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An ab Initio/IGLO/NMR Study of the *nido*-Carborane $C_2B_6H_{10}$[†,1]

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The structure of the eight-vertex *nido*-carborane $C_2B_6H_{10}$ has been investigated by employing the ab initio/IGLO/NMR method. The experimental ^{11}B NMR chemical shifts for $C_2B_6H_{10}$ are compatible with three different structures (one static and two requiring fluxionality). Ab initio calculations were not able to locate a minimum corresponding to one of the structures requiring fluxionality, but the other two structures are minima on the potential surface. Theoretical IGLO ^{11}B NMR chemical shift calculations strongly support the static structure and rule out the remaining dynamic structure.

Introduction

The eight-vertex *nido*-carborane $C_2B_6H_{10}$ was originally synthesized and investigated[2] to solve the discrepancy between the X-ray structure for the borane B_8H_{12}[3] and its "expected" configuration. On the basis of the original geometrical systematics,[4] the anticipated gross structure of B_8H_{12} (bridge hydrogens are omitted) would be generated (see Figure 1) by removing a high coordination vertex from a nine-vertex polyhedron (**1**), giving an eight-vertex, five-membered open-face nido geometry (**2**, ni-8⟨V⟩). However, the X-ray crystal structure of B_8H_{12} (**3**) indicated a nido six-membered open-face geometry (ni-8⟨VI⟩) differing from the ni-8⟨V⟩ structure **2** simply by the absence of one edge connection. B_8H_{12}, which possesses four bridge hydrogens, was originally thought to adopt the ni-8⟨VI⟩ structure **3** to avoid *76*-bridge hydrogens.[5]

The structure of $C_2B_6H_{10}$ (isoelectronic with B_8H_{12}) was originally proposed[2] on the basis of its ^{11}B NMR spectrum (δ −22 and +8 in a 2:4 ratio) to be either the static ni-8⟨VI⟩ structure **4** or the dynamic ni-8⟨V⟩ structure **5** (see Figure 2). The static ni-8⟨VI⟩ structure **4** (similar to B_8H_{12}) and the dynamic ni-8⟨V⟩ structure **5** (the "predicted" structure based upon the 1971 geometrical systematics[4]) were both compatible with the experimental ^{11}B NMR values. Attempts to "freeze out" the proposed dynamic structure **5** by acquiring the ^{11}B NMR spectrum at −80 °C failed.[2]

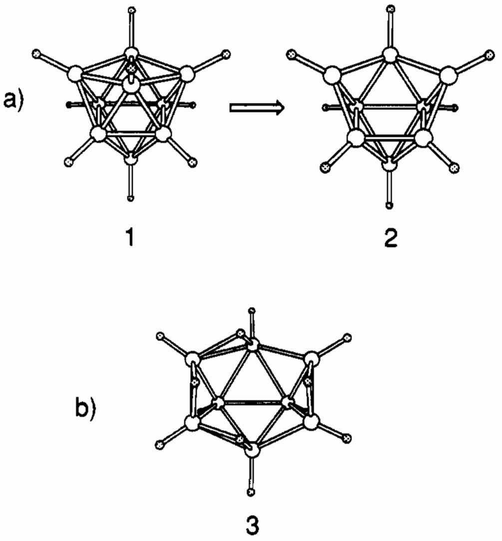

Figure 1. (a) Generation of the "expected" eight-vertex nido framework **2** of B_8H_{12} (bridge hydrogens not included) from a nine-vertex polyhedron **1** based upon geometrical systematics.[4] (b) Actual geometry of B_8H_{12} (**3**) as determined via X-ray diffraction.[3] Large circles represent boron, and small circles, hydrogen.

Another dynamic ni-8⟨VI⟩ structure (**6**) is also plausible.[6] Two synchronized skeletal diamond–square–diamond (DSD) rearrangements would make the four borons neighboring the bridge hydrogens in **6** (see Figure 2) equivalent as required by the ^{11}B NMR spectrum. Support for this type of rearrangement comes from *nido*-$R_4C_4B_8H_8$ (R = alkyl) in which two sets of skeletal carbons and several sets of borons coalesce at almost ambient conditions into "one kind" of carbon and fewer kinds of boron.[7] The dynamic ni-8⟨VI⟩ structure **6** would be favored over structures **4** and **5** if "charge smoothing" arguments involving carbon were dominant, while "charge smoothing" arguments involving only bridge hydrogens would favor structure **4**.[5]

We decided to investigate the alternative *nido*-$C_2B_6H_{10}$ structures (Figure 2) using the combined ab initio/IGLO[8]/NMR[9] method, a relatively new method of structural determination and

