

Decisive Electron Correlation Effects on Computed ^{11}B and ^{13}C NMR Chemical Shifts. Application of the GIAO-MP2 Method to Boranes and Carbaboranes

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Abstract: The performance of ^{11}B NMR chemical shift computations at a *correlated* (GIAO-MP2/TZP') level of ab initio theory is assessed for the first time. For molecules where SCF based methods (e.g. IGLO or GIAO-SCF) perform well, correlation effects on δ are negligible and IGLO, GIAO-SCF, and GIAO-MP2 results are equally satisfactory. But for problem cases e.g. 1,5- $\text{C}_2\text{B}_3\text{H}_5$ (**1**) and B_4R_4 (**3c**, R = *t*-Bu), the large (10–35 ppm) errors obtained with *uncorrelated* wave functions are corrected at GIAO-MP2: excellent accord is achieved with the experimental values. While correlation effects on $\delta^{11}\text{B}$ are negligible for the third problem molecule, 1,2- $\text{C}_2\text{B}_3\text{H}_7$ (**2**), the discrepancies proved to be due to inaccuracies in the early experimental $\delta^{11}\text{B}$ values. Remeasurements show the published IGLO predictions to have been correct. However, the GIAO-MP2 computed $\delta^{13}\text{C}$ values for **2**, and for **1** as well, are superior to the IGLO results. For the elusive B_4F_4 (**3e**), $\delta^{11}\text{B} = 44.7$ is predicted. Calibration is provided by B_2F_4 , B_2Cl_4 , and B_4Cl_4 (**3d**), as well as by B_4H_{10} (**4**), B_3H_9 (**5**), the two $\text{C}_2\text{B}_4\text{H}_6$ isomers (**6** and **7**), and $\text{C}_2\text{B}_5\text{H}_7$ (**8**) whose accurate structures were established earlier by means of the combined ab initio/IGLO/NMR method: the correlated MP2/TZP' chemical shifts result in comparably good agreement with the experimental values. A number of the ^{13}C chemical shifts in these carbaboranes improve at the MP2/TZP' level as well.

Introduction

The combination of high-level ab initio optimized geometries, theoretically computed NMR chemical shifts, and experimental NMR data affords a structural tool^{1–3} that can now be routinely applied for structural elucidations as well as the characterization of newly synthesized compounds.⁴ This is now possible due to the development, implementation, and extensive performance tests of several practical methods for chemical shift calculations: GIAO (gauge including atomic orbitals),⁵ IGLO (individual gauge for localized orbitals),⁶ and LORG (localized orbitals, local origin).⁷

Extensive investigations on boron hydrides and carboranes have established² that experimental ^{11}B NMR chemical shifts for almost all of these compounds can be reproduced satisfactorily at the IGLO-SCF/II'/MP2/6-31G* level of theory. In view of the superior performance of geometries when optimized at *correlated* levels (MP2 vs both SCF and experimental structures),² it is remarkable that *noncorrelated* wave functions often compute ^{11}B chemical shifts within $\Delta\delta \approx 2\text{--}3$ of the experimental values.⁸

Nevertheless, two problem molecules, which gave significantly poorer agreement, were identified in our earlier survey.² The carboranes 1,5- $\text{C}_2\text{B}_3\text{H}_5$ (**1**) and 1,2- $\text{C}_2\text{B}_3\text{H}_7$ (**2**) (see Figure 1) gave maximum deviations from experiment of $\Delta\delta \approx 10$ and 8, respectively. Because of the high symmetry of **1** (D_{3h}) and its excellent experimental⁹ and computational^{2,10} characterization, this case was particularly bothersome. The possibility was suggested that these "small strained carboranes ... require even higher (e.g. correlated) levels of theory for a correct description of geometries and chemical shifts."²

(7) Hansen, A. E.; Bouman, T. D. *J. Chem. Phys.* **1984**, *82*, 5035; **1989**, *91*, 3552.

(8) (a) Note that the "direct" correlation effects on the calculated chemical shifts are usually less important than the "indirect" correlation effects via changes in the molecular geometries (calculated chemical shifts are more accurate when correlated geometries are employed). The good performance of SCF chemical shift calculations is due in part to the cancellation of errors, when relative chemical shifts, δ (the difference between two shielding constants), are employed. This compensates to some extent for the lack of correlation effects. The importance of electron correlation is usually much more pronounced in the calculation of absolute shielding constants (see ref 16a). (b) The high absolute (ca. 2–3 ppm) accuracy of computed with experimental boron chemical shifts should not be expected for other nuclei, e.g. ^{31}P , where deviations of 10 ppm constitute good agreement. The ^{11}B NMR scale covers only ca. 150 ppm, in contrast to the much larger ^{31}P scale of ca. 1000 ppm.

(9) (a) McNeill, E. A.; Gallaher, K. L.; Scholer, R. F.; Bauer, S. H. *Inorg. Chem.* **1973**, *12*, 2108. (b) Todd, L. J. *Pure Appl. Chem.* **1972**, *30*, 587. (c) Grimes, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 1895.

(10) McKee, M. L. *Inorg. Chem.* **1988**, *27*, 4241.

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(1) See the extensive bibliography in ref 2 and e.g. the following as well as references therein: Schleyer, P. v. R.; Carneiro, J. W. de M. *J. Am. Chem. Soc.* **1990**, *112*, 4046. Koch, W.; Schleyer, P. v. R.; Buzek, P.; Liu, B. *Croat. Chim. Acta* **1992**, *65*, 655. Buzek, P.; Schleyer, P. v. R.; Sieber, S. *Chem. Unserer Zeit* **1992**, *26*, 116. The most recent applications to boron compounds include: Mebel, A.; Charkin, O. P.; Bühl, M.; Schleyer, P. v. R. *Inorg. Chem.* **1993**, *32*, 463, 469. McKee, M. L.; Bühl, M.; Schleyer, P. v. R. *Inorg. Chem.* **1993**, *32*, 1712. Hynk, D.; Bühl, M.; Schleyer, P. v. R.; Holden, H. V.; Gunderson, S.; Müller, J.; Paetzold, P. *Inorg. Chem.* **1993**, *32*, 2442. Bühl, M.; Mebel, A. M.; Charkin, O. P.; Schleyer, P. v. R. *Inorg. Chem.* **1992**, *31*, 3769. Bühl, M.; Schleyer, P. v. R. *Struct. Chem.* **1993**, *4*, 1.

