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O—H···O and O—H···N hydrogen bonds in the complex of DABCO mono-betaine with *p*-hydroxybenzoic acid studied by X-ray diffraction, DFT calculations and spectroscopic methods

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ABSTRACT

DABCO mono-betaine (1,4-diazabicyclo[2.2.2]octane-1-acetate) forms a complex with *p*-hydroxybenzoic acid (HBA) at the 1:1 ratio. The crystals are monoclinic, space group $P2_1/m$. The HBA and DABCO mono-betaine molecules are linked into infinite chains through the COOH···OOC and O—H···N hydrogen bonds of 2.604(1) and 2.771(2) Å, respectively. The DABCO mono-betaine is located on a mirror plane and the HBA molecule lies on this plane. In the structure of the 1:1 complex optimized by the B3LYP/6-31G(d,p) approach, the DABCO ring has a planar conformation, while in the chains formed by two complexes, the DABCO moieties assume the propeller conformations. The FTIR spectrum shows several bands attributed to the O—H, O—H···O, O—H···N, C=O and COO stretching vibrations. ^{1}H and ^{13}C chemical shifts assignments were confirmed by the magnetic isotropic shielding constants, calculated by the GIAO/B3LYP/6-31G(d,p) approach.

1. Introduction

The Menschutkin reaction with alkyl halides results in the formation of a variety of 1-alkyl and 1,4-dialkyl-1,4-diazabicyclo[2.2.2]octane halides [1]. Similarly as 1,4-dimethylpiperazine [2], 1,4-diazabicyclo[2.2.2]octane (DABCO) forms two betaines: DABCO mono-betaine [3] and DABCO di-betaine [4]. DABCO mono-betaine crystallizes as mono-hydrate in orthorhombic space group $Pmn2_1$ [3] and forms a complex with HCl and water at the 2:3:2 ratio [5].

In this paper we extent our investigation to the synthesis of the 1:1 complex of DABCO mono-betaine with *p*-hydroxybenzoic acid, HBA, **1** (Scheme 1) and its characterization by X-ray diffraction, FTIR and NMR spectroscopies, and DFT calculations. DABCO mono-betaine has two non-equivalent proton-acceptor centers, the carboxylate group ($pK_1 = 1.97$) and the tertiary nitrogen atom ($pK_2 = 2.85$) [5], while *p*-hydroxybenzoic acid has two different proton-donor groups, COOH ($pK_{a1} = 4.67$) and OH ($pK_{a2} = 9.37$ [6], hence the molecular complex studied could give new interesting information of the O—H···O and O—H···N hydrogen bonds, crystal packing, molecular interactions and the DABCO ring conformation. We intended to compare the crystal structure of the complex investigated with those of the complexes of DABCO di-betaine with HBA and water (which it is formed at the ratio 1:2.5:2) [7], and 1,4-dimethylpiperazine mono- and di-betaines with HBA [8,9]. This study continues our search for new functional materials using hydrogen bonds as the main means of binding molecules and ions. For this purpose we need to understand the role of hydrogen bonds for the molecular aggregation and for the formation of unsolvated and solvated compounds.

2. Experimental

2.1. Synthesis

DABCO mono-betaine was prepared according the procedure described in Ref. [3]. The 1:1 complex of DABCO mono-betaine with *p*-hydroxybenzoic acid, **1**, was obtained by mixing of equimolar amounts of substrates in methanol. Complex **1** was recrystallized from a methanol–water (10:1) solution; m.p. 238–239°. Elemental analysis for $C_{15}H_{20}N_2O_5$, found: %C, 58.24; %H, 6.52; %N, 9.07; calcd.: %C, 58.43; %H, 6.54; %N, 9.09.

2.2. Measurements

The crystal structure of the complex of DABCO mono-betaine with *p*-hydroxybenzoic acid (**1**) was determined by X-ray diffraction, measured with a KUMA KM-4 CCD diffractometer [10,11]. The structure was solved by direct methods using SHELXS-97

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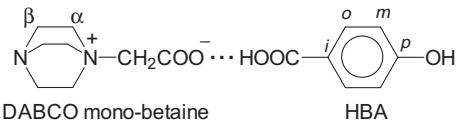

Scheme 1. Molecular formula of the complex of DABCO mono-betaine with *p*-hydroxybenzoic acid (**1**).

and refined on F^2 by full-matrix least-squares with SHELXL-97 [12]. The crystal data, details of data collection and structure refinement are 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 815756).

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.

NMR spectra were recorded on a Varian VMNRS-400 spectrometer operating at 402.641 and 101.243 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.

2.3. DFT calculations

The DFT calculations were performed with the GAUSSIAN-03 program package [13]. The calculations employed the B3LYP exchange–correlation functional, which combines the hybrid exchange functional of Becke [14,15] with the gradient-correlation functional of Lee et. al. [16] and the split-valence polarized 6-31G(d,p) basis set [17]. The magnetic isotropic shielding constants were calculated with the standard GIAO/B3LYP/6-31G(d,p) (Gauge-Independent Atomic Orbital) approach with the GAUSSIAN-03 program package using the conductor-like screening solvating model (COSMO) [18]. The X-ray geometry was used as a starting point for the calculations.

Table 1
Crystal data and structure refinement for the 1:1 complex of DABCO mono-betaine with *p*-hydroxybenzoic acid.

