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Deuteration of Closo-1,2- and 1,7-$C_2B_{10}H_{12}$ Using $C_6D_6/AlCl_3$: Mechanistic Considerations

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ABSTRACT

Regioselective deuteration of 1-X-$C_2B_{10}H_{12}$ (X = 2, 7) cage systems with $C_6D_6/AlCl_3$ is correlated to ab initio calculational results on a $[C_2B_{10}H_{13}]^+$ intermediate. Full geometry optimizations of pertinent $[C_2B_{10}H_{13}]^+$ isomers, derived from each of the two 1-X-$C_2B_{10}H_{12}$ carborane isomers, result in cage geometries not unlike the (nearly) icosahedral starting carborane. Each isomer contains a BH_2 group having an acute H-B-H angle, long B–H bonds, and a very short $H\cdots H$ distance, hinting that the pertinent boron shares the electrons of a hydrogen molecule σ pair. It is suggested that the structural differences between the BH_2 group of $[C_2B_{10}H_{13}]^+$ and the CH_2 group of the benzenium ion, $[C_6H_7]^+$ (the intermediate strongly intimated upon protonation of benzene), can be explained, in part, by (a) the availability of the π-ring electrons for bonding to the (extra) proton in the latter and (b) the unavailability of π electrons from the carborane. Thus, the $C_2B_{10}H_{12}$ cage is most probably very reluctant to give up a cage electron pair in order to assist in bonding to an (externally bound) proton. Instead, it is more probable that "hydridic" B–H sigma electrons could very well play the important role in providing bonding to the attacking proton. © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:95–102, 1998

INTRODUCTION

The polyboron hydride B_5H_9 can undergo hydrogen/deuterium isotope exchange in the presence of $C_6D_6/AlCl_3$ [1], and the results are essentially identical to that observed when B_5H_9 is placed in the presence of $DCl/AlCl_3$ [2]. To our knowledge, the use of $C_6D_6/AlCl_3$ reagent combination for H/D isotope exchange has not been extended to carboranes. Previously reported methods of deuterating carboranes involved, variously, D_2O, DCl, B_2D_6, or D_2 as the deuterium source [3–6]. The possibility of hydrolysis/cage-breakdown with D_2O, and the awkwardness, or inconvenience, of handling significant quantities of three of these reagents (DCl, B_2D_6, D_2) in the gas phase leaves much to be desired. In some cases, a deuterated polyborane has been used as a precursor to the preparation of a deuterated carborane [4]; however, many polyboranes are air unstable and difficult to work with outside a high-vacuum or other special apparatus.

Our interest in preparing deuterated carboranes stemmed initially from the desire to obtain deuterated $C_2B_5H_7$ derivatives. However, the procedure (using $C_6D_6/AlCl_3$ as the reagent combination) we had hoped would lead to regiospecific deuterated derivatives of this carborane was only moderately successful [7]. In scanning the reactivity of this $C_6D_6/AlCl_3$ reagent combination with other carboranes, we found that two isomers (1,2- and 1,7-) of the $C_2B_{10}H_{12}$ system (Figure 1) were ideal for studying a step-by-step regio selective deuteration of these systems. In the course of this experimental work, we also carried out some germane calculational studies,

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Dedicated to Prof. William McEwen on the occasion of his seventy-fifth birthday.

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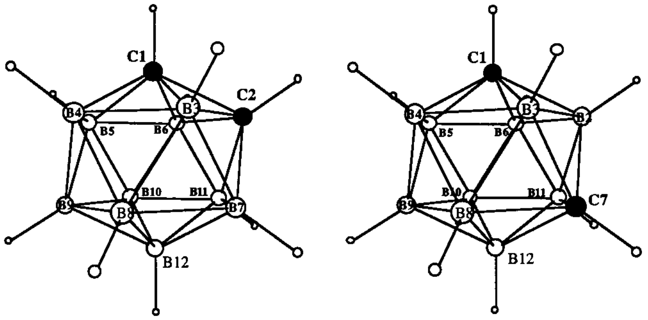


FIGURE 1 Structures of the closo-$C_2B_{10}H_{12}$ isomers used in the present study.

and this resulted in what we believe are significant mechanistic implications.

