An ab Initio/IGLO/NMR Study[1] of *closo*-$C_2B_6H_8$, *closo*-$CB_7H_8^-$, *closo*-$B_8H_8^{2-}$, and $C_3B_5H_7$

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The closo electron count compounds $C_2B_6H_8$, $B_8H_8^{2-}$, $CB_7H_8^-$, and $C_3B_5H_7$ have been studied using the combined ab initio/IGLO/NMR method. $C_2B_6H_8$ and the "high-temperature" isomer of $B_8H_8^{2-}$ have been reconfirmed as having the same bisdisphenoidal structures in the fluid phase as in the crystalline phase. The structure of the second "low-temperature" isomer of $B_8H_8^{2-}$ in solution remains unresolved. The carborane $CB_7H_8^-$ is also shown to have a fluxional closo geometry in solution. The carborane $C_3B_5H_7$ probably does not have the closo geometry in solution as has been suggested.

Introduction

The first *closo*-carboranes were reported[2] in the period 1959–1962. They were 1,5-$C_2B_3H_5$ (**1**), the 1,2- and 1,6-isomers of $C_2B_4H_6$ (**2** and **3**) and 2,4-$C_2B_5H_7$ (**4**)[3] (see Figure 1). From the structures of these four compounds three structural patterns were recognized: (a) the structures appeared to have shapes resembling the most spherical deltahedra (which results in the most uniformly connected vertices[4]); (b) the skeletal carbons tended to occupy the lowest connected vertices when options were available; (c) the skeletal carbons were separated from each other in the most stable configurations (e.g., the less stable 1,2-$C_2B_4H_6$ (**2**) was assumed to have rearranged into the more stable 1,6-$C_2B_4H_6$ (**3**) during synthesis, and this assumption was confirmed in 1963[3]).

The three patterns made it easy to anticipate the correct structure for the "one-boron-larger" *closo*-carborane, $C_2B_6H_8$. A specific dodecahedron[4] (a bisdisphenoid of D_{2d} symmetry) was (a) the most spherical, (b) had carbons in the lowest coordinated positions, and (c) had locations for separated carbons (structure **5** in Figure 2). A small amount of the dimethyl derivative of *closo*-$C_2B_6H_8$ was prepared[5a] for structural determination by Williams and Gerhart in 1965 by heating *nido*-hexaborane, B_6H_{10}, and dimethylacetylene. The ^{11}B NMR spectrum for a static bisdisphenoidal structure (**5** in Figure 2) should have contained three resonances reflecting three sets of two borons apiece (2:2:2), but instead the ^{11}B spectrum at 12.8 MHz revealed one set of four borons and one set of two borons (4:2) even at substantially reduced temperatures.[5a,b]

It was obvious that the observed spectrum for the dimethyl derivative of $C_2B_6H_8$ could be interpreted in one of the following ways: (a) the anticipated geometry **5** was correct but there was an accidental overlap of two resonances, (b) the anticipated geometry **5** was correct but fluxional behavior allowed two sets of two borons to become equivalent in the NMR spectrum, (c) the correct solution phase structure had one square open face (**6**), or (d) the structure had an Archimedean antiprism geometry (**7**). Williams and Gerhart[5a] relied upon the empirical patterns derived from the known carboranes (vide infra[3]) and concluded that the ^{11}B NMR spectrum resulted from either a coincidental overlap or fluxional behavior and selected **5** as the correct geometry for the dimethyl derivative of $C_2B_6H_8$.

A subsequent ^{11}B NMR study[6] in 1966 on $(CH_3)_2C_2B_6H_6$ confirmed the same 4:2 ratio in the 19.3 MHz ^{11}B NMR spectrum. These authors, however, favored the Archimedean antiprism geometry (**7** in Figure 2) rather than structure **5** although they suggested further NMR studies at higher fields to resolve the possible ambiguity.

In 1966, Lipscomb[7] proposed a general mechanism (termed the "diamond–square–diamond" mechanism or DSD) for the isomerization of deltahedral structures. A dynamic system fluctuating between two or all three of the aforementioned structures (**5**, **6**, and **7**) was considered possible, but unlikely, since other *closo*-carborane rearrangements had required higher temperatures. In 1967 Lipscomb and Hart[8] carried out a low temperature (−50 °C) single-crystal X-ray diffraction study[7] on $(CH_3)_2C_2B_6H_6$. The structure was shown to have the bisdisphenoid geometry **5** with the skeletal carbons in nonadjacent, low-coordination positions as predicted by Williams and Gerhart;[5a] the structure in solution was assumed to be the same.

