

Isolating Benzenium Ion Salts

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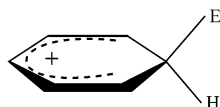
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Abstract: When partnered with carborane anions, arenium ions are remarkably stable. Previously investigated only at subambient temperatures in highly superacidic media, protonated benzene is readily isolated as a crystalline salt, thermally stable to >150 °C. Salts of the type [H(arene)][carborane] have been prepared by protonating benzene, toluene, *m*-xylene, mesitylene, and hexamethylbenzene with the carborane superacid H(CB₁₁HR₅X₆) (R = H, Me; X = Cl, Br). They have been characterized by elemental analysis, X-ray crystallography, NMR and IR methods. Solid-state ¹³C NMR spectra are similar to those observed earlier in solution, indicating that lattice interactions are comparable to solution solvation effects. The acidic proton(s) of the arenium cations interact weakly with the halide substituents of the anion via ion pairing. This is reflected in the dependence of the C–H stretching frequency on the basicity of the carborane anion. Bond lengths in the arenium ions are consistent with predominant cyclohexadienyl cation character, but charge distribution within the cation is less well represented by this resonance form. Structural and vibrational comparison to theory is made for the benzenium ion (C₆H₇⁺) with density functional theory at B3LYP/6-31G* and B3P86/6-311+G(d,p) levels. The stability of these salts elevates arenium ions from the status of transients (Wheland intermediates) to reagents. They have been used to bracket the solution-phase basicity of C₆₀ between that of mesitylene and xylene.

Introduction

Electrophilic aromatic substitution is one of the most studied reactions of organic chemistry,¹ and arenium ions are widely accepted as obligatory intermediates in these reactions.^{2–4} They are commonly called Wheland⁵ intermediates but might more accurately be ascribed to von Pfeiffer and Wizinger,⁶ who laid out the principles for bromination in 1928. Following Brown and Pearsall,⁷ they are widely believed to have σ -complex structures.



Starting in the 1940s and 1950s, observations of persistent arenium ions were made in strong acids in the labs of Norris,⁸ Brown,⁷ Olah,⁹ Mackor,¹⁰ Doering,¹¹ and Gillespie.¹² The advent of NMR spectroscopy and the use of superacids allowed extensive investigations of arenium ions to be made, culminating in the characterization of the benzenium ion (C₆H₇⁺) at dry ice temperatures in 1971.¹³ Arenium ions have been isolated with most of the more basic arenes (e.g., methylated benzenes) but in a very comprehensive review in 1984, Koptuyg³ remarked how little the most reliable structural tool of X-ray crystallography had been applied to their characterization. This reflected the culture of organic chemistry, where NMR rather than X-ray crystallography was the structural tool of choice. It also reflects the difficulty of growing and collecting single crystals at subambient temperatures in viscous superacid media, although persistent efforts have paid off in SbF₅-based systems for some alkyl carbocations.¹⁴

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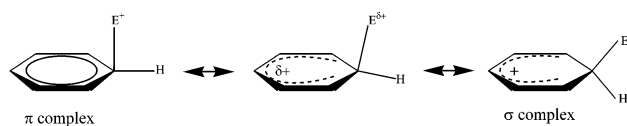
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Structural models for arenium ion intermediates can be found in the chemistry of benzenes that are highly substituted with electron-donating groups. For example, the heptamethylbenzenium ion ($C_6Me_7^+$) is stable at room temperature and its chloroaluminate salt was characterized by X-ray crystallography as early as 1968.¹⁵ The structure conformed to expectations of a σ complex. More recently, Hubig and Kochi⁴ have been successful in using hexamethylbenzenes and related benzenes to isolate adducts with selected electrophiles at dry ice temperatures. A variety of other stabilizing substituents such as pyrrolidine,¹⁶ transition metal,¹⁷ or silyl¹⁸ groups have been exploited to render arenium ion salts isolable for X-ray crystallographic characterization.

The need for accurate structural data on authentic intermediates (rather than highly substituted models) has become more pressing because conventional wisdom about the structure of arenium ions is being challenged. In 1993, Lambert et al.¹⁹ reported the structure of a silylarenium ion that did not conform to the structural expectations of a σ complex. The expected sp^3 character of the silylated carbon atom was only partially developed. We proposed that the structure should be viewed neither as a traditional σ complex^{20–22} nor as a π complex²³ but as a point along a σ – π continuum.^{24–26}



This viewpoint is gaining momentum with its adoption and elaboration in recent reviews by Lambert et al.²⁷ and by Hubig and Kochi.⁴ A closely related structure has also been found in aluminum arene chemistry.²⁸ When the electrophile is a large carbocation (e.g., *tert*-butyl) in the gas phase, π complexes are believed to be only slightly higher in energy than σ complexes.^{29,30}

The isolation and X-ray crystallographic characterization of the benzenium ion has remained elusive for a long time. It has been our thesis that this is not because it is intrinsically unstable. Rather, the conditions under which it has been generated lead to decomposition. High acidity is an obvious necessity to prevent simple deprotonation, but in addition, the conjugate base (i.e., the counterion) must be inert. Typically, the strong acids and

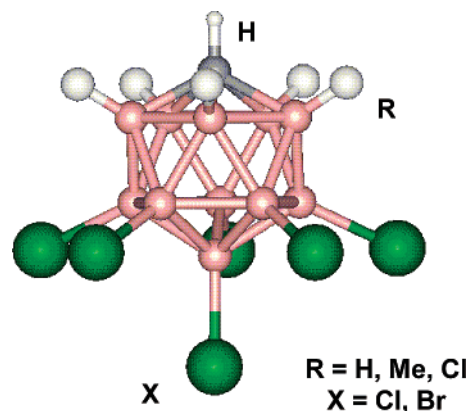


Figure 1. Icosahedral carborane anions used in this work, $CB_{11}HR_5X_6^-$ ($R = H, Me; X = Cl, Br$).

superacids that have been used to investigate arenium ions have been based on halo- or oxyanion conjugate bases. The intrinsic stability of these anions and their nucleophilicity limits the stability of cation partners in a number of identifiable ways. Haloanions frequently decompose at room temperature to give hydrogen halides and a Lewis acid. For example, although protonated toluene has been isolated as a BF_4^- salt at low temperature, it decomposes above $-50^\circ C$ to toluene, HF, and BF_3 .³¹ The anions of oxyacids (e.g., HSO_4^-) can be both nucleophiles and oxidants, leading to decomposition. The reaction of SO_2 with arenes, originally thought to be an inert solvent for superacids, caused considerable confusion in the early characterization of arenium ions because of sulfonation reactivity.³² The strongest superacids (e.g., Magic acid) are based on the addition of SbF_5 to a Brønsted acid. However, SbF_5 is a potent oxidant and this oxidative capacity is probably responsible for the decomposition of many arenes and arene-like molecules, e.g., C_{60} .³³ Clearly, the limitations of typical superacids in stabilizing arenium ions lie in the nature of their conjugate bases. Only with more inert, less nucleophilic anions can the stability of cations be increased.

