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Structural, spectroscopic, and theoretical studies of a very short OHO hydrogen bond in bis(4-(*N*-methylpiperidinium)-butyrate) hydrobromide

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The molecular structure of bis(4-(*N*-methylpiperidinium)-butyrate) hydrobromide, $(MPBu)_2HBr$, has been characterized by single crystal X-ray diffraction, infrared and NMR spectroscopies, and by DFT calculations. The crystals of the title compound at 140 K are monoclinic, space group *C*2/*c*, with $a = 11.7118(4)$, $b = 7.8737(2)$, $c = 23.9240(8)$ Å, $\beta = 90.431(3)°$, $V = 2206.1(1)$ Å^3, and $Z = 4$. Two 4-(*N*-methylpiperidinium)-butyrate moieties are joined by a very short and centrosymmetric O.H.O hydrogen bond of 2.436(2) Å. The piperidine ring adopts a chair conformation with the methyl group in the equatorial and the bulky —$(CH_2)_3COO$ substituent in the axial position. The broad absorption band below 1500 cm^{-1} in the FTIR spectrum confirms the existence of a very short O·H·O hydrogen bond. The ^1H and ^{13}C NMR spectra are interpreted on the basis of 2D experiments and the calculated GIAO/B3LYP/6-31G(d,p) magnetic isotropic shielding tensors. In the optimized structure of the complex, a 4-(*N*-methylpiperidinium)-butyrate zwitterion interacts with a 4-(*N*-methylpiperidinium)-butyric acid cation forming an O···H—O hydrogen bond of 2.580 Å. Copyright © 2008 John Wiley & Sons, Ltd.

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Keywords: 4-(*N*-methylpiperidinium)-butyrate; homoconjugated cation; short OHO hydrogen bond; X-ray diffraction; FTIR; Raman and NMR spectra; DFT calculations

INTRODUCTION

Betaines (ammonium alkanoates) are zwitterions (inner salts) because they possess formally charged ammonium and carboxylate groups separated by one or more sp^3 carbon atoms. In betaines, the positively charged nitrogen atom is inert as a hydrogen-bonding center, whereas the carboxylate group is basic, and can interact with different proton donors. The basicity of the carboxylate group decreases, but its hydrophilicity increases, with the number of methylene groups separating the positive and negative charge centers.[1–4] The electrostatic attraction between the two charged centers depends strongly on the flexibility of the linker and on the bulkiness, hydration and protonation of the charged groups.[3–6] Betaines with a hydrophobic chain of 8–20 carbon atoms exhibit unique properties characteristic of amphoteric surfactants and find interesting industrial applications in toiletries and personal care products.[7]

From the several zwitterionic forms of dialkylamino acids, $R_2N^+H—(CH_2)_nCOO^-$, and betaines, $R_3N^+—(CH_2)_nCOO^-$, with more than one methylene group in the tether, only two examples have been published reporting the formation of a 2:1 complex with a short O·H·O hydrogen bond, namely bis(3-pyridiniumpropionate) hydrobromide[8] and bis(4-pyridiniumvalerate) hydrogen perchlorate.[9] The O···O distances range from 2.39 to 2.45 Å and the hydrogen bond varies from crystallographically symmetric to very asymmetric. Olovsson *et al*.[10] have divided all complexes with very short OHO hydrogen bonds into four groups: (a) symmetric or centered, with the proton located precisely at the centre of the O···O distance; (b) statistically disordered, with the proton closer to one or the other oxygen atom in different domains in the crystal; (c) dynamically disordered, where the proton jumps between the two positions in the same hydrogen bonds as in (b); and (d) asymmetric, with the proton closer to one of the oxygen atoms.

The present paper reports the molecular structure of and hydrogen bonding in bis(4-(*N*-methylpiperidinium)-butyrate) hydrobromide, $(C_5H_{10}N(CH_3)CH_2CH_2CH_2COO)_2HBr$ [$(MPBu)_2HBr$], which contains three methylene groups in the tether, in the

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crystal and in the isolated molecule. In addition, the title complex is characterized by FTIR, Raman, and NMR spectroscopies.

