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Crystal structure and spectroscopic properties of the 1:1 complex of pyridine betaine with *p*-hydroxybenzoic acid

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ABSTRACT

Crystal structure of the 1:1 complex of pyridine betaine (PyB) with *p*-hydroxybenzoic acid (HBA) has been determined by X-ray diffraction. The crystals are monoclinic, space group $P2_1/c$ with the unit cell parameters $a = 11.9009(4)$, $b = 10.3283(3)$, $c = 11.0616(4)$ Å and $\beta = 104.252(4)^\circ$, $Z = 4$, $R = 0.038$. Both oxygen atoms of the carboxylate group of PyB are linked with the carboxylic and hydroxyl groups of HBA of the neighboring molecules, through two O–H···O hydrogen bonds of 2.589(1) and 2.588(2) Å, respectively. The PyB and HBA molecules are connected into infinite chains parallel to the *x*-axis. The FTIR spectrum of the solid complex is consistent with the X-ray results. ^{1}H and ^{13}C chemical shifts of the title complex in D_2O and DMSO-d_6 and the GIAO/B3LYP/6-31G(d,p) calculated magnetic isotropic shielding tensors (σ) using the screening solvation model (COSMO), $\delta_{exp} = a + b\sigma$, are reported. In the theoretically optimized structures of the complex investigated the O···O distances between PyB and HBA are not the same.

1. Introduction

Carboxybetaines are inner salts (zwitterionic compounds) consisting of an anionic carboxylate group and the positively charged nitrogen atom [1–3]. Several complexes of betaines with inorganic and organic acids display interesting physical properties exhibiting nonlinear optical properties and phase transitions [4–7]. Recently, we have studied some complexes of *p*-hydroxybenzoic acid (HBA) with betaines of alicyclic amines: e.g. *N*-methylmorpholine [8], *N*-methylpiperidine [9], *N,N*-dimethylpiperazine [10,11], and complexes of amino acids, e.g. piperidine-acetic acid [12] and piperidine-3-carboxylic acid [13] with HBA.

The present paper is a continuation of this project. We extend the study on preparation and structure of a complex of pyridine betaine (PyB) with *p*-hydroxybenzoic acid (HBA) to get more information on the role of the hydroxyl substituent as an additional proton-donor center in the acid molecule, on the hydrogen bonds and structures.

2. Experimental

Pyridine betaine (*N*-carboxymethylpyridinium inner salt) was prepared as described previously in Ref. [14]. The 1:1 complex of pyridine betaine with *p*-hydroxybenzoic acid (PyB·HBA) was obtained by mixing the equimolar amounts of PyB and HBA, in methanol. The precipitate was filtered off and dried over P_2O_5. The crystals were grown from a methanol–acetonitrile mixture (1:1), m.p. 135 °C. The deuterated complex was prepared by exchange with D_2O, followed by removal of excess of D_2O in vacuum.

Diffraction measurements were carried out at ambient temperature on a KUMA-KM 4 diffractometer equipped with CCD detector, using Mo Kα radiation. Data reduction was carried out with the KUMA-CCD software [15,16]. The structure was solved by direct methods using SHELXS-97 program [17]. All non-hydrogen atom positions were found from E-map and hydrogen atoms were found from a difference Fourier map. Parameters of non-hydrogen atoms were refined with anisotropic displacement parameters and the parameters of hydrogen atoms were refined isotropically using SHELXL-97 program [18]. The final *R*-factor is 0.038 for 2827 independent reflections and 234 refined parameters. The crystal data and details of data processing are given in Table 1 and the final fractional atomic coordinates in Table 2. The supplementary information in the CIF form is available from Cambridge Crystallographic Database Center, No. CCDC 715725.

The DFT calculations were performed with the GAUSSIAN 03 program package [19]. The calculations employed the B3LYP exchange-correlation functional, which combines the hybrid exchange functional of Becke [20,21] with the gradient-correlation functional of Lee, Yang and Parr [22] and the split-valence polarized 6-31G(d,p) basis set [23]. The magnetic isotropic shielding tensors were calculated with the standard GIAO/B3LYP/6-31G(d,p) (Gauge-Independent Atomic Orbital) approach using the conductor-like screening continuum solvation model (COSMO) [24].

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Table 1
Crystal data and structure refinement for the complex of pyridine betaine with *p*-hydroxybenzoic acid (PyB·HBA).

