

Density Functional Theory/Finite Perturbation Theory Calculations of Nuclear Spin–Spin Coupling Constants for Polyhedral Carboranes and Boron Hydrides

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Abstract: An extensive study is presented of nuclear spin–spin coupling constants in 25 polyhedral boranes using density functional theory/finite perturbation theory (DFT/FPT) methods to determine the Fermi contact term. Scalar couplings were obtained at either the UB3LYP/6-311G** or the UB3LYP/6-311++G** level, with molecular structures fully optimized at the B3LYP/6-31G* DFT level. The calculated results are in good agreement with the solution experimental data for a wide range of directly bonded, geminal, vicinal, and long-range coupling constants. The largest disparities occur for $^1J(^{11}\text{B}-^1\text{H})$ and $^1J(^{13}\text{C}-^1\text{H})$ values greater than 120 Hz. These are underestimated on average by about 5%, a value close to that expected (4%) from the effects of motional averaging on directly bonded coupling constants. The accurate prediction of coupling constants in polyhedral boron compounds will be extremely helpful in their detailed NMR spectral analyses.

I. Introduction

The complexity of polyhedral boron-containing compounds often makes structural assignments difficult. For this purpose, the accurate predictions of ^{11}B NMR chemical shifts using ab initio molecular orbital methods (such as IGLO and GIAO) provide powerful new structural methods.^{1–9} In contrast, there are few theoretical studies of nuclear spin–spin coupling in boron compounds.^{10–12} In view of the extensive applications of coupling constants in other molecular systems, this may seem surprising. Perhaps the most important factor is the extreme difficulty of obtaining accurate coupling constants in polyboranes since even the smaller compounds such as diborane exhibit exceedingly complex NMR spectra.^{10,13–16} The occurrence of numerous chemically equivalent but magnetically nonequivalent

nuclei can lead to spectra requiring spectral analyses even in the absence of second-order features in the spectra.^{16,17} For boron-containing compounds the situation is more difficult because the two boron isotopomers (80:20 ratio for ^{11}B : ^{10}B) produce a superposition of 2^N spectra, where N denotes the number of boron atoms in the molecule. There can also be broadening by quadrupolar relaxation^{18,19} and even possible exchange effects. These difficulties have prevented extension of the diborane spectral analysis¹⁴ to polycyclic boron compounds. In these situations, available NMR spectral data are based on a variety of techniques, including isotopic substitutions, homo- and heteronuclear decoupling, and two-dimensional NMR.

The success of ab initio calculations of magnetic shielding has recently been extended to nuclear spin–spin coupling constants. The Fermi contact (FC) contributions, which generally dominate the coupling interactions, are much more sensitive to the inclusion of electron correlation effects.^{20–23} As a consequence, ab initio calculations based on the usual many-body techniques have been generally limited to relatively small

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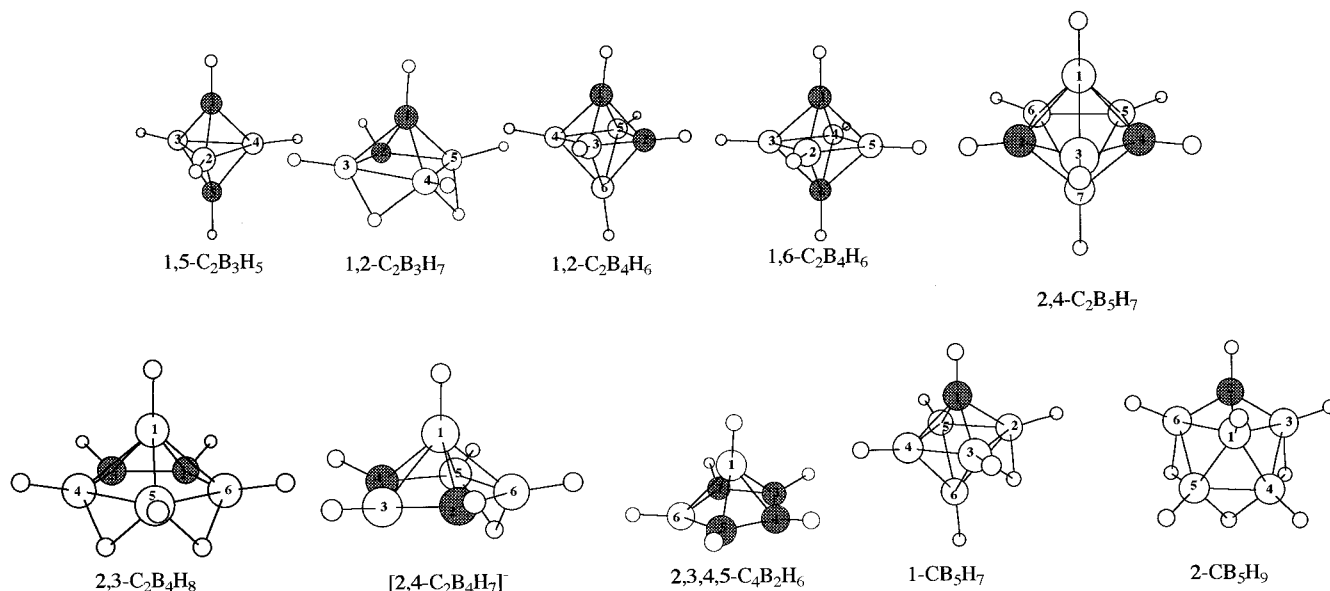


Figure 1. Framework structures for the polyborane structures in this study.

molecules.^{10–12,24–33} Because electron correlation is accurately treated in density functional theory (DFT),^{34–37} it seems ideally suited to the problem of calculating the FC contributions to nuclear spin coupling constants. This becomes especially important in larger molecules which are not easily accommodated by many-body techniques.^{38–41} The present study examines the usefulness of DFT and finite perturbation theory (FPT) methods for calculating FC contributions to coupling constants in the series of polyhedral carboranes and boron hydrides depicted in Figures 1 and 2. It is fortunate that the FC contributions are expected to be most important for these compounds since we are not yet able to perform DFT computations of the noncontact mechanisms.

