Study of Cyclic Quaternary Ammonium Bromides by B3LYP Calculations, NMR and FTIR Spectroscopies

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Abstract: N,N-dioctyl-azepanium, -piperidinium and -pyrrolidinium bromides 1-3, have been obtained and characterized by FTIR and NMR spectroscopy. DFT calculations have also been carried out. The optimized bond lengths, bond angles and torsion angles calculated by B3LYP/6-31G(d,p) approach have been presented. Both FTIR and Raman spectra of 1-3 are consistent with the calculated structures in the gas phase. The screening constants for 13C and 1H atoms have been calculated by the GIAO/B3LYP/6-31G(d,p) approach and analyzed. Linear correlations between the experimental 1H and 13C chemical shifts and the computed screening constants confirm the optimized geometry.

Keywords: N,N-dioctyl-azepanium; -piperidinium; -pyrrolidinium bromides; DFT calculations; FTIR and NMR spectra

1. Introduction

Quaternary ammonium compounds (QACs) were introduced as antimicrobial agents by Domagk over seventy years ago [1]. The first generation of QACs were standard benzalkonium chlorides, i.e. alkylbenzyltrimethylammonium chloride, with specific alkyl distributions, i.e., C12, 40%; C14, 50% and C16, 10% [2]. The second generation of QACs was obtained by substitution of the aromatic ring in alkylbenzyltrimethylammonium chlorides by chlorine or alkyl groups to get products like alkylmethylbenzyltrimethylammonium chloride with C12, 50%; C14, 30%; C16, 17% and C18, 3% alkyl distribution. Dual quaternary ammonium salts are the third generation of QACs. These products are a
mixture of equal proportions of alkyltrimethylbenzylammonium chloride with alkyl distribution C\textsubscript{12}, 68%; C\textsubscript{14}, 32% and alkyltrimethylethylbenzylammonium chloride with alkyl distribution C\textsubscript{12}, 50%; C\textsubscript{14}, 30%; C\textsubscript{16}, 17% and C\textsubscript{18}, 3%. The twin chain quaternary ammonium salts, like didecyldimethylammonium chloride are the fourth generation of QACs. The concept of synergistic combinations of dual QACs has been applied to twin chain quaternary ammonium salts. The mixture of dialkyldimethylethylammonium chloride (dioctyl, 25%; didecyl, 25%, octyldodecyl, 50%) with benzalkonium chloride (C\textsubscript{12}, 40%; C\textsubscript{14}, 50%; C\textsubscript{16}, 10%) is the newest blend of quaternary ammonium salts which represents the fifth generation of QACs [2]. Because of the increasing resistance of microorganisms to commonly used disinfectants, the synthesis of new types of microbiocides is very important. One of the new groups with good antimicrobial activity are the cyclic quaternary ammonium salts [3]. The aim of this work was the synthesis of cyclic N,N-dioctyl quaternary ammonium salts, i.e. N,N-dioctylazepanium, N,N-dioctylpiperidinium and N,N-dioctylpyrrolidinium bromides, with potential antimicrobial activity. Some cyclic quaternary ammonium salts have previously been obtained by intramolecular cyclisation of amine derivatives [4-9]. Another way, i.e. reaction of alkyl halides with cyclic amines, can lead to chiral cyclic quaternary ammonium salts [10].

In recent years numbers of applications of the quaternary ammonium salts has been continuously increasing. They are used as biocides [11-15], and phase-transfer catalysts, especially in enantioselective reactions [16-21]. Pyrrolidinium salts are analogues of oxotremorine and are used as muscarinic agonists [5]. Some quaternary ammonium salts exist as ionic liquids, which can be used as “green solvents” [22-26] and electrolytes for liquid batteries [27,28].

The molecular structures of $N,N$-dioctyl-azepanium (1), -piperidinium (2) and -pyrrolidinium (3) bromides analyzed by FTIR and NMR spectroscopy and B3LYP calculations are presented in this paper. The above compounds belong to the cyclic quaternary ammonium bromide family investigated in our laboratory in order to better understand the mechanism of their biological activity.

