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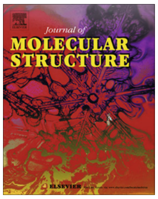

Molecular structures of N-ethylpiperidine betaine hydrate and its 1:1 complex with squaric acid

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HIGHLIGHTS

- X-ray and DFT structures of the centrosymmetric dimer of N-ethylpiperidine betaine hydrate.
- Hydrogen bonds in the complex of squaric acid with N-ethylpiperidine betaine.
- Preference of the carboxymethyl substituent to a hydrogen-bond formation.
- 2D NMR spectra determine the chemical shifts of methylene groups in betaine unit.

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ABSTRACT

N-ethylpiperidine betaine, (N-carboxymethyl-N-ethylpiperidinium inner salt, EtPB) crystallizes as a hydrate. EtPB and water molecules are bonded by intermolecular O—H···O hydrogen bonds of 2.817(1) and 2.863(1) Å, into a centrosymmetric dimer, in which only one carboxylate oxygen atom is involved in H-bonds formation. In the complex of EtPB with squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione, H_2SQ) both carboxylate oxygen atoms are engaged in the hydrogen bonds which links molecules through two short, non-symmetric O—H···O hydrogen bonds of 2.489(1) and 2.500(1) Å. The preferences of the conformation of the EtPB unit in the hydrogen bond formation have been studied by X-ray diffraction, FTIR and NMR spectroscopy and the results are supported by DFT calculations. EtPB, in hydrate and in the complex, has a chair conformation with the CH_3CH_2 group in the axial position and the CH_2COO substituent in the equatorial position.

1. Introduction

Ammonium alkanocarboxylates are zwitterions (or inner salts, or betaines) because they posses formally charged ammonium and carboxylate groups separated by one or more sp^3 carbon atoms. Alkylbetaines nowadays constitute a group of products of interest for cosmetic, household and industrial applications [1]. In betaines, the quaternary nitrogen atom is inert as a hydrogen bond center, whereas the carboxylate group is basic and can interact with different proton-donors. The nitrogen atom can be surrounded by alkyl groups or be included in heteroaliphatic or heteroaromatic ring, e.g. N-alkylpiperidine betaines. The conformations of pentamethylene heterocycles are important in mechanistic, pharmacological, synthetic and theoretical investigations [2–5]. The orientation of the substituents around the quaternary nitrogen atom depends on the C—N rotation, nitrogen inversion and ring inversion [6,7]. The piperidine ring in 1-carboxyalkyl-1-alkylpiperidinium inner salt has a chair conformation and the substituents can occupy axial or equatorial positions [8–11]. In the crystals of N-methylpiperidine betaine (N-carboxymethyl-N-methylpiperidinium inner salt, MPB) the piperidine ring adopts the chair conformation with the CH_3 group in the axial and the CH_2COO^- group in the equatorial positions, however in the MPB molecule optimized by the B3LYP/6-311++G(d,p) approach the conformer with the axial CH_2COO^- group is slightly more stable than the equatorial one [12,13]. In the following discussion in this work, the terms axial and equatorial will refer to the position of the CH_2COO^- substituent. In continuation of our earlier investigation, we report the structures of N-ethylpiperidine betaine hydrate, (N-carboxymethyl-N-ethylpiperidinium inner salt, EtPB), **1**, and its hydrogen-bonded complex with squaric acid, H_2SQ, **2** (Fig. 1). The structural study is supported by quantum chemical calculations and by spectroscopic methods. In EtPB there are two bulky, slightly different groups attached to the quaternary nitrogen atom of piperidinium ring, ethyl and carboxymethyl. Therefore, we have determined the crystal structure of EtPB to know its conformational preferences to form hydrogen bonds. This study was also

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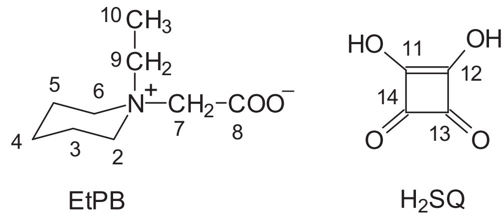

Fig. 1. Molecular structures of N-ethylpiperidine betaine, EtPB and squaric acid, H_2SQ.

aimed at analyzing the EtPB behavior as a proton-acceptor in the reaction with squaric acid, which is a diprotic acid [14–16] and comparing the results with those obtained earlier for the complex of MPB with squaric acid [17]. The interaction of H_2SQ with bases results in a variety of hydrogen-bonding complexes [18]. H_2SQ by transferring one proton to a base generates a hydrogen squarate anion, HSQ^-, or by transferring two protons it generates a squarate dianion, SQ^{2-}. The hydrogen squarate anion can be aligned to form a head-to-tail chain through strong O—H···O hydrogen bonds, or head-to-tail cyclic dimer or tetramer [19–23]. From the point of view of material science, the information on the formation of crystal structure of the complex of N-ethylpiperidine betaine with squaric acid is essential for understanding the role of hydrogen bonds and other intermolecular forces in the association of ions in the crystalline state.

