

Gaseous Supramolecules of Imidazolium Ionic Liquids: “Magic” Numbers and Intrinsic Strengths of Hydrogen Bonds

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Abstract: Electrospray ionization mass spectrometry (ESI-MS) is found to gently and efficiently transfer small to large as well as singly to multiply charged $[X^+]_n[A^-]_m$ supramolecules of imidazolium ion (X^+) ionic liquids to the gas phase, and to reveal “magic numbers” for their most favored assemblies. Tandem mass spectrometric experiments (ESI-MS/MS) were then used to dissociate, via low-energy collision activation, mixed and loosely bonded $[A\cdots X\cdots A']^-$ and $[X\cdots A\cdots X']^+$ gaseous supramolecules, as well as their higher homologues, and to estimate and order via Cooks’ kinetic method (CKM) and B3LYP/6-311G(d,p) calculations the *intrinsic* solvent-free magnitude of hydro-

gen bonds. For the five anions studied, the relative order of intrinsic hydrogen-bond strengths to the 1-*n*-butyl-3-methylimidazolium ion $[X^+]^+$ is: $CF_3CO_2^-$ (zero) > BF_4^- (−3.1) > PF_6^- (−10.0) > $InCl_4^-$ (−16.4) and BPh_4^- (−17.6 kcal mol^{−1}). The relative hydrogen-bond strength for $InCl_4^-$ was measured via CKM whereas those for the other anions were calculated and used as CKM references. A good correlation coefficient ($R=0.998$) between fragment ion ratios and calculated hy-

drogen-bond strengths and an effective temperature (T_{eff}) of 430 K demonstrate the CKM reliability for measuring hydrogen-bond strengths in gaseous ionic liquid supramolecules. Using CKM and T_{eff} of 430 K, the intrinsic hydrogen-bond strengths of BF_4^- for the three cations investigated is: 1-*n*-butyl-3-methyl-imidazolium ion (0) > 1,3-di-[(*R*)-3-methyl-2-butyl]-imidazolium ion (−2.4) > 1,3-di-[(*R*)- α -methylbenzyl]-imidazolium ion (−3.0 kcal mol^{−1}). As evidenced by “magic” numbers, greater stabilities are found for the $[(X^1)_2(BF_4)_3]^-$ and $[(X^1)_5A_4]^+$ supramolecules ($A \neq InCl_4^-$).

Keywords: hydrogen bonds • ionic liquids • kinetic method • mass spectrometry • supramolecular chemistry

Introduction

Room temperature ionic liquids,^[1] in particular those based on the 1-*n*-butyl-3-methylimidazolium ion,^[2] display a very unique combination of physicochemical properties: negligible vapor pressure, low viscosity, high thermal, chemical and

electrochemical stabilities, and distinct solubility in both polar and non-polar solvents. Owing to these outstanding characteristics, ionic liquids have found applications in many areas particularly as a new class of materials and solvents for green chemistry.^[3] As such, ionic liquids have been used as recyclable solvents for organic synthesis, immobilizing agents for organometallic and bio-catalysis, liquid supports for analytical and physical chemistry, as appropriate media for size-controlled growth of nanoparticles,^[4] and as nearly noise-free matrixes for MALDI-MS.^[5]

The unique set of properties of ionic liquids is attributed to a dual behavior resulting from their “quasi-molecular” structures^[6] formed by three-dimensional supramolecular^[7] polymeric networks of anions and cations linked mainly by C-H hydrogen bonds.^[8] In the solid state, supramolecular assemblies of ionic liquids has been evidenced by X-ray diffraction analysis.^[9] In solution, such assemblies has been demonstrated mainly by NMR^[10] and electrochemical studies.^[11] Knowledge of the intimate nature, type and strength of hydrogen-bonding in these supramolecular assemblies is therefore fundamental to understand the very unique prop-

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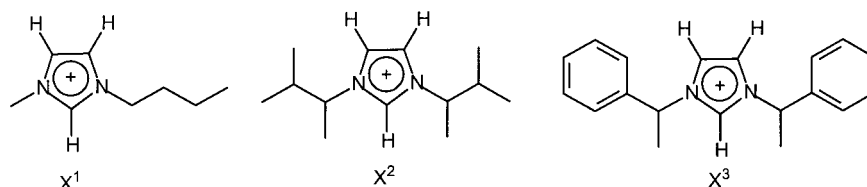
erties of ionic liquids. Attempts have been therefore made using NMR and IR spectroscopy to measure the magnitudes of such CH hydrogen bonds in the condensed phase.^[6,9] In the gas phase, the extremely low vapor pressure of ionic liquids has restricted the advantageous use of mass and tandem mass spectrometry techniques^[12] to form and isolate solvent-free gaseous ionic liquid supramolecules so as to measure their intrinsic physicochemical properties.

Electrospray ionization (ESI)^[13] has, however, revolutionized the way molecules are ionized and transferred to the gas phase for mass spectrometric (MS) analysis, and has greatly expanded the range of MS-compatible molecules including now those of much greater polarity, molecular complexity and higher mass.^[14] ESI is, in fact, an interesting “ion fishing” technique since either negative or positive ions are formed in solution and then transferred by ESI directly to the gas phase. ESI is also characterized by the gentleness by which the gaseous ions are formed, being able to transfer to the gas phase very labile, loosely bonded supramolecules such as, for instance, hydrogen-bonded amino-acid assemblies (the serine octamer and analogues) displaying “magic” numbers and enantioselective assemblies.^[15] ESI-MS is also rapidly becoming the major technique for mechanistic studies^[16] and high-throughput screening of homogenous catalysis,^[17] and to study salt cluster ion formation and properties.^[18] We^[19] therefore used ESI-MS to, for the first time, “fish” loosely bonded supramolecules of ionic liquids and transfer then to a mass spectrometer to investigate their assemblies and to compare and measure via collision-induced dissociation (CID) the *intrinsic* “solvent-free” strengths of their hydrogen bonds.

