J. Am. Chem. Soc. **1996,** *118,* 4405−4410

^{13}C NMR Studies on Carboranes and Derivatives: Experimental/Calculational Correlations

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Received December 9, 1995⊗

Abstract: The measured ^{13}C chemical shifts of over forty carborane compounds correlate very well with ab-initio/IGLO/NMR calculated values at both the DZ//3-21G and DZ//6-31G* (IGLO-NMR//Gaussian-geometry-optimized) levels of theory as well as with the ab-initio/GIAO/NMR values at the 6-31G*//6-31G* level of theory. For the carboranes in this study, the linear relationships $\delta(^{13}\text{C-IGLO-DZ//6-31G*}) = 0.941\delta(^{13}\text{C-exp}) - 1.897$ ($r^2 = 0.990$) and $\delta(^{13}\text{C-GIAO-6-31G*//6-31G*}) = 0.893\delta(^{13}\text{C-exp}) - 2.554$ ($r^2 = 0.991$) are derived. Combined together with recently reported ^{11}B NMR correlations between experiment and theory, a significant means is added to the arsenal of carborane NMR structure proof methods available to the experimentalist having access to only modest computational resources. And this procedure, of course, also has the additional feature of yielding reasonably good structural information (bond distances, angles, etc.).

Introduction

NMR studies on carboranes, $C_nB_mH_{n+m+x}$ ($n = 1$ to 4, $m = 2$ to 10, $x = 0$ to 4)[1] and related polyhedral compounds, have dealt primarily with ^{11}B and ^{1}H nuclei.[2] Accounts of ^{13}C NMR chemical shifts of carboranes, following two brief initial reports[3,4] and one early review,[5] are sparse and have been principally confined to individual chemical shift determinations for a few specific compounds in the course of synthetic studies.[2] Theoretical calculations of carborane ^{13}C chemical shifts are meager, but an important IGLO/NMR study[6] that principally emphasized ^{11}B correlations[7] between theoretical and experimental findings did also result in ^{13}C chemical shift predictions for a few carboranes. The IGLO[8] study[6] included ^{13}C information for *closo*-1,5-$C_2B_3H_5$, *closo*-1,2- and 1,6-$C_2B_4H_6$, *closo*-CB_5H_7, *nido*-2-CB_5H_9, *nido*-2,3-$C_2B_4H_8$, and *nido*-2,3,4,5-$C_4B_2H_6$. In the instances of 1,2-$C_2B_4H_6$, CB_5H_7, 2-CB_5H_9, and 2,3,4,5-$C_4B_2H_6$, no experimental work was heretofore available; but for the remaining three carboranes in this previous study the match between theoretical and experimental ^{13}C chemical shifts was found to be within a few ppm at the DZ//MP2/6-31G* (IGLO//ab-initio geometry optimization level) level of computation; i.e., $\delta = 78.5$ (expt), 80.3 (theor) ppm for 1,6-$C_2B_4H_6$; $\delta = 122$ (expt), 123.9 (theor) ppm for 2,3-$C_2B_4H_8$; and $\delta = 103$ (expt), 96.9 (theor) ppm for 1,5-$C_2B_3H_5$.

⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1996.

(1) Although many combinations of *n*, *m*, and *x* are known,[2] all possible combinations, of course, have not yet been reported.

(2) For the many primary sources consult the references and reviews cited in the pertinent volumes of the Boron Compound series of the *Gmelin Handbook of Inorganic and Organometallic Chemistry,* in particular: *Gmelin Handbook of Inorganic Chemistry*; Springer-Verlag: Berlin, FRG, 1974, 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; 1977, Borverbindungen *15*; 1977, Borverbindungen *18*; 1978, 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, 4th Suppl. Vol. 4, pp 178−321.

