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The Structure of *arachno*-$[B_6H_{11}]^-$, at −25 °C in $(CD_3)_2O$, Is Resolved via the ab Initio/IGLO-GIAO/NMR Procedure

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The *arachno*-$[B_6H_{11}]^-$ solution structure at −25 °C was clarified as fluxional compound **2** by applying the ab initio/IGLO/NMR method. The anion **2** can be derived from *arachno*-B_6H_{12}, **1**, by the removal of the B2/B3 bridging hydrogen (**2**). No minimum on the potential energy surface could be found for an asymmetric complex, **a**, between $[B_5H_8]^-$ and BH_3, which had been proposed originally. A C_s-symmetric $[\mu\text{-}(BH_3)B_5H_8]^-$ complex, **A**, only 3.2 kcal mol^{-1} higher in energy than **2**, is the intermediate in the fluxional rearrangement observed on the NMR time scale. The transition structure [**D**] connecting **2** ($E_{rel} = 0.0$) and **A** ($E_{rel} = 3.2$) has a relative energy of 9.7 kcal mol^{-1}. The elimination of both **a** and **A** as “most stable structure” candidates of *arachno*-$[B_6H_{11}]^-$ reinforces the early geometrical bonding systematics for boranes and carboranes.

Introduction

In 1975 Shore and co-workers[1] reported that the lithium and potassium salts of *nido*-$[B_5H_8]^-$ reacted with B_2H_6 to form the *arachno*-$[B_6H_{11}]^-$ anion (eq 1a). The NMR spectrum is identical with that of the anion obtained by deprotonation of B_6H_{12} (eq 1b). Protonation of $[B_6H_{11}]^-$ gives B_6H_{12}, **1**.

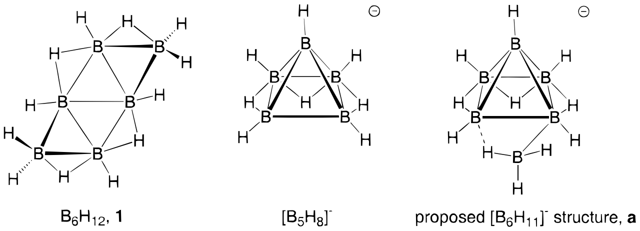
$$[B_5H_8]^- + (1/2)B_2H_6 \rightarrow [B_6H_{11}]^- \qquad (1a)$$

$$[B_5H_8]^- + B_6H_{12} \rightarrow [B_6H_{11}]^- + B_5H_9 \qquad (1b)$$

$$[B_6H_{11}]^- + H^+ \rightarrow B_6H_{12} \qquad (1c)$$

A solution of KB_6H_{11} in $(CD_3)_2O$ gave a ^{11}B NMR spectrum at −25 °C with four signals at 14.0, 1.6, −0.9, and −34.6 ppm in a ratio of 2:1:2:1. This implied that at least four kinds of borons were present. It is important to remember that Shore’s ^{11}B NMR spectra were obtained, a quarter of a century ago, at 28.8 Hz, *less than one-fifth the resolution available today*. The lone boron resonance at highest field was attributed to the presence of an “apex” boron atom. Considering the known structure of *nido*-$[B_5H_8]^-$ (Chart 1), it was concluded that the BH_3 moiety had “entered the vacant bridging site in the $[B_5H_8]^-$ ion, leaving the boron framework intact (in a topological sense)” to form a complex of *nido*-$[\mu\text{-}(BH_3)B_5H_8]^-$. “The apparent absence of spin coupling of terminal hydrogens with the inserted boron” in the −25 °C ^{11}B NMR spectrum was taken to be “suggestive of dynamic character”. However, the ^1H NMR spectrum at −125 °C showed nine different resonances, “believed to represent an effectively static structure on the ^1H NMR time scale”. In this static structure “the symmetry has been reduced by the act of the borane group assuming a static position such that one of its hydrogen atoms is in what is nearly a bridging position.” Therefore, the structure **a** was drawn asymmetrically (as reproduced in Chart 1) with one B−B and one H−B interaction between BH_3 and $[B_5H_8]^-$.

