The Superacid HBr/AlBr3: Protonation of Benzene and Ordered Crystal Structure of [C6H7]+[Al2Br7]−**

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Abstract: *Crystalline and properly ordered protonated benzene as the $[C_6H_7]^+[Al_2Br_7]^-\cdot(C_6H_6)$ salt **1** are obtained by the combination of solid $AlBr_3$, benzene, and HBr gas. Compound **1** was characterized and verified by NMR, Raman and X-Ray spectroscopy. This unexpected simple and straight forward access shows that $HBr/AlBr_3$ is an underestimated superacid that should be used more frequently.*

Arenium ions, commonly called Wheland[1] intermediates, but more correctly ascribed to Pfeiffer and Wizinger,[2] are widely accepted to be intermediates in electrophilic aromatic substitution reactions. First spectroscopic evidence for the protonation of an aromatic hydrocarbon was reported by Gold and Tye for anthracene,[3] and by Reid for alkylbenzene.[4] Later protonated aromatic hydrocarbons were observed in classical superacidic media.[5] Stable arenium ion salts were first isolated with electron-donating groups, for example $[C_6(CH_3)_7]^{+[6]}$, or those with pyrrolidinium[7] or silyl[8] substituents.

The simplest and thus non-stabilized arene that can be protonated is benzene, yielding the benzenium ion $[C_6H_7]^+$ for which three different structures have been proposed: the σ-(C_{2v}), the bridged π- (C_s) and the face-centered π-structure (C_{6v}; Scheme 1). Extensive NMR spectroscopy studies of **1** in $HF/SbF_5/SO_2ClF$ at $-78\,°C$, $-129\,°C$, and $-140\,°C$,[9] IR spectroscopy,[10,11] UV spectroscopy,[11] and theoretical studies[12] provide convincing evidence for the σ-structure as the most stable form.
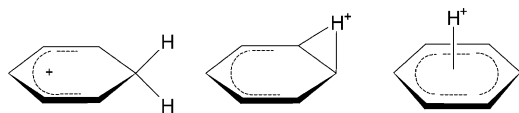
Scheme 1. $[C_6H_7]^+$ structures: σ- (left, C_{2v} symmetry), bridged π- (middle, C_s), and face-centered π-structure (right, C_{6v}).

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Although solid-state NMR and IR studies of $[C_6H_7]^+[CB_{11}H_6Cl_6]$ and $[C_6H_7]^+[CB_{11}HMe_5Br_6]$[13,14] were carried out, only the X-ray crystal structures of the $[C_6H_7]^+$ salt with the $[CB_{11}HMe_5Br_6]^-$ ion were published, containing a highly disordered benzenium ion which meant that it was not possible to differentiate between the three alternatives shown in Scheme 1.[13–15] Thus, crystallographic evidence for the preference of the σ-structure in the solid state is still missing.

Recently, we turned our attention to the $HBr/AlBr_3$ system: By combination of the Brønsted acid HBr with the Lewis superacid $AlBr_3$,[16] Brønsted superacidity can be reached.[17] This system allowed X-ray crystallographic structure determinations of delicate protonated compounds, such as the *tert*-butyl cation as its $[Al_2Br_7]^-$ salt, which is a room-temperature ionic liquid,[18] or even the non-classical 2-norbornyl cation salt $[C_7H_{11}]^+[Al_2Br_7]^-\cdot(CH_2Br_2)$.[19] Thus we were interested to see, if the $HBr/AlBr_3$ system was also able to stabilize an ordered structure of a non-substituted benzenium ion salt. Indeed, this was possible and herein we present the well-ordered crystal structure of protonated benzene as its benzene solvate $[C_6H_7]^+[Al_2Br_7]^-\cdot(C_6H_6)$ (**1**).

$AlBr_3$ is moderately soluble in HBr, but its solubility increases by addition of aromatic or aliphatic hydrocarbons leading to deeply colored oily liquids of high density.[20] Earlier NMR work showed that $HBr/AlBr_3$ and, to a lesser extent, also $HCl/AlCl_3$ protonate weak bases such as mesitylene, and even benzene,[21–23] which is 10^9 times less basic than mesitylene.[24] However, no isolation of any crystalline—even of a substituted—benzenium ion salt in this system was reported to date. ^{13}C NMR studies suggested that the $HBr/AlBr_3$ system completely protonates benzene at $AlBr_3$:benzene ratios of 2:1 or higher and a HBr ratio of 4 mole per mole $AlBr_3$.[23,25] Although it was reported that transparent crystalline cubes were separated, no crystal structure could be obtained. Based on this knowledge, we prepared mixtures with the following stoichiometric ratios: $AlBr_3$:benzene:HBr 1:1:1 (Mix 1), 2:1:3 (Mix 2), and 2:1:9 (Mix 3). From repeated efforts on Mix 3 no crystals could be isolated. Mix 2 reproducibly led to transparent cubic crystals, similar to those described in Ref. [23]. According to our Raman measurements as well as an X-ray single crystal structure determination, these crystals are solid Al_2Br_6. Only from Mix 1 (1:1:1 ratio), were colorless crystals with the composition $[C_6H_7]^+[Al_2Br_7]^-\cdot(C_6H_6)$ **1** reproducibly obtained after storage for 3 to 4 days at $0\,°C$ [Eq. (1)].