Empirical formula	$C_{14}H_{13}NO_5$
Formula weight	275.25
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a	11.9009(4) Å
b	10.3283(3) Å
c	11.0616(4) Å
β	104.252(4)°
Volume	1317.80(8) Å^3
Z	4
Calculated density	1.387 g/cm^3
Absorption coefficient	0.107 mm^{-1}
$F(000)$	576
Crystal size	0.1 × 0.5 × 0.6 mm
θ range for data collection	2.65–27.71°
Index ranges	$-15 \leqslant h \leqslant 15$
	$-5 \leqslant k \leqslant 13$
	$-12 \leqslant l \leqslant 14$
Reflections collected/unique	6211/2837 [R(int) = 0.0116]
Completeness to 2θ = 25.00	99.0%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2837/0/234
Goodness-of-fit on F^2	1.089
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0378, wR_2 = 0.1087
R indices (all data)	R_1 = 0.0503, wR_2 = 0.1190
Extinction coefficient	0.023(3)
Largest diff. peak and hole	0.386 and −0.266 e Å^{-3}

Table 2
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for PyB·HBA.

Atom	x	y	z	U(eq)
N(1)	10088(1)	262(1)	7423(1)	38(1)
C(2)	9513(2)	720(2)	6302(1)	51(1)
C(3)	8378(2)	401(2)	5830(2)	60(1)
C(4)	7811(1)	−358(2)	6513(2)	54(1)
C(5)	8411(1)	−808(2)	7659(2)	47(1)
C(6)	9555(1)	−492(1)	8097(1)	40(1)
C(7)	11314(1)	599(2)	7949(2)	45(1)
C(8)	11520(1)	1556(1)	9033(1)	38(1)
O(1)	10685(1)	2075(1)	9342(1)	47(1)
O(2)	12561(1)	1730(1)	9524(1)	53(1)
C(11)	6616(1)	1872(1)	8150(1)	40(1)
C(12)	6208(1)	2477(2)	7003(2)	60(1)
C(13)	5051(1)	2413(2)	6396(2)	61(1)
C(14)	4284(1)	1728(1)	6909(1)	43(1)
C(15)	4698(1)	1069(2)	8016(2)	63(1)
C(16)	5851(1)	1148(2)	8629(2)	56(1)
C(17)	7844(1)	1913(1)	8831(1)	40(1)
O(3)	8536(1)	2526(1)	8243(1)	50(1)
O(4)	8213(1)	1425(1)	9847(1)	58(1)
O(5)	3146(1)	1631(1)	6342(1)	56(1)
H(2)	9964(16)	1280(2)	5904(18)	68(5)
H(3)	7969(18)	720(2)	5050(2)	77(6)
H(4)	7001(17)	−582(19)	6224(18)	68(5)
H(5)	8040(16)	−1308(19)	8169(17)	59(5)
H(6)	10029(13)	−781(15)	8899(15)	46(4)
H(7A)	11736(16)	−200(2)	8267(18)	66(5)
H(7B)	11601(15)	941(17)	7273(17)	57(5)
H(12)	6780(18)	2960(2)	6630(2)	76(6)
H(13)	4784(19)	2880(2)	5630(2)	84(7)
H(15)	4140(2)	630(2)	8360(2)	84(6)
H(16)	6152(17)	701(19)	9440(19)	71(5)
H(3A)	9333(19)	2359(19)	8702(19)	71(6)
H(5A)	2984(19)	2190(2)	5740(2)	81(7)

U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

FTIR spectra were measured on a Bruker IFS 66v/S instrument, evacuated to avoid water and CO_2 absorptions, with the resolution of 2 cm^{-1}, in Nujol and Fluorolube suspensions using KBr plates. Each spectrum consisted of 64 scans.

The NMR spectra were recorded on a Varian Gemini 300 VT spectrometer operating at 300.07 and 75.46 MHz for ^{1}H and ^{13}C, respectively. The spectra were measured in D_2O and DMSO-d_6 relative to internal standard of 3-(trimethylsilyl)propionic-d_4 acid sodium salt and TMS, respectively. The 2D (COSY, HETCOR) spectra were obtained with standard Varian software.