At about the same time as the Hart and Lipscomb X-ray study[8] on 1,7-$(CH_3)_2C_2B_6H_6$, Muetterties et al. synthesized[9] the eight-vertex polyborane *closo*-$B_8H_8^{2-}$ (isoelectronic and arguably isostructural with $C_2B_6H_8$) and obtained a single crystal of the $Zn(NH_3)_4^{2+}$ salt. An X-ray study[10] showed the $B_8H_8^{2-}$ salt also had the bisdisphenoidal geometry **8** (Figure 3). The ^{11}B NMR spectrum of the cesium salt of $B_8H_8^{2-}$ in water consisted of a single resonance. A static bisdisphenoid structure like that found in the solid state (**8**) should possess two resonances of equal intensity. Although a static Archimedean antiprism structure **9** along with a dynamic system fluctuating between **8** and **9** was considered to explain the observed spectrum, the result was still assumed to be due to coincidental chemical shifts.[9]

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(1) (a) All of this material, with the exception of *closo*-$CB_7H_8^-$ and $C_3B_5H_7$, was presented at the BUSA-II Meeting at Research Triangle, NC, June, 1990, by J. W. Bausch, G. K. S. Prakash, and R. E. Williams. (b) See also reference 83 on p 91 of *Electron Deficient Boron and Carbon Clusters*, Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, 1991.

(2) (a) Williams, R. E.; Good, C. D.; Shapiro, I. *Abstracts of Papers*; 140th National Meeting of the American Chemical Society, 1961; American Chemical Society: Washington, DC, 1961; Abstr. 14N, p 36. (b) Good, C. D.; Williams, R. E. U.S. Patent 3030289, 1959; *Chem. Abstr.* **1962**, *57*, 12534b.

(3) Onak, T. P.; Gerhart, F. J.; Williams, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 3378.

(4) Deltahedra are polyhedra with triangular facets only. Three of the common deltahedral dodecahedra are the hexagonal bipyramid (flatest with six 4*k* and two 6*k* vertices), the bicapped trigonal prism (longest with two 3*k* and six 5*k* vertices), and the bisdisphenoid (most spherical with four 4*k* and four 5*k* vertices).

(5) (a) Williams, R. E.; Gerhart, F. J. *J. Am. Chem. Soc.* **1965**, *87*, 3513. (b) Muetterties, E. L.; Hoel, E. L.; Salentine, C. G.; Hawthorne, M. F. *Inorg. Chem.* **1975**, *14*, 950.

(6) Tebbe, F. N.; Garrett, P. M.; Young, D. C.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1966**, *88*, 609.

(7) Lipscomb, W. N. *Science* **1966**, *153*, 373.

(8) (a) Hart, H.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1967**, *89*, 4220. (b) Hart, H.; Lipscomb, W. N. *Inorg. Chem.* **1968**, *7*, 1070.

(9) Klanberg, F.; Eaton, D. R.; Guggenberger, L. J.; Muetterties, E. L. *Inorg. Chem.* **1967**, *6*, 1271.

(10) Guggenberger, L. J. *Inorg. Chem.* **1969**, *8*, 2771.

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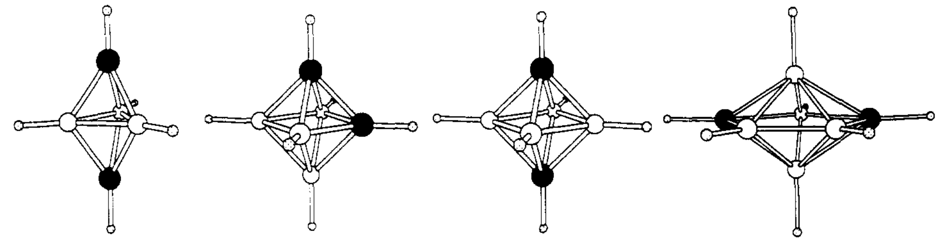
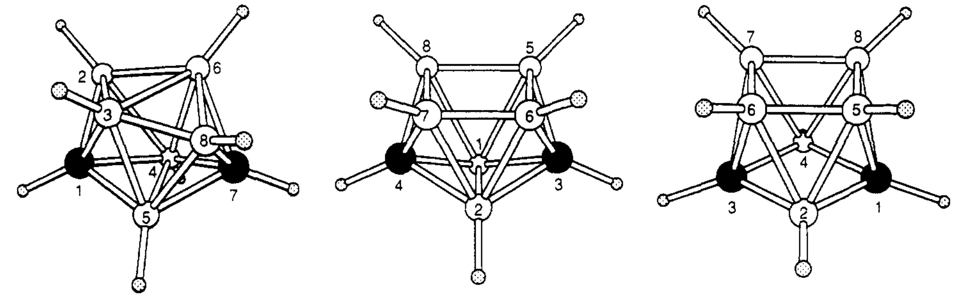


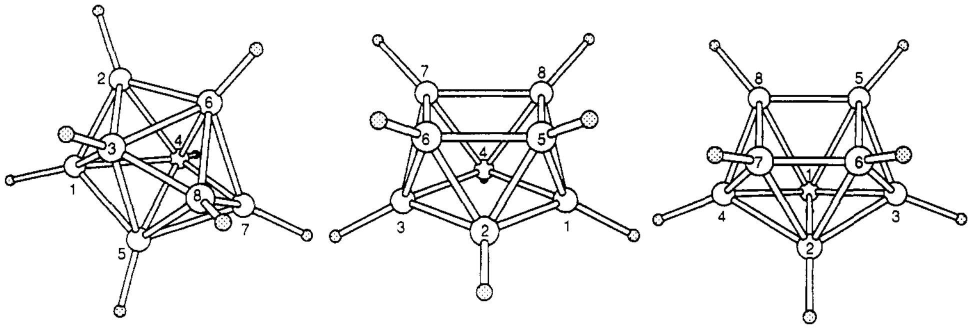
1 2 3 4

Figure 1. The first small *closo*-carboranes discovered: 1,5-$C_2B_3H_5$ (**1**), 1,2-$C_2B_4H_6$ (**2**), 1,6-$C_2B_4H_6$ (**3**), and 2,4-$C_2B_5H_7$ (**4**).