EXPERIMENTAL

Reaction of 1,2-$C_2B_{10}H_{12}$ with $C_6D_6/AlCl_3$: Deuteration Sequence

A 50 mg quantity of 1,2-$C_2B_{10}H_{12}$ (^{11}B NMR shown in Figure 2), 0.5 mL of C_6D_6 (99.6 atom% deuterium), and ≈10 mg $AlCl_3$ were placed in a 5 mm NMR tube under dry bag conditions. Deuterated benzene and $AlCl_3$ are of commercial grade (Aldrich). Using standard vacuum line techniques, several tubes with this sample mixture were sealed. One sample was then allowed to stand at room temperature for about 12 hours after which a ^{11}B NMR spectrum of the sample clearly showed that deuteration had occurred completely at the (9,12) positions [8] (Figure 2); further standing for an additional 26 days at ambient temperatures showed that deuteration had occurred to a significant extent at the (8,10) positions as well. [It is to be noted that the doublets observed in the ^{11}B NMR spectrum of the carborane are an indication that a hydrogen is still attached to the pertinent borons while singlets (usually as a result of overlap of three closely spaced 1:1:1 area peaks in which the coupling constant between the overlapping peaks should theoretically be close to one-seventh that of the corresponding B–H coupling) give evidence of an isotope exchange, indicating the presence of a deuterium (spin I = 1) at the pertinent boron.] At 57 days, an ^{11}B NMR analysis revealed a spectrum very similar to that of the one taken at 26 days, i.e., there was no indication at that point that deuteration was occurring at boron positions other than (9,12) and (8,10). An ^{11}B NMR spectrum of a sample taken after it was heated at 68°C for 48 hours showed only partial deuteration of the B(4,5,7,11) positions. Heating at 100°C for 51 hours gave rise to a deuterated carborane that exhibited essentially complete deuteration at the B(4,5,7,11) position(s) while B(3,6) remain largely undeuterated (Figure 2). Further heating at 150°C for 24 hours and subsequent NMR analysis indicated that deuteration at B(3,6) had not yet occurred to any significant extent. Heating beyond 150°C was avoided because of a hint of carborane degradation indicated by the appearance of an ^{11}B impurity peak at $\sim\delta = +7$.

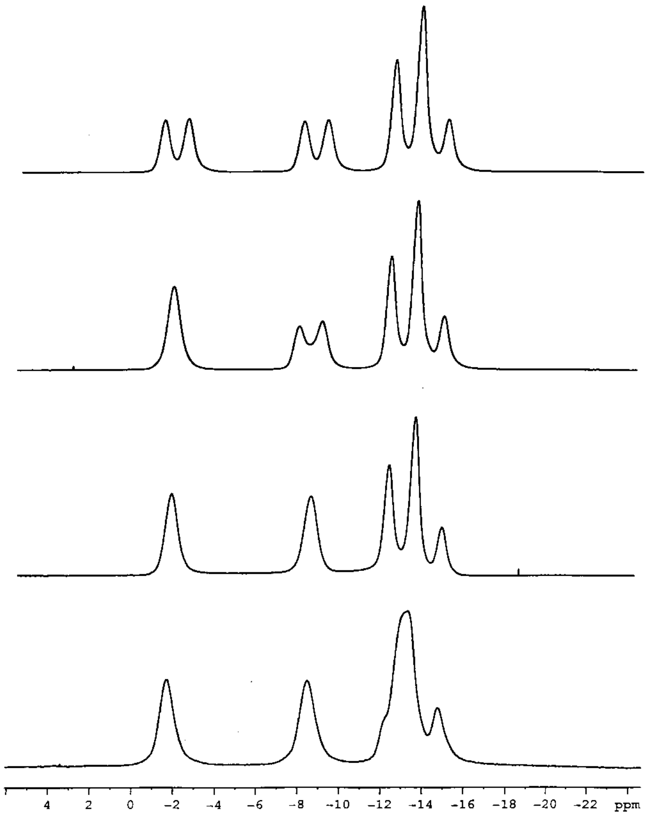


FIGURE 2 The ^{11}B NMR spectra of closo-1,2-$C_2B_{10}H_{12}$ and its deuterated species; all spectra taken in C_6D_6 as the solvent. Top spectrum is that of undeuterated 1,2-$C_2B_{10}H_{12}$, four nonequivalent borons resulting in four ^{11}B–^{1}H doublets in an area ratio of 2:2:4:2 assigned to B(9,12), B(8,10), B(4,5,7,11), and B(3,6) [8], respectively, proceeding from low to high field. The latter two doublets are overlapped and observed together as a skewed triplet. The chemical shift scale is referenced with respect to $BF_3 \cdot OEt_2$; next to the top spectrum is that of 9,12-D_2-1,2,-$C_2B_{10}H_{10}$ with B(8,10) only partially deuterated; next to the bottom spectrum is that of 8,9,10,12-D_4-1,2-$C_2B_{10}H_8$; the bottom spectrum is that of 4,5,7,8,9,10,11,12-D_8-1,2-$C_2B_{10}H_4$.

