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Unusual molecular structure of the 1:2.5:2 complex of DABCO di-betaine (1,4-diacetate-1,4-diazoniumbicyclo[2.2.2]octane) with *p*-hydroxybenzoic acid and water

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ABSTRACT

The molecular structure of the 1:2.5:2 complex of DABCO di-betaine, *p*-hydroxybenzoic acid (HBA) and water (**1**) has been characterized by single-crystal X-ray diffraction, infrared spectroscopy and DFT calculations. The crystals **1** are triclinic, space group $P\bar{1}$. The carboxylate groups of DABCO di-betaine are engaged in the COO···HOOC and COO···HO hydrogen bonds with two HBA molecules of 2.750(2) and 2.621(2) Å, respectively. Two water molecules and one HBA, disordered over the inversion center in two orientations with half occupancies, play a role of the bridge between the DABCO di-betaine·$(HBA)_2$ complexes. Three structures of DABCO di-betaine with HBA and water of different stoichiometry (**2**–**4**) have been optimized at the B3LYP/6-31G(d,p) level of theory. The $\nu C{=}O$ and $\nu_{as}COO$ vibrations are distinguished in the solid-state FTIR spectrum of **1** and confirmed by the second-derivative spectrum of **1** and the calculated spectrum of **2** by the B3LYP/6-31G(d,p) approach.

1. Introduction

1,4-Diazabicyclo[2.2.2]octane, $N(CH_2CH_2)_3N$, abbreviated as DABCO, is a globular molecule of high symmetry. It crystallizes as anhydrous compound or as hydrates [1–4]. Crystals of DABCO undergo a structural phase transition [5–8]. DABCO is a common chemical reagent with a wide range of applications. Its complexes with mineral acids have interesting and promising physical and chemical properties. The spontaneous polarization of the N^+–H···N bond is responsible for ferroelectric properties of DABCO salts [9–13].

DABCO, as a 3°-amine, in the reaction with alkyl halides forms a variety of quaternary 1,4-dialkyl-1,4-diazabicyclo[2.2.2] octane dihalides [14]. Wu and Mak have synthesized and solved the crystal structures of 1,4-dicarboxymethyl-1,4-diazabicyclo [2.2.2]octane inner salt (1,4-diacetate-1,4-diazoniumbicyclo[2.2.2] octane, DABCO di-betaine) and its hydrochloride [15].

In this paper we investigated the structure of the complex formed between DABCO di-betaine and *p*-hydroxybenzoic acid (HBA, Scheme 1). It is a continuation of our previous study of the molecular structures of complexes of alicyclic and aromatic betaines with HBA [16–22]. It was our intention to investigate the hydrogen bonds in the DABCO di-betaine·HBA complex by X-ray diffraction and FTIR spectroscopy, as well as comparison of molecular structures in the crystals and in isolated molecules, optimized at the B3LYP/6-31G(d,p) level of theory.

2. Experimental

2.1. Materials

1,4-Diacetate-1,4-diazoniumbicyclo[2.2.2] octane, DABCO di-betaine, was prepared according to the method described in Ref. [15]. The crystals of the complex of DABCO di-betaine with *p*-hydroxybenzoic acid (HBA) were grown from a mixture of the components dissolved in the CH_3OH–H_2O solution, m.p. 245–248 °C. Analysis for $C_{27.5}H_{35}N_2O_{13.5}$; calcd.: %C, 54.19; %H, 5.79; %N, 4.60; found: %C, 53.70; %H, 5.95; %N, 4.59. The deuterated complex was prepared by threefold crystallization from CH_3OD and the excess of solvent was removed under the reduced pressure on heating.

2.2. Measurements

The crystal structure of the complex of DABCO di-betaine with HBA (**1**) was determined by X-ray diffraction, measured with a KUMA KM-4 CCD diffractometer [23,24]. The structure was solved by direct methods using SHELXS-97 [25] and refined on F^2 by

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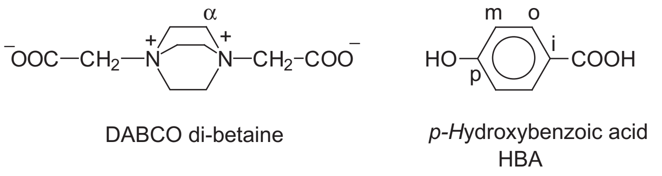

Scheme 1. Molecular structures of DABCO di-betaine and *p*-hydroxybenzoic acid (HBA).

full-matrix least-squares with the SHELXL-97 [26]. The disordered *p*-hydroxybenzoic acid was refined with the benzene ring and its hydrogens idealized and fixed as a rigid group; the hydroxyl and acid hydrogens were assigned by using the AFIX instruction of SHELXL. The numbering of atoms is shown in Fig. 1. The crystal data, details of data collection and structure refinement are given in Table 1. The final atomic coordinates listed in Table A and the bond lengths, bond and torsion angles given in Table B are included in the Supplementary material. The complete set of structural parameters in CIF format is available as an Electronic Supplementary Publication from the Cambridge Crystallographic Data Centre (CCDC 803377).

The DFT calculations were performed with the GAUSSIAN-03 program package [27]. The calculations employed the B3LYP exchange–correlation functional, which combines the hybrid exchange functional of Becke [28,29] with the gradient-correlation functional of Lee, Yang and Parr [30] and the split-valence polarized 6-31G(d,p) basis set [31]. All the calculated IR frequencies for complexes **2**–**4** were positive and confirmed that the optimized structures were in the states of minimum energies. The geometry of **1** was used as a starting point for the calculations.