5 6 7

Figure 2. Various geometries considered for $C_2B_6H_8$: bisdisphenoid **5**, square open-face **6**, and square antiprism **7**.



8 9 10

Figure 3. Various geometries proposed for $B_8H_8^{2-}$: bisdisphenoid **8**, square antiprism **9**, and square open-face **10**.

In 1973, Muetterties, Wiersama, and Hawthorne reported[11] an NMR study of the behavior of $B_8H_8^{2-}$ as a function of solvent, cation, and temperature. From a temperature-dependent ^{11}B NMR study, they found that $Na_2B_8H_8{\cdot}xH_2O$ in 1,2-dimethoxyethane contains two isomers in rapid equilibrium with each other. At low temperatures an isomer containing three ^{11}B resonances in a 2:4:2 ratio was found, while at higher temperatures another isomer with one ^{11}B resonance was preferred. The "high-temperature" isomer had the same single resonance as the $Cs_2B_8H_8$ salt in water. Muetterties et al.[11] interpreted these results as indications of an equilibrium between the D_{4d} symmetry isomer **9** and the C_{2v} symmetry isomer **10** (see Figure 3), both of which differed from the solid-state D_{2d} symmetry isomer **8**. They speculated that specific cation–anion or solvent–anion interactions potentially stabilized the square open faces of **9** and **10** in solution.

In 1979, Lipscomb and Kleier reported molecular orbital calculations[12a] on $B_8H_8^{2-}$ using PRDDO theory[13] in order to study its fluxional behavior. The D_{2d} form **8** was found to be the most stable isomer with a symmetry-allowed low-energy path (<4 kcal/mol) for rearrangement (via the DSD mechanism) into the C_{2v} form **10**. No computational evidence was found for a stable D_{4d} form **9**. Lipscomb and Kleier interpreted the single resonance ^{11}B NMR spectra of $Na_2B_8H_8{\cdot}xH_2O$ in dimethoxyethane and $Cs_2B_8H_8$ in water as arising from a fluxional D_{2d} structure **8** that permuted the two different boron environments using the C_{2v} geometry **10** as the "transitional structure".[12b] They suggested various ion-pairing phenomena to explain the "low-temperature" ^{11}B NMR spectrum of $Na_2B_8H_8$ in 1,2-dimethoxyethane, but admitted further experimental work was still needed.

The probable existence of at least two isomeric structures for *closo*-$B_8H_8^{2-}$ resurrected the remote possibility that *closo*-$(CH_3)_2C_2B_6H_6$ might have a different structure in solution than in the crystal.

Various other computational studies support the proposed fluxionality for $B_8H_8^{2-}$ and isomers of $C_2B_6H_8$. Stone's tensor harmonic theory (TSH) supports[14] a degenerate rearrangement for the D_{2d} structure for $B_8H_8^{2-}$ passing through a slightly distorted C_{2v} structure **10**. Using ab initio theory, Gimarc and Ott studied the isomerization of $C_2B_6H_8$ isomers,[15] and they appear to follow the DSD pathway(s).

In 1971, a carborane of formula $C_3B_5H_7$ (presumed to be

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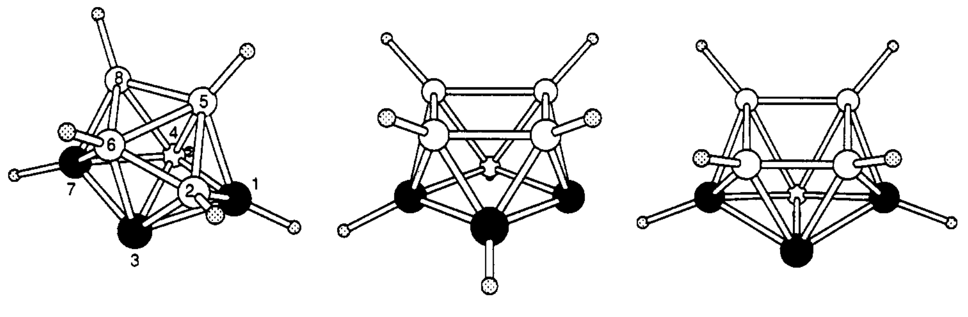
[11] Muetterties, E. L.; Wiersama, R. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 7521.

[12] (a) Kleier, D. A.; Lipscomb, W. N. *Inorg. Chem.* **1979**, *18*, 1312. (b) By "transitional structure" Lipscomb et al. imply either an intermediate or a transition state.

