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Application of IGLO and GIAO Structure/NMR Analyses to a Novel Isomer of the Dicarbaoctaborane(11) Anion, [*arachno*-2,6-$C_2B_6H_{11}$]$^-$, Prepared from the Reaction of *closo*-1,6-$C_2B_7H_9$ with Fluoride Ion

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Abstract: The structure of a new carborane anion [*arachno*-2,6-$C_2B_6H_{11}$]$^-$, prepared from the reaction of *closo*-1,6-$C_2B_7H_9$ with tetrabutylammonium fluoride in tetrahydrofuran, is determined from a combination of experimentally observed ^{11}B, 2D ^{11}B–^{11}B, and ^{13}C NMR results and the application of ab-Initio/IGLO/NMR and ab-Initio/GIAO/NMR methods. The skeletal structure of the new ion is related to both the known $C_2B_6H_{10}$ and the proposed [2,3-$C_2B_6H_{11}$]$^-$ ion, but with a single bridging hydrogen between the borons 3 (*3k*) and 4 (*4k*) of the six-atom open face, a BH_2 group at position 5 (*3k*), and a CH_2 group at position 6 (*3k*). The 2D NMR observations are consistent with the B–B bond distance trends derived from ab Initio optimized geometries obtained at both the 3-21G and 6-31G* levels of theory.

Introduction

Fluoride ion, in aprotic solvents, such as acetonitrile or tetrahydrofuran, has been found to be effective in the (partial) cage opening of *closo*-carboranes such as 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, 1,2-$C_2B_{10}H_{12}$, and 1,7-$C_2B_{10}H_{12}$.[1,2] The reactions usually proceed at a moderate rate at ambient temperatures, and nearly quantitative conversions to *nido*-carboranes are observed. In the case of the (near) octahedral *closo*-1,6-$C_2B_4H_6$ the product is the [5-F-*nido*-2,4-$C_2B_4H_6$]$^-$ ion, the pentagonal pyramidal framework of which contains a fluorine atom terminally attached to one of the two equivalent basal borons of the parent [*nido*-2,4-$C_2B_4H_7$]$^-$ ion. The other three *closo*-carboranes produce a *nido*-carborane that is expected from a removal of single skeletal boron. Specifically, the action of fluoride ion on the pentagonal bipyramidal *closo*-2,4-$C_2B_5H_7$ produces the [*nido*-2,4-$C_2B_4H_7$]$^-$ ion,[1] a product expected from the removal of a single high-coordination boron. This reaction is analogous to the removal of a single vertex of *closo*-2,4-$C_2B_5H_7$ by amides,[3] and the earlier reported removal of a single boron vertex from *closo*-1,2- and 1,7-$C_2B_{10}H_{12}$ using hydroxide ion, or alkoxide ion, in alcohol.[4] The reaction of fluoride ion with both the 1,2- and 1,7-isomers of the (near) icosahedral *closo*-$C_2B_{10}H_{12}$ mimics the action of the [OH]$^-$/ROH reagent combination in that the products are the same, the 7,8- and 7,9-isomers, respectively, of the [*nido*-$C_2B_9H_{12}$]$^-$ ion. It is to be noted, however, that the conversion of *closo*-1,7-$C_2B_{10}H_{12}$ to [*nido*-7,9-$C_2B_9H_{12}$]$^-$ appears to be more facile when carried out with tetrabutylammonium fluoride in THF than with the [OH]$^-$/ROH reagent combination. The temperature at which the production of [*nido*-7,9-$C_2B_9H_{12}$]$^-$ from *closo*-1,7-$C_2B_{10}H_{12}$/[OH]$^-$/ROH takes place is reported[4] to be in the range of 150–160 °C, whereas the use of fluoride ion[1,2] to effect the same conversion takes place at a reasonable rate at ambient temperature. To summarize, the action of fluoride ion on 2,4-$C_2B_5H_7$ or on the two $C_2B_{10}H_{12}$ isomers differs from the reaction of the same reagent on 1,6-$C_2B_4H_6$ in that the latter involves attachment of the fluorine to the carborane with no loss of boron, whereas the other three carboranes result in debor type reaction products. It was then of some interest to see which of these two (or perhaps other) routes would be taken upon treating the tricapped-trigonal-prismatic 1,6-$C_2B_7H_9$ [5,6] with tetrabutylammonium fluoride. As described herein, a new carborane anion is formed, a product that was difficult to isolate for traditional structural analyses. Nevertheless, a unique structural assignment for this compound is made by application of the ab-initio/IGLO/NMR (and the related ab-initio/GIAO/NMR) method,[7-9] a structure determination technique that now rivals the high confidence levels associated with diffraction methods.

Experimental Section

A solution of tetrabutylammonium fluoride (1 M, Aldrich Chemical Co.) in tetrahydrofuran was dried over CaH_2; after 2 days two liquid layers formed and 0.12 mL of the lower layer (which contained ca. 2 M fluoride ion solution) was added to an NMR tube to which was attached at one end a 1-mL bulb. The transfer was carried out in a drybag filled with nitrogen. The NMR tube/bulb and its contents were subsequently attached to a high-vacuum line and frozen to −190 °C. To this frozen mixture was sublimed 1,6-$C_2B_7H_9$ [ca. 0.12 mmol; ^{11}B NMR data: δ = +31.4 (area 1; J = 161 Hz); δ = −7.5 (area 2; J = 180 Hz); δ = −12.6 (area 4; J = 167 Hz)].[5,6] The NMR tube/bulb was sealed and its contents were subsequently warmed to room temperature. As the mixture approached ambient temperature it bubbled rather vigorously for about 2 min. The solution slowly turned from a near colorless mixture to a pale yellow liquid. No solids were formed. A ^{11}B NMR (128.4 MHz) spectrum