2. Results and Discussion

2.1. Synthesis

$N,N$-dioctyl-azepanium, -piperidinium and -pyrrolidinium bromides 1-3 were obtained by reaction of $N,N$-dioctylamine with dibromohexane, dibromopentane and dibromobutane, respectively. The reaction of secondary amines with 1,5-dichloropentane and 1,4-dichlorobutane to produce dialkylpiperidinium and dialkylpyrrolidinium salts has previously been described by Ericsson and Keps [4]. In our work, using dibromoalkanes instead of dichloroalkanes, we formed five-, six- and seven-membered ammonium compounds in much higher yields and after shorter reaction times. In the first step of reaction of dioctylamine with $\alpha,\alpha$-dibromoalkane, the halogenated tertiary amine is formed, which shows a strong tendency to form cyclic quaternary ammonium salts.

2.2. B3LYP Calculations

The structures and numbering for 1-3 are given in Figure 1. The structures optimized at the B3LYP/6-31G(d,p) level of theory are shown in Figure 2.
Figure 1. The structure and numbering for $N,N$-dioctylazepanium bromide (1), $N,N$-dioctylpiperidinium bromide (2) and $N,N$-dioctylpyrrolidinium bromide (3).
Figure 2. Structures of (a) $N,N$-dioctylazepanium (1), (b) $N,N$-dioctylpiperidinium (2), (c) $N,N$-dioctylpyrrolidinium (3) bromides optimized by the B3LYP/6-31G(d,p) method.

The computed B3LYP geometry parameters, energy and dipole moments are given in Table 1. The calculated energy for $N,N$-dioctylazepanium bromide (1) is about 1.2% lower than for $N,N$-dioctyl-piperidinium bromide (2) and 2.4% lower in comparison to $N,N$-dioctylpyrrolidinium bromide (3). The bromide anions in 1-3 are engaged in three non-linear weak intramolecular interactions with carbon atoms. Bromide anions additionally interact via Coulombic attractions with positively charged nitrogen atom. The $N^+\cdots\text{Br}^-$ distances are 3.888 Å, 3.709 Å, and 3.674 Å, for 1, 2, and 3, respectively.
Table 1. Selected parameters of investigated molecules 1-3 estimated by B3LYP/6-31G(d,p) calculations.

| Parameters                        | 1                | 2                | 3                |
|-----------------------------------|------------------|------------------|------------------|
| Energy (a.u)                      | -3495.20808      | -3453.27811      | -3413.96044      |
| Dipol moment (Debye)              | 13.4951          | 11.4097          | 11.4657          |
| Bond length (Å)                   |                  |                  |                  |
| N⁺…Br⁻                              | 3.888            | 3.709            | 3.674            |
| C(1)-H…Br⁻                           | 3.636            | 3.536            | 3.486            |
| C(1')-H…Br⁻                           | 3.686            |                  |                  |
| C(4)-H…Br⁻                           | 3.551            | 3.570            | 3.616            |
| C(4')-H…Br⁻                           |                  | 3.360            | 3.346            |
| N-C(1)                               | 1.535            | 1.538            | 1.532            |
| N-C(1')                              | 1.533            | 1.514            | 1.513            |
| N-C(4)                               | 1.548            | 1.542            | 1.529            |
| N-C(4')                              | 1.531            | 1.551            | 1.543            |
| Bond angle (°)                     |                  |                  |                  |
| N-C(1)-C(2)                           | 119.5            | 115.3            | 106.2            |
| N-C(1')-C(2')                         | 116.9            | 114.2            | 106.2            |
| N-C(4)-C(5)                           | 117.9            | 116.3            | 115.6            |
| N-C(4')-C(5')                         | 120.2            | 119.9            | 118.6            |
| Dihedral angle (°)                  |                  |                  |                  |
| N-C(1)-C(2)-C(3)                     | -70.3            | -49.5            |                  |
| N-C(1')-C(2')-C(3')                  | 88.6             |                  |                  |
| N-C(1)-C(2)-C(2')                    |                  | 57.8             |                  |
| N-C(1')-C(2')-C(2')                  |                  | -18.2            |                  |
| N-C(4)-C(5)-C(6)                      | -176.8           | -177.4           | -176.9           |
| N-C(4')-C(5')-C(6')                   | -176.5           | -172.3           | -170.0           |