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S0002-7863(95)04089-3 CCC: $12.00

Table 1. ^{13}C NMR Chemical Shifts, Obtained Experimentally and Obtained from IGLO and GIAO Calculations on ab Initio Optimized Geometries, with δ Given in ppm Relative to Tetramethylsilane

compd	carbon position	δ, exptl	δ, IGLO DZ//3-21G[a]	δ, IGLO DZ//6-31G* [a]	δ, GIAO 6-31G*//6-31G*
2,3,4,5-$C_4B_2H_6$	C(2,5)	88.9	86.1[g]	86.2[g]	77.3
2,3,4,5-$C_4B_2H_6$	C(3,4)	101.4	109.6[g]	104.2[g]	92.5
6-Me-2,3,4,5-$C_4B_2H_5$	$C_{cage}(2,5)$	86.9	80.7	82.3	74.2
6-Me-2,3,4,5-$C_4B_2H_5$	$C_{cage}(3,4)$	99.9	109.1	103.6	92.0
6-Me-2,3,4,5-$C_4B_2H_5$	Me	−2.5	−2.9	−3.4	−3.0
1,5-$C_2B_3H_5$	C(1,5)	103.3[b,c]	96.5[g]	94.9[g]	88.0
1,2-$C_2B_4H_6$	C(1,2)	50.3	46.1[g]	42.6[g]	37.5
1,6-$C_2B_4H_6$	C(1,6)	78.5[b,c]	80.7[g]	76.3[g]	70.6
2-Cl-1,6-$C_2B_4H_5$	C(1,6)	81.1	80.8	78.0	69.8
2,4-Cl_2-1,6-$C_2B_4H_4$	C(1,6)	80.9	82.2	79.2	70.1
2,3-$C_2B_4H_8$	C(2,3)	123.7[b]	128.6[g]	121.1[g]	114.4
2-Me-2,3-$C_2B_4H_7$	$C_{cage}(2)$	141.3	141.2	132.8	129.4
2-Me-2,3-$C_2B_4H_7$	$C_{cage}(3)$	125.7	128.1	121.8	114.5
2-Me-2,3-$C_2B_4H_7$	Me	26.2	21.3	21.4	22.8
2,3-Me_2-2,3-$C_2B_4H_6$	$C_{cage}(2,3)$	136.7	138.9	131.6	126.8
2,3-Me_2-2,3-$C_2B_4H_6$	Me	20.3	17.7	17.8	18.6
$[2,4\text{-}C_2B_4H_7]^-$	C(2,4)	75.2	69.5	68.3	58.0
3-Me_3N-2,4-$C_2B_4H_6$	C(2,4)	63.4	60.1	59.1	51.0
3-Me_3N-2,4-$C_2B_4H_6$	Me	54.1	47.6	46.1	45.4
1-Me-B_5H_8	Me	−11.2[d]	−10.5	−10.3	−10.5
1-CB_5H_7	C(1)	58.7	42.9[g]	45.5[g]	41.0
2-Me-1-CB_5H_6	$C_{cage}(1)$	58	44.5	46.9	42.5
2-Me-1-CB_5H_6	Me	−5.5	−4.9	−5.3	−6.5
2-CB_5H_9	C(2)	107.6	103.2[g]	98.9[g]	91.4
2-Me-2-CB_5H_8	$C_{cage}(2)$	127.4	117.3	111.7	108.6
2-Me-2-CB_5H_8	Me	24.2	20.1	20.3	21.3
3-Me-2-CB_5H_8	$C_{cage}(2)$	104.8	97.3	94.4	87.7
3-Me-2-CB_5H_8	Me	2.3	1.3	1.4	1.2
4-Me-2-CB_5H_8	$C_{cage}(2)$	106.4	101.9	97.4	90.0
4-Me-2-CB_5H_8	Me	−2.6	−2.9	−2.8	−2.7
2,4-$C_2B_5H_7$	C(2,4)	80.0[b,c]	77.1[g]	73.9[g]	70.5
1-Me-2,4-$C_2B_5H_6$	$C_{cage}(2,4)$	83.3	77.0	73.9	70.8
1-Me-2,4-$C_2B_5H_6$	Me	−3.5	−3.5	−3.7	−4.2
