Ab Initio/NMR Studies on Per-*B*-F and Per-*B*-Cl Derivatives of $C_4B_2H_6$ and $C_2B_4H_6$: “Classical” vs “Carborane-Cage” Structures. Correlation of ^{11}B, ^{19}F, and ^{35}Cl NMR Data among Related Fluoroboron and Chloroboron Compounds

Thomas Onak,*,† Martin Diaz,† and Michael Barfield*,‡

Contribution from the Departments of Chemistry, California State University, Los Angeles, California 90032, and University of Arizona, Tucson, Arizona 85721

Received July 18, 1994®

Abstract: Ab initio IGLO/^{11}B-NMR and IGLO/^{35}Cl-NMR calculations as well as GIAO/NMR studies on two plausible B-Cl_4-$C_2B_4H_2$ structures lead to the conclusion that the only known compound of that formula most probably prefers a “classical” structure rather than a *closo* configuration of carbon and boron atoms. IGLO and GIAO calculations on a [2.1.1] bicyclic system, perhaps fluxional in nature, with the two carbon atoms at the bridgehead positions are reasonably consistent with available NMR data. The proposed static planar structure for the known B,B′-difluoro derivative of $C_4B_2H_6$ is supported by IGLO/^{11}B-NMR and IGLO/^{19}F-NMR, as well as corresponding GIAO/NMR results. Calibration of the ^{11}B, ^{19}F, and ^{35}Cl NMR correlative approaches involved the comparison of calculated and experimental NMR shifts for the simple haloboron compounds, $XB(CH{=}CH_2)_2$, $X_2BCH{=}CH_2$, $XBMe_2$, X_2BMe, BX_3, BX_4^- ion, (X = F, Cl), $ClBF_2$, and Cl_2BF.

Introduction

The parent compounds of the formula $C_2B_nH_{n+2}$ (n = 3−10) all appear to take on *closo*-carborane type cage geometries, i.e. deltahedral skeletal cage configurations.[1] There have been indications that the placement of halogens on boron atoms of these and related carborane cages might well result in some degree of cage opening, or in cage fluxionality.[2,3] Also, it has been generally accepted that the known B,B′-difluoro derivative of $C_4B_2H_6$ (known as its per-C-alkyl derivative) adopts a “classical” planar C_4B_2 configuration (**IV**, Figure 1)[4] rather than the *nido* arrangement known for the parent $C_4B_2H_6$ (**I**).[5] It has been rationalized that the “unshared” electrons of the fluorine atoms could back-donate electrons to the attached borons, and thus increase the cage electron density; this could then have the effect of opening up the otherwise “electron-deficient” nido cage to give the proposed planar configuration. In order for this cage opening to occur, it might well require that every boron atom in the molecule be attached to a halogen. The known *B*-monohalo and *B*-dihalo carboranes of the small *closo* carboranes (e.g. 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$ (**VII**), 2,4-$C_2B_5H_7$) have not shown any indication of cage opening or fluxionality under ambient conditions.[3,6] And it is satisfying that MO calculations on several of the monochloro and dichloro systems generally support greater stability for the carborane cage configuration rather than for isomeric structures with “classical” bonding.[7]

A *B*-tetrachloro derivative of $C_2B_4H_6$ has been reported in which a shift of +62.76 ppm (relative to $F_3B{\cdot}OEt_2$) was found for the single boron NMR resonance.[8] This high-frequency chemical shift value is considered unusual for a *closo* compound. Most all parent *closo* carboranes exhibit ^{11}B chemical shifts that

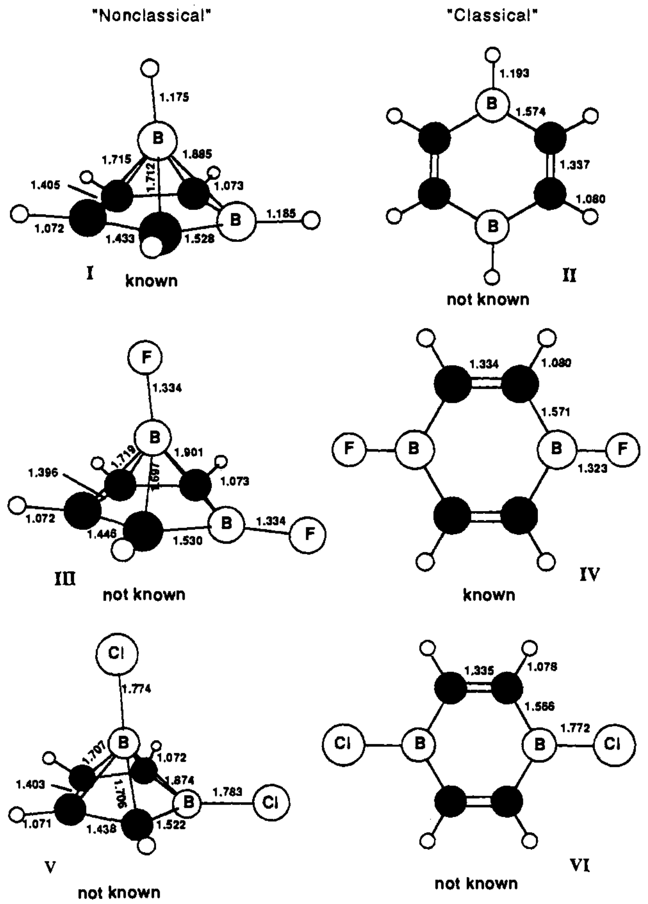

Figure 1. Vibrationally stable structures of $C_4B_2H_6$ systems obtained from ab initio calculations carried out at the 6-31G* level of theory. Bond distances are given in Å.

[†] California State University.

[‡] University of Arizona.

[®] Abstract published in *Advance ACS Abstracts,* December 15, 1994.

(1) Williams, R. E. *Chem. Rev.* **1992,** *92,* 177−207 and references therein.

(2) Camp, R. N.; Marynick, D. S.; Graham, G. D.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978,** *100,* 6781−6783.

(3) Abdou, Z. J.; Abdou, G.; Onak, T.; Lee, S. *Inorg. Chem.* **1986,** *25,* 2678, 2683.

(4) Maddren, P. S.; Modinos, A.; Timms, P.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1975,** 1272−1277; Timms, P. L. *J. Am. Chem. Soc.* **1968,** *90,* 4585−4589.

(5) Pasinski, J. P.; Beaudet, R. A. *J. Chem. Soc., Chem. Commun.* **1973,** 928; *J. Phys. Chem.* **1974,** *61,* 683.

0002-7863/95/1517-1403$09.00/0

are found in a low-frequency region, between $\delta = -65$ and $+20$ ppm.[9] For example, the ^{11}B shift of the parent *closo*-1,6-$C_2B_4H_6$ is $\delta = -17$ ppm,[6i,10,11] and the three types of borons in the pentagonal pyramidal *closo*-2,4-$C_2B_5H_7$ fall in the region of $\delta = -23$ to $+8$ ppm.[6a,h,m,10b,11] From available data it can be expected that replacement of a terminal hydrogen with a halogen such as chlorine on any given boron of these cages should deshield the boron resonance, perhaps 10−15 ppm, and probably not less than 5 ppm nor more than 25 ppm.[3,6a,c,g,h,m,9,11,12,13] So at most, a substitution of this kind should deshield the ^{11}B resonance the *closo*-dicarbahexaborane to a position no further downfield than about $\delta = +5$ ppm, and certainly not in the same region as the observed $\delta = +62$ ppm for the known *B*-Cl_4-$C_2B_4H_2$. Additionally, strict application of a ^{11}B chemical shift additivity relationship[6i]

$$(\sigma_{\text{total}} = \sigma_{\text{parent}} + \Delta\sigma_{\text{contiguous}} + \Sigma\Delta\sigma_{\text{nearest-neighbor}} + \Delta\sigma_{\text{antipodal}})$$

to *B*-halogenated 1,6-$C_2B_4H_6$ compounds would lead to a predicted shift for *B*-Cl_4-*closo*-1,6-$C_2B_4H_2$, **XI**, of around $\delta = -16.1$ ppm $[= -17.6 + 9.3 + 2(1.4) - 10.6]$[6i,11] to $\delta = -13.5$ ppm $[= -18.7 + 9.9 + 2(2.3) - 9.3]$,[14] depending upon which set of experimental data for the known monochloro and dichloro derivatives are utilized.

