

Full Paper

## Synthesis, Molecular Structure and Spectral Properties of Quaternary Ammonium Derivatives of 1,1-Dimethyl-1,3-propylenediamine

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**Abstract:** 1,1-Dimethyl-3-oxo-1,4-diazepan-1-ium chloride (**1**) and 1,1-dimethyl-1-carboxymethyl-3-aminopropyl ammonium hydrochloride (**2**) have been obtained by the reactions of 1,1-dimethyl-1,3-propylenediamine with ethyl chloroacetate and chloroacetic acid, respectively. The products have been characterized by FTIR, Raman and NMR spectroscopy. B3LYP calculations have also been carried out. The screening constants for  $^{13}\text{C}$ - and  $^1\text{H}$ - atoms have been calculated by the GIAO/B3LYP/6-31G(d,p) approach and analyzed. The FTIR and NMR spectra of the investigated compounds **1** and **2** are in excellent agreement with the structures optimized by Density Functional Theory (DFT) calculations.

**Keywords:** 1,1-Dimethyl-3-oxo-1,4-diazepinium chloride; 1,1-dimethyl-1-carboxymethyl-3-aminopropylammonium hydrochloride; FTIR, Raman and NMR spectra; DFT calculations.

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### Introduction

Quaternary alkyl ammonium salts (QAC) play an important role in the living organisms and many functions of prokaryotic and eukaryotic cells have been shown to be alkyl ammonium salt dependent [1,2]. These compounds also exhibit excellent antimicrobial activity, therefore they are used as antiseptics, bactericides and fungicides, and as therapeutic agents, as well. The above group mainly consists of alkyltrimethyl-, dialkyldimethyl- and alkyldimethylbenzyl ammonium salts. The quaternary

nitrogen atom in QAC can also form part of aromatic or aliphatic rings. In general, ammonium salts which show good antimicrobial activities contain one or two alkyl chains of lengths in the C<sub>8</sub> to C<sub>14</sub>. For use as softeners and hair conditioning agents chain lengths between C<sub>16</sub> to C<sub>18</sub> are used [3-7]. The use of the same type of quaternary alkyl ammonium salts for a long time may cause an increase of resistance of microorganisms, which is considered a very serious problem. To avoid this problem the structures and types of microbiocides used have to be continuously changed. Among the new microbiocides currently studied and applied are quaternary aminopropylalkyl ammonium salts [8]. These new QACs, containing an additional aminopropyl group, display excellent antimicrobial activities.

One type of quaternary ammonium derivatives are the betaines, zwitterionic molecules, in which a carboxylate group is connected by one or more methylene groups with a quaternary nitrogen,  $\geq N^+-(CH_2)_n-COO^-$ . Betaines have a variety of applications in medicine, pharmacy, biology because of their biocidal properties [9]. Betaines which contain a hydrophobic chain in the range of  $n = 8-20$  carbon atoms, show unique amphoteric surfactant properties and their current industrial applications are mainly in the toiletries and personal care products areas. Many of these complexes display interesting physical properties, exhibiting phase transitions with ferroelectric, antiferroelectric and ferroelastic behaviour as well as phases with commensurate and incommensurate superstructures [10].

From the structural point of view quaternary ammonium halides containing COOH group can be considered as bifunctional compounds. The cohesion forces in the crystals of these compounds are dominated by COOH...X<sup>-</sup> hydrogen bonds, N<sup>+</sup>...X<sup>-</sup> and N<sup>+</sup>...O electrostatic interactions, and C-H...X<sup>-</sup> contacts [11]. The electrostatic attractions depend on the number of methylene groups in the tether connecting the positively charged nitrogen atom with COO<sup>-</sup> or COOH groups, the counter anions and also on additional substituents.

