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Synthesis of the *arachno*-4-$CB_8H_{12}^{2-}$ Monocarbaborane Dianion and NMR/Computational Studies of the Fluxional Processes Observed in the Isoelectronic Nine-Vertex *arachno* Anions: *arachno*-4-$CB_8H_{12}^{2-}$, *arachno*-4-$CB_8H_{13}^{-}$, and *arachno*-4-$SB_8H_{11}^{-}$

Daniel E. Kadlecek and Larry G. Sneddon*

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

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The new monocarbaborane dianion, *arachno*-4-$CB_8H_{12}^{2-}$ has been synthesized from the reaction of *arachno*-4-CB_8H_{14} with 2 equiv of NaH in polar solvents. DFT/GIAO computations at the B3LYP/6–311G*//B3LYP/6–311G* level, in conjunction with 1D and 2D NMR spectroscopic studies, have confirmed that the dianion results from deprotonation of both the *endo*-CH and one bridging hydrogen of the parent *arachno*-4-CB_8H_{14}. While the DFT calculations indicate that a C_1 symmetric structure is lowest in energy, the experimental solution NMR data are consistent with the dianion having a C_s symmetric structure, thus suggesting that it is fluxional in solution. Transition state calculations located a low-energy pathway with an activation energy of only 2.7 kcal/mol that allows the migration of the bridging hydrogen between the two enantiomeric forms of the dianion. The process can occur by a single-step, simple rotation through a transition state structure containing a –BH_2 group at the B7 boron. Averaging the calculated ^{11}B NMR chemical shifts of the resonances for those atoms in the static enantiomeric structures that become equivalent by this fluxional process then gives excellent agreement with the solution NMR data. Transition state calculations of the fluxional behavior previously observed for the isoelectronic *arachno*-4-$CB_8H_{13}^{-}$ and *arachno*-4-$SB_8H_{11}^{-}$ monoanions have likewise revealed related low-energy (0.3 and 5.0 kcal/mol, respectively) rearrangement mechanisms involving the simultaneous rotation of three hydrogens (two bridging and one –BH_2) through a C_s symmetry transition state containing three –BH_2 groups.

Introduction

Stíbr et al. originally achieved the synthesis of *arachno*-4-CB_8H_{14} in 1976 through the ferric chloride mediated oxidative hydrolysis of 6-$(CH_3)_3$N-6-CB_9H_{11}.[1] A more convenient route was later developed based on the degradation of readily available *o*-carborane.[2] Solution NMR studies[3] and MP2 calculations[4] concluded that *arachno*-4-CB_8H_{14} has the expected *arachno*-type cage framework and contains one $-CH_2$ group and four bridging hydrogens spanning the four B−B bond edges of the six-membered open face. Deprotonation of *arachno*-4-CB_8H_{14} with 1 equiv of base was found to yield the *arachno*-4-$CB_8H_{13}^{-}$ monoanion.[3] A crystallographic determination carried out on the Proton Sponge salt of the monoanion confirmed that one of the bridging protons was removed; however, ab initio/IGLO computations, in conjunction with experimental NMR studies, revealed the structure to be dynamic in solution, rearranging through a fluxional process involving the rapid equilibration of *endo*-BH and B−H−B bridging hydrogens.[2] In this paper we report the first synthesis of the *arachno*-4-$CB_8H_{12}^{2-}$ dianion, along with DFT/GIAO studies of the three isoelectronic anions *arachno*-4-$CB_8H_{13}^{-}$, *arachno*-4-$CB_8H_{12}^{2-}$, and *arachno*-4-$SB_8H_{11}^{-}$ that elucidate the mechanisms of their fluxional rearrangements observed in solution.

Experimental Section

All manipulations were carried out using standard high-vacuum or inert-atmosphere techniques as described by Shriver.[5]

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* Author to whom correspondence should be addressed. E-mail: lsneddon@sas.upenn.edu.

