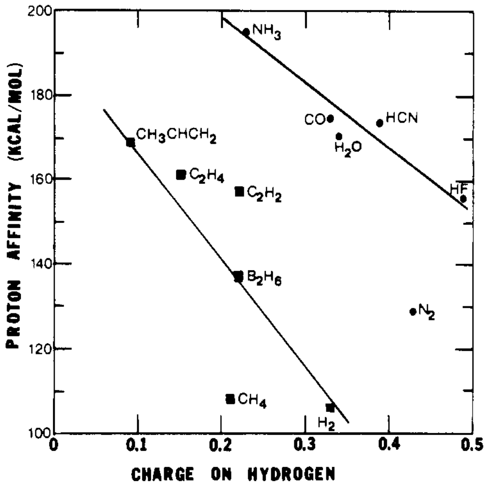

**Figure 2.** Plot of calculated proton affinity vs. resultant charge on the hydrogen atom.

proton. Such results are presented in Table V for eight molecules. It is clear that the frontier orbital theory and the charge on the attacked atom can serve as useful guidelines to predict the site of proton attack. In four of the eight cases both guidelines predict the same site of attack, in two cases the atomic charge alone predicts the correct site, and in two cases the frontier orbital theory alone predicts the correct site. In all cases except pyridine and aniline, the most stable site of attack results in the least positive charge on the proton.

**Proton Affinity Correlations.** In Figures 1 and 2 we present plots of calculated proton affinity vs. ionization energy (Koopmans' theorem) and vs. resultant charge on the proton. These plots are presented for a select few simple molecules of the sort for which we previously have examined the experimental data.[5b] There does appear to be a hint of the type of correlation we observed before. That is, substrate molecules can be classified as to whether they are lone-pair electron donors or bond-pair electron donors.

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**Supplementary Material Available:** A listing of calculated MNDO heats of formation and ionization energies from Koopmans' theorem and a figure showing calculated structures for $H^+(CO)_3$ (6 pages). Ordering information is given on any current masthead page.

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# MNDO Studies of Proton Affinity as a Probe of Electronic Structure. 2. Boranes and Carboranes

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The protonation of the boranes and carboranes $B_4H_{10}$, $B_nH_{n+4}$ ($n$ = 2, 5, 6), $C_2B_nH_{n+2}$ ($n$ = 3, 4, 5, 10), $CB_5H_9$, and $B_nH_n^{2-}$ ($n$ = 4, 6, 7) has been studied by the MNDO method. Calculated proton affinities and protonated structures are reported. The calculations predict B–B edge protonation for $B_6H_{10}$ and 1,6-$C_2B_4H_6$, B–B–B face protonation for $B_6H_6^{2-}$, $B_7H_7^{2-}$, 2,4-$C_2B_5H_7$, and 1,12-$C_2B_{10}H_{12}$, proton attack resulting in a three-center B–$H_2$ bond for $B_2H_6$, $B_4H_{10}$, and $B_5H_9$, carbon protonation for 1,5-$C_2B_3H_5$ and 2-$CB_5H_9$, and formation of a two-center B–H bond upon protonation of $B_4H_4^{2-}$. The site of protonation is correlated with the electronic structure of the substrates. Selected ab initio calculations employing the 3-21G basis set have been performed.

## Introduction

The boranes[1] and carboranes[2] from a class of molecules of exceeding interest from a structure and bonding viewpoint. Studies in the past decade have shown that it is useful to relate the structure and bonding of transition-metal organometallic cluster molecules to those of the main-group boranes and carboranes through the isolobal principle.[3]

In this work we set out to use the proton as a probe of the electronic structure of the boranes and carboranes. Our approach is to use the MNDO molecular orbital method,[4] building on our earlier work of MNDO proton affinity studies.[5] We shall pay particular attention to the site of proton attack on the substrate molecule and the resulting geometry changes and charge redistribution caused by protonation.

The experimental proton affinities are known for a few boranes[6] and carboranes[7] from gas-phase studies, but the protonated structures are unknown. Protonation of $B_6H_{10}$ has been carried out in solution, and NMR studies show that the B–B edge has been protonated to form $B_6H_{11}^+$.[8] We were also intrigued by the fact that ion cyclotron resonance experiments[7] on 1,6-$C_2B_4H_6$ have indicated it to have a basicity (proton affinity) equal to that of ammonia, in spite of the fact that it is an "electron deficient" molecule. Therefore, one of our goals was to determine whether the MNDO method could provide a rationale for the high basicity of 1,6-$C_2B_4H_6$.

A study of the scope that we have undertaken would be next to impossible using ab initio methods with a high-quality basis set. It is well-known that ab initio methods have difficulty obtaining the correct structure for a borane as small as $B_4H_{10}$, even when configuration interaction is included.[9] We have

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(5) Part 1: DeKock, R. L.; Jasperse, C. P., preceding paper in this issue.

(6) (a) Solomon, J. J.; Porter, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 1443. (b) Pierce, R. C.; Porter, R. F. *Ibid.* **1973**, *95*, 3849.