2.3. FTIR and Raman Spectra Study

Room-temperature solid-state FTIR and Raman spectra as well as the calculated spectra of 1 are shown in Figure 3.

Figure 3. Spectra of N,N-dioctylazepanium bromide (1); (a) FTIR, (b) Raman and (c) calculated spectra.
The observed and calculated harmonic frequencies and their tentative assignments are listed in Table 2. In general, the calculated frequency values with B3LYP 6-31G(d,p) basis set are close to experimental values of vibrational frequency.

Table 2. FTIR and Raman frequencies of \(N,N\)-dioctylazepanium bromide (1).

| Raman  | IR        | IR(calc.) | INT   | Proposed assignment |
|--------|-----------|-----------|-------|---------------------|
| 2973m  | 2956s     | 3016      | 43.7  | νOH                 |
|        | 3013      | 62.3      |       | νCH\(_2\)           |
|        | 3011      | 64.9      |       | νCH\(_2\)           |
|        | 2999      | 23.3      |       | νCH\(_2\)           |
|        | 2987      | 63.2      |       | νCH\(_2\)           |
|        | 2974      | 18.6      |       | νCH\(_2\)           |
|        | 2943      | 112       |       | νCH\(_2\)           |
| 2926s  | 2925s     | 2934      | 61.4  | νCH\(_2\)           |
|        | 2919      | 6.4       |       | νCH\(_2\)           |
| 2864s  | 2856s     | 2914      | 200   | νCH\(_2\)           |
| 2781vw |           |           |       | νCH\(_2\)           |
| 2727vw |           |           |       | νCH\(_2\)           |
| 2709vw | 2696vw    |           |       | νCH\(_2\)           |
| 2669vw | 2670vw    |           |       | νCH\(_2\)           |
| 1490vw | 1485m     | 1501      | 21.9  | νCC                 |
|        |           | 1481      | 4.7   |                     |
| Mode  | cm⁻¹   | Int. | vCC, βCH₂ |
|-------|--------|------|-----------|
| 1448w | 1468m  | 1467 | 8.0       |
|       |        | 1456 | 7.9       |
|       |        | 1452 | 2.3       |
| 1392w | 1396   | 1377 | 1.5       |
|       |        | 1376 | 3.5       |
|       |        | 1372 | 1.6       |
| 1358vw| 1360w  | 1354 | 4.9       |
| 1349vw| 1338w  | 1344 | 1.4       |
| 1313vw| 1310w  | 1308 | 2.7       |
|       |        | 1321 | 2.8       |
| 1280vw| 1277w  | 1281 | 3.4       |
| 1263vw| 1251vw | 1264 | 2.8       |
| 1217vw| 1218vw | 1205 | 0.63      |
|       |        | 1186 | 1.3       |
| 1141vw| 1141vw | 1169 | 3.3       |
| 1115vw| 1115vw | 1115 | 2.4       |
| 1087vw| 1088w  | 1075 | 15.3      |
| 1069vw| 1068vw | 1055 | 1.6       |
| 1048vw| 1047vw | 1029 | 3.8       |
| 1014vw| 1007w  | 1014 | 2.9       |
| 960vw | 962w   | 997  | 2.6       |
| 930vw | 930vw  | 944  | 2.0       |
|       |        | 933  | 9.7       |
| 865vw | 875w   | 878  | 13.7      |
| 846vw | 847vw  | 853  | 4.6       |
| 831vw | 832w   |      |           |
| 803vw | 800vw  | 788  | 2.5       |
| 767vw | 765vw  | 742  | 19.5      |
| 741vw | 738w   |      |           |
|       | 723w   | 714  | 4.0       |
| 706vw |        |      |           |
| 659vw | 651vw  | 616  | 1.8       |
| 580vw | 578vw  |      |           |
| 542vw | 538vw  |      |           |
| 498vw | 499vw  | 499  | 3.8       |
| 403vw | 403vw  | 439  | 1.5       |

