

FULL PAPER

## The Hydronium Tetrafluoroborate Dimer in Nonpolar Media and its Proton NMR Spectrum

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**Abstract** Hydronium tetrafluoroborate ion pairs,  $\text{H}_3\text{O}^+\cdot\text{BF}_4^-$  have been shown computationally to be unstable toward decomposition, in the absence of solvation or electrostatic interactions existing in crystals. As the proton NMR spectrum of a hydronium salt with the octanesulfonate-antimony pentachloride complex anion was reported in the nonpolar solvent, we investigated the hypothesis that larger ionic clusters were present in the nonpolar solvent. It was found that the dimer  $(\text{H}_3\text{O}^+\cdot\text{BF}_4^-)_2$  was stable at the MP2/6-31G\* level. GIAO-B3LYP chemical shift calculations with the same basis set and also with the 6-31G\*\*, 6-31++G\*\*, 6-311++G\*\*, dzvp, tzp, tz2p, and qz2p basis sets conducted on the hydronium fluoroborate dimer reproduce the main features of the experimental spectrum: the existence of two signals with a two-to-one intensity ratio and the more intense resonance at higher frequency (more deshielded). The alternative structures, of hydronium tetrafluoroborate ion pairs with one and with two hydrogen bonds between anion and cation, give calculated chemical shifts which are farther from the experimental values.

**Keywords** Hydronium tetrafluoroborate, Ion pairs, Ion clusters, *Ab initio* calculations, GIAO-B3LYP chemical shift calculations

### Introduction

In our investigations of acid strength of liquid and solid acid catalysts, we have concentrated on two groups of probe bases suitable for investigation by NMR: alkenones [1] and aromatic hydrocarbons [1d, 2]. There have been, however, a number of acidity studies in which water was used as probe

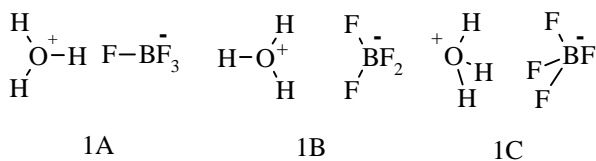
base for acidity studies. The earliest work sought to determine the acidity function of  $\text{FSO}_3\text{H}\cdot\text{SbF}_5$  (14-82 mol%  $\text{SbF}_5$ ) from the lifetime of dissolved hydronium ions, measured by dynamic NMR spectroscopy [3]. The low sensitivity of the NMR method required the use of high concentrations of water (4-15 mol %) [3], conditions under which the  $H_o$  parameter [4] does not measure the actual acid strength [1c]. We have shown that the determination of acidity functions by NMR requires an extrapolation to zero indicator concentration (infinite dilution) [2]. Moreover, the whole treatment [3] was based on the acidity of the hydronium ion (the  $\text{p}K_{\text{BH}^+}$  value of water), a property found later to be highly variable with the acid anion [5]. The reported acid strengths [3] and basicity constants [6] should, therefore, be very much in error.

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Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70<sup>th</sup> birthday

In recent years, an evaluation of relative acid strengths of various media, especially solids, was attempted from the extent of hydration of near-stoichiometric quantities of water. Among the methods of analysis used were the high-resolution  $^1\text{H}$  MAS-NMR spectroscopy at room temperature [7], the deconvolution of broad-band  $^1\text{H}$  NMR spectra of frozen water at 4 K [8], IR spectroscopy [9], and neutron diffraction [10]. Theoretical calculations of the extent of hydration of water by molecules modeling the zeolites were also published [11]. As pointed out earlier, these methods gave conflicting results [2]. The controversy stimulated us to examine the applicability of  $^{17}\text{O}$  NMR as a tool of determining the extent of hydration of water in an acid. The result was negative, because the  $^{17}\text{O}$  chemical shift did not vary smoothly from pure water to pure hydronium salt, but showed instead a maximum for the composition  $\text{H}_5\text{O}_2^+$ . Along both branches of the  $\delta^{17}\text{O}$  vs. composition plot ( $\text{H}_3\text{O}^+\cdot\text{BF}_4^-$  to  $\text{H}_5\text{O}_2^+\cdot\text{BF}_4^-$  and  $\text{H}_5\text{O}_2^+\cdot\text{BF}_4^-$  to  $\text{H}_2\text{O}$ ) the chemical shift variation was nonlinear [12].

