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Ab Initio/IGLO/NMR Investigation of *nido*-$C_4B_7H_{11}$ Configurations: Structural Assignment of the Three Known Isomers and Reconfirmation of Empirical Carbon Placement Patterns

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The ab initio/IGLO/NMR method has been successfully applied to establish the structures of the three known isomers of *nido*-$C_4B_7H_{11}$. The method confirms the previously proposed structure, *nido*-7,8,9,10-$C_4B_7H_{11}$, **1a**, as one of the three known isomers. Of four candidates considered for the second isomer, one of the previously proposed structures, *nido*-1,7,8,10-$C_4B_7H_{11}$, **2b**, is selected. Of four candidates considered for the third isomer, structure *nido*-2,7,9,10-$C_4B_7H_{11}$, **3b**, which had not been previously proposed, is established. The relative order of stability is **1a** > **2b** > **3b**. A comparison of the relative energies of the nine cage structures considered in this study shows that, in complete agreement with previous empirically determined patterns, the most stable structures are those in which the carbons occupy low coordinate sites. This preference is more important than avoiding carbon−carbon connections.

Introduction

In this paper we demonstrate that the ab initio/IGLO/NMR method can be used to correctly establish the structures of the three known *nido*-$C_4B_7H_{11}$ carboranes. Furthermore, the relative energies of these and other possible cage structures are compared to predictions using empirical patterns governing carbon placement. The nido 11-vertex cage is ideally suited for the testing of these empirical rules as it contains only three kinds of vertices, and no complications are expected due to the lack of structural vertex homogeneity.

In the early 1980s Kutzelnigg and Schindler developed an ab initio based method for the calculation of NMR chemical shifts based upon the individual gauge for localized orbitals (IGLO).[1] The Schleyer group recognized the potential of the IGLO method to distinguish between structural alternatives for a variety of polyboranes and carboranes *provided that accurate structures are employed as input for the IGLO calculations*.[2] They found that ab initio optimized geometries at a high level of theory usually give better results than the best available experimental structures. They called this technique the ab initio/IGLO/NMR method.

The three-step ab initio/IGLO/NMR computational method can be summarized as follows: (1) the ab initio geometries are optimized for all candidate structures potentially compatible with the experimental NMR data, (2) the NMR chemical shifts are calculated using the IGLO method for each of the various ab initio optimized geometries, and (3) the IGLO calculated chemical shifts for the various candidate structures are compared with the experimentally observed NMR chemical shift values. Ideally, the calculated NMR shifts of *one, and only one*, of the candidate structures correlate with the observed experimental data and it is thus determined to be the correct structure in solution. The method has been successful in the structural elucidation of a number of boranes, carboranes, and related systems.[3]

Computational Section

The various candidate structures were fully optimized within the specified symmetry constraints employing the GAUSSIAN92 program[4] (using the standard Pople basis sets included) on either an IBM RS6000

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(1) (a) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 192−200. (b) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919−1933. (c) Schindler, M.; Kutzelnigg, W. *Mol. Phys.* **1983**, *48*, 781−798. (d) Schindler, M.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1983**, *105*, 1360−1370. (e) Schindler, M.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1987**, *109*, 1020−1033. (f) Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR, Basic Principles and Progress*; Diehl, P., Fluck, E., Günther, H., Kosfeld, R., Seelig, J., Eds.; Springer-Verlag: Berlin, 1991; Vol. 23, pp 165−262.

(2) Bühl, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 477−491.