The abbreviations used are: s, strong; m, medium; w, weak; vw, very weak; v, stretching; β, in plane bending; δ, deformation; γ, out of plane bending; and τ, twisting.
2.4. $^1$H-NMR and $^{13}$C-NMR Spectra

The proton chemical shift assignments (Tables 3-5) 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 $^1$H and $^{13}$C chemical shifts ($\delta_{\text{exp}}$) and the GIAO (Gauge-Independent Atomic Orbitals) isotropic magnetic shielding ($\sigma_{\text{calc}}$) for 1 is shown in Figure 4. Both correlations are linear, described by the relationship: $\delta_{\text{exp}} = a + b \cdot \sigma_{\text{calc}}$. The parameters $a$ and $b$ are given in Tables 3-5. The very good correlation coefficients ($r^2=0.9379$) for $^1$H and ($r^2=0.9984$) for $^{13}$C confirm the optimized geometry of 1-3.

**Figure 4.** Plots of the experimental chemical shifts ($\delta_{\text{exp}}$) vs the magnetic isotropic shielding ($\sigma_{\text{calc}}$) from the GIAO/B3LYP/6-31G(d,p); $N,N$-dioctylazepanium bromide (1) $\delta_{\text{pred}} = a + b \cdot \sigma_{\text{calc}}$. (a) carbon-13; (b) proton.

|       | $\delta_{\text{exp}}$ | $\delta_{\text{calc}}$ | $\sigma_{\text{calc}}$ | $\delta_{\text{exp}}$ | $\delta_{\text{calc}}$ | $\sigma_{\text{calc}}$ |
|-------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| C(1)  | 63.1                   | 57.4                   | 118.0                  | H(1)                   | 3.70                   | 3.85                   | 27.44                  |
| C(2)  | 22.2                   | 23.3                   | 155.4                  | H(2)                   | 2.01                   | 1.62                   | 30.27                  |
| C(3)  | 27.3                   | 21.7                   | 157.1                  | H(3)                   | 1.79                   | 2.06                   | 29.72                  |
| C(4)  | 61.3                   | 64.6                   | 110.1                  | H(4)                   | 3.45                   | 3.25                   | 28.20                  |
| C(5)  | 22.6                   | 25.7                   | 152.7                  | H(5)                   | 1.71                   | 1.59                   | 30.32                  |
| C(6)  | 26.4                   | 27.1                   | 151.2                  | H(6)                   | 1.27                   | 1.23                   | 30.77                  |
| C(7)  | 29.1                   | 30.3                   | 147.7                  | H(7)                   | 1.27                   | 1.33                   | 30.65                  |
| C(8)  | 29.0                   | 30.3                   | 147.7                  | H(8)                   | 1.27                   | 1.31                   | 30.67                  |
| C(9)  | 31.6                   | 32.2                   | 145.6                  | H(9)                   | 1.27                   | 1.27                   | 30.72                  |
| C(10) | 22.6                   | 24.1                   | 154.5                  | H(10)                  | 1.27                   | 1.34                   | 30.63                  |
| C(11) | 14.0                   | 12.4                   | 167.3                  | H(11)                  | 0.88                   | 1.05                   | 31.00                  |

| a     | -0.9113                | a                      | 0.7865                 |
| b     | 164.9046               | b                      | 25.4318                |
| $r^2$ | 0.9622                 | $r^2$                  | 0.9609                 |

