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# Hydrogen bonding Part 59. NMR study of N,N,N-trimethyl-1-adamantylammonium, trimethyl-*i*-pentylammonium, and tetra-*i*-pentylammonium ions; an explanation for the anomalous hydration behavior of N,N,Ntrimethyl-1-adamantylammonium ion salts

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#### Abstract

The halide and hydroxide salts of the N,N,N-trimethyl-1-adamantylammonium ion have hydration behaviors which are different from the common patterns shown by all other quaternary ammonium ion halide and hydroxide salts we have studied. These differences include formation of higher iodide and bromide hydrates, failure to form halide monohydrates, and the existence of unusual molecular ions with three-center covalent hydrogen bonding in the lower fluoride and hydroxide hydrates. The <sup>1</sup>H NMR spectrum of N,N,N-trimethyl-1-adamantylammonium ion is not consistent with that expected from application of conventional chemical shift rules. Comparison with the model compounds trimethyl-*i*pentylammonium and tetra-*i*-pentylammonium ions, which have similar C–H arrangements but lack the tricyclic cage, demonstrate that through-cage interactions spread positive charge over the whole structure of the N,N,N-trimethyl-1adamantylammonium ion. The diffusely charged nature of the ion is correlated with the observed anomalous hydration behavior of its salts.

## 1. Introduction

Over the last two decades, we have studied the hydrates of the halides, and in most cases the hydroxides, of 12 quaternary ammonium ions; these include mono- and dications of tetra-*n*alkylammonium and bicyclic ammonium ions, as well as choline and acetylcholine. In all, close to 100 hydrates have been examined. While there are differences in hydration behavior, in general, all of these hydrates can be arranged in a logical pattern where trends in behavior are accounted for by factors of cation size and charge, cation symmetry, and anion electronegativity [1]. The hydration behavior of salts of the N, N, N-trimethyll-adamantylammonium ion (TMAA<sup>+</sup>) do not fit into the pattern shown by the other quaternary ammonium ion salts; salts of this ion have completely unique ways of interacting with H<sub>2</sub>O, for example:

(1) all other iodides form iodide ion monohydrates but no higher hydrates; TMAAI forms

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only a clathrate hydrate with 12  $H_2O$  molecules and no monohydrate [2].

(2) all other bromides but one form bromide ion monohydrates (one forms only a hemihydrate) but no higher hydrates; TMAABr forms only a trihydrate and no monohydrate [2].

(3) all other chlorides but one form chloride ion monohydrates (one forms only a hemihydrate) and several form higher hydrates; TMAACl forms only a pentahydrate and no monohydrate [2].

(4) all other fluorides form fluoride ion monohydrates with planar  $(H_2O \cdot F^-)_2$  clusters and all but one form higher hydrates; TMAAF forms a trihydrate and a hemihydrate, but no monohydrate [3].

All other hydroxides that form hydroxide ion monohydrates have planar  $(H_2O \cdot OH^-)_2$  clusters, and cannot be further dehydrated; TMAAOH forms a monohydrate which is not a planar cluster and a hemihydrate [4].

In all other quaternary ammonium ion hydrates, H<sub>2</sub>O, while sometimes very tightly bound, is still H<sub>2</sub>O with characteristic IR absorptions; in TMAAF  $\cdot 0.5H_2O$  and TMAAOH  $\cdot H_2O$ , and TMAAOH  $\cdot 0.5H_2O$  the H<sub>2</sub>O has lost its identity in forming covalently bonded FHOHF<sup>2-</sup> and HOHOH<sup>-</sup> molecular ions [3, 4].

The <sup>1</sup>H NMR pattern of chemical shifts for  $TMAA^+$  is not that which would be predicted by applying standard textbook values, and it has appeared possible that the apparent spectral anomalies could be accounted for by dispersion of positive charge by orbital interaction within the tricyclic cage. Trimethyl-i-pentylammonium (TMIPA<sup>+</sup>) and tetra-*i*-pentylammonium ions  $(TIPA^+)$  are analogs of the TMAA<sup>+</sup> structure which lack the tricyclic cage. We have prepared these two ions and compared their NMR spectra with that of  $TMAA^+$  to determine if there are special effects associated with the cage compound, and to see if an explanation of these effects could account for the unusual hydration behavior of TMAA<sup>+</sup> salts.