(3) For example: (a) Schleyer, P. v. R.; Bühl, M.; Fleischer, U.; Koch, W. *Inorg. Chem.* **1990**, *29*, 153−155. (b) Bühl, M.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 886−888. (c) Bühl, M.; Schleyer, P. v. R. In *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, 1991; Chapter 4, p 113. (d) Williams, R. E. In *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, 1991; Chapter 4, p 91 (see footnote 83). (e) Bühl, M.; Schleyer, P. v. R.; McKee, M. L. *Heteroatom. Chem.* **1991**, *2*, 499−506. (f) Bühl, M.; Schleyer, P. v. R.; Havlas, Z.; Hnyk, D.; Heřmánek, S. *Inorg. Chem.* **1991**, *30*, 3107−3111. (g) Bühl, M.; Steinke, T.; Schleyer, P. v. R.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1160−1161. (h) Reference 1f, pp 210−212. (i) Köster, R.; Seidel, G.; Wrackmeyer, B.; Blaeser, D.; Boese, R.; Bühl, M.; Schleyer, P. v. R. *Chem. Ber.* **1992**, *125*, 663; **1991**, *124*, 2715−2724. (j) Kang, S. O.; Bausch, J. W.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1992**, *31*, 3763−3768. (k) Bausch, J. W.; Prakash, G. K. S.; Bühl, M.; Schleyer, P. v. R.; Williams, R. E. *Inorg. Chem.* **1992**, *31*, 3060−3062. (l) Bausch, J. W.; Prakash, G. K. S.; Williams, R. E. *Inorg. Chem.* **1992**, *31*, 3763−3768. (m) Bühl, M.; Mebel, A. M.; Charkin, O. P.; Schleyer, P. v. R. *Inorg. Chem.* **1992**, *31*, 3769−3775. (n) Onak, T.; Tseng, J.; Tran, D.; Herrera, S.; Chan, B.; Arias, J.; Diaz, M. *Inorg. Chem.* **1992**, *31*, 3910−3913. (o) Onak, T.; Tseng, J.; Diaz, M.; Tran, D.; Arias, J.; Herrera, S.; Brown, S. *Inorg. Chem.* **1993**, *32*, 487−489. (p) Mebel, A. M.; Charkin, O. P.; Bühl, M.; Schleyer, P. v. R. *Inorg. Chem.* **1993**, *32*, 463−468. (q) Mebel, A. M.; Charkin, O. P.; Schleyer, P. v. R. *Inorg. Chem.* **1993**, *32*, 469−473. (r) McKee, M. L.; Bühl, M.; Schleyer, P. v. R. *Inorg. Chem.* **1993**, *32*, 1712−1715. (s) Onak, T.; Tran, D.; Tseng, J.; Diaz, M.; Arias, J.; Herrera, S. *J. Am. Chem. Soc.* **1993**, *115*, 9210−9215. (t) Onak, T.; Diaz, M.; Barfield, M. *J. Am. Chem. Soc.* **1995**, *117*, 1403−1410.

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Model 580 workstation or a Silicon Graphics International IRIS 4D/440VGX computer. A vibrational frequency analysis was also carried out on each optimized geometry to determine the nature of the stationary point. A true minimum was found for all nine structures considered (i.e. one that possesses no imaginary frequencies).

The input structure for a geometry optimization at the HF/STO-3G level of theory was a monocapped pentagonal antiprism (an icosahedron with one vertex removed) containing B−B, B−C, and C−C bond lengths of 1.7 Å and exo-polyhedral B−H and C−H bonds of 1.1 Å. For all but one isomer (**3a**), an optimized geometry closely resembling the input structure was found, and the optimized geometry served as the input for higher level geometry optimizations. Each C_1 symmetry isomer was optimized up to the HF/6-31G* level of theory, and each C_s symmetry isomer was optimized up to the electron-correlated level MP2(FULL)/6-31G*. For the relative energy determination, a single point calculation at MP2(FULL)/6-31G* using the HF/6-31G* optimized geometry was carried out for each structure. Cartesian coordinates of the optimized geometries at the highest level of theory employed are available in the supplementary material.

The NMR chemical shifts were calculated using the IGLO program employing the DZ basis set contracted as follows: B and C 7s3p {4111,21}, H 3s {21}. For structures **2a**, **2b**, and **2d**, basis set II (as denoted by the Bochum group[1f]) was employed and is contracted as follows: B and C 9s5p1d {51111,2111,1}, d exponents 0.5 (B), 1.0 (C); H 5s1p {311,1}, p exponent 0.65. B_2H_6 is the primary reference for the ^{11}B NMR chemical shifts, and the δ values were converted to the experimental $BF_3{\cdot}O(C_2H_5)_2$ scale using the experimental value of $\delta(B_2H_6) = 16.6$ ppm.[5] Due to the lack of unambiguous 2D ^{11}B-^{11}B NMR spectra for compounds **II** and **III**, the experimental ^{11}B NMR data was assigned (with intensities correct) in order to obtain the best agreement with the calculated shifts. A comparison of the calculated and available experimental ^{1}H NMR data for compounds **I**, **II**, and **III** has not been included because ^{1}H shifts are difficult to accurately calculate.[3c] Experimental ^{13}C shifts have only been reported for compound **II**; therefore, direct comparison with theory for compounds **I** and **III** is not possible. The IGLO calculated ^{13}C NMR data for all structures have been included in Supporting Table 1 although previous studies[2,6] indicate the level of theory employed in this study may not be suitable for the accurate calculation of cage carbons in carboranes.[7]

Results and Discussion

Three compounds (**I**,[8] **II**,[9] and **III**[8]) of molecular formula *nido*-$C_4B_7H_{11}$ have been synthesized by the following methods:

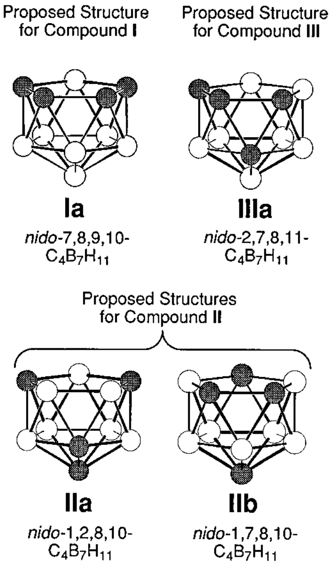

Figure 1. Four previously proposed structures for the three known isomers of the *nido*-$C_4B_7H_{11}$ carboranes: **Ia**, **IIa** and **IIb**, and **IIIa**. Borons are white and carbons are shaded circles; hydrogens have been omitted for clarity.

$$\textit{arachno-}\mu\text{-6,9-}CH_2\text{-5,6,9-}C_3B_7H_{11} + NaH \xrightarrow{\Delta} \underset{\textbf{I}}{\textit{nido-}C_4B_7H_{11}} \quad (1)$$

$$\textit{closo-}1,5\text{-}C_2B_3H_5 \xrightarrow[\text{hot/cold reactor}]{400\ ^\circ C/0\ ^\circ C} \underset{\textbf{II}}{\textit{nido-}C_4B_7H_{11}} \quad (2)$$

$$\textit{arachno-}4,5\text{-}C_2B_7H_{13} + HC{\equiv}CH \xrightarrow[\text{hexane}]{120\ ^\circ C} \underset{\textbf{III}}{\textit{nido-}C_4B_7H_{11}} \quad (3)$$

On the basis of skeletal electron counting rules,[10] all three compounds were proposed to have an open-cage structure consisting of a monocapped pentagonal antiprism. The three initially proposed structures, **Ia**, **IIa**, and **IIIa** for compounds **I**, **II**, and **III**, respectively, are shown in Figure 1, along with a recently proposed[11] alternative structure, **IIb**, for compound **II**.

Isomer I. Compound **I** was proposed to have the structure *nido*-7,8,9,10-$C_4B_7H_{11}$, **Ia** (Figure 1), on the basis of 1D ^{11}B and 2D COSY ^{11}B-^{11}B NMR experiments. Structure **Ia** is also that originally predicted by geometrical systematics[10a] to have the most stable arrangement of carbons. Of the eighteen arrangements of four carbons over the nido 11-vertex icosahedral fragment with C_s symmetry, only six of these would give the 2:2:1:1:1 ratios of boron resonances experimentally observed. On the basis of this fact combined with the 2D NMR spectra, the method of synthesis, and the geometrical preferences of carbon, the proposed structure, **Ia**, appeared secure.

Structure **Ia** was subjected to the ab initio/IGLO/NMR method. The ab initio optimized geometry for *nido*-7,8,9,10-$C_4B_7H_{11}$, **1a**, is given in Figure 2 along with the calculated ^{11}B NMR chemical shifts which are compared with the experimental values for **I**. The agreement between the calculated and experimental values is excellent, thus the proposed isomer, **Ia**, is reconfirmed as correct by the ab initio/IGLO/NMR method.

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(4) Gaussian 92: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA.

(5) Onak, T. P.; Landesman, H. L.; Williams, R. E. *J. Phys. Chem.* **1959**, *21*, 1533−1535.

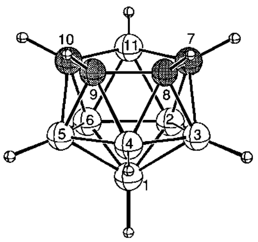
(6) (a) Schleyer, P. v. R.; Gauss, J.; Bühl, M.; Greatrex, R.; Fox, M. A. *J. Chem. Soc., Chem. Commun.* **1993**, 1766−1768. (b) Bühl, M.; Gauss, J.; Hofmann, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1993**, *115*, 12385−12390.

(7) Although IGLO basis set II (or II′) has been shown to accurately calculate ^{11}B NMR chemical shifts,[2,3] this level of theory has not been extensively applied to ^{13}C NMR shifts in carboranes due to the lack of experimental ^{13}C data. In the limited comparisons that have been made, it appears that IGLO ^{13}C chemical shifts are too far upfield compared to the experimental data.[2] However, the GIAO−MP2 method has been shown to give very good correlation of the calculated ^{13}C data with experiment for these limited cases.[6] For example, in *nido*-1,2-$C_2B_3H_7$ the IGLO method (II′//MP2/6-31G*) predicts the two carbons too far upfield by 9.3 and 13.3 ppm from the experimental values, while the GIAO−MP2 method (MP2/6-31G*//MP2/6-31G*) predicts the two carbons within 2 ppm of the experimental values.[6] Hence, Schleyer et al. concluded that for carboranes "the inclusion of electron correlation influences the ^{13}C chemical shifts significantly and improves the agreement with experiment...this behavior is likely to be general...".[6b] Application of the GIAO−MP2 method to molecules as large as $C_4B_7H_{11}$ is currently too computationally demanding.