Experimental Section

ESI mass and tandem mass spectra in both the negative and positive ion modes were acquired using a Micromass (Manchester, UK) QToF instrument of ESI-QqToF configuration with 7.000 mass resolution in the TOF mass analyzer. The following typical operating conditions were used: 3 kV capillary voltage, 40 V cone voltage and desolvation gas temperature of 100 °C. Tandem ESI-MS/MS spectra were collected after 5 eV collision induced dissociation (CID) of mass-selected ions with argon. Mass-selection was performed by Q1 using a unitary *m/z* window, and collisions were performed in the rf-only quadrupole collision cell, followed by mass analysis of product ions by the high-resolution orthogonal-reflectron TOF analyzer. Ionic liquids of three analogous imidazolium ions (see below) with CF_3CO_2^- , BF_4^- , PF_6^- , InCl_4^- and BPh_4^- counteranions were available from previous studies.^[6,20]

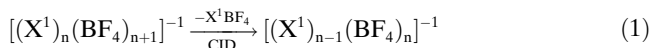
Geometries and electronic energies of fully optimized structures were calculated via Gaussian 98 B3LYP/6-



311+G(d,p) calculations.^[21] These data are available from the authors upon request.

Results and Discussion

Singly charged gaseous supramolecules: Using ESI, a series of singly negatively and positively charged supramolecules of all ionic liquids investigated herein (excepted for InCl_4^- for which higher supramolecules were very minor^[20]), linked via weak CH hydrogen bonds, are found to be efficiently transferred directly from their acetonitrile solutions to the gas phase. Fortunately therefore, loosely hydrogen-bonded polymeric supramolecular networks for ionic liquids are conserved to a great extent during the ESI ion evaporation process.^[13] For X^1BF_4 , for instance, this network is clearly seen in the ESI(−) mass spectrum by the series of singly negatively charged $[(\text{X}^1)_n(\text{BF}_4)_{n+1}]^{-1}$ homologous supramolecules (Figure 1) with $n=0$ up to 12 (using a threshold of 0.1% relative intensity) of *m/z* 313, 540, 766, 991, 1218, 1444, 1670, and so on ($\Delta m/z$ 226 for ^{11}B) with nearly logarithmically decreasing intensities, excepted for that of *m/z* 540 with “magic number” assemblies, see below. The isotopologue anion of *m/z* 86 ($^{10}\text{BF}_4^-$) and the more abundant one of *m/z* 87 ($^{11}\text{BF}_4^-$) for which $n=0$ are also clearly detected. Mass-selection and CID via tandem MS/MS experiments (spectra not shown) reveal that all of the $[(\text{X}^1)_n(\text{BF}_4)_{n+1}]^{-1}$ supramolecules dissociate via a characteristic and predictable fashion: owing to their H-bonded nature, they sequentially loose neutral X_1BF_4 molecules [Eq. (1)].



Similarly, ESI mass spectrum in the positive ion mode shows X^1 of *m/z* 139 and the corresponding series of singly

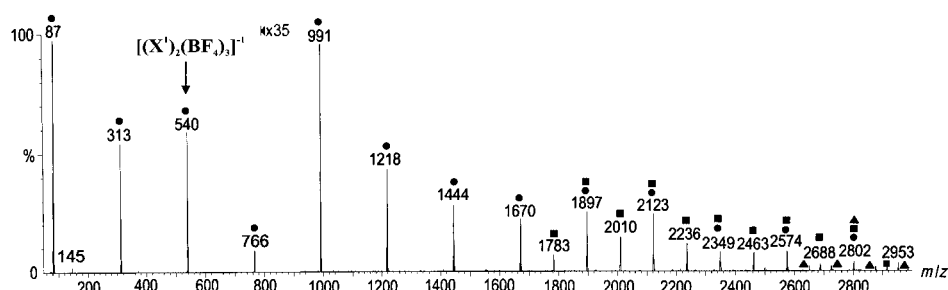


Figure 1. ESI-MS mass spectrum in the negative ion mode of an acetonitrile solution of X^1BF_4 . Note the series of singly negatively charged gaseous $[(\text{X}^1)_n(\text{BF}_4)_{n+1}]^{-1}$ supramolecules of *m/z* 313, 540, 766, 991, etc. ($\Delta m/z$ 226 for ^{11}B). The intensity scale has been increased from *m/z* 900 to show more clearly the series of doubly charged supramolecules $[(\text{X}^1)_n(\text{BF}_4)_{n+2}]^{-2}$ ($n=13-25$) of *m/z* 1783, 1897, 2010, etc. ($\Delta m/z$ 113 for ^{11}B), and the triply charged ones $[(\text{X}^1)_n(\text{BF}_4)_{n+3}]^{-3}$ ($n=34-39$) of *m/z* 2648, 2723, 2799, 2802, etc. ($\Delta m/z$ 75.3 for ^{11}B). The “magic” number supramolecule $[(\text{X}^1)_2(\text{BF}_4)_3]^{-1}$ is indicated. ●: singly, ■: doubly, ▲: triply charged.

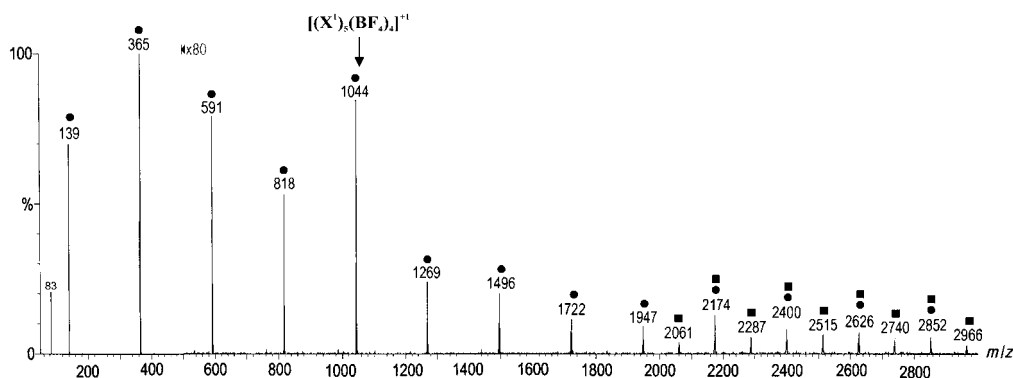


Figure 2. ESI-MS mass spectrum in the positive ion mode of an acetonitrile solution of X^1BF_4 . Note the series of singly positively charged $[(X^1)_{n+1}(BF_4)_n]^+$ supramolecules of m/z 365, 591, 818, 1044, etc. ($\Delta m/z$ 226 for ^{11}B). The intensity scale has been increased from m/z 500 to show more clearly the series of doubly charged species $[(X^1)_{n+2}(BF_4)_n]^{+2}$ ($n=15-26$) of m/z 2061, 2174, 2287, etc. ($\Delta m/z$ 113 for ^{11}B). The “magic” number supramolecule $[(X^1)_5(BF_4)_4]^{+1}$ is indicated. ●: singly, ■: doubly charged.