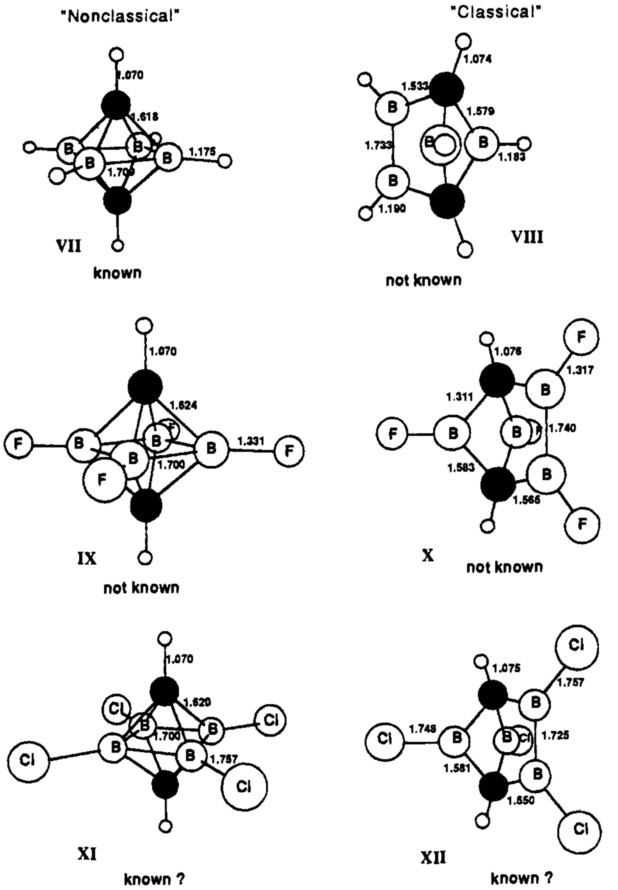

Figure 2. Vibrationally stable structures of $C_2B_4H_6$ systems obtained from ab initio calculations carried out at the 6-31G* level of theory. Bond distances are given in Å.

It is well-known that the boron compounds having a more "classical" structure such as R_2BCl or $RBCl_2$ (R = alkyl, vinyl) are to be found at the high-frequency region (i.e., $\delta = +52$ to $+77$ ppm) of the ^{11}B NMR spectrum.[15] This raises the following question: Is the $\delta(^{11}B) = +62.76$ ppm shift found for the *B*-tetrachloro derivative of $C_2B_4H_6$ more consistent with a "classical" structure (e.g. **XII**, Figure 2) than that with a carborane-like cage structure, **XI**? There is now strong support for the use of ab initio methods such as IGLO (individual gauge for localized molecular orbitals)[16] and GIAO (gauge including atomic orbitals)[17] for making strong structural inferences concerning boron-containing compounds. These methods involve the comparison of calculated ^{11}B chemical shifts of MO optimized structures with experimentally obtained chemical shifts.[18] We presently examine, by means of the ab initio/IGLO/NMR and ab initio/GIAO/NMR methods, carborane-cage, and alternative, structures for $C_4B_2H_6$ and for $C_2B_4H_6$ systems and some of their per-*B*-halogenated (halogen = F, Cl) derivatives, Figures 1 and 2. In the course of this work we found it instructive to study, in parallel, several simple fluorboron and chloroboron compounds ($XB(CH{=}CH_2)_2$, $X_2BCH{=}CH_2$, $XBMe_2$,

---

(6) (a) Nam, W.; Onak, T. *Inorg. Chem.* **1987**, *26*, 48−52. (b) Ng, B.; Onak, T. J. *Fluorine Chem.* **1985**, *27*, 119−125. (c) Ng, B.; Onak, T.; Fuller, K. *Inorg. Chem.* **1985**, *24*, 4371−4376. (d) Dobbie, R. C.; DiStefano, E. W.; Black, M.; Leach, J. B.; Onak, T. *J. Organomet. Chem.* **1976**, *114*, 233−238. (e) Spielman, J. R.; Warren, R. G.; Bergquist, Allen, J. K.; Marynick, D.; Onak, T. *Synth. React. Inorg. Metal-Org. Chem.* **1975**, *5*, 347−356. (f) Beltram, G. A.; Jasperse, C.; Cavanaugh, M. A.; Fehlner, T. P. *Inorg. Chem.* **1990**, *29*, 329. (g) Abdou, Z. J.; Soltis, M.; Oh, B.; Siwap, G.; Banuelos, T.; Nam, W.; Onak, T. *Inorg. Chem.* **1985**, *24*, 2363−2367. (h) Ng, B.; Onak, T.; Banuelos, T.; Gomez, F.; DiStefano, E. W. *Inorg. Chem.* **1985**, *24*, 4091−4096. (i) Takimoto, C.; Siwapinyoyos, G.; Fuller, K.; Fung, A. P.; Liauw, L.; Jarvis, W.; Millhauser, G.; Onak, T. *Inorg. Chem.* **1980**, *19*, 107−110. (j) Beltram, G. A.; Fehlner, T. P. *J. Am. Chem. Soc.* **1979**, *101*, 6237−6244. (k) Maraschin, N. J.; Lagow, R. J. *Inorg. Chem.* **1975**, *14*, 1855−1859. (l) Gomez, F.; Onak, T.; Arias, J.; Alfonso, C. *Main Group Met. Chem.* **1990**, *13*, 237−246. (m) Warren, R.; Paquin, D.; Onak, T.; Dunks, G.; Spielman, J. *Inorg. Chem.* **1970**, *9*, 2285−2287. (n) Olsen, R. R.; Grimes, R. N. *Inorg. Chem.* **1971**, *10*, 1103−1105. (o) Reilly, T. J.; Burg, A. B. *Inorg. Chem.* **1973**, *12*, 1450−1451. (p) McKown, G. L.; Beaudet, R. A. *Inorg. Chem.* **1971**, *10*, 1350−1354. (q) Olsen, R. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1970**, *92*, 5072−5075.

(7) Onak, T.; O'Gorman, E.; Banuelos, T.; Alfonso, C.; Yu, M. *Inorg. Chem.* **1990**, *29*, 335−340. Onak, T., unpublished studies.

(8) Hosmane, N. S.; Islam, M. S.; Burns, E. G. *Inorg. Chem.* **1987**, *26*, 3236−3237.

(9) For references to, and chemical shift values of, polyboranes see: *Gmelin Handbook of Inorganic Chemistry*; Springer-Verlag: Berlin, FRG, 1974; pp 249−288, Borverbindungen 2, pp 1−288. Also see: *Gmelin Handbook of Inorganic Chemistry*; Springer-Verlag: Berlin, FRG, 1975, Borverbindungen 6, pp 1−150; 1977, Borverbindungen 11, pp 1−207; 1977, Borverbindungen 12, pp 1−306; 1977, Borverbindungen 14, pp 149−233; 1978, Borverbindungen 18, pp 206−227; 1979, Borverbindungen 20, pp 1−239; 1980, Boron Compounds, 1st Suppl. Vol. 1, pp 84−108; 1980, Boron Compounds, 1st Suppl. Vol. 3, pp 105−256; 1983, Boron Compounds, 2nd Suppl. Vol. 1, pp 84−204; 1982, Boron Compounds, 2nd Suppl. Vol. 2, pp 223−335; 1987, Boron Compounds, 3rd Suppl. Vol. 1, pp 90−240; 1988, Boron Compounds, 3rd Suppl. Vol. 4, pp 153−254; 1993, Boron Compounds, 4rd Suppl. Vol. 4, pp 178−321.

(10) (a) Williams, R. E.; Good, C. D.; Shapiro, I. *J. Am. Chem. Soc.* **1962**, *84*, 3837−3840. (b) Onak, T.; Gerhart, F. J.; Williams, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 3378−3380.

(11) Nam, W.; Onak, T. *Inorg. Chem.* **1987**, *26*, 1581−1586.

(12) Siwapinyoyos, G.; Onak, T. *Inorg. Chem.* **1982**, *21*, 156−163.

(13) (a) Siedle, A. R. *Annu. Rept. Nucl. Magn. Reson. Spectrosc.* **1988**, *20*, 205. (b) Siedle, A. R. *Annu. Rept. Nucl. Magn. Reson. Spectrosc.* **1982**, *12*, 177.

(14) Fehlner, T. P.; Czech, P. T.; Fenske, R. F. *Inorg. Chem.* **1990**, *29*, 3103.

(15) Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag, New York, 1978.

(16) The IGLO method employed here was designed by the following: (a) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. (b) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919. (c) Schindler, M.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1983**, *105*, 1360−1370. (d) Schindler, M.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1987**, *109*, 1020−1033. (e) Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR, Principles and Progress*; Springer-Verlag: Berlin, 1990; Vol. 23, pp 165−262.

