Synthesis and structural studies of a new class of quaternary ammonium salts, which are derivatives of cage adamanzane type aminal 1, 3, 6, 8-tetraazatricyclo[4.3.1.1^3,8]undecane (TATU)

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Abstract

Background: Novel mono N-alkyl quaternary ammonium salts (3a-f) were prepared using the Menschutkin reaction from the cage adamanzane type aminal 1,3,6,8-tetraazatricyclo[4.3.1.1^3,8]undecane (TATU) and alkyl iodides, such as methyl, ethyl, propyl, butyl, pentyl and hexyl iodide (2a-f), in dry acetonitrile at room temperature.

Results: The structures of these new quaternary ammonium salts were established using various spectral and electrospray ionization mass spectrometry (ESI-MS) analyses. Compound (3b) was also analyzed using X-ray crystallography.

Conclusion: It was noted that alkyl chain length did not significantly affect the reaction because all employed alkyl iodide electrophiles reacted in a similar fashion with the aminal 1 to produce the corresponding mono N-quaternary ammonium salts, which were characterized by spectroscopic and analytical techniques.

Background

Cage aminals of the adamanzane type are tricyclic tertiary tetraamines, which can act as bases or as nucleophiles. The main subject of research in our laboratory (Universidad Nacional, Bogotá) is the reactivity of these polyamine bases toward nucleophiles and electrophiles. In recent years, we became interested in the cage aminal 1,3,6,8-tetraazatricyclo[4.3.1.1^3,8]undecane (TATU, 1) because of its interesting molecular structure, which contains two pairs of non-equivalent nitrogen atoms [1-6]. To the best of our knowledge, only two available studies in the literature have investigated reactions of 1 with electrophilic reagents [4,5], but its nucleophilicity has not been investigated. To gain further insight into the nucleophilic properties of this aminal, which has four active nucleophilic centers and, consequently, offers a series of alternative possibilities for alkylation, we reacted 1 with several primary alkyl halides using the Menschutkin reaction, i.e., N-alkylation of tertiary amines with haloalkyls [7]. We found that no reaction occurred when N-alkylation was attempted using alkyl bromides and chlorides. Compound 1 reacts with alkyl iodides in dry acetonitrile at room temperature to produce mono N-alkyl ammonium quaternary salts (3a-f) (Scheme 1) with a yield of approximately 80-90%. Attempts to quaternize more than one nitrogen atom failed, even in the presence of excess alkylating agent, and only one of the four possible quaternary ammonium derivatives was obtained. We attribute this behavior to the stereoelectronic factors that govern the N-C-N (aminal) group. As prior studies have demonstrated [8], the activity of amines in quaternization with alkyl halides primarily depends on the spatial structure and induction effects of substituents at the nitrogen atom. Other interactions, such as the anomeric effect, have been observed to produce changes in the molecular geometry of aminals. Molecular orbital studies at the ab initio level implicate (n N ®s*C-N) type interactions between a lone pair on N and an antiperiplanar σ* orbital of the adjacent C-N bond as being responsible for the anomeric effect [9]. In fact, in N-protonated aminals, the existence of a strong anomeric effect has been...
clearly established [10,11]. Our results suggest that the anomeric effect evidenced by the shortening and lengthening of N-C-N bond lengths and reduces the N-pyramidalities, thereby making the nitrogen less nucleophilic [12]. In summary, these quaternary ammonium salts provide new evidence characterizing anomeric effects in amines that possess one nitrogen atom with a full positive charge. These results demonstrated that the nucleophilicity of the specific nitrogen atoms varies and increases with higher sp³ character. Compounds (3a-f) were characterized with ESI-MS, FT-IR, and ¹H and ¹³C NMR spectral studies. Unequivocal assignments of methylene hydrogens were achieved by ¹H-¹H COSY experiments. The structure of compound 3b was confirmed by a structural study using X-ray crystallography.

Quaternary ammonium salts have multiple uses in industry, in laboratories and in the household. These compounds act as disinfectants, antiseptic agents, surfactants, fabric softeners, corrosion inhibitors, emulsifiers and anti-static agents (e.g., in shampoos). In organic syntheses, these compounds are used as phase transfer catalysts for a wide range of organic reactions involving immiscible solvent systems [13]. In recent years, interest in ammonium salts has concerned their utilization in templating organic molecules in the synthesis of zeolites, e.g., in photoreactions of chirally modified zeolites [14], in the synthesis and mechanism of decomposition study of triazenes [15], in the obtention of ionomers with photoluminescent properties [16] and for obtaining new Rh and Ag complex [17], and the use of these ammonium salts as ionic liquids and energetic molecular compounds [18]. These quaternary ammonium salts can react with alkyl halides, leading to the formation of new ammonium salts, which are promising candidates for new zeolite templates and energetic molecular compounds.