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

(3) E.g.: (a) Bausch, J. W.; Prakash, G. K. S.; Williams, R. E. *Inorg. Chem.* **1992**, *31*, 3763. (b) Bausch, J. W.; Prakash, G. K. S.; Williams, R. E.; Bühl, M.; Schleyer, P. v. R. *Inorg. Chem.* **1992**, *31*, 3060. (c) Bühl, M.; Mebel, A. M.; Charkin, O. P.; Schleyer, P. v. R. *Inorg. Chem.* **1992**, *31*, 3769.

(4) Onak, T.; Tseng, J.; Tran, D.; Herrera, S.; Chan, B.; Arias, J.; Diaz, M. *Inorg. Chem.* **1992**, *31*, 3910.

(5) (a) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789. (b) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251. (c) Häser, M.; Ahlrichs, R.; Baron, H. P.; Weis, P.; Horn, H. *Theor. Chim. Acta* **1992**, *83*, 455.

(6) (a) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. (b) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919. (c) Review: Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR, Basic Principles and Progress*; Springer Verlag: Berlin, Heidelberg, 1990; Vol. 23, p 165.

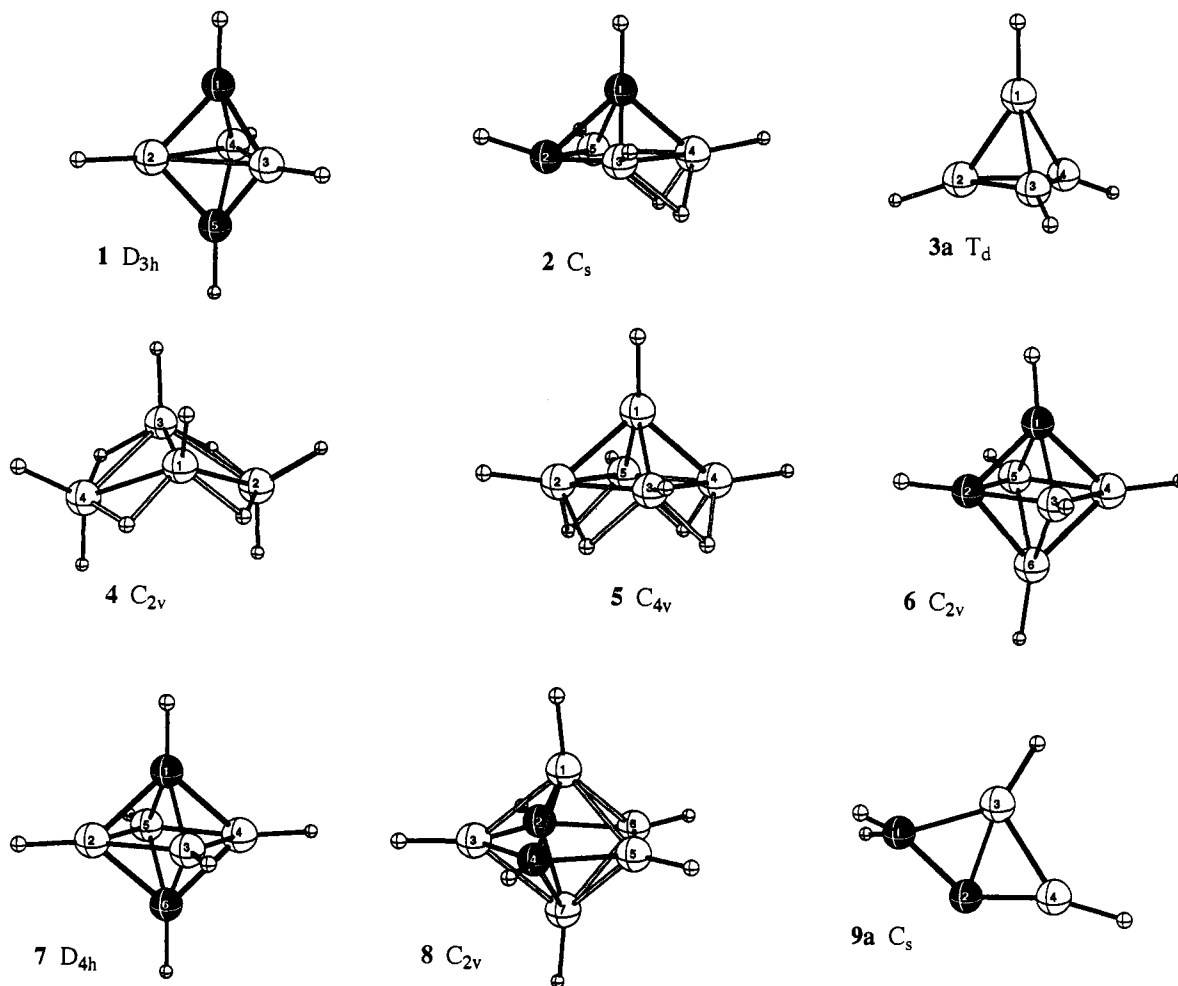


Figure 1. Representation of the MP2/6-31G* geometries of the boranes and carbaboranes considered in this study. The carbon atoms are darkened. With the exception of 3 and 9, these have been taken from ref 2. The geometries of 3a and its B_4R_4 derivatives, R = CH₃ (3b), R = tBu (3c), R = Cl (3d), and R = F (3e), are given in the footnotes of Table II. The geometries of 9a reported in ref 17 were refined at MP2/6-31G*. See Table IV for the experimentally-studied derivatives of 9a: 9b and 9c.

A third problem case with an unambiguous tetrahedral geometry, $B_4(t\text{-Bu})_4$ (3c),^{11,12} has been identified more recently. The IGLO¹¹ B chemical shifts, computed for the reasonable model, $B_4\text{Me}_4$ (3b), are 40 ppm in error.