A sample with a mol ratio 21:1 of C_6D_6:1,2-$C_2B_{10}H_{12}$, without the $AlCl_3$ catalyst, was examined for possible deuteration. After the sample had been allowed to stand at room temperature for several days, no deuteration at the boron sites occurred. Also, no D/H exchange was evident after heating the sample to 150°C for 24 hours.

Reaction of 1,7-$C_2B_{10}H_{12}$ with $C_6D_6/AlCl_3$: Deuteration Sequence

An ≈50 mg quantity of 1,7-$C_2B_{10}H_{12}$, 0.5 mL of C_6D_6 (99.6 atom% deuterium), and ≈10 mg $AlCl_3$ were placed in a 5 mm NMR tube under N_2/dry bag conditions. Deuterated benzene and $AlCl_3$ are of commercial grade (Aldrich). Using vacuum line techniques, nitrogen gas was pumped off and the sample was sealed under vacuum, preventing air from entering the reaction tube. The sample was monitored by ^{11}B NMR spectra, recorded on a Bruker 400-MHz instrument.

Figure 3 depicts the ^{11}B NMR spectrum of 1,7-$C_2B_{10}H_{12}$ [9], four nonequivalent borons resulting in four doublets ranging from -5 to -20 ppm with respect to $BF_3 \cdot OEt_2$. Also depicted in Figure 3 is a spectrum of 1,7-$C_2B_{10}H_{12}$ that has undergone deuteration with $C_6D_6/AlCl_3$ for a period of 26 days at room temperature; the B(9,10) peak appears as a singlet, indicating that deuterium exchange has taken place at that position, while the other boron peaks remain as doublets, showing no observable signs of deuterium exchange. After 47 days at room temperature, an ^{11}B NMR spectrum was taken of the same sample, which shows evidence of deuteration starting to occur at the B(5,12) position (Figure 3). The cavity between the two members of the B(5,12) doublet is beginning to fill up. Peaks associated with B(4,6,8,11) and B(2,3) remain as doublets, showing no evidence of collapsing at this time. Heating at 68°C for 48 hours promoted essentially complete deuteration at B(5,12) and partial deuteration at B(4,6,8,11). The B(2,3) positions still showed no evidence of deuteration. When the compound had been heated at 110°C for 6 hours, the B(4,6,8,11) positions were completely deuterated while B(2,3) remained undeuterated. The sample was further heated to 150°C for 24 hours, and B(2,3) still remained largely undeuterated (Figure 3). At 150°C, new smaller ^{11}B peaks began to appear, the carborane perhaps decomposing under the imposed conditions. Heating to higher temperatures was avoided to prevent further degradation of the 1,7-$C_2B_{10}H_{12}$ carborane.

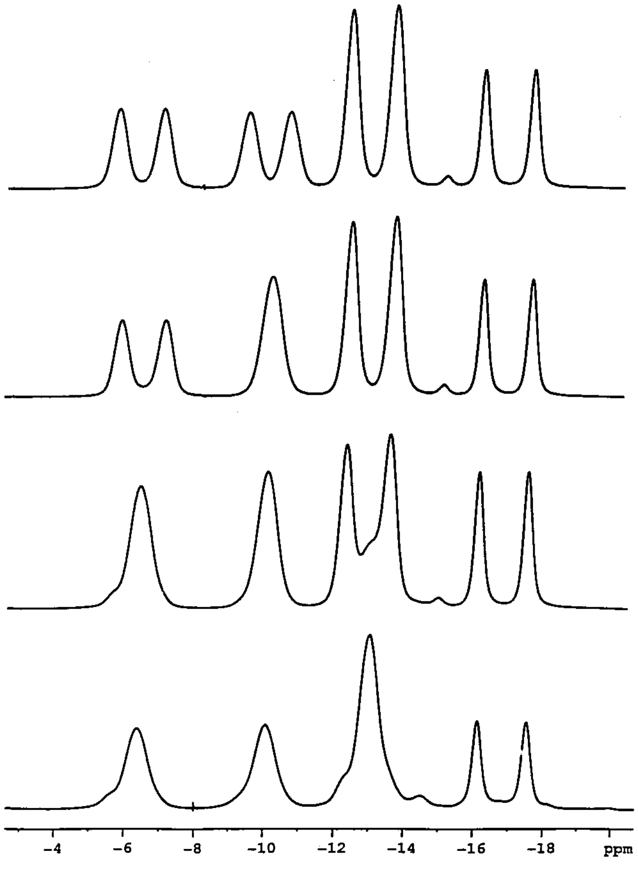


FIGURE 3 The ^{11}B NMR spectra of closo-1,7-$C_2B_{10}H_{12}$ and its deuterated species; all spectra taken in C_6D_6 as the solvent. Top spectrum is that of undeuterated 1,7-$C_2B_{10}H_{12}$, four nonequivalent borons resulting in four ^{11}B–^1H doublets in an area ratio of 2:2:4:2 assigned to B(5,12), B(9,10), B(4,6,8,11), and B(2,6) [9], respectively, proceeding from low to high field with respect to $BF_3 \cdot OEt_2$; next to the top spectrum is that of 9,10-D_2-1,7-$C_2B_{10}H_{10}$; next to the bottom spectrum is that of 5,9,10,12-D_4-1,7-$C_2B_{10}H_8$ with B(4,6,8,11) only partially deuterated; the bottom spectrum is that of 4,6,8,5,9,10,11,12-D_8-1,7-$C_2B_{10}H_4$.