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Table 1. NMR Data for *arachno*-4-$CB_8H_{12}^{2-}$

nucleus	δ (multiplicity, intensity, assignment, J(Hz))
$^{11}B^{a,b}$	3.6 (d, B5,9, J_{BH} 119), −18.9 (d, B2,3, J_{BH} 122), −33.2 (d, B7, J_{BH} 121), −37.3 (t, B6,8, J_{BH} 101), −50.4 (d, B1, J_{BH} 141)
$^{11}B-^{11}B^{a,b}$	obsd cross peaks: B1−B2,3; B1−B5,9; B2,3-B5,9; B2,3-B6,8; B2,3−B7
$^{1}H\{^{11}B\}^{a,c}$	2.77 (2, BH), 2.51 (s, 1, cage-CH), 1.10 (2, BH), 0.07 (1, BH), −0.17 (2, BH), −1.31 (1, BH), −1.38 (2, BH), −3.89 (1, BHB)
$^{13}C\{^{1}H\}^{a,d}$	71.3 (C4)

[a] CD_3CN. [b] 64.2 MHz. [c] 500.4 MHz. [d] 125.8 MHz.

Materials. Oil-dispersed sodium hydride was purchased from Aldrich, washed with dry hexanes under a N_2 atmosphere, and then dried under vacuum. Acetonitrile, tetrahydrofuran (THF), and dimethoxyethane (DME) were dried by being passed through an activated alumina column prior to use. The monocarbaborane *arachno*-4-CB_8H_{14} was prepared according to the literature procedure.[2]

Physical Measurements. ^1H NMR spectra at 500.4 MHz and ^{13}C NMR spectra at 125.8 MHz were obtained on a Bruker AM-500 spectrometer. ^{11}B NMR spectra at 64.2 MHz were obtained on a Bruker AF-200 spectrometer. Both spectrometers were equipped with the appropriate decoupling accessories. All ^{11}B chemical shifts are referenced to external $BF_3{\cdot}O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All ^1H and ^{13}C chemical shifts were measured relative to internal residual protons or carbons in the lock solvent and are referenced to Me_4Si (0.00 ppm).

Synthesis of *arachno*-4-$CB_8H_{12}^{2-}$. To a 100-mL, two-neck, round-bottom flask fitted with a vacuum adapter, magnetic stirbar, and septum was added 0.11 g (1.0 mmol) of *arachno*-4-CB_8H_{14} under a flow of N_2. To this flask was then added via syringe 5.0 mL of acetonitrile with stirring to dissolve the solid. The solution was maintained at 0 °C while 0.06 g (2.5 mmol) of NaH was added through one neck of the flask. After bubbling ceased, ^{11}B NMR analysis of the reaction mixture indicated quantitative conversion to *arachno*-4-$CB_8H_{12}^{2-}$. Samples for spectroscopic analysis were obtained by filtering the reaction mixture in the glovebag to remove excess NaH, and then concentrating the filtrate under reduced pressure. Removal of the solvent initially gave an oily solid. Further drying overnight on the high-vacuum line overnight yielded 0.087 g (44% yield) of a very air-sensitive powdery white solid which elemental analyses indicated contained an acetonitrile solvate. Anal. Calcd for $Na_2CB_8H_{12}{\cdot}CH_3CN$: C, 18.23; H, 7.65; N, 7.09; Found: C, 18.95; H, 7.49; N, 5.62. NMR data are given in Table 1.

Computational Studies. The DFT/GIAO method,[6] using the Gaussian 98[7] program, was used in a manner similar to that previously described.[8] The geometries were fully optimized at the B3LYP/6−311G* level within the specified symmetry constraints (using the standard basis sets included) on a (2)-processor Origin 2000 computer running IRIX 6.5.5 or a (6)-processor Power Challenge XL computer running IRIX 6.5.6. A vibrational frequency analysis was carried out on each optimized geometry at the B3LYP/6−311G* level with a true minimum found for each structure (i.e., possessing no imaginary frequencies). The NMR chemical shifts were calculated at the B3LYP/6−311G* level using the GIAO option within Gaussian 98. ^{11}B NMR GIAO chemical shifts are referenced to $BF_3{\cdot}O(C_2H_5)_2$ using an absolute shielding constant of 102.24.[9,10] The ^{13}C NMR GIAO chemical shifts were referenced to TMS using an absolute shielding constant of 184.38 according to the method described by Schleyer.[11]

For the reaction pathway transition state calculations, all geometries were optimized at the B3LYP/6−311G* level. Vibrational frequencies were calculated at the same levels to determine the nature of the stationary point and to make zero-point corrections. The stationary points for *arachno*-4-$CB_8H_{12}^{2-}$, *arachno*-4-$CB_8H_{13}^{-}$, and *arachno*-4-$SB_8H_{11}^{-}$ were judged to be true transition states, with each possessing only one imaginary frequency, of magnitudes −621.7, −695.4, and −756.8 cm^{-1}, respectively. IRC calculations were carried out to confirm the reaction pathways from the located transition states in both directions.

