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Structure of 1-methyl-6-oxyquinolinium betaine dihydrate studied by X-ray diffraction, DFT calculations, vibrational and NMR spectra

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Dedicated to Prof. Austin Barnes on the occasion of his 65th birthday.

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ABSTRACT

The crystals of 1-methyl-6-oxyquinolinium betaine dihydrate, 6QB·2H_2O, are triclinic, space group $P\bar{1}$. The oxygen atom of 6QB exhibits an extremely rare capability of accepting four hydrogen bonds. It is engaged in four hydrogen bonds to water molecules of the 2.823, 2.825, 2.833 and 2.849 Å; each water molecule interacts with two neighbouring 6QB molecules linking them into infinite sheets. Differences in geometrical parameters between the X-ray and calculated molecules reflect changes in their structures between zwitterion and quinonoid forms. The probable assignments of the experimental FTIR solid spectrum have been made on the basis of B3LYP/6-311G(d,p) calculated frequencies in vacuum. Both ^{1}H and ^{13}C chemical shifts are solvent dependent. Linear correlations between the experimental ^{1}H and ^{13}C NMR chemical shifts of 6QB·2H_2O in solutions and the GIAO/B3LYP/6-311G(d,p) calculated magnetic isotropic shielding tensors (σ_{cal}) using the screening solvation model, $\delta_{exp} = a + b\sigma_{cal}$, are reported.

1. Introduction

Betaines are zwitterions (inner salts, dipolar ions) with two oppositely charged units. An important group of betaines are pyridinium-, isoquinolinium- and quinolinium-olates and their complexes with acids [1–7]. An interesting betaine is 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-phenoxide known as the Reichardt's type dye [8,9], which was used to evaluate solvent polarity $E_T(30)$ values for several hundred solvents from the peak wavenumbers (ν) of the longest UV wavelength charge transfer absorption band. Another attractive molecule is 1-methyl-8-oxyquinolinium betaine (1-methylquinolinium-8-olate), 8QB. On the basis of this molecule, the polarities E_T(8QB) of 28 pure solvents were determined and were found to correlate linearly with the corresponding $E_T(30)$ scale [2–4]. Recently, we have studied spectroscopic properties of 1-methyl-8-oxyquinolinium betaine [5].

Another interesting molecules are cations of 6-hydroxyquinolinium and 1-methyl-6-hydroxyquinolinium, which are well-known as strong photoacids exhibiting photoinduced solute–solvent proton transfer (PT) in aqueous solution and alcohols [10].

In this paper, 1-methyl-6-oxyquinolinium betaine dihydrate (1-methylquinolinium-6-olate), 6QB·2H_2O, has been studied by X-ray diffraction, DFT calculations, FTIR, Raman and NMR spectroscopic techniques. In the crystal the oxygen atom of 6QB is engaged in four hydrogen bonds with water molecules. The water molecule additionally interacts with two neighbouring 6QB molecules, linking them into infinite sheets.

2. Experimental and calculations

1-Methyl-6-hydroxyquinolinium iodide was prepared following the method described by Bardez et al. [6a]: 6-hydroxyquinoline (3 g) in dry acetonitrile (15 ml) was refluxed with methyl iodide (2 ml, 4.6 g) for 8 h. The solvent was evaporated and the residue was purified by heating for 15 min with charcoal in methanol and recrystallized from ethanol to give green crystals as plates (5.1 g, 85% yield), m.p. 231–233 °C (lit. [6c] 234–235.5 °C).

1-Methyl-6-oxyquinolinium betaine dihydrate, 6QB·2H_2O, was prepared by dissolving iodide salt (2 g) in hot methanol (10 ml) and treating it with aqueous solution of K_2CO_3 (0.6 g). The solvent was evaporated and the residue after recrystallization from ethyl acetate–ethanol (1:3) gives yellow-orange crystals as needles (1.1 g, 81% yield), m.p. 156–159 °C.