(8) Štíbr, B.; Jelínek, T.; Drdáková, E.; Heřmánek, S.; Plešek, J. *Polyhedron* **1988**, *8*, 669−670.

(9) Astheimer, R. J.; Sneddon, L. G. *Inorg. Chem.* **1983**, *22*, 1928−1934.

(10) (a) Williams, R. E. *Inorg. Chem.* **1971**, *10*, 210−214. (b) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1−66. (c) Williams, R. E. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 67−142. (d) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446−452. (e) Williams, R. E. In *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, 1991; pp 11−93. (f) Williams, R. E. *Chem. Rev.* **1992**, *92*, 177−207.



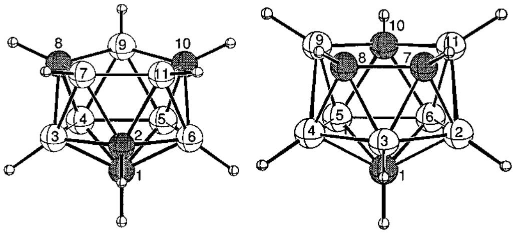
1a

optimized geometry for
nido-7,8,9,10-$C_4B_7H_{11}$

^{11}B NMR data

	Exp't (I)	IGLO
B1	-46.3	-47.7
B4	-23.5	-26.6
B2,6	-15.3	-15.3
B3,5	-14.5	-15.9
B11	-14.0	-15.1

Figure 2. Ab initio optimized geometry and IGLO calculated ^{11}B NMR chemical shifts for *nido*-7,8,9,10-$C_4B_7H_{11}$, **1a**.



2a

optimized geometry for
originally proposed
nido-1,2,8,10-$C_4B_7H_{11}$

2b

optimized geometry for
subsequently proposed
nido-1,7,8,10-$C_4B_7H_{11}$

^{11}B NMR data

	IGLO	Exp't (II)	IGLO
(B4,5)	-25.0	-23.7	-24.7 (B2,4)
(B7,11)	-22.6	-16.6	-16.6 (B5,6)
(B9)	-10.0	-15.6	-15.2 (B3)
(B3,6)	-15.0	-14.1	-16.0 (B9,11)

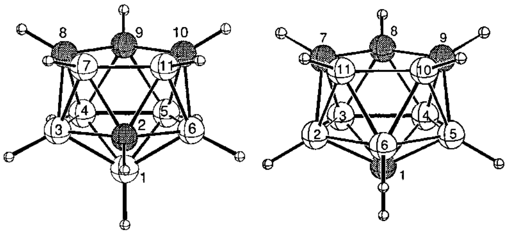
Figure 3. Ab initio optimized geometries and IGLO calculated ^{11}B NMR chemical shifts for the proposed *nido*-1,2,8,10-$C_4B_7H_{11}$, **2a**, and the alternative isomer *nido*-1,7,8,10-$C_4B_7H_{11}$, **2b**.

Isomer II. Compound **II** was first proposed[9] to be *nido*-1,2,8,10-$C_4B_7H_{11}$, **IIa**, and later[11] to have the structure *nido*-1,7,8,10-$C_4B_7H_{11}$, **IIb** (Figure 1). There are 12 arrangements of four carbons over the 11-vertex icosahedral fragment with C_s symmetry that would be compatible with the multiplicities observed in the ^{11}B NMR spectrum (2:2:2:1 ratios). Both proposed structures (**IIa** and **IIb**) contain a mirror plane and were initially selected on the basis of two conflicting empirical viewpoints. Structure **IIa** was originally proposed[9] primarily on empirical line-width patterns in its 1D ^{11}B NMR spectrum, the 1D ^{13}C NMR spectrum (2:1:1 ratios), and the absence of a boron atom in the "apex" position. Additional support came from the fact that this structure maximizes boron−carbon interactions in the cage, but it was acknowledged at the time that alternative structures such as the 1,7,8,10 isomer (**IIb**) could not be ruled out. Subsequently it was proposed[11] that **IIb** should, in fact, be the favored geometry, based upon carbon's preference for occupying low coordination sites in carborane structures.