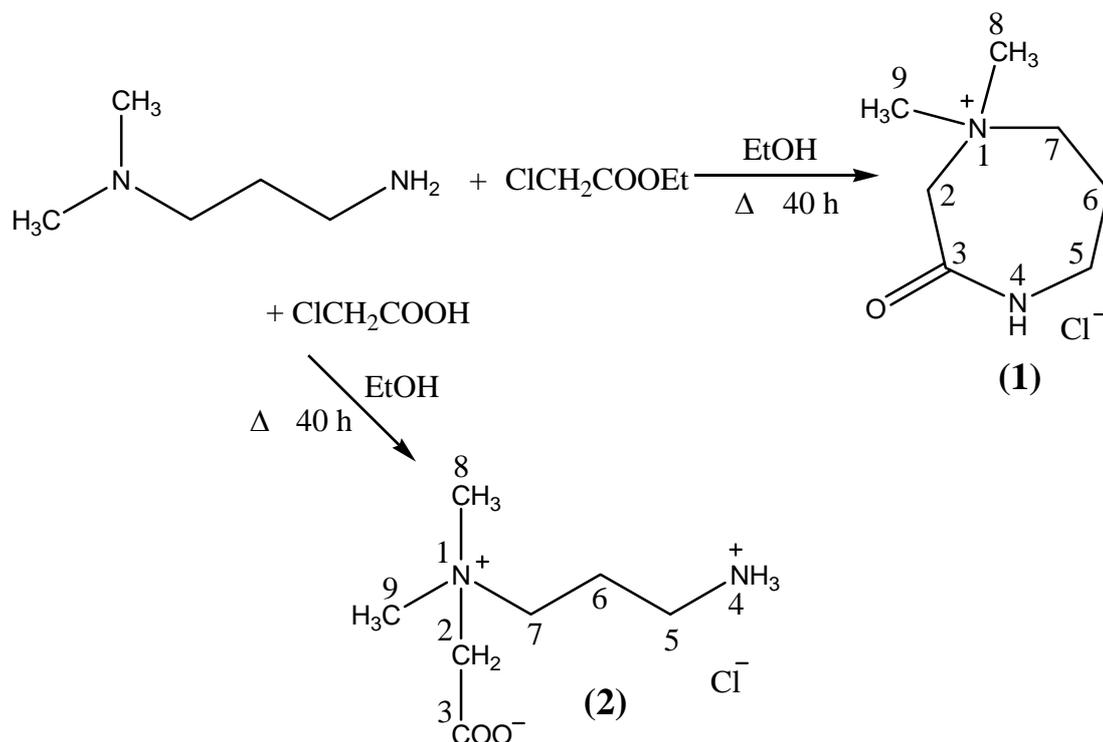
In order to better understand the mechanism of antimicrobial activity of bifunctional quaternary ammonium compounds we have synthesized a new series of betaines. In this work the reaction of 1,1-dimethyl-1,3-propylenediamine with chloroacetic acid and ethyl chloroacetate using the procedure developed by Kröhnke *et al.* [12] is presented and the structures of the resulting products analyzed.

## Results and Discussion

Quaternization of 1,1-dimethyl-1,3-propylenediamine with ethyl chloroacetate in anhydrous ethanol gave 1,1-dimethyl-3-oxo-1,4-diazepan-1-ium chloride (**1**), and with chloroacetic acid gave 1,1-dimethyl-1-carboxymethyl-3-aminopropyl ammonium hydrochloride (**2**) (Scheme 1).

It has been reported in the literature [13-15] that the 2-NHR-pyridines upon quaternization with  $\omega$ -halopropionic acids and esters form both zwitterionic compounds and cyclic products. The cyclic product **1** has been previously obtained by Melandri in an intramolecular conversion of amidoamines, which were obtained by reaction of chloroacetaldehyde and appropriate amines [16]. Seven-membered heterocyclic rings like 3-oxo-1,4-diazepine derivatives are very important compounds because of their therapeutic properties and large numbers of strategies have been developed to prepare these compounds. [17].

**Scheme 1.** Synthesis of 1,1-dimethyl-3-oxo-1,4-diazepan-1-ium chloride (**1**) and 1,1-dimethyl-1-carboxymethyl-3-aminopropyl ammonium hydrochloride (**2**).



The geometry of the investigated compounds **1** and **2** have been optimized at the B3LYP/6-31G(d,p) level of theory (Figure 1).

**Figure.1.** Structures of a) 1,1-dimethyl-3-oxo-1,4-diazepan-1-ium chloride (**1**) and b) 1,1-dimethyl-1-carboxymethyl-3-aminopropyl ammonium hydrochloride (**2**) calculated by the B3LYP/6-31G(d,p) method.