Results and Discussion

As reported by Howarth et al.,[3b] a previous attempt to prepare the *arachno*-4-$CB_8H_{12}^{2-}$ dianion by the deprotonation of *arachno*-4-CB_8H_{14} with *n*-BuLi in THF was unsuccessful. This failure was attributed to the poor solubility of the product in the reaction solvents and/or cluster degradation. However, in contrast to this earlier study, we have now found that the synthesis of this dianion is readily achieved by the reaction of *arachno*-4-CB_8H_{14} with an excess of NaH in polar solvents such as acetonitrile, THF, or DME (eq 1).

$$\textit{arachno}\text{-4-}CB_8H_{14} + 2NaH \xrightarrow{CH_3CN,\ THF,\ or\ DME} Na^{+}{}_2[\textit{arachno}\text{-4-}CB_8H_{12}{}^{2-}] + 2H_2 \quad (1)$$

The reactions appear quantitative by ^{11}B NMR, and following filtration to remove the excess unreacted sodium hydride, such solutions of the dianion can then be used for further reactions without purification or isolation.[12] When the reaction is carried out in acetonitrile, the product, in the form of an acetonitrile solvate, $Na^{+}{}_2$ [*arachno*-4-$CB_8H_{12}^{2-}$]$\cdot$$CH_3CN$, can be obtained as a very air-sensitive white solid in a 44% isolated yield.

The *arachno*-4-$CB_8H_{13}^{-}$ monoanion has been shown[2,3] to contain four potentially acidic hydrogens, an *endo*-CH, an *endo*-BH, and two bridging hydrogens, any one of which

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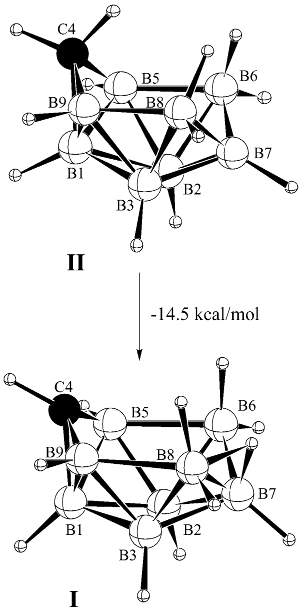

Figure 1. DFT optimized geometries and energies calculated at the B3LYP/6−311G* level for two possible structures (**I** and **II**) of *arachno*-4-$CB_8H_{12}^{2-}$. Energies (ZPE corrected): **I**, −244.0488643 H; **II**, −244.0257157 H.

could, in principle, be removed to form the *arachno*-4-$CB_8H_{12}^{2-}$ dianion. All of these possibilities were investigated using DFT/GIAO computations at the B3LYP/6−311G*//B3LYP/6−311G* level. The two optimized geometries, **I** and **II**, shown in Figure 1, were found to be of lowest energies with **I** being favored by 14.5 kcal/mol over **II**. Both structures have two *endo*-BH hydrogens, but in **I** the third hydrogen is bridging the B7−B8 edge, while in **II** the third hydrogen is in the *endo* position of the $-CH_2$ group. Because of the different placement of the three hydrogens on the open face, the two structures have different symmetries, i.e., **I** has C_1 symmetry, while **II** has C_s symmetry.

The 64.2 MHz ^{11}B NMR spectrum of *arachno*-4-$CB_8H_{12}^{2-}$ (Figure 2) consists of five peaks of relative intensity 2:2:1:2:1 indicating a C_s symmetric solution structure. Four of the five peaks are doublets, but the intensity-2 peak at −37.3 ppm appears as a triplet that can be assigned to two equivalent $-BH_2$ units. The 500.4 MHz ^{11}B-decoupled ^1H NMR spectrum is also consistent with C_s symmetry, containing eight singlets of intensity 2:1:2:1:2:1:2:1 that can be assigned as shown in Figure 3 to eight terminal −BH, two *endo*-BH, one −CH, and one B−H−B hydrogens. The 125.8 MHz ^1H-decoupled ^{13}C NMR spectrum shows the cage-carbon peak at 71.3 ppm.