# 2. Experimental

NMR spectra were recorded on a Varian T-60

instrument in  $D_2O$  solvent with TMS as external reference. TCI (Tokyo) *i*-pentylammonium bromide and iodide and tri-*i*-pentylamine, and trimethylamine Aldrich (Milwaukee, WI) were used as supplied.

Tri-*i*-pentylamine and a 50% mol excess of *i*-pentylammonium bromide were dissolved in ethanol. Since reaction appeared slow at 25°C (solution stayed basic) the mixture was refluxed for 5 days. Evaporation of solvent and unreacted reagents in vacuo left an oil. This was covered with ether and stored for 2 days at  $-20^{\circ}$ C. This afforded tetra-*i*-pentyl ammonium bromide as white crystals. The yield was not determined, but was quite low. *i*-Pentylammonium iodide was dissolved in ether and the solution saturated with trimethylamine. White crystals of trimethyl-*i*-pentylammonium iodide precipitated slowly over a period of several days. Again the yield was not determined, but appeared to be essentially quantitative.

#### 3. Results and discussion

## 3.1. Choice of compounds

The most noteworthy feature of the NMR spectrum of TMAA<sup>+</sup> is that the  $\gamma$ -hydrogens of the cage are further downfield (more deshielded) than the  $\beta$ -hydrogens, whereas simple chemical shift predictions for alkyl compounds would suggest that they should absorb at approximately the same  $\delta$  value. Similar deshielding was observed for the  $\gamma$ -hydrogens of the 1-adamantyl cation, and has been ascribed to intracage orbital interaction between  $\gamma$ -C-H bonds and the cationic site [5, 6]. The situation in the TMAA<sup>+</sup> ions is different, as there is a  $(CH_3)_3N^+$  group attached to an sp<sup>3</sup> carbon at the 1-position, rather than an  $sp^2$  carbon with an empty orbital. It was not clear if what was observed in the spectrum of TMAA<sup>+</sup> was a unique feature of the cage or perhaps a general effect in quaternary ammonium ions. To examine this, we wanted an analogous compound which lacked the cage structure.

The structure of the TMAA<sup>+</sup> cation is shown in Fig. 1. If the 1-position designated  $\alpha$  (to the  $(CH_3)_3N^+$  group), there are then three  $\beta$ -CH<sub>2</sub>



Fig. 1. Structure of the N, N, N-trimethyl-1-adamantyl-ammonium ion.

groups, three  $\gamma$ -CHs, and three  $\delta$ -CH<sub>2</sub>s. Since chemical shift effects on methylene and methyne hydrogens might differ, we desired model compounds which would have both  $\beta$ -CH<sub>2</sub> and  $\gamma$ -CH hydrogens, *i*-pentylammonium ions satisfy this condition.

Fig. 2 shows the relationship between the hydrogens of TMAA<sup>+</sup> and those of TMIPA<sup>+</sup> and TIPA<sup>+</sup> ions. Both TMAA<sup>+</sup> and TMIPA<sup>+</sup> have  $(CH_3)_3N^+$ groups; we have designated these hydrogens  $\alpha'$ . TMIPA<sup>+</sup> and TIPA<sup>+</sup> have  $\alpha$ -CH<sub>2</sub> groups; due to the cage structure, there are no analogous hydrogens of TMAA<sup>+</sup>. The  $\beta$  and  $\gamma$  hydrogens — those of greatest interest — of all three ions, have a similar bonding environment. The *i*-pentyl substituted ions have CH<sub>3</sub> groups in the  $\delta$  position, rather than the CH<sub>2</sub> groups of TMAA<sup>+</sup>; however, further extension of the chain to put CH<sub>2</sub> groups in the  $\delta$ positions would lead to unnecessarily complex molecules. It is possible to take the difference in the  $\delta$  groups into account (see section 3.2.).



Fig. 2. Comparison of the hydrogen patterns of (A) N,N,N-trimethyl-1-adamantylammonium ion and (B) trimethyl-*i*-pentylammonium ion. The pattern of the tetra-*i*-pentyl-ammonium ion resembles (B), except that three *i*-pentyl groups replace the  $\alpha'$ -methyl groups.



Fig. 3. <sup>1</sup>H NMR spectra at 60 MHz (250 Hz sweep width) of (A) N,N,N-trimethyl-1-adamantylammonium ion, (B) trimethyl-*i*-pentylammonium ion and (C) tetra-*i*-pentylammonium ion. See Table 1 for assignment of absorptions.