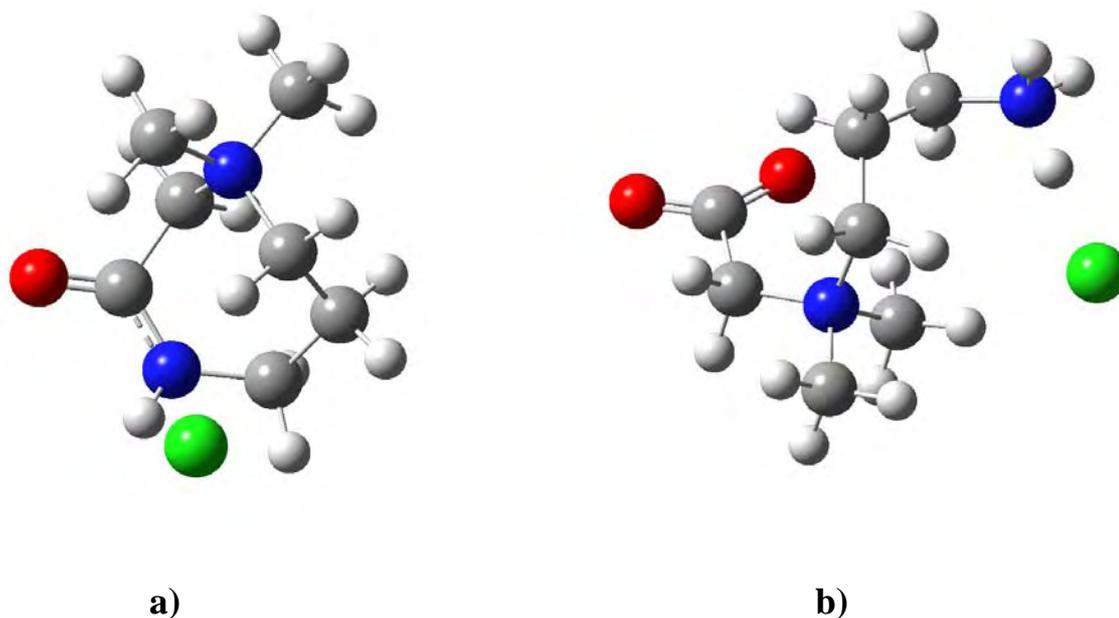


Table 1 shows the energies, dipole moments and selected geometrical parameters calculated at the B3LYP/6-31G(d,p) level of theory for compounds **1** and **2**. In **2** the N<sup>+</sup>H<sub>3</sub> group forms a hydrogen bond with chloride anion, NH...Cl = 2.906 Å, and its protons are not equivalent. Additionally the N<sup>+</sup>(CH<sub>3</sub>) group is engaged in an intramolecular interaction with the COO<sup>-</sup> group. In **1** the chloride anion interacts *via* Coulombic attractions with the adjacent positively charged nitrogen atom and also has close contacts with NH group.

**Table 1.** Selected parameters of investigated compounds (**1**) and (**2**) estimated by B3LYP/6-31G(d,p) calculations.

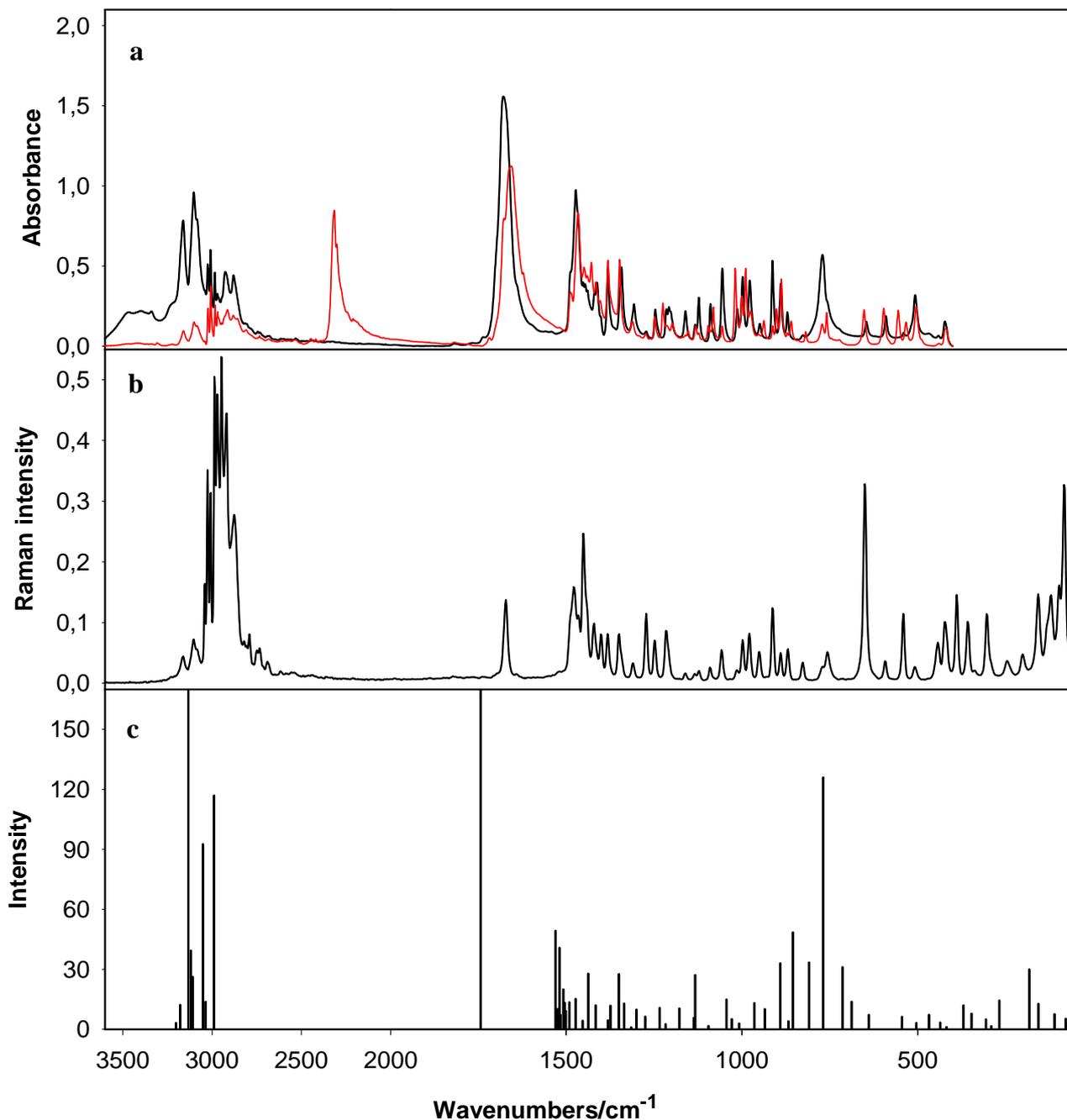
Parameters	Compound	
	1	2
Energy (a.u)	-920.693398	-997.308310
Dipole moment (Debye)	14.9394	5.7351
C(3)=O (Å)	1.227	1.253, 1.232
N(4)...Cl (Å)	3.001	2.906
N(4)-H (Å)	1.042	1.133
N(4)-H·Cl (deg.)	135.3	177.1
N(1)... Cl (Å)	4.470	4.066
N(1)... O (Å)	3.201	2.944
C(7)... O (Å)	3.201	2.901
N(4)-C(3) (Å)	1.351	-
N(4)-C(5)-C(6)-C(7) (deg)	-8.58	-67.64
N(1)-C(2)-C(3)-N(4) (deg)	-81.64	-
N(1)-C(2)-C(3)-O (deg)	93.13	9.75, -170.8
N(1)-C(7)-C(6)-C(5) (deg)	-67.74	-73.15
C(2)-C(3)-N(4)-C(5) (deg)	0.35	-