[13] Halgren, T. A.; Lipscomb, W. N. *J. Chem. Phys.* **1973**, *58*, 1569.

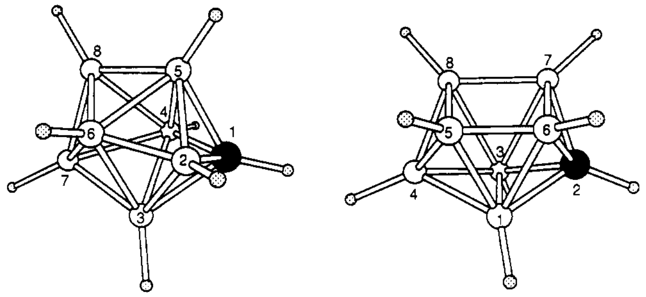
[14] Wales, D. J.; Stone, A. J. *Inorg. Chem.* **1987**, *109*, 1388.

[15] Gimarc, B. M.; Ott, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 1388. Interestingly, they show the 1,2-isomer of $C_2B_6H_8$ to be metastable relative to the experimentally known 1,7-isomer and predict its preparation and isolation should be feasible. In Williams and Gerhart's paper[5] describing the preparation of $(CH_3)_2C_2B_6H_6$, they found in trace amounts another molecule of the same mass and suggested it may be the 1,2-isomer.



11 12 13

Figure 4. Various structures for $C_3B_5H_7$: bisdisphenoid **11**, square antiprism **12**, and square open-face **13**.



14 15

Figure 5. Structures considered for $CB_7H_8^{1-}$: bisdisphenoid **14** and square open-face **15**.

isoelectronic and isostructural with $B_8H_8^{2-}$ and $C_2B_6H_8$) was reported in a communication.[16] The 32.2 MHz ^{11}B NMR spectrum contained three resonances in a ratio of 2:2:1. Along with the ^1H NMR spectrum and IR data, the structure was interpreted as having a fluxional bisdisphenoidal geometry (**11**; see Figure 4) passing through a square antiprism intermediate structure (**12**) to explain the ^{11}B NMR spectrum. In contrast, a static bisdisphenoidal structure **11** would possess five resonances (assuming no overlap). There has been no subsequent work reported on this intriguing molecule which has been proposed to possess a "bare" carbon atom in the polyhedral framework.

Recently, another eight-vertex *closo*-carborane was synthesized,[17] 1-$CB_7H_8^-$. The ^{11}B NMR spectrum of the Me_4N^+ salt in acetone consisted of two resonances in a 4:3 ratio, and a fluxional bisdisphenoid structure (**14**; see Figure 5) was proposed. A static bisdisphenoid structure **14** of C_s symmetry would possess four resonances in a 2:2:1:1:1 ratio. Thus, it appeared likely that $CB_7H_8^-$ is fluxional in solution.

We decided to investigate these four eight-vertex systems computationally using the combined ab initio/IGLO[18]/NMR procedure,[19a] a relatively new method of structural determination and assessment that the Schleyer group has achieved considerable success in refining the structures for many compounds including boranes and borane anions,[19b,c] carboranes,[19c] and *closo*-heteroboranes.[20] To sum up this procedure, the geometries of all "potentially correct" structures for a molecule are calculated using ab initio theory and then each of these geometries are used as input for an IGLO/NMR chemical shift calculation. The structure for which the theoretical IGLO calculated NMR chemical shifts accurately correlates with the experimental NMR values is deemed the best representation for the molecule in solution. The theoretical and experimental values are strikingly precise for the correct structures while incorrect structures generate gross mismatches between the calculated and experimental values.

Table I. Calculated Energies of Eight-Vertex Systems ($B_8H_8^{2-}$, $C_2B_6H_8$, $CB_7H_8^-$, and $C_3B_5H_7$)

structure	level	energy[a]
	$B_8H_8^{2-}$	
8 (D_{2d})	HF/3-21G	−126039.6 (0)
	HF/6-31G*	−126755.0 (0)
9 (D_{4d})	HF/3-21G	−126003.8 (2)
	HF/6-31G*	−126730.9 (2)
10 (C_{2v})	HF/3-21G	−126037.3 (0)
	HF/6-31G*	−126752.2 (0)
	$C_2B_6H_8$	
5 (C_2)	HF/3-21G	−142568.8 (0)
	HF/6-31G*	−143386.6 (0)
6 (C_{2v})	HF/3-21G	−142567.7 (0)
	HF/6-31G*	−143384.6 (1)
7 (C_{2v})	HF/3-21G	−142371.1 (2)
	$CB_7H_8^-$	
14 (C_s)	HF/3-21G	−134361.2 (0)
	HF/6-31G*	−135127.6 (0)
15 (C_s)	HF/3-21G	−134359.5 (0)
	HF/6-31G*	−135124.7 (0)
	$C_3B_5H_7$	
11 (C_1)	HF/3-21G	−150341.7 (0)
	HF/6-31G*	−151207.7 (0)

[a] In kcal/mol with the number of imaginary frequencies in parentheses.

