Contents lists available at ScienceDirect

Vibrational Spectroscopy

Spectroscopic and theoretical studies of bis(dimethylphenyl betaine) hydrochloride monohydrate

Mirosław Szafran *, Anna Komasa, Zofia Dega-Szafran

Faculty of Chemistry, Adam Mickiewicz University, Umułtowska 89b, 61614 Poznań, Poland

ABSTRACT

Bis(dimethylphenyl betaine) hydrochloride monohydrate was prepared and characterized by FTIR, Raman spectroscopes, and B3LYP/6-311++G(d,p) calculations. In the optimized structure of the complex, two betaine moieties are joined by a very strong asymmetric hydrogen bond with an $O\cdots O$ distance of 2.439 Å. The water molecule is H-bonded to one oxygen atom of dimethylphenyl betaine and chloride anion via $O(w)\cdots O(2)$ and $O(w)\cdots Cl$ distances of 3.099 and 3.167 Å, respectively. The potential energy distributions (PED) were used for the assignments of IR and Raman frequencies in the experimental and calculated spectra of the title compound. Chloride anion interacts electrostatically with N^+ atoms.

Published by Elsevier B.V.

1. Introduction

The 'short-strong' (SSHB) or 'low-barrier' (LBHB) [1] $O\cdots O$ hydrogen bonds ($O\cdots O$ distances <2.5 Å) are present in the following three classes of complexes: (i) acid salts of carboxylic acids $(AHA)^- M^+$, where M = Na, K, Rb, Cs, NH_4, $N(Me)_4$ [2–7], (ii) basic salts of heterocyclic N-oxides and other oxygen bases with acids $(BHB)^+ X^-$ [8–13], and (iii) basic salts of betaines (zwitterionic molecules, inner salts) with acids $(BHB)^+ X^-$ [14–22], where X = Cl, Br, I, ClO_4, BF_4, $SbCl_6$, AsF_6. These types of complexes are characterized by the continuous absorption below 1800 cm^{-1}. Also notable is the absence of any distinct broad absorption in the region above 1800 cm^{-1}.

Previously, we have reported on the crystal and molecular structures, and spectroscopic properties of dimethylphenyl betaine hydrochloride [23] and dimethylphenyl betaine hydrate [24]. In this paper, we extend our investigation to bis(dimethylphenyl betaine) hydrochloride monohydrate (Scheme 1) as a new complex of a basic salt of the betaine.

2. Experimental

2.1. Synthesis

Bis(dimethylphenyl betaine) hydrochloride monohydrate was prepared by mixing dimethylphenyl betaine hydrochloride (0.01 M) [23] and dimethylphenyl betaine monohydrate (0.01 M) [24] in an aqueous solution. After evaporation of water in air for several days, colorless bis(dimethylphenyl betaine) hydrochloride monohydrate (2:1 complex) was obtained of m.p. 185–186 °C. Elemental analysis for $C_{20}H_{26}N_2O_4Cl\cdot H_2O$ calc.: C%, 58.18; H%, 7.08; N%, 6.78; found: C%, 58.21, H%, 7.06, N%, 6.81. The 2:1 complex during recrystallization from methanol decomposes to dimethylphenyl betaine and its hydrochloride. Hence the suitable crystals of the 2:1 complex to single-crystal X-ray analysis were not obtained.

2.2. FTIR and Raman spectra

Solid-state FTIR spectrum was recorded in Nujol and Fluorolube mulls on a Bruker IFS 66 v/S spectrometer, evacuated to avoid water and CO_2 absorptions at 2 cm^{-1} resolution. Each FTIR spectrum was accumulated by acquisition of 64 scans. The Raman spectrum of crystalline sample was measured on a Bruker FRA-106/S instrument operating at the 1064 nm exciting line of Nd:YAG laser with the resolution of 1 cm^{-1}. The spectrum was accumulated by acquisition of 200 scans.

* Corresponding author. Tel.: +48 61 8291714; fax: +48 61 8291555.
E-mail address: szafran@amu.edu.pl (M. Szafran).
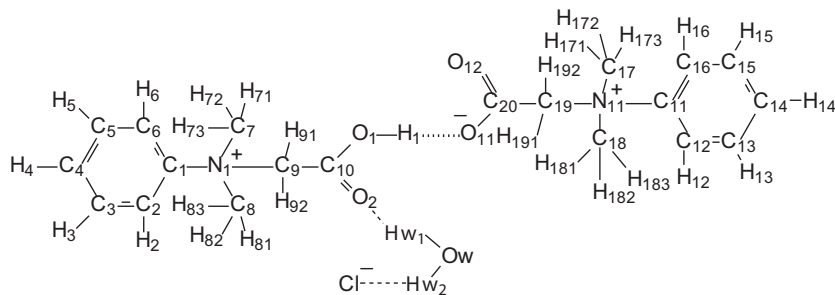
Scheme 1. Molecular structure of bis(dimethylphenyl betaine) hydrochloride hydrate and numbering of atoms.

2.3. Computational details

The DFT calculations were performed using the Gaussian 09 program package [25]. The optimum geometries were obtained employing B3LYP [26,27] functional in conjunction with 6-311++G (d,p) basis set [28]. Subsequently the vibrational IR and Raman spectra were calculated at harmonic approximation. All the calculated frequencies were real, which confirm that the optimized structures correspond to minimum energies.

The internal coordinates of the molecule were converted to the local-symmetry coordinates. The vibrational potential energy distribution (PED) was determined using VEDA 4 program [29] made available by Jamroz [30].