Two of the least nucleophilic classes of anions available to modern chemistry are the perfluorinated tetraphenylborates and carboranes.³⁴ In 1999, $F_{20}-BPh_4^-$ was used to obtain the X-ray structure of a protonated pentamethylbenzene salt, $[C_6Me_5H_2]-[F_{20}-BPh_4]^-$.³⁵ At the same time, the icosahedral carborane $CB_{11}H_6Cl_6^-$ was used to prepare the first isolable salt of the benzenium ion.³⁵ With a recent new variant of the anion, single crystals of a benzenium ion salt suitable for X-ray diffraction were obtained.³⁶ The boron–phenyl bonds in the $F_{20}-BPh_4^-$ anion are subject to room temperature cleavage at the acidity of the xylenium ion, so only carborane anions (Figure 1) are suitable for isolating the arenium ion salts of the most weakly basic arenes.

Methods for preparing the conjugate acids of carborane anions, H(carborane), have recently been developed,³³ and these acids are ideal reagents for protonating arenes. This paper is

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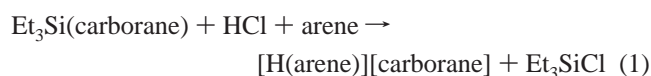
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the full account arising out of our preliminary communications in this area.^{35,36}

Results and Discussion

Synthesis and Isolation. The main arenes used in this study were benzene, xylene, toluene, mesitylene, and hexamethylbenzene. The carborane counterions were $\text{CB}_{11}\text{H}_6\text{X}_6^-$ ($\text{X} = \text{Cl}$ or Br) and their 2,3,4,5,6-pentamethylated counterparts $\text{CB}_{11}\text{HMe}_5\text{X}_6^-$ (Figure 1).

The key to generating the high Brønsted acidity needed to protonate arenes is the strong Lewis acidity of trialkylsilylium ion-like species, $\text{R}_3\text{Si}^{\delta+}(\text{carborane}^{\delta-})$. While these species do not contain free silylium ions, they behave like silylium ions.²⁶ They are extremely potent halophiles and have been used to extract chloride ion from a variety of sources. The greater strength of the $\text{Si}-\text{Cl}$ bond (ca. $113 \text{ kcal}\cdot\text{mol}^{-1}$) relative to the $\text{H}-\text{Cl}$ bond ($103 \text{ kcal}\cdot\text{mol}^{-1}$) provides the driving force for the in situ preparative reaction of the carborane superacids, $\text{H}(\text{carborane})$ (eq 1). Ethyl groups on Si are chosen so that the metathesis byproduct, Et_3SiCl , is volatile and easily removed.



Alternatively, isolated carborane superacids can be reacted directly with an arene:



For volatile arenes such as benzene, a simple gas/solid reaction with the solid superacid is sometimes sufficient to produce the arenium ion salts. For liquid arenes, straightforward addition and vacuum removal of excess arene gives clean product in essentially quantitative yield. For solid arenes such as hexamethylbenzene, a less basic arene solvent (e.g., benzene or toluene) is used and addition of hexanes precipitates crystalline products in excellent yield. Exclusion of water is critical to the success of this chemistry. Solvent volumes must be kept to a minimum, glassware is silylated with Me_3SiCl , and solvents must be very carefully dried. Handling is done in a drybox that is in excellent condition ($\text{H}_2\text{O} < 0.5 \text{ ppm}$). Even when isolated, the crystalline salts act as desiccants, forming H_3O^+ or H_5O_2^+ salts. This conversion can be monitored by IR spectroscopy (see below).

Acid-catalyzed rearrangements of substituted benzenes are well-known and are presumed to occur via 1,2-shifts in arenium ions.^{3,37} One of the most familiar is the isomerism of xylenes to an equilibrium mixture where *m*-xylene predominates. It was not surprising, therefore, to find that on the synthetic time scale at room temperature the carborane acids are strong enough to convert *o*-xylene to *m*-xylene. The isolated salt from *o*-xylene was shown to contain the *m*-xylenium cation by X-ray structure. In addition, low-temperature ^1H NMR after low-temperature redissolution in $\text{CH}_2\text{Cl}_2-d_2$ was used to confirm the *m*-isomer.

It takes several orders of magnitude of acidity above 100% H_2SO_4 to protonate benzene, so the carborane acids readily qualify as superacids. We therefore investigated the protonation of arenes less basic than benzene itself, i.e., benzenes with electron-withdrawing groups. When carborane acids are added

to *o*-dichlorobenzene and *o*-difluorobenzene, solids consistent with arenium ion formation can be isolated by evaporation. However, isomerization is evident, and in time, some decomposition occurs so analytically pure products were not isolated. The ^{13}C cross-polarization magic-angle spinning (CPMAS) spectrum of the solid from *o*-dichlorobenzene showed two carbocationic centers (180, 190 ppm) and two methylene sites (44, 55 ppm), consistent with a mixture of ortho and meta isomers.³ The corresponding spectrum from *o*-difluorobenzene was too complex to interpret. Arenes containing CF_3 substituents showed rapid decomposition, presumably because of elimination of HF.

Finally, we note that intermolecular proton transfer rates are sufficiently fast that ring C–H/C–D exchange occurs rapidly on the synthetic time scale in deuterated solvents. In this way, samples of ring-deuterated arenium ions were readily prepared for IR spectroscopy. Deuterium also washes into the B–H bonds of the nonmethylated carborane anions when they are partnered with the more acidic deuterated arenium ions, such as the benzenium and toluenium ions.

Thermal Stability. Thermal stability of the isolated salts was investigated by differential thermal analysis (DTA) with the instrument inside a drybox. At heating rates of 4 deg/min, unsolvated salts showed no significant weight loss (<2%) up to 150 °C. To show sample integrity after heating, IR spectra were run on a sample of $[\text{H}(\text{benzene})][\text{CB}_{11}\text{HMe}_5\text{Br}_6^-]$ before and after heating to 150 °C for 5 min. They were identical (see Supporting Information Figure S8). With time above these temperatures, the salts do not melt but slowly turn brown and lose weight. ^1H NMR spectroscopy on a sample of $[\text{C}_6\text{H}_7][\text{CB}_{11}\text{H}_6\text{Cl}_6^-]$ that had been decomposed at ca. 200 °C in a sealed tube revealed the presence of benzene and chlorobenzene. Evidently, at elevated temperatures the B–Cl bonds of the carborane anion are susceptible to protonation, loss of HCl, and possible intervention of benzene as a nucleophile. Nevertheless, thermal stability to ca. 150 °C illustrates the extraordinary stability imparted to the benzenium ion when partnered with a carborane counterion.