Very recently, methods for correlated chemical shift calculations have been devised, namely GIAO-MP2 [or GIAO-MBPT-(2)]¹³ and two (nearly) gauge-origin independent versions of SOPPA (second-order polarization propagator approximation).¹⁴ In addition, a multiconfigurational SCF version of IGLO has been formulated and implemented.¹⁵ The first applications of the GIAO-MP2 method, e.g., to the chemical shifts of carbon, nitrogen, oxygen, aluminum, etc.,^{13,16} show, in some cases, significant, and even decisive improvements in accuracy over the chemical shift results computed at the SCF level. We now assess the effect of dynamic electron correlation on the ¹¹B chemical shifts for the first time. We focus on the problem cases, 1, 2, and

3. While our calibration study establishes that correlation effects are negligible for boranes, like e.g. B_4H_{10} (4), which were well-behaved in our earlier work, they can be very large, e.g. $\Delta\delta \approx 35$ for $B_4\text{Me}_4$ (3b). In addition, the halogenated boranes, B_2X_4 and B_4X_4 (X = F and Cl), are examined in this context.

Also included are results for boracyclopropylideneborane 9a, a promising candidate for electron-correlated chemical shift calculations because of its nonclassically bridged C=B double bond (see Figure 1).^{17,18} Consistent with the unique geometrical configuration at carbon C2, its computed NMR ¹³C chemical shift (unlike that of B4 which also participates in the double bond) is sensitive to electron correlation effects. This also is found to be true for the ¹³C shifts in some of the other carbaboranes included in this study.

Methods, Basis Sets, and Geometries

Geometries have been fully optimized in the designated symmetry employing standard methods¹⁹ and the Gaussian 90,^{20a} CADPAC,^{20b} and ACES II²¹ program packages. Chemical shifts have been evaluated using the IGLO⁶ and the GIAO-MP2^{13,21} programs employing various

(11) (a) Davan, T.; Morrison, J. A. *J. Chem. Soc., Chem. Commun.* **1981**, 250. (b) Klusik, H.; Berndt, A. *J. Organomet. Chem.* **1982**, 234, C17.

(12) Mennekens, T.; Paetzold, P.; Boese, R.; Bläser, D. *Angew. Chem., Int. Ed. Engl.* **1991**, 30, 173.

(13) Gauss, J. *Chem. Phys. Lett.* **1992**, 191, 614.

(14) (a) Bouman, T. D.; Hansen, A. E. *Chem. Phys. Lett.* **1990**, 175, 292. (b) Sauer, S. P. A.; Paldarova, I.; Oddershede, J. *Mol. Phys.*, in press. *Theor. Chim. Acta* Submitted for publication.

(15) (a) Kutzelnigg, W.; van Wüllen, C.; Fleischer, U.; Franke, R.; v. Mourik, T. In *Nuclear Magnetic Shieldings and Molecular Structure*; Tossell, J. A., Ed.; Kluwer Academic: Amsterdam, 1993. (b) van Wüllen, C.; Kutzelnigg, W. *Chem. Phys. Lett.* **1993**, 205, 563.

(16) (a) Gauss, J. *J. Chem. Phys.* **1993**, 99, 3629. (b) Gauss, J.; Schneider, U.; Ahlrichs, R.; Dohmeier, C.; Schnöckel, H. *J. Am. Chem. Soc.* **1993**, 115, 2402.

(17) (a) Budzelaar, P. H. M.; Schleyer, P. v. R.; Krogh-Jespersen, K. *Angew. Chem., Int. Ed. Engl.* **1984**, 23, 825. (b) Budzelaar, P. H. M.; Krogh-Jespersen, K.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1985**, 107, 2773. (c) Frenking, G.; Schaefer, H. F., III *Chem. Phys. Lett.* **1984**, 109, 521.

(18) (a) Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1983**, 22, 877. (b) Wieczorek, C.; Allwohn, J.; Schmidt-Lukasch, G.; Hunold, R.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 398.

(19) Hehre, W.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

basis sets: DZ—B,C (7s3p,4s2p), H (3s,2s);²²II'—B,C (9s5p1d,5s4p1d); H (3s,2s);²² DZP—B,C,F (9s5p1d,4s2p1d);^{23a} Si (12s8p1d,6s4p1d);^{23a} Cl (11s7p1d,6s4p1d);^{23b} H (4s1p,2s1p);^{23a} TZP—B,C,F (11s6p1d,5s3p1d);^{23a} Si (13s10p1d,8s6p1d);^{23b} Cl (12s9p1d,7s5p1d);^{23b} H (5s1p,3s1p);^{23a} TZP'—B,C same as TZP, but DZP for H. The GIAO calculations on B₄Me₄ (3b) have been carried out without polarization functions on the hydrogen atoms. Unless otherwise noted, MP2/6-31G* optimized geometries (in the FULL, i.e. all-electron correlated approximation) have been used for the chemical shift calculations.

The ¹¹B and ¹³C chemical shifts (δ values) are reported relative to the experimental standards, BF₃·OEt₂ and tetramethylsilane (TMS), respectively. For δ ¹³C, each calculated absolute chemical shielding (σ) is compared directly with the σ for TMS computed at the same level: IGLO/DZ 218.13 ppm, IGLO/II' 192.1 ppm, GIAO-SCF/DZP 199.2 ppm, GIAO-SCF/TZP' 196.4 ppm, GIAO-MP2/DZP 203.5 ppm, GIAO-MP2/TZP' 201.6 ppm. For δ ¹¹B, where it is inconvenient to compute the experimental NMR standard, B₂H₆ (which has δ 16.6 vs BF₃·OEt₂) is used instead. The σ values for B₂H₆ are as follows: IGLO/DZ 114.88 ppm, IGLO/II' 101.85 ppm, GIAO-SCF/DZP 105.8 ppm, GIAO-SCF/TZP' 103.5 ppm, GIAO-MP2/DZP 102.8 ppm, and GIAO-MP2/TZP' 100.7 ppm.