While the C_s symmetry of structure **II** is consistent with the symmetry found in the NMR spectra of *arachno*-4-$CB_8H_{12}^{2-}$, this structure can be eliminated as a possibility since the GIAO calculated chemical shifts and assignments (Table 2) are quite different from the experimentally observed values, with the ^{11}B NMR chemical shifts differing by as much as 73 ppm, and the carbon shift differing by 75.5 ppm. Structure **II** is also inconsistent with the fact that it has two CH hydrogens, whereas the ^1H NMR spectrum of *arachno*-4-$CB_8H_{12}^{2-}$ clearly shows only one CH, with the other hydrogen being present as a B−H−B bridge.

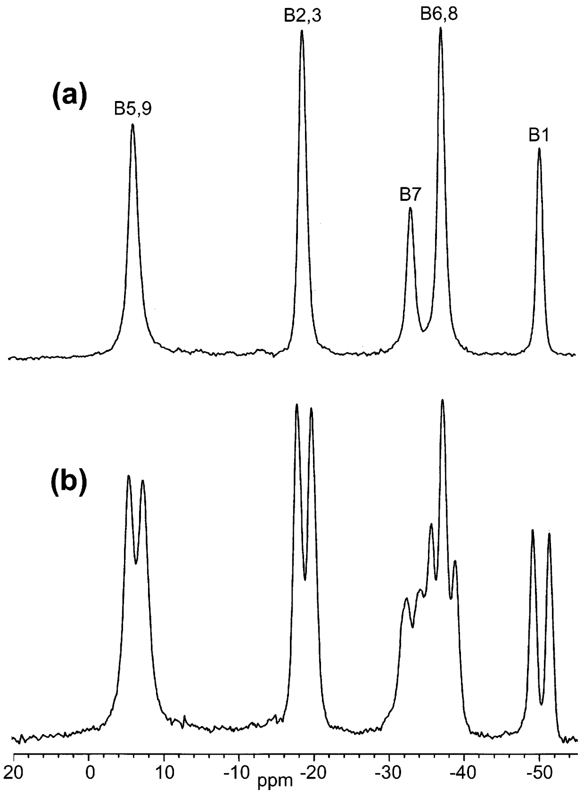

Figure 2. 64.2 MHz ^{11}B NMR spectra for *arachno*-4-$CB_8H_{12}^{2-}$: (a) ^1H decoupled, (b) ^1H coupled.

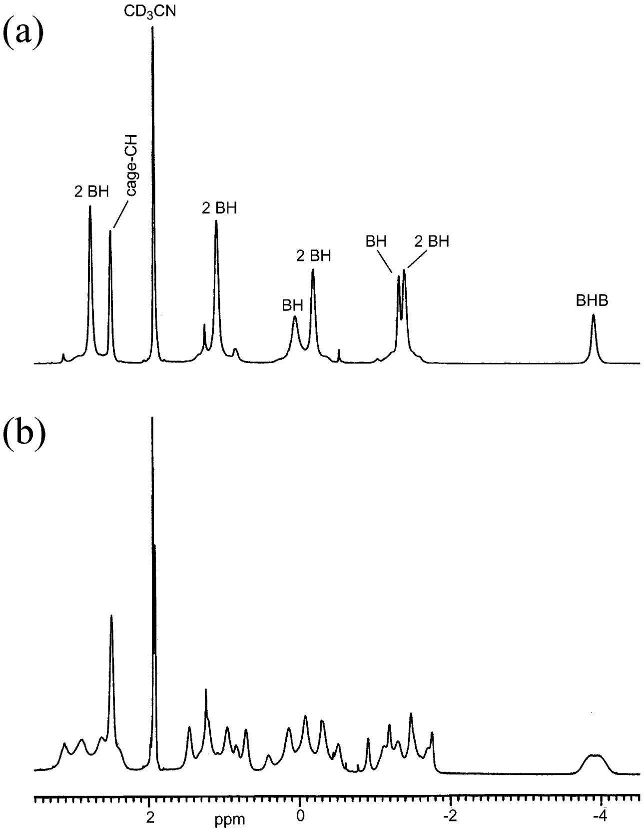

Figure 3. 500.4 MHz ^1H NMR spectra of *arachno*-4-$CB_8H_{12}^{2-}$: (a) ^{11}B decoupled, (b) ^{11}B coupled.