Methods

The geometries were fully optimized within symmetry constraints employing the GAUSSIAN86 program[21] (using the standard basis sets included) on an Alliant FX/40 computer. The ^{11}B chemical shifts were calculated using the IGLO program[18a] employing a double-ζ (DZ) basis set of Huzinaga.[22] Gaussian lobes contracted as follows:[18b] C and B, 7s3p (4111, 21); H, 3s (21). B_2H_6 is the primary reference and the δ values were converted to the $BF_3{\cdot}OEt_2$ scale using the experimental value of $\delta(B_2H_6)$ = 16.6 ppm.[23]

Results and Discussion

***closo*-$B_8H_8^{2-}$.** In 1989 we decided[1] to investigate $B_8H_8^{2-}$ due to the high degree of symmetry which results in lessened

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(17) Plesek, J.; Jelinek, T.; Stibr, B.; Hermanek, S. *J. Chem. Soc., Chem. Commun.* **1988**, 348.

(18) (a) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. (b) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919. (c) Review: Kutzelnigg, W.; Fleisher, U.; Schindler, M. *NMR, Basic Principles and Progress*; Springer Verlag: Berlin, 1991; p 165.

(19) (a) The combined ab initio/IGLO/NMR method was first used by Schleyer et al. See ref 19b and references therein. (b) Schleyer, P. v. R.; Buhl, M. In *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley-Interscience: New York, 1991; Chapter 4, p 113. (c) Buhl, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 477.

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Table II. IGLO-Calculated ^{11}B NMR Chemical Shifts[a] of Eight-Vertex Systems $B_8H_8^{2-}$, $C_2B_6H_8$, $CB_7H_8^-$, and $C_3B_5H_7$

structure	level	B1,2,7,8	B3,4,5,6	ϕ
8 (D_{2d})	DZ//3-21G	−0.1	−9.7	−4.9
	DZ//6-31G*	−1.5	−11.7	−6.6
	expt[b]			−6.8

structure	level	B1–8
9 (D_{4d})	DZ//3-21G	6.0
	DZ//6-31G*	5.0
	expt[b]	−6.8

structure	level	B1,2	B3,4	B5,6,7,8
10 (C_{2v})	DZ//3-21G	−13.6	7.7	13.3
	DZ//6-31G*	−14.3	8.3	11.0
	expt[b]	−22.2	9.5	−3.6

$C_2B_6H_8$

		B2,8	B3,6	B4,5	ϕ(B2,8,3,6)
5 (C_2)	DZ//3-21G	24.1	−5.0	−2.8	9.6
	DZ//6-31G*	22.7	−6.3	−6.4	8.2
	expt[c]			−8.8	7.7

		B1,2	B5,6,7,8
6 (C_{2v})	DZ//3-21G	−8.9	19.9
	DZ//6-31G*	−11.1	18.7
	expt[c]	−8.8	7.7

$CB_7H_8^-$

structure	level	B2	B3,5	B4	B6	B7,8	ϕ-(B2,3,4,5)	ϕ-(B6,7,8)
14 (C_s)	DZ//3-21G	14.2	−8.8	1.3	−5.4	9.5	−0.5	4.5
	DZ//6-31G*	12.7	−11.7	−0.8	−6.5	8.2	−2.9	3.3
	expt[d]						−4.4	3.1

structure	level	B1,3	B6,7	B4	B5,8	ϕ(B1,3,6,7)	ϕ(B4,5,8)
15 (C_s)	DZ//3-21G	−10.9	22.2	6.5	13.3	5.7	11.0
	DZ//6-31G*	−10.3	17.9	0.8	12.6	3.8	8.7
	expt[d]					−4.4	3.1

$C_3B_5H_7$

structure	level	B2	B5	B6	B8	B4	ϕ(B2,6)	ϕ(B5,8)
11 (C_1)	DZ//3-21G	26.6	6.2	−8.5	27.8	11.6	9.1	17.0
	DZ//6-31G*	22.7	4.9	−9.0	33.4	−1.1	6.8	19.1
	expt[e]					3.5	7.0	−17.1

[a] In ppm versus $BF_3{\cdot}OEt_2$ (0.0 ppm). [b] Reference 11. [c] Personal communication from Prof. T. P. Onak. [d] Reference 17. [e] Reference 16.

computational time and space requirements. The three structures considered (Figure 3) were the D_{2d} symmetry bisdisphenoid **8**, the D_{4d} symmetry square antiprism **9**, and the four-membered open-face C_{2v} symmetry structure **10**. Each of these geometries were optimized using ab initio technique[20] at the HF/6-31G* level of theory. The D_{2d} isomer **8** was calculated to be 2.9 kcal/mol more stable than the C_{2v} isomer **10** and 24.2 kcal/mol more stable than the D_{4d} structure **9** (see Table I), which is in agreement with the previously reported PRDDO method[13] and MNDO calculated[24] order of stability for the $B_8H_8^{2-}$ isomers. A frequency calculation at the same level of theory revealed that isomers **8** and **10** are true minima on the potential energy surface (i.e., possess zero imaginary frequencies). However, the square antiprism **9** is a higher order stationary point as it possesses two imaginary frequencies.