EXPERIMENTAL

$(MPBu)_2HBr$ was prepared by mixing of equivalent amounts of 4-(*N*-methylpiperidinium)-butyric acid bromide, MPBuHBr (m.p. 181–182 °C)[2] and 4-(*N*-methylpiperidinium)-butyrate (m.p. 82–83 °C)[2] in methanol. The solvent was removed under reduced pressure and the residue was dried over P_2O_5. The solid compound was recrystallized from methanol, m.p. 184–185 °C. Analysis for $C_{20}H_{39}N_2O_4Br$, calculated/found: %C, 52.83/53.01; %H, 8.69/8.71; %N, 6.14/6.21. The deuterated complex was prepared by isotope exchange with D_2O, followed by azeotropic removal of excess D_2O in vacuum. The residue was recrystallized from CH_3OD.

Single crystals were grown from a 5:1 methanol–acetonitrile mixture. X-ray diffraction measurements were carried out using graphite-monochromated Mo $K\alpha$ radiation and a KM4-CCD diffractometer[11] equipped with an Oxford Instruments low-temperature device.[12] Eight hundred seventy-six ω scans were recorded in six orientations of the crystal with 0.68° oscillation and an exposure time of 6 s. Integrated intensities were obtained using the CrysAlis program.[13] The dataset consisted of 6973 observations which were reduced to 2248 unique data. The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least squares minimization of $\Sigma w(F_o^2 - F_c^2)^2$ using SHELXL-97.[14] All hydrogen atoms were derived from a difference Fourier map and included in the refinement with isotropic B factors. The refinement converged with a very low *R* factor of 0.0205 (Table S1). Atomic coordinates and equivalent displacement parameters are listed in Table S2. The atom numbering system is shown in Fig. 1. Molecular illustrations were prepared using ORTEPII[15] and the XP package.[16] Atomic parameters in the CIF format are available as Electronic Supplementary Publication from Cambridge Crystallographic Data Centre (CCDC 693894).

FTIR and Raman spectra were measured on a Bruker IFS 66v/S instrument, evacuated to avoid water and CO_2 absorption. FTIR spectrum was recorded 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 ^1H and ^{13}C, respectively. The spectra were measured in D_2O relative to 3-(trimethylsilyl)propionic-d_4 acid sodium salt as internal reference. The 2D (COSY, HETCOR) spectra were obtained with standard Varian software.

The DFT calculations were performed with the GAUSSIAN-03 program package.[17] The calculations employed the B3LYP exchange-correlation functional, which combines the hybrid exchange functional of Becke[18,19] with the gradient-correlation functional of Lee, Yang, and Parr,[20] and the split-valence polarized 6-31G(d,p) basis set.[21]

RESULTS AND DISCUSSION

Crystal structure

The crystal structure of $(MPBu)_2HBr$ is shown in Fig. 1. Bond lengths, bond angles, and selected torsion angles are listed in Table S3. The investigated compound crystallizes in the *C*2/*c* space group. The asymmetric unit consists of one-half of the centrosymmetric, hydrogen bonded bis(4-(*N*-methylpiperidinium)-butyrate cation and of one-half of the bromide anion, which is located on the two-fold axis. The two components of the cation are connected by a very short O···H···O hydrogen bond with an O···O distance of 2.436(2) Å, which classifies it as very strong (Table 1).[22] Similar symmetric hydrogen-bonded dimers exist in type A acid salts of monocarboxylic acids, for example, $(RCOO)_2HK$.[23] Homoconjugated cations with symmetric O···H···O hydrogen bonds were found in several structures of betaines, for example, bis(betaine) hydrochloride monohydrate,[24] bis(betaine)nitrate,[25] bis(homarine)hydrogen perchlorate,[26] bis(*N*-methylpiperidine betaine) hydrobromide,[27] bis(*N*-methylpiperidine betaine) hydroiodide,[28] and bis(*N*-methylpiperidine betaine) hydrochloride.[29] Very short O···H···O hydrogen bonds were also found in hydrogen squarate derivatives.[30,31] However, the O···H···O hydrogen bond in the investigated compound is by 0.009–0.011 Å shorter than in bis(*N*-methylpiperidine betaine) hydrohalides, $(MPB)_2HX$.[27–29] The B_{iso} displacement parameter of the H atom in the O···H···O bridge [8.4(10) Å^2] is higher than the component of the B_{aniso} tensor of the terminal O atoms along the O···O line [1.58(4) Å^2], indicating that although this hydrogen bond is crystallographically centrosymmetric, the proton may be distributed either dynamically or statically on both sides of the inversion center. However, with an O···O distance of 2.436(2) Å, its expected deviation from the midpoint of the O···O vector is small, about 0.09 Å.[32]