(17) (a) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251−8260. (b) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789. (c) Rohlfing, C. M.; Allen, L. C.; Ditchfield, R. *Chem. Phys.* **1984**, *87*, 9. (d) Pulay, P.; Hinton, J. F.; Wolinsky, K. In *Nuclear Magnetic Shieldings and Molecular Structure*; Tossell, J. A., Ed.; Kluwer: Boston, 1993; pp 243−262. (e) Sulzback, H. M.; Schleyer, P. v. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1994**, *116*, 3967−3972.

X_2BMe, BX_3, BX_4^- ion (X = F, Cl); $ClBF_2$; and Cl_2BF) for which ^{11}B and halogen NMR data have been gathered.

Calculational Methods for the Geometry Optimizations and for IGLO/NMR and GIAO/NMR Chemical Shift Determinations

Energy optimized structures for all molecules were carried out using the ab initio Gaussian-90 codes[19] with split valence basis sets at the HF/3-21G level and with polarization functions at the HF/6-31G* level of theory. Except as noted below, each geometry optimization resulted in a vibrationally stable structure. The total energies for those molecules which are a part of this study are given in Table 1. Depicted in Figures 1 and 2 are the carborane molecules which were optimized at the HF/6-31G* level. The energy optimized structures were used to calculate the chemical shieldings using both IGLO[16,18,20,21] and GIAO[17] methods. These make use of Huzinaga Gaussian lobe functions[22] and Cartesian Gaussian functions, respectively. All IGLO calculations were performed with a double-ζ set (DZ) in the contractions (21) for H, (4111/21) for first row elements, and (511111/3111) for second row (Cl) atoms. Calculations were also performed with a (9/5) set contracted to a (51111/2111) set with one set of (5) d-type functions on first row elements and for H a (311) set with one set of p-functions (orbital exponent 0.65). This set is denoted Basis Set II in the notation of the Bochum group.[16e] The exponent of the d-type functions is 0.7 for boron and 1.0 for elements C to F. The contraction scheme for Cl is (5111111/211111) with two sets of d-functions having d-orbital exponents of 0.4 and 1.6. Available computational resources limited the IGLO computations at the Basis Set II level to those compounds smaller than **III**, **IV**, **XI**, and **XII**. All GIAO chemical shielding results made use of 6-31G basis sets (Tables 2–5).

All calculated ^{11}B shielding values σ were referenced to B_2H_6 as the primary reference point. The resulting chemical shifts δ in Table 2 were converted to the standard $F_3B{\cdot}OEt_2$ scale using the experimental value of +16.6 ppm for $\delta(B_2H_6)$;[23] thus,

$$\delta(^{11}\text{B of cpd}) = \sigma(^{11}\text{B of B}_2\text{H}_6) - \sigma(^{11}\text{B of cpd}) + 16.6\text{ ppm}$$

The shielding for B_2H_6 [σ(^{11}B of B_2H_6)] is 114.9 ppm at the double-ζ level, which then implies that the shielding for $F_3B{\cdot}OEt_2$ is 131.5 ppm. For Basis Set II, the values are 102.3 and 118.9 ppm, respectively. A similar method is used to obtain the ^{19}F chemical shifts. These are first obtained relative to HF (computed at the same level of theory) and then converted to the standard $FCCl_3$ scale,

$$\delta(^{19}\text{F of cpd}) = \sigma(^{19}\text{F of HF}) - \sigma(^{19}\text{F of cpd}) - 214\text{ ppm}$$

where the constant is the experimental difference between the chemical shifts of HF and $FCCl_3$.[16e,24] Similarly, the ^{35}Cl chemical shifts are given by

$$\delta(^{35}\text{Cl of cpd}) = \sigma(^{35}\text{Cl of CH}_3\text{Cl}) - \sigma(^{35}\text{Cl of cpd}) + 50.0\text{ ppm}$$

where CH_3Cl is a secondary standard which is 50 ppm deshielded from the primary standard, Cl^-(aqueous) ion. The $\sigma(^{35}Cl)$ values of CH_3Cl are 887.2 ppm for IGLO/DZ//3-21G (this abbreviated basis set designation implies an IGLO calculation carried out at the double-ζ level for a geometry which was previously optimized at the ab initio 3-21G level), 971.6 for IGLO/DZ//6-31G*, 897.8 for IGLO/Basis-II/3-21G, 942.2 for IGLO/Basis-II/6-31G*, and 1002.7 for GIAO/6-31G//6-31G*. The IGLO and GIAO results are summarized in Tables 2–5. Calculations performed with Basis II (IGLO) and 6-31G (GIAO) with HF/6-31G* optimized geometries represent the highest levels of theory that could be applied to all the compounds (with the exception of IGLO/Basis-II for **II**, **IV**, **XI**, and **XII**) by means of the computational resources available to us. Geometry differences between optimizations carried out at the 3-21G and 6-31G* levels did not usually cause significant changes in calculated chemical shifts. All calculations were carried out, variously, on Multiflow-Trace, Convex C220, Convex C240, and Alliant FX/2800 minisupercomputers.

Results and Discussion

The ab initio/IGLO/NMR and ab initio/GIAO/NMR ^{11}B data for both the D_{4h} and [2.1.1] bicyclic forms (**XI** and **XII**, Figure 2) of a tetra-*B*-chlorodicarbahexaborane, $C_2B_4H_2Cl_4$, are summarized in Table 2. The assumption of a "near"-octahedral D_{4h} carborane cage framework for **XI** leads to inconsistency between the experimental and calculated ^{11}B NMR data; i.e., $\delta = +62.76$ vs -13.2 ppm, respectively. The computed value was obtained at the DZ//3-21G (IGLO//Geometry-optimization) level; at the DZ//6-31G* level the calculated value is not much different, $\delta = -13.4$ ppm. The calculated energies of the geometry optimized isomers indicate that the *closo* structure **XI** is less stable than the bicyclo[2.1.1] isomer **XII** depicted in Figure 2 by 24 kcal/mol at the highest level of theory (6-31G*) that available computer resources would allow. The static [2.1.1] bicyclic compound **XII** in Figure 1 would lead to two ^{11}B resonances unless accidental overlap occurred. On the other hand, if fast equilibration takes place between the several degenerate forms of the bicyclic isomer **XII** (i.e. via various sequential *B*–*B* rotations),[25] a single resonance could be expected. The calculated average ^{11}B chemical shift is $<\delta>$

---

(18) For examples of the application of IGLO to boron compounds see: (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. *Heteroat. Chem.* **1991**, *2*, 499–506. (f) Bühl, M.; Schleyer, P. v. R.; Havlas, Z.; Hnyk, D.; Hermanek, 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) Bühl, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 477–491. (i) Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR, Principles and Progress*; Springer-Verlag: Berlin, 1990; Vol. 23, pp 210–212. (j) Köster, R.; Seidel, G.; Wrackmeyer, B.; Blaeser, D.; Boese, R.; Bühl, M.; Schleyer, P. v. R. *Chem. Ber.* **1992**, *125*, 663; **1991**, *24*, 2715–2724. (k) Kang, S. O.; Bausch, J. W.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1992**, *114*, 6248–6249. (l) Bausch, J. W.; Prakash, G. K. S.; Bühl, M.; Schleyer, P. v.- R.; Williams, R. E. *Inorg. Chem.* **1992**, *31*, 3060–3062. (m) Bausch, J. W.; Prakash, G. K. S.; Williams, R. E. *Inorg. Chem.* **1992**, *31*, 3763–3768. (n) Bühl, M.; Mebel, A. M.; Charkin, O. P.; Schleyer, P. v. R. *Inorg. Chem.* **1992**, *31*, 3769–3775. (o) Onak, T.; Tseng, J.; Tran, D.; Herrera, S.; Chan, B.; Arias, J.; Diaz, M. *Inorg. Chem.* **1992**, *31*, 3910–3913. (p) Onak, T.; Tseng, J.; Diaz, M.; Tran, D.; Arias, J.; Herrera, S.; Brown, D. *Inorg. Chem.* **1993**, *32*, 487–489. (q) Mebel, A. M.; Charkin, O. P.; Bühl, M.; Schleyer, P. v. R.; *Inorg. Chem.* **1993**, *32*, 463–468. (r) Mebel, A. M.; Charkin, O. P.; Schleyer, P. v. R. *Inorg. Chem.* **1993**, *32*, 469–473. (s) McKee, M. L.; Bühl, M.; Schleyer, P. v. R. *Inorg. Chem.* **1993**, *32*, 1712–1715. (t) Onak, T.; Tran, D.; Tseng, J.; Diaz, M.; Arias, J.; Herrera, S. *J. Am. Chem. Soc.* **1993**, *115*, 9210–9215.