#### 3.2. NMR spectral comparisons

The <sup>1</sup>H NMR spectra of the three ions are shown in Fig. 3. Due to the rigid cage of TMAA<sup>+</sup>, all hydrogens are in fixed conformational relationship to each other. The  $\beta$ -H atoms have a  $\gamma$ -H atom gauche to each of them, the  $\gamma$ -H atoms have two  $\beta$ -H atoms gauche, one  $\delta$ -H atom gauche, and one  $\delta$ -H atom trans to them, while one  $\delta$ -H is gauche to two  $\gamma$ -Hs and the other is trans to two  $\gamma$ -Hs. This results in small coupling constants and complex patterns that cannot be resolved at 60 MHz; thus all three types of hydrogens give unresolved multiplets (Fig. 3(A)).

Minimized structures of  $TMIPA^+$  and  $TIPA^+$ are shown in Fig. 4. The structure chosen for



Fig. 4. Structures of trimethyl-*i*-pentylammonium ion (left) and tetra-*i*-pentylammonium ion (right).

TIPA<sup>+</sup> is similar to the cross-like  $D_{2d}$  structure shown by tetraethyl- and tetrapropylammonium ions in crystal structures [7, 8]. Examination of these structures shows that free rotation of the  $\alpha$ and  $\beta$  carbons is highly unlikely, and rotation of the  $\gamma$  carbons questionable. Thus restriction of conformational averaging again leads to poorly resolved multiplets for the  $\alpha$ -H and  $\beta$ -H of TMIPA<sup>+</sup> (Fig. 3(B)) and TIPA<sup>+</sup> (Fig. 3(C)). In both ions, the  $\gamma$ -H, which would be split into a nonet in a conformationally equilibrating chain, absorbs at essentially the same point as the  $\beta$ -H; the presence of the combined absorptions is demonstrated by integration. Only the  $\delta$ -CH<sub>3</sub> groups of these two ions appear to be freely rotating and thus show the expected doublet pattern.

Chemical shift values for the three ions are shown in Table 1. For each signal the center point of the area of absorption is listed. The absorptions of the methyl groups of TMIPA<sup>+</sup> and TIPA<sup>+</sup> have also been corrected to methylene values (shown in parentheses) by addition of 0.50 ppm, a reasonable estimate of the chemical shift between otherwise similar CH<sub>3</sub> and CH<sub>2</sub> groups.

#### 3.3. Chemical shifts

In addition to chemical shifts, Table 1 lists  $\Delta\delta$  values, i.e. the amount in ppm that the absorptions of hydrogens of TMIPA<sup>+</sup> and TIPA<sup>+</sup> differ from those of TMAA<sup>+</sup>. The  $\alpha'$ -(CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup> hydrogens of TMAA<sup>+</sup> show an upfield shift of 0.10 ppm relative to those of TMIPA<sup>+</sup>, and of 0.20 ppm relative to the methyl groups of the tetramethylammonium ion, which absorb at 3.23 ppm. All the hydrogens of the cage show downfield shifts from the corresponding hydrogens of the open (non-cage) ions. When compared with TIPA<sup>+</sup>, the corresponding hydrogens of TMAA<sup>+</sup> show downfield shifts of  $\beta$ -H 0.49 ppm,  $\gamma$ -H 0.66 ppm, and  $\delta$ -H 0.24 ppm (corrected to CH<sub>2</sub>).

We conclude that the presence of the tricyclic cage results in lowered positive character for the  $\alpha'$ -(CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup> carbons of TMAA<sup>+</sup>, and increased positive character for all carbons of the cage —

Table 1

NMR chemical shifts in  $D_2O^{a,b}$  of hydrogens of the TMAA<sup>+</sup> ion relative to the corresponding hydrogens of the TMIPA<sup>+</sup> and TIPA<sup>+</sup> ions

Hydrogens <sup>c</sup>	TMAA <sup>+</sup>	TMIPA <sup>+</sup>	$\Delta \delta^{\mathbf{d}}$	TIPA <sup>+</sup>	$\Delta \delta^{\mathbf{d}}$
$\alpha'$	3.03 s (9H)	3.13 s (9H)	-0.10	e	
α	e	3.30 m (2H)	-	3.28 m (8H)	
β	2.21 m (6H)	1.83 m (2H) <sup>f</sup>	0.38	1.72 m (8H) <sup>g</sup>	0.49
$\gamma$	2.38 m (3H)	$1.83 \text{ m} (1 \text{H})^{\text{f}}$	0.55	1.72 m (4H) <sup>g</sup>	0.66
δ	1.86 m (6H)	1.18 d (6H)	0.68 (0.18) <sup>h</sup>	1.12 d (24H)	0.74 (0.24) <sup>h</sup>

<sup>a</sup> Chemical shifts are in  $\delta$  (ppm) relative to TMS as external reference.