Table 3. Chemical shifts ($\delta$, ppm) in CDCl$_3$ and calculated GIAO nuclear magnetic shielding ($\sigma_{\text{calc}}$) for $N,N$-dioctylazepanium bromide (1). 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.
Table 4. Chemical shifts (δ, ppm) in CDCl₃ and calculated GIAO nuclear magnetic shielding (σ_{calc}) for N,N-dioctylpiperidinium bromide (2). The predicted GIAO chemical shifts were computed from the linear equation \( δ_{exp} = a + b \cdot σ_{calc} \) with \( a \) and \( b \) determined from the fit the experimental data.

|       | δ_{exp} | δ_{calc} | σ_{calc} | δ_{exp} | δ_{calc} | σ_{calc} |
|-------|---------|----------|----------|---------|----------|----------|
| C(1)  | 58.9    | 54.8     | 129.6    | H(1)    | 3.78     | 3.28     | 27.90    |
| C(2)  | 20.0    | 20.5     | 167.8    | H(2)    | 1.90     | 1.67     | 29.95    |
| C(3)  | 26.4    | 20.5     | 167.8    | H(3)    | 1.90     | 1.47     | 30.23    |
| C(4)  | 58.1    | 61.0     | 122.7    | H(4)    | 3.46     | 3.88     | 27.12    |
| C(5)  | 21.7    | 23.2     | 161.8    | H(5)    | 1.65     | 1.77     | 29.84    |
| C(6)  | 22.5    | 25.7     | 162.1    | H(6)    | 1.27     | 1.42     | 30.30    |
| C(7)  | 29.0    | 29.2     | 158.1    | H(7)    | 1.27     | 1.33     | 30.41    |
| C(8)  | 28.9    | 29.2     | 158.1    | H(8)    | 1.27     | 1.37     | 30.36    |
| C(9)  | 31.6    | 30.7     | 156.5    | H(9)    | 1.27     | 1.30     | 30.45    |
| C(10) | 20.6    | 23.1     | 164.9    | H(10)   | 1.27     | 1.39     | 30.33    |
| C(11) | 14.0    | 13.6     | 175.5    | H(11)   | 0.88     | 1.02     | 30.81    |

\[ a = 170.9303 \]
\[ b = -0.8962 \]
\[ r^2 = 0.9640 \]

Table 5. Chemical shifts (δ, ppm) in CDCl₃ and calculated GIAO nuclear magnetic shielding (σ_{calc}) for N,N-dioctylpyrrolidinium bromide (3). The predicted GIAO chemical shifts were computed from the linear equation \( δ_{exp} = a + b \cdot σ_{calc} \) with \( a \) and \( b \) determined from the fit the experimental data.

|       | δ_{exp} | δ_{calc} | σ_{calc} | δ_{exp} | δ_{calc} | σ_{calc} |
|-------|---------|----------|----------|---------|----------|----------|
| C(1)  | 62.9    | 61.9     | 126.0    | H(1)    | 3.85     | 3.69     | 27.57    |
| C(2)  | 21.8    | 18.6     | 169.5    | H(2)    | 2.31     | 1.77     | 29.81    |
| C(4)  | 59.4    | 59.7     | 128.2    | H(4)    | 3.43     | 3.32     | 28.00    |
| C(5)  | 23.4    | 24.2     | 163.9    | H(5)    | 1.70     | 2.43     | 29.04    |
| C(6)  | 26.3    | 27.5     | 160.6    | H(6)    | 1.27     | 1.30     | 30.49    |
| C(7)  | 29.0    | 29.2     | 158.9    | H(7)    | 1.27     | 1.26     | 30.24    |
| C(8)  | 28.9    | 30.2     | 157.8    | H(8)    | 1.27     | 1.25     | 30.41    |
| C(9)  | 31.5    | 31.1     | 156.9    | H(9)    | 1.27     | 1.40     | 30.40    |
| C(10) | 22.5    | 23.3     | 164.8    | H(10)   | 1.27     | 1.18     | 30.35    |
| C(11) | 14.0    | 12.5     | 175.6    | H(11)   | 0.88     | 0.91     | 30.80    |

\[ a = 187.2433 \]
\[ b = -0.9949 \]
\[ r^2 = 0.9920 \]

The correlation between the experimental chemical shifts and calculated isotropic screening constants are 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. 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. For this
reason the agreement between the experimental and the calculated data for proton is worse than for $^{13}$C.