3. Results and discussion

3.1. Crystal structure

The complex between pyridine betaine (PyB) and *p*-hydroxybenzoic acid (HBA) is formed in the stoichiometry 1:1. The numbering scheme of atoms in PyB and HBA moieties is shown in Fig. 1. The bond lengths, bond angles and selected torsion angles of PyB·HBA are given in Table 3. The phenyl ring of HBA and pyridine ring of PyB in the complex investigated show small deviations from planarity, as indicated by the torsion angles (Table 3). The hydroxyl group of HBA is nearly coplanar with the phenyl ring, while the plane of the carboxyl group is twisted relative to the best plane of the phenyl ring by 4.6(2)°. The angle between the plane of the pyridine ring and the plane of CH_2COO group in PyB is 74.4(1)°. Both oxygen atoms of the carboxylate group of PyB are engaged in the hydrogen bonds with the carboxylic and hydroxyl groups of two molecules of HBA, respectively, without the proton transfer from acid to betaine. The O(3)···O(1) and O(5)^{i}···O(2) distances are 2.589(1) and 2.588(2) Å, respectively [i: symmetry code: $x+1$, $-y+0.5$, $z+0.5$] (Fig. 2). In the O(3)–H···O(1) hydrogen bond the O–H bond is 0.97(2) Å and the H···O(1) distance is 1.62(2) Å, while in the O(5)–H···O(2) hydrogen bond the O–H bond is shorter by 0.10(2) Å and the H···O(2) distance is longer by 0.10(3) Å (Table 4). However the total O–H···O distances and bond angles are the same from the statistical point of view. In the complex investigated PyB and HBA molecules form an infinite hydrogen bonded chain parallel to the *x*-axis (Fig. 3). There are some C–H···O contacts, involving the C–H atoms at C(6) and C(7) positions of PyB and the oxygen atoms of the neighboring molecules of HBA, which stabilize the crystal structure (Table 4).

A similar arrangement in chain of the interacting molecules, was found in the complex of *N*-methylmorpholine betaine with HBA [8], however the COO···HOOC hydrogen bond was shorter (2.587(2) Å) than the COO···HO ones (2.677(2) Å). In the complex of *N*-methylpiperidine betaine with HBA, two molecules of betaine and two molecules of HBA are linked together forming a centro-

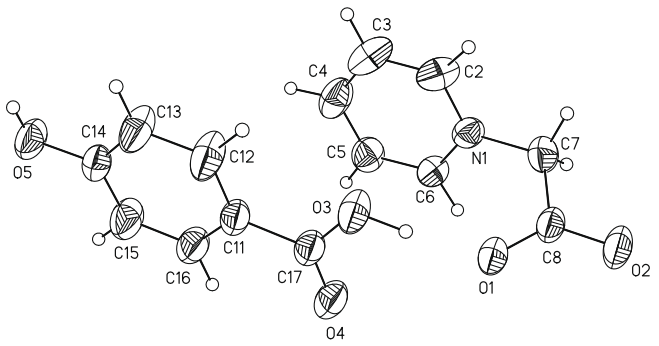

Fig. 1. Atom numbering scheme of pyridine betaine and *p*-hydroxybenzoic acid, showing 50% probability displacement ellipsoids.

Table 3
Experimental and calculated bond lengths (Å), bond and torsion angles (°) for PyB·HBA.