The calculated ^{11}B chemical shifts for the C_1 symmetric structure **I** also do not match the ^{11}B NMR spectra observed

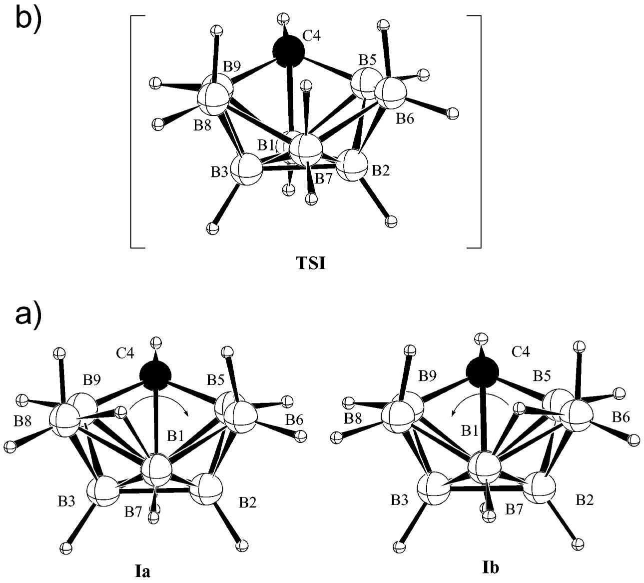

Figure 4. (a) Enantiomeric forms of structure **I** formed by bridge-hydrogen migration between B7−B8 and B7−B6 edges. (b) DFT optimized transition state structure **TSI** calculated at the B3LYP/6−311G* level for the fluxional process illustrated in part a. **TSI** energy (ZPE corrected): −244.0444959 H.

Table 2. Comparisons of the Experimental ^{11}B and ^{13}C NMR Data for *arachno*-4-$CB_8H_{12}^{2-}$ with the DFT/GIAO Calculated Values for Structures **I** and **II**

	calcd		
exptl	**Ia**	**I** (averaged)	**II**
		^{11}B	
3.6 (B5,9)	7.6 (B9) −2.7 (B5)	2.4 (B5,9)	39.5 (B7)
−18.9 (B2,3)	−10.1 (B2) −31.7 (B3)	−20.9 (B2,3)	3.6 (B5,9)
−33.2 (B7)	−41.7 (B7)	−41.7 (B7)	−16.4 (B1)
−37.3 (B6,8)	−42.5 (B6) −37.2 (B8)	−39.9 (B6,8)	−24.5 (B2,3)
−50.4 (B1)	−55.4 (B1)	−55.4 (B1)	−45.8 (B6,8)
		^{13}C	
71.3 (C4)	84.5 (C4)	84.5 (C4)	−4.2 (C4)

for *arachno*-4-$CB_8H_{12}^{2-}$. However, good agreement between the calculated and experimental values can be obtained by assuming that in solution the dianion is exhibiting fluxional behavior resulting from the rapid migration of the bridging hydrogen between the B7−B8 and B7−B6 edges of the cluster. As shown in Figure 4a, such a process corresponds to an interconversion between the two enantiomeric forms of structure **I**. If this process occurs rapidly compared to the NMR time scale, then this has the effect of equilibrating three pairs of boron atoms: B2 and B3, B5 and B9, and B6 and B8. As shown in Table 2, averaging the GIAO calculated chemical shift values for the three pairs of borons in the static structure that become equivalent in the fluxional process yields excellent agreement with the experimental ^{11}B spectrum. The calculated assignments of the resonances also are in complete agreement with the connectivities that were determined by $^{11}B-^{11}B$ COSY experiments.