Chart 1



B_6H_{12}, **1** $[B_5H_8]^-$ proposed $[B_6H_{11}]^-$ structure, **a**

Structure **a**, incorporating a fluxional BH_3 group, and C_s-symmetric **A** or **[B]**,[2] both lacking the single hydrogen bridge invoked for **a** but differing in the orientation of the BH_3 group, satisfy the 2:1:2:1 boron ratio observed by NMR: there are four “kinds of boron”, one unique apex boron, and one unique basal boron plus two pairs of equivalent basal borons. Hence, configurations resembling **A**, **[B]**, or **a** were favored over structures **2** and **F**, both of which have six different borons (see Figure 1). However, this assignment required the purported apex boron signal (at −34.6 ppm) in **A**, [**B**], or **a** to be at 10−15 ppm lower field compared to the chemical shift values of all similar apex-borons in derivatives of *nido*-B_5H_9 or *arachno*-B_5H_{11}.[3] Moreover, on the basis of structural systematics, the most probable configurations for *arachno*-$[B_6H_{11}]^-$ were[4] **2** and **F** (Figure 1).[2] Both candidates **2** and **F** may be derived from

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(2) In this paper all *established* structures are given numbers (e.g., **1**, **2**, etc.), while all configurations that are unknown experimentally, but that are shown to be energy minima by ab initio calculations, are given letters (e.g., **A**, **B** etc.). transitions states are enclosed in brackets (**[F]**). Structures for which no stationary point could be found are given lower case letters (e.g., **a**).

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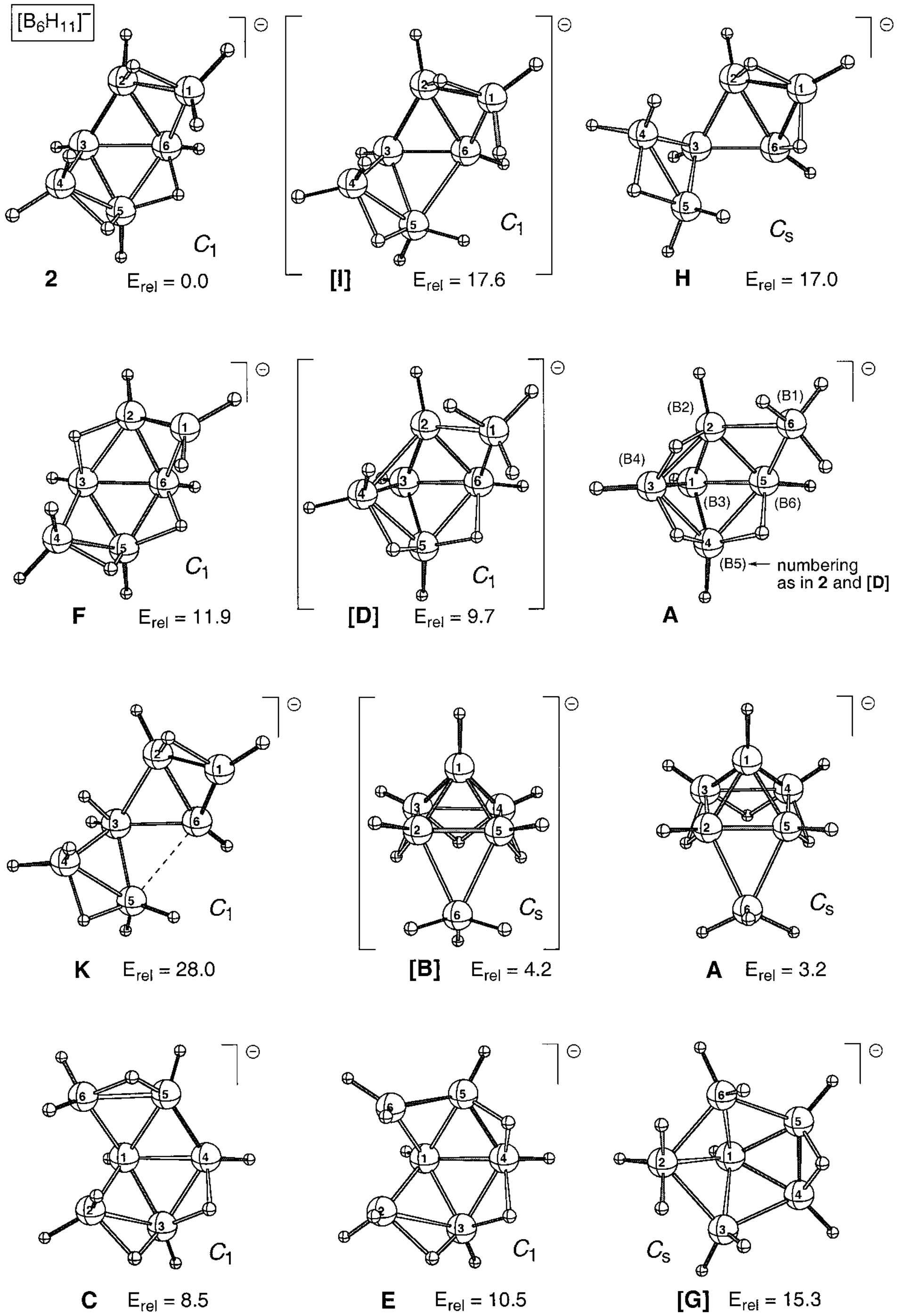