X-ray Structures. Single crystals of arenium ion salts suitable for X-ray crystallography were grown at ambient temperature. The anion was the hexabromocarborane, $\text{CB}_{11}\text{H}_6\text{Br}_6^-$, for the four methylated arenes: toluenium, *m*-xylenium, mesitylenium, and hexamethylbenzenium. For crystallizing the benzenium ion, the pentamethylated carborane anion, $\text{CB}_{11}\text{HMe}_5\text{Br}_6^-$, was the most successful. Disorder was evident in the benzenium ion structure, where the C_6H_7^+ cation is located at a special position requiring a center of symmetry. It was modeled as a 50:50 mixture of benzenium ions whose protonated (C_1) and para (C_4) carbon atoms are interchanged.

As shown in Figure 2, the structures consist of essentially discrete cations and anions. The acidic protons on the sp^3 carbon atoms of the arenium ions are within van der Waals contact of Br atoms of the carborane anions, indicating some degree of ion pairing (dashed lines). H---Br distances are in the range 2.6–3.3 Å and can be considered as weak H-bonds. The proximity of the Br atoms to the acidic C–H bond(s) is consistent with a Mulliken population analysis of the benzenium ion that shows the C–H bonds on the protonated carbon atom are the most polar (Figure 3). The valence bond representation of the benzenium ion as a cyclohexadienyl cation is misleading in this

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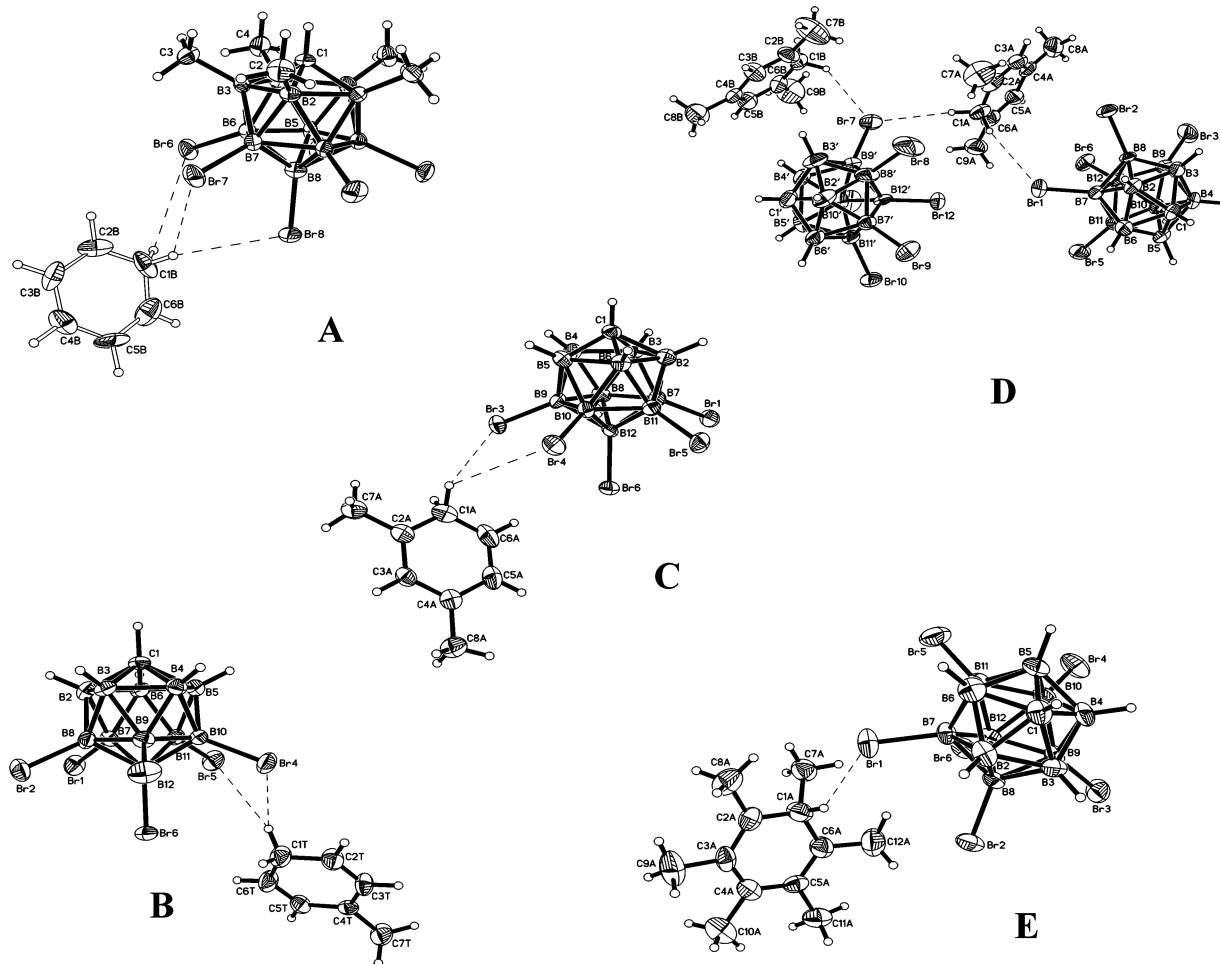


Figure 2. Thermal ellipsoid (50%) representations of the crystal structures of arenium ions. (A) Benzenium in $[\text{C}_6\text{H}_7][\text{CB}_{11}\text{H}(\text{CH}_3)_5\text{Br}_6]$. (B) Toluenum in $[\text{HC}_6\text{H}_5(\text{CH}_3)][\text{CB}_{11}\text{H}_6\text{Br}_6]$. (C) *m*-Xylenium in $[\text{HC}_6\text{H}_4(\text{CH}_3)_2][\text{CB}_{11}\text{H}_6\text{Br}_6]$. (D) Mesitylenium in $[\text{HC}_6\text{H}_3(\text{CH}_3)_3][\text{CB}_{11}\text{H}_6\text{Br}_6]$. (E) Hexamethylbenzenium in $[\text{HC}_6(\text{CH}_3)_6][\text{CB}_{11}\text{H}_6\text{Br}_6]$. Solvate molecules have been omitted for clarity. Since only the asymmetric unit is shown for B–E, not all C–H...Br interactions are indicated with dashed lines.

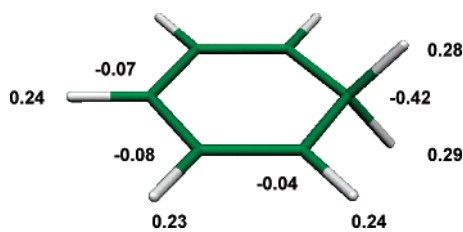
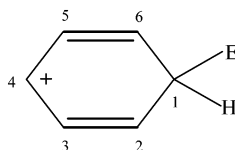


Figure 3. Mulliken population analysis calculated for the C_6H_7^+ ion.

regard because it places the positive charge on a carbon atom, para (or ortho) to the site of protonation.