Deuterium exchange of 1,7-$C_2B_{10}H_{12}$ with C_6D_6 as the deuterium source appears dependent on the presence of $AlCl_3$ as indicated by the following observations: After combining 1,7-$C_2B_{10}H_{12}$ and C_6D_6 (without $AlCl_3$), and allowing the mixture to stand at room temperature for several days, the ^{11}B NMR spectrum gave no signs of deuteration. Heating the sample at 110°C for 6 hours, and then at 150°C for 24 hours, still did not show any indication of deuterium exchange by an ^{11}B NMR analysis; however, some new ^{11}B NMR peaks formed, indicating possible degradation of 1,7-$C_2B_{10}H_{12}$ under the conditions of this experiment.

CALCULATIONAL METHODS AND RESULTS

Energy-optimized calculated structures for molecules, including the $[1,X\text{-}C_2B_{10}H_{13}]^+$ (X = 2, 7) isomers, in this study were obtained by application of the ab initio Gaussian-94 codes [10]. Those full-geometry optimizations resulting in stable structures gave no imaginary frequencies upon subjecting each compound to a vibrational frequency calculation. Total energies, along with relative energies, for the $[C_2B_{10}H_{13}]^+$ isomers are given in Tables 1 and 2. In Table 3 are cited the B–H, H···H distances and

TABLE 1 Total (in Hartrees) and Relative (in Kcal/mol) Energies for the $[1,2\text{-}C_2B_{10}H_{13}]^+$ Isomers

Location of BH_2 Group	*Total Energy (3-21G) (A.U.)*	*Relative Energy (Kcal)*
9 or 12	−328.006889	0.0
8 or 10	−328.001053	3.7
4,5,7 or 11	−327.984059	14.3
3 or 6	−327.962225	28.0

TABLE 2 Total (in Hartrees) and Relative (in Kcal/mol) Energies for the $[1,7\text{-}C_2B_{10}H_{13}]^+$ Isomers

Location of BH_2 Group	*Total Energy (3-21G) (A.U.)*	*Relative Energy (Kcal)*
9 or 10	−328.033556	0.0
5 or 12	−328.020117	8.4
4,6,8 or 11	−328.014765	11.8
2 or 3	−327.997526	22.6

TABLE 3 Geometry Data for the BH_2 Group in Each of the Fully Optimized Stable $[C_2B_{10}H_{13}]^+$ Isomers

	Bond Distance, Å		*H(1)···H(2)* Distance, Å	H-B-H Angle, degrees
Ion Isomer	*B-H(1)*	*B-H(2)*		
9-H-1,2-	1.377	1.379	0.789	33.3
8-H-1,2-	1.369	1.367	0.793	33.7
4-H-1,2-	1.358	1.358	0.800	34.3
3-H-1,2-	1.374	1.374	0.793	33.6
9-H-1,7-	1.364	1.363	0.795	33.9
5-H-1,7-	1.370	1.370	0.795	33.8
4-H-1,7-	1.355	1.358	0.800	34.3
2-H-1,7-	1.356	1.345	0.806	34.7

H-B-H angles of the BH_2 group in each of the $[C_2B_{10}H_{13}]^+$ isomers.

Nucleus-independent chemical shift (NICS) calculations were carried out as described by Schleyer et al. [11]. The Gaussian-94 application [10] allows for the placement of "ghost atoms" at any arbitrary spatial point relative to the position of the molecule in order to compute GIAO-derived magnetic properties at that point. Placement of a ghost atom at the nonweighted mean of the heavy atom coordinates of a cage or ring molecule produced the NICS values cited in Table 4.

Calculations were carried out on, variously, SUN 4/280 and SUN SPARC station model 10 computers. The Gaussian-94 code was also employed at the SDSC Cray C90 regional facility.