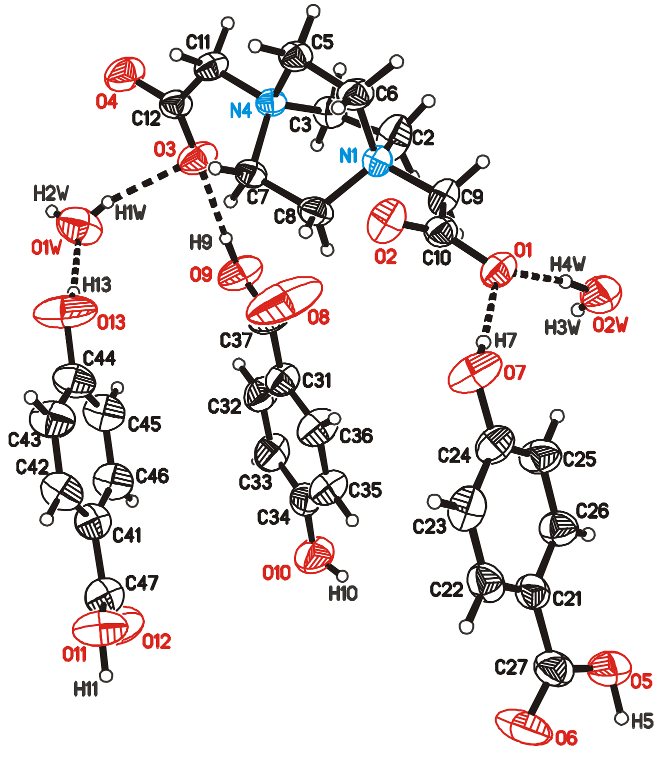

Fig. 1. The symmetry-independent part of the unit cell of the 1:2.5:2 complex of DABCO di-betaine with *p*-hydroxybenzoic acid and H_2O (**1**). The *p*-hydroxybenzoic acid [C(41)–C(47)] is located on an inversion center (located approximately between C(42) and C(46)) and hence disordered in two orientations (with half occupancies) and only one of them has been shown for clarity. The hydrogen bonds have been indicated by the dashed lines. The thermal ellipsoids have been drawn at the 50% probability level.

Table 1
Crystal data and structure refinement for the 1:2.5:2 complex of DABCO di-betaine (1,4-diacetate-1,4-diazoniumbicyclo[2.2.2]-octane) with *p*-hydroxybenzoic acid and water.

Empirical formula	$C_{27.50}H_{35}N_2O_{13.50}$
Formula weight	609.57
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 7.8300(9) Å
	b = 14.461(2) Å
	c = 14.6827(14) Å
	α = 60.897(12)°
	β = 88.998(9)°
	γ = 82.905(11)°
Volume	1439.8(3) $Å^3$
Z	2
Calculated density	1.406 g/cm^3
Absorption coefficient	0.113 mm^{-1}
F(0 0 0)	644
Crystal size	0.21 × 0.18 × 0.13 mm
θ range for data collection (°)	2.97–29.00
Max/min. indices h, k, l	−9/10, −12/19, −17/18
Reflections collected/unique	11960/6500 [R(int) = 0.0164]
θ_{Max}(°)/completeness (%)	29.00/84.8%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6500/4/451
Goodness-of-fit on F^2	1.022
Final R indices [$I > 2\sigma_I$]	$R1$ = 0.0429, $wR2$ = 0.1033
R indices (all data)	$R1$ = 0.0733, $wR2$ = 0.1107
Largest diff. peak and hole	0.222 and −0.207 e A^{-3}

FTIR spectra were measured on a Bruker IFS 66v/S instrument, with the resolution of 2 cm^{-1}. The FTIR solid state spectra were recorded in Nujol and Fluorolube suspensions using KBr plates.

The NMR spectra were recorded on a Varian Gemini 300 VT spectrometer operating at 300.07 and 75.46 MHz for ^1H and ^{13}C, respectively. The spectra were measured in D_2O relative to internal standard of 3-(trimethylsilyl)propionic-d_4 acid sodium salt. δ^1H (ppm): 4.14 (CH_2), 4.26 (CH_2 ring), 6.94 (H-m), 7.90 (H-o); $\delta^{13}C$ (ppm): 54.29 (C-ring), 67.05 (CH_2), 118.20 (C-m), 126.02 (C-i), 134.95 (C-o), 163.11 (C-p), 170.39 (COOH), 174.63 (COO).

3. Results and discussion

3.1. Crystal structure

The hydrogen-bonded complex **1** of DABCO di-betaine with *p*-hydroxybenzoic acid (HBA) crystallizes as dihydrate at the ratio 1:2.5:2 in triclinic $P\bar{1}$ group. The structure of complex **1** with atom labeling is shown in Fig. 1. The selected bond lengths, bond and torsion angles are given in Table 2 and the H-bond distances in Table 3. One of the HBA molecules, labeled C(41)–C(47) lies on an inversion center, located approximately between atoms C(42) and C(46). Hence, it is disordered in two antiparallel orientations, each half occupied. Only one of these orientations has been shown in Fig. 1, for clarity. The disordered HBA molecules in their both orientations over the inversion centers are shown in Figs. 2 and 3. The space-filling drawing in Fig. 3 illustrates the close packing of the structure, including the disordered HBA molecules. DABCO di-betaine in the complex is in the double zwitterionic form. The C(10)–O(1), C(10)–O(2), C(12)–O(3) and C(12)–O(4) bond lengths are 1.268(2), 1.230(2), 1.235(2) and 1.244(2) Å, respectively (Table 2). The O(1) and O(3) oxygen atoms of the carboxylate groups, as proton-acceptors, are bonded to HBA and water molecules by the medium–strong hydrogen bonds (Table 3). However, the O(3) oxygen atom is engaged in the O(3)···H(9)–O(9) hydrogen bond of 2.750(2) Å with the carboxylic group of one of the HBA