Our NMR spectroscopic investigations of the neat liquid Mix 1 suggest the presence of an estimated 30% fraction of the $[C_6H_7]^+$ ion. The results are in line with a rapid equilibrium of sigma C_{2v} structures as in earlier reports[22,23]

$$\text{benzene} + AlBr_3 \xrightarrow[HBr]{0\,^{\circ}C} 0.5 \left[\begin{array}{c} H^1 \; H^2 \\ \text{[benzenium]} \\ {[Al_2Br_7]^-} \end{array} \right] + 0.5 \; \text{benzene} \qquad (1)$$
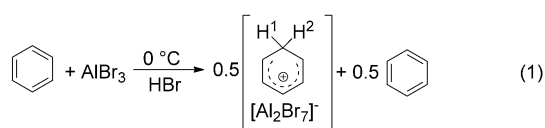
and is not discussed in detail herein. A more detailed discussion and more data are available in the Supporting Information. After about 2 h at room temperature, the liquid Mix 1 turns to a dark yellow brown, which indicates decomposition reactions. The most characteristic vibrational modes of the benzenium ion are the methylene stretching vibrations $v_{as}(CH_2)$ and $v_s(CH_2)$ that are almost degenerate. For crystalline **1** they resonate at 2852 cm^{-1} and are clearly visible in the low-temperature Raman Spectrum at $-196\,^{\circ}C$ (see Supporting Information).

The solid-state structure of **1** was determined with X-ray diffraction methods at 100 K. Figure 1 a shows the asymmetric unit of the molecular structure of **1** ($P2_1/n$, $R_1 = 3.23\,\%$, $wR_2 = 6.97\,\%$). The positions of all the hydrogen atoms were found in the difference Fourier map and the hydrogen positions were allowed to refine freely with a same-distance restraint for all C–H distances. The structural details of the dimeric $[Al_2Br_7]^-$ ion are close to those found in $K[Al_2Br_7]$,[26] $NH_4[Al_2Br_7]$,[27] and $[C(CH_3)_3]^+[Al_2Br_7]^-$.[18] The asymmetric unit of **1** includes protonated benzene and one molecule of co-crystallized neutral benzene that is located at a special position. The structural parameters of **1** and for comparison those of a disordered and a calculated structure are included with Table 1.

The C–C distances of the neutral benzene molecule are indistinguishable within the standard deviation and average
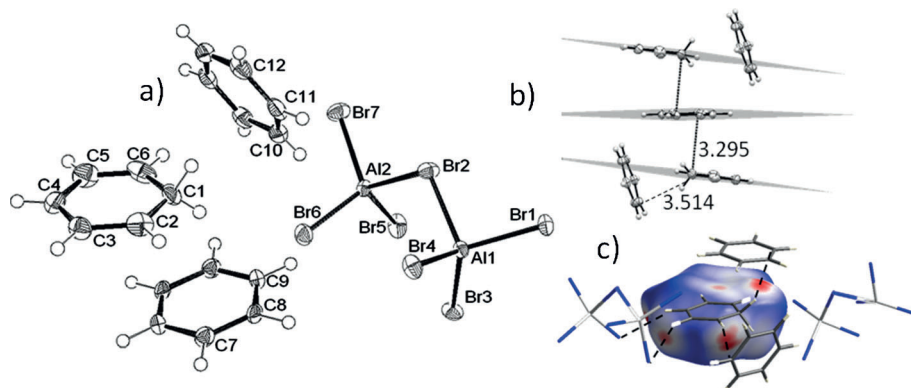
to 1.377(7) Å. This is in fine agreement with literature.[28] The benzenium ion is planar and the C-C-C bond angles range from 117.9(5) to 122.8(6)°. The C–C distances around C2, C3, C4, C5, and C6 are consistent with a delocalized electronic structure related to a pentadienyl cation moiety and average within 3σ to 1.378(8) Å. The C1–C2 and C1–C6 bond lengths to the protonated carbon atom C1 of 1.423(8) and 1.419(8) Å are longer, but considerably shortened if compared to the sp^2–sp^3 bond of 1.51 Å in $CH_2(Ph_2)$[29] and to a C–C single bond (1.54 Å). In contrast the structure determined for $[C_6H_7]^+$-$[HCB_{11}(CH_3)_5Br_6]^-$ (included in Table 1) shows a complete disorder of the cation.[14] Whereas, all the observed C–C distances and C-C-C bond angles of $[C_6H_7]^+$ in **1** are in good agreement with the calculated MP2/def2-QZVPP data. Thus, to our knowledge **1** contains the first well-ordered structure of the benzenium ion. The minimum C–C distances between the $[C_6H_7]^+$ ion and the co-crystallized benzene molecules are 3.295 and 3.514 Å and lie close to the sum of the van der Waals radii (3.4 Å),[30] as also follows from the visualization of the cation with the Hirshfeld surface (Figure 1 c).[31] The sandwiched structure of one of the benzene molecules (C9, C8, and C7) and the benzenium ion is in accordance with an η^2- to η^3-inter-ring interaction. The benzene molecule is slightly tilted towards the direction of the methylene group, slightly reducing the π–π stacking interaction (see Figure 1 b). The averaged H–Br contact distance between cation and anion is 2.914 Å and lies a bit below the sum of the van der Waals radii (3.05 Å).[30]