The piperidine ring adopts the chair conformation and the endocyclic dihedral angles vary between 54.9(1) and 58.0(2)°. The

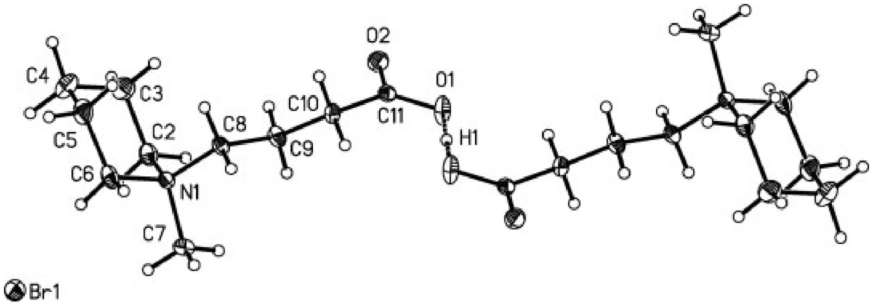

Figure 1. An ORTEP plot of bis(4-(*N*-methylpiperidinium)-butyrate) hydrobromide with atom labeling scheme. Anisotropic displacement ellipsoids have been drawn at the 50% probability level. H atoms are represented as spheres of arbitrary radius. The second MPBu moiety is generated by a center of symmetry at which the acidic hydrogen atom is located. The Br^- ion is placed on a two-fold axis. Symmetry operation for the generation of the second half of the $(MPBu)_2H^+$ dimer: −1−x, 2−y, 1−z

Table 1. Hydrogen bonds for bis(4-(*N*-methylpiperidinium)-butyrate) hydrobromide (Å and °)

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
X-ray				
O(1)···H(1)···O(1)[a]	1.218(1)	1.218(1)	2.436(2)	180
C(5)–H(5E)···O(2)[b]	0.96(2)	2.49(2)	3.388(2)	155(2)
C(6)–H(6E)···O(1)[c]	0.96(2)	2.52(2)	3.410(2)	154(1)
C(8)–H(82)···O(2)[d]	0.93(2)	2.50(1)	3.304(2)	145(1)
C(9)–H(91)···O(2)[c]	0.91(2)	2.51(2)	3.409(2)	170(1)
C(9)–H(92)···O(2)	0.93(2)	2.57(1)	2.892(2)	101(1)
C(10)–H(101)···O(2)[d]	0.98(2)	2.56(2)	3.435(2)	149(1)
C(10)–H(102)···O(1)[a]	0.96(2)	2.51(2)	3.214(2)	131(1)
B3LYP/6-31G(d,p)				
O(1)–H(1)···O(1)	1.011	1.578	2.580	170.2
C(8)–H···O(2)	1.097	2.202	3.281	168.7

Symmetry codes: [a] $-x-1, -y+2, -z+1$; [b] $-0.5-x, 0.5-y, 1-z$; [c] $0.5-x, 1.5-y, 1-z$; [d] $-1-x, 1-y, 1-z$.

—$CH_2CH_2CH_2COO^-$ substituent is in the axial position and is linked by the O···H···O hydrogen bond with its centrosymmetric copy within the dimeric $(MPBu)_2H^+$ cation. It is of note that in $(MPB)_2HX$ complexes[27–29] the —CH_2COO^- group is in the equatorial position, while in the 1:1 complexes the —$(CH_2)_nCOO^-$ substituent has been also found in the axial position, for example, in 4-(*N*-methylpiperidinium)-butyric acid bromide,[33] *N*-methylpiperidine betaine hydrochloride,[34] and hydrobromide.[35] Both positions of the —CH_2COO^- substituent are observed in complexes of MPB with hexafluorosilicic acid[36,37] and tartaric acid.[38]

In the $(MPBu)_2H^+$ cation, one unit of positive charge is located at each of the N(1) atoms whereas one unit of negative charge is distributed symmetrically between O(1) and O(1′). The carboxylic group is characterized by the following bond lengths: 1.226(2) and 1.289(1) Å for the C(11)=O(2) and C(11)—O(1)···H bonds, respectively, which are typical for zwitterionic betaine molecules engaged in hydrogen bonds in similar $(MPB)_2HX$ complexes.[27–29] However, the present case is very unusual in that the proton in the COO···H bond assumes the *trans* orientation, the O(2)—C(11)—O(1)···H(1) torsion angle being 177.2(1)°.