2-Me-2,4-$C_2B_5H_6$	$C_{cage}(2)$	86.0	84.8	80.7	82.9
2-Me-2,4-$C_2B_5H_6$	$C_{cage}(4)$	82.9	76.1	73.1	69.1
2-Me-2,4-$C_2B_5H_6$	Me	20.6	16.6	16.7	17.6
3-Me-2,4-$C_2B_5H_6$	$C_{cage}(2,4)$	81.3	74.5	71.8	69.4
3-Me-2,4-$C_2B_5H_6$	Me	−2.5	−1.3	−1.4	−2.5
5-Me-2,4-$C_2B_5H_6$	$C_{cage}(2)$	80.1	74.3	72.1	68.6
5-Me-2,4-$C_2B_5H_6$	$C_{cage}(4)$	82.7	77.8	74.3	71.2
5-Me-2,4-$C_2B_5H_6$	Me	−3.5	−2.8	−2.8	−3.1
1-Cl-2,4-$C_2B_5H_6$	C(2,4)	82.7	75.8	74.2	70.7
3-Cl-2,4-$C_2B_5H_6$	C(2,4)	81.2	75.4	73.3	69.1
5-Cl-2,4-$C_2B_5H_6$	C(2)	78.3	72.7	71.0	66.9
5-Cl-2,4-$C_2B_5H_6$	C(4)	83.7	80.6	78.1	73.5
5,6-Me_2-2,4-$C_2B_5H_5$	$C_{cage}(2,4)$	82.1	74.9	72.4	69.3
5,6-Me_2-2,4-$C_2B_5H_5$	Me	−3.7	−3.5	−3.4	−4.0
1,5-Cl_2-2,4-$C_2B_5H_5$	C(2)	80.6	71.9	71.6	67.4
1,5-Cl_2-2,4-$C_2B_5H_5$	C(4)	85.7	80.8	78.6	73.7
3,5-Cl_2-2,4-$C_2B_5H_5$	C(2)	76.1	67.8	69.5	64.5
3,5-Cl_2-2,4-$C_2B_5H_5$	C(4)	83.0	79.4	77.2	71.9
5,6-Cl_2-2,4-$C_2B_5H_5$	C(2,4)	82.1	81.3	74.9	69.6
1,5,6-Me_3-2,4-$C_2B_5H_4$	$C_{cage}(2,4)$	83.2	75.4	73.0	70.1
1,5,6-Me_3-2,4-$C_2B_5H_4$	Me(1)	−4.7	−3.4	−3.7	−4.5
1,5,6-Me_3-2,4-$C_2B_5H_4$	Me(5,6)	−4.3	−3.3	−3.3	−3.9
1,3,5,6,7-Me_5-2,4-$C_2B_5H_2$	$C_{cage}(2,4)$	83.9	73.1	71.2	69.8
1,3,5,6,7-Me_5-2,4-$C_2B_5H_2$	Me(1,7)	−4.1	−4.2	−4.3	−5.2
1,3,5,6,7-Me_5-2,4-$C_2B_5H_2$	Me(5,6)	−2.4	−3.0	−3.0	−3.9
1,3,5,6,7-Me_5-2,4-$C_2B_5H_2$	Me(3)	−0.9	−0.3	−0.4	−1.9
1,7-$C_2B_6H_8$	C(1,7)	72.9	72.8	65.4	63.0
$[1,3\text{-}C_2B_6H_9]^-$	C(1)	34.5	34.4	29.3	25.0
$[1,3\text{-}C_2B_6H_9]^-$	C(3)	76.0	67.9	71.5	64.8
$[2,6\text{-}C_2B_6H_{11}]^-$	C(2)	82.9	82.9	79.7	70.0
$[2,6\text{-}C_2B_6H_{11}]^-$	$C(6)H_2$	−22.4	−20.0	−21.6	−23.9
1,6-$C_2B_7H_9$	C(1,6)	70.3[c]	61.3	64.6	61.7
1,6-$C_2B_8H_{10}$	C(1)	57.7[c]	40.6	40.6	40.4
1,6-$C_2B_8H_{10}$	C(6)	35.4[c]	40.5	35.1	32.6
1,10-$C_2B_8H_{10}$	C(1,10)	102.9	94.2	91.0	89.0
2,3-$C_2B_9H_{11}$	C(2,3)	88.8[c]	83.8	83.3	81.0
$[7,8\text{-}C_2B_9H_{12}]^-$	C(7,8)	*ca.* 45[e]	39.0	35.3	31.1
$[7,9\text{-}C_2B_9H_{12}]^-$	C(7,9)	*ca.* 35[f]	27.4	24.7	19.3