II. Theoretical Section

a. Finite Perturbation Theory for the Fermi Contact Term.

Coupled Hartree–Fock theory has been used extensively for calculation of nuclear spin–spin coupling constants. The perturbation of the electronic system by nuclei N and N' , with nuclear spin operators μ_N and $\mu_{N'}$, can be described by the Hamiltonian,

$$H = H_0 + \mathbf{A}_N \cdot \mu_N + \mathbf{A}_{N'} \cdot \mu_{N'} \quad (1)$$

where H_0 is the unperturbed Hamiltonian and \mathbf{A}_N , for example, is the Fermi contact term for nucleus N ,

$$\mathbf{A}_N = (16\pi\beta/3) \sum_{\mu} \delta(r_{\mu N}) \mathbf{S}_{\mu} \quad (2)$$

where $\delta(r_{\mu N})$ is the Dirac delta function and \mathbf{S}_{μ} is the electron spin operator for the μ th electron. The FPT formulation of Pople, McIver, and Ostlund⁴² is a variant that requires open-shell calculations. At nucleus N , a FC perturbation $\lambda(\phi_{\mu}|\delta(r_{\mu N})|\phi_{\nu})$, where λ is a perturbation parameter,³⁸ is added to the $\mu\nu$ th element of the α -spin matrix elements of H_0 , and it is subtracted from the corresponding matrix elements of β -spin. This has the effect of producing unpaired spin density $\rho_{\mu\nu}(\mu_N)$ which propagates through the molecule as self-consistency is achieved. Using finite difference methods,⁴² the FC coupling can be put into the form

$$J_{NN'} = (\hbar/2\pi)(8\pi\beta/3)^2 \gamma_N \gamma_{N'} \lambda^{-1} \sum_{\mu\nu} \rho_{\mu\nu}^{N'}(\mu_N) \langle \phi_{\mu} | \delta(r_{N'}) | \phi_{\nu} \rangle \quad (3)$$

where γ_N denotes the magnetogyric ratio for nucleus N and $\rho_{\mu\nu}^N(\mu_N)$ denotes the $\mu\nu$ th element of the spin density matrix evaluated at nucleus N' .

b. Computational Methods. With few exceptions, good-quality structural data are not available for the compounds of this study. Therefore, the geometries of all compounds were fully optimized at the B3LYP/6-31G* level of theory using the Gaussian 94 suite of programs.^{43,44} The B3LYP method makes use of Becke's three-parameter exchange functional³⁷ and the nonlocal correlation functional of Lee, Yang, and Parr.³⁶ For consistency, optimized structures were also used in cases where experimental structural data are available.

Fermi contact contributions to the scalar coupling constants for the optimized structures were obtained at the UB3LYP/6-311G** triple-split level with polarization functions on hydrogens and heavier atoms.

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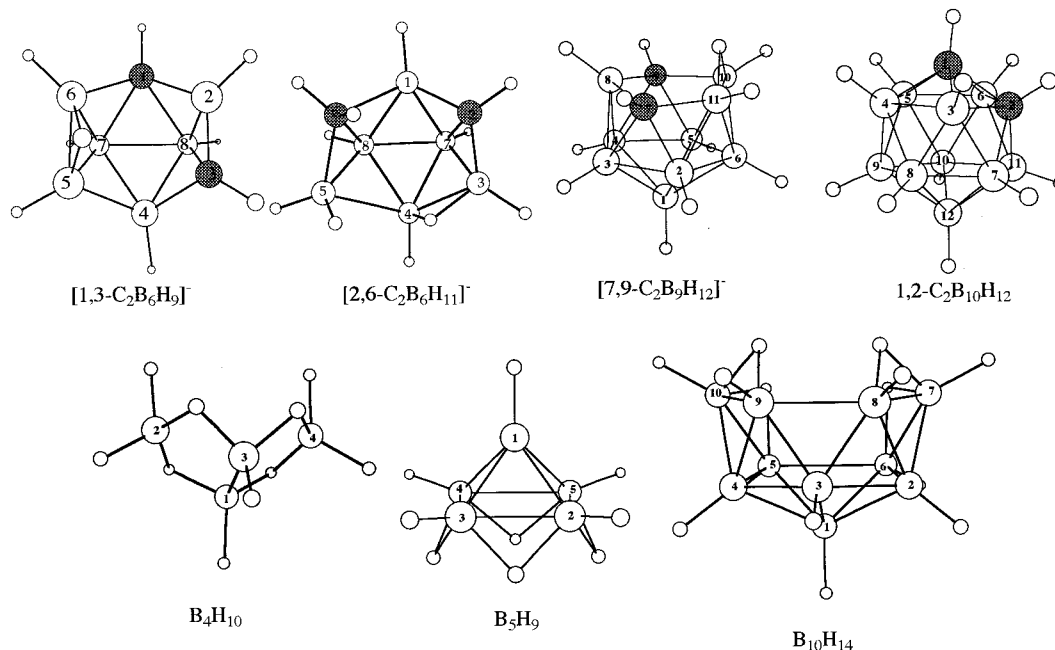


Figure 2. Framework structures for the remaining polyborane structures in this study.