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Table I. ^{11}B NMR Data (*J* in Parentheses) for the [*arachno*-2,6-$C_2B_6H_{11}$]$^-$ Ion

atom	δ^a	coupling^a
B(1)	−2.2	d (134)
B(3)	+9.1	dd (143, 40)
B(4)	−6.1	d (160)
B(5)	−24.9	t (119)
B(7)	−56.7	d (149)
B(8)	−13.7	d (140)

^{a} Line widths are the following (broad to narrow): B(4) > B(8) > B(7) > B(3) > B(5). When line narrowing techniques are employed in a manner to narrow the peak at $\delta = -6.1$ (B(4)) to *ca.* 50 Hz, the peak at $\delta = -24.9$ (B(5)) exhibits a width at half-height of *ca.* 20 Hz. Further attempts at resolution enhancement do not reveal new information. δ values are in ppm, *J* values are in Hz.

of the mixture indicated that no 1,6-$C_2B_7H_9$ (^{11}B data given above) was present and in its place a number of new strong resonances were observed (Table I). NMR spectra that were taken at later times indicated that no further change occurred, implying that the reaction had proceeded to completion within a relatively short period of time. The NMR tube and its contents were attached to a high-vacuum line and the volatile materials collected in a separate container. To the nonvolatile, gel-like fraction was added dried deuterated tetrahydrofuran (99.5% D), and the liquid mixture was sealed into a 5-mm quartz NMR tube for analyses (^{11}B, $^{11}B\{^1H\}$, ^1H, $^1H\{^{11}B\}$), see Table I. An area analysis of the ^{11}B NMR spectrum of the sample indicated *ca.* 85% conversion to the [*arachno*-2,6-$C_2B_6H_{11}$]$^-$ion (Figure 1) and monoboron compounds of the type $[B(OR)_xF_y]^-$ $(x + y = 4)$,[1a,10a] the latter giving rise to resonances appearing in the region of $\delta = 0$ to $+2$ ppm; the remaining 15% is a mixture of mostly $[B_3H_8]^-$ ($\delta^{11}B = -29.5$, nonet, $J_{BH} = 33$ Hz),[10b,c] $[BH_4]^-$($\delta^{11}B = -37$, quintet, $J_{BH} = 82$ Hz)[10d,e] and some compound(s) exhibiting several very small impurity peaks at $\delta(^{11}B)$ −28.1, −21.5, −16.6, −12.6, −11.0, +5.5, and +19.3 ppm. A proton NMR spectrum of the [*arachno*-2,6-$C_2B_6H_{11}$]$^-$ion taken at 400 MHz was measured both with and without ^{11}B decoupling. The spectrum was dominated by the peaks of the tetabutylammonium ion, $\delta = 0.95$ (relative area 12), 1.38 (8), 1.69 (8), 3.31 (8); however, a broad (*ca.* 150 Hz width at half-height) peak at −3.24 ppm which sharpened considerably upon ^{11}B decoupling was assigned to a bridging hydrogen. A 1:1:1:1 quartet of peaks centered at $\delta = -1.51$ ppm, $J = 150$ Hz (assigned to HB7), collapsed to a singlet upon ^{11}B decoupling; the area of this singlet was equal (±10%) to that of the peak at $\delta = -3.24$ ppm (Hμ). The $^1H\{^{11}B\}$ spectrum also revealed two additional HB resonances at $\delta = +2.82$ and $+3.13$ ppm (each area 1 relative to each of the resonances at $\delta = -3.24$ ppm (Hμ) and $\delta = -1.51$ ppm (HB7)). All product(s) of the reaction appear to be stable indefinitely at room temperature in solution; however, isolation of the principal carborane anion, [*arachno*-2,6-$C_2B_6H_{11}$]$^-$, has proved elusive. No insoluble tetraalkylammonium salt could be obtained in a crystalline form for diffraction studies.

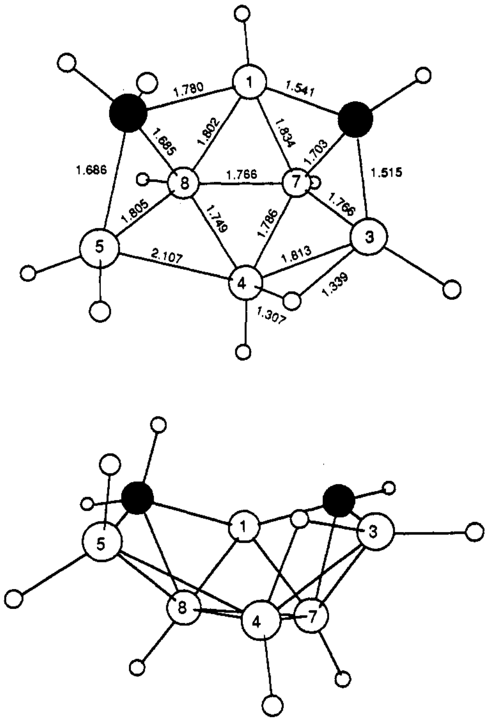

Figure 1. Two perspectives of the 6-31G* geometry-optimized (vibrationally stable) structure for the [*arachno*-2,6-$C_2B_6H_{11}$]$^-$ion; bond distances are given in angstroms.