3. Conclusions

$N,N$-dioctyl-azepanium, -piperidinium, -pyrrolidinium bromides 1-3 have been obtained by reaction of $N,N$-dioctylamine with dibromohexane, dibromopentane and dibromobutane, respectively. The structure of the investigated compounds has been analyzed by FTIR and NMR spectroscopy and B3LYP calculations. Both the FTIR and Raman spectra of 1-3 are consistent with the observed structures in the gas phase. The good correlations between the experimental $^{13}$C and $^1$H chemical shifts in D$_2$O solution and GIAO/B3LYP/6-31G(d,p) calculated isotropic shielding tensors ($\delta_{\text{exp}} = a + b \cdot \sigma_{\text{calc}}$) have confirmed the optimized geometry of 1-3.

4. Experimental

4.1. General

The NMR spectra were measured with a Varian Gemini 300VT spectrometer, operating at 300.07 and 75.4614 MHz for $^1$H and $^{13}$C, respectively. Typical conditions for the proton spectra were: pulse width 32°, acquisition time 5s, FT size 32 K and digital resolution 0.3 Hz per point, and for the carbon spectra pulse width 60°, FT size 60 K and digital resolution 0.6 Hz per point, the number of scans varied from 1200 to 10,000 per spectrum. The $^{13}$C and $^1$H chemical shifts were measured in CDCl$_3$ relative to an internal standard of TMS. All proton and carbon-13 resonances were assigned by $^1$H (COSY) and $^{13}$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 ($^1$H) and 150.963 MHz ($^{13}$C), and equipped with a 5 mm triple-resonance inverse probehead [$^1$H/$^{31}$P/BB] with a self-shielded $z$ gradient coil (90° $^1$H pulse width 9.0 μs and $^{13}$C pulse width 13.3 μs). Infrared spectra were recorded in the KBr pellets using a FT-IR Bruker IFS 66 spectrometer. The Raman spectrum was recorded on a Bruker IFS 66 spectrometer. The ESI (electron spray ionization) mass spectra were recorded on a Waters/Micromass (Manchester, UK) ZQ mass spectrometer equipped with a Harvard Apparatus syringe pump. The sample solutions were prepared in methanol at the concentration of approximately $10^{-5}$M. The standard ESI – MS mass spectra were recorded at the cone voltage 30V.

4.2. Computational Details

The calculations were performed using the Gaussian 03 program package [29] at the B3LYP [30,31] levels of theory with the 6-31G(d,p) basis set [30]. The NMR isotopic shielding constants were calculated using the standard GIAO (Gauge-Independent Atomic Orbital) approach [29-32] of GAUSSIAN 03 program package [33].
4.3. General procedure for the synthesis of N,N-dioctylcycloalkylammonium salts 1-3

Dioctylamine (5 g, 0.02 mol) was mixed with the appropriate dibromoalkane (0.02 mol) in the presence of anhydrous sodium carbonate (4.14 g, 0.04 mol). The reaction mixture was heated under reflux for 15 h. The solvent was evaporated under reduced pressure and the residue was dried over P₄O₁₀ and then recrystallized from a suitable solvent, as indicated.