Table 1 (Continued)

compd	carbon position	δ, exptl	δ, IGLO DZ//3-21G^a	δ, IGLO DZ//6-31G* ^{a}	δ, GIAO 6-31G*//6-31G*
1,2-$C_2B_{10}H_{12}$	C(1,2)	55.5^{b,c}	47.9	43.2	41.9
1,7-$C_2B_{10}H_{12}$	C(1,7)	55.1^{b,c}	46.3	43.8	44.5
1,12-$C_2B_{10}H_{12}$	C(1,12)	63.5^c	64.4	60.6	58.1

[a] The designation before the // marks represents the level of calculation carried out with the IGLO/NMR, or GIAO/NMR, method. The designation after the // marks represents the level of calculation used for the geometry optimization procedure using the Gaussian code. [b] Our experimentally measured values agree reasonably well with those reported earlier: 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. (1,5-$C_2B_3H_5$ 103.3; 1,6-$C_2B_4H_6$ 78.5; 2,3-$C_2B_4H_8$ 122; 2,4-$C_2B_5H_7$ 80; 1,2-$C_2B_{10}H_{12}$ 56.4; 1,7-$C_2B_{10}H_{12}$ 56.3). [c] Our experimentally measured values for certain carboranes agree quite well with those reported earlier: Todd, L. J. *Pure Appl. Chem.* **1972**, *30*, 587 (1,5-$C_2B_3H_5$ 102.4; 1,6-$C_2B_4H_6$ 77.2; 2,4-$C_2B_5H_7$ 80; 1,6-$C_2B_7H_9$ 70.3; 1,6-$C_2B_8H_{10}$ C(1) 57.1, C(6) 33.4; 2,3-$C_2B_9H_{11}$ 86.5; 1,2-$C_2B_{10}H_{12}$ 55.5; 1,7-$C_2B_{10}H_{12}$ 55.4). The value reported for 1,12-$C_2B_{10}H_{12}$, $\delta = 63.5$, was not rechecked by us. [d] Our experimentally measured value for 1-Me-B_5H_8 agrees well with that, $\delta = -12.2$, reported by Hall et al. (Hall, L. W.; Lowman, P. D.; Ellis, J. D.; Odom, J. D. *Inorg. Chem.* **1975**, *14*, 580). [e] Our experimentally measured value for $[7,8\text{-}C_2B_9H_{12}]^-$ agrees reasonably well with that, $\delta = 47.8$, reported by Howe et al. (Howe, O. V.; Jones, C. J.; Wiesema, R. J.; Hawthorne, M. F. *Inorg. Chem.* **1971**, *10*, 2516) but is somewhat different than that, $\delta = 38.0$, reported by Clouse et al. (Clouse, A. O.; Doddrell, D.; Kahl, S. B.; Todd, L. J. *Chem. Comm.* **1969**, 729). [f] Our experimentally measured value for $[7,9\text{-}C_2B_9H_{12}]^-$ agrees reasonably well with that, $\delta = 38.0$, reported by Clouse et al. (Clouse, A. O.; Doddrell, D.; Kahl, S. B.; Todd, L. J. *Chem. Commun.* **1969**, 729) but is somewhat more different than that, $\delta = 28.8$, reported by Howe et al. (Howe, O. V.; Jones, C. J.; Wiesema, R. J.; Hawthorne, M. F. *Inorg. Chem.* **1971**, *10*, 2516). [g] This value agrees with that reported earlier by Bühl et al. (Bühl, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 477−491).

We extend the ab-initio/IGLO/NMR approach here to include our recently collected ^{13}C NMR information on >40 carborane compounds available to us and to further evaluate the predictive value of the IGLO calculational tool. The confidence level for a linear relationship between ^{13}C chemical shifts, experimentally obtained *vs* calculated values, is determined. In this respect it should be mentioned that previous studies[9] have shown that ^{13}C shifts have been usefully predicted for many organic systems by the IGLO/NMR//ab-initio technique.