As shown in Figure 3, the positive charge is delocalized onto the H atoms and is greatest at the site of protonation.

On the other hand, the cyclohexadienyl resonance form is a very good representation from the point of view of bond lengths and angles (Table 1). When data on the benzenium (which suffer from disorder) are excluded, the bond lengths to the protonated (C_1) carbon atom in the methylated arenium ions (1.40–1.47

Å) are the longest, as expected for sp^2 – sp^3 bonds. The C_2 – C_3 and C_5 – C_6 bond lengths (1.33–1.39 Å) are the shortest, consistent with double bonds. The C_3 – C_4 and C_4 – C_5 bond lengths (1.37–1.43) are also mostly short, consistent with sp^2 – sp^2 bonds to a formally carbocationic center. Inclusion of cyclohexadienyl resonance forms with the positive charge located at the ortho (rather than para) carbon atoms rationalizes these short bonds. The bond angles show little in the way of trends, all being within 4° of idealized values of 120° . A natural bond orbital analysis of the calculated benzenium ion structure indicates that the principal resonance contribution corresponds to the cyclohexadienyl structure with formal double bonds C_2 – C_3 and C_5 – C_6 .³⁸ An atoms-in-molecules analysis supports this view with these bonds having the greatest ellipticity (C_1 – C_2 , 0.13; C_2 – C_3 , 0.21; C_3 – C_4 , 0.05).^{39–40}

The six-atom cores are essentially planar. The greatest deviation of any particular carbon atom from the mean plane is found at the protonated carbon atom, C_1 . We measure this

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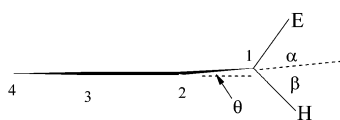
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Table 1. Selected Bond Lengths and Angles for Chemically Equivalent Bonds in Arenium Ions^a

cation	C ₁ –C ₂	C ₂ –C ₃	C ₃ –C ₄	C ₆ –C ₁ –C ₂	C ₁ –C ₂ –C ₃	C ₂ –C ₃ –C ₄	C ₃ –C ₄ –C ₅
	C ₁ –C ₆	C ₅ –C ₆	C ₄ –C ₅		C ₅ –C ₆ –C ₁	C ₄ –C ₅ –C ₆	
benzenium (calcd)	1.473 ^b	1.373	1.413	117.0	120.9	119.1	123.0
benzenium (exptl)	1.461 ^c	1.366	1.406	117.4.0	120.8	119.0	123.0
	1.381(6)	1.345(6)	1.391(6)	119.8(3)	120.1(3)	120.2(3)	119.8(3)
toluenium	1.391(6)	1.345(6)	1.381(6)	116.0(5)	120.2(3)	120.1(3)	119.5(5)
	1.451(8)	1.336(8)	1.394(7)		121.2(5)	121.0(5)	
<i>m</i> -xylenium	1.448(8)	1.334(8)	1.409(7)	119.2(5)	121.5(5)	120.7(5)	119.6(4)
	1.429(6)	1.376(6)	1.382(6)		118.7(4)	120.4(4)	
mesitylenium	1.400(8)	1.377(7)	1.427(6)	120.6(8)	121.5(5)	118.9(4)	120.0(7)
	1.414(12)	1.384(11)	1.370(10)		118.2(7)	121.7(7)	
pentamethylbenzenium ^d	1.425(12)	1.387(11)	1.380(10)	119.4(2)	117.5(7)	121.8(7)	123.3(2)
	1.455(3)	1.358(4)	1.426(4)		120.4(2)	118.3(2)	
hexamethylbenzenium	1.463(8)	1.356(8)	1.413(8)	117.0(5)	120.3(5)	118.7(5)	123.5(5)
heptamethylbenzenium ^e	1.467(8)	1.383(8)	1.387(8)	115.4(8)	121.1(9)	119.7(5)	122.8(9)
	1.490(9)	1.36(1)	1.407(9)				

^a Atoms are numbered sequentially from the protonated atom (C₁). Bond lengths are given in angstroms; bond angles are given in degrees. ^b B3LYP/6-31G*. ^c B3P86/6-311+G(d,p). ^d Reference 35. ^e Reference 15.

displacement as the dihedral angle (θ) between the C₂–C₁–C₆ plane and the least-squares plane of the five-atom C₂–C₆ core.



These tilt angles are greatest in the hexamethylbenzenium ion (3.7°) and one of the two independent mesitylenium ions (4.3°). The variation is ascribed to asymmetric interactions of the acidic protons (and possibly the C₁ methyl groups) with Br atoms of the anion, i.e., to packing forces.

The angles of elevation (α , β) subtended by the substituents (E, H) on the protonated carbon atom are of interest in describing arenium ions as σ complexes or as points along a σ – π continuum. An idealized π complex, such as that observed⁴² with E = Ag⁺, has $\alpha = 90^\circ$ and $\beta = 0^\circ$. An idealized σ complex, with a tetrahedral sp³ C₁ carbon atom would have α and $\beta = 55^\circ$. The angle α is well-defined in the case of the hexamethylbenzenium ion because the out-of-plane substituent E is a methyl group whose C atom is accurately located by X-ray crystallography. In all the other present structures, E is a hydrogen atom. These were located experimentally from electron density difference maps, but the usual caution must be taken in assigning precise positions for H atoms from X-ray structures. They are probably reliable to within ca. 5°. Table 2 lists available α and β angles for the present structures and selected arenium ions from the literature. The data are portrayed pictorially in Figure 4, which illustrates how the electrophiles lie as points on a σ – π continuum. The shaded sector represents the arenium ions reported in the present work. It is clear they are all classical σ complexes. The assumption that methylated benzenium ions are good structural models for less basic benzenium ions is seen to have had good validity. Softer electrophiles such as Br⁺ and R₃Si⁺ have greater π character.

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 (42) Shelly, K.; Finster, D. C.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 5955–5959.

Table 2. Angles of Elevation for Substituents in Arenium Ions

arenium ion	E	α , deg	β (to H), deg
benzenium (calcd)	H	50	50
benzenium (exptl)	H	53(2)	53(2)
toluenium	H	44–53	44–53
<i>m</i> -xylenium	H	38–64	38–64
mesitylenium	H	43–62	43–62
pentamethyl ^a	H	50	50 (to CH ₃)
hexamethyl	CH ₃	41	50 (to CH ₃)
heptamethyl ^b	CH ₃	56	56 (to CH ₃)
(chloromethyl)hexamethyl ^c	CH ₂ Cl	43	63 (to CH ₃)
chlorohexamethyl ^d	Cl	56	50 (to CH ₃)
bromohexamethyl ^d	Br	68	42 (to CH ₃)
triethylsilyl-4-methyl ^e	Et ₃ Si	76	<i>f</i>
toluene–Al(C ₆ F ₅) ₃ ^g	Al(C ₆ F ₅) ₃	84	10
Ag ⁺ π complex ^h	Ag ⁺	90	0

^a Reference 35. ^b Reference 15. ^c Reference 41. ^d Reference 4. ^e Reference 19. ^f H not located. ^g Reference 28. ^h Reference 42.