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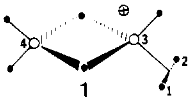
employed the MNDO method since it has been shown to be efficient in terms of computation time and to provide accurate heats of formation and structures of molecules.[10] Deficiencies of the MNDO method have been delineated in part 1.[5]

The MNDO method has been applied successfully to the boranes[11] and carboranes,[12] and one paper has reported its use to study the protonation of $B_5H_9$, $B_6H_{10}$, and $B_6H_6^{2-}$.[13] Each of these studies shows that the MNDO method must be used with care since it tends to underestimate the strengths of multicenter bonds.[11,12] Hence, incorrect geometries are calculated for 1,6-$C_2B_4H_6$, $CB_5H_7$, and $B_5H_9$. In our study, for each case that an open "classical" structure rather than the observed cage structure was calculated, it was possible to impose a few symmetry constraints during the geometry optimization and arrive at a structure close to the experimental one. We began our study with sufficient cynicism to warrant due caution in accepting the calculated structures provided by MNDO. Except where symmetry constraints were required to maintain a correct structure, we have optimized the geometry completely for both the molecular substrates and the protonated species. Our work on the substrates corroborates that of Dewar and McKee.[11,12] The proton affinities were calculated from the computed heats of formation and by utilization of the experimental heat of formation of the proton, 365.7 kcal/mol.[14]

## Results

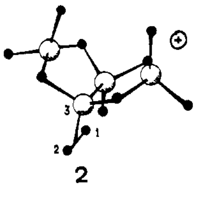
**$B_2H_6$/$B_2H_7^+$.** The calculated structure of $B_2H_7^+$ is presented in **1**. It essentially corresponds to a $B_2H_5^+$–$H_2$ complex, with an $H^1$–$H^2$ bond length of 0.74 Å compared to an MNDO optimized bond length of 0.66 Å for free $H_2$. The three-center $B^3$–$H^1$($H^2$) distance is 1.53 Å, considerably longer than the two-center B–H distance of 1.16 Å. Our 3-21G ab initio calculations[15] are in structural agreement with the MNDO result; the $H^1$–$H^2$ distance is 0.79 Å, and the $B^3$–$H^1$($H^2$) distance is 1.41 Å. MNDO assigns to the $B_2H_5$ fragment a 0.66+ charge and the ab initio method assigns a 0.53+ charge.



**1**

The overall $B_2H_6$ structure is only minimally distorted upon protonation. The only real change is the tightening of the bridging hydrogens toward the protonated boron, the bonds shortening from 1.35 to 1.26 Å. Structure **1** agrees with the proposed structure of Pierce and Porter.[16]

**$B_4H_{10}$/$B_4H_{11}^+$.** Protonation of $B_4H_{10}$ is similar to that of $B_2H_6$ in that an $H_2$ complex is formed of the sort $B_4H_9^+$–$H_2$ (**2**). The $H^1$–$H^2$ bond length is 0.76 Å, and the $B^3$–$H^1$ and $B^3$–$H^2$ bond lengths are 1.49 and 1.51 Å. The calculated charge on the $B_4H_9$ fragment is 0.62+. Each wing boron is 0.20+, the protonated boron is 0.14–, the other hinge boron is 0.22–, and the bridging hydrogen atoms are all about 0.10+.



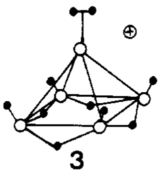
**2**

The tetraborane structure is only minimally affected by protonation. The central B–B distance actually shortens, by 0.02 Å, and the wing borons flatten slightly, increasing the dihedral angle from 117 to 130°. The hinge-to-wing boron distances, originally 1.88 Å, increase to 2.02 and 1.92 Å; the protonated boron essentially pushes the wing borons away. One of the two planes of symmetry is maintained, however. A structure that is similar to **2** but is without a central B–B bond has been postulated by Pierce and Porter.[16]

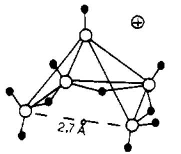
Two other less stable sites of $B_4H_{10}$ protonation were considered. Protonating a wing boron gives a structure calculated to be 5.6 kcal/mol less stable than **2**. This energy difference is not surprising, for it is intuitively reasonable that formation of electron-deficient bonds be preferred at the more electron-rich boron, and in $B_4H_{10}$ MNDO calculates 0.24– charges for the hinge borons and 0.09+ charges for each of the wing borons. Formation of a central B–H–B bond is also found to give a less stable structure than **2**, by 12.7 kcal/mol. The site of protonation on $B_4H_{10}$ also can be rationalized with use of the frontier orbital approach.[17] The HOMO of $B_4H_{10}$ is calculated to consist of 5% character from each of the wing-tip boron atoms and 19% from each of the hinge boron atoms.

Calculations were also done ab initio at the 3-21G level. These results confirm that the formation of a B–$H_2$ bond at a central boron is favored and that the protonated boron is more negative than the other hinge boron, which is in turn more negative than the wing borons.