Table 2. Geometry Optimized (ab Initio) Energies (au)

compd	HF/3-21G	HF/6-31G*
2,3,4,5-$C_4B_2H_6$	−203.144 41	−204.310 21
6-Me-2,3,4,5-$C_4B_2H_5$	−241.982 06	−243.356 09
1,5-$C_2B_3H_5$	−151.819 03	−152.686 57
1,2-$C_2B_4H_6$	−176.909 65	−177.936 21
1,6-$C_2B_4H_6$	−176.917 62	−177.946 22
2-Cl-1,6-$C_2B_4H_5$	−633.679 83	−636.890 06
2,4-Cl_2-1,6-$C_2B_4H_4$	−1090.439 69	−1095.831 73
2,3-$C_2B_4H_8$	−176.907 07	−179.088 53
2-Me-2,3-$C_2B_4H_7$	−216.883 93	−218.126 70
2,3-Me_2-2,3-$C_2B_4H_6$	−255.704 97	−257.161 65
1,2,3-Me_3-2,3-$C_2B_4H_5$	−294.540 61	−296.204 23
$[2,4\text{-}C_2B_4H_7]^-$	−177.540 25	−178.550 22
3-Me_3N-2,4-$C_2B_4H_6$	−349.284 55	−351.230 83
1-Me-B_5H_8	−166.653 35	−167.618 80
1-CB_5H_7	−164.348 46	−165.306 91
2-Me-1-CB_5H_6	−203.186 36	−204.353 03
2-CB_5H_9	−165.514 39	−166.476 37
2-Me-2-CB_5H_8	−204.333 37	−205.510 56
3-Me-2-CB_5H_8	−204.351 99	−205.522 68
4-Me-2-CB_5H_8	−204.348 98	−205.521 05
2,4-$C_2B_5H_7$	−202.082 11	−203.245 12
1-Me-2,4-$C_2B_5H_6$	−240.920 73	−242.290 92
2-Me-2,4-$C_2B_5H_6$	−240.903 37	−242.281 12
3-Me-2,4-$C_2B_5H_6$	−240.92162	−242.292 60
5-Me-2,4-$C_2B_5H_6$	−240.919 27	−242.290 47
1-Cl-2,4-$C_2B_5H_6$	−658.844 13	−662.189 41
3-Cl-2,4-$C_2B_5H_6$	−658.848 38	−662.192 91
5-Cl-2,4-$C_2B_5H_6$	−658.848 42	−662.192 10
5,6-Me_2-2,4-$C_2B_5H_5$	−279.756 45	−281.335 64
1,5-Cl_2-2,4-$C_2B_5H_5$	−1115.608 81	−1121.135 14
3,5-Cl_2-2,4-$C_2B_5H_5$	−1115.613 09	−1121.138 78
5,6-Cl_2-2,4-$C_2B_5H_5$	−1115.612 58	−1121.13 75
1,5,6-Me_3-2,4-$C_2B_5H_4$	−318.594 76	−320.381 25
1,3,5,6,7-Me_5-2,4-$C_2B_5H_2$	−396.271 71	−398.473 90
1,7-$C_2B_6H_8$	−227.201 34	−228.504 49
$[1,3\text{-}C_2B_6H_9]^-$	−227.201 34	−229.081 40
$[2,6\text{-}C_2B_6H_{11}]^-$	−227.785 16	−230.226 64
1,6-$C_2B_7H_9$	−252.333 42	−253.782 42
1,6-$C_2B_8H_{10}$	−277.924 56	−279.056 99
1,10-$C_2B_8H_{10}$	−277.469 75	−279.096 82
2,3-$C_2B_9H_{11}$	−302.598 19	−304.328 07
$[7,8\text{-}C_2B_9H_{12}]^-$	−303.206 56	−304.930 43
$[7,9\text{-}C_2B_9H_{12}]^-$	−303.240 55	−304.962 30
1,2-$C_2B_{10}H_{12}$	−327.744 66	−329.620 84
1,7-$C_2B_{10}H_{12}$	−327.775 52	−329.649 38
1,12-$C_2B_{10}H_{12}$	−327.778 19	−329.653 14

In order to include several fairly large carboranes (i.e. those with eight or more non-hydrogen atoms) we undertook to correlate the experimental data with IGLO results obtained at the DZ level on 6-31G*, as well as on 3-21G, optimized

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(8) The IGLO method employed here was designed by: (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. *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.