Parameters	X-ray	B3LYP/6-31G(d,p)
Bond lengths		
N(1)–C(2)	1.347(2)	1.353
C(2)–C(3)	1.363(2)	1.381
C(3)–C(4)	1.375(3)	1.395
C(4)–C(5)	1.374(2)	1.392
C(5)–C(6)	1.367(2)	1.385
N(1)–C(6)	1.340(2)	1.354
N(1)–C(7)	1.473(2)	1.472
C(7)–C(8)	1.527(2)	1.592
O(1)–C(8)	1.248(2)	1.268
O(2)–C(8)	1.237(2)	1.226
C(11)–C(12)	1.391(2)	1.400
C(12)–C(13)	1.376(2)	1.392
C(13)–C(14)	1.382(2)	1.400
C(14)–C(15)	1.381(2)	1.401
C(15)–C(16)	1.375(2)	1.388
C(11)–C(16)	1.380(2)	1.402
C(14)–O(5)	1.349(2)	1.365
C(11)–C(17)	1.470(2)	1.493
C(17)–O(3)	1.329(2)	1.325
C(17)–O(4)	1.212(2)	1.229
Bond angles		
N(1)–C(2)–C(3)	119.9(2)	121.10
C(2)–C(3)–C(4)	120.1(2)	119.21
C(3)–C(4)–C(5)	119.0(2)	119.01
C(4)–C(5)–C(6)	119.5(2)	119.68
N(1)–C(6)–C(5)	120.5(2)	120.43
C(6)–N(1)–C(2)	120.9(1)	120.53
C(2)–N(1)–C(7)	120.7(1)	120.40
C(6)–N(1)–C(7)	118.5(1)	118.65
N(1)–C(7)–C(8)	114.5(1)	111.73
O(1)–C(8)–C(7)	120.6(1)	113.15
O(2)–C(8)–C(7)	112.9(1)	114.22
O(1)–C(8)–O(2)	126.5(1)	132.59
C(11)–C(12)–C(13)	120.4(2)	120.54
C(12)–C(13)–C(14)	120.5(2)	119.90
C(13)–C(14)–C(15)	119.2(1)	120.09
C(14)–C(15)–C(16)	120.2(2)	119.48
C(15)–C(16)–C(11)	121.0(1)	121.07
C(16)–C(11)–C(12)	118.6(1)	118.93
C(12)–C(11)–C(17)	122.3(1)	122.07
C(16)–C(11)–C(17)	119.1(1)	119.01
O(5)–C(14)–C(13)	122.4(1)	122.54
O(5)–C(14)–C(15)	118.3(1)	117.37
O(3)–C(17)–C(11)	114.9(1)	113.21
O(4)–C(17)–C(11)	123.4(1)	122.08
O(4)–C(17)–O(3)	121.7(1)	124.71
Torsion angles		
N(1)–C(2)–C(3)–C(4)	1.8(3)	1.02
C(2)–C(3)–C(4)–C(5)	−1.4(3)	0.34
C(3)–C(4)–C(5)–C(6)	0.1(2)	−0.16
C(4)–C(5)–C(6)–N(1)	0.7(2)	−1.38
C(5)–C(6)–N(1)–C(2)	−0.3(2)	2.76
C(6)–N(1)–C(2)–C(3)	−0.9(2)	−2.59
C(7)–N(1)–C(2)–C(3)	−179.9(2)	−175.06
C(7)–N(1)–C(6)–C(5)	178.6(1)	175.34
C(2)–N(1)–C(7)–C(8)	107.3(2)	108.64
C(6)–N(1)–C(7)–C(8)	−71.7(2)	−63.97
N(1)–C(7)–C(8)–O(1)	−6.1(2)	37.20
N(1)–C(7)–C(8)–O(2)	174.0(1)	−144.98
C(11)–C(12)–C(13)–C(14)	−1.0(3)	0.01
C(12)–C(13)–C(14)–C(15)	−2.4(3)	−0.05
C(13)–C(14)–C(15)–C(16)	3.2(3)	0.01
C(14)–C(15)–C(16)–C(11)	−0.7(3)	0.06
C(15)–C(16)–C(11)–C(12)	−2.7(3)	−0.10
C(16)–C(11)–C(12)–C(13)	3.5(3)	0.06
C(12)–C(13)–C(14)–O(5)	−179.5(2)	179.95
C(16)–C(15)–C(14)–O(5)	−179.6(2)	−179.99
C(17)–C(11)–C(12)–C(13)	179.9(2)	−179.96
C(17)–C(11)–C(16)–C(15)	−179.2(2)	179.92
C(12)–C(11)–C(17)–O(3)	−2.6(2)	0.65
C(16)–C(11)–C(17)–O(3)	173.7(1)	−179.37
C(12)–C(11)–C(17)–O(4)	177.7(2)	−179.49
C(16)–C(11)–C(17)–O(4)	−5.9(2)	0.49

symmetric dimer by two COO···HOOC and two COO···HO hydrogen bonds of lengths 2.622(1) and 2.617(1) Å, respectively [9].