Results and Discussion

1,5-C₂B₃H₅ (1). D_{3h} symmetric **1**, the smallest carborane in our systematic IGLO study,² displayed the largest discrepancy between computed and experimental ¹¹B chemical shifts, Δδ ≈ 10 at the IGLO-SCF/II'/MP2/6-31G* level. Geometries optimized at still higher levels, as well as those in which selected parameters were varied, failed to give any significant improvement. Practically the same deviation as IGLO is found at GIAO-SCF/TZP'/MP2/6-31G* (see Table I); both levels are of comparable quality. However, in going from GIAO-SCF to the correlated GIAO-MP2 level, the computed ¹¹B value decreases from δ = 11.8 to 1.9 (Table I), i.e. to almost perfect agreement with experiment (δ = 1.4). In addition, the experimental ¹³C chemical shift²⁴ also is reproduced excellently at GIAO-MP2 (δ = 104.2 vs expt. δ = 103.3, cf. GIAO-SCF, δ = 95.4). Hence, as surmised earlier,² correlation effects are necessary to reproduce the chemical shifts of **1** accurately.

1,2-C₂B₃H₇ (2). We expended a great deal of effort on this molecule. In contrast to **1**, the accurate structure of the rather unstable **2** has not been established with certainty. Grimes et al. isolated **2** in modest yield from the gas-phase reaction of B₄H₁₀ with acetylene.^{25a,b} The ¹¹B (but not ¹³C) chemical shifts were determined. The IR spectra suggested "a relatively large CC bond order". This interpretation was supported by the reaction chemistry which was "strongly suggestive of an ethylene-like carbon-carbon bond".^{25a} Beaudet's preliminary microwave-derived CC distance, 1.453 Å,²⁶ is *not* supported by the ab initio geometries, in which much longer separations are found (e.g.

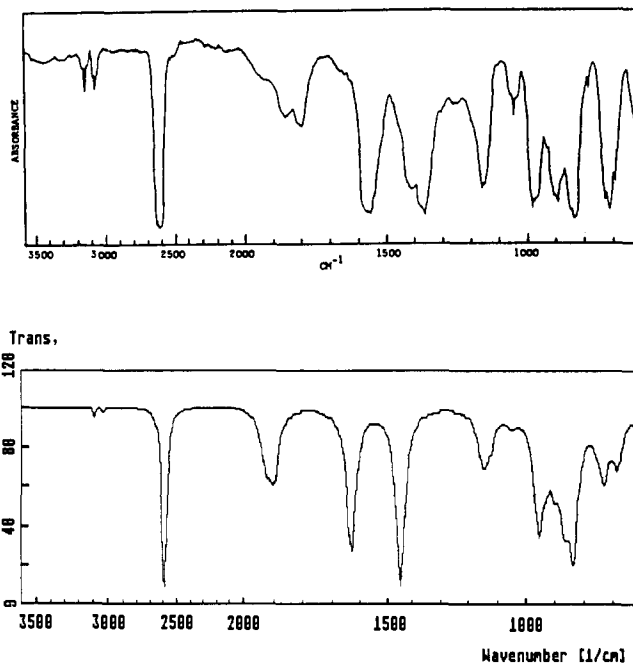


Figure 2. Comparison of the experimental (top) and computed (MP2/6-31G*, scaled by 0.93) infrared spectra of C₂B₃H₇ (**2**). The experimental spectrum is derived from that presented in ref 25b. The computed spectrum has been adjusted to correspond to the nonlinear experimental scale. Note the weak CH stretching frequencies at ca. 3100 cm⁻¹. The fine overall agreement, as well as the match between the computed and the experimental chemical shifts, confirms the correctness of the assigned structure.

1.604 Å at MP2/6-31G*²). Even though our combined ab initio/IGLO/NMR study gave better agreement between the experimental δ ¹¹B shifts and those computed using the best ab initio rather than the experimental structure, the Δδ ≈ 8 deviations encountered for both types of borons in 1,2-C₂B₃H₇ (**2**)² were much larger than the average difference between theory and experiment. We hoped that this discrepancy also might be resolved at correlation levels.

However, as shown in Table I, the GIAO-MP2 ¹¹B chemical shifts of **2** do not differ notably from those at GIAO-SCF or IGLO-SCF levels, and still deviate by Δδ ≈ 7 and 8 for B_{3,5} and B₄, respectively, from the early experimental data. We first suspected that the accuracy of the MP2/6-31G* optimized geometry employed in the chemical shift calculations might not be sufficient. However, reoptimization at the somewhat higher MP2/6-311G* level resulted in only minor geometrical changes (all bonds are elongated by ca. 0.01 Å). Consequently, only slightly different δ ¹¹B values are computed (δ = -12.0 and -13.9, IGLO-SCF/DZ//MP2/6-311G*). We then carried out extensive searches for alternative C₂B₃H₇ structures, but these failed to reveal lower energy minima or geometries which gave satisfactory agreement between computed and experimental chemical shifts.

An even more convincing demonstration of the correctness of the general structure proposed for **2** was provided by the agreement of the gas-phase IR spectrum^{25b} with that computed at MP2-(FC)/6-31G*, i.e., with the frozen core approximation (Figure 2). If the structure of **2** really is correct, why do the computed and the experimental ¹¹B chemical shifts differ? The reported experimental shifts were in error!

Greatrex and Fox recently repeated the difficult preparation of 1,2-C₂B₃H₇ (**2**).^{25c} Their remeasured δ ¹¹B values did not

(26) Beaudet, R. A. In *Advances in Boron and the Boranes*; Liebmann, J. F., Greenberg, A., Williams, R. E., Eds.; Verlag Chemie: Weinheim, 1988; Chapter 20, p 417.

(27) (a) Biffar, W.; Nöth, H.; Pommerening, H. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 56. (b) Schlüter, K.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 57.

(20) (a) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzales, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, 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 90*; Gaussian Inc.: Pittsburgh, PA, 1990. (b) Amos, R. D.; Rice, J. E. *CADPAC: The Cambridge Analytical Derivative Package*; Issue 4.0, Cambridge, 1987.

(21) ACES II, an ab initio program system by J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, and R. J. Bartlett, Quantum Theory Project, University of Florida, Gainesville, FL 1991.

(22) Huzinaga, S. *Approximate Atomic Wavefunctions*; University of Alberta: Edmonton, 1971.

