

Diprotic Superacids

Superacidity of Boron Acids $H_2(B_{12}X_{12})$ ($X = Cl, Br$)*

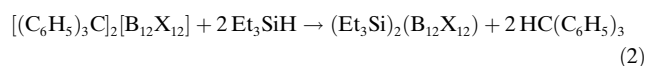
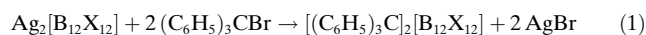
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The finding that monoprotic carborane acids of the type $H(CHB_{11}X_{11})$ ($X = Cl, Br$) are the strongest pure acids isolated to date^[1,2] suggests that the analogous diprotic boron acids $H_2(B_{12}X_{12})$ may have comparable or even higher acidity. The hydrated acids $[H(H_2O)_n]^+[B_{12}X_{12}^{2-}]$ were prepared many years ago from aqueous solutions of their alkali metal salts using an ion-exchange resin in acid form^[3] and were shown to be slightly stronger acids than H_2SO_4 in aqueous solution. However, the anhydrous acids are unknown. Can they be synthesized? Are they superacids? Of further interest is that the $B_{12}H_{12}^{2-}$ ion starting material is considerably cheaper than the isoelectronic $CB_{11}H_{12}^-$ carborane ion, so there is potential for cost savings relative to carborane acids, which are too expensive for widespread use.

An indication that the all-boron acids $H_2(B_{12}X_{12})$ should show comparable acid strengths to their analogous carborane acids $H(CHB_{11}X_{11})$ comes from the position of their anions on the $\nu(NH)$ basicity scale. In this ranking, the N–H stretching frequencies of contact-ion-pair trioctylammonium salts $Oct_3N^+H\cdots anion^-$ are compared in CCl_4 solution.^[2,4] The higher the $\nu(NH)$ frequency, the lower the basicity of the anion. As shown in Table 1, the $B_{12}Cl_{12}^{2-}$ salt has almost the same $\nu(NH)$ frequency as the $CHB_{11}Cl_{11}^-$ salt. This result is surprising inasmuch as the dinegative charge on the $B_{12}Cl_{12}^{2-}$ ion might have been expected to render it more basic than the uninegative $CHB_{11}Cl_{11}^-$ ion. It suggests that chloride substituents on both anions form an effective screen for negative charge that is delocalized and buried within the icosahedral

cage. Similar conclusions can be drawn from the data on the $B_{12}Br_{12}^{2-}$ ion, although low solubility of its trioctylammonium salt in CCl_4 allow comparisons to be made only for crystalline salts. It is also clear from the data in Table 1 that the boron anions are much less basic than the $(HSO_4)_2^{2-}$ ion, so their conjugate acids are expected to be much stronger than 100 % H_2SO_4 , whose acidity ($H_0 = -12$ on the Hammett scale) defines the onset of superacidity.

The synthetic pathway to the anhydrous diprotic acids exploits multistep metathesis reactions similar to those used in the preparation of $H(CHB_{11}Cl_{11})$.^[1] Starting with the silver salts of $B_{12}Br_{12}^{2-}$ and $B_{12}Cl_{12}^{2-}$, their respective trityl ($C(C_6H_5)_3^+$) salts [Eq. (1)] and triethylsilylium compounds [Eq. (2)] have been prepared and characterized by X-ray crystallography.^[5]



The structures of the trityl salts are unremarkable and similar to that of the $B_{12}F_{12}^{2-}$ ion,^[6] but those of the triethylsilylium derivatives are informative with regard to how the dianions act as Lewis bases. As illustrated in Figure 1 for the $B_{12}Cl_{12}^{2-}$ ion, the triethylsilyl groups adopt 1,12 or *trans* positions, presumably to minimize electrostatic repul-

Table 1: $\nu(NH)$ frequencies of tri-*n*-octylammonium salts (in cm^{-1}).

Anion	$\nu(NH)$ in CCl_4	$\nu(NH)$ solid
$CHB_{11}Cl_{11}^-$ ^[a]	3163	3180
$B_{12}Cl_{12}^{2-}$	3165	3167
$CHB_{11}Br_{11}^-$ ^[a]	3140	3150
$B_{12}Br_{12}^{2-}$	insoluble	3140
$(HSO_4)_2^{2-}$	3021, 2660	3080

[a] Ref. [4].