Calculated DFT/FPT results are based on eq 3 using the FC output of the FIELD option of Gaussian 94.⁴³ It was also of interest to explore the importance of including diffuse functions to the coupling constants for the ionic and/or dipolar (zwitterion) species. For molecules such as $[\text{BH}_4]^-$, H_3NBH_3 , and Me_3NBH_3 , the DFT/FPT approach was also used to obtain coupling constants at the UB3LYP/6-311⁺⁺G** level. As expected, the use of diffuse functions gave substantial improvement for $^1J(^{11}\text{B}-^1\text{H})$ in $[\text{BH}_4]^-$. However, there was no overall improvement in the linear correlation ($r^2 = 0.994$) on including the results for ionic and dipolar species computed with diffuse functions.

Coupling constants for the molecules B_2H_6 , CH_4 , and C_2H_6 were included here because they could be considered as "standards". Of the four mechanisms generally considered to be important for nuclear spin-spin coupling, only the FC components were computed. Except for coupling to fluorine, the FC contributions are often the most important. Based on recent ab initio results for diborane,¹⁰⁻¹² the assumption of FC dominance is probably reasonable for the polyhedral boranes. Entered in Table 1 are the calculated FC and non-FC contributions to all of the B_2H_6 coupling constants. These were based on an equations-of-motion coupled-cluster singles and doubles method (EOM/CCSD).^{11,12} These values are in good agreement with the experimental data and the DFT/FPT results of the present study, which are also included in the second and third columns of Table 1. The magnitude of non-FC contributions in the next-to last column does not exceed 2.2 Hz, even though it is a large fraction of this geminal $^{11}\text{B}-^{11}\text{B}$ coupling constant. In fact, the average of the noncontact contributions in Table 1 is only -0.3 Hz.

The semiempirical INDO/FPT⁴² and INDO/SCPT⁴⁵ methods for determining nuclear spin-spin coupling constants have been used extensively for a wide range of systems and have given useful qualitative insights.²⁰ For example, the INDO/SCPT approach was used to examine a number of $^{13}\text{C}-^{11}\text{B}$ nuclear spin-spin coupling constants.⁴⁶ At an early stage in this study, the INDO/FPT method was

Table 1. Comparison of Spin-Spin Coupling Data for B_2H_6^a

coupling	exp ^b	DFT/FPT, ^c FC	EOM/CCSD ^d		
			FC	non-FC	total
¹ $J[\text{B}-\text{Ht}]$	133.5	128.0	122.1	0.1	122.2
¹ $J[\text{B}-\text{Hb}]$	46.3	45.2	42.0	0.7	42.7
² $J[\text{B}-\text{B}]$	-3.8	-3.3	-3.6	-2.2	-5.8
² $J[\text{Ht}-\text{Hb}]$	-7.4	-6.1	-7.1	-0.1	-7.2
² $J[\text{Ht}-\text{Ht}(\text{gem})]$	4.5	1.5	-1.4	0.0	-1.4
³ $J[\text{B}-\text{Ht}']$	4.0	5.3	4.9	-0.5	4.4
⁴ $J[\text{Ht}-\text{Ht}'(\text{cis})]$	4.5	3.0	3.0	-0.2	2.8
⁴ $J[\text{Ht}-\text{Ht}'(\text{trans})]$	14.8	11.0	11.4	-0.4	11.0

^a All values are given in hertz. ^b Reference 14; for consistency, the J value is assumed to have same sign as calculated by DFT/FPT. ^c UB3LYP/6-311G**//B3LYP/6-31G*, present study. ^d Reference 12.

used to compute the FC contributions in all of the polyhedral boron compounds of this study. In general, the trends for $^1J(^{11}\text{B}-\text{Ht})$ are reasonable, but the computed $^1J(^{11}\text{B}-\text{Hb})$ values are poor in comparison with the DFT/FPT results (for notation, see footnote *a* of Table 2). The INDO/FPT results for the polyhedral boranes are not included.

III. Results and Discussion

Entered in Table 2 are the calculated coupling constants, $J(\text{calc})$, for the 25 polyhedral boron compounds depicted in Figures 1 and 2. Results for several smaller molecules and experimental data from the literature are also included. These are the DFT/FPT results obtained at the UB3LYP/6-311G**//B3LYP/6-31G* levels. Coupling constants for ions and dipolar species at the UB3LYP/6-311⁺⁺G** level are given in parentheses. The only criterion for inclusion of these carboranes and polyhedral boron hydrides was unambiguous structural assignments. As a consequence, data have been omitted for polyhedral compounds that are known, or even suspected, to involve tautomerism or cage fluxionality (e.g., $[\text{B}_3\text{H}_8]^-$, $[2,3-\text{C}_2\text{B}_4\text{H}_7]^-$, B_5H_{11} , $\text{C}_4\text{B}_8\text{H}_{12}$). Except for the diborane experimental data in Table 1, full NMR spectral analyses have not been reported.^{10,13,14} Some of the NMR spectra of symmetrical polyboranes could also be complicated by the occurrence of chemically equivalent but magnetically nonequivalent nuclei.