(23) (a) Dunning, T. H. *J. Chem. Phys.* 1970, 53, 2823; 1971, 55, 716. The polarization functions are the following: *d*(B) = 0.386, *d*(C) = 0.654, *d*(F) = 1.58, *d*(Si) = 0.28, and *p*(H) = 0.7 (see also: Redmon, L. T.; Purvis, G. D.; Bartlett, R. J. *J. Am. Chem. Soc.* 1979, 101, 2856). (b) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* 1992, 97, 2571. The polarization function exponents employed are *d*(Cl) = 0.65 and *d*(Si) = 0.4.

(24) (a) Todd, L. J. *Pure Appl. Chem.* 1971, 30, 587. (b) Olah, G. A.; Prakash, G. K. S.; Liang, G.; Henold, K. L.; Haigh, G. B. *Proc. Natl. Acad. Sci. U.S.A.* 1977, 74, 5217.

(25) (a) Franz, D. A.; Grimes, R. N. *J. Am. Chem. Soc.* 1970, 92, 1438. (b) Franz, D. A.; Miller, V. R.; Grimes, R. N. *J. Am. Chem. Soc.* 1972, 94, 412. (c) Schleyer, P. v. R.; Gauss, J.; Bühl, M.; Greatrex, R.; Fox, M. A. *J. Chem. Soc., Chem. Commun.* In press.

Table I. Relative Chemical Shifts of 1,5-C₂B₃H₅ (**1**) and 1,2-C₂B₃H₇ (**2**) Computed with Various Methods^a and Basis Sets (MP2/6-31G* Optimized Geometries)

level of theory	$\delta^{13}\text{C}$	$\delta^{11}\text{B}$			
1,5-C ₂ B ₃ H ₅ (1) <i>D</i> _{3h}	C1,5	B2,3,4			
IGLO-SCF/DZ	96.9	12.0			
IGLO-SCF/II'	97.5	11.4			
GIAO-SCF/DZP	87.8	10.2			
GIAO-SCF/TZP'	95.4	11.8			
GIAO-MP2/DZP	93.4	-0.1			
GIAO-MP2/TZP'	104.2	1.9			
experiment	103.3 ^b	1.4, ^c 3.5 ^d			
1,2-C ₂ B ₃ H ₇ (2) <i>C</i> ₂	C1	C2	B3,5	B4	
IGLO-SCF/DZ	-24.3	64.2	-12.7	-14.6	
IGLO-SCF/II'	-34.8	48.6	-13.6	-15.7	
GIAO-SCF/DZP	-35.8	47.2	-13.4	-14.8	
GIAO-SCF/TZP'	-30.5	51.7	-13.3	-14.7	
GIAO-MP2/DZP	-28.5	51.0	-14.6	-15.9	
GIAO-MP2/TZP'	-23.1	57.4	-14.6	-16.0	
experiment 1972 ^e			-21.7	-23.7	
experiment 1993 ^d	-21.5	57.9	-13.39	-15.07	

^a IGLO values from ref 2. ^b Reference 24. ^c Grimes, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 1895. ^d Reference 25c. ^e Reference 25a.

agree with the earlier experimental literature either, but accorded almost perfectly with the 1992 IGLO predictions.¹² Evidently, the reference scale of the original $\delta^{11}\text{B}$ measurements (which were by no means routine in the early days) had inadvertently been shifted by about 8 ppm.

Greatrex and Fox also determined the $\delta^{13}\text{C}$ values for **2**.^{25c} While these did not correspond very well to the 1992 IGLO predictions,² GIAO-MP2 gave excellent results (Table I). As with **1**, correlated levels of theory are needed to reproduce $\delta^{13}\text{C}$ values in demanding situations.

B₄R₄ (**3**). Recently, the tetrahedral B₄ arrangement in B₄(tBu)₄ (**3c**) was confirmed by X-ray structure analysis.¹² The ¹¹B nuclei in **3c** are extremely deshielded ($\delta = 135$)¹¹ and e.g. resonate more than $\Delta\delta = 30$ downfield from "classical" tetraalkyldiborane(2) derivatives, R₂B-BR₂.²⁷

The initial chemical shift calculations on the parent compound B₄H₄ (**3a**, *T_d* symmetry), though somewhat basis set dependent, also indicated strong deshielding for boron. However, even with the largest basis sets employed, the magnitude of the downfield shift is greatly overestimated at the SCF level ($\delta = 197$ and 198 at IGLO-SCF/II and GIAO-SCF/TZP, respectively, see Table II). The effect of alkyl substitution on the chemical shift is substantial ($\Delta\delta = 11$ –33 for the tetramethyl derivative **3b** and $\Delta\delta \approx 15$ ppm for B₄tBu₄ (**3c**)), but a $\Delta\delta = 33$ –45 difference to the experimental result remains. (The GIAO-SCF calculation on **3c** was performed at the suggestion of a referee to provide a check on the reliability of B₄Me₄ as a suitable model compound for B₄tBu₄. As the large basis set GIAO-SCF and GIAO-MP2 calculations could not be carried out due to the size of **3c**, the shifts at higher levels were estimated by interpolation. See Table II.)

The interpolated GIAO-SCF/TZP' estimate, $\delta \approx 180$, for B₄tBu₄ (**3c**) deviates considerably from the experimental $\delta^{11}\text{B} = 135$. This deviation is even larger than the deviation of the theoretical value for the methyl compound (cf. the calculated GIAO-SCF/TZP' value for B₄Me₄ (**3b**), $\delta = 168$). As the GIAO-MP2 calculations reveal, these large discrepancies at the SCF level are due to electron correlation effects. The GIAO-MP2/TZP' $\delta = 132.5$ for B₄Me₄ (**3b**) as well as the interpolated $\delta \approx 139$ for B₄tBu₄ (**3c**) are both in excellent agreement with the experimental value, $\delta = 135$ for **3c**. This qualitatively correct description of **3c** undoubtedly constitutes a major success of the GIAO-MP2 method.

