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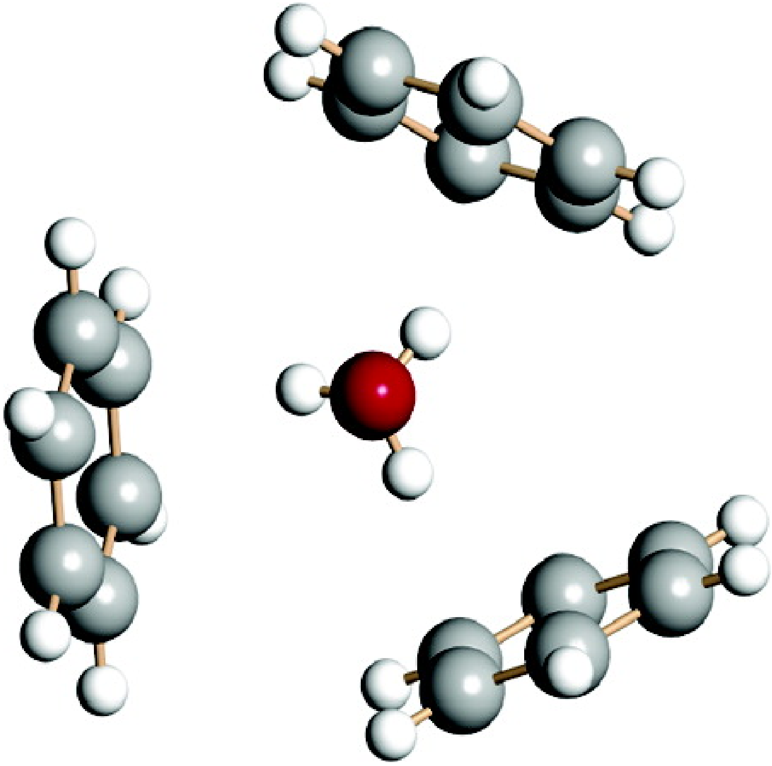

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The Structure of the H_3O^+ Hydronium Ion in Benzene

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Writing H^+ or $H_{solv}{}^+$ frequently suffices for the description of the active protonating species in an acid-catalyzed reaction, reflecting how little attention is paid to the exact nature of strong acids in organic solvents. In O-atom donor solvents, such as ethers, alcohols, and ketones, proton *di*solvates prevail because of the stability of short, strong, low-barrier (SSLB) H-bonds in linear two-coordinate $[solv-H^+-solv]^+$ cations.[1,2] Much less is known about the ionization of acids in weak donor solvents, such as arenes or halocarbons, and there is the additional problem of the role of trace water. Its ubiquitous presence in organic solvents means that hydronium ions (H_3O^+, $H_5O_2{}^+$, etc.) are likely candidates for the active protonating agents in many acid-catalyzed reactions.

In this communication, we show how newly developed carborane acids provide insight into the solvation environment of the H_3O^+ ion in benzene. Carborane acids are chosen because they are the strongest (yet gentlest) pure Brønsted acids presently known,[3] and their large, charge-delocalized conjugate bases allow the isolation of salts whose cations are more discrete than previously accessible. The very weak attraction of carborane anions to cations minimizes ion pairing, better allowing a cation to reveal its response to the solvent environment.

In benzene, the carborane acid $H(CHB_{11}Cl_{11})^3$ protonates water at the 1 equiv level to give relatively concentrated solutions ($\sim 10^{-2}$ M) of the H_3O^+ ion. Single crystals of a tetrabenzene solvate $[H_3O][CHB_{11}Cl_{11}]\cdot 4C_6H_6$, **1**, are deposited upon standing at 6 °C. A novel feature of the X-ray structure is π-complexation of H_3O^+ by three of the benzene solvate molecules (Figure 1). Cation/anion interactions, typical of previous structural analyses of H_3O^+ salts,[4] are absent. The π-interactions of O−H bonds with aromatic acceptors are recognized in H_2O solvates[5] and in benzene/water gas-phase clusters,[6] but the only precedent with H_3O^+ is an ion-paired structure having a benzyl group as part of an anion.[7]

The H-atoms of the pyramidal H_3O^+ ion in **1** lie inside the C−C bond framework of benzene, but do not point directly at the center of the ring. The O···C distances lie in the range of 3.06−3.74 Å. The H···plane normal distances are 2.13, 2.16, and 2.26 Å (black dots in insert a, Figure 1). The vectors of the O−H bonds point somewhat closer to the C−C bonds (black dots in insert b, Figure 1). The DFT-calculated structure of $H_3O(benzene)_3{}^+$ (B3LYP/6-311+G(d,p)) shows a very nearly C_{3v} symmetry structure with the O−H vectors pointing close to a carbon atom of benzene (red dots in Figure 1 inserts; H···C = 2.005 Å, ∠O−H···C = 173.3°). Tribenzene solvation of the H_3O^+ ion is conceptually related to triwater solvation in the familiar "Eigen-type" $H_9O_4{}^+$ ion of aqueous acid solution, which was isolated as a discrete carborane salt some time ago.[8] Tribenzene solvation of H_3O^+ also rationalizes the solubility of a small cation in a nonpolar solvent. It is reminiscent of Ag^+ salts which are soluble in arene solvents because of conceptually analogous π-complexation.