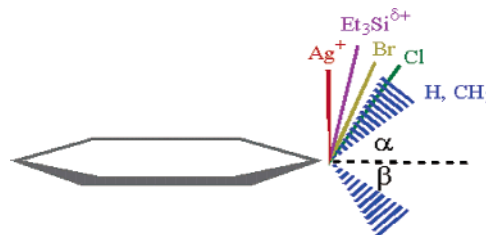


Figure 4. Graphical display of arenium ion structures illustrating the σ – π continuum. The shaded sectors represent the structures reported in this paper.

NMR Spectroscopy. Given the past reliance on solution NMR spectroscopy to characterize arenium ions, there is a fundamental question concerning the degree to which solvation and/or ion pairing in acidic media is important for their stabilization. This has been addressed by Haw and co-workers⁴³ for arenium ions on an AlBr₃ surface. To probe the congruency of solution, surface and crystalline state structures, we measured the CPMAS ¹³C NMR spectra of two of the more exposed arenium ions (benzenium and toluenium). Data for solution and solid state are compared in Table 3. Differences between the crystalline state, surface-absorbed state, and liquid superacid

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Table 3. Comparison of Solid-State and Solution ^{13}C NMR Spectra of Arenium Ions

ion	state	temp ($^{\circ}\text{C}$)	C_1	C_2	C_3	C_4	C_5	C_6
benzenium ^a	crystalline	-120	52	184	136	176	136	184
benzenium ^b	$\text{HSO}_3/\text{SbF}_5/\text{SO}_2\text{ClF}$	-135	52.2	186.6	136.9	178.1	136.9	186.6
benzenium ^c	$\text{HBr}/\text{AlBr}_3/\text{surface}$	-195	53	185	138	178	138	185
toluenium ^d	crystalline	25	45	179	126	203	126	179
toluenium ^d	crystalline	-70	47	180	139	208	139	180
toluenium ^e	$\text{HSO}_3\text{F}/\text{SbF}_5$	-80	46.7	178.6	138.5	201.0	138.5	178.6
toluenium ^c	$\text{HBr}/\text{AlBr}_3/\text{surface}$	-195	49	179	139	200	139	179

^a Anion = $\text{CB}_{11}\text{H}_6\text{Cl}_6^-$. ^b Reference 13. ^c Reference 43. ^d Anion = $\text{CB}_{11}\text{H}_6\text{Br}_6^-$. ^e Reference 13.

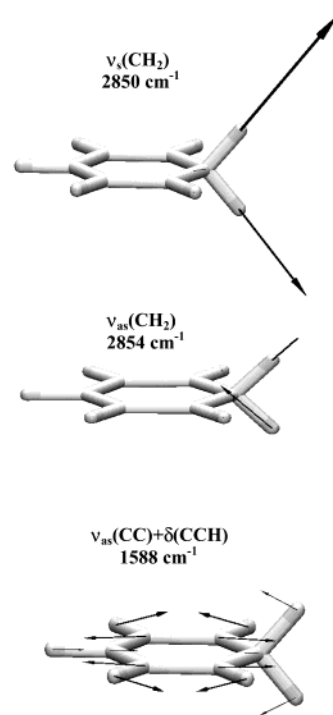
media are small. This suggests that anisotropic solvation of these arenium ions has a minimal effect on charge distribution within the cation. It is consistent with arenium ions being basically free cations and with the role of carboranes as weakly interacting spectator anions.

IR Spectroscopy. The infrared spectroscopy of arenium ions has not been studied extensively because of experimental difficulties associated with the production of good quality samples that do not react with the cell window materials.³ Spectra for methylated benzenium ions were obtained in 1964 in the labs of Koptuyg³ and Perkampus⁴⁴ with haloaluminate or gallate counterions, and low-resolution spectra of the C_6H_7^+ and C_6D_7^+ ions have also obtained.⁴⁴ With stable crystalline salts and modern calculational methods, we are able to make a significantly improved study.

(a) Benzenium Ion. From the DFT-calculated structure of the anion-free C_6H_7^+ ion, the vibrational modes of the benzenium ion were calculated and appropriately scaled (0.96).^{45a} Three of the more important IR-active modes for the present study are illustrated in Figure 5, and frequencies are listed in Table 4. The full analysis is available as Supporting Information. Modes due to $\nu_{\text{as}}(\text{CH}_2)$ and $\nu_{\text{s}}(\text{CH}_2)$ are diagnostic of the acidic methylene group. They occur at almost identical frequencies near 2850 cm^{-1} . Symmetry lowering leads to IR activity of an A_1 symmetry mode of benzene, $\nu(\text{CC}) + \delta(\text{CCH})$, at 1588 cm^{-1} in the benzenium ion. Compared to free benzene ($\nu\text{C-H} = 3090, 3071, 3036\text{ cm}^{-1}$), all the aromatic-type C-H stretching frequencies increase because of the positive charge that is delocalized over all H atoms.

A well-resolved spectrum for the $\nu\text{C-H}$ region is shown in Figure 6 for $[\text{C}_6\text{H}_7][\text{CB}_{11}\text{HMe}_5\text{Br}_6]$. The entire spectrum (available as Supporting Information) shows the same bands as predicted by theory, but the frequencies are shifted due to an effect of the counterion. The most strongly perturbed bands are associated with the acidic methylene group, where $\nu(\text{CH})$ frequencies move ca. 100 cm^{-1} to lower energy (Table 4). This was anticipated from the earlier studies on methylated arenium ions with aluminate and gallate counterions³ and from the present X-ray structures, which show interactions of the acidic C-H bonds with Br atoms of the carborane anions. A weakening of the C-H bonds, and consequent lowering of the stretching frequencies, is readily understood in terms of the C-H \cdots Br hydrogen bonding and charge redistribution associated with ion pairing.