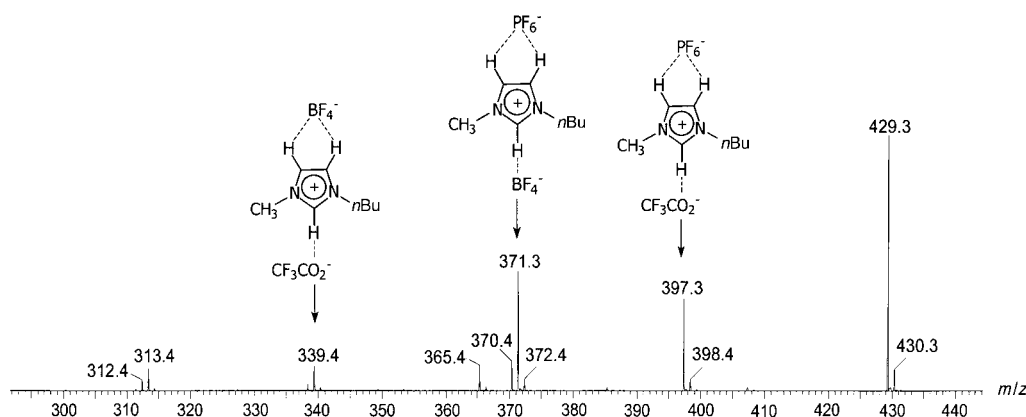


Figure 3. ESI-MS mass spectrum in the negative ion mode of an equimolar mixture of X^1BF_4 , X^1PF_6 , and $X^1CF_3CO_2$. The homogeneous supramolecules are those of m/z 313 $[BF_4 \cdots X^1 \cdots BF_4]^-$, m/z 365 $[CF_3CO_2 \cdots X^1 \cdots CF_3CO_2]^-$, and m/z 429 $[PF_6 \cdots X^1 \cdots PF_6]^-$. The target mixed supramolecules $[A_1 \cdots X^1 \cdots A_2]^-$ of m/z 339, 371, and 397 are indicated. The loosely bonded structures shown are those predicted as the global minimum by B3LYP/6-311G+(d,p) calculations.

positively charged $[(X^1)_{n+1}(BF_4)_n]^{+1}$ supramolecules (Figure 2) of m/z 365, 591, 818, 1044, 1289, 1498, 1722, 1947 and so on ($\Delta m/z$ 226 for ^{11}B) with nearly logarithmically decreasing intensities (excepted for the “magic number” supramolecule of m/z 1044). These homologous supramolecules also dissociate via CID by sequential losses of neutral X^1BF_4 molecules.

Doubly and triply charged gaseous supramolecules: Notably, we learn from the ESI(−) mass spectrum that large enough gaseous $(X^1BF_4)_n$ supramolecules are also able to accommodate two ($n=13$ and mass=2938 u or higher) or even three ($n=34$ and mass=7684 u or higher) additional BF_4^- anions; hence doubly and even triply negatively charged gaseous supramolecules are also unequivocally detected (Figure 1). The series of doubly charged supramolecules $[(X^1)_n(BF_4)_{n+2}]^{-2}$ ($n=13-25$) is composed of those of m/z 1556, 1670, 1783, 1897, and so on ($\Delta m/z$ 113), and that of the triply charged ones $[(X^1)_n(BF_4)_{n+3}]^{-3}$ ($n=34-39$) of those of m/z 2648, 2723, 2802 and so on ($\Delta m/z$ 75.3).

In the ESI(+) mass spectrum (Figure 2), the series of doubly charged species $[(X^1)_{n+2}(BF_4)_n]^{+2}$ ($n=15-26$) of m/z

1835, 1947, 2061, 2174, and so on ($\Delta m/z$ 113) is also clearly detected. Triply positively charged supramolecules of $[(X^1)_{n+3}(BF_4)_n]^{+3}$ composition are, apparently, not intrinsically stable^[22] in the gas phase and are therefore not observed.

“Magic numbers” for assemblies of ionic liquid supramolecules: Interestingly, supramolecules of higher than average stability are evident in the ESI-MS spectra for both the negative and, more generally, in the positive ion series. For the negative ion series (Figure 1), if one considers the normal logarithmically decreasing intensity pattern, the abundance of $[(X^1)_2(BF_4)_3]^{-1}$ of m/z 540 is considerably out of range. No negatively charged “magic number” supramolecules were observed in the ESI(−)-MS spectra of the other ionic liquids.

For the positive ion series, the abundances of the $[(X^1)_5(BF_4)_4]^{+1}$ supramolecule of m/z 1044 is also clearly out of range, which indicates its greater *intrinsic* solvent-free gas-phase stability. Positively charged “magic number” supramolecules of $[(X^1)_5A_4]^{+1}$ composition were also apparent in the ESI(+)-MS spectra of the other ionic liquids except

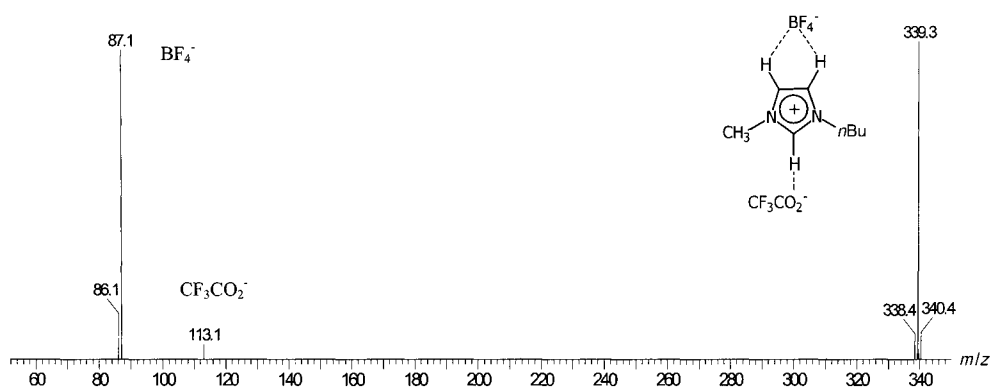
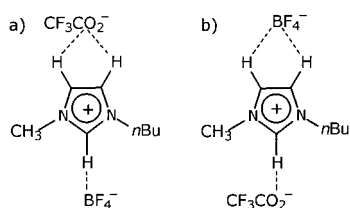