(19) (a) GAUSSIAN-90: Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whitesides, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A.; Gaussian, Inc., Pittsburg PA. (b) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

(20) Barfield, M. In *Nuclear Magnetic Shieldings and Molecular Structure*; Tossell, J. A., Ed.; Kluwer: Boston, 1993; pp 523–537. Jiao, D.; Barfield, M.; Hruby, V. J. *J. Am. Chem. Soc.* **1993**, *115*, 10883–10887. Barfield, M. *J. Am. Chem. Soc.* **1993**, *115*, 6916–6928. Jiao, D.; Barfield, M.; Combariza, J. E.; Hruby, V. J. *J. Am. Chem. Soc.* **1992**, *114*, 3639–43. Jiao, D.; Barfield, M.; Hruby, V. J. *Magn. Res. Chem.* **1993**, *31*, 75–79. Barfield, M.; Yamamura, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 4747–4758.

(21) Keller, W.; Barnum, G. A.; Bausch, J. W.; Sneddon, L. G. *Inorg. Chem.* **1993**, *32*, 5058–5066.

(22) Huzinaga, S. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: New York, 1984.

(23) Onak, T.; Landesman, H. L.; Williams, R. E.; Shapiro, I. *J. Phys. Chem.* **1959**, *63*, 1533.

(24) Jameson, C. J.; Jameson, A. K.; Burrell, P. M. *J. Chem. Phys.* **1980**, *73*, 6013.

Table 1. Geometry Optimized (ab Initio) Energies (au)

compd[a]	Gaussian HF/3-21G opt	Gaussian HF/6-31G* opt
B_2H_6	−52.497 81	−52.812 40
1,6-$C_2B_4H_6$ (closo), **VII**	−176.917 62	−177.946 22
1,4-$C_2B_4H_6$ (2.1.1 bicyclic), **VIII**	−176.928 99	−177.930 03
2,3,4,5-$C_4B_2H_6$ (nido), **I**	−203.144 41	−204.310 21
$C_4B_2H_6$ (1,4-B,B′ planar), **II**	−203.164 66	−204.297 38
B-Cl_4-1,6-$C_2B_4H_2$ (closo), **XI**	−2 003.957 24	−2 013.713 87
B-Cl_4-1,4-$C_2B_2H_2$ (2.1.1 bicyclic), **XII**	−2 004.017 01	−2 013.751 73
B-Cl_2-2,3,4,5-$C_4B_2H_4$ (nido), **V**	−1 116.675 35	−1 122.204 65
B-$Cl_2C_4B_2H_4$ (1,4-B,B′ planar), **VI**	−1 116.724 68	−1 122.223 29
$ClB(CH{=}CH_2)_2$, W form	−635.971 17	−639.146 62
$ClB(CH{=}CH_2)_2$, Z form	−635.969 69	−639.146 18
$ClB(CH{=}CH_2)_2$, U form	−635.966 84	−639.145 11
$Cl_2BCH{=}CH_2$	−1 016.258 56	−1 021.205 00
$ClBMe_2$	−560.699 27	−563.456 13
Cl_2BMe	−978.622 48	−983.359 58
BCl_3	−1 396.533 11	−1 403.254 34
$ClBF_2$	−679.821 36	−683.213 91
Cl_2BF	−1 038.177 39	−1 043.233 03
BCl_4^- ion	−1 853.972 74	−1 862.846 88
HCl	−457.869 43	−460.059 98
Cl^- ion (gas)	−457.353 59	−459.526 00
CH_3Cl	−496.689 48	−499.093 15
B-F_4-1,6-$C_2B_4H_2$ (closo), **IX**	−570.470 13	−573.553 15
B-F_4-1,4-$C_2B_4H_2$ (2.1.1 bicyclic), **X**	−570.577 02	−573.631 69
B-F_2-2,3,4,5-$C_4B_2H_4$ (nido), **III**	−399.941 81	−402.132 42
B-$F_2C_4B_2H_4$ (1,4-B,B′ planar), **IV**	−400.005 41	−402.168 84
$FB(CH{=}CH_2)_2$, W form	−277.610 46	−279.120 68
$FB(CH{=}CH_2)_2$, Z form	−277.609 09	−279.119 82
$FB(CH{=}CH_2)_2$, U form	−277.605 96	−279.117 54
$F_2BCH{=}CH_2$	−299.545 62	−301.161 90
$FBMe_2$	−202.340 50	−203.429 60
F_2BMe	−261.911 75	−263.317 05
BF_3	−321.465 84	−323.195 49
BF_4^- ion	−420.492 47	−422.725 15
$FCCl_3$	−1 508.381 68	−1 515.711 64
HF	−99.460 22	−100.002 91

[a] The geometries for the 6-31G* optimized carboranes are found in Figures 1 and 2. The 6-31G* optimized energies for CH_3Cl and $CFCl_3$ are in agreement with those in: Ignacio, E. W.; Schlegel, H. B. *J. Phys. Chem.* **1992**, *96*, 5830−5837. The 6-31G* optimized geometry measurements for CH_3Cl are 1.077 Å for CH, 1.784 Å for CCl, 108.45° for HCCl; for $CFCl_3$, 1.322 Å for FC, 1.757 Å for FC, 107.99° for FCCl. The literature geometry measurements (Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*: *Techniques of Chemistry*, 3rd ed.; Wiley: NY, 1984; Vol. 18. Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619−721) for CH_3Cl are CH 1.09 Å, CCl 1.781 Å, and HCCl 108.0°; and for $CFCl_3$ CF1.33 Å, CCl 1.76 Å, ClCCl 109.40°. The 6-31G* optimized geometrical parameters for CH_3BF_2 are 1.313 Å for BF, 1.568 Å for BC, 1.086 Å for HC, 116.1° for FBF, and 111.0° for HCB; for CH_3BCl_2 they are 1.762 Å for BCl, 1.567 Å for BC, 1.085 Å for HC, 117.8° for ClBCl, and 110.9° for HCB. This compares with the literature (Cox, A. P. *J. Mol. Struct.* **1983**, *97*, 61. Hubbard, S. D.; Cox, P. A. *J. Mol. Spectrosc.* **1986**, *115*, 118−214. Cheung, C.-C. S.; Beaudet, R. A. *J. Mol. Spectrosc.* **1971**, *36*, 337−340; Bauer, S. H.; Hastings, J. M. *J. Am. Chem. Soc.* **1942**, *64*, 2686) experimental values of BC 1.559 Å, BF 1.324 Å, HC 1.104 Å, FBF 116.0°, HCB 110.6° for CH_3BF_2 and: HC 1.102 Å, BCl 1.753 Å, BC 1.563 Å, ClBCl 117.8°, HCB 110.4° for CH_3BCl_2. The BCl experimental bond distance in BCl_3 is measured to be 1.742 Å (Dewar, M. J. S.; Jie, C.; Zoebisch, F. G. *Organometallics* **1988**, *7*, 513−21. Kanaka, S.; Marata, Y.; Kuchitsu, K.; Morino, Y.; *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1134−1146); our 6-31G* optimized distance is 1.745 Å. The 6-31G* optimized geometry of BF_3 yields a B−F bond distance of 1.301 Å which is comparable to the 1.31 Å distance found by K. Kuchitsu and S. Konaka (*J. Chem. Phys.* **1965**, *45*, 4342−4347) and to the 1.309 Å found by S. G. W. Ginn, J. K. Kennedy and J. Overend (*J. Chem. Phys.* **1968**, *48*, 1571). Geometry data from the 6-31G* optimization of $CH_2{=}CHBF_2$: BF 1.313 Å; BC 1.551 Å; FBF 116.7°; CCB 121.5°; CCBF 0.0°; from microwave data (Durig, J. R.; Carter, R. O.; Odom, J. D. *Inorg. Chem.* **1974**, *13*, 701), assuming that the vinyl structure is unchanged from that of propene, BC 1.536 Å ± 0.02; BF 1.336 Å; FBF 114.5°; CCB 120.2° and that the compound is either planar or very nearly planar. Reference 14 in P. H. Blustin (*J. Chem. Phys.* **1977**, *66*, 5648−5655) gives the HCl bond distance as 1.274 Å; our 6-31G* optimized distance is 1.266 Å. Our 6-31G* optimized geometrical parameters for the other compounds in the table are: for $ClB(CH{=}CH_2)_2$ (W configuration): BCl 1.793 Å, BC 1.556 Å, CC 1.328 Å, CH 1.075−1.080 Å, CBC 121.3°, CBClC 180.0°; for $FB(CH{=}CH_2)_2$ (W configuration): BF 1.333 Å, BC 1.561 Å, CC 1.327 Å, CH 1.076−1.079 Å, CBC 124.5°, CBFC 180.0°; for $ClB(CH_3)_2$: BCl 1.788 Å, BC 1.574 Å, CH 1.084−1.086 Å, CBC 123.9°, CBClC 180.0°; for $FB(CH_3)_2$: BF 1.329 Å, BC 1.579 Å, CH 1.085−1.091 Å, CBC 124.8°, CBFC 180.0°; for $[BCl_4]^-$: BCl 1.873 Å; for $[BF_4]^-$: BF 1.329 Å; for $FBCl_2$: BF 1.299 Å, BCl 1.746 Å, ClBF 119.1°; for $ClBF_2$: BF 1.299 Å, BCl 1.748 Å, ClBF 120.3°; for HF: HF 0.911 Å.