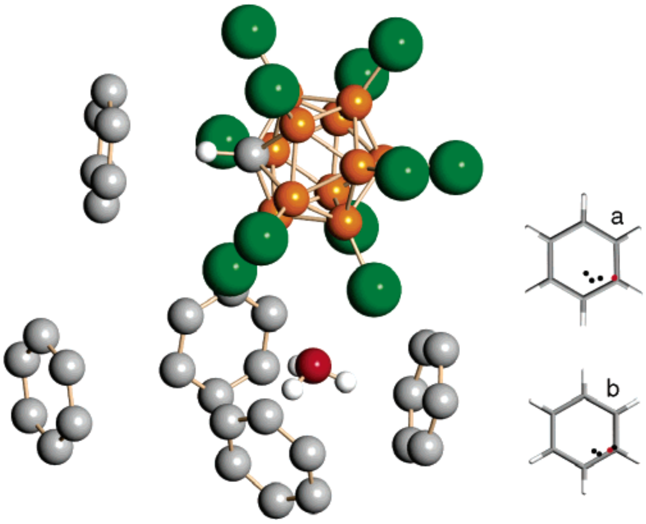

Figure 1. X-ray structure of $[H_3O\cdot 3C_6H_6][CHB_{11}Cl_{11}]\cdot C_6H_6$, **1**, showing tribenzene solvation of H_3O^+. Two lattice benzene solvate molecules sit on symmetry sites so only half of each is contained in the asymmetric unit. $\angle H-O-H_{avg} = 105.6°$ (calcd 112.1°). Insert a: Experimental (black) and calculated (red) positions of the H-atoms normal to the benzene planes. Inset b: Points where the experimental (black) and calculated (red) O−H vectors intersect the benzene planes.

The solid-state IR spectrum of **1** shows two sets of bands for benzene, ascribable to those π-bonded to H_3O^+ and those described as solvating the anion or "free" in the lattice. These two types are best distinguished in the frequency range of the combination bands at 1950−2000 and 1800−1850 cm^{-1} (Figure 2) and the C−H rock (ca. 700 cm^{-1}). Those ascribed to H_3O^+-complexed benzene are the most significantly shifted relative to those of liquid benzene (Table 1). We note in passing that the benzene molecule solvating the anion has a weak π-interaction with the C−H bond of the carborane anion (upper left in Figure 1), enough to lower νC−H of the carborane by 15 cm^{-1} relative to a nonbenzene solvated sample of $[H_3O][CHB_{11}Cl_{11}]$.

The IR spectrum of the H_3O^+ moiety in **1** might be expected to be sensitive to the crystallographic site inequivalency of the three O−H···benzene interactions. However, the doubly degenerate ν_4(E) bend in C_{3v} symmetry is not split, only broadened (Table 2). The O−H interactions with the benzene π-electron density are apparently not particularly sensitive to their precise location over the ring. The observation of a first overtone of ν_4(E) at 3163 cm^{-1}, enhanced by a Fermi resonance interaction with the $\nu_1(A_1)$ stretch, is in agreement with the calculation that the symmetric $\nu_1(A_1)$ vibration has a frequency higher than that of asymmetric ν_3(E) (Table 2).

When $[H_3O][CHB_{11}Cl_{11}]$ is produced in the absence of benzene, where ion pairing (and H-bonding) of H_3O^+ to Cl substituents on the carborane anion can be safely assumed, the frequencies of the H_3O^+ cation are very similar to those in benzene-solvated **1** (Figure

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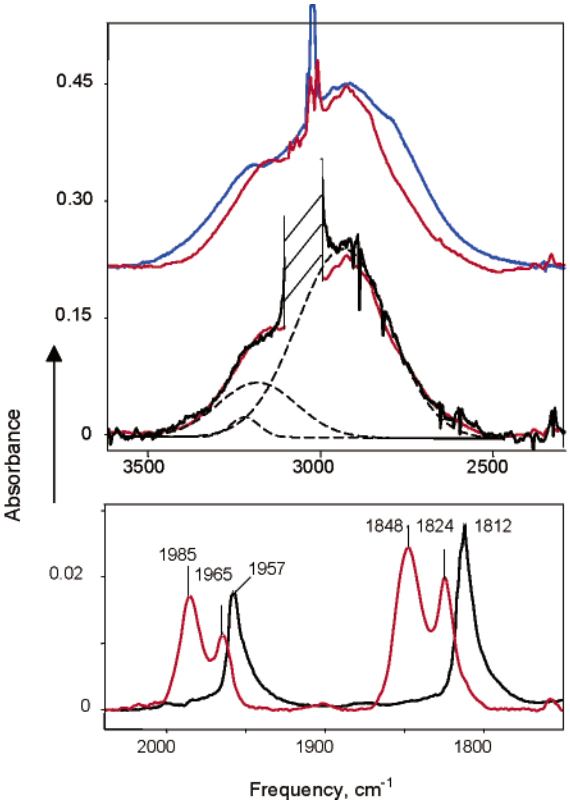

Figure 2. Selected regions of $H_3O(benzene)_3^+$ of **1** in solid state (red) and in benzene solution (black, dashed deconvolution), and of nonsolvated $[H_3O][CHB_{11}Cl_{11}]$ in solid state (blue). In the 2000−1800 cm^{-1} range, the absorbance scale is 15 times smaller for the solution spectrum than that for the solid. The shaded region is nontransparent in benzene solution.