### FTIR study

Room-temperature solid-state FTIR, Raman and calculated spectra of **1** and **2** are shown in Figures 2 and 3, respectively. The stretching vibration,  $\nu(\text{C}=\text{O})$ , of **1** appears in the FTIR spectrum as a broad and intense band at  $1687\text{ cm}^{-1}$ , which is characteristic for carbonyl groups in cyclic structures. In the Raman spectrum this absorption is very small and lies at  $1671\text{ cm}^{-1}$ . The strong absorption in the  $3170\text{--}3080\text{ cm}^{-1}$  region arises from the NH stretching vibrations. This absorption shifts to lower wavenumbers after deuteration and one broad band at  $2315\text{ cm}^{-1}$  which corresponds to the ND group is present. No absorption of the ND group is observed in the Raman spectrum (Figure 2b). The bands at  $1416$  and  $859\text{ cm}^{-1}$  are shifted to  $1096$  and  $555\text{ cm}^{-1}$  when the proton in NH is replaced by deuterium (Figure 2a). Thus, these bands correspond to the NH and ND in-plane and out-in-plane bending modes, respectively. The strong absorption of (**2**) in the  $3070\text{--}2370\text{ cm}^{-1}$  region corresponds to the  $\nu(\text{N}^+\text{H}\cdots\text{Cl})$  band which is typical for hydrogen bonds with an N...Cl distance between 2.8 and 2.9 Å (Figure 3a). In the Raman spectrum of (**2**) (Figure 3b) this absorption is absent. The  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  for