**$B_5H_9$/$B_5H_{10}^+$.** The MNDO protonation of $B_5H_9$ has been reported to result in the formation of a three-center B–$H_2$ bond, at the apical and most negative boron (**3**).[13] Our study also finds this structure, but MNDO prefers by 16.8 kcal/mol a more classical structure (**4**) in which a B–H–B bond has broken in favor of two classical two-center B–H bonds. Although this energy difference is significant, structure **3**, where the $B_5$ cluster is relatively undisturbed, is probably more realistic.[18]



**3**



**4**

It is not unusual for MNDO to predict cluster decomposition. Dewar and McKee have shown for unprotonated $B_5H_9$ itself that MNDO prefers by 9 kcal/mol a more classical structure over the experimentally observed $C_{4v}$ symmetry cluster;[11a] that the MNDO structure should distort even further upon protonation is hardly surprising. MNDO also improperly prefers a classical $CB_5H_7$ structure by 17 kcal/mol over the microwave structure, and the empirical octahedral structure for 1,6-$C_2B_4H_6$ is not even calculated to be a local energy minimum.[12] Several of the clusters in the work reported here are predicted by MNDO to break up when protonated. Dewar

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(10) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 5558.

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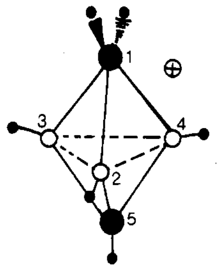
(18) Solomon, J. J.; Porter, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 1443.

$C^1B^2$ = 1.78
$C^1B^3$ = 1.63
$B^2B^3$ = 1.97
$B^3B^4$ = 2.08
$C^5B^2$ = 1.57
$C^5B^3$ = 1.57
$<HC^1H$ = 96.3



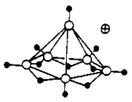
$C^1$ = -0.39
$C^5$ = -0.10
$B^2$ = +0.33
$B^3$ = +0.13

**Figure 1.** Structure and calculated charges for $C_2B_3H_5{-}H^+$.

and co-workers attribute MNDO's mistakes to an underestimation of the strengths of multicenter bonds.[11a] Diagrams of subsequent classical structures will be relegated to the supplementary material.

Several other $B_5H_9$ protonation sites were considered. Protonation of a basal rather than the apical boron gave a structure 3.5 kcal/mol less stable than **3**; protonation along an apical boron–basal boron edge gave a structure 11.8 kcal/mol less stable than **3**; face protonation gave a structure that relaxed to **3**, and protonation in or below the basal boron plane gave structures more than 100 kcal/mol less stable than **3**. The site of protonation for $B_5H_9$ occurs at the most negative (apical) position. However, this is also the position at which the HOMO percent character is concentrated. The apical boron contributes 30% to the HOMO whereas each basal boron atom contributes only 8%.

**$B_6H_{10}$/$B_6H_{11}^+$.** The MNDO structures for $B_6H_{10}$ and $B_6H_{11}^+$ also have been previously reported;[11,13] protonation occurs at the unbridged equatorial B–B edge to form a fifth B–H–B bond (**5**). $B_6H_{11}^+$ is the only protonated borane or carborane whose structure has been experimentally inferred, and the MNDO structure agrees with the solution NMR results.[8] Whereas $B_6H_{10}$ has $C_s$ symmetry, $B_6H_{11}^+$ has $C_{5v}$ symmetry. Edge protonation was calculated to be preferred by 25 kcal/mol over apical boron protonation, and other attempted protonation sites gave structures that relaxed toward **5**.



**5**

It is interesting that in this case the site of protonation is not determined by the atomic charges in $B_6H_{10}$. The most negative site is the apical boron atom (0.24–) followed by the unique basal boron atom (0.13–). The two atoms in the B–B bond are each only 0.06–. This site of protonation may be best explained by the 48% localized character of the HOMO on the two boron atoms that are bridged.

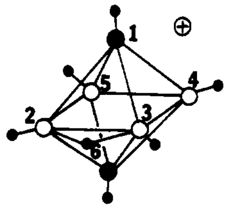
**1,5-$C_2B_3H_5$/1,5-$C_2B_3H_6^+$.** MNDO correctly calculates the experimental trigonal-bipyramidal structure of $C_2B_3H_5$, with both carbons apical.[12] Upon protonation, however, MNDO calculates a classical structure in which each of the carbons has four bonds (supplementary material).

A more likely structure is shown in Figure 1; here protonation has occurred at a carbon and the trigonal bipyramid is maintained. A plane of symmetry remains. Structurally, the borons are pushed away from the protonated carbon toward the unprotonated carbon, the boron in the plane of symmetry more so than the other two.

The charge disturbance is far more radical. Before protonation the carbons were charged 0.18– each and the borons 0.02+ each. Carbon protonation has occurred at the most negative site, but the protonated carbon has become significantly more negative by 0.21 charge unit.