Figure 1. Candidate *arachno*-$[B_6H_{11}]^-$ configurations, **2**, **A**, [**B**], **C**, [**D**], **E**, **F**, [**G**], **H**, [**I**], and **K** (labeled in order of decreasing stability; transition structures are in brackets).

the known structure of *arachno*-B_6H_{12}, **1**,[5] by the removal of different bridge hydrogens. They might also be considered as the most probable structures in light of the deprotonation and protonation reactions, eqs 1b and 1c.

The observation that the ^{11}B NMR spectrum obtained at −76 °C differed significantly (and reversibly as a function of temperature) from the ^{11}B NMR spectrum obtained at −25 °C also is remarkable: at −76 °C there are three peaks at 15.2, 1.0, and −21.7 (3:2:1), and the 15.2 ppm peak is due to two overlapping signals. In addition, the ^1H NMR spectrum at −125 °C revealed wholesale asymmetry. It seemed reasonable (in 1975) to assume that the precursor $[B_5H_8]^-$ and BH_3 fragments probably had formed an alternative isomeric structure (or structures) of *nido*-$[\mu\text{-}(BH_3)B_5H_8]^-$, at −76 and −125 °C (possibly structure **a** in Chart 1). However, if **a** were the correct structure at −76 °C, the deviation of the chemical shift of the apex boron (−21.7 ppm) from that of B_5H_9 (−55.2 ppm) and B_5H_{11} (−55.2 ppm) models[3] must be doubled in magnitude. The chemical shift ($\delta(^{11}B) = -21.7$ ppm) of the presumed "apex boron" atom was found at even lower field, i.e., by 25−30 ppm, at −76 °C than observed for any other *nido*-B_5H_9 derivative.

The IGLO (individual gauge for localized orbitals) program of Kutzelnigg and Schindler[6] constituted the first practical method for the ab initio computation of magnetic properties, NMR chemical shifts in particular. The first applications, e.g.,

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on carbocations, used experimental or standard geometries which often resulted in calculated chemical shift values that were in relatively poor agreement with the experimental data. These deviations were ascribed at first to solvent effects and/or counterion interactions. Later, it was realized that accurate "input" geometries were critical for the calculation of good chemical shift values.[7]

The demonstration of outstanding performance of the IGLO approach for calculating ^{11}B NMR chemical shifts using computed geometries[8] established the basis of the ab initio/IGLO/NMR method.[9] This is now accepted as a reliable structural tool.[10] Comparison of the experimental $\delta(^{11}\mathrm{B})$ values with those computed for different geometries allows the "best" geometry to be selected. Chemical shifts computed for even closely related candidate structures usually differ from each other in one or more ways. Usually one, and only one, set of calculated chemical shift values matches the experimentally determined values, and thus the correct structure can be selected from among the alternatives. Using these techniques, many "decades-old" contentious structures have been mediated successfully. For example, an *arachno*-1-CB_4H_{10} derivative[11] has been confirmed. A *closo*-$C_2B_6H_8$ structure[12] has been reconfirmed, and the structures of several mono- and dimethyl derivatives of *nido*-B_6H_{10} have been deduced and/or supported.[13] The *nido*-8⟨VI⟩ structure for *nido*-$B_8H_{10}L$[14] has been established, and two of three *nido*-11⟨V⟩ structures for isomers of *nido*-$C_4B_7H_{11}$[15] structural proposals for alkyl derivatives of *closo*-1,2-$C_2B_3H_5$[16] and of *closo*-$C_3B_5H_7$[12] have been purged from the literature. However, a substantial "*reservoir*" of less disputatious structures in the older literature remains to be examined by the ab initio/IGLO or GIAO/NMR method.