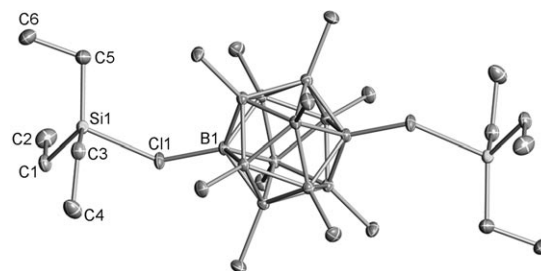


Figure 1. X-ray crystal structure of $(Et_3Si)_2(B_{12}Cl_{12})$.

sions between the electropositive silicon centers and to pack most efficiently in the crystal lattice. The sum of the C–Si–C angles, whose approach towards 360° is used as a measure of developing silylium ion character in an $R_3Si^{\delta+}$ moiety,^[7,8] is 348.3° . This value is close to 349.5° in $Et_3Si(CHB_{11}Cl_{11})$,^[9] thus indicating similar low Lewis basicities of the $B_{12}Cl_{12}^{2-}$ and $CHB_{11}Cl_{11}^-$ ions.

A further illustration of the comparable Lewis basicities of the $B_{12}Cl_{12}^{2-}$ and $CHB_{11}Cl_{11}^-$ ions comes from the formation of the hydride-bridged cation $[Et_3Si-H-SiEt_3]_2^+[B_{12}Cl_{12}]$ when excess silane is used in Equation (2). This

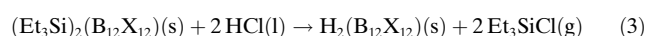
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cation forms reversibly when silane competes with the anion for coordination to the Et_3Si^+ moiety and is readily identified by its $\nu(\text{Si-H-Si})$ band at approximately 1870 cm^{-1} in the IR spectrum of the isolated solid.^[9] Similarly, halocarbon solvents such as *o*-dichlorobenzene (ODCB) are sufficiently basic to compete with the anion for coordination to the Et_3Si^+ moiety.^[9] Since excess silane and solvent molecules can interfere with the subsequent formation of the unsolvated $\text{H}_2(\text{B}_{12}\text{X}_{12})$ acids, thus lowering their purity, considerable care must be taken to remove them from the silylium derivatives by drying under vacuum. Such contaminants include toluene that can be carried through from the trityl salt preparation.

Silylium ion character in the $(\text{Et}_3\text{Si})_2\text{B}_{12}\text{X}_{12}$ derivatives is sufficiently strong that chloride abstraction from anhydrous HCl proceeds readily according to Equation (3) at sub ambient temperatures to give the desired acids $\text{H}_2(\text{B}_{12}\text{X}_{12})$ as nearly colorless solids in essentially quantitative yields.



Both $\text{H}_2(\text{B}_{12}\text{Br}_{12})$ and $\text{H}_2(\text{B}_{12}\text{Cl}_{12})$ are distinctively characterized in their solid-state IR spectra by broad, low-energy absorptions associated with short, strong, symmetrical X-H-X hydrogen bonding.^[10,11] As shown in Figure 2, these bands appear at 1200 and approximately 620 cm^{-1} for $\text{H}_2(\text{B}_{12}\text{Cl}_{12})$ compared to 1100 and 615 cm^{-1} in $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$. In the analogous bromide, they appear at 1080 and approximately 570 cm^{-1} . The lower-energy band is particularly strong, but its exact frequency is made uncertain by Evans holes.^[11] Given the overarching tendency of strongly acidic protons to attain symmetrical (or nearly symmetrical) di-solvation,^[10] and by analogy to $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$ whose X-ray structure shows $\text{Cl-H}^+-\text{Cl}$ bridges in a 2D polymeric chain structure,^[11] a 3D network structure with $\text{X-H}^+-\text{X}$ bridges is the only reasonable structure for $\text{H}_2(\text{B}_{12}\text{X}_{12})$ acids. This 3D structure would also explain why these acids cannot be sublimed under vacuum up to 200°C for purification and possible single-crystal growth, even though carborane acids can be vaporized around 150°C .^[11]