At the same time, we conducted GIAO-B3LYP calculations of the  $^{17}\text{O}$  chemical shifts of  $\text{H}_3\text{O}^+\cdot\text{BF}_4^-$  (**1**) and  $\text{H}_5\text{O}_2^+\cdot\text{BF}_4^-$ , in order to compare them with the experimental data and with calculations run on the isolated cations [13]. Three possible relative orientations of ions in the ion pairs were considered for **1**, as represented in Scheme 1: with one (Structure **1A**), two (Structure **1B**), and three hydrogen bonds (Structure **1C**) [12].



**Scheme 1** Relative orientations of ions in hydronium tetrafluoroborate ion pairs (**1**)

The calculations showed **1** to be unstable for all three relative orientations, decomposing into water, hydrogen fluoride, and boron trifluoride. (A fourth orientation, **1D**, in which the cation has one hydrogen facing the anion, like in **1A**, and the anion has three fluorine atoms facing the cation, like in **1C**, was also unstable.) Obviously, hydronium fluoroborate owes its stability to the interaction of **1** with surrounding ions in the crystal. The hydronium ions might perhaps exist as such in a strong anion-stabilizing solvent of low basicity, like hexafluoroisopropanol or perfluoro-*tert*-butanol [1c,d,2d,14]. Geometry optimizations on the individual ion pair **1** could be conducted only for fixed interionic distances. This constraint did not affect the reliability of our calculations, as we had found that geometry optimization at fixed interionic distances gives the correct structures for carbocations in ion pairs and aggregates [15]. As for the NMR chemical shift calculations, valid predictions had been reported even for structures

which were not energy minima [16], but had one [16b,c] or two negative frequencies [16a] in the force constant matrices.

The instability of **1** was intriguing, however, because proton NMR experiments had indicated that hydronium ions can be generated by the reaction of water with one equivalent of octanesulfonic acid and one equivalent of antimony pentachloride in a nonpolar solvent (mixture of freons) [17]. We did not expect that particular Lewis acid-Brønsted acid pair to represent a strong superacid [1c]. It was possible, however, that the elementary species present were not ion pairs, but larger aggregates, stabilized by multiple electrostatic interactions. As the authors of the  $^1\text{H}$  NMR study did not determine (for example by osmometry) what was the size of the ionic clusters in their solution, we decided to test this idea and seek computationally the size of the smallest aggregate in our system,  $(\text{H}_3\text{O}^+\cdot\text{BF}_4^-)_n$ , between the ion pair ( $n = 1$ ) and the crystal ( $n = \infty$ ), which is stable in the absence of a polar solvent.

## Computational method

The calculations were conducted with the Gaussian 98 programs [18]. Geometry optimizations were performed at the MP2/6-31G\* level. In preliminary calculations, the relative positions of the ions and the symmetry of the cluster were controlled with the use of dummy atoms [12]. Afterwards, the dummy atoms were removed from the Z-matrix. No symmetry constraints were imposed in the calculations.