In contrast to the 1:1 MPBuHBr complex,[33] the present 2:1 complex, $(MPBu)_2HBr$, does not form a discernible ion pair. Although the molecular geometry of the MPBu unit in both complexes is more or less similar, the type of intermolecular interactions is different. In the 1:1 complex, the Br^- ion is associated with 'its' $MPBuH^+$ cation via an O—H···Br^- interaction of 3.141(1) Å. In the case of bis(4-(*N*-methylpiperidinium)-butyrate hydrobromide, the architecture of the crystal structure is more similar to that of the isomorphous $(MPB)_2HCl$ and $(MPB)_2HBr$ complexes,[27,29] which also crystallize in the *C*2/*c* space group. There are also other similarities between the above $(MPB)_2HX$ complexes and the $(MPBu)_2HBr$ structure: (i) the homoconjugated cations are symmetrically disposed around the inversion center with the acidic proton placed on it (Fig. 2), (ii) each anion is surrounded by two N^+ atoms from the piperidine rings related by the two-fold

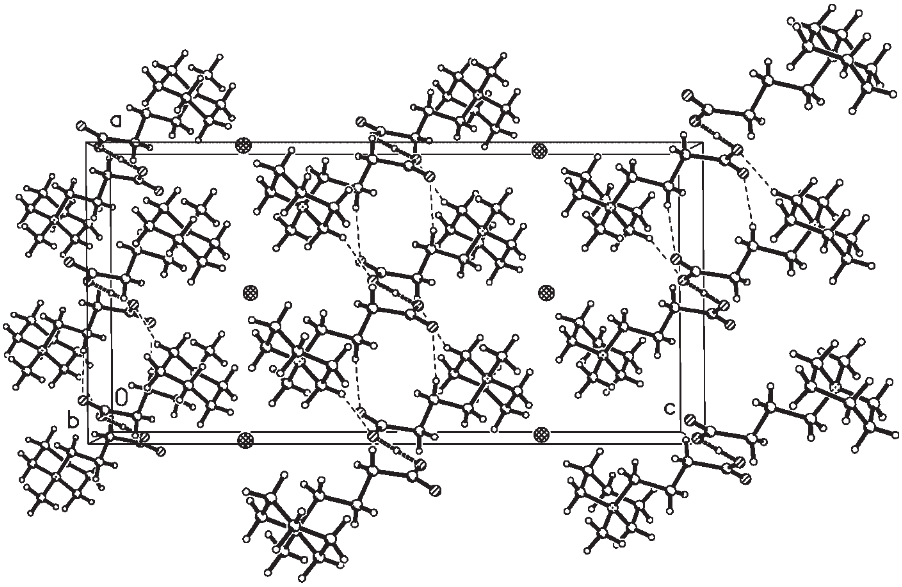

Figure 2. Crystal packing of bis(4-(*N*-methylpiperidinium)-butyrate) hydrobromide viewed along [010]

axis and by two other piperidine rings from neighboring molecular layers, with $Br^{-}\cdots N^{+}$ distances of about 4.4 Å. Some differences in the crystal-packing pattern are caused by the elongation of the aliphatic tether. There are two C—H···O(2) contacts (Table 1) between two $(MPBu)_2H^{+}$ cations, which additionally stabilize the crystal structure.

Vibrational spectra

The solid-state FTIR spectrum of $(MPBu)_2HBr$ (Fig. 3a) is different from the spectrum of MPBuHBr.[33] The most characteristic feature of the spectrum of the 2:1 complex is a broad and intense absorption in the 1500–400 cm^{-1} region. This absorption is attributed to the νOHO and γOHO vibrations of the strong O···H···O hydrogen bond.[39,40] This continuous absorption is broken by several Evans windows. The center of gravity, ν_H, calculated for the 1500–400 cm^{-1} region is at 980 cm^{-1} and shifts to 990 cm^{-1} after deuteration. This ν_H/ν_D isotope ratio of 0.99 confirms the strong character of the hydrogen bond in the investigated complex.[39,41,42] Notably, there are no distinct absorption bands in the region above 1800 cm^{-1}, except those corresponding to the CH_2 and CH_3 stretching vibrations.

The ν_{as}COO vibration appears at 1677 cm^{-1}. After deuteration, this band is split into two bands at 1674 and 1644 cm^{-1}, which suggests that the ODO bond becomes asymmetric in the deuterated species.