1-Methyl-6-oxyquinolinium betaine anhydrous, 6QB, was obtained as red needles after drying at 80 °C in vacuum over P_2O_5, m.p. 239–243 °C. The dehydrated sample was very hygroscopic and the last trace of water was very hard to remove [6b]. The anhydrous sample converts to dihydrate when left in an open vessel.

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X-ray diffraction measurements were carried out on a KUMA KM4-CCD diffractometer [11]. The structure was solved by direct methods with the SHELXS-97 program [12] and refined with the SHELXL-97 program [13]. All non-hydrogen atoms were anisotropically refined. Four H-atoms at water molecules O(1W) and O(2W) were located from the difference Fourier maps and refined with isotropic temperature factors. All other H-atoms were located from the molecular geometry and their $U_{\text{iso's}}$ were related to the thermal vibrations of their carriers. The crystal data, together with the details concerning their collection and structure refinement are given in Table 1. The molecular structure and atom numbering of 6QB·2H_2O are shown in Fig. 1 and the crystal packing in Figs. 2 and 3. The parameters in the CIF form are available as Electronic Supplementary Information from the Cambridge Crystallographic Database Centre (CCDC 752767). Molecular illustrations were prepared using ORTEPII [14] package.

FTIR and Raman spectra were recorded on a Bruker IFS 113v spectrometer at a 2 cm^{-1} resolution. FTIR spectra were measured in Nujol and Fluorolube emulsions. Raman spectrum was measured for the crystal sample. The samples of anhydrous betaine were prepared in a dry-box.

^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 VT spectrometer operating at 300.07 and 75.46 MHz for proton and carbon-13, respectively, in DMSO-d_6, CD_3CN and D_2O solutions, in 5 mm tubes. The concentration of samples was 0.05 mol l^{-1}. The chemical shifts were measured with respect to internal standard TMS (organic solutions) and 3-(trimethylsilyl)propionic-d_4 acid sodium salt (D_2O). The assignments of the chemical shifts were confirmed by COSY, HETCOR and HMBC experiments.

The calculations were performed using the Gaussian 03 program package [15] and B3LYP [16,17] method in conjunction with 6-311G(d,p) [18] basis set. The conductor like screening solvation model was applied to calculate the structure of 6QB·2H_2O as isolated molecule and in DMSO, CH_3CN and H_2O solutions [19]. Geometrical parameters are listed in Table 2 and the energies, dipole moments and H-bond distances in Table 3. The vibrational FTIR spectra (harmonic wavenumbers and absolute intensities) were calculated at the B3LYP/6-311G(d,p) level of theory. The harmonic force fields, determined initially in the Cartesian coordinates, were transformed to the force fields in the internal local-symmetry coordinates. The local-symmetry coordinates, defined in terms of the internal valence coordinates following the IUPAC recommendation [20,21], are given in Table 4. In this way, the redundant internal coordinates were removed. The force fields thus determined were used to calculate the vibrational potential energy distribution (PED) of the normal coordinates. PED is defined as recommended by Keresztury and Jalsovszky [22] and was calculated with the program PACK [23,24]. The contributions greater than 10% are given in Table 5. The

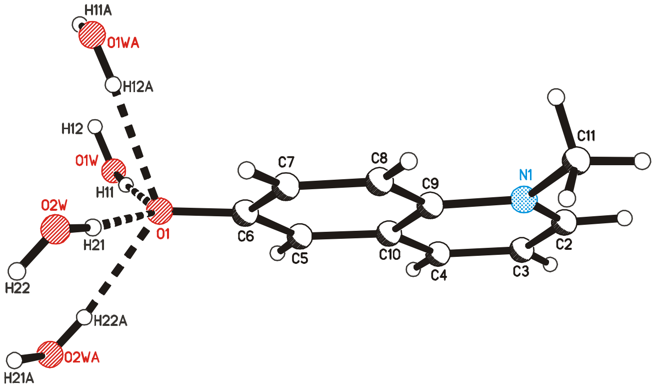

Fig. 1. The asymmetric unit of 1-methyl-6-oxyquinolinium betaine dihydrate (6QB·2H_2O) and two other symmetry dependent water molecules included in this drawing to illustrate the 4-fold H-acceptor capacity of the C(6)–O(1) group and the atom labelling. The hydrogen bonds are indicated by the dashed lines.