Although bands due to $\nu_{\text{as}}(\text{CH}_2)$ and $\nu_{\text{s}}(\text{CH}_2)$ are expected to be sufficiently close in frequency so as to appear as a single

**Figure 5.** Three key vibrational modes calculated for the C_6H_7^+ ion.

band, a split band (separated by about 50 cm^{-1}) is observed experimentally (Table 4). The deuterated ion shows the same pattern with expected increased mass ratios of 1.35 and 1.37. This splitting presumably arises from asymmetry in the C-H \cdots Br interactions, as seen in the X-ray crystal structure. Sometimes a second band appears, indicative of a second type of environment for the cation. The sensitivity of these bands to the nature of the anion leads to an ordering of anion interaction strength that reflects the basicity of the anion interaction. As shown in Table 4, the average frequency for $\nu(\text{CH}_2)$ decreases in the order no anion > $\text{CB}_{11}\text{H}_6\text{Cl}_6^-$ > $\text{CB}_{11}\text{H}_6\text{Br}_6^-$ > $\text{CB}_{11}\text{H}_6\text{I}_6^-$ > $\text{CB}_{11}\text{HMe}_5\text{Br}_6^-$. With one minor exception, understandable in terms of the presence of two types of ions, this is also reflected in the decreasing order of the highest energy frequency for $\nu(\text{CH})_{\text{aromatic}}$. The ordering is understood as the result of polarizability of the halide substituents on the anion ($\text{Cl} < \text{Br} < \text{I}$). Pentamethylation of the hexabromocarborane anion is seen to increase its basicity, consistent with an electron-donating effect.

The interaction of C_6H_7^+ with anions was modeled in computer with methyl bromide. As shown in Figure 7, it has a stable configuration with a monodentate interaction of the Br atom with the acidic methylene group. The H \cdots Br distance is 2.77 \AA . This is shorter than the distances seen in the X-ray structure ($2.95\text{--}3.05\text{ \AA}$), presumably because the interaction is monodentate for an isolated ion. Figure 7 illustrates one of the two $\nu(\text{CH}_2)$ modes, which occur at 2852 and 2775 cm^{-1} . The average value (2813 cm^{-1}) places methyl bromide approximately midway between no anion and the weakest interacting carborane anion ($\text{CB}_{11}\text{H}_6\text{Cl}_6^-$). It suggests that halocarborane anions have donor properties not much greater than those of halocarbon solvents.

(b) Methylated Arenium Ions. The stretching frequencies of the acidic C-H protons in the arenium ions derived from methylated arenes are listed in Table 5. The bands are faithfully

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Table 4. Frequencies of the $C_6H_7^+$ Ion as a Function of Counterion^a

counterion (or complex)	$\nu(CH_2)$ (average)	$\nu(CH)_{aromatic}$	$\nu(CC) + \delta(CCH)$
none (calcd)	2854, 2850 (2853)	3109, 3093, 3083	1588
CH ₃ Br (calcd)	2852, 2775 (2813)	3132, 3111, 3082, 3080, 3074	1584
N ₂ ^b	2809, 2792, (2801)	3081, 3109	
CB ₁₁ H ₆ Cl ₆ ⁻	2770, 2720 (2745)	3100, 3072, c, 3040, 3028	1601
CB ₁₁ H ₆ Br ₆ ⁻	2757, 2714 (2736)	3095, 3073, 3066, c, 3023	1600
CB ₁₁ H ₆ I ₆ ⁻	2746, 2696 (2721)	3088, 3068, 3060, c, c	1598
CB ₁₁ HMe ₅ Br ₆ ⁻	2700, 2672 (2686), 2785 ^d	3093, 3087, 3067, 3060, 3034	1598
CB ₁₁ HMe ₅ Br ₆ ⁻	(2043, 1981) ^e		(1558) ^e

^a Frequencies are given in reciprocal centimeters. ^b Reference 45b. ^c Band is overlapped by $\nu(CH)$ of anion. ^d Assigned to a second type of molecule. ^e Values for $C_6D_7^+$.

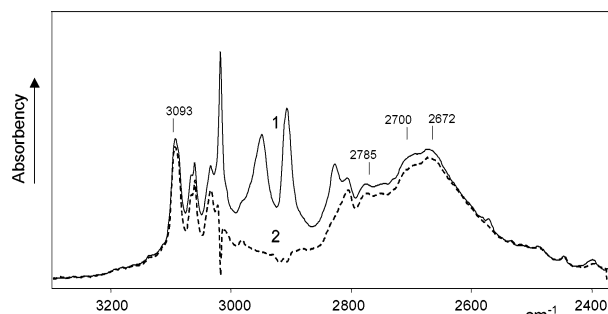


Figure 6. IR spectra of the $\nu(CH)$ region of $[C_6H_7][CB_{11}HMe_5Br_6]$ (solid line) and the $C_6H_7^+$ ion (dashed line) after subtraction of anion bands. The anion spectrum was obtained from the difference spectrum of $[C_6H_7][CB_{11}HMe_5Br_6]$ and $[C_6D_7][CB_{11}HMe_5Br_6]$.

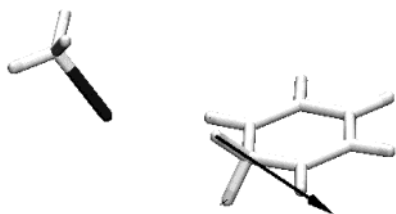


Figure 7. Calculated structure of the $CH_3Br \cdot C_6H_7^+$ adduct, showing one of the $\nu(CH)$ modes.

Table 5. C–H Stretching Frequencies for the Acidic Methylene Proton(s) as a Function of Arene with Two Different Bromocarborane Anions^a

arenium	anion	$\nu C-H$	$\nu C-D$
benzenium	CB ₁₁ HMe ₅ Br ₆ ⁻	2672, 2700, 2785 ^b	1981, 2043 ^b
mesitylenium	CB ₁₁ HMe ₅ Br ₆ ⁻	2776	2055
hexamethylbenzenium	CB ₁₁ HMe ₅ Br ₆ ⁻	2876 ^b	2118 ^b
benzenium	CB ₁₁ H ₆ Br ₆ ⁻	2757, 2714	
toluenium	CB ₁₁ H ₆ Br ₆ ⁻	2777	
m-xylenium	CB ₁₁ H ₆ Br ₆ ⁻	2776	
hexamethylbenzenium	CB ₁₁ H ₆ Br ₆ ⁻	2758, 2884 ^b	

^a Frequencies are given in reciprocal centimeters. ^b Possibly due to arenium ion without significant H-bonding to Br atom of anion.

reproduced in ring-deuterated samples with increased mass ratios of 1.35. In some cases, only a single band arises from the two C–H bonds on the acidic CH₂ group, indicating that both protons interact with Br atoms of the anion in an equivalent manner. A single band is expected for the hexamethylbenzenium ion. It has not previously been located because of overlap with other $\nu(CH)$ bands. It was located by difference spectroscopy by use of the deuterated analogue (see Supporting Information Figure S7). Since *two* bands are observed, at significantly different energies, two different environments must be present. Possibly one has a significant C–H \cdots Br interaction and the other does not. All things being equal, $\nu(CH)$ might be expected

to reflect the arenium ion acidity: benzenium > toluenium > *m*-xylenium > mesitylenium > hexamethylbenzenium. However, this correlation is not convincingly revealed in the data of Table 5. While crystal packing effects and differential interactions of the C–H bonds with Br atoms of the anions are likely to perturb any correlation, it is also true that acid strength has more to do with solvation energies and charge distribution in the anion than C–H bond strengths. This probably explains why $\nu(CH)$ is not very sensitive to the nature of the arene.