Van Wüllen and Kutzelnigg recently reported another correlated study of the chemical shifts of B₄H₄ (**3a**) using the MC-IGLO method.^{15b} This resulted in a significantly larger correlation

Table II. Computed Relative ¹¹B Chemical Shifts of B₄R₄ Compounds (**3a**–**e**) in *T_d* Symmetry (MP2/6-31G* Geometries Except As Noted)

level of theory	B ₄ H ₄ 3a ^a	B ₄ Me ₄ 3b ^b	B ₄ tBu ₄ 3c	B ₄ Cl ₄ 3d ^c	B ₄ F ₄ 3e ^d
IGLO-SCF/DZ	208.3	175.1			
	(208.8) ^e				
IGLO-SCF/II	196.6				
GIAO-SCF/DZP	185.9	162.4	176.2 ^f	110.1	58.8
GIAO-SCF/TZP'	197.1	167.9	(180 estim) ^h	116.6	64.3
	(197.6) ^f				
GIAO-MP2/DZP	133.5	122.8		70.9	37.4
GIAO-MP2/TZP'	150.0	132.5	(139 estim) ^h	81.4	44.7
	(150.1) ^f				
experiment			135.4 ⁱ	85.5 ^j	

^a MP2/6-31G* geometry (Å): BB 1.681, BH 1.187. ^b CH bonds (Å) and BB edges eclipsed; MP2/6-31G* geometry: BB 1.688, BC 1.562, CH 1.095, BCH 1.11.3°; the staggered conformer is 2.3 kcal/mol higher in energy at the SCF/6-31G* level. ^c MP2(FC)/6-31G* geometry employed (Å) (frozen core approximation): BB 1.690, BC 1.721. ^d MP2/6-31G* geometry (Å): BB 1.709, BF 1.324. ^e In parentheses: SCF/6-31G* geometry employed. ^f In parentheses: TZP basis set employed. ^g The GIAO-SCF calculation (Schneider, V.; Gauss, J. Unpublished results) was performed with the TURBOMOLE program package (Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165; also see ref 5c) using a HF/svp optimized geometry and the dzp basis set (see: Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571). ^h Estimated by interpolation using the GIAO-SCF/DZP result for **3c** and the data for **3a** and **3b**. This gives a correlation correction of 41 ppm for **3c** at GIAO-MP2/TZP'. ⁱ Reference 12. ^j Reference 30.

correction (about 70 ppm) than the GIAO-MP2 method. In light of the good results obtained with the GIAO-MP2 method and the large alkyl effects found for B₄Me₄ (**3b**) as well as for B₄tBu₄ (**3c**), it seems that MC-IGLO overestimates the electron correlation correction by at least 10–20 ppm. However, more accurate calculations are certainly required to provide a final answer on the accuracy and reliability of the MC-IGLO as well as the GIAO-MP2 method in this particularly difficult case.

The same large correlation correction for $\delta^{11}\text{B}$ is found for the tetrachloro derivative, B₄Cl₄ (**3d**), which possesses the idealized tetrahedral symmetry in the gas phase²⁸ and nearly so in the solid state.²⁹ Compared to **3a**–**3c** ($\delta^{11}\text{B} > 135$), the deshielding of boron is much attenuated in **3d** ($\delta 85.5$).³⁰ As for **3a**–**3c**, chemical shift calculations at SCF levels greatly overestimate this deshielding (e.g. GIAO-SCF/TZP, $\delta 116.6$). Again, the $\Delta\delta \approx 30$ deviation is due to correlation effects, as the GIAO-MP2/TZP result ($\delta 81.4$) affords very good accord with experiment.

A slightly smaller effect of electron correlation, on $\delta^{11}\text{B}$, $\Delta\delta \approx 20$, is computed for the unknown tetrafluoro derivative, B₄F₄ (**3e**, compare SCF and MP2 values in Table II). The ¹¹B chemical shift predicted at the GIAO-MP2/TZP level, $\delta 44.7$, should be reliable and may facilitate the experimental characterization of this yet elusive compound. Attempts to synthesize B₄F₄ (**3e**) have been unsuccessful,³¹ even though high level ab initio calculations (employing DZP basis set and including electron correlation at CI and CPF levels) indicate that **3e** might be a sufficiently stable, isolable molecule.³²

B₂X₄. In contrast to the tetraborane(4) derivatives **3a**–**e**, the effects of electron correlation on $\delta^{11}\text{B}$ in classical diborane(4) compounds are negligible. For both B₂Cl₄³³ and B₂F₄,³⁴ the

(28) Brain, P. T.; Downs, A. J.; Fanfarillo, M.; Goode, M. J.; Massey, A. C.; Rankin, D. W. H.; Robertson, H. E. *J. Mol. Struct.* **1989**, *192*, 163.

(29) Atoji, M.; Lipscomb, W. N. *Acta Crystallogr.* **1952**, *6*, 547; *J. Chem. Phys.* **1953**, *21*, 127. For a more recent X-ray structure of B₄Cl₄, see: Thier, D. Dissertation, Universität Stuttgart, 1992. The B–B = 1.640(10) Å and B–Cl = 1.656(9) Å bond lengths are in somewhat better agreement with our MP2(FC)/6-31G* values.

(30) Ahmed, L.; Castilla, J.; Morrison, J. A. *Inorg. Chem.* **1992**, *31*, 1858.

(31) Massey, A. G. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 1.

(32) Swanton, D. J.; Ahlrichs, R. *Theor. Chim. Acta* **1989**, *75*, 163. A binding energy of **3e** with respect to four BF monomers of ca. 120 kcal/mol has been calculated.

GIAO-SCF/TZP and GIAO-MP2/TZP values are almost identical: δ 67.8 and 67.9, respectively, for B₂Cl₄, and δ 26.2 and 26.6, respectively, for B₂F₄. The degree of agreement with the experimental data, δ = 62.4³⁵ and 23.8,³⁶ respectively, while satisfactory, is somewhat lower than usual. We wondered if this might be at least partially due to the low barriers to rotation around the BB bonds of B₂F₄ and B₂Cl₄, computed at MP2/6-31G* to be only 0.2 and 2.3 kcal/mol, respectively.³⁷ However, the chemical shifts of the staggered (*D*_{2d}) and planar (*D*_{2h}) forms are close and taking their average does not improve the agreement with experiment. As for B₂F₄ and B₂Cl₄, no large correlation effects are found for BF₃ (the GIAO-MP2 value is 3 ppm higher than that at GIAO-SCF) and both MP2 and SCF-based methods (also see ref 6c for IGLO) yield good δ ¹¹B results.