The bridge hydrogen migration between the B7−B6 and B7−B8 edges in *arachno*-4-$CB_8H_{12}^{2-}$ would seem to be most reasonably accomplished in a straightforward manner by a simple process involving a ~60° rotation about the B7−H7 bond axis. Indeed, transition state calculations at the B3LYP/6−311G* level yielded a low-energy pathway with an activation energy of only 2.7 kcal/mol for such a process. As shown in Figure 4b, the expected transition state structure was located in which the bridging hydrogen was rotated into the *endo* position at the BH_2 group at the B7 boron. The *arachno*-4-$CB_8H_{12}^{2-}$ dianion is isoelectronic with, and has a cage framework similar to that of, the *arachno*-$B_9H_{14}^-$ and *arachno*-$B_9H_{13}^{2-}$ anions. Computational studies by Hofman and Schleyer have shown that both of the borane anions favor C_1 symmetry structures in the solid state, but can rearrange through C_s symmetry transition states in solution.[13] The rapid rearrangement between the B6−H−B7 and B7−H−B8 positions in *arachno*-$B_9H_{14}^-$, as in *arachno*-4-$CB_8H_{12}^{2-}$, was found to involve a 60° rotation of a single bridging hydrogen through a transition state structure having an *endo* hydrogen at the B7 boron. The 2.7 kcal/mol barrier for the *arachno*-4-$CB_8H_{12}^{2-}$ rearrangement is comparable to the calculated energy differences between the C_1 (with a B−H−B group) and C_s (with a $-BH_2$ group) symmetry isomers of *arachno*-$B_9H_{14}^-$ (2.3 kcal/mol) and thus provides a value that can be associated with such a rotation step at the 7-boron position of a nine-vertex *arachno* cluster system. These activation energies also appear reasonably consistent with those found for related single-step rotations found in *nido*-7,8-$C_2B_9H_{12}^-$ (1.4 kcal/mol)[14] and B_5H_{11} (1.1 kcal/mol).[15] Naturally, such low barriers preclude the observation of the static structures of these species by the normal low-temperature NMR methods used to study fluxional processes.

Fluxional behavior involving hydrogen migrations over the open face of a polyborane cluster is a well-known phenomenon; however, in most cases the rearrangement mechanisms are more complex than that found for *arachno*-4-$CB_8H_{12}^{2-}$, since they can require the simultaneous movements of several hydrogens (or even cage atoms). In this regard, we have used DFT calculations to reexamine the fluxional process previously observed for two monoanions, *arachno*-4-$CB_8H_{13}^-$ [2] and *arachno*-4-$SB_8H_{11}^-$,[16] that are isoelectronic with *arachno*-4-$CB_8H_{12}^{2-}$.

In agreement with the earlier HF/6-31G* calculations,[2] DFT calculations at the B3LYP/6−311G* level showed that the C_1 symmetry structure **III**, which can exist in the two enantiomeric forms (**IIIa** and **IIIb**) shown in Figure 5, is lowest in energy for *arachno*-4-$CB_8H_{13}^-$. The structure contains two inequivalent B−H−B bridging hydrogens, as well as $-CH_2$ and $-BH_2$ groups, and is thus inconsistent with the experimental ^{11}B NMR spectrum which exhibits only five doublet resonances in 1:2:1:2:2 ratios. However, as presented in Table 3, excellent agreement between the apparent C_s symmetry observed in the experimental ^{11}B NMR spectrum of the anion and the DFT calculated structure **III** can be obtained by simply averaging the calculated ^{11}B NMR chemical shifts of the resonances for those atoms in the

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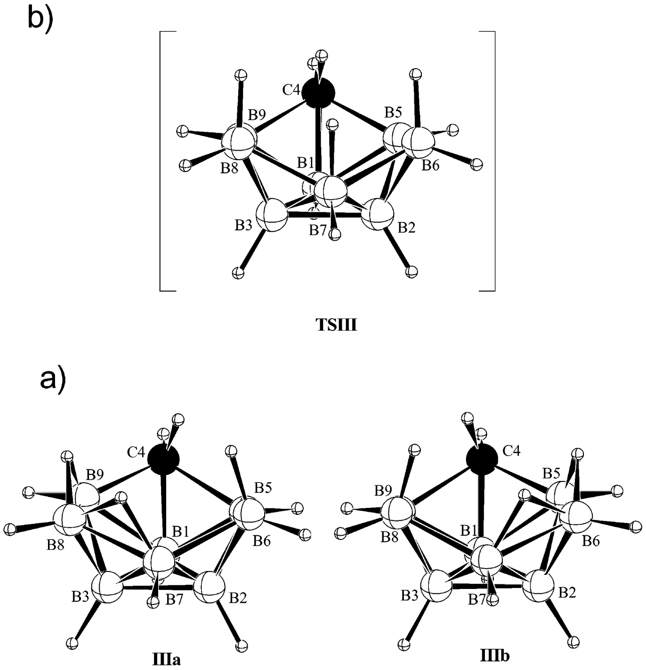