The NMR shielding constants ( $\sigma$ ) were calculated with the DFT-GIAO method, at the B3LYP level [19]. Two groups of basis sets were used (a) 6-31G\*, 6-31G\*\*, 6-31++G\*\*, and 6-311++G\*\*, and (b): dzvp (9s5p1d/3s2p1d for B, O, F and 5s/2s for H) [20a], tzp (9s5p1d/5s3p1d for B, O, F and 5s1p/3s1p for H) [20b] tz2p (11s6p3d/5s3p2d for B, O, F and 5s3p/3s2p for H) [20c], and qz2p (11s7p2d/6s4p2d for B, O, F and 6s2p/3s2p for H) [20d]. The polarization exponents and contraction coefficients for each of them were listed previously [12,21]. Note that polarization exponents for the qz2p basis set for boron were not publicly available [20c]. The chemical shifts were deduced relative to methane, for which the shielding constants with the same basis sets were calculated on the MP2/6-311G\*\* optimized structure [21]. The methane  $\sigma$  values were: 31.99 (6-31G\*), 31.54 (6-31G\*\*), 31.51 (6-31++G\*), 31.76 (6-311++G\*\*), 32.10 (dzvp), 31.74 (tzp), 31.61 (tz2p), and 31.55 ppm (qz2p). The conversion of chemical shifts from the methane scale to the TMS scale was achieved by adding 0.2 ppm [22].

The projections of molecular geometry shown in the paper were generated with the program MOLDEN 3.4 [23].

## Results and discussion

Formation of ion pairs by acid-base reactions in nonpolar (or rather non-hydrogen-bond-forming) solvents is predicated

**Table 1** Geometrical parameters for  $(H_3O^+ \cdot BF_4^-)_2$  (**2**) at MP2/6-31G\* [a]

Parameter	Value
d(O-Ha), d(O-Ha') [b]	1.022
d(O-Hb) [c]	0.990
d(Ha...Fa), d(Ha', Fa') [d]	1.513
d(Hb...Fb), d(Hb...Fb') [d]	2.023
d(Fb...Fb')	2.783
$\theta$ (Ha-O-Ha')	108.8
$\theta$ (Ha-O-Hb), $\theta$ (Ha'-O-Hb)	102.6
$\theta$ (O-Ha...Fa), $\theta$ (O-Ha'-Fa')	163.3
$\theta$ (O-Hb...Fb), $\theta$ (O-Hb-Fb')	121.0
$\theta$ (Fb...Hb...Fb')	86.8
$\varphi$ (HaHa'OHb)	109.2

[a] Distances in Ångströms, bond angles ( $\theta$ ) and dihedral angles ( $\varphi$ ) in degrees.

[b] Two hydrogens.

[c] One hydrogen [d] Fa, Fa' are in different anions and so are Fb and Fb'.

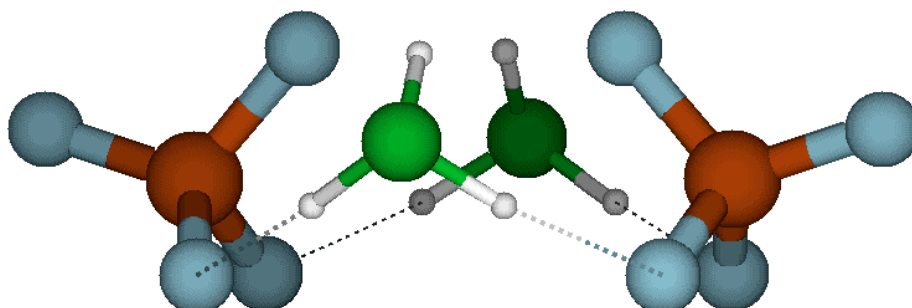
upon the formation of strong hydrogen bonds between anions and cations in undissociated ion pairs and aggregates [24]. More hydrogen bonds per ion can be formed in larger than in smaller aggregates. To establish which is the smallest hydronium fluoroborate aggregate which can exist in nonpolar solvents, we started with the four-ion cluster,  $(H_3O^+ \cdot BF_4^-)_2$  (Structure **2**), which in the end was found to be stable.

A representation of the cluster **2** is shown in Figure 1. It exhibits a symmetrical arrangement of the ions, such that the two cations have identical structures and environments, as do the two anions. In each cation there are two equal and long O-H bonds and one shorter O-H bond. The two hydrogen atoms with long O-H bonds (Ha) are strongly hydrogen-bonded to fluorine atoms in different anions (Fa). These hydrogen bonds connect each cation with the two anions. The third hydrogen of each cation (Hb) is interacting with two other fluorine atoms (Fb and Fb'), one in each anion, at longer distance. The distance between these two fluorine atoms,

$d(Fb \cdots Fb') = 2.783 \text{ \AA}$ , represents the shortest distance between the anions. At the same time, the separation between the hydrogens with short OH bonds in each cation,  $2.940 \text{ \AA}$ , is the shortest distance between the two cations in the cluster. The aggregation of the four ions creates a cavity in its center. The main geometrical parameters of **2** are listed in Table 1.