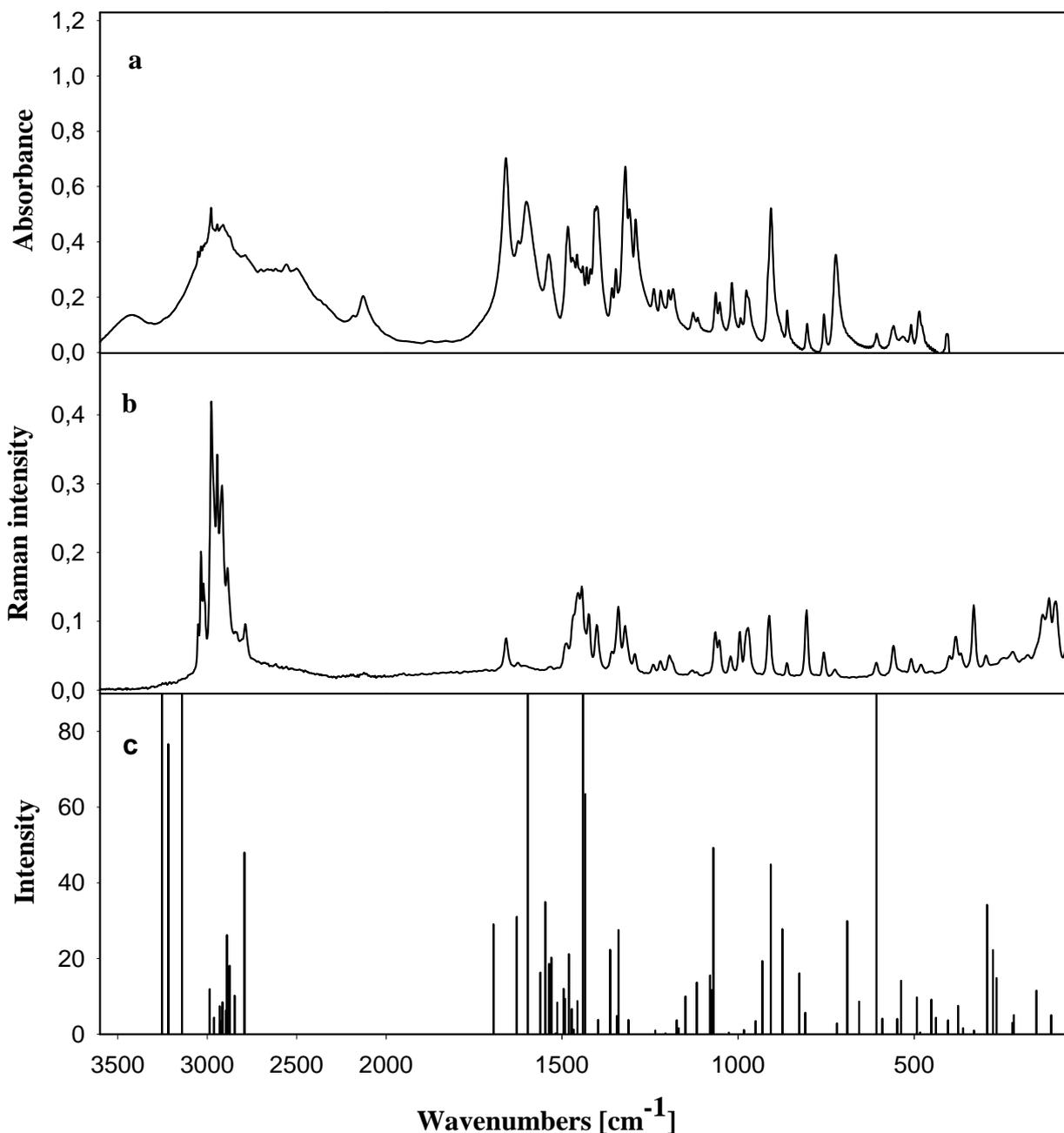
1,1-dimethyl-1-carboxymethyl-3-aminopropyl ammonium hydrochloride (**2**) are located at 1658 and 1382  $\text{cm}^{-1}$  and they have the slightly higher wavenumbers in comparison to betaines [18,19].

**Figure 2.** Spectra of 1,1-dimethyl-3-oxo-1,4-diazepan-1-ium chloride (**1**): (a) FTIR (suspension in Nujol and Fluorolube, red line – deuterated analogue), (b) Raman and (c) calculated spectra.



The DFT harmonic vibrational wavenumbers are usually higher than the experimental values because of the neglect of anharmonicity, incomplete treatment of electron correlation and the use of finite on-particle basis sets. However, in this case the overall agreement between the experimental and calculated frequencies for **1** and **2** is good (Figures 2c and 3c).

**Figure 3.** Spectra of 1,1-dimethyl-1-carboxymethyl-3-aminopropyl ammonium hydrochloride (**2**): (a) FTIR (suspension in Nujol and Fluorolube), (b) Raman and (c) calculated spectra.