Brønsted Acid Reagents. One goal of this work was to elevate arenium ions from solution observables to the status of weighable reagents for the clean delivery of protons at prescribed acidities. Benzene and hexamethylbenzene span ca. 10¹⁰ range of acidity, so $[H(arene)][carborane]$ salts offer acidity that is leveled from that of the “bare” superacid to that of the arenium ion of choice.

Illustrative of this use is the bracketing of the acidity of the HC₆₀⁺ ion. *o*-Dichlorobenzene solutions of C₆₀ (10⁻⁴ M) were treated with 1 equiv of various arenium ion salts and monitored by visible spectroscopy for conversion to HC₆₀⁺. The *m*-xylenium ion was strong enough to cause significant protonation, but the mesitylenium ion was not. This indicates that C₆₀ has a solution basicity between that of mesitylene and *m*-xylene.

Another use of the arenium ions as reagents is in the protonation of other organic solvents. This leads to isolable carborane salts of H(solvent)₂⁺ (solvent = diethyl ether, tetrahydrofuran, nitrobenzene, etc.) and allows the solvated structures of ionized acids to be probed.⁴⁶ H(solvent)₂⁺ cations have short, strong, low-barrier (SSLB) H-bonds and show very unusual IR effects.

Conclusion

Carborane anions confer remarkable stability on arenium ion salts such that even the benzenium ion can be isolated and characterized at ambient temperature by methods not previously available. The next challenge will be to isolate protonated arenes having common substituents, so that more of the intermediates of electrophilic aromatic substitution can be studied as stable ions. It is likely that more points on the $\sigma-\pi$ continuum can be established.

Experimental Section

All manipulations were carried out under dry conditions using Schlenkware or an inert atmosphere glovebox (H₂O, O₂ < 0.5 ppm). Carborane anions^{36,47} were prepared by literature methods and solvents

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Table 6. Summary of X-ray Crystal Data and Structure Refinement for Arenium Salts

	structure (ID code)				
	benzenium (ucr851m)	toluenium (ucr492f)	m-xyleneium (ucr521m)	mesitylenium (ucr621m)	hexamethyl-benzenium (ucr641m)
empirical formula	C ₁₂ H ₂₃ B ₁₁ Br ₆	C ₁₅ H ₂₃ B ₁₁ Br ₆	C ₁₇ H ₂₇ B ₁₁ Br ₆	C ₃₃ H ₄₆ B ₂₂ Br ₁₂ Cl ₄	C ₁₃ H ₂₃ B ₁₁ Br ₆
formula weight	765.67	801.70	829.76	1769.23	779.70
temp, K	223(2)	213(2)	213(2)	213(2)	213(2)
crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic	orthorhombic
space group	Pnma	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	C ₂	<i>P</i> 2 ₁ 2 ₁ 2 ₁
unit cell dimensions					
<i>a</i> , Å	14.1517(10)	23.499(4)	9.1191(15)	22.500(2)	13.1503(10)
<i>b</i> , Å	17.1870(13)	9.3870(15)	12.701(2)	11.7084(11)	13.9660(10)
<i>c</i> , Å	10.4898(8)	25.538(4)	24.710(4)	23.329(2)	14.1644(11)
β , deg		101.507(3)		97.041(2)	
volume, Å ³	2551.4(3)	5520.0(15)	2862.0(8)	6099.4(10)	2601.4(3)
<i>Z</i>	4	8	4	4	4
density (calcd), Mg/m ³	1.993	1.929	1.926	1.927	1.991
absorption coeff, mm ⁻¹	9.442	8.733	8.426	8.083	9.262
<i>F</i> (000)	1440	3024	1576	3344	1472
crystal size, mm ³	0.67 × 0.28 × 0.18	0.24 × 0.14 × 0.10	0.70 × 0.55 × 0.45	0.47 × 0.46 × 0.34	0.48 × 0.26 × 0.20
θ range for data collection, deg	2.27–28.28	1.63–26.37	1.65–26.37	1.76–26.37	2.05–26.37
Index ranges	18 ≤ <i>h</i> ≤ 18 22 ≤ <i>k</i> ≤ 22 13 ≤ <i>l</i> ≤ 13	29 ≤ <i>h</i> ≤ 29 11 ≤ <i>k</i> ≤ 11 31 ≤ <i>l</i> ≤ 31	11 ≤ <i>h</i> ≤ 7 14 ≤ <i>k</i> ≤ 15 30 ≤ <i>l</i> ≤ 30	28 ≤ <i>h</i> ≤ 26 14 ≤ <i>k</i> ≤ 14 25 ≤ <i>l</i> ≤ 29	16 ≤ <i>h</i> ≤ 16 15 ≤ <i>k</i> ≤ 17 15 ≤ <i>l</i> ≤ 17
reflns collected	25 987	25 102	16 878	19 692	17 247
indep reflns [<i>R</i> (int)]	3265 [0.0408]	5649 [0.0730]	5858 [0.0287]	9508 [0.0343]	5315 [0.0379]
completeness, % (θ , deg)	100.0 (28.49)	99.9 (26.37)	99.9 (26.37)	100.0 (26.37)	100 (26.37)
absorption correction	SADABS	SADABS	SADABS	SADABS	SADABS
max, min transmission	0.2813, 0.0613	0.4755, 0.2284	0.1157, 0.0668	0.1697, 0.1155	0.2588, 0.0950
refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
data/restraints/parameters	3265/0/159	5649/0/317	5858/1/344	9508/198/756	5315/0/305
goodness-of-fit on <i>F</i> ²	1.024	1.016	1.018	1.021	1.024
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]					
<i>R</i> ₁	0.0252	0.0420	0.0279	0.0353	0.0317
<i>wR</i> ₂	0.0612	0.0886	0.0587	0.0746	0.0699
<i>R</i> indices (all data)					
<i>R</i> ₁	0.0343	0.0638	0.0347	0.0510	0.0408
<i>wR</i> ₂	0.0651	0.0922	0.0602	0.0797	0.0733
largest diff peak/hole, e ⁻ Å ³	0.556/−0.573	0.779/−0.593	0.538/−0.430	0.730/−0.525	0.629/−0.317

were dried by standard methods.⁴⁸ ¹³C CPMAS NMR spectra were measured on a Bruker BZH 400/89 spectrometer with cross polarization and magic-angle spinning. Samples were packed in a zirconium ceramic rotor (4 × 18 mm) inside a glovebox and sealed from air by jamming Teflon tape between the cap and the rotor. IR spectra were run on a Shimadzu-8300 FT-IR spectrometer in the 4000–400 cm⁻¹ range (32 scans, resolution 2 cm⁻¹). Samples were prepared as thin wafers pressed between 3-μm FEP Teflon films to ensure there was no reaction with pellet media.