Both the ^{11}B and ^1H spectra were gathered on a 400-MHz Bruker instrument; ^{13}C data were obtained by using a 300-MHz Bruker instrument. The ^{13}C data for the carborane anion are reported in the Discussion section below; the tetrabutylammonium cation exhibited ^{13}C resonances (relative to TMS) at $\delta = +57.5$ ppm (1:2:1 triplet,143 Hz) for CH_2N, +22.8 ppm (1:2:1 triplet, 126 Hz) for CH_2, +18.7 ppm (1:2:1 triplet, 125 Hz) for CH_2, and +12.3 ppm (1:3:3:1 quartet, 125 Hz) for CH_3; the deuterated THF solvent exhibited ^{13}C resonances at $\delta = +23.7$ ppm (C-D coupling of 20.5 Hz) and +65.8 ppm (C–D coupling of 22 Hz).

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Table II. IGLO and GIAO ^{11}B NMR Chemical Shifts for the [*arachno*-2,6-$C_2B_6H_{11}$[$^-$ Ion (See Figure 3)

atom type	δ,[a] IGLO (DZ//6-31G*)	δ,[a] GIAO (6-31G//6-31G*)	δ(exp)[a]
B(1)	-0.2	0.9	-2.2
B(3)	12.0	10.9	9.2
B(4)	-7.1	-3.6	-6.1
B(5)	-21.8	-21.2	-24.9
B(7)	-59.0	-55.3	-56.7
B(8)	-15.1	-11.5	-13.7

[a] δ values are in ppm.

Calculational Methods for the Geometry Optimizations and for IGLO/NMR and GIAO/NMR Chemical Shift Determinations

Geometry optimization of the [*arachno*-2,6-$C_2B_6H_{11}$]$^-$ ion (Figure 1) was carried out by using the Gaussian-90 code[11] at each of the following levels of theory: STO-3G, 3-21G, and 6-31G*. Each geometry optimization resulted in a vibrationally stable optimized structure; HF(STO-3G) = -227.37774 AU, HF(3-21G) = -228.92456 AU, and HF(6-31G*) = -230.22664 AU. In a similar fashion geometry optimization of the [*arachno*-2,5-$C_2B_6H_{11}$]$^-$ ion resulted in vibrationally stable entities, HF(STO-3G) = -227.36766 AU, HF(3-21G) = -228.91375 AU, and HF(6-31G*) = -230.21653 AU. For the [*arachno*-2,3-$C_2B_6H_{11}$]$^-$ ion HF(STO-3G) = -227.35715 AU, HF(3-21G) = -228.90002 AU, and HF(6-31G*) = -230.20963 AU. At the 6-31G* level the *relative* energies (in kcal/mol) of the [*arachno*-$C_2B_6H_{11}$]$^-$ ion isomers are 0.00 for the 2,6-, 6.34 for the 2,5-, and 10.67 for the [*arachno*-2,3-$C_2B_6H_{11}$]$^-$ ions, respectively.

The Gaussian calculations were carried out, variously, on Alliant FX/2800 and Multiflow-Trace minisupercomputers. The structures for the molecules were verified by constructing ball and stick models of each species directly from the optimized coordinates using the Molecular Editor application on a Mac-IIci computer.

The (Gaussian) geometry optimized coordinate output for each molecule was subsequently used as the input coordinate set for IGLO calculations[7-9] which were then carried out at the the DZ level. The consequent ^{11}B chemical shielding values, determined from IGLO calculations, were referenced to B_2H_6 as the primary reference point, and these δ values were then converted to the standard $F_3B{\cdot}OEt_2$ scale with use of the experimental value of +16.6 ppm for $\delta(B_2H_6)$[12] (Table II). Proton[13] and ^{13}C NMR chemical shifts were referenced relative to tetramethylsilane. The IGLO derived chemical shift values reported here are those carried out at the DZ//6-31G* (IGLO//Gaussian-geometry-optimized) level (Table II). However, the chemical shift results obtained by using the geometries optimized at lower levels of theory (i.e. STO-3G and 3-21G) were not significantly different than that obtained by using the 6-31G* optimized geometry.

A parallel approach was used for the GIAO calculations. The GIAO program[14] was made available to us by P. Pulay at the University of Arkansas; all GIAO calculations were carried out at the 6-31G basis set level on the [*arachno*-$C_2B_6H_{11}$]$^-$ ion optimized geometries which had been previously treated at various levels of theory (see above). The ^{11}B chemical shift values reported here for the [*arachno*-2,6-$C_2B_6H_{11}$]$^-$ ion (Table II) are those carried out at the highest level, 6-31G//6-31G* (GIAO//Gaussian), that was allowed by the computational resources available to us. A best fit linear relationship, $\delta(GIAO) = 1.008\delta(exp) + 2.56$ ($r^2 = 0.999$), was derived for the [*arachno*-2,6-$C_2B_6H_{11}$]$^-$ ion from the ^{11}B data in Table II. A standard deviation of 0.9 ppm is determined from a consideration of the difference between the calculated δ(GIAO), from the above equation, and δ(exp). A similar relationship, $\delta(IGLO) = 1.056\delta(exp) + 1.42$ ($r^2 = 0.993$), standard deviation of 1.9 ppm, was found for the IGLO(DZ//6-31G*)/experimental comparison.

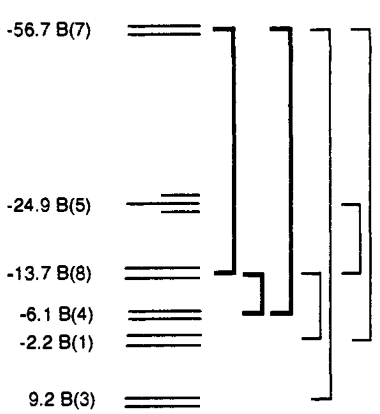

Figure 2. 2D ^{11}B–^{11}B NMR interactions (strong lines represent stronger interactions) for the [*arachno*-2,6-$C_2B_6H_{11}$]$^-$ion (see also Table I).