### $^1\text{H}$ - and $^{13}\text{C}$ -NMR study

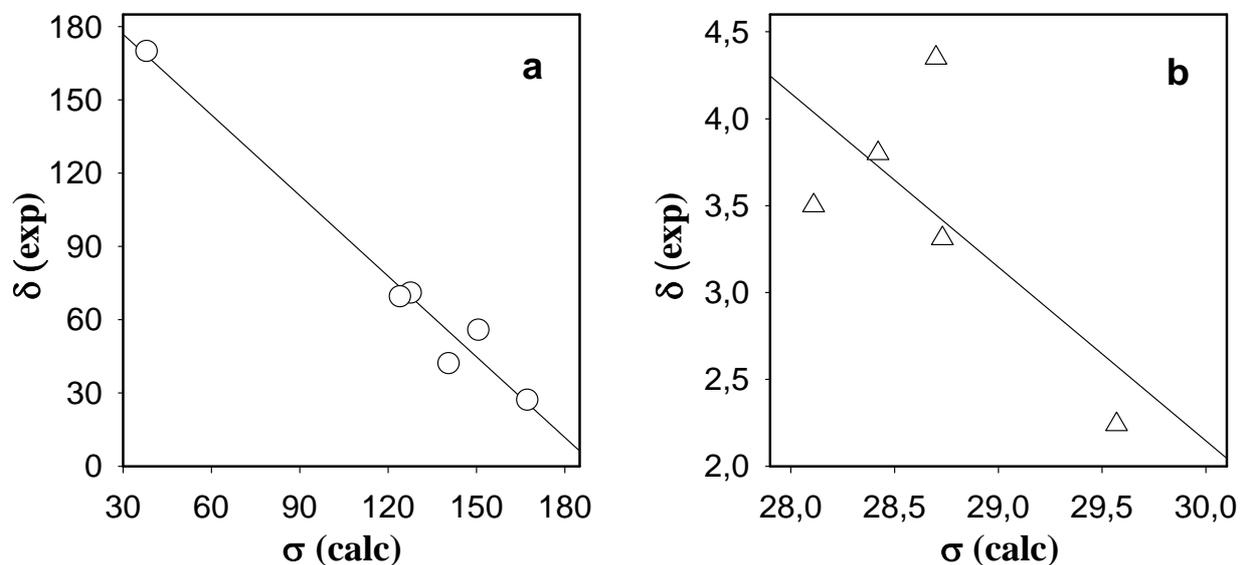
The proton chemical shift assignments (Table 2) are based on 2D COSY experiments, in which the proton-proton connectivity is observed through the off-diagonal peaks in the counter plot. The relations between the experimental  $^1\text{H}$ - and  $^{13}\text{C}$ - chemical shifts ( $\delta_{\text{exp}}$ ) and the GIAO (Gauge-Independent Atomic Orbitals) isotropic magnetic shielding tensors ( $\sigma_{\text{calc}}$ ) are shown in Figures 4 and 5. Both correlations are linear, described by the relationship:  $\delta_{\text{exp}} = a + b \cdot \sigma_{\text{calc}}$ . The  $a$  and  $b$  parameters are

given in Table 2. It has been reported in the literature [20] that the correlation between the experimental chemical shifts and calculated isotropic screening constants are usually better for  $^{13}\text{C}$  atoms than for protons. The protons are located on the periphery of the molecule and thus are supposed to be more efficient in intermolecular (solute-solvent) effects than carbons. For this reason the agreement between the experimental and the calculated data for proton is worse than for  $^{13}\text{C}$ . The differences between the exact values of the calculated and experimental shifts for protons are probably due to the fact that the shifts are calculated for single molecules in gas phase.

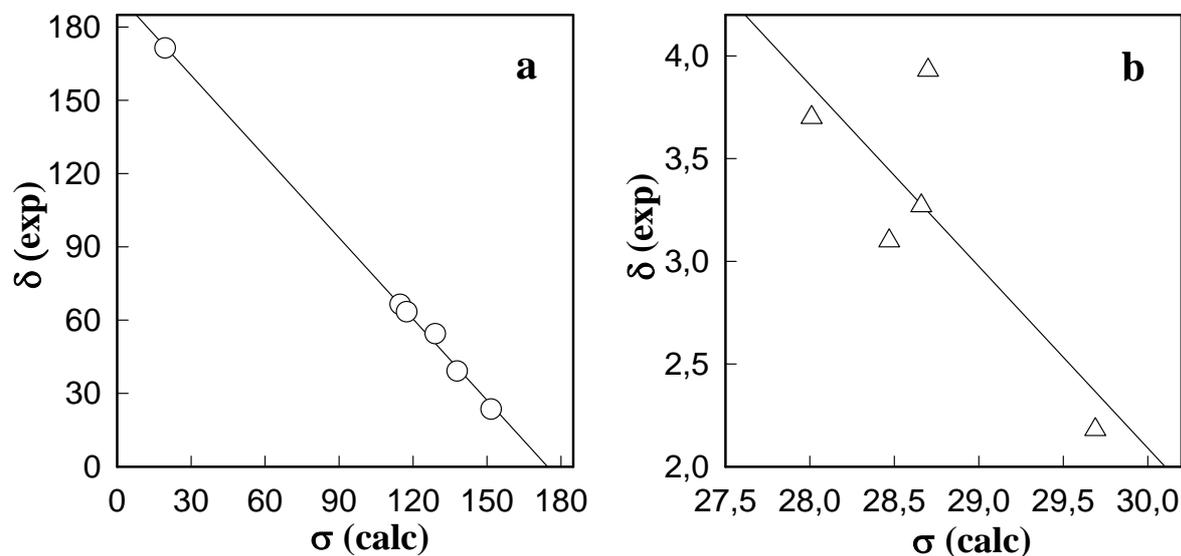
**Table 2.** Chemical shifts ( $\delta$ , ppm) in  $\text{D}_2\text{O}$  calculating GIAO nuclear magnetic shielding tensors ( $\sigma_{\text{calc}}$ ) for 1,1-dimethyl-3-oxo-1,4-diazepan-1-ium chloride (**1**) and 1,1-dimethyl-1-carboxymethyl-3-aminopropyl ammonium hydrochloride (**2**). The predicted GIAO chemical shifts were computed from the linear equation  $\delta_{\text{exp.}} = a + b \cdot \sigma_{\text{calc}}$  with  $a$  and  $b$  determined from the fit the experimental data ( $r$  is the correlation coefficient).