IGLO ^{11}B NMR shift calculations at the double-ζ level using the HF/6-31G* optimized geometries (DZ//6-31G*) were carried out on isomers **8** and **10** as well as the energetically unfavorable isomer **9**. The square antiprism structure **9**, with eight equivalent boron atoms, gave an IGLO-calculated ^{11}B NMR shift of δ 5.0, which is in poor agreement with the experimental "high-temperature" isomer value of δ −6.8 (see Table II). The D_{2d} isomer **8**, which possesses two different boron environments, gave calculated values of δ −11.6 and −1.5. If fluxionality is assumed (via a single DSD mechanism), the two types of boron environments in isomer **8** can be permuted to yield an average calculated shift of δ −6.6, which is in excellent agreement with the experimental value of δ −6.8 for the "high-temperature" isomer. The intermediate for the fluxional D_{2d} isomer **8** would be the C_{2v} isomer **10**, which is only ~3 kcal/mol less stable.

A dilemma became apparent. The C_{2v} isomer **10** (Figure 3) had been considered[11] responsible for the experimental "low-temperature" (2:4:2 ratio) ^{11}B NMR spectrum. While the C_{2v} isomer **10** could, in principal, give rise to the experimentally observed 2:4:2 spectrum, it could not be both the static observable independent species and at the same time the fluxional intermediate which makes all of the borons NMR equivalent in the D_{2d} isomer **8**. At intermediate temperatures in low polarity solvents, the "high-temperature" isomer exists as separate noninterchanging species on the NMR time scale. If the C_{2v} isomer **10** is the intermediate that allows all the borons in the D_{2d} isomer **8** to become equivalent, then it cannot also be the low-temperature isomer as well (unless some kind of solvent and/or ion-pairing equilibria is occurring).

Support for this comes from the IGLO-calculated ^{11}B NMR chemical shift values for the C_{2v} isomer **10** (see Table II) which are δ −14.3, 8.3, and 11.0 (in a 2:2:4 ratio) to be compared with the experimental values of δ −22.2, 9.5, and −3.6, respectively. The correlation between the calculated and experimental values is poor. We conclude that the "low-temperature" isomer of $B_8H_8^{2-}$ does not have the C_{2v} structure **10**. Neither isomer **8** or **9** could give rise to the 2:4:2 ratio spectrum observed.

***closo*-$C_2B_6H_8$.** Having shown that the predominant structure in both the solid state and in solution for *closo*-$B_8H_8^{2-}$ was isomer **8** and that it was fluxional probably using the slightly less stable isomer **10** as the intermediate suggested that a similar intermediate might be involved in the assumed to be fluxional structure of *closo*-$C_2B_6H_8$. Extrapolating from the energy calculations of the $B_8H_8^{2-}$ isomers, we assumed that the bisdisphenoidal isomer **5** of C_2 symmetry would probably be the most stable geometry and that the four-membered open-face C_{2v} symmetry isomer **6** would be the next most stable geometry for the fluid-phase structure of the *closo*-carborane $C_2B_6H_8$. As a check for the unsuitability of the square antiprism geometry **7**, we carried out an HF/3-21G geometry optimization which showed it to be ~200 kcal/mol higher in energy than **5** or **6** as well as a higher order stationary point (possessing two imaginary frequencies).

At the HF/6-31G* level of ab initio theory, isomer **5** of C_2 symmetry is only 1.93 kcal/mol more stable than isomer **6** of C_{2v} symmetry (Table I). Frequency analyses at the same level showed both **5** and **6** to be true minima on the potential energy surface.

IGLO-calculated ^{11}B NMR chemical shifts (DZ//6-31G*) for the C_{2v} isomer **6** yielded values of δ −11.1 and 18.7 for the borons in a 2:4 ratio, to be compared with the experimental values for the parent $C_2B_6H_8$ of δ −8.8 and 7.7. The correlation between theory and experiment is unacceptable (Table II).

The IGLO-calculated ^{11}B NMR chemical shift values (DZ//6-31G*) for the C_2 isomer **5** (with three types of boron environments in a 2:2:2 ratio) are δ −6.4, −6.3, and 22.7. If **5** is assumed to be fluxional, such that two sets of boron environments coalesce (δ −6.3 and 22.7 average to δ 8.2), then the calculated values become δ −6.4 and 8.2 (in a 2:4 ratio) which correlate quite well with the experimental values of δ −8.8 and 7.7. The mechanism for this fluxionality that permutes two sets of boron environments in **5** most likely is a single DSD rearrangement where the "transitional structure" is the C_{2v} isomer **6** (see Figure 6). Thus, there is one and only one "connection" in **5** (between the borons labeled "b") that is "broken" to give **6**, that "re-forms" between adjacent borons (labeled "a") that regenerates **5** and thus permutes two sets of borons.