To investigate the reaction thermodynamics leading to solid **1**, we constructed a Born–Fajans–Haber cycle (Scheme 2) by combining lattice-energy calculations with highly correlated quantum chemical calculations (see Supporting Information for details).[32] Lattice Gibbs energies/enthalpies were calculated with an approach developed for ionic liquids in our group.[33] According to this cycle, the reaction of benzene with solid $AlBr_3$ and the formation of solid non-solvated $[C_6H_7]^+[Al_2Br_7]^-$ was calculated to be slightly exergonic. The main driving force for the reaction is the gain of lattice energy in the condensed solid phase. The gas-phase reaction is energetically very disfavored because of charge separation. The observed more favorable formation of the benzene-solvated compound **1** compared to the non-solvated one in the cycle may be attributed to the energy gain through additional C–H-π and π–π stacking interactions of benzene and protonated benzene, which cannot be considered in the calculation of the lattice energies.

The superacidic medium HBr/$AlBr_3$ is also able to stabilize pro-

Figure 1. a) Molecular structure of **1**. Thermal ellipsoids are set at 50% probability. The positions of all the hydrogen atoms were found in the difference Fourier maps. Selected bond lengths [Å] and angles [°]: Br1-Al1 2.2586(14), Br2-Al1 2.4449(14), Br3-Al1 2.2596(13), Br4-Al1 2.2602(13), Br2-Al2 2.4111(14), Br5-Al2 2.2514(13), Br6-Al2 2.2717(14), Br7-Al2 2.2615(14), C7-C8 1.376(7), C8-C9 1.384(7), C7-C9' 1.374(7), C10-C11 1.378(7), C11-C12 1.364(8), C12-C10' 1.387(8); Br1-Al1-Br3 113.99(6), Br1-Al1-Br4 114.406, Br3-Al1-Br4 112.39(6), Br1-Al1-Br2 99.41(5), Br3-Al1-Br2 107.14(5), Br4-Al1-Br2 108.28(6), Br5-Al2-Br7 111.73(6), Br5-Al2-Br(6) 112.84(6), Br7-Al2-Br6 112.84(6), Br5-Al2-Br2 110.06(6), Br7-Al2-Br2 101.92(5), Br6-Al2-Br2 106.75(5), Al2-Br2-Al1 112.27(5), C7-C8-C9 119.5(4), C8-C7-C9' 120.6(4), C7'-C9-C8 120.0(4), C12-C11-C10 120.8(5), C11-C10-C12 119.7(5), C11-C12-C10' 119.4(5). b) Stacking of the arene moieties in the solid state, the minimum C–C distances between the $[C_6H_7]^+$ ion and the co-crystallized benzene are given in Å. c) Hirshfeld surface of the cation of **1** with surrounding counterions and benzene molecules. Red indicates contact distances below, blue above the sum of the van der Waals radii.

Table 1: Comparison of bond lengths [Å] and angles [°] of $[C_6H_7]^+$ as its $[Al_2Br_7]^-$ salt with the disordered $[C_6H_7]^+[HCB_{11}(CH_3)_5Br_6]^-$ salt and the ab initio calculation (C_{2v} symmetry, MP2/def2-QZVPP).