Results and Discussion

Reaction of tetrabutylammonium fluoride in tetrahydrofuran with *closo*-1,6-$C_2B_7H_9$ results in the removal of a single boron and yields the [*arachno*-2,6-$C_2B_6H_{11}$]$^-$ ion (Figure 1). The structure for this ion is derived from 1D ^{11}B NMR (Table I), 2D ^{11}B–^{11}B NMR spectra (Figure 2), ^{13}C NMR, ^1H NMR, and ab-Initio/IGLO/NMR and ab-Initio/GIAO/NMR results (Table II), as well as an intercorrelation of all of these results for self-consistency. The ^{11}B NMR data point to a structure with C_1 symmetry; i.e., all six ^{11}B resonances, in an area ratio of 1:1:1:1:1:1, are unique (Table I). Five of the six borons are each attached to a single terminal hydrogen, and the remaining boron is attached to two terminal hydrogens. Although many of the proton NMR resonances of the [*arachno*-2,6-$C_2B_6H_{11}$]$^-$ ion are apparently obscured by intense peaks of the counterion, tetrabutylammonium cation, it is readily determined that there is one bridging hydrogen (found at high field, $\delta^1H = -3.24$ ppm) per molecule; additionally, three of the seven H_tB proton resonances are observed, each in a 1:1 area ratio with the bridging hydrogen. The skeletal structure proposed for the new ion is related to the known $C_2B_6H_{10}$,[15,16] but unlike the latter molecule the carbons of the [*arachno*-2,6-$C_2B_6H_{11}$]$^-$ ion are in *low* coordination (i.e. 3*k*)[17] non-adjacent 2,6-positions, a single bridging hydrogen positioned between the borons 3 and 4, a BH_2 group located at position 5, and a CH_2 group located at position 6.

Geometry optimization of the [*arachno*-2,6-$C_2B_6H_{11}$]$^-$ ion at the 6-31G* level of MO theory gives a structure (Figure 1) which is vibrationally stable. The four shortest of the nine B–B bond distances in the 6-31G* optimized structure are the B(4)–B(8), B(7)–B(8), B(4)–B(7), and B(3)–B(7) bonds. The first three of these give the strongest cross peaks in the ^{11}B–^{11}B 2D NMR and

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[12] Onak, T.; Landesman, H. L.; Williams, R. E.; Shapiro, I. *J. Phys. Chem.* **1959**, *63*, 1533.

[13] The proton chemical shifts, as calculated by both IGLO (DZ//6-31G*) and GIAO (6-31G//6-31G*) methods, are as follows for the [*arachno*-2,6-$C_2B_6H_{11}$]$^-$ ion (the first number is the IGLO δ value and the second number is the GIAO δ value): +4.39, +3.53 for H_t1; +2.86, +2.81 for H_t2; +4.98, +3.61 for H_t3; +3.51, +3.06 for H_t4; +0.97, +1.11 for H_t5(endo); +1.94, +1.68 for H_t5(exo); -2.93, -1.23 for H_t6(endo); -2.44, -1.75 for H_t6(exo); -0.98, -1.61 for H_t7; +2.33, +1.60 for H_t8; -6.39, -4.84 for $H_\mu3,4$.

[14] (a) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251–8260. (b) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789.

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[16] Reilly, T. J.; Burg, A. B. *Inorg. Chem.* **1974**, *13*, 1250.

[17] (a) Williams, R. E. In *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, 1991; Chapter 2, pp 11–93 and references therein. (b) Williams, R. E. *Inorg. Chem.* **1971**, *10*, 210. (c) Williams, R. E. Adv. *Inorg. Chem. Radiochem.* **1976**, *18*, 67 and references therein. (d) Williams, R. E. *Chem. Rev.* **1992**, *92*, 177–207 and references therein for all of the above.

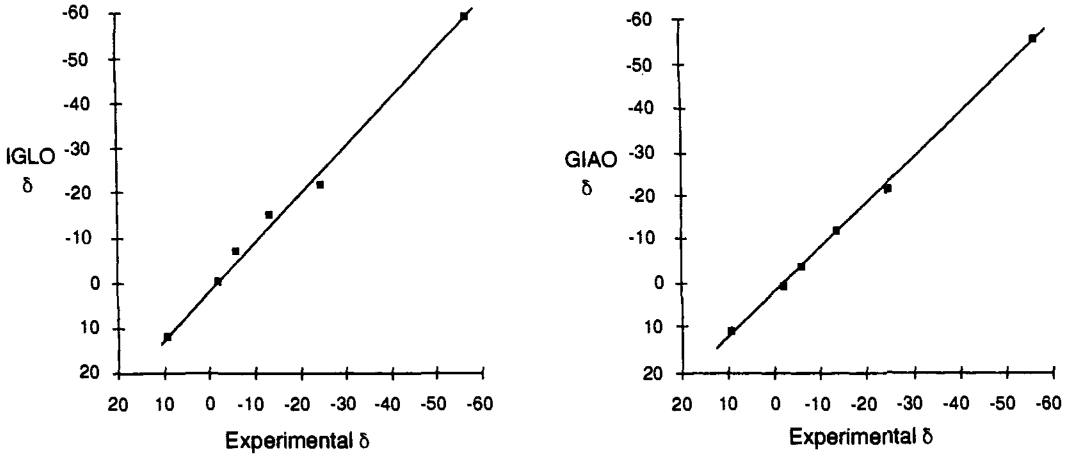

Figure 3. Graphical correlations between IGLO (dz//6-31G*) and GIAO (6-31G//6-31G*) vs experimental ^{11}B chemical shifts for the [*arachno*-$2,6-C_2B_6H_{11}]^-$ ion; see Table II.

the last gives a medium strength cross peak (Figure 2). The only ^{11}B–^{11}B cross peaks that are not observed between adjacent borons are for the two bonds B(3)–B(4) and B(4)–B(5); and these two B–B bonds are calculated to be among the longest in the molecule ion. In fact, the unusually long length of the B(4)–B(5) bond, 2.1 Å, is about the same length as the longest B–B bonds in $1,6-C_2B_7H_9$[18,19] and $2,3-C_2B_9H_{11}$[20] and indicates that the bond order for this B–B "linkage" is obviously not very substantial at all.