**Results and Discussion**

Reaction of 1 with alkyl iodides 2a-f produced 3a-f in good to excellent yields using the standard protocols for the alkylation of amines. The reaction products were separated by precipitation from dry acetonitrile solution. In the FT-IR spectra of 3a-f (in KBr), alkyl chains showed absorption bands at 2960-2830 cm⁻¹ for asymmetric and symmetric stretching vibrations. Absorption bands at 1148-1136 cm⁻¹, which were related to symmetric C-N stretching vibrations, were observed. The signals at the masses of 169.1449, 183.1587, 197.1730, 211.1923, 225.2120, 239.2291, and 253.2441 in the ESI-MS spectra in the positive ion mode were assigned to the respective charged quaternary ammonium ions of compounds 3a-f. The fragmentation patterns of these spectra were found to be similar to one another.

A close inspection of the ¹H NMR spectral patterns for the aminalic protons of 3a-f suggests that a mono-N-alkyl ammonium salt was obtained. The quaternary ammonium group reduced the symmetry of 3a-f relative to 1, making them readily differentiated from 1 by ¹H NMR. The positive charge on one of the nitrogen atoms is evident in the ¹H NMR spectra of 3a-f, which exhibit signals that are shifted downfield with more complex splitting patterns. The largest effect was observed for the Ha proton, which appears at approximately 4.83 ppm, while the corresponding signal in the ¹H NMR spectrum of compound 1 resonates at 3.62 ppm [3].

The characteristic signals of aminal cage structure in the ¹H NMR spectra of 3a-f are grouped into four AB spin systems belonging to the four methylene bridgehead protons (H₂a, H₂b, H₂c and H₂d) and single hydrogens at 3.43 (NCH₂CH₂N) and 4.82 ppm (NCH₂N), which can be observed in the low field region of the spectra. The homonuclear coupling constant value indicated that doublets form AB pairs. However, the 1D spectrum was not sufficient for a complete assignment. Figure 1 shows the ¹H NMR of 3b as an example.

Because there is long-range coupling between hydrogen atoms that are in the W conformation, the ¹H NMR spectrum alone was not definitive in assigning all protons. ¹H-¹H COSY experiments allowed the assignment of the signals of all of the W-positioned hydrogen atoms. For instance, in the ¹H-¹H-COSY spectrum (Figure 2), one cross peak involved the W-coupling between H₄ hydogen of methylene groups 7 and 10, and the H₄ hydrogens of methylene groups 2 and 11 appears between the doublets at 4.00 ppm and 4.83 ppm. Therefore, the signals at 4.64 and 4.83 ppm can be unequivocally assigned to H₄ and H₄ protons, respectively.

The structures of 3a-f were determined from the correlations found in the ¹H-¹H COSY, HMQC and HMBC contour plots. The number of signals observed indicates that C₂ᵥ symmetry is not maintained in the cage structure. Instead, the polycyclic structure adopts a C₄ᵥ symmetry. This conformation cannot explain the NMR results because the ethylene bridge of 3a-f is virtually
symmetrical; however, a single resonance at 3.43 ppm is observed, and the doublet or triplet expected for the ethylene bridge protons is collapsed to a single line. The equivalence of these protons can be explained in two different ways, either by rapid interconverting conformers of the 1,3,5-triazepane ring, which can adopt two conformations (Figure 3) on the NMR time scale, or by the virtual chemical equivalence of these protons. In the case of the aminal cage structure, some conformational freedom for small rotations of the ethylene bridge [19]. To test this hypothesis, we conducted single-point energy calculations of the $S_4$ and $D_{2d}$ ethylene residue conformations of $1$ using a Gaussian software package [20] at the Hartree-Fock level with a 6-31G* basis set, but our results revealed that the $S_4$ conformation is 64.0 kcal/mol higher in energy than is the $D_{2d}$ conformation.