TABLE 4 NICS Values[a] (ppm) for $1,X\text{-}C_2B_{10}H_{12}$ and $[1,X\text{-}C_2B_{10}H_{13}]^+$ (X = 2, 7) Isomers

Location of BH_2 Group	*NICS Value,[a,b] ppm, of $[1,2\text{-}C_2B_{10}H_{13}]^+$*
9 or 12	−30.8
8 or 10	−29.8
4,5,7 or 11	−29.6
3 or 6	−29.7
Parent 1,2- $C_2B_{10}H_{12}$	−29.31
	NICS Value,[a,b] ppm, of $[1,7\text{-}C_2B_{10}H_{13}]^+$
9 or 10	−29.7
5 or 12	−30.5
4,6,8 or 11	−29.5
2 or 3	−29.5
Parent $1,7\text{-}C_2B_{10}H_{12}$	−29.27

[a] NICS [11] values (ppm) calculated at the 3-21G//3-21G level of theory; geometric NICS center determined by averaging coordinates of all nonhydrogen *cage* atoms.

[b] Negative values are upfield.

RESULTS AND DISCUSSION

The general reaction equation for deuterating a boron position on a carborane with C_6D_6 is given:

$$\text{carborane} + C_6D_6 \xrightarrow{AlCl_3} \text{D-carborane} + C_6D_5H$$

Under the conditions described in Experimental, facile deuterium isotopic exchange occurs in a regioselective fashion for both 1,2- and $1,7\text{-}C_2B_{10}H_{12}$. The sequence of boron site deuteration of $1,2\text{-}C_2B_{10}H_{12}$ (Figure 2) and of $1,7\text{-}C_2B_{10}H_{12}$ (Figure 3) follow similar patterns in that borons that are farthest away from the cage carbon atoms become deuterated prior to other boron sites that are closer to the carbons. The boron deuteration pattern for $1,2\text{-}C_2B_{10}H_{12}$ is as follows: B(9,12) > B(8,10) > B(4,5,7,11) > B(3,6) (Figures 2 and 4). This parallels the observations noted in Fielding's thesis [6], where he reports the use of $DCl/AlCl_3$ as the source of deuterium. There are some differences. Fielding indicates that there may be a slight difference in the rate of exchange (using $DCl/AlCl_3$) of the (9,12) and (8,10) positions, whereas we can deuterate the (9,12) well before there is much indication that the (8,10) positions are affected at all. Furthermore, Fielding only obtains partial deuteration of the 4,5,7,11 positions (at high DCl pressures), whereas we are able to completely deuterate (using $C_6D_6/AlCl_3$) those positions at 100°C without effecting any significant deuteration at the remaining boron (3,6) positions.

There are two sets of borons, B(9,12) and B(8,10), that are not bonded directly to a carbon. Deuterium/hydrogen exchange occurs at B(9,12) prior to that at B(8,10), but both of these types of positions are deuterated before the boron positions that are directly attached to a carbon. This evidence, along with the 1,7-$C_2B_{10}H_{12}$ deuteration pattern (discussed below), suggests, as mentioned earlier, that deuteration of borons on $C_2B_{10}H_{12}$ is roughly dependent on the boron's spatial distance to the carbon atom. The order of boron distances from both carbon atoms is B(9,12), B(8,10), B(4,5,7,11), and B(3,6), with B(3,6) being the closest. And as previously mentioned, this is the same order in which deuterium exchange occurs, with B(9,12) being the initial position to be deuterated. No deuterium/hydrogen exchange at the B(3,6) position(s) is evident using the conditions cited in the Experimental section.

Systematic sequential deuteration of 1,7-$C_2B_{10}H_{12}$ is depicted in Figures 3 and 5. The B(9,10) positions are the favored deuteration sites for this carborane, and this is noted by ^{11}B NMR (^{1}H-undecoupled) spectra (Figure 3). Complete deuteration at B(9,10) is followed by deuteration at B(5,12), and then the B(4,6,8,11) positions.