3.2. B3LYP/6-31G(d,p) calculations

The structures of PyB·HBA optimized by the B3LYP/6-31G(d,p) approach are shown in Fig. 6. The calculated bond lengths, bond and torsion angles are given in Table 3. Structure (a) shows a monomer of PyB·HBA complex in which the carboxylic group of HBA interacts with the carboxylate group of PyB, through the O(3)–H···O(1) hydrogen bond of 2.574 Å, shorter by 0.015 Å than in the crystal (Table 4). In the optimized structure (b) the hydroxyl group of HBA is engaged in the O(5)–H···O(2) hydrogen bond, which is by 0.086 Å longer than in the crystal, and by 0.100 Å longer than in structure (a). However, when two molecules of PyB·HBA are linked into chain, as is shown in the optimized structure (c), the O(3)–H···O(1) and O(5)–H···O(2) hydrogen bonds are longer than in the crystal, but not the same (Table 4). The calculated energies of the optimized structures (a), (b) and (c) suggest that structure (c) is more stable, than structures (a) and (b), however (a) is by 0.21 kcal/mol more stable than (b) (Table 4).

3.3. FTIR spectrum

The solid-state FTIR spectrum of the PyB·HBA complex is shown in Fig. 4. There is a broad absorption in the region between 3390 and 2550 cm^{-1}, attributed to the νOH modes. After deuteration three bands at 2500, 2200 and 2060 cm^{-1} appear in the FTIR spectrum. The frequencies of the νOH bands are consistent with the O···O distances in the hydrogen bonds in the crystalline complex. The bands at 1448, 1293 are attributed to the δOH vibrations, while at 933 cm^{-1} to the γOH vibrations. In the spectrum of the deuterated complex these bands appear at 1360, 1044 (δOD) and 774 (γOH) cm^{-1}. The νC=O and ν_{as}COO bands appear at 1690 and 1675 cm^{-1}, respectively. The band at 1245 cm^{-1} is attributed to the ν_sCOO vibration.

3.4. NMR spectra

The proton and carbon-13 chemical shifts of PyB·HBA in D_2O and DMSO-d_6 are given in Table 5. The assignments are based on two-dimensional ^1H–^1H (COSY) and ^1H–^{13}C (HECTOR) experiments [25,26]. The doublets and two triplets due to the pyridine ring protons and two doublets of doublets of the phenyl ring protons are observed in the range 7–9 ppm in the ^1H NMR spectrum. The signal of methylene protons appears at 5.23 ppm. The ^1H and ^{13}C resonance signals of H(2), H(6), H(3), H(5), C(3), C(5) and C(12) shift to the low magnetic field in the DMSO-d_6 solution, while the other to the high magnetic field in comparison to the spectrum run in D_2O. The relation between the experimental ^1H and ^{13}C chemical shifts (δ_{exp}) and the gauge including atom orbitals (GIAO) magnetic isotropic shielding tensors (σ) are usually linear and described by the following equation: $\delta = a + b\sigma$ [27,28]. The calculations of σ are performed for the structure (a) of the monomeric complex of PyB·HBA. The data in Table 5 and Fig. 5 show that the agreement between the experimental and predicted values of the chemical shifts is good only for ^{13}C and much better when the conductor-like screening continuum solvation model was used. The protons are located on the periphery of the molecule and thus are supposed to be more efficient in intermolecular (solute–solute) effects than the carbon atoms [29]. As revealed by the crystal structure, some protons of the pyridine betaine moiety are engaged in the weak intermolecular C–H···O hydrogen bonds (Table 4).

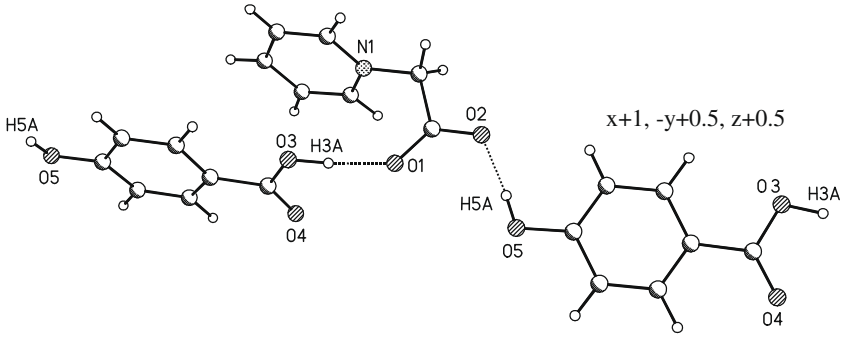

Fig. 2. The chains formed by pyridine betaine with *p*-hydroxybenzoic acid. Dashed lines show hydrogen bonds.