The higher-energy conformer could be avoided at room temperature, and the equivalence could be caused by close shifts of the signals of the NCH$_2$CH$_2$N fragment. Using X-ray crystallography, structural investigation of aminal cage structures indicated an almost planar ethylene bridge with a $D_{2d}$ conformation and large distortions of the N-C-N and the C-N-C bond angles [19,21]. We expected that the incorporation of these alkyl substituents would not affect the structure of the aminal cage. Several attempts were made to recrystallize the products from a warm saturated water solution, but only single crystals of compound 3b could be grown (Table 1).

The molecular structure and atom-numbering scheme are shown in Figure 4. The asymmetric unit consists of one quaternary ammonium cation and three iodide anions. The iodide atoms are located in specific positions such that the sum formula contains one iodide and one quaternary ammonium cation. The atom numbering diagram shows that the cation adopts a $D_{2d}$ conformation with a torsion angle in the ethylene bridge fragment of $-4.2(3)^\circ$. Within the aminal cage structure, the bond distances are comparable to the bond distances in the 1,3,6,8-tetraazatricyclo[4.3.1.1$^{3,8}$]undecan-1-ium cation 1 [6]. C-N bond distances provide structural evidence for a strong anomeric effect, due to the presence of the quaternary nitrogen atom, which distorts the aminal cage. The C-N bond lengths involving the quaternary N3 atom are significantly longer than the other C-N bond lengths. The anomeric effect is also responsible for the distortion of the C-N1-C bond angles with respect to the neutral aminal cage structure [2]. The charge of the N3 atom leads to an increase in the bond order of the N1-C4 bond and makes the C4-N1-C2 and C4-N1-C1 angles greater than the comparable angles in the uncharged aminal cage by $2^\circ$. Also, the presence of this positive charge has a strong and direct influence on the reactivity of the aminal cage. In fact, our preliminary analysis of the chemical reactivity of 3a-f with phenols showed that the rate of reaction is greater than that of TATU. Furthermore, the Fukui

![Figure 1](http://journal.chemistrycentral.com/content/5/1/55)
index was used to localize possible sites in which chemical reactivity is enhanced. The Fukui index for 3b suggests that the most reactive site for nucleophilic attack in the cation is C-4 (Table 2).

Thus, the formation of the carbon-nitrogen bond increases the reactivity compared with TATU. The Fukui index results (Table 2) are consistent with the electron density isosurface (with an isovalue of 0.02) for 3b (Figure 5) where an attractive interaction results in negative potential energy (colored in dark blue).

The X-ray diffraction experiments showed that the ethyl group adopts a preferential orientation with respect to the ethylene bridge. Theoretical calculations were performed for this compound in order to estimate the more stable geometries that were possible. The equilibrium geometries of the low-energy conformers of 3b were fully optimized at the HF level of theory with the 6-31G(d) basis set. In both conformers, the ethyl group is coplanar with the mean plane of the aminal cage. However, the rotational energy barrier is only 28.21 kJ/mol, suggesting a ‘rapid rotation’ of the ethyl group around the N3-C8 bond. The organization of the crystal packing for the title compound exhibits a network interconnecting through C-H...I (3.137 Å) short contact (Figure 6) with a distance shorter than the sum of the Van der Waals radii of I and H (rI = 2.20 Å).
The structure solution was complicated by twinning and by the presence of heavy atoms, namely iodine atoms, which made it difficult to recognize the organic molecule and disentangle the twinning. In the diffraction pattern, every third layer contains strong reflections, while the intervening layers are much weaker. This phenomenon is observed because the iodine atoms occupy positions that make a 9-fold smaller subcell, and the true cell is created only by the organic moieties. The crystal used for the structure solution was an especially well-ordered one in which the superstructure reflections are sharp and can be integrated. The structure has a layered structure along c with layers of organic molecules separated by layers of iodine with hexagonal symmetry. The organic molecules are aligned one on the top of one another, and, between them, there are nearly empty channels that are filled by the ethyl groups of the molecules. It is not surprising that, under non-equilibrium crystallization conditions, the layers tend to stack in a disordered fashion, and, sometimes, the next layer is stacked such that its molecules lie above the channels in the bottom layer. If such a stacking fault occurs frequently, we obtain a completely disordered crystal with, on average, nine times a smaller unit cell. For less frequently occurring stacking faults, the crystal can be better modeled as a twin. This property is observed in the case of the current structure. The twinning law is a mirror plane perpendicular to a (or, equivalently, b).