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Table 2. Nuclear Spin–Spin Coupling Constants for a Series of Polyhedral Boranes and Carboranes

compound	$J[\text{N}-\text{N}']^a$	$J(\text{expt})^b$	$J(\text{calc})^c$	$J[\text{N}-\text{N}']^a$	$J(\text{expt})^b$	$J(\text{calc})^c$
1,5-C ₂ B ₃ H ₅ ^{d,e}	¹ J[C–H]	192	182.6	³ J[C1–H5]	19.7	18.6
	¹ J[B2–H2]	189	182.5	³ J[H1–H2]	2.1	1.9
	² J[C1–C5]	15	15.1	⁴ J[H1–H5]	10.8	8.7
1,2-C ₂ B ₃ H ₇ ^f	¹ J[B3(5)–Ht]	172	165.7	¹ J[B3(5)–Hb]	34	38.0
	¹ J[B4–Ht]	172	159.5	¹ J[B4–Hb]	48	48.5
1,2-C ₂ B ₄ H ₆ ^d	¹ J[B3,5–H]	185	178.0	³ J[H1–H4]	1.5	0.4
	¹ J[B4,6–H]	162	164.9	⁴ J[H3–H5]	6.9	6.1
	³ J[H1–H3(5)]	1.5	1.9	⁴ J[H1–H6]	11.1	8.7
1,6-C ₂ B ₄ H ₆ ^{d,e}	¹ J[C–H]	187	174.5	⁴ J[H1–H6]	14	11.0
	¹ J[B–H]	184	183.6	⁴ J[H2–H4]	7.1	6.1
	³ J[HCBH]	0.6	0.4			
2,4-C ₂ B ₅ H ₇ ^{d,e,g}	¹ J[B1–H]	179	170.4	³ J[H2–H3]	6.7	5.7
	¹ J[B3–H]	182	174.1	³ J[H1–H2]	0.2	0.0
	¹ J[C–H]	190	171.6	³ J[H1–H3]	1.1	1.1
	¹ J[B5–H]	169	165.0	³ J[H1–H5]	0.6	0.6
	¹ J[B1–B5]	9.5	11.8	⁴ J[H1–H7]	9.7	7.6
	³ J[H2–H6]	8.6	7.6	⁴ J[H2–H5]	1.5	1.1
CB ₅ H ₇ ^{d,h}	¹ J[B2(3)–H]	184	177.4	¹ J[B6–H]	174	167.8
	¹ J[B4(5)–H]	162	168.1	⁴ J[HB6–CH]	12.4	9.5
CB ₅ H ₉ ^{i,j}	¹ J[B1–Ht]	166	159.9	¹ J[B3–Hb]	40.5	37.1
	¹ J[B3–Ht]	160	156.1	¹ J[B4–Hb3(4)]	40	45.1
	¹ J[B4–Ht]	163	152.4	¹ J[B4–Hb4(5)]	40	34.5
	¹ J[C2–Ht]	150	142.9	¹ J[B1–B4]	19.5	22.1
	¹ J[B1–Ht]	165	159.0	¹ J[B4–Ht]	157	152.1
2-CH ₃ -CB ₅ H ₈ ^k	¹ J[B3–Ht]	159	152.2	¹ J[B3–Hb]	41	38.3
	¹ J[B1–Ht]	163	157.5	¹ J[B3–Hb3(4)]	36	32.9
3-CH ₃ -CB ₅ H ₈ ^{k,l}	¹ J[B6–Ht]	162	155.3	¹ J[B6–Hb5(6)]	39	36.8
	¹ J[B1–Ht]	165	157.1	¹ J[B1–B4]	19	23.0
4-CH ₃ -CB ₅ H ₈ ^{k,l}	¹ J[B5–Ht]	157	149.8	¹ J[B1–B5]	18	21.6
	¹ J[B1–B3]	7	7.5	¹ J[B1–B6]	7	7.6
	¹ J[B4(6)–Hb]	48	46.0	¹ J[B1–B5]	26.5	32.0
	¹ J[B1–Ht]	179	173.4	¹ J[C–H]	160	148.8
[2,4-C ₂ B ₄ H ₇] ^o	¹ J[B4(6)–Ht]	158	152.5	¹ J[C2–B6]	50	56.5
	¹ J[B5–Ht]	164	151.1			
	¹ J[B3–Ht]	120	116.0 (115.5)	¹ J[B5(6)–Ht]	135	127.8 (126.5)
2,3,4,5-C ₄ B ₂ H ₆ ^{i,p}	¹ J[B1–Ht]	158	148.0 (146.2)	¹ J[B4(5)–H]	142.5	142.4
	¹ J[B2(3)–H]	203.5	194.5	¹ J[B8–Ht]	147	134.6 (132.8)
[1,3-C ₂ B ₆ H ₉] ^q	¹ J[B7–Ht]	136	144.3 (142.5)	¹ J[B6–Hb]	46	48.6 (48.4)
	¹ J[B2–Ht]	144	132.8 (131.8)	¹ J[B4–B5]	47	45.5 (45.1)
	¹ J[B4–Ht]	115	114.3 (112.9)			
	¹ J[B6–Ht]	150	140.6 (138.9)	¹ J[B6–Hb]	40	45.0 (44.6)
4-(CH ₃) ₃ N-1,3-C ₂ B ₆ H ₈ ^q	¹ J[B2–Ht]	152	149.2 (148.3)			
	¹ J[B6–Ht]	160	156.1 (154.7)			
	¹ J[B1–Ht]	134	127.0 (125.0)	¹ J[B7–Ht]	149	141.0 (138.9)
[2,6-C ₂ B ₆ H ₁₁] ^r	¹ J[B3–Ht]	143	133.0 (131.1)	¹ J[B8–Ht]	140	133.0 (130.7)
	¹ J[B4–Ht]	160	133.0 (131.2)	¹ J[B3–Hb]	40	43.4 (43.5)
	¹ J[B1–Ht]	145	131.9 (130.5)	¹ J[B8–Ht]	135	126.5 (124.4)
	¹ J[B2(5)–Ht]	145	139.7 (137.7)	¹ J[B10(11)–Ht]	132	125.0 (123.1)
[7,9-C ₂ B ₉ H ₁₂] ^s	¹ J[B3(4)–Ht]	144	138.0 (136.0)	¹ J[B10(11)–Hb]	56	51.6 (51.5)
	¹ J[B6–Ht]	140	131.3 (129.3)			
	¹ J[B3,6–H]	178	168.2	¹ J[B8(10)–H]	151	145.4
	¹ J[B9(12)–H]	151	144.9	¹ J[B4(5,7,11)–H]	164	157.0
1,7-C ₂ B ₁₀ H ₁₂ ^{e,v}	¹ J[B5(12)–H]	162	156.4	¹ J[B9(10)–H]	151	145.4
	¹ J[B2(3)–H]	178	170.3	¹ J[B4(6,8,11)–H]	164	157.5
	¹ J[C–H]	184	165.9			
B ₄ H ₁₀ ^{m,w}	¹ J[B2–Hb]	30	29.6	¹ J[B1–B3]	20.4	21.6
	¹ J[B1–Ht]	155	150.0			
1-CH ₃ B ₄ H ₉ ^x	¹ J[B3–Ht]	161	148.1	¹ J[B1–Hb]	40	45.4
	¹ J[B2(4)–Hte]	129	127.3	¹ J[B2(4)–Hb]	26	33.1
	¹ J[B2(4)–Hta]	129	120.5			
B ₅ H ₉ ^{y,z,aa,bb}	¹ J[B1–Ht]	175	169.5	¹ J[B2–Hb2(3)]	33	34.1
	¹ J[B1–B2]	19.2	22.6	³ J[H1–Hb2(3)]	5.7	4.5
	¹ J[B2–Ht]	166	159.2	³ J[H1–H2]	5.7	5.7
1-CH ₃ -B ₅ H ₈ ^{y,z,cc,dd}	¹ J[C–H]	120.1	112.0	¹ J[B2–Ht]	166	156.0
	¹ J[B1–C]	73	71.9	¹ J[B2–Hb]	36	34.2
	¹ J[B1–B2]	18.9	22.5	² J[HC–B1]	–6.8	–5.3
2-CH ₃ -B ₅ H ₈ ^{y,cc}	¹ J[C–H]	120.8	113.0	¹ J[B3(5)–Ht]	166	156.0
	¹ J[B2–C]	64	64.8	¹ J[B4–Ht]	164	159.0
	¹ J[B1–Ht]	173	165.7	³ J[Hb–C–H]	3.3	2.9
B ₁₀ H ₁₄ ^{ee}	¹ J[B6(9)–Ht]	160	157.1	¹ J[B5(7,8,10)–Ht]	161	154.5