Figure 4. Tandem ESI-MS/MS product ion mass spectrum for 5 eV CID of the mixed and singly negatively charged ionic liquid supramolecule $[\text{CF}_3\text{CO}_2\cdots\text{X}_1\cdots\text{BF}_4]^{-1}$. The isotopologue ions $^{11}\text{BF}_4^-$ of m/z 87 and $^{10}\text{BF}_4^-$ of m/z 86 are lost preferentially since the hydrogen bond with BF_4^- is weaker than that with CF_3CO_2^- .

for $\text{A}=\text{InCl}_4^-$. We are currently investigating via DFT calculations the effects governing the extra stabilities of the singly charged $[(\text{X}^1)_5\text{A}_4]^{+1}$ ionic liquid supramolecules.^[22]

Relative strengths of hydrogen bonds: The observation that ESI is able to transfer loosely bound ionic liquid supramolecules of $[(\text{X}^1)_n(\text{BF}_4)_{n+1}]^{-1}$ composition to the gas phase gave us the unprecedented opportunity to form, isolate via mass-selection, and then gently dissociate by low-energy CID, mixed gaseous $[\text{A}\cdots\text{X}^1\cdots\text{A}']^{-1}$ supramolecules (as well as higher homologues) so as to measure, for the first time, the *intrinsic* solvent-free relative strengths of their weak, but so relevant, CH hydrogen bonds. To form such mixed supramolecules, first an acetonitrile solution of X^1BF_4 , X^1PF_6 , and $\text{X}^1\text{CF}_3\text{CO}_2$ was prepared, and its ESI(−) mass spectrum recorded (Figure 3).

Both series of “mixed” and “homogeneous” supramolecules were found to be efficiently transferred to the gas phase, and each of the mixed ones: $[\text{CF}_3\text{CO}_2\cdots\text{X}^1\cdots\text{BF}_4]^{-1}$ of m/z 339, $[\text{BF}_4\cdots\text{X}^1\cdots\text{PF}_6]^{-1}$ of m/z 371, and $[\text{CF}_3\text{CO}_2\cdots\text{X}^1\cdots\text{PF}_6]^{-1}$ of m/z 397 were mass-selected and then dissociated by 5 eV collisions with argon. As the spectrum of Figure 4 shows for $[\text{CF}_3\text{CO}_2\cdots\text{X}^1\cdots\text{BF}_4]^{-1}$ of m/z 339, the stronger $\text{CF}_3\text{CO}_2\cdots\text{X}^1$ hydrogen bond favors the loss of a neutral $\text{X}^1\text{CF}_3\text{CO}_2$ species, and consequently BF_4^- of m/z 87 is formed as the main ionic fragment, whereas CF_3CO_2^- of m/z 113 is of minor abundance. For $[\text{CF}_3\text{CO}_2\cdots\text{X}^1\cdots\text{BF}_4]^{-1}$, two loosely bonded isomers could be formed, **a** and **b** in Scheme 1, but B3LYP/6-311+G(d,p) calculations predict **b** as the global minimum.



Scheme 1.

Similarly, PF_6^- is the main ionic fragment of $[\text{BF}_4\cdots\text{X}^1\cdots\text{PF}_6]^{-1}$. For $[\text{CF}_3\text{CO}_2\cdots\text{X}^1\cdots\text{PF}_6]^{-1}$, however, in which PF_6^- interacts more weakly to $[\text{X}^1]^+$ than CF_3CO_2^- , PF_6^- is formed exclusively. The gaseous $[\text{BPh}_4\cdots\text{X}^1\cdots\text{PF}_6]^{-1}$ and $[\text{InCl}_4\cdots\text{X}^1\cdots\text{PF}_6]^{-1}$ supramolecules were also formed and dissociated in similar experiments, as

Table 1. Relative abundances (I) of fragment ions in the tandem ESI-MS/MS spectra for CID of $[\text{A}\cdots\text{X}^1\cdots\text{A}']^{-1}$ and $[\text{X}\cdots\text{BF}_4\cdots\text{X}']^{+1}$ mixed supramolecules.

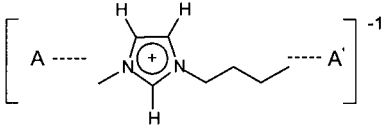
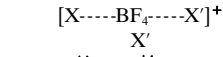
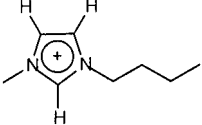
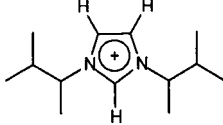
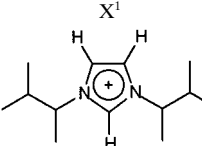
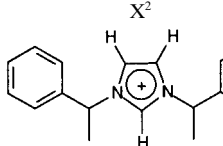
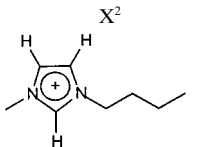
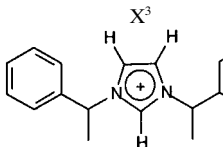
			
A	A'	I_A	$I_{A'}$
CF_3CO_2^-	BF_4^-	4.4	100
BF_4^-	PF_6^-	0.05	100
PF_6^-	InCl_4^-	0.02	100
InCl_4^-	BPh_4^-	12.5	100
		I_X	$I_{X'}$
		5.7	100
		50.6	100
		2.0	100

Table 1 summarizes. From Table 1 therefore, the qualitative order of intrinsic hydrogen bond strength to X^1 for the five anions studied is: $\text{CF}_3\text{CO}_2^- > \text{BF}_4^- > \text{PF}_6^- > \text{InCl}_4^- > \text{BPh}_4^-$. The order above is also corroborated when the

higher homologue mixed supramolecules were mass-selected and dissociated. For instance, the dissociation of $[\text{CF}_3\text{CO}_2(\text{X}^1)_2(\text{BF}_4)_2]^{-1}$ occurs by the loss of both $\text{X}^1\text{CF}_3\text{CO}_2$ and X^1BF_4 neutral species, but again the loss of the more strongly hydrogen-bonded $\text{X}^1\text{CF}_3\text{CO}_2$ species dominates.