Empirical formula	$C_{15}H_{20}N_2O_5$
Formula weight	308.33
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/m$
Unit cell dimensions	a = 6.7164(3) Å
	b = 6.8899(4) Å
	c = 15.8923(6) Å
	β = 96.289(4)°
Volume	730.99(6) $Å^3$
Z	2
Calculated density	1.401 g/cm^3
Absorption coefficient	0.106 mm^{-1}
F(0 0 0)	328
Crystal size	0.32 × 0.23 × 0.20 mm
θ range for data collection (°)	3.05–28.37
Max/min. indices h, k, l	−8/8, −9/8, −19/20
Reflections collected/unique	9516/1796 [R(int) = 0.0299]
θ_{Max}(°)/Completeness (%)	28.37/91.4
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1796/0/173
Goodness-of-fit on F^2	1.020
Final $R1/wR2$ indices [$I > 2\sigma$]	0.0431/0.1075
$R1/wR2$ indices (all data)	0.0586/0.1195
Largest diff. peak and hole	0.161 and −0.245 e $Å^{-3}$

Table 2
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the 1:1 complex of DABCO mono-betaine with *p*-hydroxybenzoic acid. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
N(1)	−2831(2)	2500	−1234(1)	24(1)
C(2)	−4106(2)	4296(2)	−1195(1)	33(1)
C(3)	−5787(2)	4242(2)	−1927(1)	37(1)
N(4)	−5653(2)	2500	−2458(1)	33(1)
C(5)	−3702(3)	2500	−2792(1)	35(1)
C(6)	−1973(3)	2500	−2071(1)	34(1)
C(9)	−1106(3)	2500	−542(1)	28(1)
C(10)	−1616(3)	2500	379(1)	28(1)
O(1)	−49(2)	2500	893(1)	48(1)
O(2)	−3350(2)	2500	553(1)	43(1)
C(11)	1028(3)	2500	3894(1)	30(1)
C(12)	−791(3)	2500	4233(1)	35(1)
C(13)	−853(3)	2500	5099(1)	38(1)
C(14)	904(3)	2500	5642(1)	35(1)
C(15)	2731(3)	2500	5311(1)	42(1)
C(16)	2783(3)	2500	4444(1)	39(1)
C(17)	1175(3)	2500	2973(1)	30(1)
O(3)	−560(2)	2500	2494(1)	42(1)
O(4)	2764(2)	2500	2674(1)	46(1)
O(5)	774(2)	2500	6490(1)	47(1)
H(21)	−4600(20)	4270(20)	−637(10)	39(4)
H(22)	−3250(30)	5400(30)	−1245(11)	52(5)
H(31)	−7090(30)	4230(30)	−1706(11)	53(5)
H(32)	−5710(20)	5370(30)	−2278(12)	54(5)
H(51)	−3610(20)	3630(20)	−3129(10)	40(4)
H(61)	−1170(20)	3720(30)	−2062(10)	45(4)
H(91)	−320(20)	3690(20)	−638(10)	38(4)
H(12)	−1990(40)	2500	3853(16)	47(7)
H(13)	−2120(40)	2500	5312(16)	48(7)
H(15)	3940(40)	2500	5688(17)	54(7)
H(16)	4010(40)	2500	4232(16)	50(7)
H(3)	−380(40)	2500	1880(20)	72(9)
H(5)	2040(50)	2500	6770(20)	78(10)

3. Results and discussion

3.1. Crystal structure

DABCO mono-betaine forms a crystalline complex with *p*-hydroxybenzoic acid (HBA), **1**, at the 1:1 ratio. The crystals are monoclinic, space group $P2_1/m$. Fig. 1 shows the labeling system of atoms in the complex **1**, while the bond lengths, bond and torsion angles are given in Table 3. The atoms N(1), N(4), C(5), C(6), C(9), C(10), O(1) and O(2) of DABCO mono-betaine unit are located on a mirror plane, perpendicular to the *y*-axis, hence only half of the molecule is asymmetric, while the remaining atoms of the ethylene bridges in the DABCO mono-betaine unit can be generated by the symmetry code: x, $-y + 0.5$, z. The ethylene bridges in the DABCO mono-betaine unit are planar, the N(1)—C—C—N(4) torsion angles are ca. 1° (Table 3). A similar planar conformation has been observed in DABCO mono-betaine hydrate [3], while in its hydrated complex with HCl three ethylene bridges are twisted by about 12° [5] and the crystal mirror-plane symmetry is broken. In DABCO salts with inorganic acids at room and higher temperatures the conformation of the ring is planar, while the propeller conformation was assumed at low temperature [19–22]. In complex **1**, *p*-hydroxybenzoic acid molecule is coplanar with the DABCO mono-betaine moiety in the crystallographic mirror plane (Figs. 2 and 3a, Table 2).

DABCO mono-betaine unit exists in a zwitterionic form and its carboxylate group, as a proton-acceptor, is involved in the O(3)—H(3)···O(1) hydrogen bond of 2.604(1) Å with the carboxylic group of HBA. Hence, the C(10)—O(1) bond of 1.260(2) Å is longer than C(10)—O(2) of 1.225(2) Å. The hydroxyl group of HBA interacts with the N(4) nitrogen atom of the neighboring DABCO