In $C_2B_3H_5$ and $C_2B_3H_6^+$ the B–B bond lengths are very long, at or above 1.94 Å. Thus, if we ignore B–B bonding, we can consider $C_2B_3H_5$ to be classical, each carbon with four bonds and each boron with three. That protonation should occur at the more electron-rich carbon rather than at a boron is therefore not unexpected. The site of protonation could also have been predicted on the basis of the percent character of the HOMO. It contains 31% character from each C atom and 13% character from each B atom. Protonation of a boron gives a structure with a by now familiar B–$H_2$ bond, a structure that is 14.2 kcal/mol less stable than the one in Figure 1. Attempts to protonate a BB edge and a BBC face gave structures that both relaxed to the one in Figure 1.

$C^1B^2$ = 1.78
$C^1B^4$ = 1.62
$B^2B^3$ = 1.66
$B^3B^4$ = 1.84
$B^4B^5$ = 1.91
$B^2H^6$ = 1.38



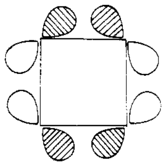
$C^1$ = -0.17
$B^2$ = -0.03
$B^4$ = +0.13
$H^6$ = +0.23

**Figure 2.** Structure and calculated charges for $C_2B_4H_6{-}H^+$.

**1,6-$C_2B_4H_6$/1,6-$C_2B_4H_7^+$.** Although $C_2B_4H_6$ is considered to be "electron deficient", an ICR study has found it to have a proton affinity greater even than that of ammonia.[7] This system is thus of special interest, so that in addition to MNDO calculations we have done ab initio calculations.

The experimentally observed octahedral 1,6-$C_2B_4H_6$ structure is not found by MNDO calculations to be even a local energy minimum.[11a] It is thus no great surprise that upon complete relaxation the MNDO 1,6-$C_2B_4H_7^+$ cluster distorts to a classical structure (supplementary material). When the cluster is not fully relaxed, however, the most stable site of protonation is along a B–B edge, resulting in a structure with $C_{2v}$ symmetry as shown in Figure 2. The C–B and B–B distances in the neutral molecule were 1.67 and 1.74 Å, respectively. Surprisingly, the bridged B–B distance is shortened to 1.64 Å. It is generally assumed that hydrogen-bridged bonds are lengthened. The opposite $B^4$–$B^5$ edge lengthens to 1.91 Å. The 3-21G ab initio calculations do not agree that the bridged bond is shortened; the bridged B–B distance is calculated to be 1.80 Å, compared to 1.64 Å in neutral 1,6-$C_2B_4H_6$. However, the ab initio calculations agree with MNDO that the bridged bond is shorter than the unbridged bonds; the opposite $B^4$–$B^5$ length is 1.84 Å.

This unexpected bond length trend can be rationalized by considering the approach of the proton to attack the HOMO of 1,6-$C_2B_4H_6$. This orbital is B–B bonding and contains no carbon character (**6**). Proton attack at a given BB bond causes electronic charge to cluster in the BHB bridge, thereby weakening and lengthening the unbridged BB bonds. This hypothesis is borne out by the following charge analysis.



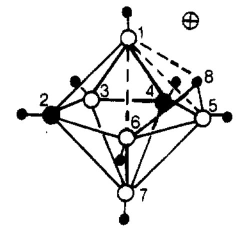
**6**

The carbons gain electronic charge when the B–B edge protonates, going from 0.03+ to 0.17– each. The borons were originally 0.17–; the bridged borons, although they lose charge and end up 0.03–, do not contribute nearly as much charge as the unbridged borons, which are 0.13+. In the ab initio calculations, the carbons each stay at 0.85–, the bridged borons each stay at 0.31+, and the unbridged borons each become 0.51+.

The calculated proton affinities are 160 kcal/mol by MNDO and 157 kcal/mol by ab initio, considerably lower than the ICR value of 208 kcal/mol.[7]

$B^1C^2$ = 1.62
$B^1B^3$ = 1.93
$B^1B^5$ = 2.29
$B^1B^7$ = 2.56
$B^1H^8$ = 2.24
$B^5B^6$ = 1.83

$C^2B^3$ = 1.63
$C^2B^6$ = 1.63
$B^7C^2$ = 1.90
$B^7B^3$ = 1.77
$B^7B^5$ = 1.78
$B^5H^8$ = 1.38



$B^1$ = +0.12
$C^2$ = −0.13
$B^3$ = +0.04
$B^5$ = +0.02
$B^7$ = +0.01
$H^8$ = +0.10

**Figure 3.** Structure and calculated charges for $C_2B_5H_7$–$H^+$.

MNDO calculations of face and C–B edge protonated structures all gave higher heats of formation or else were passed over during optimization in preference for the edge-protonated structure shown in Figure 2. We have also attempted protonation at the center of the cluster. This site is less stable than the edge-protonated site by 300 kcal/mol. We have attempted protonation at the center of other closo structures in this study; never did we find them to represent the most stable configuration.

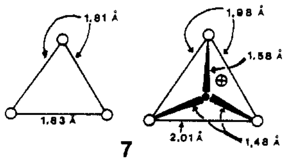
**2,4-$C_2B_5H_7$/2,4-$C_2B_5H_8^+$.** Both carbon atoms in $C_2B_5H_7$ are empirically known to be equatorial, and both possible 2,4- and 2,3-isomers have in fact been observed. MNDO favors the 2,4-isomer,[12] and it is this isomer whose protonation is considered here.