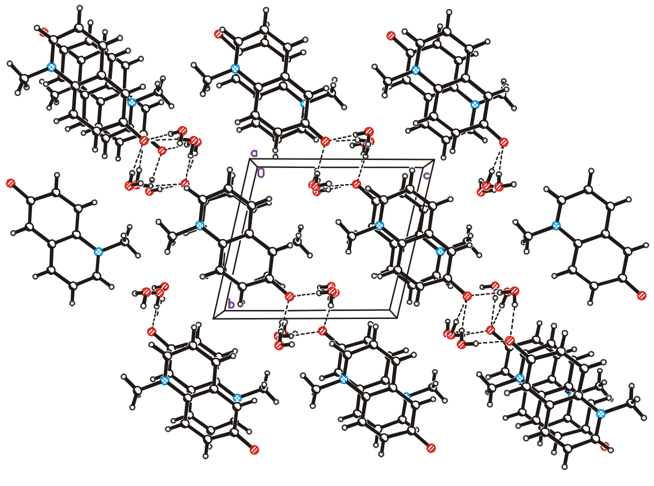

Fig. 2. The crystal structure of 6QB·2H_2O viewed as an autostereographic projection down the [1 0 0] axis [34]. The hydrogen bonds are indicated by the dashed lines.

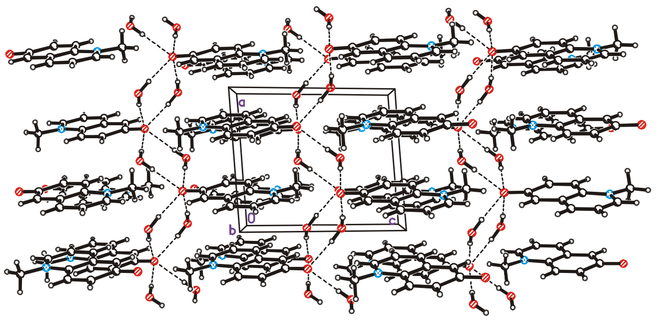

Fig. 3. Autostereographic projection [35] of the molecule packing in the crystal structure of 6QB·2H_2O. The hydrogen bonds are indicated by the dashed lines.

Table 1
Crystal data and structure refinement for 1-methyl-6-oxyquinolinium betaine dihydrate, 6QB·2H_2O.

Empirical formula	$C_{10}H_9NO·2H_2O$
Formula weight	195.21
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 7.304(1) Å
	b = 7.686(1) Å
	c = 8.676(1) Å
	α = 102.77(1)°
	β = 93.73(1)°
	γ = 92.96(1)°
Volume	472.9(1) $Å^3$
Z	2
Calculated density	1.371 g/cm^3
Absorption coefficient	0.102 mm^{-1}
F(0 0 0)	208
Crystal size	0.25 × 0.15 × 0.075 mm
θ Range for data collection (°)	2.80–29.44°
Max./min. indices	$-9 \leq h \leq 8$, $-10 \leq k \leq 9$, $-11 \leq l \leq 11$
Reflections collected/unique	6114/2299 R_{int} = 0.0330
Completeness to θ_{max} = 28.77°	88.0%
Refinement method	Full-matrix-block least-squares on F^2
Data/restraints/parameters	2299/0/143
Goodness-of-fit on F^2	1.037
Final R indices [$I > 2\sigma_I$]	R_1 = 0.0600, wR_2 = 0.1277
R indices (all data)	R_1 = 0.1560, wR_2 = 0.1618
Largest diff. peak and hole	0.254 and −0.173 $eÅ^{-3}$