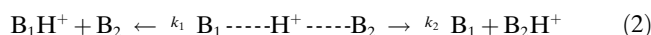
ESI-MS in the positive ion mode allows us to perform another unprecedented series of experiments with gaseous ionic liquid supramolecules: the formation, isolation, and gentle dissociation of gaseous $[\text{X}^1\text{---A}^1\text{---X}^2]^+1$ positively charged supramolecules now with mixed imidazolium ions, and to compare the intrinsic strength of their hydrogen bonds. Three such mixed supramolecules were formed from an acetonitrile solution of BF_4^- salts of the X^1 , X^2 and X^3 imidazolium ions. Figure 5 shows the tandem product ion mass spectrum of one such supramolecule, $[\text{X}^2\text{---BF}_4\text{---X}^3]^+1$ of m/z 573. Upon dissociation, the two imidazolium ions compete for the central BF_4^- anion, and the more loosely hydrogen-bonded ion is expelled preferentially as the main ionic fragment. Since X^3 of m/z 277 is formed with an abundance nearly twice as that of X^2 of m/z 209 (Table 1), we conclude that X^2 is more strongly hydrogen bonded to BF_4^- .

To complete the order, the $[\text{X}^2\text{---BF}_4\text{---X}^1]^+1$ supramolecule of m/z 493 was also dissociated, and X^2 of m/z 209 was found to be formed with an abundance nearly twenty times as great as that of X^1 of m/z 109 (Table 1); hence, X^1 is more strongly hydrogen-bonded to BF_4^- than X^2 . The $[\text{X}^1\text{---A}^1\text{---X}^3]^+1$ supramolecule of m/z 503 was also formed and dissociated via similar experiments (Table 1). From these experiments, the order of H-bond strength to BF_4^- is therefore: $\text{X}_1 > \text{X}_2 > \text{X}_3$. This order likely reflects increasing electron-donating or steric effects, or both, of the N-substituents weakening hydrogen bonds to the imidazolium ions.

Relative hydrogen-bond energies by Cooks' kinetic method

(CKM): The kinetic method proposed by Cooks and co-workers^[23] has been used to determine thermochemical properties based on rates of competitive dissociations of gaseous mass-selected ionic supramolecules as measured via MS experiments. Because of the ease of use, broad applicability, high sensitivity to small thermochemical differences

(typically as small as $0.1 \text{ kcal mol}^{-1}$), and high precision, the CKM has found a multitude of applications.^[24] In its simplest form, the method relies on the following major assumptions: a) negligible differences in the entropy requirements for the competitive channels; b) negligible reverse activation energies; and c) the absence of isomeric forms of the activated cluster ion. When these conditions are well satisfied, the ratio of the fragment ion abundance for, for instance, a proton bound dimer $\text{B}_1\text{---H}^+\text{---B}_2$ as described in Equation (2), in which k_1 and k_2 are the rate constants for the competitive dissociations, is related to the proton affinity difference of the two bases, $\Delta(\text{PA})$, by Equation (3). T_{eff} is the effective temperature, a thermodynamic quantity^[25] apparently related to the internal energy of the dissociating ions, and $\Delta(\Delta S)$ is the reaction entropy difference between the two fragmentation channels.



$$\ln\left(\frac{k_1}{k_2}\right) = \ln\left(\frac{[\text{B}_1\text{H}^+]}{[\text{B}_2\text{H}^+]}\right) \approx \frac{\text{PA}(\text{B}_1) - \text{PA}(\text{B}_2)}{RT_{\text{eff}}} - \frac{\Delta(\Delta S)}{R} \quad (3)$$

From Equation (3), the CKM reliability and whether or not a significant entropic effect operates is verified by investigating the dissociation of cluster ions formed by a set of reference compounds of known ion affinities (ΔPA for proton affinity) and by plotting $\ln(k_1/k_2)$ versus ΔPA . Thus, a straight line with high correlation coefficient intercepting the origin indicates the reliability of the method and the absence of significant entropic effects, and from its slope T_{eff} is then calculated. From such a plot, the affinity of an unknown can therefore be determined by forming and dissociating ion clusters of the unknown with reference compounds. For systems where entropy effects are relevant, "extended" CKM versions have been developed.^[26] Different instrumental conditions are employed so as to vary the effective temperature, and to extract apparent entropy differences between pairs of cluster ions.

To verify whether CKM is applicable to measure relative intrinsic hydrogen-bond strengths in gaseous ionic liquid supramolecules, we plot $\ln(I_A/I_A)$ versus the relative X^1 affinities for CF_3CO_2^- , BF_4^- , PF_6^- , and BPH_4^- as estimated by

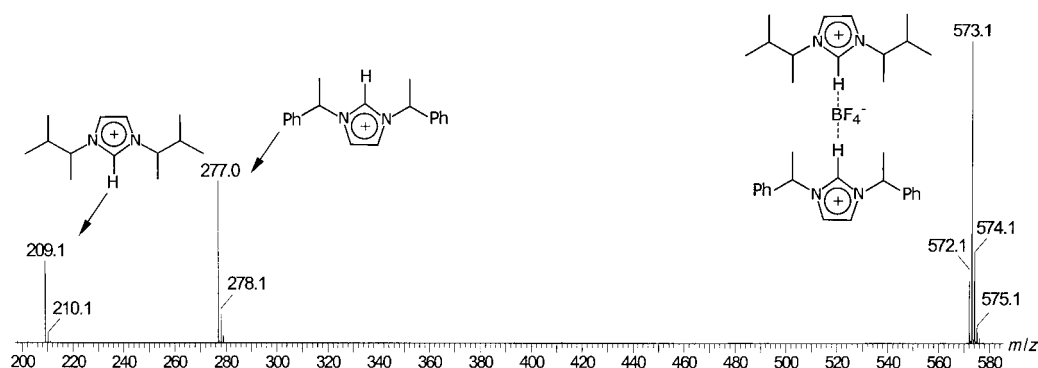


Figure 5. Tandem ESI-MS/MS product ion mass spectrum for 5 eV CID of the mixed and singly positively charged ionic liquid supramolecule $[\text{X}^2\text{---BF}_4\text{---X}^3]^+1$. Because the H-bond of X^2 of m/z 209 to BF_4^- is stronger than that of X^3 , the X^3 fragment ion of m/z 277 is formed to a greater extent.