Figure 5. (a) DFT optimized geometries **III** for the enantiomeric structures of *arachno*-4-$CB_8H_{13}^-$ at the B3LYP/6−311G* level. (b) DFT optimized transition state structure **TSIII** for the interconversion of structures **IIIa** and **IIIb**. Energies (ZPE corrected): **III**, −244.7078976 H; **TSIII**, −244.7074894 H.

Table 3. Comparisons of the Experimental ^{11}B NMR Data for *arachno*-4-$CB_8H_{13}^-$ with the DFT/GIAO and HF/IGLO Calculated Values for **III**

	DFT/GIAO		HF/IGLO
exptl[a]	calcd **IIIa**	calcd (averaged)	calcd[a] (averaged)
4.0 (B5,9)	10.1 (B5) −5.7 (B9)	2.2 (B5,9)	2.6 (B5,9)
−3.9 (B7)	−5.0 (B7)	−5.0 (B7)	3.4 (B7)
−21.5 (B1)	−21.8 (B1)	−21.8 (B1)	−17.0 (B1)
−30.4 (B2,3)	−14.3 (B2) −53.7 (B3)	−34.0 (B2,3)	−32.2 (B2,3)
−35.2 (B6,8)	−48.7 (B6) −31.2 (B8)	−39.9 (B6,8)	−35.2 (B6,8)

[a] Reference 2.

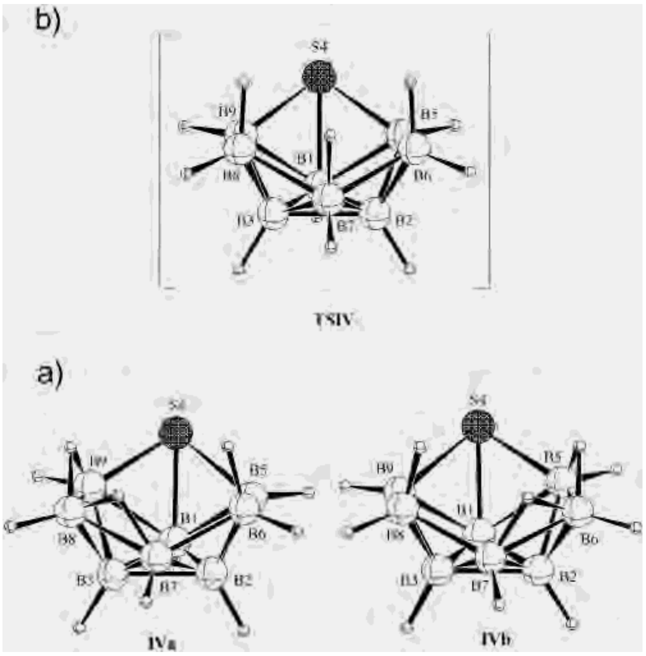

Figure 6. (a) DFT optimized geometries **IV** for the enantiomeric structures of *arachno*-4-$SB_8H_{11}^-$ at the B3LYP/6−311G* level. (b) DFT optimized transition state structure **TSIV** for the interconversion of structures **IVa** and **IVb**. Energies (ZPE corrected): **IV**, −603.6927911 H; **TSIV**, −603.6897947 H.

Table 4. Comparisons of the Experimental ^{11}B NMR Data for *arachno*-4-$SB_8H_{11}^-$ with the DFT/GIAO Calculated Values for **IV**

	DFT/GIAO calcd	
exptl[a]	**IVa**	averaged
3.9 (B5,9)	6.2 (B5) 5.8 (B9)	6.0 (B5,9)
−5.7 (B7)	−6.1 (B7)	−6.1 (B7)
−29.5 (B1)	−28.0 (B1)	−28.0 (B1)
−27.5 (B2,3)	−50.1 (B2) −9.0 (B3)	−29.6 (B2,3)
−38.0 (B6,8)	−33.0 (B6) −51.0 (B8)	−42.0 (B6,8)

[a] Reference 16.