If the geometrical systematics proposed in 1971 are followed,[4,17] the three proposed $[B_6H_{11}]^-$ candidates, **A**, **[B]** (Figure 1), and **a** (Chart 1),[1] are "structural pariahs" in contrast to the "acceptable" **2** (or less likely **F**). Both structures **A** and **[B]** incorporate one apical B atom which is 4-fold coordinated to other cluster atoms ($4k_C$). *This is without precedent among all other arachno-borane structures*. The departure from the pattern[4 17] illustrated in Figure 2 led us to wonder about the structures **A**, [**B**], and **a** from time to time. Despite our misgivings, these structures have been universally accepted (ourselves included) as the most reasonable configurations that seemingly matched Shore's ^{11}B NMR spectra.[1]

In view of the new investigational developments, we have now subjected the $[B_6H_{11}]^-$ "structural alternatives" (i.e., structures **2** and **F** versus **A** and [**B**] (Figure 1) as well as **a** (Chart 1)) to the ab initio/IGLO or GIAO/NMR procedure.

Computational Details

All geometries were fully optimized within the given symmetry at the Hartree−Fock and second-order Møller−Plesset levels in the frozen core approximation (MP2(fc)) with the Gaussian 94 program.[18] Standard 6-31G* and 6-31+G* basis sets were used. Vibrational frequencies were derived analytically at HF/6-31G* to characterize the nature of the stationary points and for zero-point vibrational energy corrections (ZPE). Relative energies (E_{rel}) given in Figure 1 correspond to our final level MP2(fc)/6-31+G* + 0.89ZPE(HF/6-31G*).[19] Chemical shifts were computed with the IGLO program[6] using the DZ or II′ basis sets (based on Huzinaga basis sets[20]) in the recommended contraction schemes. DZ has 7s3p contracted to [4111,21] on B and 3s contracted to [21] for H; II′ is the same for H but provides 9s5p contracted to [51111,2111] plus a set of d polarization functions for B. B_2H_6 was used as the primary reference, and a gas-phase chemical shift value of 16.6 ppm[21] was used for the conversion to the experimental $BF_3{\cdot}OEt_2$ scale.

Discussion and Results

The Structure of *arachno*-$[B_6H_{11}]^-$ at −25 °C. The following *arachno*-$[B_6H_{11}]^-$ candidate structures were computed: **2** and **F** were derived from B_6H_{12} by removing one bridge hydrogen between B2/B3 and B1/B2, respectively. Structures **A** and **[B]** both correspond to $[B_5H_8]^-{\cdot}BH_3$ complexes but differ in the orientation of the bridging BH_3 group. Structure **a** is not a stationary point at all. Optimization of a starting geometry corresponding to **a** converged to **A**. Optimization of a starting geometry with five hydrogen bridges within the C_s symmetry point group converged to **[G]**, where the BH_3 is inserted into a basal B−B edge of $[B_5H_8]^-$ (Figure 1), only one H is in a bridging position (B4/B5), and four H atoms are terminally endo bound. Candidate **[G]** turned out to be a transition state and geometry optimization without symmetry constraints converged to **E**, which can formally be derived from **F**: The positions of the $B1H_2$ and the H bridging B2−B3 in **F** are exchanged in **E**. In a similar fashion, **C** and **2** are related: The $B1H_2$ group together with one bridging H of **2** is located above the B2−B3 edge in **C** (note the different numbering for **2** and **C**). Optimization of a starting geometry with the *endo*-hydrogen atom removed from B1 in B_6H_{12} converged to **K**, which is much higher in energy (28 kcal mol^{-1}).

Among all $[B_6H_{11}]^-$ isomers considered, **2**, which lacks the B2−B3 hydrogen bridge of B_6H_{12}, is lowest in energy. The