<sup>b</sup> symbols used: s, singlet; d, doublet; m, multiplet.

<sup>c</sup> See Fig. 2.

<sup>d</sup> (Chemical shift of  $TMAA^+$ ) – (chemical shift of ion).

<sup>e</sup> None present.

<sup>f</sup>Cannot distinguish between  $\beta$  and  $\gamma$  protons; total area of multiplet is 3 H.

<sup>g</sup> Cannot distinguish between  $\beta$  and  $\gamma$  protons; total area of multiplet is 12 H.

<sup>h</sup> Value in parentheses is calculated value if -CH<sub>3</sub> were -CH<sub>2</sub>-, by a 0.50 ppm downfield shift.

with the greatest effect seen at the  $\gamma$ -position than would be found for a normal tetraalkylammonium ion. The result is that TMAA<sup>+</sup>, rather than having a point charge on the N atom surrounded by alkyl material, is actually a diffusely charged species, with positive character distributed to some extent to all carbons of the cage.

# 3.4. The anomalous hydration behavior of $TMAA^+$

Consideration of the diffusely charged nature of the TMAA<sup>+</sup> cation can assist in explaining some of the anomalous hydration behavior of TMAA<sup>+</sup> which was outlined in the Introduction.

Dispersion of charge throughout the cage of TMAA<sup>+</sup> would help to stabilize a shell of  $H_2O$  molecules about the ion, and thus could account for the unexpected formation of the 12  $H_2O$  crystalline clathrate seen with TMAAI [2]. This presumably also accounts for the fact that only TMAA<sup>+</sup>, of all quaternary ammonium ions we have studied, stabilizes a bromide hydrate above the monohydrate level [2].

The TMAA<sup>+</sup> cation is protected from decomposition by Hofmann elimination from attack of base on  $\beta$ -H by the gauche relationship of  $\beta$ -H to the  $(CH_3)_3N^+$  group and by the bridgehead position of the  $(CH_3)_3 N^+$  group. This is also true of ions such as N, N'-dimethyltriethylenediammonium and N-methylquinuclidinium; however these ions decompose by  $S_N 2$  attack by base on  $CH_3N^+$  methyl when an attempt is made to dehydrate hydroxides or fluorides below the monohydrate level [9, 10]. It is possible that the lowered positive nature of the  $(CH_3)_3N^+$  methyl groups in TMAA<sup>+</sup> by siphoning of charge into the cage lowers the susceptibility to S<sub>N</sub>2 attack, and allows the formation of fluoride and hydroxide hemihydrates, which cannot be prepared with any other quaternary ammonium ions we have studied.

Similarly, diffusion of charge throughout the cage may lower the propensity of the  $(CH_3)_3N^+$  group to form hydrogen bonds to the anion (recently confirmed for tetramethylammonium fluoride monohydrate [11]). This could result in the hydroxide or fluoride ion being a stronger acceptor of hydrogen bonds from H<sub>2</sub>O, and lead to the formation of the covalently bonded

FHOHF<sup>2-</sup> and HOHOH<sup>-</sup> molecular ions observed in TMAAF  $\cdot$  0.5H<sub>2</sub>O, TMAAOH  $\cdot$  H<sub>2</sub>O, and TMAAOH  $\cdot$  0.5H<sub>2</sub>O.

Perhaps the most puzzling feature of TMAA<sup>+</sup> hydration is the failure to form monohydrates, whether of the Type I cluster or Type II linear variety which are so common with other quaternary ammonium ion salts [1]. The only monohydrate of a TMAA<sup>+</sup> salt that we have observed is TMAAOH $\cdot$ H<sub>2</sub>O. Presumably, formation of the three-center covalent type hydrogen bond in the HOHOH<sup>-</sup> ion believed to be present in this hydrate is energetically favored over normal electrostatic hydrogen bonding in the Type I  $(H_2O \cdot OH^-)_2$  structure found with all other quaternary ammonium hydroxide monohydrates that we have prepared. Similarly, formation of two three-center covalent type hydrogen bonds in FHOHF<sup>2-</sup> lends extraordinary stability to this ion in TMAAF  $\cdot 0.5H_2O$ ; even if an  $(H_2O \cdot F^-)_2$ cluster were to exist transiently, it would be expected to expel H<sub>2</sub>O and go to the much more stable  $FHOHF^{2-}$  ion. Thus the unique formation of molecular clusters with very strong bonds could account for the failure of TMAAOH and TMAAF to form cluster monohydrates.