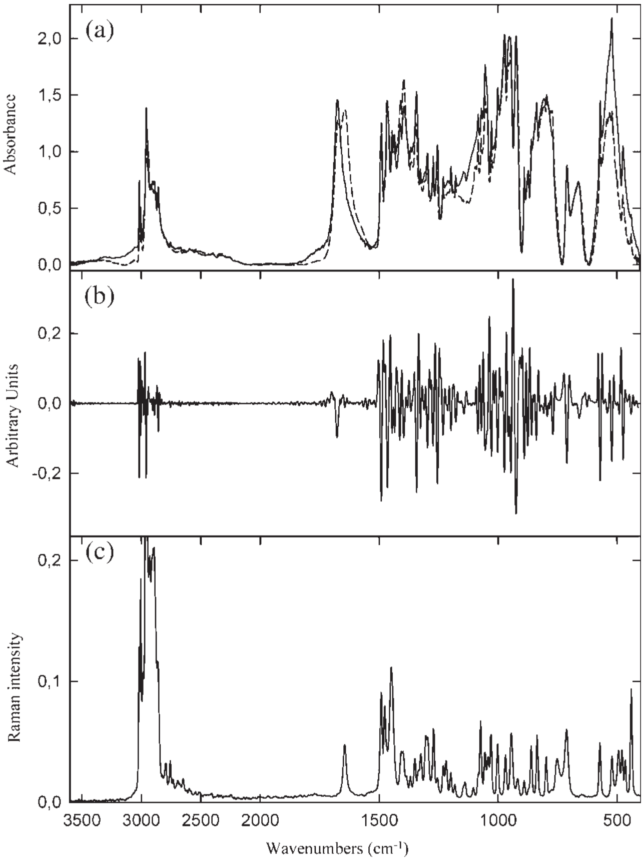

Figure 3. Infrared spectra of the bis(4-(*N*-methylpiperidinium)-butyrate) hydrobromide complex: (a) FTIR spectrum in Nujol and Fluorolube emulsions (dashed line after deuteration); (b) the second-derivative FTIR spectrum; and (c) the Raman spectrum

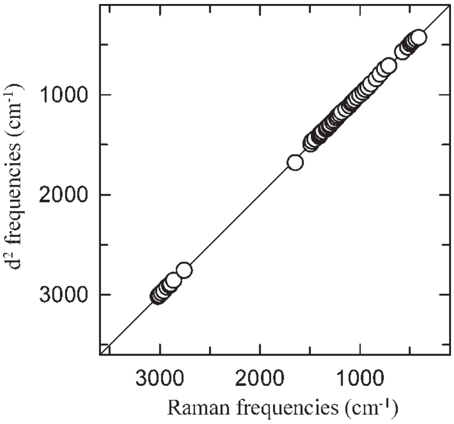

Figure 4. A plot of the second-derivative FTIR frequencies (d^2) *versus* the Raman frequencies (R) for bis(4-(*N*-methylpiperidinium)-butyrate) hydrobromide. The linear regression line has the equation $d^2 = 1.5138 + 0.9998\nu_{Raman}$; $r = 0.9999$, $n = 49$

The continuous absorption of the OHO vibration in the 1500–400 cm^{-1} region overlaps the in-plane and out-of-plane C—H, C—O, and O—H vibrations. Some of these vibrations can be distinguished in the second derivative (d^2) spectrum (Fig. 3b). The minima in the second-derivative spectrum have the same wavenumbers as the maxima in the absorbance spectrum but their relative intensities vary inversely with the square of the half-width of the absorbance bands.[43,44]

The Raman spectrum (Fig. 3c) shows very intensive bands attributed to the stretching CH_2 and CH_3 vibrations and several

Table 2. Experimental (δ_{exp}) and predicted (δ_{pred}) ^{1}H and ^{13}C chemical shifts (δ, ppm) together with calculated average magnetic isotropic shielding tensors (σ, ppm) for bis(4-(*N*-methylpiperidinium)-butyrate) hydrobromide

Atom[a]	δ_{exp}	δ_{pred}[b]	σ
^{1}H			
$C(2,6)H_2$	3.45	3.34	27.7348
$C(3,5)H_2$	1.87	1.87	30.0315
$C(4)H_2$	1.69	2.02	29.7798
$C(7)H_3$	3.05	3.10	28.1040
$C(8)H_2$	3.35	3.42	27.6116
$C(9)H_2$	2.01	1.96	29.9015
$C(10)H_2$	2.37	2.07	29.7255
^{13}C			
C(2,6)	63.96	63.70	132.4223
C(3,5)	22.34	22.58	168.8250
C(4)	23.36	21.75	169.5605
C(7)	50.63	55.03	140.0911
C(8)	64.97	62.01	133.9144
C(9)	20.49	21.33	169.9287
C(10)	34.92	34.33	158.4279
C(11)	181.46	213.27	28.2119

[a] For atom numbering scheme refer to Fig. 1.