2. Experimental

2.1. Syntheses

N-Ethylpiperidine betaine (**1**) was prepared according the procedure described previously and recrystallized from acetonitrile; m.p. 206–207 °C [24,25]. The 1:1 complex of EtPB with H_2SQ (2) was obtained by mixing 0.62 g of EtPB in 2 mL of methanol with 0.42 g of H_2SQ in 3 mL of water. The solvents were evaporated under reduced pressure and the solid residue was recrystallized from acetonitrile (0.8 g, 82%), m.p. 136–138 °C. Elemental analysis calculated for $C_{13}H_{19}NO_6$ (285.29): %C 54.73, %H 6.71, %N 4.91; found: %C 54.38, %H 6.43, %N 4.69.

2.2. Measurements

Table 2
Selected experimental and calculated by the B3LYP/6-311++G(d.p) approach bond lengths (Å), bond and torsion angles (°) for N-ethylpiperidine betaine hydrate (**1**, **1a**) and the complex of N-ethylpiperidine betaine with squaric acid (**2**, **2a**).

	1	**1a**	**2**	**2a**
	X-ray	B3LYP	X-ray	B3LYP
Bond lengths				
C(8)—O(1)	1.267(1)	1.243	1.272(1)	1.241
C(8)—O(2)	1.240(1)	1.241	1.251(1)	1.254
C(11)—O(3)			1.318(1)	1.316
C(12)—O(4)			1.299(1)	1.313
C(13)—O(5)			1.230(1)	1.205
C(14)—O(6)			1.217(1)	1.206
Bond angles				
C(11)—C(12)—C(13)			93.16(8)	92.85
C(12)—C(13)—C(14)			86.50(8)	87.04
C(13)—C(14)—C(11)			88.53(8)	87.04
C(14)—C(11)—C(12)			91.80(9)	93.07
Torsion angles				
C(8)—C(7)—N(1)—C(2)	−59.74(7)	−64.93	−71.13(12)	−65.40
C(8)—C(7)—N(1)—C(6)	−176.16(5)	177.73	172.33(9)	177.40
C(8)—C(7)—N(1)—C(9)	61.54(7)	54.85	51.15(12)	55.27
N(1)—C(7)—C(8)—O(1)	171.78(6)	−173.98	−163.01(9)	−173.52
N(1)—C(7)—C(8)—O(2)	−8.25(9)	6.57	18.81(15)	7.12
C(10)—C(9)—N(1)—C(2)	−171.03(5)	175.68	168.05(10)	175.86
C(10)—C(9)—N(1)—C(6)	−50.71(7)	−63.70	−72.67(12)	−63.84
C(10)—C(9)—N(1)—C(7)	68.47(7)	56.54	45.32(12)	55.59
O(3)—C(11)—C(12)—O(4)			−0.9(3)	0.10
O(4)—C(12)—C(13)—O(5)			−0.1(2)	−0.18
O(5)—C(13)—C(14)—O(6)			−0.5(2)	0.30
O(6)—C(14)—C(11)—O(3)			1.5(2)	−0.24

Table 1
Crystal data and structure refinement for N-ethylpiperidine betaine hydrate (**1**) and the complex of N-ethylpiperidine betaine with squaric acid (**2**).

	1	**2**
Empirical formula	$C_9H_{19}NO_3$	$C_{13}H_{19}NO_6$
Formula weight	189.25	285.29
Temperature (K)	100(1)	130(2)
Wavelength (Å)	0.71073	1.54178
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	6.9770(2)	10.1399(8)
b (Å)	7.6408(2)	7.4273(18)
c (Å)	10.0024(2)	18.2134(13)
α (°)	85.340(2)	90°
β (°)	78.995(2)	91.726(6)
γ (°)	67.257(2)	90
Volume (Å^3)	482.71(2)	1371.1(4)
Z	2	4
$D_{calculated}$ (g cm^{-3})	1.302	1.382
Absorption coefficient (mm^{-1})	0.096	0.927
F(000)	208	608
Crystal size (mm$^{3)}$	0.4 × 0.4 × 0.6	0.1 × 0.4 × 0.5
θ range for data collection (°)	3.21–29.99	4.86–75.32
Index ranges (h, k, l)	−9/9; −10/10; −14/14	−12/12; −9/8; −22/22
Reflections collected	11524	10391
Independent reflections	2808 [R(int) = 0.0105]	2749 [R(int) = 0.0138]
Completeness to θ = 25° (%)	99.9	99.2
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2808/0/194	2749/0/258
Goodness-of-fit on F^2	1.064	1.067
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0299$, $wR_2 = 0.0837$	$R_1 = 0.0323$, $wR_2 = 0.0828$
R indices (all data)	$R_1 = 0.0312$, $wR_2 = 0.0846$	$R_1 = 0.0328$, $wR_2 = 0.0831$
Largest diff. peak and hole (e·Å^{-3})	0.421 and −0.202	0.312 and −0.173