Table 2 (Continued)

compound	$J[\text{N}-\text{N}']^a$	$J(\text{expt})^b$	$J(\text{calc})^c$	$J[\text{N}-\text{N}']^a$	$J(\text{expt})^b$	$J(\text{calc})^c$
	$^1J[\text{B}2(4)-\text{Ht}]$	159	151.5	$^1J[\text{B}6-\text{Hb}]$	40	37.5
	$^1J[\text{B}1(3)-\text{Ht}]$	151	142.9	$^1J[\text{B}2-\text{B}6]$	18	21.3
$\text{H}_3\text{NBH}_3^{ff}$	$^1J[\text{B}-\text{H}]$	98	98.2 (96.5)			
$\text{Me}_3\text{NBH}_3^{gg}$	$^1J[\text{B}-\text{H}]$	92.5	99.3 (98.2)			
$\text{CH}_3\text{B}_2\text{H}_5^{hh}$	$^1J[\text{B}1-\text{Ht}]$	130	123.3	$^1J[\text{B}2-\text{Ht}]$	134	125.5
	$^1J[\text{B}1-\text{Hb}]$	41	41.7	$^1J[\text{B}2-\text{Hb}]$	44	46.5
$[\text{BH}_4]^-$ ⁱⁱ	$^1J[\text{B}-\text{H}]$	81	66.2 (75.3)			
CH_4^{jj}	$^1J[\text{C}-\text{H}]$	125	115.6	$^2J[\text{H}-\text{H}]$	-12.6	-9.8
$\text{C}_2\text{H}_6^{kk}$	$^1J[\text{C}-\text{H}]$	125.2	114.1	$^2J[\text{C}-\text{H}']$	-4.6	-2.3
	$^1J[\text{C}-\text{C}]$	34.6	31.4			