[b] δ_{pred} have been calculated by linear regression using the equation $\delta = a + b\sigma$; $a_H = 21.0511$, $b_H = -0.6386$, $r = 0.9281$; $a_C = 213.2710$, $b_C = -1.1295$, $r = 0.9992$.

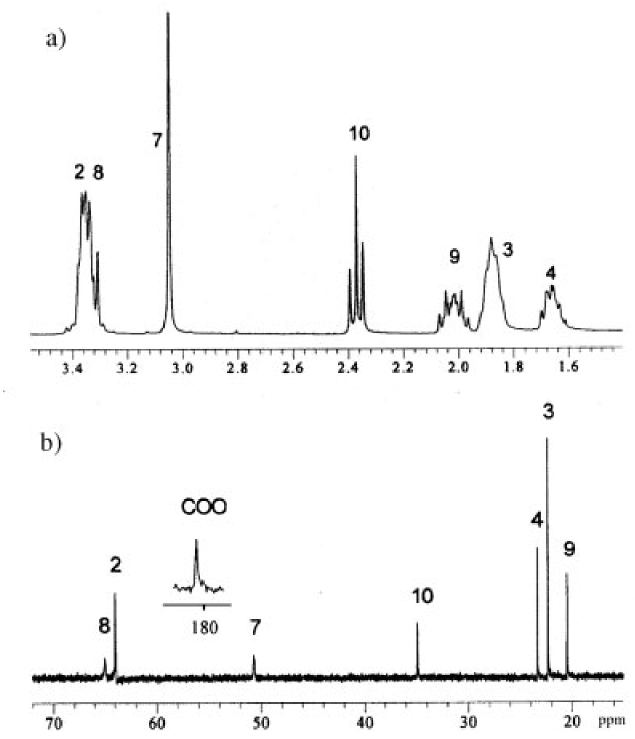

Figure 5. ^1H (a) and ^{13}C (b) NMR spectra of bis(4-(*N*-methylpiperidinium)-butyrate) hydrobromide in D_2O

weaker bands corresponding to deformation vibrations of the C—H and C—O bonds in the fingerprint region. The Raman absorption bands correlate very well with the negative bands in the second-derivative FTIR spectrum. A plot of the frequency of the negative bands in the second derivative spectrum *versus* the Raman frequencies is linear with unit slope (Fig. 4). The Raman band at 1645 cm^{-1} is attributed to the ν_{as}COO mode. In Raman spectra, the intensity of the νOH mode is usually very weak[45] and in the spectrum of $(MPBu)_2HBr$ this absorption is absent.

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

In the optimized structure of the title complex, one of the 4-(*N*-methylpiperidinium)-butyrate moieties is present in the zwitterionic form, while the second one is protonated (Figure S1). The protonated form, $MPBuH^+$, is linked to the zwitterion, MPBu, by an asymmetric O—H···O hydrogen bond with an O···O distance of 2.580 Å, which is longer by 0.144 Å than in the crystal (Table 1). This strong asymmetry of the O—H···O hydrogen bond correlates with the large dipole moment of 22.5 D. A similar asymmetric O—H···O hydrogen bond was determined for the $(MPB)_2H^+$ cation with axial–axial $—CH_2COO^-$ substituents, while for the equatorial–equatorial conformer the O···H···O hydrogen bond was symmetric.[27]

The geometrical parameters of the optimized structure are given in Table S3. The most significant differences between the crystal and optimized structures are in the C(9)—C(10)—C(11)—O(1/2) torsion angles. The bromide anion of the optimized structure is closer to the protonated moiety of the homoconjugated cation, the $Br^-\cdots N^+$ distance being 3.79 Å. The calculated energy of $(MPBu)_2HBr$ is −3767.785692 au.