Both IGLO[9-11] calculations at the DZ level and GIAO[14] calculations at the 6-31G level, performed on the 6-31G* optimized [*arachno*-$2,6-C_2B_6H_{11}]^-$ ion (Figure 1), predict ^{11}B NMR chemical shifts (Table II) that are very nearly those obtained experimentally. The IGLO and GIAO results are plotted against the experimental data in Figure 3, and it is visually obvious that excellent linear correlations are obtained.

It is not entirely surprising to find that the highest field ^{11}B chemical shift, $\delta = -56.7$ ppm, is associated with B(7), for this atom is at the apex of a pentagonal pyramid of borons and carbon (the basal atoms of which are located at the 1, 2, 3, 4, and 8 vertices). This geometrical arrangement is not unlike other pentagonal pyramidal compounds in which the apical boron resonances are found in the high-field region between $\delta = -50$ and -60 ppm.[21,22] This phenomenon could well be related to "aromatic" ring-current effects as suggested earlier.[21] The "ring-current" hypothesis appears to empirically account for the sizable high-field shifts of atoms located above the pentagon of basal atoms, and for the downfield shifts of the peripheral (basal) atoms.[21,22] The lowest chemical shift resonance of the [*arachno*-$2,6-C_2B_6H_{11}]^-$ ion, $\delta = +9.2$ ppm, is logically associated with a low coordination (B(3)) boron atom adjacent to a carbon atom in the base of the pentagonal pyramid (7-1,2,3,4,8; apical atom number followed by the positions of the five basal skeletal atoms). Because B(8) is at the apex of another pentagonal pyramid (the basal atoms of which are located at the 1, 7, 4, 5, and 6 vertices) it might initially be reasoned that this boron should be found at substantially higher field than observed, $\delta = -13.7$ ppm; however, the pentagonal base has two XH_2 (X = B,C; H = terminal hydrogen) groups which could be thought to make that segment of the base of the pyramid more "saturated" and less "aromatic" in character, and thus less capable of showing the "ring-current" chemical shift effects that are noticed in compounds such as $C_xB_{6-x}H_{10-x}$ (x = 0–4).[21,23] In other words, the presence of the two "saturated" XH_2 groups at positions 5 and 6 could be thought to quench the "aromatic" character of the pyramid that has B(8) as the apex.[24]

Before arriving at the structural assignment for the ion shown in Figure 1, a number of plausible $[C_2B_6H_{11}]^-$ ion structures were examined by Gaussian geometry optimization methods. Such structures included those formally derived from the removal of a single high-coordination boron from the tricapped-trigonal-prism structure of *closo*-$1,6-C_2B_7H_9$.[17,25] An extra terminal hydrogen was placed on a single boron (note in Table I that the ^{11}B NMR spectrum shows one BH_2 1:2:1 triplet pattern at $\delta =$ -24.9 ppm) atom in each prospective isomer, and a bridging hydrogen was positioned at a boron–boron site along an open face. The placement of an extra hydrogen on one of the two original CH carbons is strongly suggested in order to pair up all electrons. Additionally, we examined numerous $[C_2B_6H_{11}]^-$ framework structures related to the known $C_2B_6H_{10}$,[8ℓ,15] again

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(22) For references to, and chemical shift values of, typical pentagonal pyramidal compounds see pp 249–288 of the following: *Gmelin Handbook of Inorganic Chemistry*; Springer-Verlag: Berlin, FRG, 1974; Borverbindungen 2, pp 1–288. Also see: *Gmelin Handbook of Inorganic Chemistry*; Springer-Verlag: Berlin, FRG, 1975; Borverbindungen 6, pp 1–150; 1977, Borverbindungen 11, pp 1–207; 1977, Borverbindungen 12, pp 1–306; 1977, Borverbindungen 14, pp 149–233; 1978, Borverbindungen 18, pp 206–227; 1979, Borverbindungen 20, pp 1–239; 1980, Boron Compounds, 1st Suppl. Vol. 1, pp 84–108; 1980, Boron Compounds, 1st Suppl. Vol. 3, pp 105–256; 1983, Boron Compounds, 2nd Suppl. Vol. 1, pp 84–204; 1982, Boron Compounds, 2nd Suppl. Vol. 2, pp 223–335; 1987, Boron Compounds, 3rd Suppl. Vol. 1, pp 90–240; 1988, Boron Compounds, 3rd Suppl. Vol. 4, pp 153–254.

(23) It could be suggested that the equivalent situation in organic systems arises when one proceeds from the "aromatic" benzene, C_6H_6, to the partially saturated cyclohexa-1,3-diene containing two $-CH_2-$ groups. Substantial "ring-current" NMR shifts would be expected, of course, in the former molecule but not in the latter.