Table 1. Absolute (−au) and Relative (kcal/mol) Energies of *nido*-$C_4B_7H_{11}$ Structures[a]

isomer	structure	6-31G*// 6-31G*	ZPE[b]	E_{rel}[c]	MP2/6-31G*// 6-31G*	E_{rel}[d]
7,8,9,10	**1a**	330.67890	99.32	0.8	331.92467	0.0
1,7,8,10	**2b**	330.67927	98.75	0.0	331.91905	3.0
2,7,9,10	**3b**	330.66312	98.65	10.0	331.90826	9.7
2,7,8,10	**3c**	330.66339	98.53	9.7	331.90432	12.0
2,8,9,10	**2c**	330.65407	98.75	15.8	331.90117	14.2
1,7,8,9	**2d**	330.64183	98.62	23.4	331.88766	22.5
2,7,8,9	**3d**	330.62898	98.52	31.3	331.87933	27.7
1,2,8,10	**2a**	330.62927	97.70	30.3	331.86574	35.4
2,7,8,11	**3a**	330.59742	97.61	50.2	331.84489	48.4

[a] Absolute (−au) energies of C_s symmetry structures optimized at MP2(FULL)/6-31G* are the following: 331.92649 (**1a**), 331.87126 (**2a**), 331.92092 (**2b**), 331.90520 (**2c**), and 331.88966 (**2d**). [b] Zero point energy at the HF/6-31G* level. [c] Relative energy at the 6-31G*//6-31G* + ZPE (6-31G*) level; the zero point energies have been scaled by 0.89 as recommended.[13] [d] Relative energy at the MP2/6-31G*//6-31G* + ZPE (6-31G*) level; the zero point energies have been scaled by 0.89 as recommended.[13]



2c

optimized geometry for
nido-2,8,9,10-$C_4B_7H_{11}$

2d

optimized geometry for
nido-1,7,8,9-$C_4B_7H_{11}$

^{11}B NMR data

	IGLO	Exp't (II)	IGLO
(B4,5)	-27.5	-23.7	-24.0 (B3,4)
(B7,11)	-21.1	-16.6	-19.3 (B10,11)
(B1)	-50.7	-15.6	-10.8 (B6)
(B3,6)	-19.2	-14.1	-17.0 (B2,5)

Figure 4. Ab initio optimized geometries and IGLO calculated ^{11}B NMR chemical shifts for *nido*-2,8,9,10-$C_4B_7H_{11}$, **2c**, and *nido*-1,7,8,9-$C_4B_7H_{11}$, **2d**.

In order to conclusively assign the structure of compound **II**, both candidate structures, *nido*-1,2,8,10-$C_4B_7H_{11}$, **IIa**, and *nido*-1,7,8,10-$C_4B_7H_{11}$, **IIb**, (Figure 1) were subjected to the ab initio/IGLO/NMR method. The ab initio optimized structures, **2a** and **2b**, and the calculated ^{11}B NMR chemical shifts together with the experimental data for compound **II** are included in Figure 3. The correlation between the experimental data for compound **II** and the calculated ^{11}B NMR chemical shifts for structure **2b** is significantly better than with **2a**. For example, the calculated shift (in ppm) for the unique boron in structure **2b** (B3, −15.2) agrees quite well with the experimental value (−15.6), while the calculated value for the unique boron in structure **2a** (B9, −10.0) is at over 5 ppm lower field from the experimental value (−15.6). Thus, the IGLO ^{11}B NMR chemical shift calculations favor **2b** over **2a** for the structure of compound **II**; the relative energies also favor **2b** by a substantial 32.4 kcal/mol (see Table 1).

Two other candidate configurations with C_s symmetry (**2c** and **2d** in Figure 4) that are predicted to be energetically less favorable than **2b**, but more favorable than **2a** based upon carbon location preferences,[10a] were also subjected to the ab initio/IGLO/NMR method. The 2,8,9,10 isomer, **2c**, gives good agreement of the calculated shifts with the experimental data for three of the ^{11}B resonances, but the calculated shift for B1 (−50.7) is at over 36 ppm lower field than the experimental value (−15.6). Thus, **2c** is ruled out as the structure for compound **II**. The 1,7,8,9 isomer, **2d**, gives fairly good correlation of the IGLO calculated ^{11}B NMR chemical shifts with the experimental data for compound **II**, with only B6 (−10.8) differing appreciably from the experimental value (−15.6). However, the agreement between the calculated and experimental ^{11}B NMR data for **2b** is better than **2d**. In addition, isomer **2b** is calculated to be 19.5 kcal/mol more stable than **2d** (see Table 1).

The IGLO calculated ^{13}C NMR data for **2a**, **2b**, **2c**, and **2d** are given in Supporting Table 1. As mentioned earlier, the

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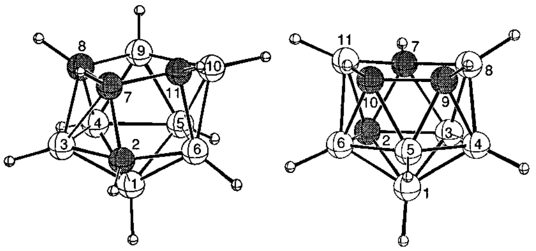
(11) (a) Reference 9f. (b) Williams, R. E. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1994; Vol. 36, pp 1−55.