NMR spectra

The proton and carbon chemical shifts based on the $^1H—^1H$ and $^1H—^{13}C$ experiments are listed in Table 2 and the NMR spectra are shown in Fig. 5. The ring H atoms at C(2), C(3), and C(4) give rise to multiplets, which prevents the estimation of the chemical shifts of the axial and equatorial protons. The methylene protons of the tether are affected by the positively charged nitrogen atom and by the carboxylate group. The resonance signal of the protons at C(9) appears as a multiplet typical of an $AA'MM'X_2$ spin system (Fig. 5), similar to that observed in the spectrum of MPBuHBr and in the spectra of other betaines with three CH_2 groups in the tether.[46] The resonance signals of the carbon atoms C(7) and C(8) attached to the $N^+(1)$ atom are of low intensity as a result of the quadrupole effect of the nitrogen atom.

The resonance signals of the CH_3 group at 3.05 and 50.63 ppm for the ^1H and ^{13}C nuclei, respectively, confirm the equatorial orientation of the methyl group at the nitrogen atom.[47,48]

The relations between the experimental ^1H and ^{13}C chemical shifts (δ_{exp}) and the magnetic isotropic shielding tensors (σ) computed by the GIAO/B3LYP/6-31G(d,p) approach are usually linear and described by the equation, $\delta_{exp} = a + b\sigma_{calc}$.[49,50] The data in Table 2 and Fig. 6 show that the agreement between the experimental (δ_{exp}) and predicted (δ_{pred}) values of the chemical shifts is much better for ^{13}C than for ^1H. The protons are located on the periphery of the molecule and thus are more susceptible to intermolecular solvent–solute effects than the carbon atoms.[51]

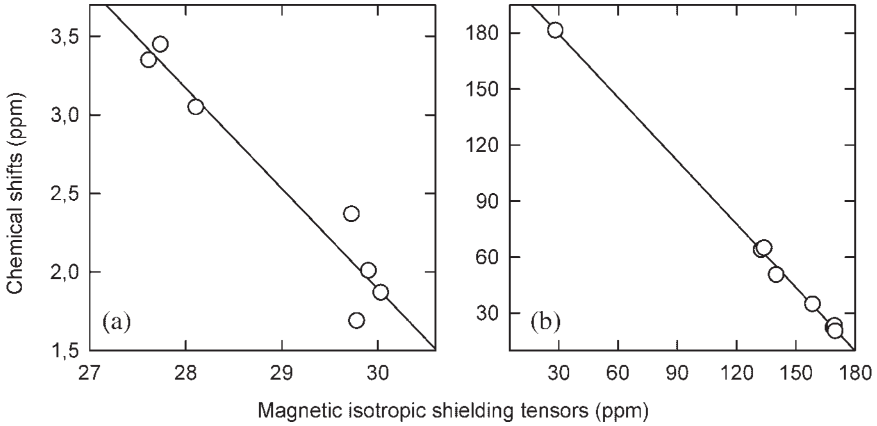

Figure 6. A plot of the experimental proton (a) and carbon (b) chemical shifts *versus* the magnetic isotropic shielding tensors from GIAO/B3LYP/6-31G(d,p) calculations for bis(4-(*N*-methylpiperidinium)-butyrate) hydrobromide

CONCLUSIONS

In the crystal structure of (MPBu)$_2$HBr two molecules of 4-(*N*-methylpiperidinium)-butyrate form a homoconjugated cation through a short, symmetric, and linear O···H···O hydrogen bond with the O···O distance of 2.436(2) Å. Although the proton in the hydrogen bond has been located at the center of symmetry, its rather high B_{iso} parameter indicates that it may deviate, either dynamically or statically, by a small displacement from the geometric center of the O···H···O bridge. The —(CH$_2$)$_3$COO$^-$ substituent is in the axial position, while the —CH$_3$ group is equatorial. In the optimized structure generated by B3LYP/6-31G(d,p) calculations, the proton is closer to one of the carboxylate groups, resulting in an COO—H···OOC hydrogen bond with 2.580 Å O···O separation. The FTIR spectrum shows a broad and intense absorption in the 1500–400 cm^{-1} region, which is characteristic of a very short O···H···O hydrogen bond. The second derivative frequencies correlate linearly with the Raman frequencies. The magnetic isotropic shielding tensors calculated by the standard GIAO/B3LYP/6-31G(d,p) approach give a good linear correlation with the experimental ^{13}C chemical shifts.

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