3. Results and discussion

3.1. Optimized structures

The most stable geometry of bis(dimethylphenyl betaine) hydrochloride monohydrate (2:1 complex) was constructed similarly to the structures of bis(4-methylammonium-benzoate) hydroiodide hydrate and its anhydrous molecule [31], and optimized at the B3LYP/6-311++G(d,p) level of theory, The optimized structure of the complex is shown in Fig. 1. The total energy and dipole moment are: $E = -1725.806386$ a.u. and $\mu = 2.876$ D. The calculated geometrical parameters are listed in Table 1. As illustrated in Fig. 1, a pair of betaines are bridged by a proton, forming a homoconjugated cation. The resulting asymmetrical O(1)-H···O(11) hydrogen bond links two carboxylate groups with the distances between them of 2.439 Å, which qualifies it as a very strong asymmetrical hydrogen bond [4]. In the crystals of bis(betaine) hydrochloride monohydrate the O···H···O hydrogen bond is 2.454(1) Å [14]. In the investigated complex the water molecule is H-bonded to one oxygen atom of dimethylphenyl betaine and chloride anion via O(w)-H(w1)···O(2) and O(w)-H(w2)···Cl hydrogen bonds with the O···O and O···Cl distances of 3.099 and 3.167 Å, respectively (Table 2). There are also some contacts between phenyl ring, methyl and methylene protons and chloride anion (Table 2). The chloride anion interacts
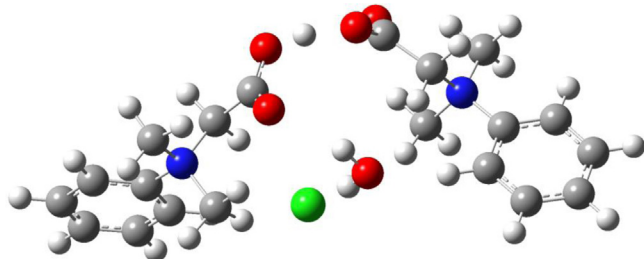
electrostatically with the positively charged nitrogen atoms, however the contacts between N(1)$^+$ and Cl$^-$ is shorter than that between N(11)$^+$ and Cl$^-$ (Table 2).

The two carboxylate-fragments participating in the hydrogen bond are planar with the dihedral angle between the O(2)–C(10)–O(1) and O(12)–C(20)–O(11) planes equal to −49.6°. The torsion angle between the planes through the phenyl rings is −113.0° and the angles between the phenyl rings and the COO$^-$ moieties are −88.8° and 41.4°, respectively.

3.2. Raman and FTIR spectra

The experimental Raman and FTIR spectra of bis(dimethyl-phenyl betaine) hydrochloride monohydrate are shown in Fig. 2a and c, respectively, and their frequencies are listed in Table 3. The FTIR spectra of bis(dimethylphenyl betaine) hydrochloride mono-hydrate (2:1 complex), dimethylphenyl betaine hydrochloride (1:1 complex) and dimethylphenyl betaine hydrate are compared in Fig 2c. The ν_{as}OH and ν_sOH bands of the water molecule appear at 3417

Fig. 1. The structures of bis(dimethylphenyl betaine) hydrochloride monohydrate optimized by the B3LYP/6-311++G(d,p) approach in vacuum.

Table 1
Calculated bond lengths (Å), bond and torsion angles (deg) for bis(dimethylphenyl betaine) hydrochloride hydrate.

Bond lengths			
N(1)–C(1)	1.509	N(11)–C(11)	1.506
N(1)–C(7)	1.526	N(11)–C(17)	1.505
N(1)–C(8)	1.504	N(11)–C(18)	1.505
N(1)–C(9)	1.532	N(11)–C(19)	1.538
C(1)–C(2)	1.395	C(11)–C(12)	1.396
C(2)–C(3)	1.394	C(12)–C(13)	1.392
C(3)–C(4)	1.391	C(13)–C(14)	1.394
C(4)–C(5)	1.390	C(14)–C(15)	1.390
C(5)–C(6)	1.396	C(15)–C(16)	1.396
C(9)–C(10)	1.531	C(19)–C(20)	1.554
C(10)–O(1)	1.295	C(20)–O(11)	1.273
C(10)–O(2)	1.223	C(20)–O(12)	1.231
O(w)–O(2)	3.099		
O(w)–Cl	3.167		
Bond angles			
N(1)–C(1)–C(2)	117.8	N(1)–C(11)–C(12)	118.2
C(1)–C(2)–C(3)	119.0	C(11)–C(12)–C(13)	119.3
C(2)–C(3)–C(4)	120.8	C(12)–C(13)–C(14)	120.8
C(3)–C(4)–C(5)	119.6	C(13)–C(14)–C(15)	119.4
C(4)–C(5)–C(6)	120.4	C(14)–C(15)–C(16)	120.5
C(5)–C(6)–C(1)	119.3	C(15)–C(16)–C(11)	119.5
C(1)–N(1)–C(7)	108.4	C(11)–N(11)–C(17)	108.8
C(1)–N(1)–C(8)	112.8	C(11)–N(11)–C(18)	112.6
C(1)–N(1)–C(9)	107.1	C(11)–N(11)–C(19)	108.4
N(1)–C(9)–C(10)	116.4	N(11)–C(19)–C(20)	116.6
C(9)–C(10)–O(1)	109.3	C(19)–C(20)–O(11)	109.7
C(9)–C(10)–O(2)	123.0	C(19)–C(20)–O(12)	121.5
Torsion angles			
C(2)–C(1)–N(1)–C(9)	63.5	C(12)–C(11)–N(11)–C(19)	58.2
C(1)–N(1)–C(9)–C(10)	178.0	C(11)–N(11)–C(19)–C(20)	−174.8
N(1)–C(9)–C(10)–O(1)	−161.5	N(11)–C(19)–C(20)–O(11)	166.1
N(1)–C(9)–C(10)–O(2)	22.1	N(11)–C(19)–C(20)–O(12)	−12.8