Once again MNDO gives a "classical" structure for 2,4-$C_2B_5H_8^+$ (supplementary material). The most stable cluster structure is found to be BBB face capped, as shown in Figure 3. The net structural effect of protonating 2,4-$C_2B_5H_7$ is a slight expansion of the cluster; the $B^1$–$B^7$ distance increases by 0.05 Å, the $B^5$–$B^6$ distance increases by 0.15 Å, and $C^2$–$B^3$ increases by 0.02 Å, while $B^3$ dips so that the $B^3$–$B^7$ distance shortens by 0.14 Å. $B^5$ and $B^6$ also dip significantly, thus enlarging the protonated face.

In terms of charge, $B^5$ and $B^6$ have each changed from 0.12− to 0.02+. $B^1$ has changed upon protonation from 0.05− to 0.12+, $B^7$ has changed from 0.05− to 0.01+, the carbons have each changed from 0.06− to 0.13−, and $B^3$ has changed from 0.14− to 0.04+.

Protonation at a carbon was found to be less stable than protonation at any of the boron atoms. Among the boron atoms, the more negative sites $B^5$ and $B^6$ were preferred over $B^1$, $B^3$, and $B^7$. The HOMO of $C_2B_5H_7$ is 55% localized in the triangular BBB face.

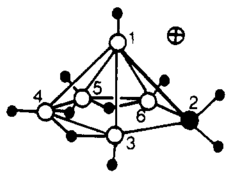
**$C_2B_{10}H_{12}$/$C_2B_{10}H_{13}^+$.** 1,12-$C_2B_{10}H_{12}$ is an icosahedron, and although it is the fourth carborane of the $C_2B_nH_{n+2}$ series that we have considered, it is the only one that contains more than one "layer". In 1,12-$C_2B_{10}H_{12}$ we find a highly symmetric $C_{5v}$ structure where two planes, each containing five borons, are staggered. Protonation is found by MNDO to cap one of the 10 equivalent BBB faces, and with the exception of the boron atom vertices of the protonated face there is almost no distortion of the cluster. 1,12-$C_2B_{10}H_{13}^+$ is thus the first protonated carborane for which MNDO does not choose a "classical" structure. An unprotonated BBB face is almost equilateral, and the proton ends up hovering almost directly above the center of that face (7). The HOMO contains 10% character from each of the boron atoms in $C_2B_{10}H_{12}$.



**7**

The charge donation comes largely from the boron bound hydrogens; each of the ten is originally charged 0.078+ but end up charged (0.125 ± 0.004)+. The two borons adjacent to the base of the protonated face, at 0.04+, are the only borons more positive than 0.06−. Each of the 10 borons was originally 0.10−.

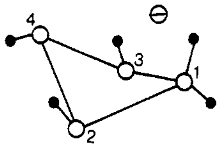
$B^1C^2$ = 1.95
$B^1B^3$ = 1.80
$B^1B^4$ = 1.77
$C^2B^3$ = 1.61
$B^3B^4$ = 1.80
$B^4B^5$ = 1.96
$<HC^2H$ = 109°
$<B^3C^2B^6$ = 115°



$B^1$ = −0.06
$C^2$ = −0.15
$B^3$ = +0.11
$B^4$ = −0.03

**Figure 4.** Structure and calculated charges for $CB_5H_9$–$H^+$.

$B^1B^2$ = 1.64
$B^2B^4$ = 1.56
$B^1B^4$ = 2.05
$B^2B^3$ = 2.38
$<HB^1H$ = 115°

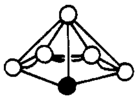


$B^1$ = −0.42
$B^2$ = −0.01
$B^4$ = −0.33

**Figure 5.** Structure and calculated charges for $B_4H_5^-$.

Protonating a carbon gave a structure calculated to be 26.5 kcal/mol less stable than the face-capped structure.

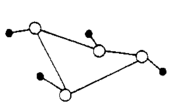
**2-$CB_5H_9$/2-$CB_5H_{10}^+$.** 2-$CB_5H_9$ is a nido cluster (8), unlike the previously discussed carboranes, all of which are closo. The molecule offers several possible sites of protonation: an equatorial carbon, a rather negative apical boron (0.25−), an equatorial B–C edge, and a BCB face. MNDO calculates a classical structure for $CB_5H_{10}^+$, which we do not report here. In the most stable 2-$CB_5H_{10}^+$ cluster, shown in Figure 4, protonation has occurred at the carbon, which if we ignore the apical boron ends up in an almost tetrahedral arrangement. The HOMO is 43% concentrated on the carbon atom. Structurally the carbon folds down and away from the cluster; the $B^1$–$C^2$ distance increases by 0.17 Å, and whereas the $B^1$–$B^3$ distance shortens by 0.09 Å the $C^2$–$B^3$ distance increases by 0.11 Å.



**8**

In terms of charge $B^1$ becomes 0.19 more positive, the protonated $C^2$ becomes 0.15 more negative, $B^3$ becomes 0.16 more positive, and $B^4$ changes only by 0.01−. Here, as so often before, we find a secondary charge effect where atoms adjacent to protonated atoms donate considerable charge while the site atom actually gains charge.