^a Ht or H refers to a terminally attached hydrogen, and Hb refers to a bridging hydrogen; values in parentheses correspond to equivalent nuclei; coupling values (in the subsequent columns of this table) to boron are to the ^{11}B isotope. ^b References to the experimental J values are given in the first column. The sign (+ or -) of each J value is deemed to be in conformity with the calculated value. ^c $J(\text{calc})$ denotes the DFT/FPT Fermi contact coupling constants. The values in parentheses are those derived from the Fermi contact value calculated using diffuse functions at the UB3LYP/6-311⁺⁺G** level of theory. The calculation at this latter level was carried out only for ions and adducts. All molecules and ions were geometry optimized at the B3LYP/6-31G* level of theory. ^d Onak, T.; Wan, E. *J. Chem. Soc., Dalton Trans.* **1974**, 665–669. Onak, T.; Jarvis, W. *J. Magn. Reson.* **1979**, *33*, 649–654. Miller, V. R.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 15–20. ^e Olah, G. A.; Prakash, G. K. S.; Liang, G.; Henold, K. L.; Haigh, G. B. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 5217–5221. ^f Franz, D. A.; Grimes, R. N. *J. Am. Chem. Soc.* **1970**, *92*, 1438–1439. ^g Nam, W.; Soltis, M.; Gordon, C.; Lee, S.; Onak, T. *J. Magn. Reson.* **1984**, *59*, 399–405. Anderson, J. A.; Astheimer, R. J.; Odom, J. D.; Sneddon, L. G. *J. Am. Chem. Soc.* **1984**, *106*, 2275–2283. ^h Onak, T.; Drake, R.; Dunks, G. *J. Am. Chem. Soc.* **1965**, *87*, 2505. ⁱ Dunks, G. B.; Hawthorne, M. F. *Inorg. Chem.* **1969**, *8*, 2667–2691. Dunks, G. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1968**, *90*, 7355. ^j Groszek, E.; Leach, J. B.; Wong, G. T. F.; Ungermaun, C.; Onak, T. *Inorg. Chem.* **1971**, *10*, 2770–2775. Onak, T.; Herrera, S. Unpublished results, 1993. ^k Onak, T.; Tseng, J.; Tran, D.; Correa, M.; Herrera, S.; Arias, J. *Inorg. Chem.* **1992**, *31*, 2161–2166. Onak, T.; Perrigan, R. Unpublished results, February 1998. ^l Onak, T.; Spielman, J. *J. Magn. Reson.* **1970**, *3*, 122–133. ^m Onak, T.; Leach, J. B.; Anderson, S.; Frisch, M. J. *J. Magn. Reson.* **1976**, *23*, 237–248. ⁿ Akitt, J. W.; Savory, C. G. *J. Magn. Reson.* **1975**, *17*, 122–124. Onak, T.; Perrigan, R. Unpublished results, April 1998. ^o Abdou, Z. J.; Gomez, F.; Abdou, G.; Onak, T. *Inorg. Chem.* **1988**, *27*, 3679–3680. Onak, T.; Lockman, B.; Haran, G. *J. Chem. Soc., Dalton Trans.* **1973**, 2115–2118. ^p Onak, T.; Wong, G. T. F.; McKenzie, M.; Alfonso, C. *Organomet. Synth.* **1988**, *4*, 430–432. ^q Onak, T.; Tseng, J.; Tran, D.; Herrera, S.; Chan, B.; Arias, J.; Diaz, M. *Inorg. Chem.* **1992**, *31*, 3910–3913. ^r Reference 4. ^s Plesek, J.; Stibr, B.; Fontaine, X.; Kennedy, J.; Hermánek, S.; Jelínek, T. *Collect. Czech. Chem. Commun.* **1991**, *56*, 1618–1635. ^t *Gmelin Handbuch der Anorganischen Chemie, Ergänzungswerk*, Vol. 43; Bor-Wasserstoff-Verbindungen, Springer-Verlag: Berlin, 1977; Borverbindungen Part 12, pp 256–257. ^u Todd, L. *J. Pure Appl. Chem.* **1972**, *30*, 587–598. ^v *Gmelin Handbuch der Anorganischen Chemie, Ergänzungswerk*, Vol. 43; Bor-Wasserstoff-Verbindungen, Springer-Verlag: Berlin, 1977; Borverbindungen Part 12, pp 258–259. ^w Leach, J. B.; Onak, T.; Spielman, J.; Rietz, R. R.; Schaeffer, R.; Sneddon, L. G. *Inorg. Chem.* **1970**, *9*, 2170–2175. ^x Jaworowski, I. S.; Long, J. R.; Barton, L.; Shore, S. G. *Inorg. Chem.* **1979**, *18*, 56–60. ^y Tucker, P. M.; Onak, T.; Leach, J. B. *Inorg. Chem.* **1970**, *9*, 1430–1441. ^z Lowman, D. W.; Ellis, P. D.; Odom, J. D. *Inorg. Chem.* **1973**, *12*, 681. ^{aa} Onak, T. *J. Chem. Soc., Chem. Commun.* **1972**, 351–352. ^{bb} Reference 16. Moniz, W. B.; Poranski, C. F.; Sojka, S. A. *J. Magn. Reson.* **1975**, *20*, 535–539. ^{cc} Onak, T.; Wan, E. *J. Magn. Reson.* **1974**, *14*, 66–71. Leach, J. B.; Onak, T. *J. Magn. Reson.* **1971**, *4*, 30–39. ^{dd} Reference 48. ^{ee} Gaines, D. F.; Nelson, C. K.; Kunz, J. C.; Morris, J. H.; Reed, D. *Inorg. Chem.* **1984**, *23*, 3252–3254. ^{ff} Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag: New York, 1978; p 284. ^{gg} Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag: New York, 1978; p 285. ^{hh} Bunting, R. K.; Jungfleisch, F. M.; Hall, C. L.; Shore, S. G. *Inorg. Synth.* **1979**, *19*, 237–239. ⁱⁱ Reference 52. ^{jj} Muller, N.; Pritchard, D. E. *J. Chem. Phys.* **1959**, *31*, 768–771, 1471–1476. Banwell, C. N.; Sheppard, N. *Discuss. Faraday Soc.* **1962**, *34*, 115–126. Anet, F. A. L.; O'Leary, D. J. *Tetrahedron Lett.* **1989**, *30*, 2755–2758. ^{kk} References 49 and 31.

In these circumstances, line separations may correspond to sums and differences of coupling constants, and the use of NMR spectral data without, e.g., isotopic substitution, could lead to data which are inappropriate for comparisons with the computed values. The good agreement between the calculated and experimental values in Table 2 suggests that these problems are no worse than the neglect of many other things, such as noncontact contributions, motional averaging, gas-to-solution shifts, and solvent effects.