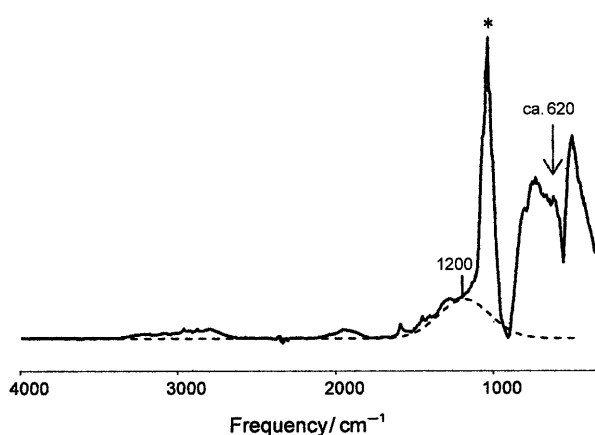


Figure 2. IR spectrum of $\text{H}_2(\text{B}_{12}\text{Cl}_{12})$ showing the two broad absorptions at 1200 (Gaussian fit shown by dashed line) and ca. 620 cm^{-1} (with Evans holes) characteristic of symmetrical $\text{Cl-H}^+-\text{Cl}$ bridge bonding. The major anion absorption is marked with an asterisk.

The acids have relatively low solubility in low-basicity solvents such as anhydrous liquid SO_2 , but the appearance of a downfield peak at $\delta = 19.3\text{ ppm}$ in the ^1H NMR spectrum of $\text{H}_2(\text{B}_{12}\text{Cl}_{12})$ is consistent with ionization to give the di-solvated $\text{H}(\text{SO}_2)_2^+$ ion.^[11] The solid anhydrous acids are moisture-sensitive. As monitored by IR spectroscopy, the gradual appearance of broad $\nu(\text{OH})$ bands in the range $3200\text{--}3600\text{ cm}^{-1}$ occurs as the broad bands associated with the acid $\text{X-H}^+-\text{X}$ group disappear, indicating the formation of H_5O_2^+ and H_7O_3^+ ions.^[12]

The protonation of benzene has become a benchmark of superacidity above and beyond that of mineral acids.^[2] The strongest traditional acids, triflic acid ($H_0 = -14$) and fluoro-sulfuric ($H_0 = -15.1$), do not protonate benzene, whereas carborane acids do.^[13] This behavior indicates that the equivalent Hammett acidities of carborane acids must be -17 or greater. Like carborane acids, the Hammett acidities of the present acids cannot be measured directly because they are unavailable in liquid form.

Stirring a suspension of $\text{H}_2(\text{B}_{12}\text{X}_{12})$ in the smallest possible volume of benzene (to minimize water contamination) converts the acids into slurries of their corresponding benzenium ion salts, formulated as $[\text{C}_6\text{H}_7]^+[\text{B}_{12}\text{X}_{12}]^-$. The presence of the C_6H_7^+ ion is established by IR spectroscopy, with diagnostic bands in the $\nu(\text{CH})$ and $\nu(\text{CC})/\delta(\text{CH})$ s regions. In particular, the $\nu(\text{CH}_2)$ frequencies of the most acidic CH_2 group at the protonated sp^3 carbon atom appear as a broad absorption centered at 2733 cm^{-1} for $\text{X} = \text{Cl}$ and 2664 cm^{-1} for $\text{X} = \text{Br}$. These frequencies are lower than those in the gas phase ($2810, 2795\text{ cm}^{-1}$)^[14] owing to H-bonding to halide atoms of the anions. The greater red shift for the bromide is consistent with the higher basicity of the $\text{B}_{12}\text{Br}_{12}^{2-}$ ion relative to the $\text{B}_{12}\text{Cl}_{12}^{2-}$ ion. As shown in Table 2, other

Table 2: Frequencies of the C_6H_7^+ ion as a function of counterion (in cm^{-1}).

Counterion	$\nu(\text{CH}_2)$ (average)	$\nu(\text{CH})_{\text{aromatic}}$	$\nu(\text{CC}) + \delta(\text{CCH})$
none ^[a]	2810, 2795 (2803)	3110, 3080	
$\text{CB}_{11}\text{H}_6\text{Cl}_6^{2-}$ ^[b]	2770, 2720 (2745)	3100, 3072, 3040, 3028	1601
$\text{B}_{12}\text{Cl}_{12}^{2-}$	2753, 2713 (2733)	3092, 3070, 3035	1600
$\text{CB}_{11}\text{H}_6\text{Br}_6^{2-}$ ^[b]	2757, 2714 (2736)	3095, 3073, 3066, 3023	1600
$\text{B}_{12}\text{Br}_{12}^{2-}$	2664	3084, 3060, 3028, 3015	1597

[a] Ref. [14]. [b] Ref. [13].

identifying bands are all very close in frequency. IR bands attributable to $\text{X-H}^+-\text{X}$ bridged moieties are absent, thus indicating that $\text{H}(\text{B}_{12}\text{X}_{12})^-$ ions, which would result from monoionization of the diprotic acids, must be absent. $\text{H}_2(\text{B}_{12}\text{X}_{12})$ behaves as a diprotic acid: both hydrogen ions are sufficiently acidic to protonate benzene. The extraordinary stability of the $\text{B}_{12}\text{X}_{12}^{2-}$ ions makes the isolation of the benzenium ion at room temperature straightforward. As expected for more basic arenes, the 2:1 arenium ion salts derived from protonating toluene and mesitylene can be isolated in a similar manner and characterized by IR spectroscopy (see the Supporting Information).