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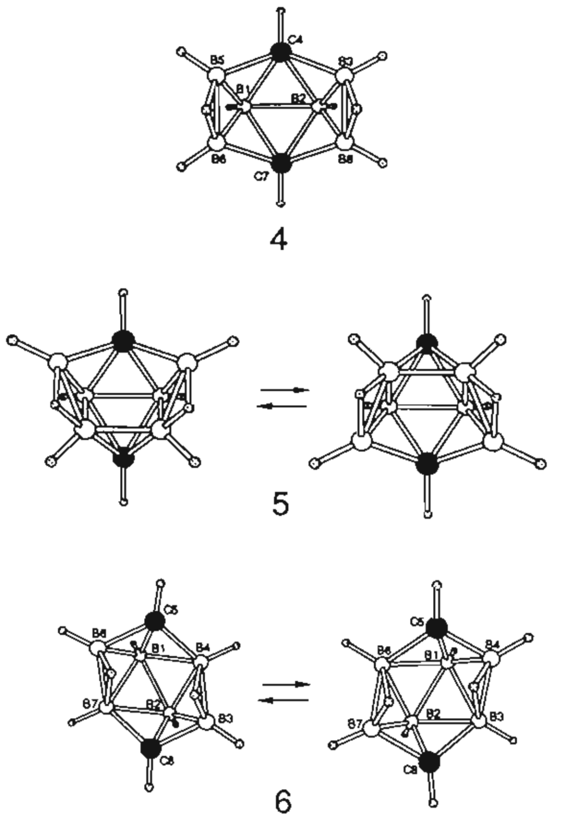

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Figure 2. Possible structures for $C_2B_6H_{10}$. Large circles represent boron, filled circles carbon, and small circles hydrogen.

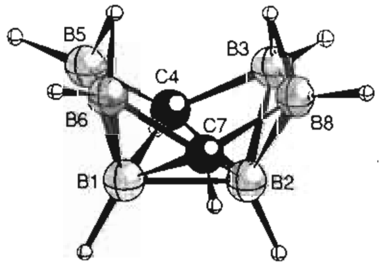

Figure 3. MP2/6-31G*-optimized bond lengths (Å) for $C_2B_6H_{10}$ (**4**): B1B2, 1.777; B1B3, 1.719; B1C4, 1.709; B3C4, 1.603; B3B8, 1.689; H_{bridge}B3, 1.326.

assessment that has achieved success in the elucidation of accurate structures of boranes and borane anions[1,9] and more recently has been applied to the investigation of the anti-podal effect in *closo*-heteroboranes.[10] To sum up this method, 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[8] NMR chemical shift calculation. The structure for which the theoretical IGLO-calculated NMR chemical shifts accurately correlates with the experimental values is deemed the best representation for the molecule in solution.

Methods

The geometries were fully optimized in the given symmetry (C_{2v} for **4** and C_2 for **6**) by employing the GAUSSIAN86 program[11a] at USC on an Alliant FX/40 computer using the standard 3-21G and 6-31G* basis sets. In addition, **4** was reoptimized at the MP2(Full)/6-31G* level of theory using the CADPAC[11b] program. Single point calculations at the MP2(FC)/6-31G* level were performed for the 3-21G geometries of **4** and **6** (notation MP2/6-31G*//3-21G). The ^{11}B chemical shifts were calculated using the IGLO program[8] and employing Huzinaga[12] Gaussian lobe basis sets contracted as follows:[8b] basis DZ, C,B 7s3p(4111,21); H, 3s(21); basis II′, C,B 9s5p1d(51111,2111,1), p-exponents 1.0 and 0.5 for C and B, respectively, H same as DZ. 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.[13]

Table I. Absolute (–au) and Relative (kcal/mol) Energies of the $C_2B_6H_{10}$ Isomers **4** and **6**

level of theory	E_{abs} **6**	E_{abs} **4**	E_{rel}[a] of **6**
ZPE (3-21G)[b]	87.9 (0)	90.0 (0)	
3-21G//3-21G	228.26657	223.32086	34.1
6-31G*//3-21G	229.57448	229.63252	36.4
MP2/6-31G*//3-21G	230.41879	230.48325	40.4
final estimate[c]			38.5

[a] $E_{rel}(4)$ = 0. [b] Zero point energy (in kcal/mol). [c] MP2/6-31G*//3-21G + ZPE(3-21G).

Table II. IGLO-Calculated ^{11}B NMR Chemical Shifts[a] of $C_2B_6H_{10}$ Isomers

structure	level of theory	B1,2	B4,7	B3,6	ϕB(3,4,6,7)	B(3,5,6,8)
6	DZ//3-21G	18.3	–2.6	23.2	10.3	
4	DZ//3-21G	–19.1				9.0
	DZ//6-31G*	–21.9				7.9
	II′//MP2/6-31G*	–19.1				9.1
expt[b]		–22				8

[a] In ppm versus $BF_3{\cdot}OEt_2$ (0.0 ppm). [b] Reference 2.