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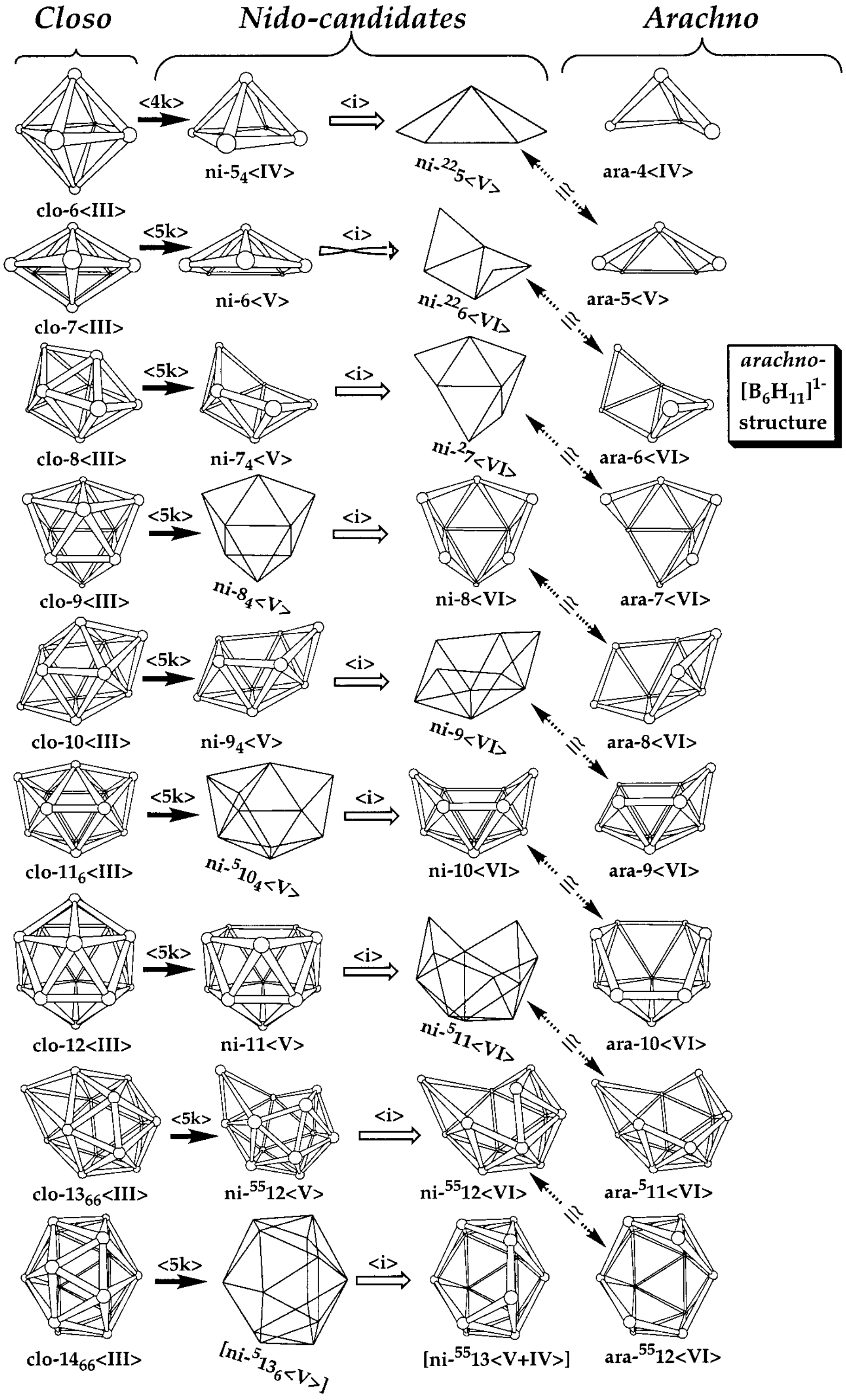

Figure 2. 1998 *Bivertex-seco* geometrical systematics. For the labels, the short forms clo, ni, and ara are used for closo, nido, and arachno cages, respectively; the total number of vertexes and the largest number of vertexes in an open face are given in Arabic and Roman numerals, respectively. The presence of perimeter (part of the largest open face) and cage vertexes with unfavorable coordination numbers *n* with respect to other vertexes is indicated by the number *n* as a superscript and subscript, respectively. See ref 17 for more details.

most prominent structural change upon deprotonation is a considerable shortening of the B2−B3 edge (from 1.791 to 1.676 Å, Figure 3). Isomers **A** and **[B]** are second best with relative energies of only 3.2 and 4.2 kcal mol^{-1}. The alternative bridge-deprotonated structure **F** is quite high in energy (11.9 kcal mol^{-1}), even higher than **C** and **E**.