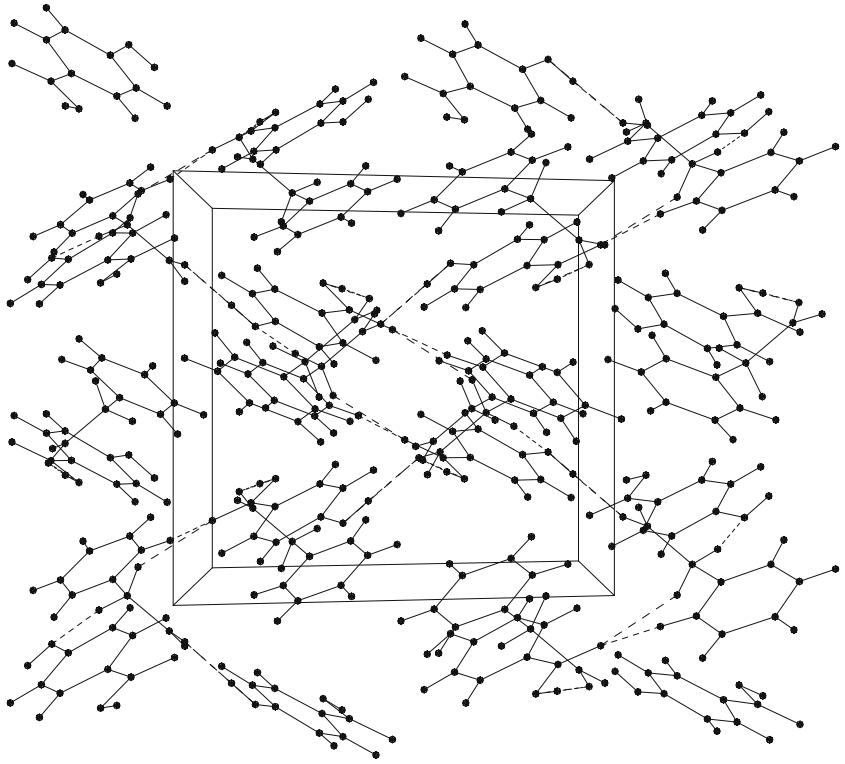

Fig. 3. Molecular arrangement of the PyB·HBA complex down the *x*-axis.

Table 4
Dimensions of hydrogen bonds in the crystal and optimized structures of PyB·HBA (distances in Å, angles in °).

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
X-ray				
O(3)–H(3A)···O(1)	0.97(2)	1.62(2)	2.589(1)	175(2)
O(5)[a]–H(5A)[a]···O(2)	0.87(2)	1.72(3)	2.588(2)	176(2)
C(6)–H(6)···O(4)[b]	0.97(2)	2.30(2)	3.191(2)	151(2)
C(7)–H(7B)···O(5)[c]	0.96(2)	2.43(2)	3.310(2)	153(2)
C(7)–H(7A)···O(4)[b]	0.99(2)	2.43(2)	3.155(2)	130(2)
B3LYP/6-31G(d,p)				
$C_5H_5N^+$ $CH_2COO^-\cdots HOOCC_6H_4OH$[d] (a)				
O(3)–H(3A)···O(1)	1.018	1.559	2.574	175.58
$C_5H_5N^+CH_2COO^-\cdots HOC_6H_4COOH$[e] (b)				
O(5)–H(5A)···O(2)	0.97	1.679	2.674	175.67
$(PyB{\cdot}HBA)_2$ chain[f] (c)				
O(3)–H(3A)···O(1)	0.989	1.683	2.670	175.69
O(5)[a]–H(5A)[a]···O(2)	0.990	1.720	2.707	173.96

Symmetry code: [a] $x+1, -y+0.5, z+0.5$; [b] $-x+2, -y, -z+2$; [c] $x+1, y, z$.
Energies HF (a.u.): [d] −972.219177; [e] −972.218846; [f] −1944.448244.