enantiomeric structures that become equivalent by a fluxional process that interconverts the two enantiomers. This fluxional process is more complex than that observed for the *arachno*-4-$CB_8H_{12}^{2-}$ dianion, since it requires the synchronized movement of three hydrogens. Thus, not only must there be a 60° rotation of a bridging hydrogen between the B7−B6 and B7−B8 edges, but there must also be correlated interconversions of two hydrogens between the B8−B9 edge and the B8 −BH_2 group and between the B6−B5 edge and the B6 −BH_2 group, respectively. Although a possible C_s transition state structure was tentatively proposed, no attempts were made in the earlier HF/6−31G* studies to locate the transition state for such a process.[2] However, transition state calculations for this rearrangement at the B3LYP/6−311G* level readily located the transition state structure **TSIII** shown in Figure 4b. As can be seen in this figure, this C_s symmetry structure contains −BH_2 groups at each of the B6, B7, and B8 borons which have been formed by rotations of the bridging hydrogens in the static enantiomeric structures (**IIIa** and **IIIb**) to the *endo* positions of the **TSIII** structure. The activation energy for this process proved to be only 0.3 kcal/mol. It is perhaps surprising that, even though the process is much more complex, the barrier for the *arachno*-4-$CB_8H_{13}^-$ rearrangement is lower than that of the single-step process found in the *arachno*-4-$CB_8H_{12}^{2-}$ dianion. However, it must be recognized that although the two anions are isoelectronic, they have different charges, and this can obviously significantly affect the energetics of the rearrangement pathways.

The *arachno*-4-$SB_8H_{11}^-$ monoanion was first prepared by Base and Wallbridge in 1989 and reported to have a ^{11}B NMR spectrum composed of five doublets in 1:2:1:2:2 ratios (Table 4) apparently supporting a C_s symmetric solution structure. However, our DFT calculations have again shown that a C_1 symmetry structure (**IV**), which can exist in the two enantiomeric forms shown in Figure 6, is lowest in energy. This structure is quite similar to that found for the *arachno*-4-$CB_8H_{13}^-$ having two inequivalent B−H−B bridging hydrogens and a single −BH_2 group. Again, simply averaging the calculated ^{11}B NMR chemical shifts of the resonances for those atoms in the enantiomeric structures (**IVa** and **IVb**) that become equivalent by a fluxional process that interconverts the two enantiomers gives excellent agreement with the experimental ^{11}B NMR data. This fluxional process must be similar to that found for the *arachno*-4-$CB_8H_{13}^-$ anion, since it can again be accomplished by the synchronized movement of three hydrogens between the B7−B6 and B7−B8 edges, the B8−B9 edge and the B8 −BH_2 group, and the B6−B5 edge and the B6 −BH_2 group, respectively. Indeed, transition state calculations readily located the C_s symmetry transition state structure **TSIV** shown in Figure 5b, which is quite similar to that found for **TSIII**. Thus, like **TSIII**, the **TSIV** structure contains −BH_2 groups at each of the B6, B7, and B8 borons as a result of the rotation of the bridging hydrogens in the static enantiomeric structures (**IVa** and **IVb**) to the *endo* positions of the **TSIV** structure. However, the activation energy for this process proved to be higher (5.0 kcal/mol) than that for the analogous process in *arachno*-4-$CB_8H_{13}^-$.

In summary, the common mechanistic steps and low activation energies (0.3−5.0 kcal/mol) found for the fluxional processes reported herein for *arachno*-4-$CB_8H_{12}^{2-}$, *arachno*-4-$CB_8H_{13}^-$, and *arachno*-4-$SB_8H_{11}^-$, as well as in the earlier studies[13] of the *arachno*-$B_9H_{14}^-$ and *arachno*-$B_9H_{13}^{2-}$ anions, appear to provide a consistent picture of the rearrangement mechanisms and energetics of nine-vertex polyborane anions. These results should now aid in the determination of common features involved in the fluxional processes in other cluster classes.

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Supporting Information Available: Tables listing Cartesian coordinates and bond distances for the DFT optimized geometries of structures **Ia**, **II**, **IIIa**, and **IVa** and Cartesian coordinates for the transition states **TSI**, **TSIII**, and **TSIV**. This material is available free of charge via the Internet at http://pubs.acs.org.

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