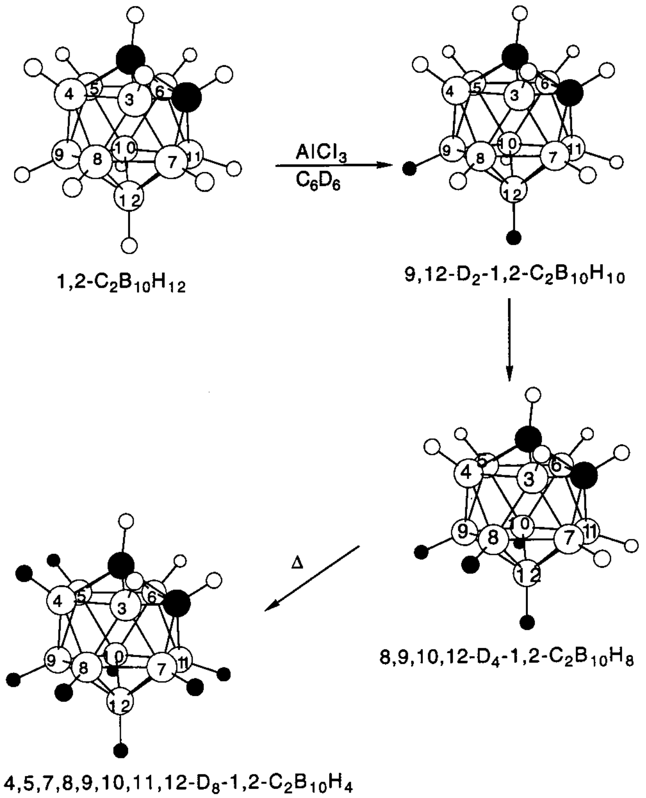


FIGURE 4 Sequential deuteration pattern of 1,2-$C_2B_{10}H_{12}$, ● = deuterium.

MECHANISM OF D/H EXCHANGE

Gaines implied, in his studies of D/H exchange involving the $C_6D_6/AlCl_3/B_5H_9$ combination, that if any HCl/DCl is present during the reaction and operating as D/H carriers, it could not be detected [1]. On the other hand, the absorption of a miniscule quantity of moisture to the surface of the reaction container(s) is hard to rule out and could lead to very small quantities of HCl/DCl that would be very difficult to detect; such quantities of moisture would be next to impossible to remove even when exceptional and laborious measures are taken. With this in mind, it is reasonable to assume that H^+/D^+ could well be present during the reaction, and it was then of interest to employ a simple deuterated (protonated, for MO calculational purposes) carborane intermediate, $[C_2B_{10}H_{13}]^+$, to account for the D/H exchange; much the same as suggested for D/H exchange under Lewis acid catalyzed conditions on benzene systems [12].

We then set about to study protonation of 1,X-$C_2B_{10}H_{12}$ (at each of the four different types of boron positions of both systems X = 2, and X = 7) by a well-established ab initio MO calculational method. Gaussian-94 geometry optimization procedures were carried out on these systems at the 3-21G basis set level of theory, the highest level we could manage when considering the resources at our disposal. The approach taken with each $[C_2B_{10}H_{13}]^+$ geometry optimization was to, initially, preserve the same cage geometry as that of the unprotonated compound but allowing the BH_2 group of the protonated carborane to geometry optimize. The resultant protonated carborane was subsequently subjected to a "full" geometry optimization using no geometry restrictions at all. For every one of the possible ion isomers (four in each of the two sets) studied in this fashion, a local minimum was located in which the (nearly) isocahedral geometry of the C_2B_{10} unit was still intact while containing a BH_2 group in the pertinent position. Next, for each of the four $[C_2B_{10}H_{13}]^+$ isomers in each set (X = 2 and X = 7), the BH_2 group was rotated approximately 90° in an attempt to locate another possible local minimum. Full-geometry optimization of each of such structures did result, in a few instances, in a slightly more stable entity. For each of the four (most stable) isomers in each set (i.e., four isomers of protonated 1,2-$C_2B_{10}H_{12}$ and four isomers of protonated 1,7-$C_2B_{10}H_{12}$), a comparison of relative energies, NICS values, and BH_2 geometries in each set was made. It is important to note that each of the four full-geometry optimized protonated carboranes in each set gave rise to a "vibrationally stable" species, (i.e., generating no negative frequencies when a frequency calculation was carried out), Figures 6 and 7. Upon comparing the

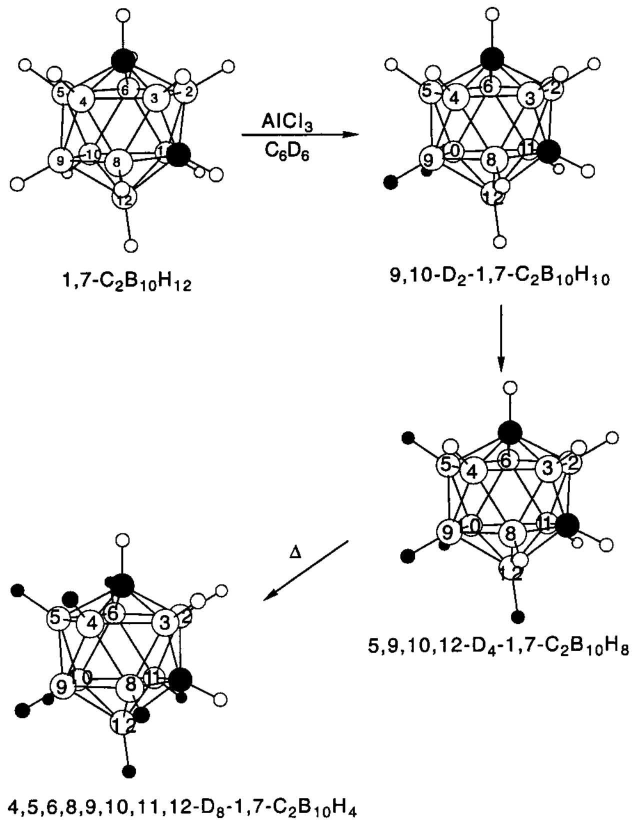


FIGURE 5 Sequential deuteration pattern on 1,7-$C_2B_{10}H_{12}$, ● = deuterium.