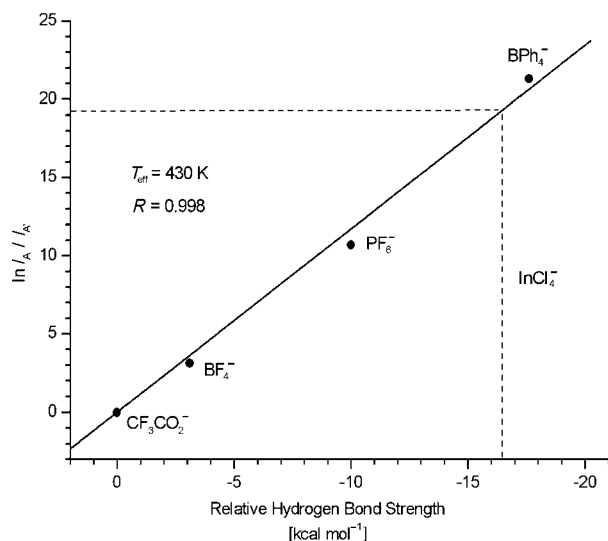


Figure 6. CKM plot used to test the reliability of the method for gaseous ionic liquid supramolecules.

B3LYP/6-311+G(d,p) calculations (Figure 6) by using CF_3CO_2^- as the reference (zero). Drawing a straight line passing through the origin results in a correlation coefficient as high as 0.998 and a T_{eff} of 430 K. This effective temperature is very typical of loosely bonded ionic species. For instance, weakly bonded clusters or supramolecules such as H^+ , Cl^+ and Br^+ bound dimers of amines and pyridines^[27] usually display T_{eff} below 700 K whereas covalently bonded species such as “electron-bound dimers” display considerably higher, greater than 1500 K, effective temperatures.^[28] These results therefore demonstrate the CKM reliability for ionic liquids and negligible entropic effects even though the nature of the anions A^- herein investigated vary considerably. We then used the plot of Figure 6 to estimate the relative hydrogen-bond strength for InCl_4^- , an “unknown” for which B3LYP/6-311+G(d,p) calculations are not applicable. Combining therefore data from the calculations and CKM, the following relative order of hydrogen bonding to 1-*n*-butyl-3-methylimidazolium ion X^1 is derived: CF_3CO_2^- (0) > BF_4^- (−3.1) > PF_6^- (−10.0) > InCl_4^- (−16.4) and BPh_4^- (−17.6 kcal mol^{−1}).^[29] Using now T_{eff} of 430 K,^[30] the ratios from Table 1, and Equation (3) (negligible entropy effects), the relative order of hydrogen bonding of the imidazolium ions to BF_4^- can also be calculated: X^1 (0) > X^2 (−2.4) > X^3 (−3.0 kcal mol^{−1}).

Figure 7 shows the geometries for the hydrogen-bonded dimers of X^1 with CF_3CO_2^- , BF_4^- , PF_6^- , and BPh_4^- as optimized by B3LYP/6-311G(d,p) calculations. Note the strong and short (1.95 and 1.88 Å) C(2)H-bond which are predicted for $\text{X}^1\text{CF}_3\text{CO}_2$ and X^1BF_4 . The C(2)H-F hydrogen bond for PF_6^- is, as compared to BF_4^- , considerably longer (2.01 Å) and therefore weaker. As BPh_4^- is considerably sterically hindered, a much weaker and longer hydrogen bond (2.43 Å) is predicted for X^1BPh_4^- ; hydrogen bonding occurs via interaction of C(2)H with the *ipso* carbon of the phenyl group, which carries the highest density of negative charge.

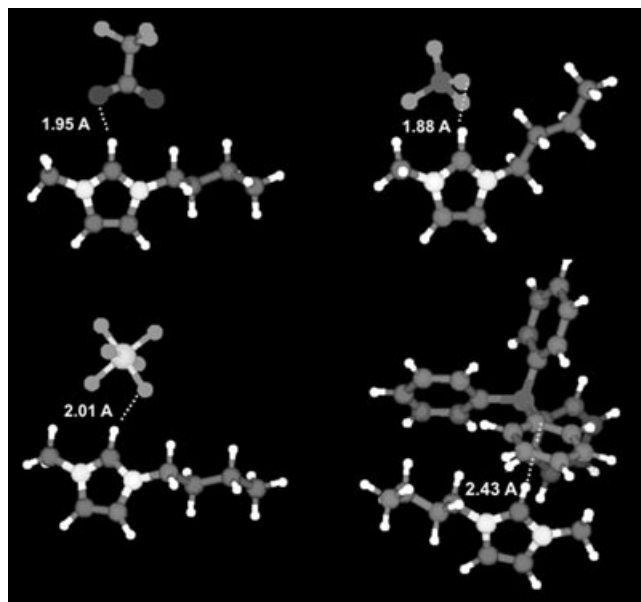


Figure 7. B3LYP/6-311G+(d,p) optimized structures of the neutral supramolecules $\text{X}^1\text{CF}_3\text{CO}_2$, X^1BF_4 , X^1PF_6 and X^1BPh_4 . The H-bond is indicated.