Conclusions

It was noted that alkyl chain length did not significantly affect the reaction because all employed alkyl iodide electrophiles reacted in a similar fashion with the aminal 1 to produce the corresponding mono N-quaternary ammonium salts, which were characterized by spectroscopic and analytical techniques. Furthermore, 1 only reacts with alkyl iodides, and the quaternization occurs regioselectively on the nitrogen with major sp³ character, which prevents its further alkylation even in a large excess of electrophile. The elucidation of the structure of compound 3b, both in the solid state and in solution, has revealed that nN-σ*CH₂-N₃R⁺ orbital overlap confirms that an anomic effect is present in the ammonium salt. This straightforward, one-step process provides a convenient preparative method for mono-N-alkylated quaternary ammonium salts and could be of interest to investigate the kinetic and thermodynamic properties of the Menschutkin reaction.

Experimental

General and Instrumentation

NMR spectra were performed in D₂O on a Bruker Avance 400 operating at 400.13 MHz (¹H) and 100.4 MHz (¹³C) at room temperature; chemical shifts were referenced to deuterium (¹H) and to external CDCl₃ (¹³C). Infrared spectra were recorded as KBr discs on a Perkin-Elmer Paragon FT-IR instrument in the range of 4000-600 cm⁻¹. MS-ESI mass spectra were obtained with a Micromass Technologies-LCT Premier XE Waters; melting points were taken in capillaries on an Electrothermal 9100 melting point apparatus and are presented without correction.

Compound 1 was synthesized according to a previously reported procedure [1]. Solvents and reagents were distilled before use. Crystals suitable for single-crystal X-ray determination were produced by keeping a solution of 3b in water for several days at room temperature.

General procedure for the synthesis of compounds 3a-f

To a solution of 1 (0.154 g, 1.0 mmol) in dry acetonitrile (5 mL) was added an equivalent amount (1.0 mmol) of the respective alkyl iodide (2a-f). The reaction mixture was stirred at room temperature for 5 h until a precipitate was observed. The resultant precipitate was filtered under vacuum, washed successively with chloroform and dried in vacuo (Scheme 1).

1-methyl-1,3,6,8-tetraazatricyclo[4.3.1.1³,8]undecan-1-i um iodide (3a)

Was isolated as a white solid highly hygroscopic, (0.216 g, 73%). M.p. = 117-118.3°C (decomposition), FT-IR (KBr)
1-ethyl-1,3,6,8-tetraazatricyclo[4.3.1.13,8]undecan-1-ium iodide (3b)

Was isolated as a white solid hygroscopic, (0.287 g, 87%), M.p. = 120-121.0°C (decomposition), FT-IR (KBr) \( v_{\text{max}} \): 2994, 2974, 2946, 1473, 1454, 1405, 1387, 1347, 1321, 1296, 1256, 1235, 1158, 1128, 1114, 1044, 1022, 993, 979, 965, 925, 881, 843, 813, 771, 737, 694, 656, 582, 529, 497, 471, 455, 423 cm\(^{-1}\). \(^1\)H NMR (400 MHz, D\(_2\)O) \( \delta \) (ppm): 2.64 (s, 3H, H-12), 3.42 (s, 4H, H-4 and H-5), 3.97 (\( d, J = 16.0 \) Hz, 2H, H-7a and H-10a), 4.57 (\( d, J = 12.0 \) Hz, 2H, H-2c and H-11c), 4.56 (\( d, J = 12.0 \) Hz, 2H, H-7b and H-10b), 4.81 (s, 2H, H-9), 4.82 (\( d, J = 12.0 \) Hz, 2H, H-2d and H-11d), \(^{13}\)C NMR (100 MHz, D\(_2\)O) \( \delta \) (ppm): 41.9 (C-12), 55.3 (C-4 and C-5), 69.1 (C-7 and C-10), 79.0 (C-9), 80.5 (C-2 and C-11). MS (ESI\(^+\)) \( m/z \): 169.1449 [C\(_7\)H\(_{14}\)N\(_4^+\)CH\(_3\)].