The results for B₂F₄ and B₂Cl₄, as well as those for BF₃, suggest that electron correlation effects are of little importance for chemical shift computations in "normal", unstrained boron compounds. The following section provides further examples.

Calibration Molecules: B₄H₁₀ (4), B₅H₉ (5), 1,2-C₂B₄H₆ (6), 1,6-C₂B₄H₆ (7), 2,4-C₂B₅H₇ (8). In order to assess the effect of electron correlation for "normal" boranes and carboranes, we reinvestigated 4–8, the δ ¹¹B values of which are already well described at the SCF level. As expected, there are no major changes of the computed ¹¹B chemical shifts in going from GIAO-SCF to GIAO-MP2 (Table III). Correlation tends to increase the shielding with respect to the standard (compare the corresponding GIAO-SCF and GIAO-MP2 values in Table III), but only slightly. The largest chemical shift change due to correlation, $\Delta\delta$ = 3.7, is found for B_{2,3,4,5} in B₅H₉ (5). In most cases, the degree of agreement is improved in going from GIAO-SCF to GIAO-MP2, but not significantly. Hence, the decisive correlation effects on δ ¹¹B of 1 and 3 are exceptional. The ¹¹B NMR chemical shifts of "normal" boranes and carboranes are described with sufficient accuracy at the SCF level. However, this is not always the case for the ¹³C shifts which may improve with GIAO-MP2 (see 1, 2, and below).

Boracyclopropylideneborane C₂B₂H₄ (9a). As predicted by ab initio calculations,¹⁷ the parent boracyclopropylideneborane C₂B₂H₄ (9a, see Figure 1) adopts a non-classically bridged structure. The X-ray C₂B₂ skeletal distances of a substituted derivative 9b were in good agreement with those predicted for 9a.^{18b} The unusual structural feature in these compounds is a formally sp²-hybridized planar carbon, C2, with all bonds arranged in one semicircle. The IGLO-SCF/II' computed chemical shift of this unique C2 in 9a, δ 141.2,³⁸ deviated substantially from the experimental values, δ 115.2 and 126.0 for derived 9b and 9c, respectively.¹⁸ Again, the use of a correlated wave function improves the agreement decisively (GIAO-MP2/TZP' δ 125.2, Table IV). The effect of electron correlation on δ ¹³C, $\Delta\delta$ \approx 18, is considerably larger than that in ethylene, CH₂=CH₂ ($\Delta\delta$ \approx 7, GIAO-MP2/TZ2P'/MP2/TZ2P level).¹⁶

The computed ¹³C chemical shift of the "classical" carbon C1 in 9a is less sensitive to correlation effects, as the difference between the GIAO-SCF and GIAO-MP2 values is $\Delta\delta$ < 3 (Table IV). Except for the IGLO-SCF/II' value (δ 19.9), all computed C1 chemical shifts are near or within the experimental range for the substituted compounds (δ 25.0–30.5).

The computed ¹¹B NMR chemical shift of the doubly bonded, bridged boron B4 shows no unusual dependence on the theoretical level employed. The GIAO-MP2/TZP' value for B4 in 9a, δ

Table III. Computed Relative Chemical Shifts (δ ¹¹B and δ ¹³C) for Reference Molecules B₄H₁₀ (4), B₅H₉ (5), 1,6-C₂B₄H₆ (7), 1,2-C₂B₄H₆ (6), and 2,4-C₂B₅H₇ (8) Employing MP2/6-31G* Geometries^a

level of theory					
B ₄ H ₁₀ (4) C _{2v}	B1,3	B2,4			
	IGLO-SCF/DZ	-42.2	-6.0		
	IGLO-SCF/II'	-40.0	-5.3		
	GIAO-SCF/DZP	-37.1	-4.0		
	GIAO-SCF/TZP'	-39.4	-3.8		
	GIAO-MP2/DZP	-40.5	-6.6		
	GIAO-MP2/TZP'	-43.7	-6.9		
experiment ^b	-41.8	-6.9			
B ₅ H ₉ (5) C _{4v}	B1	B2,3,4,5			
	IGLO-SCF/DZ	-55.2	-11.5		
	IGLO-SCF/II'	-55.1	-12.8		
	GIAO-SCF/DZP	-54.5	-12.7		
	GIAO-SCF/TZP'	-54.7	-11.4		
	GIAO-MP2/DZP	-55.8	-16.2		
	GIAO-MP2/TZP'	-56.5	-15.1		
experiment ^c	-53.1	-13.4			
1,6-C ₂ B ₄ H ₆ (7) D _{4h}	C1,6	B2,3,4,5			
	IGLO-SCF/DZ	80.3	-18.1		
	IGLO-SCF/II'	71.7	-18.6		
	GIAO-SCF/DZP	70.3	-22.0		
	GIAO-SCF/TZP'	76.7	-17.7		
	GIAO-MP2/DZP	69.4	-22.5		
	GIAO-MP2/TZP'	78.2	-17.6		
experiment ^d	78.5	-19.4			
1,2-C ₂ B ₄ H ₆ (6) C _{2v}	C1,2	B3,4	B5,6		
	IGLO-SCF/DZ	44.5	-15.1	5.4	
	IGLO-SCF/II'	37.5	-15.3	1.4	
	GIAO-SCF/DZP	36.4	-19.0	-1.4	
	GIAO-SCF/TZP'	42.9	-15.8	2.0	
	GIAO-MP2/DZP	45.4	-18.9	-4.2	
	GIAO-MP2/TZP'	53.3	-15.3	0.4	
experiment ^e		-16.3	1.6		
2,4-C ₂ B ₅ H ₇ (8) C _{2v}	C2,4	B1,7	B3	B5,6	
	IGLO-SCF/DZ	74.5	-17.9	10.7	3.4
	IGLO-SCF/II'	76.5	-21.7	8.1	3.3
	GIAO-SCF/DZP	70.7	-22.3	4.1	1.5
	GIAO-SCF/TZP'	76.6	-20.4	8.2	4.3
	GIAO-MP2/DZP	74.5	-22.5	1.0	0.2
	GIAO-MP2/TZP'	82.6	-20.5	6.2	3.6
experiment ^f	80	-23.5	5.0	2.0	

^a Geometries and IGLO values from ref 2. ^b Jaworowski, I. S.; Long, J. R.; Barton, L.; Shore, S. G. *Inorg. Chem.* **1979**, *18*, 56. ^c Tucker, P. M.; Onak, T.; Leach, J. B. *Inorg. Chem.* **1970**, *9*, 1430. ^d C: ref 24. B: Onak, T.; Gerhardt, F. J.; Williams, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 5378. ^e Onak, T.; Drake, R. P.; Dunks, G. B. *Inorg. Chem.* **1964**, *3*, 1686. ^f Warren, R.; Paquin, D.; Onak, T.; Dunks, G. B.; Spielman, J. R. *Inorg. Chem.* **1970**, *9*, 2285.