On the basis of these relative thermodynamic stabilities, **2** should represent the $[B_6H_{11}]^-$ solution structure. However, if **2** were a static structure, this geometry should give rise to six different ^{11}B NMR chemical shifts, due to its lack of symmetry. If **2** were fluxional, however, some boron atoms might exchange their chemical environments and become equivalent on the NMR time scale. Averaged chemical shifts for groups of boron atoms would result.

Having identified **2** as the most likely $[B_6H_{11}]^-$ solution structure, we next averaged the computed individual ^{11}B NMR chemical shifts to see if they would match the four experimental values 14.0, 1.6, −0.9, and −34.6 and their 2:1:2:1 relative

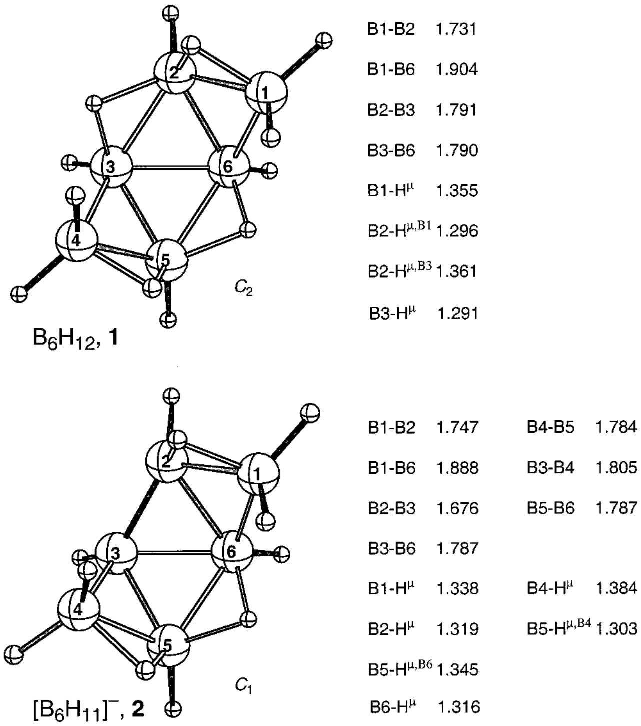

Figure 3. Solution structure of *arachno*-$[B_6H_{11}]^-$, **2**, at −25 °C, with relevant distances in angstroms in comparison to *arachno*-B_6H_{12}, **1**.

Table 1. Computed[a] ^{11}B NMR Chemical Shifts for $[B_6H_{11}]^-$ Candidate Structures

structure	B1	B3	B4	B5	B2	B6
A	−55.8	−24.5	−24.5	−5.1	−5.1	−41.3
B	−53.2	−20.7	−20.7	−9.5	−9.5	−39.1
C	−59.5	7.3	14.0	12.0	−5.7	10.8
E	−45.5	−34.6	27.1	1.8	−15.9	−14.9
F	37.1	−26.1	−8.4	27.5	3.3	−14.7
[G]	−20.2	−21.3	4.6	4.6	−76.4	−21.3
H	−50.9	−32.7	21.1	42.2	−12.3	9.1
2	5.0	−36.8	−3.8	7.8	46.1	−12.2

	B1	B3	B4/B5	B2/B6
2, av	5.0	−36.8	2.0	17.0
exptl[b]	1.6 (1)	−34.6 (1)	0.9 (2)	14.0 (2)

[a] IGLO/II′//MP2(fc)/6-31+G*. [b] In $(CD_3)_2O$ at 25 °C; at −76 °C the chemical shifts are 15.2, 1.0, and −21.7 (3:2:1). See ref 1.

intensities (Table 1). The average of the B2 (46.1) and B6 (−12.2) signals, 17.0 ppm, agrees with the experimental 14.0 ppm reasonably well. Likewise, the B4 (−3.8) and B5 (7.8) signal average, 2.0 ppm, matches the experimental 0.9. The computed shifts for B1 (5.0) and B3 (−36.8) fit the remaining experimental values 1.6 and −34.6 with unit intensities each. With this assignment, the maximum deviation between computed and experimental chemical shifts, 3.4 (for B1), is within the error expected at the level of theory applied.[8] One might add that no other structure, **A** to **H**, allows the construction of a set of averaged ^{11}B NMR chemical shifts which agrees satisfactorily with the experimental values.