(24) When a boron vertex is considered to be both an apical atom of one pentagonal pyramid and a basal atom of another pyramid, such as B7 and B8 of the $[C_2B_6H_9]^-$ ions,[8k,o] then one might expect that the ^{11}B NMR chemical shift of a boron in that environment should appear approximately midway between the presumed apical region[21,22] of $\delta = -50$ to -60 and the presumed basal region[21,22] of $\delta = +20$ to -10 depending on the number of adjacent cage carbon atoms (in general, adjacent cage-carbon atoms tend to pull the chemical shift downfield). The B7 atom of the $[1,3-C_2B_6B_9]^-$ ion[8o] can be considered both as an apical atom (the base consisting of B(1,2,3,4,8)) and as a basal boron (of the pyramid with B8 as the apex and atoms B(1,7,4,5,6) as the base) adjacent to a single carbon; the observed chemical shift, $\delta = -25.34$, is very approximately between the expected apical and basal regions. Likewise, the chemical shift of -26.6 assigned to B(8) of the same compound is approximately midway between the expected apical and basal regions. For B(7), $\delta = -36.4$, and for B(8), $\delta = -15.7$, of the $[2,3-C_2B_6H_9]^-$ ion and for B(7), $\delta = -7.3$, and for B(8), $\delta = -26.6$, of $2,3-C_2B_6H_{10}$ the observed chemical shifts[8k] are very roughly between the expected apical and basal regions. Additionally, the chemical shift of the two highest coordination (chemically equivalent) boron atoms of $1,4-C_2B_6H_{10}$[8ℓ,15] at $\delta = -22$ is in the expected "midway" chemical shift region. All of the peripheral borons (of the above compounds) that belong to only one "pyramid" are found in the lower field region of $\delta = +3.4$ to $+18.9$.

(25) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1; *J. Chem. Soc., Chem. Commun.* **1971**, 792.

with the requirements that there be one BH_2 group and one bridging hydrogen and that the molecule exhibit C_1 symmetry. Although ab-Initio calculations on these molecule anions resulted in a number of vibrationally stable structures, none were lower in energy than the one shown in Figure 1. Moreover, none gave the exceptional IGLO and GIAO correlational results (vide infra) that the structure in Figure 1 did. The closest contender (with a CH_2 in the 5 position and the BH_2 in the 6 position) gives IGLO and GIAO results that are respectable[26] to some degree, but also results in structure NMR data inconsistencies that make it a much less desirable choice; i.e., the 6-31G* optimized B–B bond distance patterns of the competitive [*arachno*-2,5-$C_2B_6H_{11}$]$^-$ molecule-ion are not found to match with the expectations of the observed 2D ^{11}B–^{11}B results. Thus, no cross peak is observed between the resonances at $\delta^{11}B = -13.7$ (B8) and +9.2 (B1) ppm and yet the the 6-31G* optimized geometry of the [*arachno*-2,5-$C_2B_6H_{11}$]$^-$ ion shows B(8)–B(1) to be the shortest bond (1.725 Å), and hence expected to be the strongest B–B bond in the molecule ion; also, one of the strongest 2D cross peaks occurs between the resonances at $\delta^{11}B = -13.7$ (B8) and -6.1 (B4) ppm, yet these resonances represent adjacent borons that are the farthest apart (1.869 Å) among the nine B–B bonds in the 6-31G* optimized geometry of the [*arachno*-2,5-$C_2B_6H_{11}$]$^-$ ion. So it is concluded that the [*arachno*-2,6-$C_2B_6H_{11}$]$^-$ ion structure fits the combination of experimental and calculational data substantially better than does its closely related [*arachno*-2,5-$C_2B_6H_{11}$]$^-$ ion isomer.

Another structure that is related to that proposed (Figure 1) in the present study is the more symmetrical [*arachno*-2,3-$C_2B_6H_{11}$]$^-$ ion, with C_s symmetry, obtained from the treatment of *closo*-1,2-$C_2B_8H_{10}$ with aqueous sodium hydroxide.[27] The [*arachno*-2,3-$C_2B_6H_{11}$]$^-$ ion is believed to have a skeletal geometry not unlike that shown in Figure 1, but with the carbons in adjacent low coordination (3*k*) positions and with two BH_2 groups in the adjacent (3*k*) positions 5 and 6. A single bridging hydrogen is placed between the adjacent BH_2 groups. (It is interesting to note that the skeletal structures of both our [*arachno*-2,6-$C_2B_6H_{11}$]$^-$ ion and the [*arachno*-2,3-$C_2B_6H_{11}$]$^-$ ion[27] are somewhat unlike the structure of the *arachno*-$C_2B_6H_{12}$ synthesized by Sneddon's group.[28]) Because ^{11}B chemical shifts of the [*arachno*-2,3-$C_2B_6H_{11}$]$^-$ ion are reported[27] it was of considerable interest to see if an IGLO NMR calculational study would provide a reinforcement of the [*arachno*-2,3-$C_2B_6H_{11}$]$^-$ structure to which the NMR assignments were previously made. We geometrically optimized the [*arachno*-2,3-$C_2B_6H_{11}$]$^-$ ion (with BH_2 groups at the 5,6 positions and with C_s symmetry) at the 6-31G* level of ab-Initio MO calculation. The outcome of the frequency calculation at this level indicated that a true energy minimum was located. IGLO analysis at the DZ//6-31G* level gives the following results (IGLO δ in italics, experimental[27] δ in boldface): B(1,4) *+7.0*, **+3.8**; B(5,6) *-34.0*, **-40.7**; B(7) *-59.5*, **-58.5**; B(8) *-22.0*, **-23.4**. The agreement between IGLO calculational and experimental results is acceptable.