Table 1. Diagnostic IR Bands (cm^{-1}) of Benzene in $H_3O{\cdot}3C_6H_6^+$

phase	type of benzene	combination bands		ρ(CH)	ν(CC) δ(CCH)
calcd	π-bonded with H_3O^+			718	1624vw
solid (**1**)	π-bonded with H_3O^+	1985	1848	700s	1600vw
	π-bonded with anion and "free" in lattice	1965	1824	684s	absent
soln	"free" liquid	1959	1814	675	absent
soln	solvating H_3O^+	1957	1812	masked	absent

Table 2. Diagnostic IR Frequencies (cm^{-1}) of H_3O^+

sample	$2\nu_4$(E)	$\nu_1(A_1)$ ν_3(E)	ν_4(E)
calcd $H_3O{\cdot}3C_6H_6^+$		3156w, 3073s	1652
1 (solid)	3163w	3200m, 2925s	1568 br
$[H_3O][CHB_{11}Cl_{11}]_{(s)}$	3200	2920 s[a]	1603, 1572
1 (benzene soln)	3223w	3170m, 2930s	~1590 br

[a] Multiple overlapping bands due to lowered symmetry.

2, Table 2). This suggests that the H-bonding acceptor abilities of the chlorocarborane anion and benzene are quite comparable. The greater width of the O−H stretch bands in the nonsolvated, ion-paired form (Figure 2, blue) and the definite splitting of the ν_4(E) bend into two components (Table 2) indicate a more significant lowering of symmetry from C_{3v} in the ion-paired form than in **1**.

In frequency, intensity, and contour, the IR spectrum of the H_3O^+ cation in benzene solution practically coincides with that of solid **1** (black and red spectra in Figure 2, respectively). This means that the molecular state of H_3O^+ in both phases is very similar and is properly described to $H_3O{\cdot}3C_6H_6^+$. Nevertheless, the spectrum of π-complexed benzene in solution differs from that in solid **1** in a manner that indicates symmetry lowering of benzene. In particular, a band at ~1600 cm^{-1} is weakly observed in solid **1** and in the calculated spectrum, but does not appear in solution (Table 1). This band is not IR active under D_{6h} symmetry but presumably gains IR allowedness as the symmetry is lowered. We note that in solid **1**, and in the calculated structure, the OH bond is directed close to a carbon atom of benzene (Figure 1, inset b), with calculated lengthening of the proximate C−C bonds by 0.006 Å relative to the remote bonds. The absence of the 1600 cm^{-1} band in solution suggests that the direction of OH bond π-interaction is closer to the center of the benzene ring, disturbing its symmetry less. Such behavior probably correlates with the softness of the $O{-}H{\cdots}C_6H_6$ π-interaction. Nevertheless, the intensity of the 1800−2000 cm^{-1} bands of π-complexed benzene in solution is ~10 times that in solid **1**. Benzene molecules from the secondary solvation shell must be affected by the cation and contribute intensity to these bands. It is clear that there is considerable subtlety and high information content in the IR spectrum of the $H_3O{\cdot}3C_6H_6^+$ ion.

Finally, there is ^{1}H NMR evidence for π-complexation of H_3O^+ by benzene in solution. In liquid SO_2, the H_3O^+ resonance appears at 11.2 ppm, similar to values observed under other conditions.[9] In benzene, however, it shifts very significantly upfield to 6.2 ppm (DFT calcd. 5.4 ppm). This is readily rationalized by a strong ring current effect.

In preliminary studies on higher hydration levels of H^+ in benzene, we find that addition of one water molecule to H_3O^+ cleanly produces the Zundel-type hydronium ion, $H_5O_2^+$. The carborane salt of this ion is even more soluble in benzene (~0.3 M) than **1**, suggesting significant π-complexation. Indeed, the X-ray structure of the isolated salt, $[H_5O_2][CHB_{11}Cl_{11}]{\cdot}C_6H_6$, **2**, shows a benzene solvate molecule π-complexed to one of the O−H bonds of the $H_5O_2^+$ cation.

In summary, π-arene complexation of hydronium ions is an important structural feature of aquated acids in benzene. In addition to their importance to the nature of the protonating species in acid catalysis, the present results are relevant to biological proton transport where "Eigen" versus "Zundel"-type hydronium ion structures are being debated.[10] Moreover, the H_3O^+ ion interacts with benzene in a manner related to that of the K^+ ion. Arene-rich membrane channels have been implicated in K^+ transport,[11] so it is not unreasonable to speculate that arene rings could participate in the biological transport of protons via π-complexed hydronium ions.

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Supporting Information Available: Experimental details of sample preparation, IR spectra, X-ray crystallography, and DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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