3a

optimized geometry for
unanticipated structure
2,7,8,11-$C_4B_7H_{11}$

3b

optimized geometry for
subsequently proposed
nido-2,7,9,10-$C_4B_7H_{11}$

^{11}B NMR data

IGLO	Exp't (**III**)	IGLO
(B4) -29.7	-51.7	-51.7 (B1)
(B1) -28.2	-25.6	-28.6 (B6)
(B6) -23.6	-25.0	-25.3 (B4)
(B5) 2.6	-18.0	-17.0 (B8)
(B3) 4.3	-17.5	-14.4 (B11)
(B10) 9.2	-15.7	-13.8 (B3)
(B9) 28.0	-13.6	-12.0 (B5)

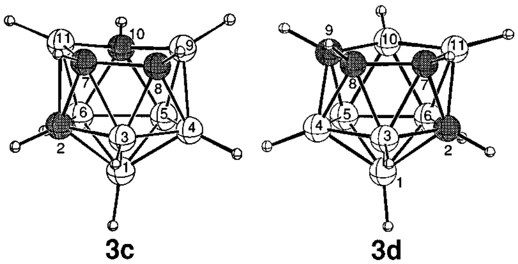
Figure 5. Ab initio optimized geometries and IGLO calculated ^{11}B NMR chemical shifts for the proposed *nido*-2,7,8,11-$C_4B_7H_{11}$, **3a**, and the favored alternative isomer *nido*-2,7,9,10-$C_4B_7H_{11}$, **3b**.

levels of theory employed in this study may not be suitable for the accurate calculation of cage carbon chemical shifts in carboranes, and neither **2a**, **2b**, **2c**, nor **2d** IGLO calculated ^{13}C shifts agree satisfactorily with the experimental data. However, the IGLO ^{13}C data for **2b**, the structure favored by the ^{11}B NMR chemical shift calculations, is shifted upfield by 12−14 ppm for all three carbons [−19.2 (C1), 14.0 (C10), 17.2 (C7,8)] compared to the experimental values (−4.7, 28.6, and 29.5 ppm).[9] Schleyer et al. found that IGLO ^{13}C shifts in carboranes are usually too far upfield from the experimental values.[2]

Isomer III. Compound **III**, with C_1 symmetry, was originally assigned the 2,7,8,11-structure, **IIIa** (Figure 1), on the basis of 1D ^{11}B and 2D COSY ^{11}B-^{11}B NMR studies.[8] A number of the resonances in the ^{11}B spectrum are closely spaced, however, making an unambiguous assignment difficult. Empirical carbon-location preferences[10a] do not favor the 2,7,8,11 isomer, **IIIa**, as it contains far too many adjacent carbon−carbon connections, an unprecedented arrangement, and would not be expected to be stable. There are a number of alternative C_1 symmetry isomers possible for compound **III**; thus, the ab initio/IGLO/NMR method appeared ideally suited for solving this structural dilemma.

An effort to determine the ab initio optimized geometry for the proposed 2,7,8,11 isomer of $C_4B_7H_{11}$, **IIIa** (Figure 1) gave an unexpected structure **3a** (Figure 5). Structure **3a** is unusual in that it contains a 4-membered square face (C2−C7−C11−B6) in addition to the anticipated 5-membered open face, with several bond distances not within normal B−B and B−C bond ranges. Apparently incorporating a triangular face of carbon atoms is disfavored, as carbon-preference systematics predicts.[10a] The calculated ^{11}B NMR chemical shifts of **3a** are shown in Figure 5 and there is poor correlation with the experimental data. Thus, the proposed structure **IIIa** may be ruled out as the structure of compound **III**.

An alternative structure, *nido*-2,7,9,10-$C_4B_7H_{11}$, appeared to be the most logical candidate for compound **III** and the ab initio optimized geometry, **3b**, is given in Figure 5. Carbon-location preferences[10a] predict configuration **3b** to be the most stable C_1 symmetry *nido*-$C_4B_7H_{11}$ structure. Structure **3b** contains three of the four carbon atoms on the open face in an "as-nonadjacent-as-possible" configuration to enhance charge smoothing. There are only two other locations available for the fourth carbon, and the 2,7,9,10 configuration, **3b**, also appears most logical based upon the synthesis from two "carbons adjacent" precursors: *arachno*-4,5-$C_2B_7H_{13}$ and acetylene. The calculated ^{11}B NMR chemical shifts of **3b** correlate well with the experimental data for compound **III** (Figure 5); thus, *nido*-2,7,9,10-$C_4B_7H_{11}$, **3b**, is favored as the revised structure for compound **III**.