Et₃Si(carborane) species were prepared in ca. 85% isolated yield by a slight modification of published methods.^{49,50} Benzene (ca. 15 mL) was added as the crystalline trityl salt [Ph₃C][carborane] (1 g), covering the solid, and triethylsilane (15 mL) was added. The mixture was stirred until the solids were completely white (ca. 1–4 days). The volatiles were removed under reduced pressure and the white solid was washed with several aliquots of hexanes. Water in the hexanes reacts with product to give hydronium ion salts, so well-dried solvent is important.

The carborane acids, H(carborane), were prepared by a slight modification of published procedures.³³ Et₃Si(carborane) (0.5 g) was placed in a thick-walled Schlenk tube and pumped under vacuum to remove any residual solvent. HCl, dried by passage through H₂SO₄ and a dry ice temperature trap, was condensed onto the solid at liquid nitrogen temperatures to obtain coverage (2–3 mL). *Caution: As a condensed gas, HCl can explode in confined glassware if the temperature is inadvertently allowed to rise. Precautions against explosion and release of a toxic gas should be taken.* The slurry was warmed to dry ice temperature and stirred for 1 h. After the mixture was refrozen to liquid N₂ temperature, the excess HCl and Et₃SiCl byproduct was removed under vacuum during gradual warming to ambient temperature, leaving an off-white solid in essentially quantitative yield.

Protonated arenes were prepared in essentially quantitative yield by adding the desired arene (ca. 1 mL) to the solid carborane acid, stirring for a few minutes, and removing the solvent under vacuum. In the case of hexamethylbenzene, 1 equiv was used in benzene as solvent.

[H(Benzene)][CB₁₁H₆Cl₆]. Anal. Calcd for C₇H₁₃B₁₁Cl₆: C, 19.63; H, 3.0. Found: C, 19.72; H, 3.98. ¹³C CPMAS: see Figure S8 in Supporting Information of ref 32. DTA: <1% weight loss to 150 °C.

[H(Benzene)][CB₁₁HMe₅Br₆]. IR: see Figures 6 and S6 and Table S3. DTA: <1.6% weight loss to 150 °C.

[H(Benzene-*d*₆)][CB₁₁HMe₅Br₆]. IR: see Figure S6.

[H(Toluene)][CB₁₁H₆Br₆]. ¹³C CPMAS NMR: see Table 3 and Figure S3. DTA: <4% weight loss to 150 °C.

[H(*m*-Xylene)][CB₁₁H₆Br₆]. ¹H NMR (CH₂Cl₂-*d*₂ at -90 °C): 8.73 (d, 1H₆, *J*_{HH} 8.5 Hz), 7.79 (s,d, 2H_{3,5}), 4.81 (s, 2H₁), 2.96 (s, 3H_{Me}), 2.85 (s, 3H_{Me}), 2.3 (br s, 1H_{carborane}); see Figure S1). Anal. for *o*-xylene solvate: Calcd for C₁₇H₂₇B₁₁Br₆: C, 24.61; H, 3.28. Found: C, 23.91; H, 3.32%.

[H(Mesitylene)][CB₁₁HMe₅Br₆]. ¹H NMR (CH₂Cl₂-*d*₂ at -20 °C): 7.54(s, H_{3,5}), 4.67 (s, 2H₁), 2.85 (s, 3H_{4-Me}), 2.73 (s, 6H_{2,6-Me}), 2.14 (s, 1H_{carborane}), 0.14 (s, 15H_{carboraneMe}); see Figure S2.

[H(Mesitylene)][CB₁₁H₆Br₆]. Anal. Calcd for C₁₀H₁₉B₁₁Br₆: C, 16.28; H, 2.59. Found: C, 15.84; H, 2.48%. DTA: <2% weight loss to 180 °C.

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[H(Hexamethylbenzene)][CB₁₁H₆Br₆]. Anal. Calcd for C₁₃H₂₅B₁₁Br₆: C, 20.02; H, 3.23. Found: C, 19.92; H, 3.38%. DTA: <0.3% weight loss to 190 °C.

[H(Hexamethylbenzene)][CB₁₁HMe₅Br₆]. IR: see Figure S7.

X-ray Structure Determinations. Single crystals of the benzenium carborane, [C₆H₇][CB₁₁HMe₅Br₆], were grown at room temperature in an hour by standing the solution obtained by dissolving [Et₃Si][CB₁₁HMe₅Br₆] (15 mg) in dry benzene (4 mL) and adding a few drops of trifluoromethanesulfonic acid. Single crystals of the toluenium carborane, [HC₆H₅(CH₃)][CB₁₁H₆Br₆]·toluene, were obtained by dissolution of the salt (20 mg) in a mixed toluene/1,2-dichlorobenzene (1:2 v/v) solvent (3 mL) (undissolved precipitates were removed by syringe filtration), followed by vapor diffusion of hexanes at room temperature. Single crystals of *m*-xylenium [HC₆H₄(CH₃)₂][CB₁₁H₅Br₆], mesitylenium [HC₆H₃(CH₃)₃][CB₁₁H₆Br₆]·2(1,2-dichlorobenzene), and hexamethylbenzenium [HC₆(CH₃)₆][CB₁₁H₆Br₆] were obtained in a manner similar to that of the toluenium carborane in 1,2-dichlorobenzene with *o*-xylene, mesitylene, and hexamethylbenzene, respectively. The structures were solved and refined by standard methods, summarized in Table 6. Details are provided in Supporting Information.

Density Functional Calculations. These were carried out with the Gaussian 98 program.⁵¹ Geometry optimization for the benzenium ion C₆H₇⁺ was carried out at the B3LYP/6-31G* and B3P86/6-311+G-(d,p) levels. The results are consistent with those of Haw and co-workers.⁴³ Full vibrational frequency calculations were made at the stationary point determined for the B3LYP/6-31G* model. Details of these calculations, frequencies, calculated IR spectra, and vibrational modes are given in Supporting Information in Figures S4 and S5 and Tables S1 and S2. For comparison with experimental spectra, the vibrational frequencies should be scaled by the factor 0.9614 as reported by Scott and Radom.^{45a}

Acknowledgment. This work was made possible by the National Institutes of Health (GM 23851), the National Science Foundation (CHE 0095206), The University of Auckland Research Committee, and by Award RC1-2399-NO-02 of the U.S. Civilian Research & Development Foundation for the Independent States of the Former Soviet Union.

Supporting Information Available: NMR spectra, IR spectra and assignments, DFT structure and vibrational data, and full crystallographic details (96 pages, print/PDF). This material is available (pdf) free of charge via the Internet at <http://pubs.acs.org>.

JA027336O

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