The ab-initio/IGLO/NMR method, when applied to the 6-31G* optimized geometry for the [*arachno*-2,6-$C_2B_6H_{11}$]$^-$ ion, predicts ^{13}C chemical shifts of $\delta = -21.6$ ppm for the CH_2 carbon and $\delta = +79.7$ ppm for the CH carbon; and it also predicts $\delta = -22.3$ ppm for the CH_2 carbon and $\delta = +104.5$ ppm for the CH carbon of the isomeric [*arachno*-2,5-$C_2B_6H_{11}$]$^-$ ion. Experimentally, two equal area $^{13}C_{cage}$ resonances are found at δ -22.4 and +82.9 ppm (Figure 4) which supports the [*arachno*-2,6-$C_2B_6H_{11}$]$^-$ ion structural assignment. The unusually high-field resonance at the $\delta = -22.4$ ppm peak appears clearly as a proton-coupled 1:2:1 triplet and thus can be manifestly assigned to the CH_2 group of the [*arachno*-$C_2B_6H_{11}$]$^-$ ion. This high-field resonance, when proton decoupled, exhibits a half-width of ≈60 Hz whereas the low-field resonance at $\delta = +82.9$ ppm is broader with a half-width of ≈150 Hz; the proton-coupled low-field resonance is broader yet with a half-width of ≈250 Hz. The differences in proton-decoupled peak width of the two ^{13}C resonances can be justified in terms of expected differences in the extent of ^{13}C–^{11}B coupling; in the 6-31G* optimized [*arachno*-2,6-$C_2B_6H_{11}$]$^-$ ion structure (Figure 1) it is noticed that two B–C bonds about the C(2)H carbon are short (between 1.51 and 1.54 Å) whereas all of the B–C bonds about the C(6)H_2 group are longer than 1.68 Å. If a greater degree of ^{11}B–^{13}C coupling is associated with shorter bond lengths then it is quite reasonable that the $^{13}C(2)$ resonance might well appear broader than the $^{13}C(6)$ resonance.

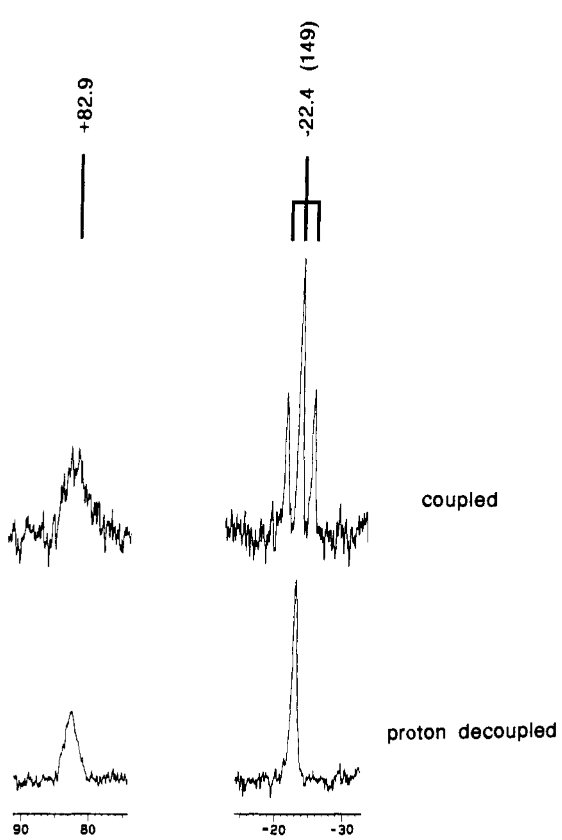

Figure 4. ^{13}C NMR data for the [*arachno*-2,6-$C_2B_6H_{11}$]$^-$ ion; chemical shifts are relative to TMS; coupling constants, in Hz, are given in parentheses.

It is interesting that the 2,6-isomer of the [$C_2B_6H_{11}$]$^-$ ion should appear the most stable of the many isomers that have been considered. In this regard it is pertinent to note that we found that the [$C_2B_6H_8$]$^{2-}$ isomer with carbon atoms in the 2,6 positions (of a skeletal framework similar to that in Figure 1) is the most stable[29] among those isomers having the carbon atoms in other positions within the same, or similar, framework. The [2,5-$C_2B_6H_8$]$^{2-}$ isomer is next in stability among the [$C_2B_6H_8$]$^{2-}$ structural isomers, and so it is intriguing that this same carbon position isomer of the [$C_2B_6H_{11}$]$^-$ ion is the next most seriously considered isomer in the present study. Be that as it may, when all reasonable isomers of the structurally related [$C_2B_6H_9$]$^-$ ion (with one bridging hydrogen present, and all carbons and borons bonded to one terminal hydrogen only) are considered for the product of hydride ion and *closo*-$C_2B_6H_8$,[8c] it is the 1,3-isomer that appears to be the most stable as examined by ab Initio

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(26) Ab-Initio/IGLO/NMR resonances for the [*arachno*-2,5-$C_2B_6H_{11}$]$^-$ molecule ion, calculated at the DZ//6-31G* level, are at $\delta^{11}B = -61.0$ (B7), -28.8 (BH_2), -7.5 (B8), -5.0 (B4), -1.9 (B3), +7.1 (B1). This logically leads to the experimental assignment of $\delta^{11}B = -56.7$ (B7), -24.9 (BH_2), -13.7 (B8), -6.1 (B4), -2.2 (B3), +9.2 (B1).

(27) Jelinek, T.; Stibr, B.; Hermanek, S.; Plesek, J. *J. Chem. Soc., Chem. Commun.* **1989**, 804–805.

(28) Corcoran, E. W.; Sneddon, L. G. *J. Am. Chem. Soc.* **1985**, *107*, 7446–7450.