**N,N-dioctylazepanium bromide (1).** Prepared from 1,6-dibromohexane (5 g) and recrystallized from acetone/acetonitrile; yield: 65%, m.p. 212-214°C. Elemental analysis for C₂₂H₄₆NBr·H₂O found (calc.) %C 62.80 (62.53); %H 11.49 (11.45); %N 3.30 (3.31); ES²MS m/z 325 (C₂₂H₄₆N); ¹H-NMR (CDCl₃): δ 3.70 (4H, t, C(1)H₂, C(1')H₂), 2.01 (4H, m, C(2)H₂, C(2')H₂), 1.79 (4H, m, C(3)H₂, C(3')H₂), 3.45 (4H, t, C(4)H₂, C(4')H₂), 1.71 (20H, m, C(5)H₂, C(5')H₂, C(6)H₂, C(6')H₂, C(7)H₂, C(7')H₂, C(8)H₂, C(8')H₂, C(9)H₂, C(9')H₂), 1.27 (4H, m, C(10)H₂, C(10')H₂), 0.88 (6H, t, C(11)H₃, C(11')H₃); ¹³C-NMR (CDCl₃): δ 63.1 (C(1), C(1')), 22.2 (C(2), C(2')), 27.3 (C(3), C(3')), 61.3 (C(4), C(4')), 22.6 (C(5), C(5')), 26.4 (C(6), C(6')), 29.1 (C(7), C(7')), 29.0 (C(8), C(8')), 31.6 (C(9), C(9')), 22.6 (C(10), C(10')), 14.0 (C(11), C(11')).

**N,N-dioctylpiperidinium bromide (2).** From 1,5-dibromopentane (4.76 g, 0.02 mol). Recrystallized from acetone; yield: 90%, m.p. 144-146°C. Elemental analysis for C₂₁H₄₄NBr found (calc) %C 64.13 (64.59); %H 12.00 (11.36); %N 3.56 (3.59); ES²MS m/z 310 (C₂₁H₄₄N); ¹H-NMR (CDCl₃): δ 3.78 (4H, t, C(1)H₂, C(1')H₂), 1.90 (6H, m, C(2)H₂, C(2')H₂ C(3)H₂), 3.46 (4H, t, C(4)H₂, C(4')H₂), 1.65 (20H, m, C(5)H₂, C(5')H₂, C(6)H₂, C(6')H₂, C(7)H₂, C(7')H₂, C(8)H₂, C(8')H₂, C(9)H₂, C(9')H₂), 1.27 (4H, m, C(10)H₂, C(10')H₂), 0.88 (6H, t, C(11)H₃, C(11')H₃); ¹³C-NMR (CDCl₃): δ 58.9 (C(1), C(1')), 20.0 (C(2), C(2')), 26.4 (C(3)), 58.1 (C(4), C(4')), 21.7 (C(5), C(5')), 22.5 (C(6), C(6')), 29.0 (C(7), C(7')), 28.9 (C(8), C(8')), 31.6 (C(9), C(9')), 20.6 (C(10), C(10')), 14.0 (C(11), C(11')).

**N,N-dioctylpyrrolidinium bromide (3).** From 1,4-dibromobutane (4.2g, 0.02 mol). Recrystallized from ethyl acetate; yield: 98%, m.p. 120-124°C; Elemental analysis for C₂₀H₄₂NBr found (calc) %C 63.47 (63.81); %H 11.76 (11.24); %N 3.78 (3.72); ES²MS m/z 296(C₂₀H₄₂N); ¹H-NMR (CDCl₃): δ 3.85 (4H, t, C(1)H₂, C(1')H₂), 2.31 (4H, m, C(2)H₂, C(2')H₂), 3.43 (4H, t, C(4)H₂, C(4')H₂), 1.70 (20H, m, C(5)H₂, C(5')H₂, C(6)H₂, C(6')H₂, C(7)H₂, C(7')H₂, C(8)H₂, C(8')H₂, C(9)H₂, C(9')H₂), 1.27 (4H, m, C(10)H₂, C(10')H₂), 0.88 (6H, t, C(11)H₃, C(11')H₃); ¹³C-NMR (CDCl₃): δ 62.9 (C(1), C(1')), 21.8 (C(2), C(2')), 59.4 (C(4), C(4')), 23.4 (C(5), C(5')), 26.3 (C(6), C(6')), 29.0 (C(7), C(7')), 28.9 (C(8), C(8')), 31.5 (C(9), C(9')), 22.5 (C(10), C(10')), 14.0 (C(11), C(11')).

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