Table IV. Computed Chemical Shifts for Boracyclopropylideneborane 9a^a

level of theory	B3	B4	C1	C2
IGLO-SCF/DZ	51.0	9.1	30.3	170.8
IGLO-SCF/II'	44.9	9.1	19.9	141.2
GIAO-SCF/DZP	43.0	9.4	23.0	133.3
GIAO-SCF/TZP'	45.7	11.9	26.0	142.4
GIAO-MP2/DZP	30.0	12.5	25.9	113.8
GIAO-MP2/TZP'	35.4	15.5	29.5	125.2
9b, experiment ^b	52	18	25.0	115.2
9c, experiment ^c	48	20	30.5	126.0

^a MP2/6-31G* geometry (Å): C₁-C₂ = 1.451; C₁-B₃ = 1.598; B₃-C₂ = 1.534; B₃-B₄ = 1.723; C₂-B₄ = 1.379. ^b Reference 18a, substituents: tBu at B₃ and B₄; two Me₃Si's at C₁. ^c Reference 18b, substituents: (2,3,5,6-tetramethylphenyl) at B₃ and B₄; two Me₃Ge's at C₁.

15.5, is close to the experimentally observed chemical shift range, δ 18–20. In contrast, a large effect of electron correlation, $\Delta\delta$ \approx 10, is apparent for δ ¹¹B of the bridging, planar tetracoordinated boron B3. In this instance, however, the agreement with experiment (δ 48–52) is worse at correlated (δ 35.4, GIAO-MP2/

(33) *D*_{2d} symmetry, MP2/6-31G* optimized parameters: B–B = 1.688 Å, B–Cl = 1.738 Å, B–B–Cl = 120.1°.

(34) The MP2/6-31G* optimized parameters, in *D*_{2h} symmetry, are: B–B = 1.718 Å, B–F = 1.327 Å, F–B–B = 121.2°.

(35) Davan, T.; Morrison, J. A. *Inorg. Chem.* **1986**, *25*, 2366.

(36) Morrison, J. A. *Chem. Rev.* **1991**, *91*, 35.

(37) An early study gave similar results: Clark, T.; Schleyer, P. v. R. *J. Comp. Chem.* **1981**, *2*, 20.

(38) (a) See footnote 15 in ref 18b. (b) MP2(Full)/6-31G* optimized parameters for 9a are given in the footnotes to Table IV.

TZP') than at SCF levels (δ 45.7, GIAO-SCF/TZP', see Table IV). Substituent effects should be taken into account, cf. B_4H_4 (3a) above.

Borane BH_3 . In their comprehensive review, Kutzelnigg, Fleischer, and Schindler included a variety of boron compounds for which IGLO gave generally satisfactory results.^{6c} They pointed out that the low-lying π MO of BH_3 was responsible for the strongly deshielding contributions of the BH bonds. As no experimental measurements have been reported on this basic molecule, we have checked IGLO prediction (δ ^{11}B = 83.7, basis II). The GIAO-SCF/TZP value, 83.8, is nearly identical, and GIAO-MP2/TZP gives 87.7.³⁹ Consequently, the effect of correlation, despite the low-lying π orbital, is quite small. This contrasts with results for the isoelectronic CH_3^+ , where GIAO-MP2 predicts ca. 35 ppm greater deshielding than at SCF. The IGLO results for $B(CH_3)_3$ agreed well with the experimental value.^{6c}

Conclusions

Our earlier survey² employing SCF-level chemical shift computations (IGLO) on boranes and carboranes demonstrated that *electron correlated geometries* gave the best agreement with experiment. The GIAO-MP2 method now has been applied to evaluate the performance of ^{11}B (and ^{13}C) NMR chemical shift computations at a correlated level of theory, particularly for those cases which did not give good IGLO results. For most "normal" boranes and carboranes (like 4–8), as well as for "classical" derivatives, e.g. B_2Cl_4 , the δ ^{11}B values computed at the correlated MP2 level of theory do not differ appreciably from

those at the SCF level. The latter were quite good already; GIAO-MP2 does not bring any significant improvement vs the experimental values. In contrast, electron correlation effects are important for the strain systems 1,5- $C_2B_3H_5$ (1) and B_4R_4 (3b,d, R = CH_3 , Cl): While the GIAO-SCF/TZP' ^{11}B chemical shifts (i.e. without electron correlation) deviate by $\Delta\delta \approx 10$ and 33 from the experimental data for 1 and 3c,d (R = t-Bu, Cl), respectively, the corresponding GIAO-MP2/TZP' values (i.e. including electron correlation) are in excellent agreement with experiment. For the still elusive B_4F_4 (3e), a ^{11}B chemical shift of $\delta \approx 45$ is predicted.

The problem case, 1,2- $C_2B_3H_7$ (2), which resisted all efforts to "improve" the computed ^{11}B chemical shifts, proved to be no exception at all. The apparent deviations were due to errors in the early experimental NMR measurements.

For a number of the molecules studied, 1, 2, and 9a (as well as 6, for which no experimental data are available), the inclusion of electron correlation influences the ^{13}C chemical shifts significantly and improves the agreement with experiment. As this behavior is likely to be general, ^{13}C chemical shifts in carboranes may provide more critical data for comparisons.

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(39) Buzek, P.; Schleyer, P. v. R. Unpublished results.