***closo*-$CB_7H_8^-$.** The two structures considered in our calculations for the $CB_7H_8^-$ anion are the bisdisphenoid **14** of C_s symmetry and the four-membered open-face structure **15**, also of C_s

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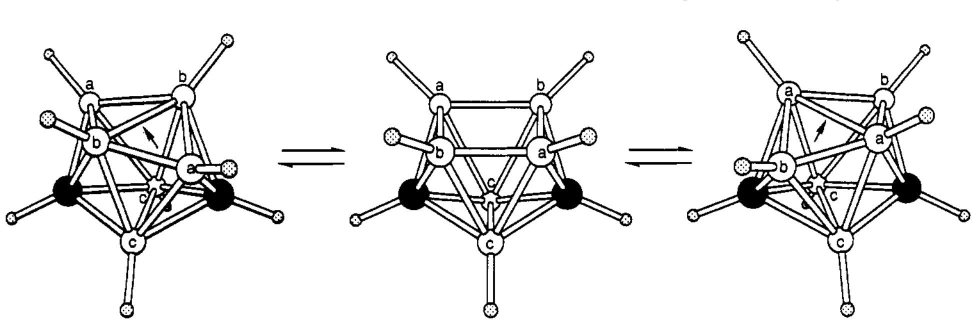
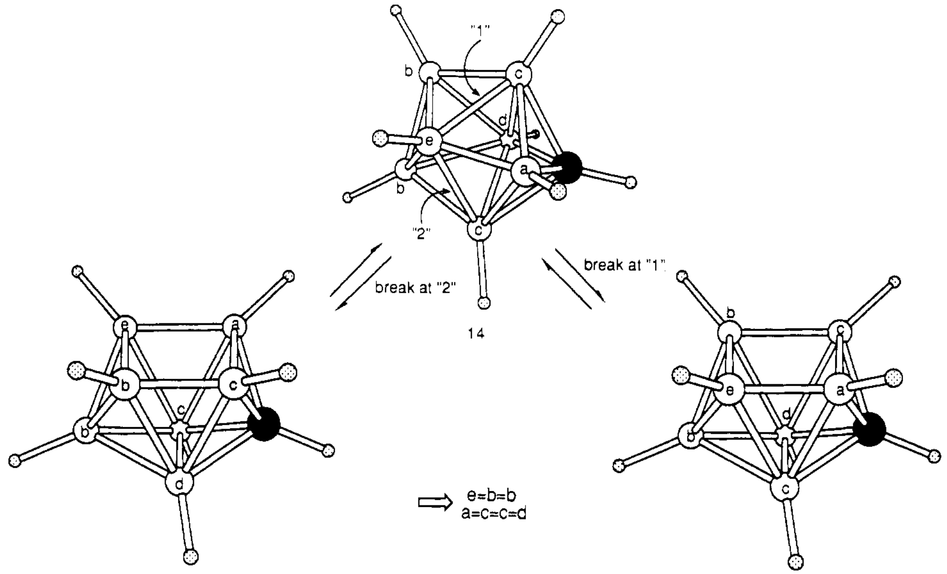


5   6   5

Figure 6. Single DSD degenerate rearrangement of 1,7-$C_2B_6H_8$ bisdisphenoid **5** that makes equivalent borons a and b via the square open-face geometry **6**.



14   15   15

Figure 7. DSD rearrangements of *closo*-$CB_7H_8^-$ (**14**) that makes equivalent borons e, b, and b and borons a, c, c, and d via the nido square open-face geometry **15**. This would account for the observed 3:4 ratio in the experimental ^{11}B NMR spectrum.

symmetry (see Figure 5). We were able to locate minima for both **14** and **15** using ab initio theory (HF/6-31G*). Isomer **14** is only 2.87 kcal/mol more stable than **15** (Table I). Frequency analyses at the same level of theory showed both structures to be true minima on the potential energy surface.

IGLO-calculated ^{11}B NMR chemical shifts (DZ//6-31G*) for the bisdisphenoid **14** are δ −11.7, −6.5, −0.8, 8.2, and 12.7 in a 2:1:1:1:2 ratio (Table II). Isomer **15** gave calculated ^{11}B NMR chemical shifts of δ −10.4, 0.8, 12.6, and 17.9 in a 2:1:2:2 ratio. The experimental ^{11}B NMR values[17] for $CB_7H_8^-$ are δ −4.4 and 3.1 in a 4:3 ratio. A fluxional $CB_7H_8^-$ seemed likely, and the likely mechanism to account for the 4:3 ratio ^{11}B NMR spectrum is almost identical to those encountered in the closely related *closo*-$B_8H_8^{2-}$ and *closo*-$C_2B_6H_8$ systems and is illustrated in Figure 7. A single DSD mechanism in **14** (at either connection "1" or "2") yields degenerate isomers **15** and makes equivalent the borons labeled a, c, and d and those labeled b and e giving the 4:3 ratio observed experimentally.

