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Structure and vibrational spectra of 1,4-dimethylpiperazine di-betaine dihydrate

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Abstract

1,4-Dimethylpiperazine di-betaine, DBPZ (1,4-dicarboxymethyl-1,4-dimethylpiperazinium inner salt) crystallizes with two molecules of water. The crystals are triclinic, space group $P\bar{1}$, $a = 6.181(2)$ Å, $b = 6.2600(18)$ Å, $c = 8.869(2)$ Å, $\alpha = 97.50(2)°$, $\beta = 94.40(2)°$, $\gamma = 112.48(3)°$, $Z = 1$, $R = 0.0418$. Double water-molecules bridges link the DBPZ molecules into infinite chains by two sequences of $O–H\cdots O$ hydrogen bonds of 2.771(2) and 2.810(2) Å. The piperazine ring has a chair conformation with the methyl groups in the axial positions and the CH_2COO^- groups in the equatorial ones. The FTIR spectra of $DBPZ(H_2O)_2$ and $DBPZ(D_2O)_2$ are interpreted and the assignment of bands to the corresponding vibrations is proposed on the grounds of the spectra calculated by the B3LYP/6-31G(d,p) level of theory. The $DBPZ(H_2O)_2$ hydrogen-bonded complex is more stable by 18.5 kcal/mol than anhydrous DBPZ.

Keywords: 1,4-Dimethylpiperazine betaines; X-ray diffraction; Hydrogen bonds; B3LYP/6-31G(d,p) calculations; FTIR spectrum

1. Introduction

Cyclohexane is a prototype of saturated six-membered ring, as well as of the molecules with one or two hetero-atoms inserted in the ring molecules, and it has been widely investigated both theoretically and experimentally [1,2]. Piperazine plays an important role as a unit present in more complex molecules studied in several fields [3–5]. Piperazine in crystals has a chair conformation with the N–H bonds in the equatorial positions and resides at the crystallographic inversion center [6]. However, the experimentally determined dipole moment of 1.47 D and the rotational spectra suggest the existence of piperazine as a mixture of the three conformers: axial–axial, equatorial–equatorial and axial–equatorial [7,8]. The conversion process of six-membered saturated heterocycles is more complex than that in cyclohexane. Their molecules can perform three different types of intermolecular motion: (i) rotation about single bonds of the ring substituent, (ii) pyramidal nitrogen inversion and (iii) ring inversion, responsible for the whole conformational dynamic processes for the six-membered aza-cycles [9]. The axial substituent in six-membered rings are less stable than the equatorial ones, in which the electronic effect does not play a direct role, because of the repulsion between 1,3-diaxial protons and the axial substituents [10]. The effect of substituent is broadly subdivided into electronic (polar or inductive) and steric components [11]. However, it has been also demonstrated that in a number of cases the axial isomers are favored, even though either steric or dipolar considerations lead to the opposite prediction [12].

In our previous studies we have demonstrated that in 1,4-dimethylpiperazine di-betaine (1,4-carboxymethyl-1,4-dimethylpiperazinium inner salt, DBPZ) complexes with hydrochloric and *p*-hydroxybenzoic acids, the bulkier CH_2COO^- substituents are in the axial positions, while the methyl groups are in the equatorial ones [13,14]. In this paper, we have focused on the structure of 1,4-dimethylpiperazine di-betaine itself, in order to obtain information on its conformation in the crystal and in isolated molecule, on hydrogen bonds and electrostatic interactions.

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2. Experimental

1,4-Dimethylpiperazine di-betaine (DBPZ) was prepared according to the method described in Ref. [13], m.p. 270 °C decomp.

Crystals of DBPZ for X-ray diffraction experiment were grown from water. The crystal structure was determined from X-ray diffraction, measured with a KUMA KM-4 CCD diffractometer [15]. The structure was solved by direct methods using SHELXS-97 [16] and refined on F^2 by full-matrix least-squares with the SHELXL-97 program [17]. The summary of the crystallographic and experimental data is given in Table 1, and the final atomic coordinates are listed in Table 2. The complete set of structural parameters in CIF format is available as an Electronic Supplementary Publication from the Cambridge Crystallographic Data Centre (CCDC 656651).

The DFT calculations were performed with the GAUSSIAN-03 program package [18]. The calculations employed the B3LYP exchange-correlation functional, which combines the hybrid exchange functional of Becke [19,20] with the gradient-correlation functional of Lee et al. [21], and the split-valence polarized 6-31G(d,p) basis set [22]. The Gauss View 3.0 program was considered to get visual animation and also for the inspection of the normal modes description.