(29) Bausch, J.; Onak, T.; Williams, R. E., work in progress.

calculations. However, the 1,3-isomer of the double negative ion, $[C_2B_6H_8]^{2-}$, is the third most stable (from Gaussian MP2/6-31G*//3-21G calculations) among the various carbon position isomers.[29] These structural findings as regards the $[C_2B_6H_9]^-$ ion system can be rationalized as follows. It has been suggested that the desire for bridging hydrogens to locate at adjacent low(est) coordination (e.g., 3*k*) boron sites is empirically more important than the known desire for cage carbon atoms to occupy low coordination sites.[17] This, coupled with the energy lowering associated with "carbons-apart" rather than "carbons-together", makes the 1,3-isomer of the $[C_2B_6H_9]^-$ ion the most logical candidate for the most stable isomer of this molecule ion. A $[2,6\text{-}C_2B_6H_9]^-$ or $[2,5\text{-}C_2B_6H_9]^-$ ion isomer cannot possess a bridging hydrogen between two adjacent 3*k* vertices since (a) bridging hydrogens are not known to attach to carbons in carboranes and (b) one carbon atom is located at each of the two pairs of adjacent 3*k* vertices in both the 2,6- and 2,5-isomers.

The structure depicted in Figure 1 for the $[2,6\text{-}C_2B_6H_{11}]^-$ ion can be derived from placing "bridging" BH_2 and CH_2 groups along adjacent edges (i.e., 4–8, 8–1) of a pentagonal pyramid (i.e., 7–1,2,3,4,8). Attempts to find other vibrationally stable isomers of the $[C_2B_6H_{11}]^-$ ion by placement of the BH_2 and CH_2 groups in *nonadjacent* bridging positions about a pentagonal pyramid (note: the pyramidal framework seems inevitable from the observation of the high-field ^{11}B resonance at $\delta = -56.7$ ppm, *vide supra*)[22] have been successful; however, such isomers are not found (from ab-Initio calculations) to be as energetically stable as when the BH_2 and CH_2 groups are placed in adjacent positions (e.g., Figure 1) along the base of a pentagonal pyramid. One reason that might be advanced for this finding is associated with the presumed energy releasing step of creating another cage bond (between a carbon of the CH_2 group and the boron of the BH_2 group) when the two bridging groups (BH_2 and CH_2) are situated in adjacent positions, as indeed they are in Figure 1. If two nonadjacent positions along the pentagonal face are selected for placement of the more "saturated" BH_2 and CH_2 groups, the "extra" bond between these two groups obviously cannot be formed. Also, the "aromaticity" (*vide supra*) of both of the pentagonal pyramids (e.g., 8–1,7,4,5,6 and 7–1,2,3,4,8) would then be expected to be adversely affected. It should be pointed out that ab-Initio/IGLO/NMR calculations carried out on all possible structural isomers of $[C_2B_6H_{11}]^-$ other than the 2,6-isomer (Figure 1) give unsatisfactory correlations to our experimental NMR data.

An enigma associated with the formation of the $[$*arachno*-$2,6\text{-}C_2B_6H_{11}]^-$ ion from *closo*-$1,6\text{-}C_2B_7H_9$ and fluoride ion is the question of where the two extra hydrogens are obtained in the course of proceeding from the *closo* reactant to the polyborane product ion. There is a plausible answer when the known difficulties of removing all the water of hydration from the fluoride ion source are considered.[1,30] We normally dry the tetrahydrofuran solution of tetrabutylammonium fluoride ion over CaH_2. Upon leaving the solution over the solid CaH_2 for too long a period of time (well over one week at room temperature) an examination of the liquid phase reveals that the concentration of soluble fluoride ion diminishes; it appears to precipitate with either of the two counterions, tetrabutylammonium or calcium. This observation suggests that a certain amount of water of hydration is necessary to keep the fluoride ion salt dissolved in tetrahydrofuran solution. It is then proposed that the stoichiometry of the reaction between the *closo* carborane and fluoride ion could well be represented by the following:

$$C_2B_7H_9 + F^- + 2H_2O \rightarrow [C_2B_6H_{11}]^- + H_2 + 1/n(BO_2F)_n$$

This would explain the formation of gas (H_2) during the reaction as well as the formation of product(s) (in addition to the $[$*arachno*-$2,6\text{-}C_2B_6H_{11}]^-$ ion) exhibiting several sharp resonances in the range of $\delta^{11}B = 0$ to $+2$ ppm. The latter range is not totally unexpected for simple boron compounds with a combination of bonded oxygen and fluorine atoms, and in particular, tetravalent boron species of a similar type[10] which could be formed in the presence of excess fluoride ion. The exact structural nature of what $1/n(BO_2F)_n$ (or any species formed by further reaction with fluoride ion) represents has evaded us, and the present designation of $1/n(BO_2F)_n$ as the monoboron side product is for the convenience of balancing the above reaction in addition to providing a reasonable guess at a product (or products) that could give rise to the NMR peak(s) at $\delta^{11}B = 0$ to $+2$ ppm.

In conclusion, ab-Initio/IGLO/NMR and ab-Initio/GIAO/NMR methods, coupled with 1D and 2D ^{11}B NMR as well as with ^{13}C and ^{1}H NMR observations, establish the structure of the principal carborane product from the reaction of fluoride ion with *closo*-$1,6\text{-}C_2B_7H_9$ to be that of the $[$*arachno*-$2,6\text{-}C_2B_6H_{11}]^-$ ion (Figure 1).

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(30) The difficulty of knowing the quantity of water present in organic solutions of fluoride ion has been commented upon earlier; see, for example: Clark, J. H. *Chem. Rev.* **1980**, *80*, 429–452, and references therein. More recently Christe et al.[31] has indicated a treatment that will remove most all water from tetramethylammonium fluoride. Also see ref 1, above.

(31) Christe, K. O.; Wilson, W. W.; Wilson, R. D.; Bau, R.; Feng, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 7619–7625.