(9) For some examples see: Barfield, M. *J. Am. Chem. Soc.* **1995**, *117*, 2862−2876. Szabo, K. J.; Cremer, D. *J. Org. Chem.* **1995**, *60*, 2257−2259. Jiao, H.; Schleyer, P. v. R. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1559−1567. Olah, G. A.; Head, N. J.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995**, *117*, 875−882. Ghose, R.; Marino, J. P.; Wiber, K. B.; Prestegard, J. H. *J. Am. Chem. Soc.* **1994**, *116*, 8827−8828. Fleischer, U.; Kutzelnigg, W.; Lazzeretti, P.; Muehlenkamp, V. *J. Am. Chem. Soc.* **1994**, *116*, 5298−5306. Born, R.; Spiess, H. W.; Kutzelnigg, W.; Fleischer, U.; Schindler, M. *Macromolecules* **1994**, *27*, 1500−1504. Lumsden, M. D.; Wasylishen, R. E.; Eichele, K.; Schindler, M.; Penner, G. H.; Power, W. P.; Curtis, R. D. *J. Am. Chem. Soc.* **1994**, *116*, 1403−1413. Buzek, P.; Schleyer, P. v. R.; Vancik, H.; Mihalic, Z.; Gauss, J. *Angew. Chem.* **1994**, *106*, 470−430; *Angew. Chem., Int. Ed. Engl.*, **1994**, *106*, 448−451. Born, R.; Spiess, H. W.; Kutzelnigg, W.; Fleischer, U.; Schindler, M. *Macromolecules* **1994**, *27*, 1500−1504. Boche, G.; Bosold, F.; Lohrenz, J. C. W.; Opel, A.; Zulauf, P. *Chem. Ber.* **1993**, *126*, 1873−1885. 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.; Hruby, V. J. *Magn. Reson. Chem.* **1993**, *31*, 75−79. Boche, G.; Bosold, F.; Lohrenz, J. C. W.; Opel, A.; Zulauf, P. *Chem. Ber.* **1993**, *126*, 1873−1885. Olah, G. A.; Bausch, J.; Rasul, G.; George, H.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1993**, *115*, 8060−8065. Olah, G. A.; Reddy, V. P.; Rasul, G.; Prakash, G. K. S. *Croat. Chem. Acta* **1992**, *65*, 721−725. Prakash, G. K. S.; Reddy, V. P.; Rasul, G.; Casanova, J.; Olah, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 3076−3078. Schleyer, P. v. R.; Carneiro, J. W. de M.; Koch, W.; Forsyth, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 3990−3992. Buzek, P.; Schleyer, P. v. R.; Vancik, H.; Sunko, D. E. *J. Chem. Soc., Chem. Commun.* **1991**, 1538−1540. Siehl, H. U.; Kaufmann, F. P.; Apeloig, Y.; Braude, V.; Danovich, D.; Berndt, A.; Stamatis, N. *Angew. Chem.* **1991**, *103*, 1546−1549 (see also: *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1479−1482). Barfield, M.; Yamamura, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 4747−4758. Schleyer, P. v. R.; Carneiro, J. W. de M.; Koch, W.; Raghavachari, K. *J. Am. Chem. Soc.* **1989**, *111*, 5475−5477. Bremer, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1989**, *111*, 1147−1148. Bremer, M.; Schoetz, K.; Schleyer, P. v. R.; Fleischer, U.; Schindler, M.; Kutzelnigg, W.; Koch, W.; Pulay, P. *Angew. Chem.* **1989**, *101*, 1063−1067. Dutler, R.; Rauk, A.; Sorensen, T. S.; Whitworth, S. M. *J. Am. Chem. Soc.* **1989**, *111*, 9024−9029. Schleyer, P. v. R.; Laidig, K.; Wiberg, K. B.; Saunders, M.; Schindler, M. *J. Am. Chem. Soc.* **1988**, *110*, 300−301.