The data in Tables 1 and 2 include 124 directly bonded and 31 coupling constants for nuclei separated by two or more bonds. In polycyclic compounds, there are possibilities for multiple coupling paths. These designations specify the shortest path. Thus, the coupling between a boron and a bridging hydrogen is called “directly bonded”, even though there is a two-bond B–B–H path which would be expected to produce large negative contributions. As the strain increases in polycyclic molecules, the role of the bridgeheads becomes an increasingly important factor affecting both the signs and magnitudes of coupling constants.⁴⁷ Since the electronic and structural factors vary widely for directly bonded, geminal, vicinal, and long-range coupling constants, it is important to examine the applicability of the theoretical methods for each of these.²⁰

All directly bonded coupling constants ($^{13}\text{C}-^1\text{H}$, $^{13}\text{C}-^{13}\text{C}$, $^{11}\text{B}-^1\text{H}$, and $^{11}\text{B}-^{11}\text{B}$) in Tables 1 and 2 are assumed to have positive signs, in agreement with the theoretical results. All five of the entries with negative signs are geminal coupling constants. Very few relative sign measurements have been performed in these series of compounds, e.g., the $^2J(^1\text{H}-\text{C}-^{11}\text{B})$ in 1- $\text{CH}_3\text{-B}_5\text{H}_8$ was determined by double-resonance experiments.⁴⁸ Spectral analysis gave the signs for $^2J(^{13}\text{C}-^1\text{H})$ and $^3J(^1\text{H}-^1\text{H})$ relative to $^1J(^{13}\text{C}-^1\text{H})$ in C_2H_6 .⁴⁹ The complexity of the diborane spectra restricted sign determinations to $^1J(^{11}\text{B}-\text{Ht})$ and $^3J(^{11}\text{B}-\text{Ht}')$,¹⁴ so the signs of all other B_2H_6 entries in Table 1 are assumed to be the same as the DFT/FPT results. A positive sign is assumed here for $^2J(\text{Ht}-\text{Ht}')$, but negative signs occur for other computations, such as the EOM/CCSD data in Table 1. However, if this coupling constant is actually negative, then the 6-Hz difference between the calculated and experimental values would be twice as large as any of the DFT/FPT results for nuclei which are not directly bonded.

The calculated directly bonded coupling constants are plotted versus the experimental values in Figure 3. Perfect agreement would have all points on the line of unit slope and zero intercept. A linear regression shows a 4.2-Hz standard deviation and

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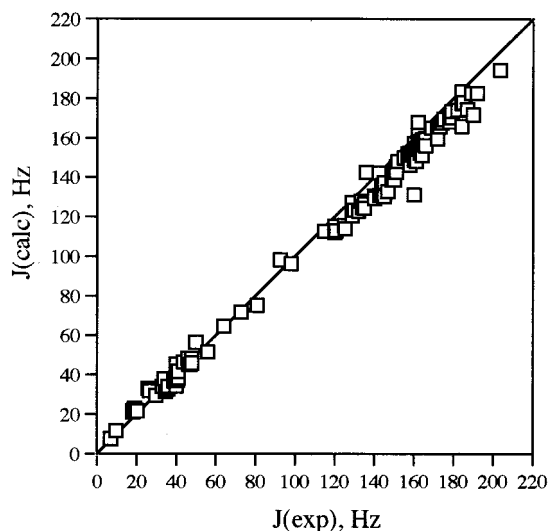


Figure 3. Directly bonded coupling constants 1J in Hz, calculated using the UB3LYP/6-311G**//B3LYP/6-31G* level of theory, except for ions and adducts (zwitterions), for which UB3LYP/6-311⁺⁺G**//B3LYP/6-31G* was used, plotted against the experimentally observed splittings. Data taken from Table 2. A unit slope, zero intercept, line is shown; however, a best-fit relationship for the data is $^1J(\text{calc}) = 0.934 ^1J(\text{exp}) + 3.2$ ($r^2 = 0.994$).

correlation coefficient $r^2 = 0.994$. The experimental data plotted in Figure 3 fall into five different ranges which overlap in a few cases. All but one of the $^{11}\text{B}-^{11}\text{B}$ coupling constants are less than 20 Hz. The ^{11}B coupling constants to the bridging hydrogens (Hb) cover a narrow range between 26 and 36 Hz. As noted above, these much smaller values are, almost certainly, a consequence of substantial negative contributions via the two-bond B-B-H paths. The three entries for $^{11}\text{B}-^{13}\text{C}$ coupling constants range from 50 to 73 Hz. The few values in the range 70–120 Hz arise from the ionic and dipolar species. By far the largest number of coupling constants in Figure 3 are for ^{11}B to terminal hydrogen, but within this range (128–204 Hz) are several $^1J(^{13}\text{C}-^1\text{H})$ values for the polyhedral compounds. These two types of coupling provide the largest deviations between the calculated and experimental results. The largest disparity occurs for $^1J(\text{B4}-\text{Ht})$ of the $[\text{2,6-C}_2\text{B}_6\text{H}_{11}]^-$ ion. It is to be noted, however, that the B4 resonance is the broadest in this C_1 system;⁴ because of strong coupling to B4 from several nuclei, it is possible that the reported value differs substantially from $^1J(\text{B4}-\text{H})$. Unfortunately, full spectral analyses may not be feasible for a spin system of this complexity.