**$B_4H_4^{2-}$/$B_4H_5^-$.** In addition to neutral boranes and carboranes, we also studied the protonation of the dianions $B_4H_4^{2-}$, $B_6H_6^{2-}$, and $B_7H_7^{2-}$, each of whose MNDO structure have been previously reported.[11b] $B_4H_4^{2-}$, isoelectronic with planar $C_4H_4^{2+}$, is a slightly folded structure of $C_{2v}$ symmetry (9). The calculated structure of $B_4H_5^-$ is shown in Figure 5. Terminal protonation has occurred to produce a classical, tetrahedral bonding situation rather than a B–$H_2$ bond. This is not surprising in light of the available charge in the dianion. Protonation causes almost no structural change. The dihedral angle increases only 1° from its original 143°, and bond lengths are similarly undisturbed. The bulk of the charge is once again donated by the secondary atoms, $B^2$ and $B^3$, each of which changes from 0.35− to 0.01−, whereas the protonated atom increases its charge from 0.35− to 0.42−.

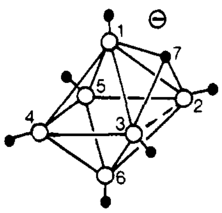


**9**

**$B_6H_6^{2-}$/$B_6H_7^-$.** The MNDO structure for $B_6H_7^-$ has been reported as an unlikely, severely distorted classical structure.[13]

$B^1B^2$ = 1.89
$B^1B^4$ = 1.79
$B^1B^6$ = 2.52
$B^1H^7$ = 1.27
$B^2H^7$ = 1.75

$B^2B^3$ = 2.20
$B^3B^4$ = 1.67
$B^4B^5$ = 1.63
$B^6B^2$ = 1.64
$B^6H^4$ = 1.90

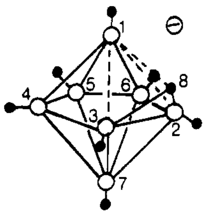


$B^1$ = -0.21
$B^2$ = -0.08
$B^4$ = -0.19
$B^6$ = -0.23
$H^7$ = +0.02

**Figure 6.** Structure and calculated charges for $B_6H_7^-$.

$B^1B^2$ = 2.33
$B^1B^4$ = 1.69
$B^1B^5$ = 1.83
$B^1B^7$ = 2.50
$B^2B^7$ = 1.80
$B^4B^7$ = 1.95

$B^5B^7$ = 1.68
$B^2B^3$ = 1.81
$B^3B^4$ = 1.66
$B^4B^5$ = 1.72
$B^1H^8$ = 2.33
$B^2H^8$ = 1.37
$B^7H^8$ = 2.57



$B^1$ = +0.07
$B^2$ = -0.10
$B^4$ = -0.29
$B^5$ = -0.11
$B^7$ = -0.10
$H^8$ = +0.04

**Figure 7.** Structure and calculated charges for $B_7H_8^-$.

But we find that MNDO also obtains a face-capped cluster, shown in Figure 6, that is barely 1 kcal/mol less stable than the Brint et al. "classical" $B_6H_7^-$.[13] The face-capped structure maintains one plane of symmetry ($C_s$). Full geometry optimization of $B_6H_7^-$ distorts the Figure 6 structure only slightly; the structure remains face capped, and the energy is 0.4 kcal/mol lower than the reported classical structure.[13]

The face-capped structure is almost certainly the actual structure; ab initio calculations (STO-3G) predict a face-capped octahedron,[13] and the isoelectronic $CB_5H_7$ is calculated to be a face-capped octahedron.[13] Also isoelectronic is 1,6-$C_2B_4H_7^+$, which we discussed earlier and which is edge rather than face protonated. The presence of face protonation for $B_6H_6^{2-}$ and edge for isoelectronic 1,6-$C_2B_4H_6$ is readily understood on the basis of the HOMO character of the two molecules. Whereas the HOMO of 1,6-$C_2B_4H_6$ is 100% localized in the $B_4$ plane (see above), the octahedral symmetry of $B_6H_6^{2-}$ has triply degenerate $t_{2g}$ HOMO orbitals occupied by six electrons. It is well-known in transition-metal chemistry from study of X-ray electron density deformation maps that a $(t_{2g})^6$ electronic configuration results in "lobes" of electron density pointing toward the faces of the octahedron.[19]

B–B bond lengths in the $B_6H_6^{2-}$ perfect octahedron were 1.73 Å. Upon protonation, the cluster expands somewhat, and the equatorial plane tilts, enlarging the face, so that the $B^2$–$B^6$ distance of 1.64 Å is shorter than the $B^1$–$B^2$ distance of 1.89 Å, whereas the $B^4$–$B^6$ distance, 1.90 Å, becomes longer than the $B^4$–$B^1$ distance, 1.79 Å. The $B^2$–$B^3$ distance has lengthened from 1.73 to 2.20 Å.

The secondary charge effect is not observed. $B^2$ and $B^3$ each have gone from 0.28– in the dianion to 0.08– in $B_6H_7^-$. The other borons donate between 0.05 and 0.09 charge unit each.