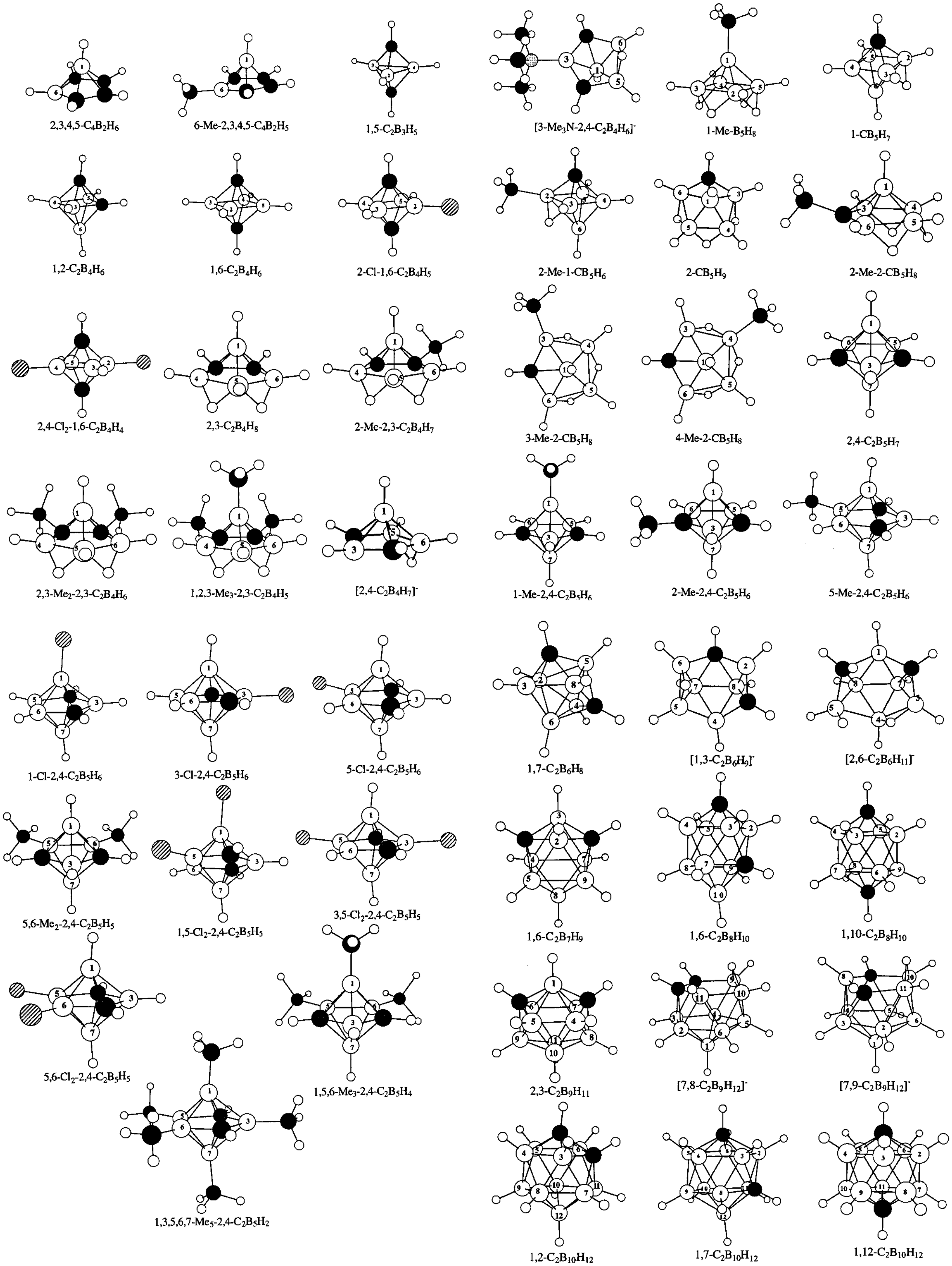

Figure 1. Structures (6-31G* geometry optimized) for the carboranes in this study.

geometries. The application of these levels of theory toward reasonable size (up to 12 non-hydrogen atoms) carboranes is attainable in many laboratories without unreasonable computational resource demands. Should high confidence levels for carborane ^{13}C correlations be found at these levels of theory, this would greatly add, along with the already developed and reported[6,7] ^{11}B NMR correlations, to the arsenal of structure proof procedures for polyhedral compounds of carbon and boron. This would not only be helpful in making overall structural assignment(s) to any new carboranes but also have the benefit of providing reasonably useful geometrical (bond-distance, bond-angle, and bond-dihedral) parameters as a result of the ab-initio geometry optimization procedure that is a part of the overall ab-initio//IGLO/NMR scheme.[6] Although this is necessarily "gas-phase" derived information, it could, in some instances, supplement any diffraction information and/or microwave derived data, or in many other instances provide the initial structural information on a compound.