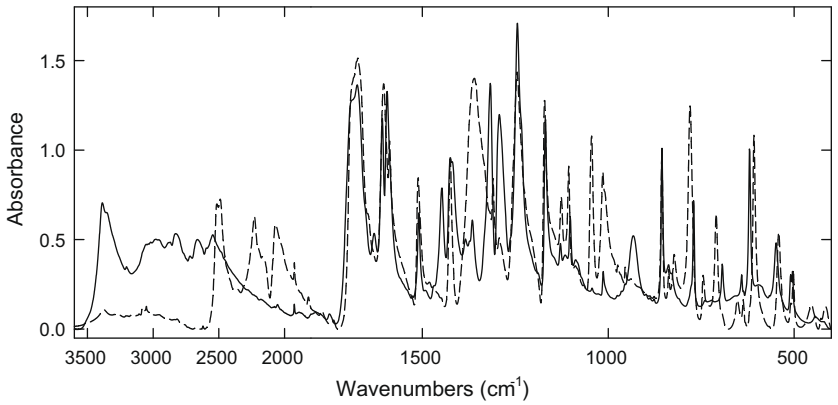

Fig. 4. FTIR spectrum of the complex of pyridine betaine with *p*-hydroxybenzoic acid; dashed line after deuteration.

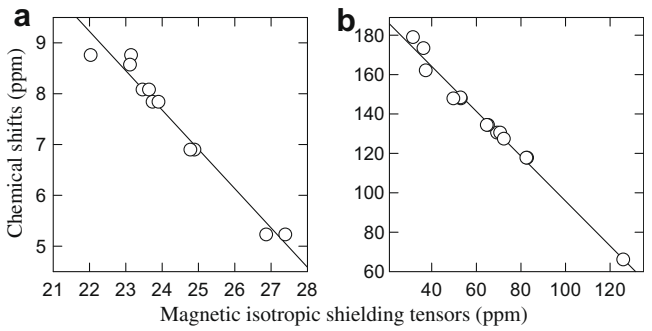

Fig. 5. Plots of the experimental ^{1}H (a) and ^{13}C (b) chemical shifts in D_2O versus the magnetic isotropic shielding tensors from the GIAO/B3LYP/6-31G(d,p) calculations for the complex of pyridine betaine with *p*-hydroxybenzoic acid.

4. Conclusions

In the complex investigated the carboxylate group of PyB is involved in two hydrogen bonds, with the same O···O distances, between the carboxylic (COO···HOOC) and hydroxyl (COO···HO) groups of HBA of the lengths 2.589(1) and 2.588(2) Å, respectively. The PyB and HBA molecules form infinite chains parallel to the *x*-axis. The solid-state FTIR spectrum of the title compound is consistent with the crystal results. ^{1}H and ^{13}C chemical shifts and the magnetic isotropic shielding tensors calculated by the GIAO/B3LYP/6-31G(d,p) approach are linear, and the predicted chemical shifts are in the good agreement with the experimental results. From two optimized structures (a) and (b) of the title complex by the B3LYP/6-31G(d,p) approach, structure (a) with COO···HOOC hydrogen bond between PyB and HBA is by 0.21 kcal/mol more stable than that with the COO···HO hydrogen bond (b). In the optimized structure of dimer (c), $(PyB{\cdot}HBA)_2$, the calculated O(3)–