A symmetrical face-bridged structure for $B_6H_7^-$ is only 2.4 kcal/mol less stable than the structure shown in Figure 6.

**$B_7H_7^{2-}$/$B_7H_8^-$.** $B_7H_8^-$, isoelectronic with 2,4-$C_2B_5H_8^+$, is found by MNDO to be face protonated. The $C_s$ symmetry structure is shown in Figure 7. As in the face-capped 2,4-$C_2B_5H_8^+$ and $B_6H_7^-$ the equatorial plane tilts and the $B^2$–$B^3$ distance increases, and as in the face-capped 2,4-$C_2B_5H_8^+$ and $B_6H_7^-$ the secondary charge effect is not observed.

The $B^2$–$B^3$ distance is 1.81 Å, longer than the $B^3$–$B^4$ distance of 1.66 Å or the $B^4$–$B^5$ distance of 1.72 Å, and the $B^1$–$B^2$ distance, 2.33 Å, is longer than the $B^1$–$B^4$ and $B^1$–$B^5$ distances of 1.69 and 1.83 Å, respectively. The proton is not in the center of the face; the $B^2$–$H^8$ distance is 1.37 Å, whereas the $B^1$–$H^8$ distance is a very long 2.33 Å. The HOMO of $B_7H_7^{2-}$ is 17% on each basal boron and 1% on each apical boron, so it is not surprising that the proton is not symmetrically situated over the triangular face.

Table I. Proton Affinities (kcal/mol)

| molecule | MNDO | expt1[a] | molecule | MNDO | expt1[a] |
|---|---|---|---|---|---|
| $B_2H_6$ | 136.6 | 146 ± 5 | 2,4-$C_2B_5H_7$ | 155.4 | 173 ± 1 |
| $B_4H_{10}$ | 144.1 | 144 ± 5 | 1,12-$C_2B_{10}H_{12}$ | 119.3 | |
| $B_5H_9$ | 154.7 | 167 ± 6 | 2-$CB_5H_9$ | 165.5 | |
| $B_6H_{10}$ | 174.3 | 195 ± 8 | $B_4H_4^{2-}$ | 460.6 | |
| 1,5-$C_2B_3H_5$ | 144.2 | | $B_6H_6^{2-}$ | 419.2 | |
| 1,6-$C_2B_4H_6$ | 160.5 | 208 ± 4 | $B_7H_7^{2-}$ | 406.7 | |

[a] For citations to the experimental work see ref 7.

The structure might almost be considered to be edge bridged, but we consider it face bridged because in the truly edge-bridged 1,6-$C_2B_4H_7^+$ case the equatorial plane of symmetry was maintained, whereas in $B_6H_7^-$ the face opens, the equatorial plane tilts, and the secondary charge effect is absent just as in the face-capped $B_6H_7^-$ and 2,4-$C_2B_5H_8^+$ cases. The difference between edge and face protonation appears to be not qualitative but quantitative, related to the contribution of the apical atom toward the bonding of the proton. The apical carbons in 1,6-$C_2B_4H_6$ contribute nothing, whereas in $B_6H_6^{2-}$ the "apical" boron contributes as much as the "basal" borons, the octahedral symmetry making the very distinction between "apical" and "basal" atoms impossible.

In $B_7H_8^-$, $B^2$ and $B^3$ have each become 0.10–, whereas $B^4$ is 0.29– and $B^5$ is 0.11–. In $B_7H_7^{2-}$ all five equatorial boron atoms were 0.28–. And where $B^1$ and $B^7$ were 0.10–, $B^1$ is now 0.07+ and $B^7$ is still 0.10–. Protonation of other sites gave structures that were all optimized toward the one in Figure 7.

**Proton Affinity.** The proton affinity of a molecule B is defined as the negative of the heat of protonation:

$$B + H^+ \rightarrow BH^+ \qquad PA = -\Delta H^\circ$$

The MNDO calculated proton affinities for the boranes and carboranes in this study are listed in Table I, and where possible they are compared to available experimental values. All the values listed were calculated by using the most stable cluster structures rather than more MNDO stable "classical" structures. Also, the experimental $\Delta H_f^\circ(H^+)$ = 365.7 kcal/mol was used throughout, rather than the 326.7 kcal/mol value given by MNDO itself. This is a strictly empirical correction, but since MNDO is parameterized to mimic experiment, the correction hardly violates the spirit of the technique.

## Discussion

The authors have assumed throughout that structures in which clusters are broken are due to artifacts of the MNDO method. Experimental support for this assumption is available in the cases of $B_5H_9$, $B_5H_{11}$,[20] 1,6-$C_2B_4H_6$, and 2-$CB_5H_9$. Ab initio calculations support it in the case of $B_6H_7^-$.[13] It is possible, though, that protonation in some cases might disrupt clusters. The energy preference for the "classical" structures is sometimes quite large. A classical structure of $C_2B_4H_7^+$, for example, is preferred by MNDO by 51 kcal/mol over the edge-protonated cluster, but in the neutral carborane the classical structure is favored by 37 kcal/mol.