While quaternary ammonium fluorides and hydroxide monohydrates (with the exception of TMAAOH) always form Type I planar clusters, chloride, bromide, and iodide monohydrates form either Type I clusters or Type II linear hydrogen bonded structures. The type shown by a particular salt monohydrate is a function of cation size, charge density, and symmetry [1]. Equilibrium vapor pressure studies demonstrate that TMAACl fails to form a monohydrate of any kind [2]. There is faint spectroscopic evidence that TMAABr and TMAAI may form linear type structures when H<sub>2</sub>O content is reduced to the monohydrate level by dehydration of  $TMAABr \cdot 3H_2O$  or TMAAI  $\cdot$  12H<sub>2</sub>O, but these "monohydrates" lose all H<sub>2</sub>O during even a rapid IR scan when warmed by the beam, and effloresce immediately on exposure to the air to give anhydrous material.

The large size of the TMAA<sup>+</sup> cation would favor monohydrate cluster formation over an extended linear form of hydrogen bonding [1]. In all quaternary ammonium salt monohydrates containing an  $(H_2O \cdot X^-)_2$  cluster whose structures have been determined by diffraction studies, the cluster lies on an inversion axis in the crystal, and it has been postulated that this feature is necessary for planar cluster formation [12]. Other quaternary ammonium ions that form cluster monohydrates [1] are of relatively high symmetry: tetramethylammonium,  $T_d$ ; tetraethylammonium and tetrapropylammonium,  $D_{2d}$ ; *N*-methyltriethylenediamine cation, *N*-methylquinuclidinium, and *N*-methyltriethylenetetramine cation,  $C_{3v}$ ; *N*, *N'*-dimethyltriethylenediammonium,  $D_{3h}$ ; *N*, *N*, *N'*, *N'*-tetramethylpiperazinium, hexamethonium, and decamethonium,  $C_{2h}$ . The TMAA<sup>+</sup> cation may well be of lower symmetry.

A simple model or drawing of TMAA<sup>+</sup> suggests that the ion would have  $C_{3v}$  symmetry. However, space filling models or molecular modeling demonstrate that either of the possible  $C_{3v}$  conformations, with the methyl groups either staggered or eclipsed with the bridgehead cage bonds, would experience significant unfavorable steric interaction between methyl hydrogens and the  $\beta$ -hydrogens of the cage. The conformation that avoids this interaction, as shown in Fig. 1, has only  $C_3$  symmetry. It is possible that the low symmetry of the TMAA<sup>+</sup> cation prevents crystal formation with the inversion axis sites required for Type I cluster formation.

It is interesting to note that if the TMAA<sup>+</sup> ion is indeed locked into a  $C_3$  conformation, this conformation is chiral, and salts of this ion could be racemic mixtures. When expanded NMR facilities are installed shortly we will investigate the conformational properties of this ion in more detail.

If monohydrate clusters are ruled out, a TMAAX monohydrate would need to either assume the extended linear structure, or some previously unobserved localized structure such as a bifurcated halide monohydrate unit or an  $HOH \cdots X^-$  unit with only one hydrogen bond. The extended linear form may well be ruled out by the bulky nature of the cation, and the last two possibilities by unfavorable energy considerations.

#### 4. Conclusion

Comparison of the <sup>1</sup>H NMR chemical shifts of

the TMAA<sup>+</sup> ion with those of TMIPA<sup>+</sup> and TIPA<sup>+</sup> demonstrates that the  $(CH_3)_3N^+$  hydrogens of TMAA<sup>+</sup> are shielded and all of the cage hydrogens are significantly deshielded relative to normal tetraalkylammonium ions which lack the tricyclic cage. This effect, which is particularly strong for hydrogens  $\gamma$  to the  $(CH_3)_3N^+$  group, is ascribed to intracage carbon orbital interaction. The compact, large, and diffusely charged nature of the TMAA<sup>+</sup> ion can account for much of the anomalous hydration of salts of the TMAA<sup>+</sup> ion, which show hydration behavior unlike that of salts of any other quaternary ammonium ion.

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