It is interesting to notice that the X-ray analysis has revealed clustering to the  $(C^+ \cdot A^-)_2$  level in the crystals of the tetramethylammonium salts of dialkyl ethylmalonates [25]. The general layout was similar to what we found for **2**: the large cations were facing each other and the anions were placed in between, each anion hydrogen-bonded to both cations (alpha methylene groups). A cavity was formed in the middle [25]. From the published representation of the cluster [25], it appears that the weakness of the hydrogen bonds (O...H distances  $2.31$ - $2.46 \text{ \AA}$ ) is compensated by the existence of hydrophobic (van der Waals) interactions between the outer butyl groups of the cation and the alkyl groups of the anion.

The application of ab initio calculations of chemical shifts for validation of chemical structures, especially of carbocations [26], has been extensively demonstrated by P. v. R. Schleyer and his group [16,27]. The existence of an experimental proton spectrum of hydronium ions in a non-hydrogen-bond-forming solvent (mixture of freons) made possible such a test for **2**. In the experimental NMR study, the spectrum of the hydronium cation consisted of a doublet (2H),  $\delta$  11.1 ppm, and a triplet (1H),  $\delta$  8.3 ppm [17]. A planar structure was preferred by the author [17] for  $H_3O^+$ , because the coupling constant, 2.8 Hz, was smaller than the value reported for water, 7.2 Hz [28]. It was also argued that a pyramidal cation should favor the orientation **1C**, in which the three hydrogens are equivalent [17]. In contrast, however, a pyramidal structure of the hydronium ion was obtained from the ab initio calculations on the isolated species [29], on **1** [12], and on **2**. We have noted that the decrease in coupling constant does not require that oxygen hybridization changes to  $sp^2$ . In fact, considering the higher electronegativity of oxygen in hydronium than in water, the variation in coupling constant upon the change in hybridization should follow the pattern of change from  $H_a-CH_2-H_b$ ,  $|J| = 12 \dots 15$ ,

**Figure 1** Optimized (MP2/6-31G\*) geometry of the  $(H_3O^+ \cdot BF_4^-)_2$  cluster (**2**)

**Table 2** Calculated (GIAO-B3LYP) Isotropic Chemical Shifts ( $\delta$ , ppm) for protons in **1A**, **1B**, and **2** [a]

Basis set [b]	H <sub>2</sub> O [c]	H <sub>3</sub> O <sup>+</sup> [d]	<b>1A</b>		<b>1B</b>		<b>2</b>	
			Ha [e]	Hb	Ha [e]	Hb	Ha [e]	Hb
6-31G*	0.2; 0.0	7.1	5.0	10.9	13.9	4.0	10.0	5.9
6-31G** [f]	0.1; 0.0	7.3	6.0	11.3	14.9	4.3	11.6	6.6
6-31++G**	0.6; 0.4	7.5	6.3	12.7	15.3	4.6	12.0	7.3
6-311++G**	0.4; 0.2	7.2	6.1	12.8	15.3	4.5	11.8	7.5
dzvp	0.9; 0.6	6.2	5.9	11.3	14.2	4.3	10.1	6.2
tzp	0.2; 0.1	6.5	6.1	12.8	14.9	5.1	11.7	6.9
tz2p	0.2; 0.2	7.3	6.4	13.2	15.5	4.6	12.2	7.3
qz2p	0.4; 0.2	7.3	6.4	13.2	15.5	4.7	12.3	7.3
Exper. for <b>3</b> [g]			11.1	8.3	11.1	8.3	11.1	8.3
Diff. (Exper. – qz2p)			4.7	-4.9	-4.4	3.6	-1.2	1.0

[a] From the isotropic shielding constants of the MP2/6-31G\*-optimized structure and those of methane. The methane shieldings with all basis sets were calculated for the structure optimized at the MP2/6-311G\*\* level. Conversion to the TMS scale was achieved by adding 0.2 ppm [22].