Table 1
Crystal data and structure refinement for 1,4-dimethylpiperazine di-betaine dihydrate

Empirical formula	$C_{10}H_{22}N_2O_6$
Formula weight	266.30
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a	6.181(2) Å
b	6.2600(18) Å
c	8.869(2) Å
α	97.50(2)°
β	94.40(2)°
γ	112.48(3)°
Volume	311.35(15) Å^3
Z	1
Calculated density	1.420 g/cm^3
Absorption coefficient	0.117 mm^{-1}
$F(000)$	144
Crystal size	0.4 × 0.3 × 0.15 mm
θ range for data collection	3.58–29.07°
Limiting indices	$-8 \leqslant h \leqslant 4$ $-8 \leqslant k \leqslant 8$ $-11 \leqslant l \leqslant 11$
Reflections collected/unique	1956/1389 [R(int) = 0.0220]
Completeness to $\theta = 29.07°$	83.1%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1389/0/93
Goodness-of-fit on F^2	0.820
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0418$, $wR_2 = 0.1311$
R indices (all data)	$R_1 = 0.0479$, $wR_2 = 0.1380$
Largest diff. peak and hole	0.201 and −0.190 eÅ^{-3}

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (Å^2 × 10^3) for 1,4-dimethylpiperazine di-betaine dihydrate

Atom[a]	x	y	z	U(eq)/U(iso)
N(1)	0.4998(2)	0.4380(2)	0.8321(1)	21(1)
C(2)	0.3474(2)	0.2649(2)	0.9241(2)	23(1)
C(6)	0.7159(2)	0.6156(2)	0.9369(2)	23(1)
C(7)	0.3632(3)	0.5599(3)	0.7571(2)	31(1)
C(8)	0.5771(2)	0.3097(2)	0.7033(1)	26(1)
C(9)	0.7225(2)	0.1694(2)	0.7478(2)	28(1)
O(1)	0.7792(2)	0.0775(2)	0.6307(2)	50(1)
O(2)	0.7707(2)	0.1526(2)	0.8824(1)	36(1)
O(1W)	1.0128(3)	−0.2223(3)	0.6291(2)	53(1)
H(21)	0.2032	0.1586	0.8586	28
H(22)	0.4310	0.1724	0.9575	28
H(61)	0.8068	0.7334	0.8797	28
H(62)	0.8144	0.5372	0.9708	28
H(71)	0.4628	0.6674	0.6989	39(5)
H(72)	0.3119	0.6445	0.8347	38(5)
H(73)	0.2279	0.4453	0.6900	46(5)
H(81)	0.6693	0.4246	0.6448	31
H(82)	0.4362	0.2023	0.6352	31
H(1W)	1.0870(50)	−0.1980(40)	0.5500(30)	58(6)
H(2W)	0.9430(50)	−0.1230(50)	0.6300(30)	67(7)

U(eq) is defined as one-third of the trace of the orthogonalized. U_{ij} tensor. The hydrogen atoms given without standard deviations were located from molecular geometry.

[a] The symmetry transformation used to generate equivalent atoms of the second half of the centrosymmetrical molecule is: $1-x$, $1-y$, $2-z$.

FTIR spectra were measured on a Bruker IFS 66v/S instrument, evacuated to avoid water and CO_2 absorptions. Solid state spectra were recorded in Nujol and Fluorolube suspensions using KBr plates. Each spectrum consisted of 64 scans. The Raman spectrum was measured on a Bruker IFS 66 instrument.

3. Results and discussion

3.1. Crystal structure

1,4-Dimethylpiperazine di-betaine dihydrate, $DBPZ(H_2O)_2$, crystallizes in the triclinic system with the centrosymmetric $P\bar{1}$ group. Only one half of the centrosymmetrical molecule of the title compound is symmetry-independent, with the piperazine ring located at the inversion center. The symmetry transformation for the second half is: $1-x$, $1-y$, $2-z$. The structure with the atom labeling is shown in Fig. 1. Because the piperazinium moiety lies at the inversion center, the atomic coordinates for N(1) and N(4), C(2) and C(5), and C(3) and C(6) are equivalent. To express this symmetry relation, the chemical numbering of the piperazine ring has been modified accordingly. Hence N(4) is labeled as N(1^i), C(5) as C(2^i) and C(3) as C(6^i), where the superscript indicates the code symmetry transformation ($1-x$, $1-y$, $2-z$). The bond length, bond and torsion angles are listed in Table 3.

The piperazine ring has a chair conformation with the methyl groups in the axial positions and the CH_2COO^- substituents in the equatorial ones. The DBPZ molecule has a zwitterionic character with the charge of −0.5352 and