If **2** really is the correct $[B_6H_{11}]^-$ solution structure, it must be fluxional. The following mechanism would render B4 and B5 as well as B2 and B6 equivalent: Breaking the B5−B6 connection allows the formation of a C_s intermediate, **H**, with a B_2H_5 and a B_3H_5 moiety coordinated to B3. Closing the B2−B4 or the B5−B6 connection in **H** leads to structure 2 with or without exchanged B2/B6 and B4/B5. However, **H** has a high relative energy of 17.0 kcal mol^{-1}, and the corresponding transition structure (**[I]**) connecting **2** and **H** is 0.6 kcal mol^{-1} higher in energy. Hence, this mechanism is unlikely.

As an alternative to breaking the B5−B6 connection, the formation of a B2−B4 connection also should be considered. Bonding between B2 and B4 requires the bridge hydrogen between B1 and B2 to become a terminal H at B1 and leads to C_s-symmetric **A** as an intermediate, thus making the B2/B6 and B4/B5 pairs equivalent. The corresponding transition structure [**D**] has a relative energy of 9.7 kcal mol^{-1}. This mechanism explains not only the fluxionality of the solution structure **2**, but also its formation from $[B_5H_8]^-$ and BH_3. Most likely, the initial adduct is structure **A**, which is 33.9 kcal mol^{-1} more stable than the isolated precursors, $[B_5H_8]^-$ and BH_3. Taking into account the complexation of BH_3 by a solvent molecule, e.g., OMe_2, the $[B_5H_8]^- + (Me_2O)BH_3 \rightarrow [B_6H_{11}]^-$ (**A**) + OMe_2 reaction energy is −11.8 kcal mol^{-1}. Only a 6 kcal mol^{-1} barrier is involved in the formation of a H bridge between B5 and B6 (or B6 and B2), which leads to the 3.7 kcal mol^{-1} more stable isomer **2** by opening the B4−B5 (or B2−B3) edge. The barrier for BH_3 rotation is only 1 kcal mol^{-1} and involves transition structure [**B**].

Structure of *arachno*-$[B_6H_{11}]^-$ at −76 °C. None of the candidate structures in Figure 1 can explain the ^{11}B NMR spectrum of *arachno*-$[B_6H_{11}]^-$ at −76 °C. We therefore considered two possibilities. First, wondering whether a solvent adduct might be formed at low temperatures, we tried to optimize adducts of $[B_6H_{11}]^-$ with a Lewis base, L = H_2O or $(CH_3)_2O$. However, most starting geometries did not converge to adduct minima, but to dissociated $[B_6H_{11}]^-$ + L. We could locate some adduct structures at the SCF level. However, they did not result in ^{11}B NMR chemical shifts that could explain the experimental values at −76 °C. Hence, these structures were not optimized at higher levels. The second idea investigated computationally was a possible dimerization at low temperatures, but again the SCF-optimized geometries failed to explain the −76 °C NMR spectra. In conclusion, we were unsuccessful in finding the structure involving $[B_6H_{11}]^-$ that is responsible for the low-temperature NMR spectra. We therefore suggest a reinvestigation of $[B_6H_{11}]^-$ with today's modern NMR techniques to obtain more experimental information on this compound.

Conclusions

The most important conclusion that emerged from applying the abinitio/IGLO/NMR method is that the −25 °C isomer of *arachno*-$[B_6H_{11}]^-$ adopts a C_1-symmetric structure, **2**, derived from B_6H_{12} by removing one proton from the B2/B3 bridging position (see Figure 1). The structure is fluxional on the NMR time scale. A C_s-symmetric complex, **A**, which is likely to be the initial product from the reaction between $[B_5H_8]^-$ and BH_3, is 3.2 kcal mol^{-1} higher in energy and an intermediate in the degenerate rearrangement, which transforms **2** into its enantiomer. The relevant transition structure [**D**] connecting **2** and **A** has a relative energy of 9.7 kcal mol^{-1}.

The formerly seemingly reasonable alternatives **A**, [**B**], and **a**[1] cannot represent the correct solution structure for *arachno*-$[B_6H_{11}]^-$ at −25 °C. The elimination of **A**, [**B**], and **a** as exceptions reinforces Williams' 1971 geometrical/electron bond systematics.[4,17] Almost all boranes and carboranes, including *arachno*-B_6H_{12}, **1**, *ara*-6⟨VI⟩ in Figure 1, have been found to comply with the 1971 set of geometrical systematics,[4] which has been upgraded to a 1998 version[17] (see Figure 2).

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