Bond lengths [Å]:	C1-C2	C2-C3	C3-C4	C4-C5	C5-C6	C6-C1
1	1.423(8)	1.386(8)	1.381(7)	1.382(8)	1.361(8)	1.419(8)
$[C_6H_7]^+$ (calcd)	1.456	1.370	1.403	1.403	1.370	1.456
$[C_6H_7]^+[CB_{11}H(CH_3)_5Br_6]^-$	1.381(1)	1.345(6)	1.391(6)	1.381(6)	1.345(6)	1.391(6)
Bond angles [°]:	C6-C1-C2	C1-C2-C3	C2-C3-C4	C3-C4-C5	C4-C5-C6	C5-C6-C1
1	117.9(5)	120.5(5)	118.5(5)	122.8(6)	119.1(5)	121.2(5)
$[C_6H_7]^+$ (calcd)	117.8	120.5	119.1	123.0	119.1	120.5
$[C_6H_7]^+[CB_{11}H(CH_3)_5Br_6]^-$	119.8(3)	120.1(3)	120.2(3)	119.8(3)	120.1(3)	120.1(3)
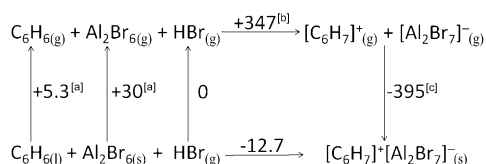
Scheme 2. Born–Fajans–Haber cycle to assess the Gibbs reaction energy in $kJ\,mol^{-1}$ at 298 K, 1 bar, [a] experimental value,[34] [b] calculated from experimental values[34] and a ccsd(t)/MP2 compound method (see Supporting Information for details), [c] calculated value (see Supporting Information for details); (g) = gaseous, (s) = solid.

tonated benzene in the solid state, allowing the protonated benzene to be isolated as its well-ordered $[Al_2Br_7]^-$ salt. An ongoing challenge to be reported later will be to classify its acidity on the basis of our recently established absolute Brønsted acidity scale.[35] This investigation shows that the HBr/AlBr$_3$ system is well suited to stabilize highly acidic protonated species and we suggest that this very available system should be used more frequently, when very high acidities are required.

Experimental Section

Techniques and instruments: All reactions were carried out in an inert atmosphere using standard vacuum and Schlenk techniques or a glove box. Special NMR tubes (J. Young) and special Schlenk flasks sealed with Teflon or glass valves were used to exclude air and moisture. All solvents were dried over CaH$_2$ and distilled afterwards. Benzene was washed with H$_2$SO$_4$ to remove tiophene, and then dried over CaH$_2$. NMR spectra were recorded unlocked at room temperature on a Bruker Biospin Avance II 400 MHz WB spectrometer and the software Topspin 2.1 was used.

1: In a typical preparation, AlBr$_3$ (0.27 g; 1.00 mmol) was weighed in the glove box into a suitable flask and benzene (0.08 g, 0.09 mL, 1.00 mmol, 1.0 equiv) was condensed to it at $-196\,°C$. Hydrogen bromide was produced in situ by adding PBr$_3$ (0.10 mL, 0.29 g, 1.05 mmol) to a suspension of CuSO$_4$·5H$_2$O (0.05 g, 0.20 mmol) in toluene (3 mL). After warming the mixture to $90\,°C$ for 60 min, the HBr (1.00 mmol, 1.00 equiv), which had formed by hydrolysis, was purified from toluene and water traces by trap-to-trap condensation (-196 to $-78\,°C$) and condensed to the mixture of AlBr$_3$ and benzene at $-78\,°C$. While stirring the mixture, it was slowly warmed to room temperature, and a bright yellow, oily liquid was formed. The compound crystallizes quantitatively in a refrigerator at $2\,°C$.

^{1}H NMR (400.17 MHz, 278 K): $\delta = 6.21$ ppm (s, 7H, CH, CH$_2$).
^{13}C NMR (100.6 MHz, 278 K): $\delta = 133.4$ ppm (s, 6C, C1, C2 C3, C4,

C5, C6). ^{27}Al-NMR (104.27 MHz, 278 K): $\delta = 87$ ppm ($\Delta\nu_{1/2} = 8600$ Hz). FT-Raman: $\tilde{\nu} = 202$ (0.31), 900 (0.50), 991 (0.75), 1610 (1.0), 2859 (0.58), 3060 cm^{-1} (0.44) (%).

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