1-propyl-1,3,6,8-tetraazatricyclo[4.3.1.13,8]undecan-1-ium iodide (3c)

Was isolated as a white solid hygroscopic, (0.292 g, 90%), M.p. = 123.2-124°C (decomposition), FT-IR (KBr) \( v_{\text{max}} \): 2957, 2935, 1459, 1402, 1389, 1345, 1324, 1260, 1226, 1161, 1112, 1049, 1033, 1009, 969, 948, 877, 814, 746, 655, 449, 423 cm\(^{-1}\). \(^1\)H NMR (400 MHz, D\(_2\)O) \( \delta \) (ppm): 0.98 (\( t, J = 4.0 \) Hz, 3H, H-14), 1.74 (\( m, J = 4.0 \) Hz, 2H, H-13), 2.91 (\( m, J = 4.0 \) Hz, 2H, H-12), 3.43 (s, 4H, H-4 and H-5), 4.00 (\( d, J = 16.0 \) Hz, 2H, H-7a and H-10a), 4.56 (\( d, J = 16.0 \) Hz, 2H, H-7b and H-10b), 4.64 (\( d, J = 12.0 \) Hz, 2H, H-2c and H-11c), 4.83 (s, 2H, H-9), 4.84 (\( d, J = 12.0 \) Hz, 2H, H-2d and H-11d). \(^{13}\)C NMR (100 MHz, D\(_2\)O) \( \delta \) (ppm): 10.6 (C-14), 14.0 (C-13), 55.3 (C-4 and C-5), 58.0 (C-12), 69.6 (C-7 and C-10), 78.2 (C-9), 78.7 (C-2 and C-11). MS (ESI\(^+\)) \( m/z \): 183.1587 [C\(_7\)H\(_{14}\)N\(_4^+\)C\(_2\)H\(_3\)].

1-buty1-1,3,6,8-tetraazatricyclo[4.3.1.13,8]undecan-1-ium iodide (3d)

Was isolated as a white solid hygroscopic, (0.287 g, 85%), M.p. = 127.2-128.1°C (decomposition), FT-IR (KBr) \( v_{\text{max}} \): 2964, 2931, 2871, 1462, 1403, 1359, 1338, 1312, 1261, 1222, 1160, 1143, 1112, 1049, 1029, 1006, 973, 938, 886, 856, 814, 780, 736, 653, 528, 453 cm\(^{-1}\). \(^1\)H NMR (400 MHz, D\(_2\)O) \( \delta \) (ppm): 0.93 (\( t, J = 8.0 \) Hz, 3H, H-15), 1.34 (\( m, J = 8.0 \) Hz, 2H, H-14), 1.67 (\( m, J = 8.0 \) Hz, 2H, H-13), 2.92 (\( m, J = 8.0 \) Hz, 2H, H-12), 3.40 (s, 4H, H-4 and H-5), 3.96 (\( d, J = 12.0 \) Hz, 2H, H-7a and H-10a), 4.52 (\( d, J = 12.0 \) Hz, 2H, H-7b and H-10b), 4.61 (\( d, J = 12.0 \) Hz, 2H, H-2c and H-11c), 4.83 (s, 2H, H-9), 4.85 (\( d, J = 12.0 \) Hz, 2H, H-2d and H-11d). \(^{13}\)C NMR (100 MHz, D\(_2\)O) \( \delta \) (ppm): 12.9 (C-15), 19.8 (C-14), 22.1 (C-13), 55.3 (C-4 and C-5), 56.3 (C-12), 69.6 (C-7 and C-10), 78.2 (C-9), 78.6 (C-2 and C-11). MS (ESI\(^+\)) \( m/z \): 211.1923 [C\(_7\)H\(_{14}\)N\(_4^+\)C\(_4\)H\(_9\)].

Single crystal X-ray measurements

Crystal data for compound 3b, C\(_7\)H\(_{14}\)N\(_4\)I, were collected using a Xcalibur Atlas Gemini ultra diffractometer of
Oxford Diffraction equipped with Mo tube with graphite monochromator, Mo-Enhanced fiber-optics collector and CCD detector Atlas. M = 310.2, trigonal, R3, a = 12.8935(3), b = 12.8935(3), c = 18.4328(4) Å, V = 2653.8 (1) Å³, Z = 9, Dcalc = 1.746 g/cm³, X-ray source Mo Kα radiation, k = 0.7107 Å, F(0 0 0) = 1386, colorless prism

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Preparation of

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The authors declare that they have no competing interests.

Competing interests

JS-B and JR-M synthesized the title compounds under the guidance of AR.

Authors’ contributions

JS-B and JR-M synthesized the title compounds under the guidance of AR. LP collected the X-ray data and solved the crystal structures under the guidance of MD. All the authors read and approved the final manuscript.

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