Results and Discussion

We were able to locate minima using ab initio theory[11] for structure **4** (C_{2v} symmetry) and **6** (C_2 symmetry) at the HF/3-21G level of theory. A frequency calculation at the same level of theory revealed both isomers are true minima on the potential energy surface (possess zero imaginary frequencies). We were not able to locate a minimum corresponding to ni-8⟨V⟩ structure **5**, as various input geometries employed (C_s symmetry) always optimized to structure **4**. On the basis of energy considerations (Table I), the static structure **4** appears to be strongly favored over structure **6**, the latter being more than 38 kcal/mol higher in energy (MP2/6-31G*//3-21G + ZPE level).

Convincing support for the static structure **4** comes from IGLO ^{11}B NMR chemical shift calculations.[14] At the DZ//3-21G level, **4** gave ^{11}B shifts of δ –19.1 and +9.1, to be compared with the experimental values[2] of δ –22 and +8, respectively (see Table II). The correlation between theory and experiment is excellent, also at higher levels. Incidentally, the IGLO values obtained at the lowest (DZ//3-21G) and at the highest level (II′//MP2/6-31G*) are nearly identical. The degree of agreement, however, is comparable to other carboranes.[9c] IGLO ^{11}B NMR chemical shift calculations (DZ//3-21G) on structure **6** (see Table II)

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(14) Of course, the IGLO method also calculates the ^{13}C and ^{1}H chemical shifts. For structure **4** the calculated (DZ/6-31G*) ^{1}H shifts (in ppm versus TMS) with the corresponding experimental values in parentheses are as follows: $H_{3,5,6,8}$ 5.6 (3.2), $H_{1,2}$ 3.6 (0.3), $H_{4,7}$ 0.2 (0.1), H_{bridge} –5.85 (–5.1). The correlation between theory and experiment is fairly good. The predicted ^{13}C chemical shift (in ppm versus TMS) for **4** is δ 11.35. The experimental ^{13}C value has not been reported. For a dynamic structure 6 (DZ/3-21G) the calculated ^{1}H values with the corresponding values in parentheses are as follows: $H_{1,2}$ 5.6 (0.3), $\phi H_{3,4,6,7}$ 4.8 (3.2), $H_{5,8}$ 7.8 (0.1), H_{bridge} –2.5 (–5.1). The correlation between theory and experiment for isomer 6 is poor. The predicted ^{13}C shift is 120.45 ppm.

gave values of δ −7.2, +22.6, and +18.2 (2:2:2 ratio) that when weighed using the DSD mechanism discussed previously give averaged shifts of δ +18.2 and +7.7 (4:2 ratio) for a fluxional **6**, which correlate poorly with the experimental values.

Conclusion

The ab initio/IGLO study of *nido*-$C_2B_6H_{10}$ reported here strongly supports the static ni-8⟨VI⟩ structure **4** for $C_2B_6H_{10}$, which is analogous to the known B_8H_{12} structure. The possible dynamic ni-8⟨V⟩ structure **5** is ruled out as it does not appear to be a true minimum on the potential surface. The possible dynamic ni-8⟨VI⟩ structure **6** is ruled out due to energy considerations and poor correlation of the IGLO-calculated ^{11}B NMR chemical shifts with the experimental values.

The determination that the ni-8⟨VI⟩ structure **4** for *nido*-$C_2B_6H_{10}$ is correct (with two carbons and two bridge hydrogens), whose structure is in between *nido*-B_8H_{12} (with four bridge hydrogens) and several isostructural species containing four carbons,[15] all of which have ni-8⟨VI⟩ configurations, suggests that all similar species, including[16] *nido*-$B_8H_{10}NEt_3$, will also be found to have the ni-8⟨VI⟩ configuration.[17]

It is known that bridge and endo hydrogens are to some extent interchangeable among *arachno*-carboranes,[18] but nido compounds may also be "forced" into having endo "groupings" rather than bridging hydrogens. Such is the situation with the *nido*-$C_2B_6H_8$ moiety when it is associated via two 2c2e bonds with an aluminum-containing group.[19]

Acknowledgment. Support at USC by the Loker Hydrocarbon Research Institute and at Erlangen by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. Prof. George A. Olah is thanked for his encouragement, and Prof. W. Kutzelnigg and his associates are thanked for supplying the IGLO programs to USC and to Erlangen. Prof. M. L. McKee also carried out preliminary computations on this problem. We thank him for this information.

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