[b] See the description and references in the Computational method section.

[c] For the first value on each line, the geometry of the water molecule was optimized at the same level as used for the shielding constant calculation. For the second value, all cal-

culations were conducted on the water structure optimized at the MP2/6-31G\*\* level.

[d] Isolated ion, geometry optimized at the same level as used for the chemical shift calculation.

[e] Two equivalent hydrogens in each structure.

[f] The calculation at this level for the ion pair with one hydrogen of the cation facing three fluorine atoms of the anions, **1D**, gave  $\delta(\text{Ha}) = 5.4$  and  $\delta(\text{Hb}) = 18.2\text{ppm}$ .

[g] From ref [17].

to H<sub>a</sub>-C(=O)-H<sub>b</sub>,  $|J| = 42$ , rather than from H<sub>a</sub>-CH<sub>2</sub>-H<sub>b</sub> to H<sub>a</sub>-C(=C<)-H<sub>b</sub>,  $|J| = 2$  to 3 [30].

Because of its size, the corresponding cluster with the anions used in the experiment



(structure **3**) could not be examined computationally, but molecular models indicate that two anions facing each other can generate a cavity with three chlorine atoms on each side, which would accommodate the pair of cations in the positions shown for **2** in Figure 1. The two sulfonate ligands are coordinated in the octahedral anions in positions away from the cavity, such that the long alkyl groups interact fully with the solvent, thus preventing the crystallization of the hydronium salt.

Examination of structure **2** reveals that the proton spectrum of the four-ion cluster should also consist of two resonances with the same splitting pattern as in the experimental spectrum. A previous investigation has shown that the chemical shifts for cations in ion pairs can be calculated with smaller anions than employed for the experimentally recorded spectra [21]. As the anion taken in the model was smaller and smaller, the basis set required to duplicate the experiment became larger and larger. We conducted, therefore, GIAO-B3LYP chemical shift calculations on **2** with basis sets of increasing size, seeking to establish (a) whether the calculated values would converge toward a limiting value and (b) whether the calculated values are in agreement with the experiment.

The calculations were conducted with basis sets of increasing size, seeking the convergence of results. Another test of the effect of basis set size on the chemical shift calculations was conducted on the isolated hydronium ion. In addition, the shielding constant and chemical shift of water (also as isolated molecule) were also calculated; these can be compared with the literature data obtained by the IGLO method [31]. Two series of calculations on water were conducted. In the first, the geometry optimization was performed with the same basis set as the chemical shift calculations. In the second, chemical shifts for the structure optimized at the MP2/6-31G\*\* level were obtained. As shown in Table 2, there is no significant difference between the two sets of values. The two orientations of the ion pair which generate two signals in the proton spectrum, **1A** and **1B**, were examined, in addition to the four-ion cluster, **2**. The results of the calculations are shown in Table 2. It is immediately observed that the ion pair with one hydrogen bond predicts a wrong ordering of chemical shifts for the two signals (the two-proton signal at lower frequency than the one-proton signal), which was intuitively expected from the respective O-H bond lengths and the calculated charge densities. The ion pair with two hydrogen bonds, **1B**, gives the right ordering of the two resonances, but the chemical shift of the two-proton signal is too large even in the calculation with the smallest basis set and converges in the wrong direction, whereas the resonance frequency of the one-proton signal is too small. The values deduced for the cluster **2** are unquestionably closer to the experimental value for **3**. The small basis sets (6-31G\* and dzvp) calculations give chemical shift values which are too small,



as observed in other cases before [21], but the results get closer to the experiment for the larger basis sets. The differences from the experimental spectrum [17] can be related to differences between the cavities formed by the anions in **2** and in **3**, in which the two cations are located.

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