For the neutral boranes we observe a general increase in proton affinity with increase in cluster size. The opposite is true for the dianions. Both trends can be rationalized from the idea that a larger molecule can more easily accommodate charge imbalance than a smaller one. Thus $B_6H_{10}$ can more

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(19) Stevens, E. D.; DeLucia, M. L.; Coppens, P. *Inorg. Chem.* **1980**, *19*, 813.

(20) In the course of our study we repeated the MNDO work of Dewar and McKee[11b] on $B_5H_{11}$. We find the cluster structure that they report, but a classical structure is calculated to be more stable by 9.1 kcal/mol.

easily accept and distribute a positive charge than can $B_2H_6$, and $B_7H_7^{2-}$ can more easily carry its dianionic charge than can $B_4H_4^{2-}$. No such pattern is discernible among the carboranes, however.

A variety of protonation types were observed. (The abstract summarizes our findings.) Some patterns emerge. Face protonation occurred always and only on closo compounds with available BBB faces. In the carborane series $C_2B_nH_{n+2}$ ($n$ = 3, 4, 5, 10) BB edge or BBB face protonation occurs for all but $n$ = 3.

Protonation tends to occur at the most negatively charged atoms in the substrate molecule. However, the percent character of the HOMO also serves as a good predictor of the site of proton attack. In fact, for $B_6H_{10}$ percent HOMO character and not charge provides the best predictor. The most negatively charged atoms are often apical, and 2-$CB_5H_9$ is the only molecule where a two-center bond is formed at an equatorial atom, that atom being carbon. B–$H_2$ bonds are observed but never C–$H_2$ bonds, and B–$H_2$ bonds are not observed upon protonation of closo compounds. These compounds undergo little structural distortion as a result of protonation.

The proton affinity results presented in Table I show significant disagreement for 1,6-$C_2B_4H_6$. Given our interest in the reported experimental[7] high proton affinity, we decided to do extensive ab initio 3-21G calculations on 1,6-$C_2B_4H_6$ and $C_2B_4H_7^+$. With optimization of both structures (except for terminal BH and CH bonds) we obtain a calculated proton affinity of 157 kcal/mol. This is close to the MNDO results but 50 kcal/mol less than that reported experimentally. At the present we have no explanation for this wide discrepancy.

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**Registry No.** $B_2H_6$, 19287-45-7; $B_4H_{10}$, 18283-93-7; $B_5H_9$, 19624-22-7; $B_6H_{10}$, 23777-80-2; 1,5-$C_2B_3H_5$, 20693-66-7; 1,6-$C_2B_4H_6$, 20693-67-8; 2,4-$C_2B_5H_7$, 20693-69-0; 1,12-$C_2B_{10}H_{12}$, 20644-12-6; 2-$CB_5H_9$, 12385-35-2; $B_4H_4^{2-}$, 12429-81-1; $B_6H_6^{2-}$, 12429-97-9; $B_7H_7^{2-}$, 12430-07-8.

**Supplementary Material Available:** A listing of calculated MNDO heats of formation and a figure showing classical structures (3 pages). Ordering information is given on any current masthead page.

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# Use of Balanced-Like-Charges Approach to Metal–Bicarbonate Reactions

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Formation reactions for several metal–bicarbonate ion pairs were written as $M^{2+} + H_2CO_3 = MHCO_3^+ + H^+$. Values of the equilibrium constants as a function of temperature could then be fit to a two-parameter equation of the form log $K = A + B/T$. The resulting equations reproduce selected published experimental formation constants to an average of ±0.5% for the following ions: Mn, Mg, Ca, Zn, and Cu.

## Introduction

The temperature dependence of formation constants for metal–bicarbonate systems are important to seawater chemistry,[1] geothermal energy studies,[2] and nuclear waste disposal.[3] Usually the temperature dependence is described by fitting to nonlinear equations such as log $K_f = A + B/T + C \ln T + DT^2$ in which either $C$ or $D$ may be zero.[1,2] An example is that of Lesht and Bauman,[1] who were unable to find a two-parameter equation consistent with their experimental log $K_f$ values. We report here an approach whereby selected formation constants are fit to a two-term linear equation that permits estimating values at high temperatures by extrapolation. The approach is based on that recently used by Lindsay,[4] Cobble et al.,[5] and Phillips and Silvester,[9] in which the charges on both sides of a chemical reaction are of like sign and are equal in number.

## Method of Calculation

The formation of a metal–bicarbonate ion pair for a divalent metal ion is written as

$$M^{2+} + HCO_3^- = MHCO_3^+ \qquad (1)$$

where

$$K_f = \frac{[MHCO_3^+]}{[M^{2+}][HCO_3^-]} \qquad (2)$$

Adding the dissociation reaction for $H_2CO_3$

$$H_2CO_3 = HCO_3^- + H^+ \qquad (3)$$

to eq 1 gives

$$M^{2+} + H_2CO_3 = MHCO_3^+ + H^+ \qquad (4)$$

It is seen that eq 4 has ions of identical sign on each side of the equation

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