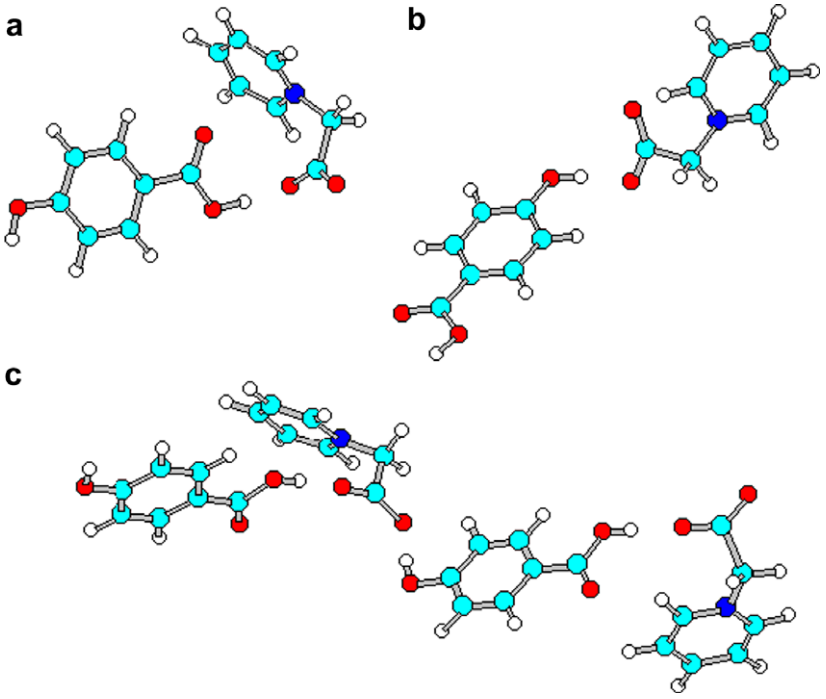

Fig. 6. The optimized structures of PyB·HBA by the B3LYP/6-31G(d,p) method, (a) monomer connected by the COOH···OOC hydrogen bond, (b) monomer connected by OH···OOC hydrogen bond and (c) dimer.

Table 5
Experimental and predicted ^{1}H and ^{13}C chemical shifts (δ, ppm) and calculated magnetic isotropic shielding tensors (σ, ppm) for the complex of pyridine betaine with *p*-hydroxybenzoic acid.

Atom[a]	D_2O	H_2O		DMSO-d_6	DMSO		Vaccum	
	δ_{exp}	$\delta_{predict}$[b]	σ	δ_{exp}	$\delta_{predict}$[b]	σ	$\delta_{predict}$[b]	σ
H-2	8.76	8.34	23.1439	8.95	8.39	23.1609	8.21	23.6606
H-3	8.08	8.10	23.4580	8.09	8.13	23.4708	7.90	24.0623
H-4	8.57	8.36	23.1129	8.53	8.42	23.1264	8.13	23.7662
H-5	8.08	7.96	23.6367	8.09	7.98	23.6495	7.80	24.1851
H-6	8.76	8.98	22.0314	8.95	9.33	22.0394	9.40	22.1000
H-7A	5.23	5.05	27.3959	5.04	4.83	27.4021	5.25	27.4996
H-7B	5.23	5.46	26.8654	5.04	5.27	26.8737	5.53	27.1394
H-12	7.84	7.88	23.7359	7.79	7.90	23.7486	8.16	23.7258
H-13	6.90	6.99	24.8870	6.84	6.93	24.9009	6.78	25.5184
H-15	6.90	7.08	24.7770	6.84	7.03	24.7835	7.12	25.0740
H-16	7.84	7.76	23.8996	7.79	7.75	23.9214	7.91	24.0437
a			26.2399			27.8252		26.4020
b			−0.7734			−0.8392		−0.7690
r			0.9826			0.9832		0.9594
C-2	147.88	149.35	52.9910	144.42	145.63	53.1023	149.12	54.8968
C-3	130.55	130.79	69.2792	131.51	128.21	69.2971	129.80	71.1432
C-4	148.40	149.47	52.8802	145.51	145.82	52.9288	146.65	56.9796
C-5	130.55	129.25	70.6322	131.51	126.76	70.6464	128.89	71.9098
C-6	147.88	153.10	49.6980	144.42	149.29	49.7037	153.33	51.3593
C-7	66.12	66.37	125.8400	64.07	67.39	125.8276	66.57	124.2971
C-8	173.42	168.40	36.2596	165.54	163.62	36.3878	163.11	43.1347
C-11	127.43	127.33	72.3193	127.02	125.09	72.1979	130.91	70.2079
C-12	134.41	135.45	65.1930	131.51	132.57	65.2458	137.76	64.4449
C-13	117.79	115.43	82.7653	115.15	113.63	82.8538	114.12	84.3199
C-14	162.15	167.21	37.3041	161.74	162.49	37.4388	167.61	39.3543
C-15	117.79	115.83	82.4141	115.15	114.06	82.4522	115.46	83.1995
C-16	134.41	136.04	64.6705	131.51	133.21	64.6563	137.73	64.4765
C-17	179.00	173.78	31.5439	167.32	168.58	31.7671	176.73	31.6907
a			209.7038			202.7688		214.4226
b			−1.1390			−1.0759		−1.1895
r			0.9938			0.9951		0.9884

[a] For numbering of atoms see Fig. 1.
[b] The predicted chemical shifts have been determined by linear regression $\delta_{predict} = a + b\sigma$.

H···O(1) and O(5)–H···O(2) distances are not the same, as in the crystal.

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