	$\delta_{\text{exp.}}$	$\delta_{\text{calc}}$	$\sigma_{\text{calc}}$		$\delta_{\text{exp.}}$	$\delta_{\text{calc}}$	$\sigma_{\text{calc}}$
<i>1,1-Dimethyl-3-oxo-1,4-diazepan-1-ium chloride (1)</i>							
	$^{13}\text{C}$				$^1\text{H}$		
C (8,9)	42.2	55.2	140.5	H (8,9)	3.31	3.42	28.73
C (2)	71.1	69.4	127.6	H (2)	4.35	3.45	28.70
C (3)	170.0	168.1	38.0	H (5)	3.50	4.04	28.11
C (5)	55.9	44.1	150.6	H (6)	2.24	2.58	29.57
C (6)	27.2	25.8	167.2	H (7)	3.80	3.73	28.42
C (7)	69.6	73.4	124.0				
a			209.9207			32.1455	
b			-1.1011			-0.9999	
r			0.9869			0.6998	
<i>1,1-Dimethyl-1-carboxymethyl-3-aminopropyl ammonium hydrochloride (2)</i>							
	$^{13}\text{C}$				$^1\text{H}$		
C (8,9)	54.4	50.4	129.0	H (8,9)	3.27	3.28	28.66
C (2)	66.5	66.3	114.8	H (2)	3.93	3.24	28.70
C (3)	171.4	172.0	19.5	H (5)	3.70	3.25	28.01
C (5)	63.4	63.4	117.4	H (6)	2.18	2.36	29.69
C (6)	23.6	25.5	151.7	H (7)	3.10	3.44	28.47
C (7)	39.2	40.7	137.9				
a			193.5479			28.6193	
b			-1.1085			-0.8843	
r			0.9992			0.8030	

**Figure 4.** Experimental chemical shifts ( $\delta_{\text{exp}}$ , D<sub>2</sub>O) in 1,1-dimethyl-3-oxo-1,4-diazepan-1-ium chloride (**1**) vs. the isotropic magnetic shielding tensors ( $\sigma_{\text{calc}}$ ) from the GIAO/B3LYP/6-31G(d,p) calculations for molecules  $\delta_{\text{exp}} = a + b \cdot \sigma_{\text{calc}}$ : (a) <sup>13</sup>C and (b) <sup>1</sup>H



**Figure 5.** Experimental chemical shifts ( $\delta_{\text{exp}}$ , D<sub>2</sub>O) in 1,1-dimethyl-1-carboxymethyl-3-aminopropyl ammonium hydrochloride (**2**) vs. the isotropic magnetic shielding tensors ( $\sigma_{\text{calc}}$ ) from the GIAO/B3LYP/6-31G(d,p) calculations for molecules  $\delta_{\text{exp}} = a + b \cdot \sigma_{\text{calc}}$ : (a) <sup>13</sup>C and (b) <sup>1</sup>H.



## Conclusions

Quaternization of 1,1-dimethyl-1,3-propylenediamine with ethyl chloroacetate gives 1,1-dimethyl-3-oxo-1,4-diazepan-1-ium chloride (**1**) and with chloroacetic acid gives 1,1-dimethyl-1-carboxymethyl-3-aminopropyl ammonium hydrochloride (**2**). The structure of the investigated products **1** and **2** have been characterized by FTIR, Raman, NMR spectroscopies and B3LYP calculations. The

FTIR spectra of the investigated compounds **1** and **2** correspond very well to the corresponding structures optimized by B3LYP calculations. Linear correlations between the experimental  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR chemical shifts and the computed screening constants confirm the optimized geometry.

## Experimental

### General

The FTIR spectra in Nujol and Florolube mulls at  $2\text{ cm}^{-1}$  resolution and Raman spectrum were recorded on a Bruker IFS 66v/S instrument, evacuated to avoid water and  $\text{CO}_2$  absorption. Each spectrum consists of 250 scans at  $31^\circ\text{C}$ . MS spectra were measured in water solutions on a Waters Micromass ZQ spectrometer. All 1D NMR spectra were measured with a Varian Gemini 300 VT spectrometer, operating at 300.07 and 75.4614 Hz for  $^1\text{H}$ - and  $^{13}\text{C}$ -, respectively. Typical conditions for the proton spectra were: pulse width  $32^\circ$ , acquisition time 5s, FT size 32 K and digital resolution 0.3 Hz per point, and for the carbon spectra pulse width  $60^\circ$ , FT size 60 K and digital resolution 0.6 Hz per point, the number of scans varied from 1200 to 10000 per spectrum. The  $^{13}\text{C}$  and  $^1\text{H}$  chemical shifts were measured in  $\text{D}_2\text{O}$  relative to PSP in  $\delta$  (ppm) relative to an internal standard of tetramethylsilane (TMS). All  $^1\text{H}$ - and  $^{13}\text{C}$ - resonances were assigned by  $^1\text{H}$  (COSY) and  $^{13}\text{C}$  (HETCOR). All 2D NMR spectra were recorded at 298 K on a Bruker Avance DRX 600 spectrometer operating at the frequencies 600.315 MHz ( $^1\text{H}$ ) and 150.963 MHz ( $^{13}\text{C}$ ), and equipped with a 5 mm triple-resonance inverse probehead [ $^1\text{H}/^{31}\text{P}/\text{BB}$ ] with a self-shielded  $z$  gradient coil ( $90^\circ$   $^1\text{H}$  pulse width 9.0  $\mu\text{s}$  and  $^{13}\text{C}$  pulse width 13.3  $\mu\text{s}$ ). The spectra were measured in  $\text{D}_2\text{O}$  solution and the sample concentration was 40 mg per 0.6 ml of solvent. The chemical shifts  $\delta$  (ppm) were referred to internal tetramethylsilane (TMS) in the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra.