$= +57.5$ ppm {i.e. $= [(+60.3) + (+54.7)]/2$} at the DZ//3-21G level and $\langle\delta\rangle = +56.1$ ppm {$= [(+58.4) + (+53.7)]/2$} at the DZ//6-31G* level. Both of these are in considerably better agreement with the reported chemical shift of $\delta = +62.76$ ppm than is that of the D_{4h} structure, **XI**. The calculated chemical shifts for the two types of borons of the static structure **XII** are sufficiently close in value to each other that accidental overlap of anticipated broad ^{11}B resonances would not be out of the question. Of course, other "classical" structures for $C_2B_4H_2Cl_4$ might be envisioned (e.g., the *B*-tetrachloro derivative of 3,4,5,6-tetraboracyclohexene),[26] but were not part of the present study.

---

(25) The bicyclic framework symmetry can be easily derived by twisting any one of the four B−B bonds of the *closo* structure, **XI**, to a position 90° from the original B_4 plane to become part of a plane that includes the two carbon atoms, as in **XII**. The detailed structural nature of such a transition state for such an isomerization was not sought but it would not be surprising to find that it may involve more than merely a simple 90° twist of a B−B bond (see: McKee, M. L. *J. Am. Chem. Soc.* **1988**, *110*, 5317−5321; **1992**, *114*, 879−881 and references therein). This would, most likely, have the effect of lowering the activation energy from that expected by the calculated energy difference (Table 1) between XI and XII.

(26) Budzelaar, P. H. M.; Kerk, S. M. v. d; Krogh-Jespersen, K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 3960−3967.

Table 2. ^{11}B NMR Chemical Shifts (ppm) Obtained Experimentally and from IGLO and GIAO Data

		δ IGLO,[b] ppm				δ GIAO,[b] ppm
compd	δ expt[a]	DZ//3-21G	DZ//6-31G*	II//3-21G	II//6-31G*	6-31G//6-31G*
$ClB(CH{=}CH_2)_2$, W form	56.7	57.4	56.4	57.3	56.0	56.5
$Cl_2BCH{=}CH_2$	52.4	65.4	64.6	56.6	55.2	58.0
$ClBMe_2$	77.2	77.6	76.1	78.2	76.0	74.3
Cl_2BMe	62.3	74.7	73.3	65.7	64.0	66.0
BCl_3	46.8	70.6	69.2	52.8	51.3	57.0
$ClBF_2$	19.8	27.9	26.4	23.8	22.3	21.2
Cl_2BF	32.3	46.4	44.8	37.2	35.5	37.8
BCl_4^- ion	6.6	16.7	13.8	15.2	12.0	17.8
$FB(CH{=}CH_2)_2$, W form	42.4	36.1	34.8	43.5	42.1	40.3
$FBMe_2$	59.0	53.4	51.8	60.1	57.3	54.6
F_2BMe	28.1	29.5	27.7	31.4	30.9	26.7
BF_3	11.6	15.1	13.9	13.2	12.0	9.2
BF_4^- ion	−1.1	−1.7	−2.0	0.7	1.3	−1.7
1,6-$C_2B_4H_6$ (closo), **VII**	−17	−16.9	−17.7	−17.0	−18.6	−17.4
1,4-$C_2B_4H_6$ (2.1.1 bicyclic), **VIII**	(−17)	48.5[d]	43.8[d]	54.0[d]	48.7[d]	46.9[d]
2,3,4,5-$C_4B_2H_6$ (nido), **I** (apex)	−60.8	−60.3	−62.3	−61.9	−63.0	−58.2
2,3,4,5-$C_4B_2H_6$ (nido), **I** (basal B)	10.3	15.5	13.1	14.3	12.0	11.9
$C_4B_2H_6$ (1,4-B,B′ planar), **II**	?	53.7	53.7	61.3	61.4	64.3
B-Cl_4-1,6-$C_2B_4H_2$ (closo), **XI**	(62.76)	−13.2	−13.4	*c*	*c*	−13.0
B-Cl_4-1,4-$C_2B_4H_2$ (2.1.1 bicyclic), **XII**	62.76	60.8[d]	59.3[d]	*c*	*c*	58.5[d]
B-F_2-2,3,4,5-$C_4B_2H_4$ (nido), **III**	(40)	−3.2[d]	−8.0[d]	*c*	*c*	−5.3[d]
B-$F_2C_4B_2H_4$ (1,4-B,B′ planar), **IV**	40	36.9	35.5	*c*	*c*	40.9

[a] Experimental chemical shifts were obtained from the following studies. For $Cl_2BCH{=}CH_2$: Good, C, D.; Ritter, D. M. *J. Am. Chem. Soc.* **1962**, *84*, 1162−1166. For $ClB(CH{=}CH_2)_2$, $ClBMe_2$, and Cl_2BMe: Barlos, K.; Kroner, J.; Nöth, H.; Wrackmeyer, *Chem. Ber.* **1977**, *110*, 2774; Wrackmeyer, B. *Z. Naturforsch.* **1980**, *35b*, 439−436. For $(CH_2{=}CH)_2BCl$: Hall, L. W.; Odom, J. D.; Ellis, P. D. *J. Am. Chem. Soc.* **1975**, *97*, 4527−4531. For $ClBF_2$, Cl_2BF, $FBMe_2$, F_2BMe, and BF_3: Fussstetter, H.; Nöth, H.; Wrackmeyer, B.; McFarlane, W. *Chem. Ber.* **1977**, *110*, 3172. For BX_4^- ion X = F, Cl: Thompson, R.; J.; Davis, J. C. *Inorg. Chem.* **1965**, *4*, 1464; Siwapinyoyos, G.; Onak, T. *J. Am. Chem. Soc.* **1980**, *102*, 420. For $FB(CH{=}CH_2)_2$ and other monoboron compounds see: Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag: New York, 1978. [b] The designation before the // marks represents the level of calculation carried out with IGLO or GIAO, respectively. The designation after the // marks represents the level of calculation used for the geometry optimization. The values in parentheses are for argument only, see text. The IGLO/DZ values for compounds **I** and **VII** are in good agreement with those in ref 18h. [c] Too large for IGLO/Basis-II calculations with available computational resources. [d] Average chemical shift.

Table 3. Fluorine-19 Chemical Shifts (ppm) and Experimental δ *vs* Calculated σ Values

		σ, IGLO[b]				σ, GIAO[b]
compd	expt[a] δ ($CFCl_3$)	DZ//3-21G	DZ//6-31G*	II//3-21G	II//6-31G*	6-31//6-31G*
$ClBF_2$	−78	302	311	285	291	306
Cl_2BF	−30	235	244	244	248	262
$F_2BCH{=}CH_2$	−89	334[d]	338[d]	303[d]	305[d]	322[d]
$FB(CH_3)_2$	−21	263	262	234	236	259
F_2BCH_3	−73	310	316	279	283	301
BF_3	−132	359	368	330	336	352
BF_4^- ion	−145	426	428	371	375	385
HF	−214	359	380	380	394	427
$F_2C_4B_2H_4$ (1,4-B,B′ planar), **IV**	−81	303	303	*c*	*c*	297
$F_2C_4B_2H_4$ (nido), **III**	(−81)	449[d]	467[d]	*c*	*c*	453[d]

[a] Experimental chemical shifts were obtained from the following studies. For $ClBF_2$, Cl_2BF, $FBMe_2$, F_2BMe, and BF_4^-: Fussstetter, H.; Nöth, H.; Wrackmeyer, B.; McFarlane, W. *Chem. Ber.* **1977**, *110*, 3172. For $ClBF_2$ and Cl_2BF: Coyle, T. D.; Stone, F. G. A. *J. Chem. Phys.* **1960**, *32*, 1892. For $F_2BCH{=}CH_2$: Coyle, T. D; Stafford, S. L.; Stone, F. G. A. *J. Chem. Soc.* **1961**, 3103. For $F_2BCH{=}CH_2$, BF_3, and BF_4^- ion: Emsley, J. W.; Phillips, L. *Prog. Nucl. Magn. Reson. Spectrosc.* **1971**, *7*, 1−526. For BF_3, $FBMe_2$, F_2BMe, and $F_2BCH{=}CH_2$: Barlos, K.; Kroner, J.; Nöth, H.; Wrackmeyer, B. *Chem. Ber.* **1977**, *110*, 2774. For HF, BF_3, and BF_4^- ion: Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR, Principles and Progress*; Springer-Verlag: Berlin, 1990; Vol. 23, pp 165−262. For HF and BF_3: Jameson, C. J.; Jameson, A. K.; Burrell, P. M. *J. Chem. Phys.* **1980**, *73*, 6013. For BF_3: Gutowsky, H. S.; Hoffman, C. J. *J. Chem. Phys.* **1951**, *19*, 1259. For $F_2C_4B_2H_4$: Timms, P. L. *J. Am. Chem. Soc.* **1968**, *90*, 4585. Value in parentheses is for argument only, see text. [b] The designation before the // marks represents the level of calculation carried out with IGLO or GIAO, respectively. The designation after the // marks represents the level of calculation used for the geometry optimization. [c] Too large for IGLO/Basis-II calculations with available computational resources. [d] Average chemical shift.

