQ with MPB are  $-0.81$  and  $1.49$ , respectively, hence we can expect strong but non-equivalent hydrogen bonds linking H<sub>2</sub>SQ with MPB. The crystal structure of H<sub>2</sub>SQ was determined at room temperature by X-ray and neutron diffraction [21–24] and by X-ray diffraction under pressure from the range 0.93–4.70 GPa [25]. H<sub>2</sub>SQ and its anions: hydrogen squarate anion, HSQ<sup>−</sup> and squarate dianion, 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 ( $sp^2$ ) electron donors of one or two lone pairs [26–28]. The crystal complexes of squaric acid with heterocyclic amino bases have been a subject of study of several scientific groups: Gilli et al. [26–28], Kolev et al. [29–31], Yesilel and Uçar et al. [32–36] and stored in the Cambridge Crystallographic Database Centre [37].

\* Corresponding author. Tel.: +48 61 8291216; fax: +48 61 8291505.

E-mail address: [degasz@amu.edu.pl](mailto:degasz@amu.edu.pl) (Z. Dega-Szafran).

Recently, we have studied the complexes of squaric acid with trigonelline (N-methyl-3-carboxypyridinium) [38], DABCO (1,4-diazabicyclo [2.2.2] octane) [39] and its mono-betaine and di-betaine [40,41]. Presently, we extend our study to the crystal structure, FTIR, NMR and B3LYP results of the complex of N-methylpiperidine betaine with squaric acid. One of the fundamental questions regarding the formation of N-methylpiperidine betaine complex with squaric acid is that of the stoichiometry of MPB to H<sub>2</sub>SQ and the conformation around the quaternary nitrogen atom of MPB.

## 2. Experimental

### 2.1. Synthesis

N-Methylpiperidine betaine, MPB, was prepared according to the procedure described in Ref. [1]. The 1:1 complex of MPB with squaric acid, H<sub>2</sub>SQ, (**1**), was obtained by mixing 0.75 g of MPB in 2 ml of water with 0.53 g of H<sub>2</sub>SQ in 10 ml of water. The solvent was evaporated under reduced pressure and the residue was

recrystallized from methanol, m.p. 156–157 °C. A deuterated sample was prepared by threefold dissolution in D<sub>2</sub>O, with subsequent removal of the solvent under reduced pressure, and finally recrystallized from CH<sub>3</sub>OD.

### 2.2. Measurements

X-ray diffraction measurements of the 1:1 complex of N-methylpiperidine betaine with squaric acid (**1**) were carried out at the ambient temperature and MoK $\alpha$  radiation on an Oxford Diffraction Super Nova diffractometer equipped with CCD detector [42]. Data reduction was performed with CrystalAliso/ECO RED program [42]. The structure was solved with direct methods using SHELXS-97 program [43]. All non-hydrogen atom positions were found from E-maps and the hydrogen atom positions from the difference Fourier maps. Parameters of non-hydrogen atoms were refined with anisotropic displacement parameters and the parameters of hydrogen atoms – isotropically, using the SHELXL-97 program [43]. The final *R* factors is 0.0467 by 3748 reflections and 241 refined parameters. The crystal data and the details of data processing are given in Table 1. The final fractional atomic coordinates listed in Table A, bond lengths, bond and torsion angles given in Tables B are included in Supplementary materials. The complete set of structural parameters in the CIF format is available from Cambridge Crystallographic Database Center under No CCDC 856122.

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

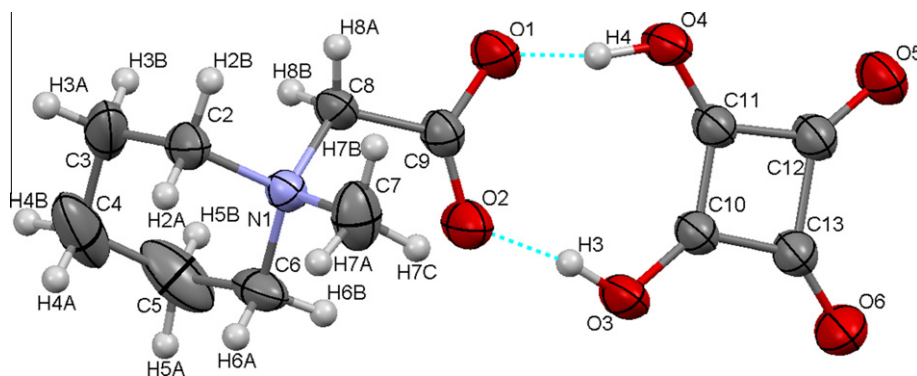
The NMR spectra for **1** were recorded using a Varian VNMRS-400 spectrometer operating at 402.6435 and 101.2440 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively. The spectra were measured in D<sub>2</sub>O relative to an internal standard of 3-(trimethylsilyl)propionic-d<sub>4</sub> acid sodium salt.

### 2.3. DFT calculations

The DFT calculations were performed with the GAUSSIAN 03 program package [44]. The calculations employed the B3LYP exchange–correlation functional, which combines the hybrid exchange functional of Becke [45,46] with the gradient-correlation functional of Lee, Yang and Parr [47] and the split-valence polarized 6-31G(d,p) basis set [48]. The X-ray geometry was used as a starting point for the calculations. The calculated IR frequencies were positive and confirmed that the optimized structures were in the states of minimum energies. The magnetic isotropic shielding constants were calculated with the standard GIAO/B3LYP/6-31G(d,p) [Gauge-Independent Atomic Orbital] approach with the

**Table 1**  
Crystal data and structure refinement for the 1:1 complex of N-methylpiperidine betaine with squaric acid (**1**).

Empirical formula	C <sub>12</sub> H <sub>17</sub> NO <sub>6</sub>
Formula weight	271.27
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
Unit cell dimensions	<i>a</i> = 17.8319(3) Å <i>b</i> = 7.11460(10) Å <i>c</i> = 20.3564(5) Å
Volume	2582.55(9) Å <sup>3</sup>
Z	8
Calculated density	1.395 g/cm <sup>3</sup>
Absorption coefficient	0.113 mm <sup>-1</sup>
F(000)	1152
Crystal size	0.4 × 0.5 × 0.6 mm
$\theta$ range for data collection	3.04–29.99°
Limiting indices	–25 ≤ <i>h</i> ≤ 25 –10 ≤ <i>k</i> ≤ 10 –28 ≤ <i>l</i> ≤ 27
Reflections collected/unique	20136/3748 [ <i>R</i> (int) = 0.0159]
Completeness to $\theta = 25.00$	99.9%
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	3748/0/241
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.036
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0466, <i>wR</i> 2 = 0.1242
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0571, <i>wR</i> 2 = 0.1326
Extinction coefficient	0.0034(9)
Largest diff. peak and hole	0.330 and –0.231 e Å <sup>-3</sup>



**Fig. 1.** Atom numbering scheme of the complex of N-methylpiperidine betaine with squaric acid. (**1**).

Download English Version:

<https://daneshyari.com/en/article/1409741>

Download Persian Version:

<https://daneshyari.com/article/1409741>

[Daneshyari.com](https://daneshyari.com)