Almost all of the large (> 120 Hz), directly bonded coupling constants in Figure 3 are underestimated by the DFT/FPT results. This can be understood without invoking the inadequacies of the spectral analyses or the neglect of the noncontact mechanisms. All computed coupling constants in the tables apply to the molecules in their equilibrium internuclear positions, while the experimental data reflect averaging over the vibrational motions. A study of the temperature dependence of $^1J(^{13}\text{C}-^1\text{H})$ in the CH_4 isotopomers showed⁵⁰ that the actual equilibrium value should be 120.78 Hz. As a consequence, the 125-Hz experimental gas phase value for methane in Table 2 reflects a nuclear motion contribution of 3.7%. By analogy, it seems likely that all of the 1J values in Table 2 associated with terminal hydrogens are overestimated by this amount. However, the role of nuclear motion for $^1J(^{11}\text{B}-\text{Hb})$ values involving *bridging hydrogens* remains to be investigated.

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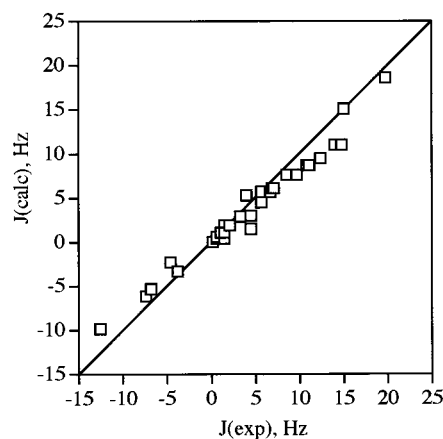


Figure 4. Nondirectly bonding coupling constants 2J , 3J , and 4J , calculated using the UB3LYP/6-311G**//B3LYP/6-31G* level of theory, plotted as a function of the experimental data. The solid line has unit slope and zero intercept. A best-fit relationship for the data is $^nJ(\text{calc}) = 0.833 ^nJ(\text{exp}) + 0.1$ ($r^2 = 0.973$).

With the exception of methane, experimental data in Table 2 were obtained in solution, often for the neat compound. With increasing density and/or condensation to the liquid, intermolecular effects will affect the measured coupling constants. Data for directly bonded $^{11}\text{B}-^1\text{H}$ coupling constants appear to be unavailable, but $^1J(^{13}\text{C}-^1\text{H})$ values increase slightly (ca. 1 Hz or less) on going from the gas to the solution phase.⁵¹ Because of the medium dependence of NMR parameters, it is preferable for comparison of calculated experimental results to use low concentrations of solute measured in a nonpolar solvent such as cyclohexane. This may not be important for species without dipole moments such as $[\text{BH}_4]^-$, where the $^{11}\text{B}-^1\text{H}$ coupling constants exhibit very little solvent dependence.⁵² However, for small *polar* solutes it has been shown that the $^1J(^{13}\text{C}-^1\text{H})$ values increase substantially with solvent polarity.⁵¹ The large dipole moments of some of the polyhedral boranes in Figures 1 and 2 could be another factor for underestimations of the directly bonded coupling constants.

In Figure 4 the DFT/FPT data for nondirectly bonded coupling constants are plotted versus the experimental data from Tables 1 and 2. Again, since the straight line corresponds to a perfect fit, the agreement is fairly good. Linear regression analysis of the 31 entries shows a 1.0-Hz standard deviation and $r^2 = 0.973$. These data fall into three overlapping ranges. Most of the 2J experimental data (from -12.6 to 15 Hz) have negative signs, but large positive values also occur. The 14 vicinal 3J values in Figure 4 range from 0.2 to 19.7 Hz. The largest of these is the $^{13}\text{C}-^1\text{H}$ coupling between a bridgehead carbon and the proton on the other bridgehead of 1,5- $\text{C}_2\text{B}_3\text{H}_5$. This is even larger than the analogous value (12.1 Hz) in bicyclo[1.1.1]pentane.⁴⁷ Twelve of the 3J values are in the range 0.2–8.7 Hz, and these correspond to vicinal coupling between cis-oriented protons. In these situations, the 3J values are expected to have an approximate $(1 + \cos \theta_1)(1 + \cos \theta_2)$ dependence on the H-X-Y and X-Y-H internal angles θ_1 and θ_2 , respectively.⁵³ The 8.5-Hz range for $^3J(\text{H}-\text{H})$ in 2,4- $\text{C}_2\text{B}_5\text{H}_7$ can be understood in terms of this dependence on internal angles. In Figure 4 there are 10 entries for long-range coupling over four bonds. These 4J values vary from 1.5 to 14.8

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Hz. The larger values occur in the most strained polyboranes and involve protons which are bonded to bridgehead carbon and boron atoms. These results are consistent with the enhanced coupling constants which have been extensively investigated in the bicycloalkane series.⁴⁷

IV. Conclusions

Density functional theory methods were used to calculate the Fermi contact contributions in a large number of polycyclic carboranes and boron hydrides. Considering the spectral complexity and size of these molecules, the results are quite reasonable and could be used to predict coupling constants in these molecules. The many possible problems that could occur for polyhedral compounds must be minor in nature, since for most of the available data, comprising more than 100 scalar couplings, there is a good linear correspondence between calculated (Fermi contact) and experimental values. Disparities averaging 5% in the directly bonded $^{13}\text{C}-^1\text{H}$ and the $^{11}\text{B}-^1\text{H}$ coupling constants associated with terminal hydrogens are close to those expected from the nuclear motion contributions.

Despite the excellent success demonstrated here for the use of DFT methods for the Fermi contact contributions applied to

polyhedral boranes, caution should be exercised in their application to other systems, such as those containing fluorine, where the noncontact mechanisms are usually substantial. Density functional theory methods are very effective in calculations of both coupling constants and chemical shifts in polyhedral boron compounds. Because the NMR spectra are complex for many of these compounds, good initial guesses of the signs and magnitudes of the NMR parameters may provide the incentive to attempt the spectral analyses.

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