It is well established that the parent 1,6-$C_2B_4H_6$, **VII**, has D_{4h} cage symmetry.[1] Previous calculations[18h] at various levels of theory (DZ//3-21G, DZ//6-31G*, DZ//MP2/6-31G*, II′//MP2/6-31G*), give reasonably good agreement between the IGLO/NMR calculated and the observed ^{11}B chemical shift measured to be in the region of $\delta = -17$ to -19 ppm.[9] In light of the above structural considerations for the tetrachloro derivative, it was of interest to predict the ^{11}B chemical shift of the parent $C_2B_4H_6$ should there be a fast equilibration between degenerate [2.1.1] bicyclic forms, **VIII** (Figure 2). A calculated ^{11}B (weighted average) chemical shift is $\langle\delta\rangle = +48.5$ ppm (=average of $\delta = +51.9$ and $+45.2$ ppm) at the DZ//3-21G level and $\langle\delta\rangle = +43.9$ ppm (=average of $+46.8$ and $+40.9$ ppm) at the DZ//6-31G* level, both of which are in very poor agreement with the reported chemical shift of $\delta = -17$ (to -19) ppm for the known 1,6-$C_2B_4H_6$. The static form of the bicyclic structure, **VIII**, does not even have a calculated resonance close to that of the experimentally observed value. Consistent with these results, the calculated energies of the two isomers indicate that the *closo* cage geometry is more stable than the bicyclic structure by 10 kcal/mol at the 6-31G* level of theory (Table 1).

It is determined, in the present study, that at the 6-31G* level of theory the [2.1.1] bicyclic configuration of the *B*-tetrafluoro

Table 4. Fluorine-19 Chemical Shifts (ppm) and Experimental vs Calculated δ Values

		δ, IGLO[b]				δ, GIAO
compd	expt[a] δ ($CFCl_3$)	DZ//3-21G	DZ//6-31G*	II//3-21G	II//6-31G*	6-31//6-31G*
$ClBF_2$	−78	−157	−145	−82	−88	−93
Cl_2BF	−30	−90	−78	−78	−68	−49
F_2BVi	−89	−189[d]	−172[d]	−137[d]	−125[d]	−109[d]
$FBMe_2$	−21	−118	−96	−68	−56	−46
F_2BMe	−73	−165	−150	−113	−103	−88
BF_3	−132	−214	−202	−164	−156	−139
BF_4^- ion	−145	−281	−262	−205	−195	−172
HF	−214	−214	−214	−214	−214	−214
$F_2C_4B_2H_4$ (1,4-B,B′ planar), **IV**	−81	−158	−137	*c*	*c*	−84
$F_2C_4B_2H_4$ (nido), **III**	(−81)	−304[d]	−301[d]	*c*	*c*	−240[d]

[a] For references see Table 3. The values in parentheses are for argument only, see text. [b] The designation before the // marks represents the level of calculation carried out with IGLO or GIAO, respectively. The designation after the // marks represents the level of calculation used for the geometry optimization. [c] Too large for IGLO/Basis-II calculations with available computational resources. [d] Average chemical shift.

Table 5. Chlorine-35 Chemical Shifts (ppm) and Experimental vs Calculated Values

		δ, IGLO[b]				δ, GIAO[b]
compd	δ, expt[a] (aq Cl^- = 0; CH_3Cl = 50)	DZ//3-21G	DZ//6-31G*	II//3-21G	II//6-31G*	6-31//6-31G*
$Cl_2BCH{=}CH_2$	220	216[d]	291[d]	168[d]	209[d]	223[d]
$ClBMe_2$	244	218	303	193	244	244
Cl_2BMe	288	275	345	217	254	264
BCl_3	300	311	373	219	253	277
HCl	90	72	123	64	85	87
CH_3Cl	50	50	50	50	50	50
$FCCl_3$	470	635	582	561	504	499
Cl^- ion (gas)	−170	−309	−225	−160	−116	−90
$Cl_4C_2B_4H_2$ (2.1.1 bicyclic), **XII**	299.7	162[d]	236[d]	*c*	*c*	174[d]
$Cl_4C_2B_4H_2$ (closo), **XI**	(299.7)	−107	−32	*c*	*c*	−59

[a] Experimental chemical shifts were obtained from the following studies. For $Cl_2BCH{=}CH_2$: Good, C. D.; Ritter, D. M. *J. Am. Chem. Soc.* **1962**, *84*, 1162−1166. For $Cl_2BCH{=}CH_2$, $ClBMe_2$, Cl_2BMe, and BCl_3: Barlos, K.; Kroner, J.; Nöth, H.; Wrackmeyer, B. *Chem. Ber.* **1977**, *110*, 2774. For HCl: Gierke, T. D.; Flygare, W. H. *J. Am. Chem. Soc.* **1972**, *94*, 7277−7283; Chesnut, D. B. *J. Chem. Phys.* **1986**, *110*, 415−420. For HCl and Cl^-(gas): Lee, C. Y.; Cornwell, C. D. *Magnetic Resonance and Related Phenomena*; Proceedings of the 19th Congress Ampere, Heidelberg, Sept. 1976; pp 261−4; Fleischer, U. Ph.D. Thesis, Ruhr-Universität Bochum, Germany. For $Cl_4C_2B_4H_2$: Hosmane, N. S.; Islam, M. S.; Burns, E. G. *Inorg. Chem.* **1987**, *26*, 3236−3237. The value in parentheses is for argument only, see text. [b] The designation before the // marks represents the level of calculation carried out with IGLO or GIAO, respectively. The designation after the // marks represents the level of calculation used for the geometry optimization. [c] Too large for IGLO/Basis-II calculations with available computational resources. [d] Average chemical shift.

derivative of $C_2B_4H_6$, **X**, is 49 kcal·mol^{-1} more stable than the *closo* D_{4h} form, **IX**. Previous calculations at the PRDDO level of theory gave essentially the same qualitative result.[2] The outcome of a frequency calculation (i.e., no negative values) at the 6-31G* level on the bicyclic form indicates that a local energy minimum was located; but the *closo* D_{4h} form, **IX**, has one calculated negative frequency at the 6-31G* level of theory, implying that the *closo* form is a transition state structure. Ab initio/IGLO/NMR calculations on *B*-F_4-*closo*-1,6-$C_2B_4H_2$, **IX**, predict ^{11}B chemical shifts of −20.3 and −20.9 ppm at the DZ//3-21G and DZ//6-31G* levels, respectively. At these same two levels of theory the average ^{11}B chemical shift expected for a (possible) fast equilibration of degenerate forms of the [2.1.1] bicyclic structure, **X**, is $\langle\delta\rangle$ = +48.3 (=average of +51.5 and +45.1 ppm) or +46.3 (=average of +49.2 and +43.3 ppm) ppm, respectively. Once the *B*-tetrafluoro derivative is prepared it will be of considerable interest to compare the experimental NMR data with that calculated in the present study, with consequent structural ramifications.