Conclusion

ESI-MS in both the positive and negative ion modes is a suitable technique to gently transfer to the gas-phase, to determine magic numbers for their assemblies, and then to measure the relative strengths of hydrogen bonding. Low energy collision dissociation of mixed loosely bonded $[\text{A} \cdots \text{X} \cdots \text{A}]^+$ and $[\text{X} \cdots \text{A} \cdots \text{X}]^-$ supramolecules (and of their higher homologues) via tandem mass spectrometric experiments (ESI-MS/MS) with the application of Cooks' kinetic method in its simplest form (entropy effects are negligible) provides relative *intrinsic* magnitudes of their weak, but very relevant, hydrogen bonds. For the five anions studied, the relative order of intrinsic hydrogen bond strengths to the 1-*n*-butyl-3-methylimidazolium ion, X^1 , is found to be: CF_3CO_2^- (0) > BF_4^- (−3.1) > PF_6^- (−10.0) > InCl_4^- (−16.4) and BPh_4^- (−17.6 kcal mol^{−1}), and for that of the three imidazolium ions to BF_4^- : X^1 (0) > X^2 (−2.4) > X^3 (−3.0 kcal mol^{−1}). As evidenced by “magic” numbers, greater stabilities are found for the $[(\text{X}^1)_2(\text{BF}_4)_3]^-$ and, more generally, for $[(\text{X}^1)_5\text{A}_4]^+$ supramolecules except for when $\text{A} = \text{InCl}_4^-$.

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[1] a) J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667; b) J. Dupont *J. Braz. Chem. Soc.* **2004**, *13*, 341.

[2] a) P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. de Souza, J. Dupont, *Polyhedron* **1996**, *15*, 1217; b) Y. Chauvin, L. Musmann,