3c

optimized geometry for
nido-2,7,8,10-$C_4B_7H_{11}$

3d

optimized geometry for
nido-2,7,8,9-$C_4B_7H_{11}$

^{11}B NMR data

IGLO	Exp't (**III**)	IGLO
(B1) -48.6	-51.7	-50.7 (B1)
(B4) -23.5	-25.6	-24.0 (B5)
(B5) -18.1	-25.0	-23.8 (B3)
(B6) -14.1	-18.0	-20.5 (B4)
(B11) -10.8	-17.5	-15.5 (B10)
(B3) -10.7	-15.7	-15.3 (B11)
(B9) -3.8	-13.6	-5.7 (B6)

Figure 6. Ab initio optimized geometries and IGLO calculated ^{11}B NMR chemical shifts for *nido*-2,7,8,10-$C_4B_7H_{11}$, **3c**, and *nido*-2,7,8,9-$C_4B_7H_{11}$, **3d**.

Two other possible candidate configurations with C_1 symmetry (**3c** and **3d** in Figure 6) of *nido*-$C_4B_7H_{11}$ that would be predicted by empirical carbon location preferences[10a] to be energetically less favorable than **3b**, but more favorable than **3a**, were also subjected to the ab initio/IGLO/NMR method. The 2,7,8,10 isomer, **3c**, gives poor correlation of the calculated ^{11}B NMR chemical shifts with the experimental data for compound **III**. For example, the calculated chemical shifts (in ppm) for B11 (−10.8) and B5 (−18.1) are at over 7 ppm lower field from the experimental values (−17.5 and −25.0, respectively).

The 2,7,8,9 isomer, **3d**, gives fairly good correlation between the calculated ^{11}B NMR chemical shifts and the experimental values for **III**, but the 2,7,9,10 isomer, **3b**, gives better correlation. In particular, the calculated shift (in ppm) for B6 (−5.7) in **3d** is located about 8 ppm lower field than the experimental value (−13.6). Thus the ab initio/IGLO/NMR method selects **3b** in favor of **3c** or **3d** as the correct structure for the asymmetrical $C_4B_7H_{11}$ carborane. There is also a substantial difference in the relative energies of **3b** and **3d**, with **3b** 18.0 kcal/mol more stable than **3d** (see Table 1). Note also that the 2D ^{11}B NMR spectrum obtained for compound **III** could be compatible with the 2,7,9,10 isomer, **3b**, due to the closely spaced resonances.

General Comments about Cage Carbon Site Preferences. The relative energies of all the *nido*-$C_4B_7H_{11}$ isomers considered in this study were determined at MP2/6-31G*//6-31G* + ZPE (6-31G*) and are included in Table 1. It is satisfying to find that the three isomers (**1a**, **2b**, **3b**) favored by the NMR chemical shift calculations are also the three most stable of those examined computationally. These results completely agree with the previously existing empirical carbon location preferences.[10a] It is also satisfying to find that the 2,7,8,11 isomer, **3a**, is calculated to be much higher in energy than all of the other isomers calculated in this study, in agreement with the prediction from carbon-location preferences that indicates any proposed structure (**IIIa**, Figure 1) containing a triangular face of three carbons should be energetically disfavored. The fact that the

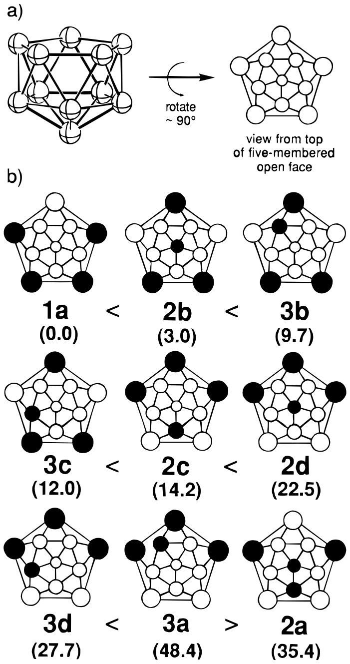


Figure 7. (a) Graphic to illustrate two views of a nido 11-vertex cluster: "side" view and "top" view. (b) Stability order among the *nido*-$C_4B_7H_{11}$ isomers (viewed from top of 5-membered open face as diagrammed in part a, with dark circles representing carbons and open circles representing borons).

optimized geometry (Figure 5) contains a square open face supports this proposition.[12]