It is well-established that the parent $C_4B_2H_6$ is both observed[5] and calculated[2] to be more stable in a *nido* (pentagonal pyramidal) configurations, **I** (Figure 1), of skeletal atoms than in a planar cyclic 1,4-$B_2C_4H_6$ configuration, **II** (Figure 1). But it has been strongly suggested that a *B,B′*-difluoro derivative of this compound has a planar C_4B_2 framework, **IV** (Figure 1).[4] The results of PRDDO calculations[2] suggest that the *B,B′*-difluoro derivative is 43 kcal/mol more stable in the planar 1,4-B_2C_4 skeletal arrangement, **IV**, than in the *nido*-C_4B_2 configuration, **III**. Our ab initio calculation at the 3-21G level of theory shows the same order of stability as that calculated by the PRDDO code, with the energy separation as 39.9 kcal·mol^{-1} (−399.941 81 au for the *nido* structure; −400.005 41 AU for the planar structure with less than 0.3 kcal/mol ZPE correction). At the 6-31G* level of theory the separation is 23.8 kcal/mol (with ZPE correction) with the planar configuration, **IV**, still found to be more stable. Our IGLO NMR calculations at the DZ level on the 3-21G optimized structures predict $\delta(^{11}B)$ = −32.9 (apex) and +26.5 (basal) ppm for the two non-equivalent borons of the 1,6-F_2-*nido*-2,3,4,5-$C_4B_2H_4$ structure, **III**, and δ = +36.9 ppm for the equivalent borons of the planar 1,4-F_2-1,4-$B_2C_4H_4$, **IV**. The IGLO calculations at the DZ level for the 6-31G* optimized structures are not much different and predict $\delta(^{11}B)$ = −37.2 (apex) and +21.2 (basal) ppm for the 1,6-F_2-*nido*-2,3,4,5-$C_4B_2H_4$ structure, **III**, and $\delta(^{11}B)$ = +35.3 ppm for the planar 1,4-F_2-1,4-$B_2C_4H_4$ configuration, **IV**. For the C-tetramethyl derivative of 1,4-F_2-1,4-$B_2C_4H_4$ an experimentally observed δ = +40.2 ppm is reported.[27] With the reasonable assumption that substitution of methyl for hydrogen on the skeletal carbons does not much affect the boron chemical shift, the agreement between calculated and experimental ^{11}B chemical shifts is quite good for the planar structure, **IV**, and very poor for the pyramidal structure, **III**, even should fast equilibration, on the NMR time scale, of apical and basal borons be invoked in the latter structure. This structural conclusion is in agreement with that of Timms et al.[4]

Similarly, geometry optimization of the *B,B′*-dichloro derivative of $C_4B_2H_6$ indicates that the planar configuration, **VI**, is

---

(27) The original report[4] cited a chemical shift value of −40.2 ppm; but since then, the signs of the boron chemical shifts have been reversed; in any case, the resonance is found downfield from the standard $BF_3{\cdot}Et_2O$.

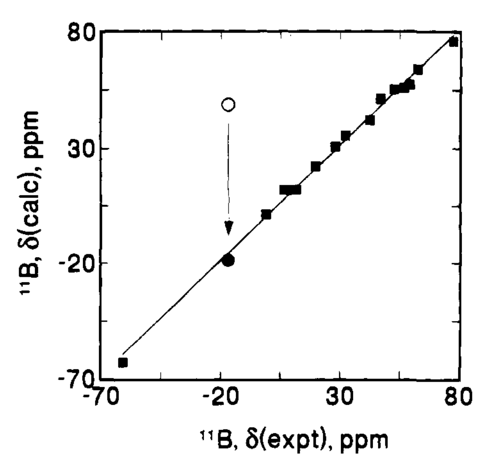

Figure 3. ^{11}B NMR chemical shift comparisons between experimental and calculated values for all those compounds in which shifts could be calculated at the IGLO II//6-31G* level of theory (see Table 2): (●) *closo*-1,6-$C_2B_4H_6$, **VII**; ○ average value for [2.1.1] bicyclic 1,4-$C_2B_4H_6$, **VIII** (see text). The relationship δ(IGLO/II//6-31G*) = δ(expt) × 1.008 + 1.028 with r^2 = 0.996 holds for the solid points.

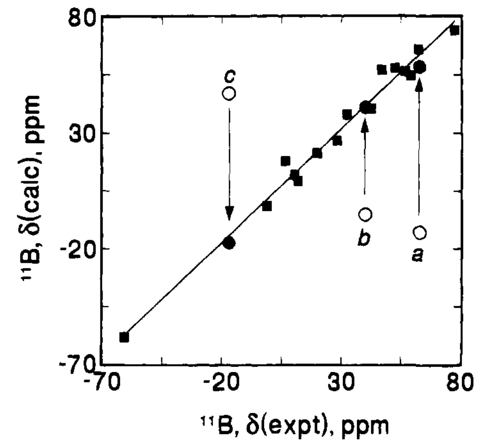

Figure 4. ^{11}B NMR chemical shift comparisons between experimental and calculated (GIAO) values (see Table 2): compound a, *B*-Cl_4-*closo*-1,6-$C_2B_4H_2$, **XI** (○) → [2.1.1] bicyclic *B*-Cl_4-1,4-$C_2B_4H_2$, **XII** (●); compound b, *nido*-*B*-F_2-2,3,4,5-$C_4B_2H_4$, **III** (○) → planar *B*-F_2-1,4-B,B'-$C_4B_2H_4$, **IV** (●); compound c, (2.1.1 bicyclic) 1,4-$C_2B_4H_6$, **VIII** (○) → *closo*-1,6-$C_2B_4H_6$, **VII** (●). For the reasons mentioned in the text of the study, an average chemical shift (Table 2) for a hypothetical fluxional molecule is assumed for each of the two [2.2.1] bicyclic systems and for the *B*-F_2-*nido*-2,3,4,5-$C_4B_2H_4$. δ(GIAO) = δ(expt) × 0.978 + 1.99 with r^2 = 0.983 holds for the solid points.

more stable than the *nido* structure, **V**, at both the 3-21G and 6-31G* levels of theory. The IGLO predicted ^{11}B NMR chemical shift(s) of both the planar and *nido* configurations of *B*,*B'*-Cl_2-$C_4B_2H_4$ are given in Table 2 and (a) the calculated value of $\delta = +54.3$ ppm for the planar structure (at the DZ//3-21G level) and $\delta = +52.9$ ppm (at the DZ//6-31G* level) is in the region expected for a boron attached to a single chlorine and two vinyl groups;[15,28] (b) the calculated values of $\delta = -39.5$ (for the apical boron) and $\delta = +24.4$ (for the basal boron) ppm of the hypothetical pentagonal pyramidal structure, **V**, are consistent with expected (ca. 10−25 ppm) deshielding from the parent $C_4B_2H_6$, **I** (apical boron −60.8 ppm, basal boron +10.4 ppm).[18h,29] When the *B*,*B'*-dichloro derivative is synthesized it will be of interest to compare the NMR data with that calculated in the present study, with the consequent structural implications.

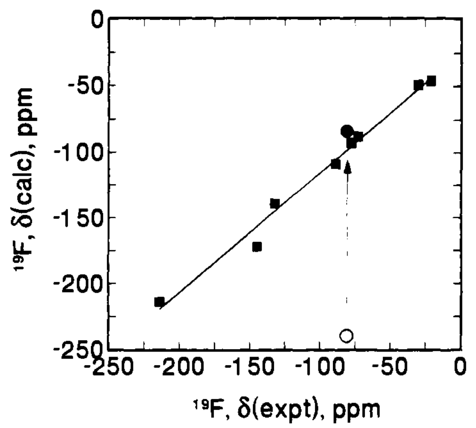

Figure 5. ^{19}F NMR chemical shift comparisons between experimental and calculated (GIAO) values (see Table 4): (○) *B*-F_2-*nido*-2,3,4,5-$C_4B_2H_4$, **III**; (●) (1,4-*B*,*B'*-planar) *B*-$F_2C_4B_2H_4$, **IV** (see text). The relationship δ(GIAO) = δ(expt) × 0.911 − 24.7 with r^2 = 0.986 holds for the solid points.

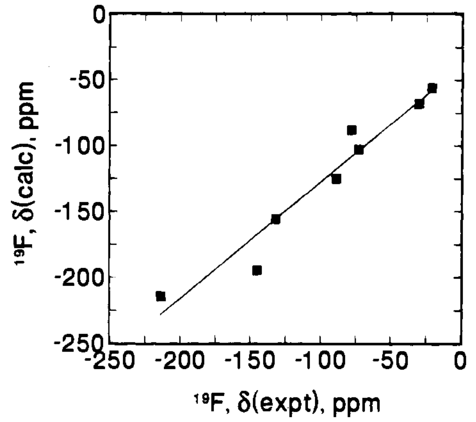

Figure 6. ^{19}F NMR chemical shift comparisons between experimental and calculated values for all those compounds in which shifts could be calculated at the IGLO II//6-31G* level of theory (see Table 4). The best fit relationship is δ(IGLO/II//6-31G*) = δ(expt) × 0.883 − 39.3 with r^2 = 0.939.