Averaging the calculated ^{11}B shifts obtained for **14**, as outlined in Figure 7 (B2, B3/B5 and B4, are borons a, c, and d and B7/B8 and B6 are borons b and e, respectively), gave values of δ −2.9 and 3.3, to be compared with the experimental values of δ −4.4 and 3.1. The correlation between theory and experiment is excellent. Thus, **15** is the intermediate in the degenerate rearrangement of **14** via a single DSD mechanism.

It is possible to consider, although the energy calculations suggest otherwise, that **14** might be the intermediate for a fluxional **15**, which also would generate the desired 4:3 ratio of boron environments as seen experimentally. Averaging the calculated ^{11}B NMR chemical shifts for **15** in this manner yields values of δ 3.8 (average of B1/B3 and B6/B7) and δ 8.7 (average of B5/B8 and B4), to be compared with the experimental values of δ −4.4 and 3.1, respectively. The correlation between theory and experiment when **15** is assumed to be the structure of $CB_7H_8^-$ in solution is unacceptable.

***closo*-$C_3B_5H_7$.** On the basis of the results discussed so far, it seemed likely that the solution structure for $C_3B_5H_7$ would be a bisdisphenoid **11** that is fluxional with the "transitional structure" (via a single DSD rearrangement) being the square open-face geometry **13**.

We employed as the starting geometry for the calculation of a bisdisphenoidal structure of $C_3B_5H_7$ (**11**, C_1 symmetry in Figure 4) the HF/6-31G*-optimized bisdisphenoid $C_2B_6H_8$ (**5**) where the appropriate B-H unit was replaced with a "bare" C unit. We located a structure corresponding to **11** at HF/6-31G* level of theory, and a frequency calculation at the same level showed it to be a true minimum. Employing the HF/6-31G*-optimized geometry of square open-face $C_2B_6H_8$ (**6**) as input geometry with the appropriate B–H replaced by a C, we have not been able to locate a minimum for a structure corresponding to the C_s symmetry square open-face geometry **13**.

It still seemed plausible that **11** is fluxional via a DSD process involving borons 2, 5, 6, and 8 but that the "transitional structure" is a distorted square open face (similar to **13**) that we were not able to locate on the potential surface. The end result would still be permuting borons 2 and 6 and borons 5 and 8. When the IGLO-calculated (DZ//6-31G*) ^{11}B chemical shifts for **11** are averaged in this manner (see Table II), the theoretical and experimental values correlate poorly. The IGLO values are δ 19.1, 6.8, and -1.1, to be compared with the experimental values of δ -17.1, 7.0, and 3.5, respectively. We conclude the structure of $C_3B_5H_7$ is not the closo structure **11** as proposed.[16]

Conclusion

We have employed the ab initio/IGLO/NMR method[19a] to investigate the experimentally known closo electron count eight-vertex polyborane and carborane systems. The structure of the *closo*-carborane 1,7-$C_2B_6H_8$ has been reconfirmed as having the same closo structure **5** (Figure 6) in solution as in the solid state as evidenced by good correlation between the calculated and experimental ^{11}B NMR chemical shifts. It appears that **5** is fluxional and that four borons become NMR equivalent by passing through the square open-face intermediate **6** (via a single DSD rearrangement).

The carborane $CB_7H_8^-$ has also been shown to be a fluxional closo structure in solution (**14**, see Figure 7) as evidenced by good correlation between the calculated and experimental ^{11}B NMR chemical shifts. Structure **14** probably passes through the square open-face intermediate **15** (via two degenerate DSD rearrangements). No crystal structure or computational studies have been reported on this recently synthesized[17] monocarbon cluster system.

The $B_8H_8^{2-}$ system, however, has only been partially resolved. The ab initio/IGLO/NMR procedure supports the previous computational studies[12] that the "high-temperature" structure in solution is the closo bisdisphenoid **8** (see Figure 3) that passes through the square open-face intermediate **10** which allows all eight borons to become NMR equivalent. The "low-temperature" solution phase structure remains unknown although it is clear that a static square open-face structure **10** is not correct for two reasons: (1) the IGLO-calculated ^{11}B chemical shifts do not correlate with the experimental values, and (2) this structure is apparently the intermediate in the degenerate rearrangement of **8**. We are currently considering several other structural options in attempts to explain the "low-temperature" $B_8H_8^{2-}$ spectra.[26]

The "bare carbon" containing cluster $C_3B_5H_7$ does not appear to be the fluxional closo structure **11** proposed by Grimes et al. as the averaged IGLO calculated ^{11}B chemical shifts correlate poorly with the experimental values. We are currently investigating **11** at even higher levels of ab initio and IGLO theory to confirm (or refute) the results we obtained at the DZ//6-31G* level. There are a number of "static" structural candidates and others requiring fluxionality that could account for the observed spectra and these will be reported in the future. Ab initio/IGLO/NMR calculations[25] on closo-2,3(-CH_2-)2,3-$C_2B_5H_5$ only marginally agree with the experimental data for $C_3B_5H_7$. An experimental reinvestigation of $C_3B_5H_7$ appears warranted as modern NMR methods (i.e., ^{13}C and various 2D techniques) would certainly help in determining the correct structure.

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