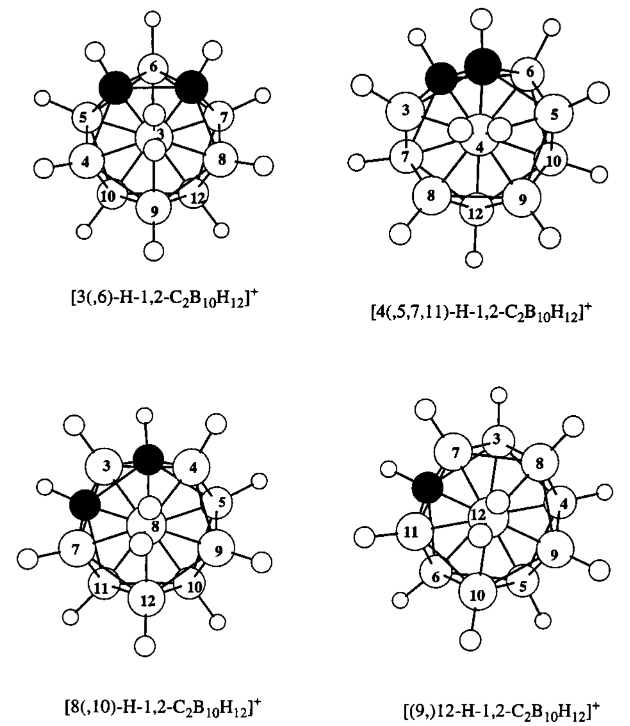


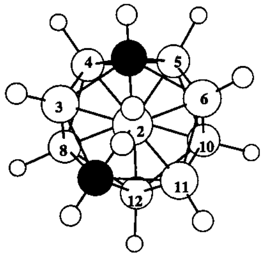
FIGURE 6 Depiction of stable *B*-protonated 1,2-$C_2B_{10}H_{12}$ species, as calculated at the 3-21G basis set level of theory. Each isomer represents the most stable configuration of the BH_2 group relative to the remainder of the molecule ion. In the case of the [9(,12)-H-1,2-$C_2B_{10}H_{13}$]$^+$ ion, the C1 atom is hidden by B12.

relative energies of all four $[C_2B_{10}H_{13}]^+$ isomers in each set (Tables 1 and 2), it is noted that the order of stabilities are calculated to be (proton at the given boron position) $9 > 8 > 4 > 3$ for the 1,2-C_2 isomer and $9 > 5 > 4 > 2$ for the 1,7-C_2 isomer of the carborane system. The is the same order (for each 1-X-isomer) as observed for the relative rate of D/H exchange as determined by ^{11}B NMR studies (vide supra). In other words, the energy of a presumed "critical" transition state for D/H exchange appears to parallel the energy of the protonated species (i.e., $[C_2B_{10}H_{13}]^+$).

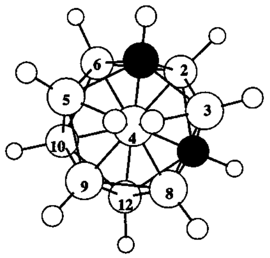
There is a consistent pattern to be found in examining the geometries of the BH_2 group of the four calculated $[C_2B_{10}H_{13}]^+$ species. When long B–H distances (1.35 to 1.39 Å) are found, relatively short H···H distances (≈0.79 Å) and rather acute H-B-H angles (Table 3) are also noted. This is not unlike the situation found in geometry optimized CH_5^+ [13] and BH_5^{2+} [14], entities containing two hydrogens that make up a CH_2 or BH_2 unit with long X–H (X = C, B) bonds and short H···H distances; in the CH_5^+ and BH_5^{2+} cases, this resembles a complex between a methyl (CH_3^+) or BH_3^{2+} cation and hydrogen molecule. This is in contrast with the protonated benzene, $C_6H_7^+$ [12] (which is thought to be involved as an intermediate in H/H proton exchange in $AlCl_3$/HCl promoted reactions); the CH_2 group has rather more standard C–H distances (≈1.1 Å) and an H···H distance (≈1.7 Å) suggesting very little H–H bonding.