### Computational Details

The calculations of geometrical parameters and FTIR frequencies were performed using the GAUSSIAN 03 package [21] at B3LYP [22-24] in conjugation with the 6-31G(d,p) [25] basis set. The NMR isotropic magnetic shielding tensors were calculated using the standard GIAO (Gauge-Independent Atomic Orbital) approach [26, 27] of Gaussian 03 program package.

### Syntheses

#### *1,1-Dimethyl-3-oxo-1,4-diazepan-1-ium chloride (1).*

1-1-Dimethyl-1,3-propylenediamine (2.19 g, 0.02 M) was mixing with ethyl chloroacetate (3.06 g, 0.02 M) in anhydrous ethanol (20 mL). The mixture was stirred at  $70^\circ\text{C}$  for 50 h. The solvent was evaporated under reduced pressure and the residue was dried over  $\text{P}_4\text{O}_{10}$  and then recrystallized from anhydrous ethanol, yield 65%, m.p.  $238\text{--}241^\circ\text{C}$ ; Elemental analysis: found (calc) %C 46.91 (47.06); %H 8.57 (8.40); %N 15.75 (15.69);  $\text{ES}^+\text{MS}$   $m/z$  143 ( $\text{C}_7\text{H}_{15}\text{N}_2\text{O}$ );  $^1\text{H}$ -NMR ( $\text{D}_2\text{O}$ ):  $\delta$  4.35 (2H, s, C(2)H<sub>2</sub>), 3.50 (2H, t, C(5)H<sub>2</sub>), 2.24 ((2H, qw, C(6)H<sub>2</sub>), 3.80 (2H, t, C(7)H<sub>2</sub>), 3.31 (6H, s, C(8)H<sub>3</sub>,

C(9)H<sub>3</sub>); <sup>13</sup>C-NMR (D<sub>2</sub>O): δ 71.1 (C(2)), 170 (C(3)), 55.9 (C(5)), 27.2 (C(6)), 69.6 (C(7)), 42.2 (C(8,9)); FTIR: ν(C=O) at 1671 cm<sup>-1</sup>. The deuterated sample was obtained by dissolving the compound in D<sub>2</sub>O (twice), evaporating to dryness and recrystallization (twice) from C<sub>2</sub>H<sub>5</sub>OD.

*N,N*-dimethyl-*N*-carboxymethyl-3-aminopropyl ammonium hydrochloride (2).

1-1-Dimethyl-1,3-propylenediamine (0,098 M; 12,3 mL) was mixing with ethyl chloroacetic acid (0.098 M; 9.26 g) in anhydrous ethanol (20 mL). The mixture was stirred at 70 °C for 40 h. The solvent was evaporated under reduced pressure and the residue was dried over P<sub>4</sub>O<sub>10</sub> and then recrystallized from anhydrous ethanol, yield 69%, m.p. 211-213 °C; Elemental analysis: found (calc) %C 42.52 (42.75); %H 09.01 (8.91); %N 14.11 (14.24); ES<sup>+</sup>MS m/z 161 (C<sub>7</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>); <sup>1</sup>H-NMR (D<sub>2</sub>O): δ 3.93 (2H, s, C(2)H<sub>2</sub>), 3.70 (2H, t, C(5)H<sub>2</sub>), 2.18 ((2H, qw, C(6)H<sub>2</sub>), 3.10 (2H, t, C(7)H<sub>2</sub>), 3.27 (6H, s, C(8)H<sub>3</sub>, C(9)H<sub>3</sub>); <sup>13</sup>C-NMR (D<sub>2</sub>O): δ 66.5 (C(2)), 171.4 (C(3)), 63.4 (C(5)), 23.6 (C(6)), 39.2 (C(7)), 54.4 (C(8,9)); FTIR: ν(COO<sup>-</sup>) at 1658 cm<sup>-1</sup>.

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