In summary, the new anhydrous diprotic acids $H_2(B_{12}X_{12})$ with $X = Cl$ and Br have been prepared. They have comparable acidity to carborane acids $H(CHB_{10}X_{10})$. Because they protonate benzene, their acidities must be at least 10^5 greater than that of 100% H_2SO_4 , that is, well into the superacidity region. These are the first examples of diprotic superacids, and the finding that both protons of $H_2(B_{12}X_{12})$ are able to protonate benzene is significant inasmuch as the second ionization might be expected to be of lower strength than the first. Finally, the all-boron acids are less expensive to prepare than their analogous carborane acids, although this advantage is tempered by the generally lower solubilities of $B_{12}X_{12}^{2-}$ salts compared to those of $CHB_{10}X_{10}^-$.^[15]

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- [1] M. Juhasz, S. Hoffmann, E. S. Stoyanov, K.-C. Kim, C. A. Reed, *Angew. Chem.* **2004**, *116*, 5466–5469; *Angew. Chem. Int. Ed.* **2004**, *43*, 5352–5355.
- [2] C. A. Reed, *Chem. Commun.* **2005**, 1669–1677.
- [3] W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, E. L. Muetterties, *Inorg. Chem.* **1964**, *3*, 159–167.
- [4] E. S. Stoyanov, K.-C. Kim, C. A. Reed, *J. Am. Chem. Soc.* **2006**, *128*, 8500–8508.
- [5] CCDC 721536, 721537, 721538 and 721539 ([trityl]₂[B₁₂Br₁₂]-2 toluene, [trityl]₂[B₁₂Cl₁₂]-2 ODCB, (Et₃Si)₂(B₁₂Br₁₂)-ODCB, and (Et₃Si)₂(B₁₂Cl₁₂)) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [6] S. V. Ivanov, S. M. Miller, O. P. Anderson, K. A. Solntsev, S. H. Strauss, *J. Am. Chem. Soc.* **2003**, *125*, 4694–4695.
- [7] C. A. Reed, *Acc. Chem. Res.* **1998**, *31*, 325–332.
- [8] T. Küppers, E. Bernhardt, R. Eujen, H. Willner, C. W. Lehmann, *Angew. Chem.* **2007**, *119*, 6462–6465; *Angew. Chem. Int. Ed.* **2007**, *46*, 6346–6349.
- [9] S. P. Hoffmann, T. Kato, F. S. Tham, C. A. Reed, *Chem. Commun.* **2006**, 767–769.
- [10] D. Stasko, S. P. Hoffmann, K.-C. Kim, N. L. P. Fackler, A. S. Larsen, T. Drovetskaya, F. S. Tham, C. A. Reed, C. E. F. Rickard, P. D. W. Boyd, *J. Am. Chem. Soc.* **2002**, *124*, 13869–13876.
- [11] E. S. Stoyanov, S. P. Hoffmann, M. Juhasz, C. A. Reed, *J. Am. Chem. Soc.* **2006**, *128*, 3160–3161.
- [12] E. S. Stoyanov, I. V. Stoyanova, F. S. Tham, C. A. Reed, *J. Am. Chem. Soc.* **2008**, *130*, 12128–12138.
- [13] C. A. Reed, K.-C. Kim, E. S. Stoyanov, D. Stasko, F. S. Tham, L. J. Mueller, P. D. W. Boyd, *J. Am. Chem. Soc.* **2003**, *125*, 1796–1804.
- [14] N. Solcà, O. Dopfer, *Angew. Chem.* **2002**, *114*, 3781–3784; *Angew. Chem. Int. Ed.* **2002**, *41*, 3628–3631.
- [15] Note added in proof: Parallel synthetic studies on the precursors to the acids have recently been published: V. Geis, K. Guttsche, C. Knapp, H. Scherer and R. Uzun, *Dalton Trans.*, **2009**, DOI: 10.1039/b821030f.