A comparison of the relative energies of the *nido*-$C_4B_7H_{11}$ carboranes calculated in this study also enables us to address a residual question concerning the relative importance of the previously mentioned carbon-location preferences[10a] for (a) low coordinated sites vs (b) nonadjacent locations when both are available. The first seven isomers of *nido*-$C_4B_7H_{11}$, in terms of estimated relative stability based upon empirical geometrical systematics, are the first seven structures illustrated in Figure 7b, drawn in a fashion (as illustrated in Figure 7a) to facilitate easy determination of vertex connectivity (the vertices on the open face are 4-coordinate and the rest are 5-coordinate) and number of carbon−carbon contacts. The order chosen assumes that the preference for carbons to occupy low coordination sites is significantly more important than the preference for carbons to occupy non-adjacent locations. The ab initio determined relative energies (from Table 1) are given in parentheses. That the top seven configurations displayed in Figure 7b match the top entries in Table 1 confirms this assumption. Prior to this study some residual uncertainty remained regarding low coordination versus adjacent carbon preferences. For example, structure **1a**, which is 3.0 kcal/mol more stable than **2b** (see Table 1), incorporates *three* C−C carbons-adjacent situations (which is associated with instability) while structure **2b** incorporates only *one* C−C carbons-adjacent situation but does contains *one* carbon in a higher coordinated location (also indicative of instability). Apparently, as previously proposed based upon empirical observations, the occupation of one additional low coordinated site (a positive effect) more than offsets the destabilizing effects of adding two additional carbons-adjacent situations.

Further examination of the structures in Figure 7b confirms these trends. Decreasing stability results as the single carbon not on the open face in **2b** moves adjacent to the lone peripheral carbon in **3b**, then adjacent to one of the pair of peripheral carbons in **3c**. An analogous trend is found upon examining structures **2c**, **2d**, **3d**, and **3a**, each having three adjacent carbons on the open face. As the lone carbon not on the open face in **2c** migrates closer to the open face carbons in **2d** and **3d**, the result is decreased stability. When this carbon makes contact with two peripheral carbons, a highly unstable situation occurs and the cage instead adopts the arachno geometry **3a**.

It was originally noted[9] (1983) that compound **II**, shown in this study to be structure **2b**, undergoes isomerization via thermolysis at 330 °C to give an unisolated material with ^{11}B NMR resonances of −13.0, −14.0, −22.9, and −45.5 ppm. These chemical shifts are similar to those reported for compound **I** (isolated in 1988), shown in this study to be structure **1a**, and reexamination of the original (1983) ^{11}B NMR spectrum of the material from the isomerization confirms this assignment. This isomerization is consistent with the relative energies of **1a** and **2b** with **2b** being only 3 kcal/mol higher in energy (see Table 1).

Conclusion

The ab initio/IGLO/NMR method has been successfully applied to establish the structures of the three isomers of *nido*-$C_4B_7H_{11}$. The method confirms compound **I** to be *nido*-7,8,9,10-$C_4B_7H_{11}$, **1a**, and compound **II** to be *nido*-1,7,8,10-$C_4B_7H_{11}$, **2b** (rather than structures **2a**, **2c**, or **2d**), and determines compound **III** to be *nido*-2,7,9,10-$C_4B_7H_{11}$, **3b** (rather than **3a**, **3c**, and **3d**).

The relative eneriges obtained from the ab initio optimized geometries indicate the thermodynamically most stable arrangement of carbon atoms in these 11-vertex nido clusters has all four carbon atoms in adjacent, low coordinate positions about the open face, structure **1a**. Thus, in complete agreement with the empirically determined trends, carbon occupation of low coordinated sites appears to be a more important factor than avoiding carbon−carbon connections in the cage. However, moving adjacent carbons from the open face to nonadjacent higher coordination vertices remains of secondary importance.

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Supporting Information Available: Tables of the IGLO calculated ^{13}C NMR chemical shifts and Cartesian coordinates for the optimized geometries at the highest level of theory employed for all the *nido*-$C_4B_7H_{11}$ systems calculated in this study (6 pages). Ordering information is given on any current masthead page.

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(12) Several years ago when structure **IIIa** (Figure 1) was first proposed in the literature[8] there was no reason to believe that the NMR data had been misinterpreted to suggest the wrong set of connectivities. Rather, it was thought[10f,11b] that the connectivities were correct but one connection in the triangle of three carbons "should disappear" with the result that an electron precise HC−group would be formed which would be connected via three 2-center 2-electron bonds to an electron deficient *arachno*-$C_3B_7H_{10}$ cluster. It was predicted that the C2−C7 connection would be "broken" (see Figure 25, ref 11b), but the calculations indicate the C2−C11 connection is in fact "broken" to give the four-membered open face. It should be noted that **3d** is high in energy compared to the other *nido*-$C_4B_7H_{11}$ clusters calculated in this study and contains some C−C and B−C bond lengths and various bond angles not within values normally found in carboranes.

(13) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; DeFrees, D.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. F.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Chem., Symp.* **1981**, *15*, 269−278.