The above arguments and conclusions depend on the reliability of ab initio/NMR computational results on known boron systems. For ^{11}B nuclei in polyhedral boron systems, numerous studies have shown that one can expect very good to excellent correspondence between experimental and theoretical results.[18] For simple (non-polyhedral) boron systems, fewer studies have appeared in the literature.[16e] Obviously, a study of boron compounds containing F−B and Cl−B bonds would be of considerable relevance to the present study. In this regard, ^{19}F shifts for some halogenated monoboron systems have been used in calculational NMR correlations,[30] and in connection with halopolyboron compounds in the present study it was convenient to include those fluoromonoboron and chloromonoboron molecules for which both ^{19}F/^{11}B or ^{35}Cl/^{11}B pairs of experimental information were available. This includes the following: $XB(CH{=}CH_2)_2$, $X_2BCH{=}CH_2$, $XBMe_2$, X_2BMe, BX_3, BX_4^- ion (X = F, Cl); $ClBF_2$; and Cl_2BF. Additional, a few non-boron "standards" for the halogen NMR studies were included (e.g. HCl, CH_3Cl, HF). Tables 2−5 and Figures 3−9 summarize the data and correlative results for these compounds. Very acceptable ab initio/IGLO/NMR and ab initio/GIAO/NMR correlations are found for ^{11}B, ^{19}F, and ^{35}Cl at the levels of

---

(28) Hall, L. W.; Odom, J. D.; Ellis, P. D. *J. Am. Chem. Soc.* **1975**, *97*, 4527.

(29) Onak, T.; Wong, G. T. F. *J. Am. Chem. Soc.* **1970**, *92*, 5226.

(30) A few such compounds have been reported in connection with earlier ab initio/NMR studies, see ref 16e. This work also presented correlative information for ^{11}B (BF_3 included), ^{19}F (HF, BF_3, BF_4^- included), and ^{35}Cl (CH_3Cl, Cl^-_{aq} included) chemical shifts.

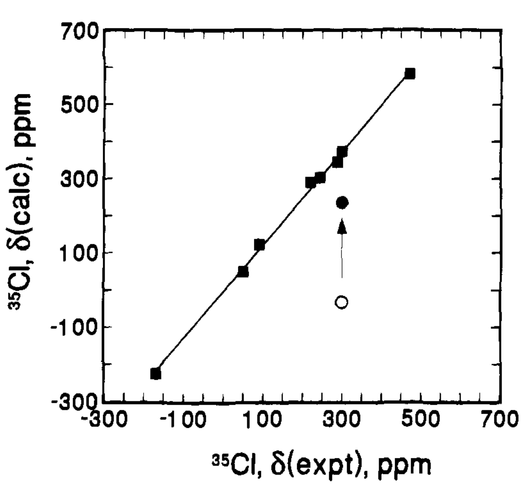

Figure 7. ^{35}Cl NMR chemical shift comparisons between experimental and calculated (IGLO; DZ//6-31G*) values (see Table 5): (○) *B*-Cl_4-*closo*-1,6-$C_2B_4H_2$, **XI**; (●) average value for [2.2.1] bicyclic *B*-Cl_4-1,4-$C_2B_4H_2$, **XII** (see text). The relationship δ(IGLO) = δ(expt) × 1.258 − 4.61, r^2 = 0.998 holds for the solid squares.

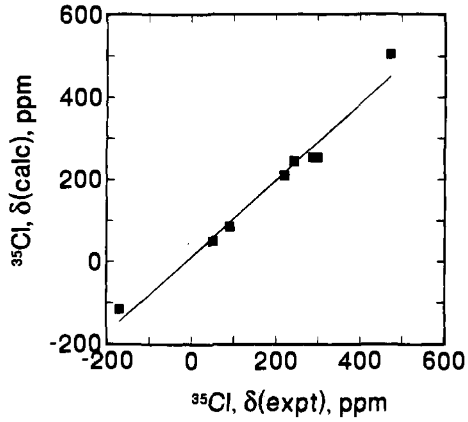

Figure 8. ^{35}Cl NMR chemical shift comparisons between experimental and calculated (IGLO; II//6-31G*) values (see Table 5). The best fit relationship is δ(IGLO/II//6-31G*) = δ(expt) × 0.930 + 11.8 with r^2 = 0.973.

theory (Figures 3−9). The large size of **III**, **IV**, **XI**, and **XII** precluded Basis-II (IGLO) NMR shift calculations on these compounds. Nevertheless, the linear correlation(s) between available experimental data and calculated chemical shifts, shown in the several figures, are quite convincing and show that the conclusions reached earlier in the present study are reliable. In each graph of Figures 3, 4, 5, 7, and 9, one to three points are not compatible with the linear relationships derived from the simple non-cage compounds. In every one of these cases, arguments were presented earlier in this discussion section to invalidate the assignment(s) of experimental shift(s) to a compound of that structure. In these instances an arrow in the figure(s) points to the piece of data associated with a structural isomer that is in much better agreement with the linear correlative NMR results. Thus (2.1.1 bicyclic) *B*-Cl_4-1,4-$C_2B_4H_2$, **XII**, gives calculated ^{11}B and ^{35}Cl NMR chemical shifts in considerably better agreement with the experimental data than does the isomeric *B*-Cl_4-*closo*-1,6-$C_2B_4H_2$, **XI**. Additionally, the planar *B*-F_2-1,4-B,B′-$C_4B_2H_4$, **IV**, results in calculated ^{11}B and ^{19}F NMR chemical shifts that are more consistent with available experimental data than does the isomeric *nido*-*B*-F_2-2,3,4,5-$C_4B_2H_4$, **III**.

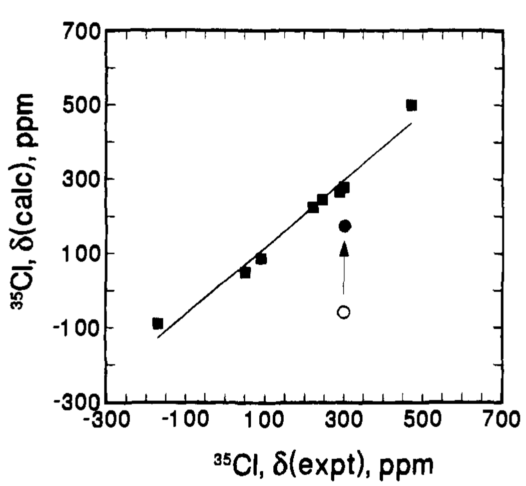

Figure 9. ^{35}Cl NMR chemical shift comparisons between experimental and calculated (GIAO) values (see Table 5): (○) *B*-Cl_4-*closo*-1,6-$C_2B_4H_2$, **XI**; (●) [2.1.1] bicyclic *B*-Cl_4-1,4-$C_2B_4H_2$, **XII**. The relationship δ(GIAO) = δ(expt) × 0.906 +25.7 with r^2 = 0.975 holds for the solid squares. An average chemical shift for a hypothetical fluxional molecule (see text) is assumed for the [2.1.1] bicyclic system.

The configuration of $XB(CH{=}CH_2)_2$ (X = F and Cl) is unknown among the three logical planar (or near planar) rotamers: U-shaped, Z-shaped, and W-shaped. With both X = F and Cl, the calculated energies, Table 1, suggest that the planar W-shaped configuration is the most favored. A ^{11}B IGLO calculation on each optimized configuration indicated insignificant differences in chemical shift between the three conformers. The U-shaped isomer (X = F) is the one most related to *B*-F_2-1,4-B,B′-$C_4B_2H_4$, **IV**, and it is satisfying that the ^{11}B NMR chemical shifts for the two (the latter as the C-methyl derivative) are not very much different.

A comparison of both IGLO and GIAO results reported in this study shows essentially the same trends. At the highest levels of theory that could reasonably be employed for all of the compounds, the ^{11}B and ^{35}Cl results are quite comparable and only the ^{19}F results appear to agree slightly better with the application of the GIAO approach than with the highest level of theory available to us via the IGLO approach, cf. Figures 5 and 6. The agreement between the two calculational approaches, at the examined levels of theory, is consistent with previous work.[16−18]

Acknowledgment. The authors thank the NSF (CHE-9222375) for partial support of this project. M.D. thanks the MBRS-NIH program (Grant S06GM08101) for partial support. California State University, Sacramento, CA, provided access to the Multiflow Trace (NSF Grant No. CHE-8822716) minisupercomputer facilities. NSF is thanked for the Convex 220 minisupercomputer located at the University of Arizona. We also thank M. Schindler for permission to use the IGLO program designed by W. Kutzelnigg and M. Schindler. The GIAO program was made available to us by P. Pulay at the University of Arkansas. We thank U. Fleischer, Ruhr-Universität Bochum, for sending us a portion of his thesis containing information concerning ^{35}Cl shifts of various standards, for valuable advice about the IGLO code, and for helpful comments on the manuscript.

JA942335K