Thus, the calculated structure for the protonated carborane species could well imply that the boron of the BH_2 group is sharing a pair of H–H σ electrons, just as it could be implied [14] for the special bonding situation in "stable species" of CH_5^+ and BH_5^{2+}.

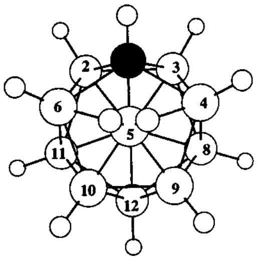
If we turn for a moment to a comparison of the NICS [11] values of benzene to its protonated species, we note that the positive NICS value, ca. 9 ppm upfield (in which an upfield value is indicative of aromatic systems, a downfield value indicative of antiaromatic systems, and an ≈nil value indicative of nonaromatic systems) [11] for benzene changes to ≈nil value (≈0.4 ppm downfield at the 6-31G*//6-31G* or 3-21G//3-21G level of theory) upon protonation to give a $C_6H_7^+$ species such as that previously proposed [12]. This is not unexpected when it is considered that the CH_2 group of the protonated species, $C_6H_7^+$, breaks the π-ring system of benzene. In contrast, the NICS values of all four boron protonated



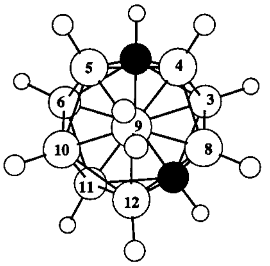
[2(,3)-H-1,7-$C_2B_{10}H_{12}]^+$



[4(,6,8,11)-H-1,7-$C_2B_{10}H_{12}]^+$



[5(,12)-H-1,7-$C_2B_{10}H_{12}]^+$



[9(,10)-H-1,7-$C_2B_{10}H_{12}]^+$

FIGURE 7 Depiction of stable *B*-protonated 1,7-$C_2B_{10}H_{12}$ species, as calculated at the 3-21G basis set level of theory. Each isomer represents the most stable configuration of the BH_2 group relative to the remainder of the molecule ion. In the case of the [5(,12)-H-1,7-$C_2B_{10}H_{12}]^+$ ion, the C7 atom is hidden by B5.

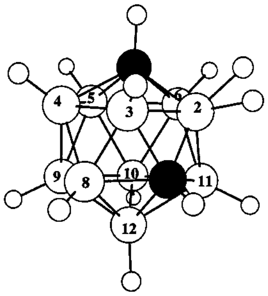


FIGURE 8 Another depiction, at a different viewing angle, of the stable [2(or 3)-H-1,7-$C_2B_{10}H_{12}$]+ ion.

[1,2-$C_2B_{10}H_{13}]^+$ species remain (at the highest basis set level of theory, 3-21G, at which these fairly large molecules could be reasonably calculated with available resources) very close to the value (ca. 29 to 31 ppm upfield) as that calculated for the neutral 1,2-$C_2B_{10}H_{12}$ (29 ppm upfield). A similar comparison between the $[C_2B_{10}H_{13}]^+$ ions and the neutral $C_2B_{10}H_{12}$ is noted for the 1,7-isomer of the carborane. It is tempting, then, to think that the cage electrons associated with each of the two related carborane systems (1,2- and 1,7-) are not involved in attachment to an attacking proton, whereas in the case of the protonated benzene, one of the π-pair of electrons of benzene obviously assists in bonding to an attacking proton. This difference in the manner in which a proton bonds to the carborane as compared to that involving benzene is not unreasonable. The carborane cage is already "electron deficient" in the sense that there are many more orbitals than electrons for normal two-center bonding, and, therefore, the cage is reluctant to give up any electron pairs in order to assist in bonding to an (externally bound) proton. Conversely, benzene is electron rich with its exposed 6 $e^-\pi$ system, in which an electron pair may be more easily borrowed for bonding to the extra proton than are the "internally hidden" cage electrons of the carborane. So, in the case of the carborane, "hydridic" B–H sigma electrons could well play a very important role in providing electron density to the attacking proton. This then could easily lead to a H–H bond sharing its electrons with a boron of the cage.

A ^{13}C NMR examination of some of the foregoing deuterated products shows no indication of deuteration at the cage carbon site. Consistent with these observations are ab initio calculations at the 3-21G level of theory for the [1(or 2)-H-1,2-$C_2B_{10}H_{12}]^+$ and [1(or 7)-H-1,7-$C_2B_{10}H_{12}]^+$ ions, which indicate that they are both less stable (i.e., HF = -327.93233 A.U. for the former, HF = -327.961281 A.U. for the latter) than the boron protonated counterparts.

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