- H. Olivier, *Angew. Chem.* **1996**, *107*, 2941; *Angew. Chem. Int. Ed. Engl.* **1996**, *34*, 2698.
- [3] a) T. Welton, *Chem. Rev.* **1999**, *99*, 2071; b) P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, *112*, 3926; *Angew. Chem. Int. Ed.* **2000**, *39*, 3772; c) J. Dupont, C. S. Consorti, J. Spencer, *J. Braz. Chem. Soc.* **2000**, *11*, 337; d) R. Sheldon, *Chem. Commun.* **2001**, 2399.
- [4] G. S. Fonseca, A. P. Umpierre, P. F. P. Fichtner, S. R. Teixeira, J. Dupont, *Chem. Eur. J.* **2003**, *9*, 3263.
- [5] a) D. W. Armstrong, L. -K. Zhang, L. F. He, M. L. Gross, *Anal. Chem.* **2001**, *73*, 3679; b) L. S. Santos, R. Haddad, N. F. Höehr, R. A. Pilli, M. N. Eberlin, *Anal. Chem.* **2004**, *76*, 2144.
- [6] P. A. Z. Suarez, S. Einloft, J. E. L. Dullius, R. F. de Souza, J. Dupont, *J. Chim. Phys. Phys. Chim. Biol.* **1998**, *95*, 1626.
- [7] Supramolecules are chemical species that are bound together reversibly by intermolecular noncovalent interactions rather than by conventional covalent bonds (shared electrons) such as highly ordered hydrogen bonded materials, see J.-M. Lehn, *Angew. Chem.* **1988**, *100*, 91; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 89. Ionic liquid highly-organized aggregates held together by hydrogen bonds are therefore commonly defined as supramolecules rather than ionic clusters, see ref. [1b].
- [8] C. J. Dymek Jr., D. A. Grossie, A. V. Fratini, W. W. Adams, *J. Mol. Struct.* **1989**, *213*, 25.
- [9] a) J. S. Wilkes, M. J. Zaworotko, *J. Chem. Soc. Chem. Commun.* **1992**, 965; b) J. Fuller, R. T. Carlin, H. C. Delong, D. Haworth, *J. Chem. Soc. Chem. Commun.* **1994**, 299.
- [10] a) J. Dupont, P. A. Z. Suarez, R. F. de Souza, R. A. Burrow, J. P. Kintzinger, *Chem. Eur. J.* **2000**, *6*, 2377; b) J. F. Huang, P. Y. Chen, I. W. Sun, S. P. Wang, *Spectrosc. Lett.* **2001**, *34*, 591.
- [11] a) J. D. Wadhawan, U. Schroder, A. Neudeck, S. J. Wilkins, R. G. Compton, F. Marken, C. S. Consorti, R. F. de Souza, J. Dupont, *J. Electroanal. Chem.* **2000**, *493*, 75; b) U. Schroder, J. D. Wadhawan, R. G. Compton, F. Marken, P. A. Z. Suarez, C. S. Consorti, R. F. de Souza, J. Dupont, *New J. Chem.* **2000**, *24*, 1009.
- [12] Recently, ESI-MS has been used to determine the ionic solubility of ionic liquids in water, see: Z. B. Alfassi, R. E. Huie, P. Neta, *Anal. Bioanal. Chem.* **2003**, *377*, 159.
- [13] a) C. M. Whitehouse, R. N. Dreyer, M. Yamashita, J. B. Fenn, *Anal. Chem.* **1985**, *57*, 675; b) J. B. Fenn, M. Mann, C. K. Meng, S. F. Wong, C. M. Whitehouse, *Science* **1989**, *246*, 64; d) R. B. Cole, *Electrospray Ionization Mass Spectroscopy*, Wiley, New York, **1997**.
- [14] a) S. H. Toma, M. Uemi, S. Nikolaou, D. M. Tomazela, M. N. Eberlin, H. E. Toma, *Inorg. Chem.* **2004**, *43*, 3521; b) V. Rioli, F. C. Gozzo, A. S. Heimann, A. Linardi, J. E. Krieger, C. S. Shida, P. C. Almeida, S. Hyslop, M. N. Eberlin, E. S. Ferro, *J. Biol. Chem.* **2003**, *278*, 8547; c) E. C. Meurer, A. A. Sabino, M. N. Eberlin, *Anal. Chem.* **2003**, *75*, 4701; d) D. M. Tomazela, F. C. Gozzo, G. Ebeling, J. Dupont, M. N. Eberlin, *Inorg. Chim. Acta* **2004**, *357*, 2349; e) A. C. H. F. Sawaya, D. M. Tomazela, I. B. S. Cunha, V. S. Bankova, M. C. Marcucci, M. N. Eberlin, *Analyst* **2004**, *129*, 739.
- [15] a) K. J. Koch, F. C. Gozzo, S. C. Nanita, Z. Takats, M. N. Eberlin, R. G. Cooks, *Angew. Chem.* **2002**, *114*, 1797; *Angew. Chem. Int. Ed.* **2002**, *41*, 1721; b) R. G. Cooks, D. X. Zhang, K. J. Koch, F. C. Gozzo, M. N. Eberlin, *Anal. Chem.* **2001**, *73*, 3646; c) Z. Takats, S. C. Nanita, R. G. Cooks, *Angew. Chem.* **2003**, *115*, 3645; *Angew. Chem. Int. Ed.* **2003**, *42*, 3521.
- [16] J. Griep-Raming, S. Meyer, T. Bruhn, J. O. Metzger, *Angew. Chem.* **2002**, *114*, 2863; *Angew. Chem. Int. Ed.* **2002**, *41*, 2738; b) S. Meyer, R. Koch, J. O. Metzger, *Angew. Chem.* **2003**, *115*, 4848; *Angew. Chem. Int. Ed.* **2003**, *42*, 4700; c) E. C. Meurer, L. S. Santos, R. A. Pilli, M. N. Eberlin, *Org. Lett.* **2003**, *5*, 1391; d) A. A. Sabino, A. H. L. Machado, C. R. D. Correia, M. N. Eberlin, *Angew. Chem.* **2004**, *116*, 2568; *Angew. Chem. Int. Ed.* **2004**, *43*, 2514; e) L. S. Santos, C. H. Pavam, W. P. Almeida, F. Coelho, M. N. Eberlin, *Angew. Chem.* **2004**, *116*, 4430; *Angew. Chem. Int. Ed.* **2004**, *43*, 4330; f) J. B. Domingos, E. Longhinotti, T. A. S. Brandão, C. A. Bunton, L. S. Santos, M. N. Eberlin, F. Nome, *J. Org. Chem.* **2004**, *69*, 6024.
- [17] a) C. Hilderling, C. Adhart, P. Chen, *Angew. Chem.* **1998**, *110*, 2831; *Angew. Chem. Int. Ed.* **1998**, *37*, 2685; b) P. Chen, *Angew. Chem.* **2003**, *115*, 2938–2954; *Angew. Chem. Int. Ed.* **2003**, *42*, 2832; c) C. Raminelli, M. H. G. Precht, L. S. Santos, M. N. Eberlin, J. V. Comasseto, *Inorg. Chem.* **2004**, *23*, 3990.
- [18] a) G. Wang, R. D. Cole, *Anal. Chem.* **1998**, *70*, 873; b) C. Hao, R. E. March, *J. Mass Spectrom.* **2001**, *36*, 509.
- [19] M. N. Eberlin, F. C. Gozzo, C. S. Consorti, J. Dupont, *Proceedings of the 47th American Society Mass Spectrometry Meeting*, Orlando, FL, **2002**.
- [20] B. A. da Silveira Neto, G. Ebeling, R. S. Gonçalves, F. C. Gozzo, M. N. Eberlin, J. Dupont, *Synthesis* **2004**, 1155.
- [21] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
- [22] M. N. Eberlin, F. C. Gozzo, J. Dupont, unpublished results.
- [23] R. G. Cooks, J. S. Patrick, T. Kotiaho, S. A. McLuckey, *Mass Spectrom. Rev.* **1994**, *13*, 287.
- [24] a) R. G. Cooks, P. S. H. Wong, *Acc. Chem. Res.* **1998**, *31*, 379; b) L. Wu, E. C. Meurer, B. Young, P. Yang, M. N. Eberlin, R. G. Cooks, *Int. J. Mass Spectrom.* **2004**, *231*, 103; c) D. V. Augusti, F. Carazza, R. Augusti, W. A. Tao, R. G. Cooks, *Anal. Chem.* **2002**, *74*, 3458; d) L. Wu, E. C. Meurer, B. Young, P. Yang, M. N. Eberlin, R. G. Cooks, *Int. J. Mass Spectrom.* **2004**, *231*, 103; e) P. S. H. Wong, S. Ma, S. S. Yang, R. G. Cooks, F. C. Gozzo, M. N. Eberlin, *J. Am. Soc. Mass Spectrom.* **1997**, *8*, 68; f) M. N. Eberlin, T. Kotiaho, B. J. Shay, S. S. Yang, R. G. Cooks, *J. Am. Chem. Soc.* **1994**, *116*, 2457.
- [25] The effective temperature has been recently proposed not to be a thermodynamic quantity, but rather to depend explicitly on molecular and instrumental parameters, see: K. M. Ervin, *J. Am. Soc. Mass Spectrom.* **2002**, *13*, 435.
- [26] P. B. Armentrout, *J. Am. Soc. Mass Spectrom.* **2000**, *11*, 371, and references therein.
- [27] a) S. A. McLuckey, D. Cameron, R. G. Cooks, *J. Am. Chem. Soc.* **1981**, *103*, 1313; b) M. N. Eberlin, T. Kotiaho, S. S. Yang, R. G. Cooks, *J. Am. Chem. Soc.* **1994**, *116*, 2457; c) F. C. Gozzo, M. N. Eberlin, *J. Mass Spectrom.* **2001**, *36*, 1140.
- [28] a) G. D. Chen, P. Wong, R. G. Cooks, *Anal. Chem.* **1997**, *69*, 3641; b) E. C. Meurer, F. C. Gozzo, R. Augusti, M. N. Eberlin, *Eur. J. Mass Spectrom.* **2003**, *9*, 295.
- [29] The intrinsic gas phase order for hydrogen bonding of $\text{CF}_3\text{CO}_2^- > \text{BF}_4^- > \text{PF}_6^-$ in imidazolium ion ionic liquids is the same as that measured in solution by infrared spectroscopy for hydrogen bonding with water molecules, see: L. Cammarata, S. G. Kazarian, P. A. Salter, T. Welton, *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192.
- [30] Because KM measures small differences in thermochemical affinities, large relative variation in T_{eff} leads to small absolute errors in ion affinities, see: R. G. Cooks, J. T. Koskinen, P. D. Thomas, *J. Mass Spectrom.* **1999**, *34*, 85.

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