Experimental Section

The ^{13}C spectra were obtained, and chemical shifts (Table 1) measured, by use of a Bruker 300-MHz instrument. Prior to each ^{13}C acquisition, the identity of each carborane[2] in question was confirmed with ^{11}B and ^{1}H spectra recorded on a Bruker 400-MHz instrument. One of the obvious problems in obtaining ^{13}C data for carboranes relates not only to the low abundance of this nucleus, of course, but also to the presence of short-, medium-, and long-range couplings of ^{11}B and ^{10}B nuclei to the ^{13}C nucleus; and this often results in very broad resonances that do not emerge from the base-line until the information from a very substantial number of spectroscopic "sweeps" has been gathered and added together. Often, overnight, or longer, accumulation times were required for obtaining a reasonable signal-to-noise spectrum for a given carborane. The ^{13}C NMR chemical shifts were referenced to tetramethylsilane, with greater positive δ values associated with downfield chemical shifts.

Energy optimized (Table 2) calculated structures for all molecules were carried out using the ab initio Gaussian-90, Gaussian-92, and Gaussian-94 codes[10] with split valence basis sets at the HF/3-21G level and with polarization functions at the HF/6-31G* level of theory. Each geometry optimization gave a stable structure resulting in no imaginary frequencies upon subjecting each compound to a vibrational frequency calculation at the respective levels of theory. Depicted in Figure 1 are the carborane molecules which were optimized at the HF/6-31G* level; these differ insignificantly from the same molecules obtained from a geometry optimization at the HF/3-21G level of theory. The energy optimized structures were used to calculate the chemical shieldings using the IGLO[8] method. This method makes use of Huzinaga Gaussian lobe functions.[11] All IGLO calculations were performed with a double-ζ (DZ) set in the contractions (21) for H, (4111/21) for first row elements, and (511111/3111) for the Cl atoms. The ^{13}C NMR chemical shifts are referenced to TMS. For the GIAO calculations (carried out using the Gaussian-94 code with the NMR=GIAO option) the shielding for the 6-31G* optimized TMS [σ(^{13}C of TMS)] is 201.7 ppm at the 6-31G* level of theory. Thus for the GIAO calculations, $\delta(^{13}\mathrm{C}) = 201.7 - \sigma(^{13}\mathrm{C})$. For both $C_2B_7H_9$ and $C_2B_9H_{11}$ the IGLO and GIAO results (both ^{13}C and ^{11}B) agreed best for respective closo structures with maximum symmetry (see Figure 1) rather than for open cage structures that have been considered energetically competitive.[2,12] For the $[7,8\text{-}C_2B_9H_{12}]^-$ ion it was assumed from the literature[2] that the lone bridging hydrogen was quickly tautomerizing between two adjacent boron positions along the open face, rendering the two carbon atoms equivalent over the NMR time scale; and therefore the two calculated ^{13}C shifts for the "static" structure of the compound were averaged.

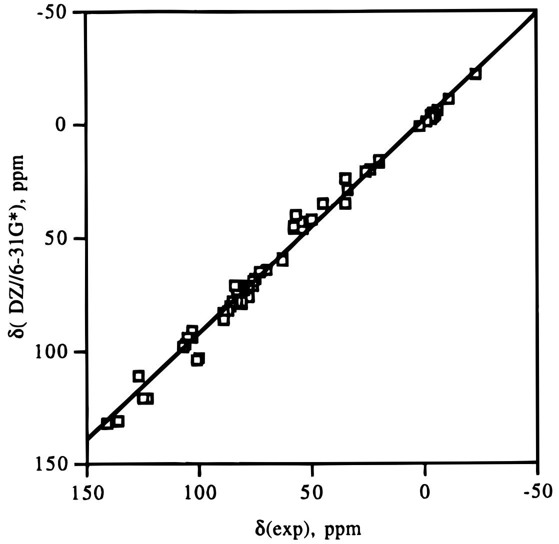

Figure 2. ^{13}C NMR chemical shift comparisons between experimental and IGLO(DZ//6-31G*) calculated values for all the compounds in Table 1; $\delta(\mathrm{DZ//6\text{-}31G^*}) = 0.941\delta(\mathrm{exp}) - 1.897$ ($r^2 = 0.990$).

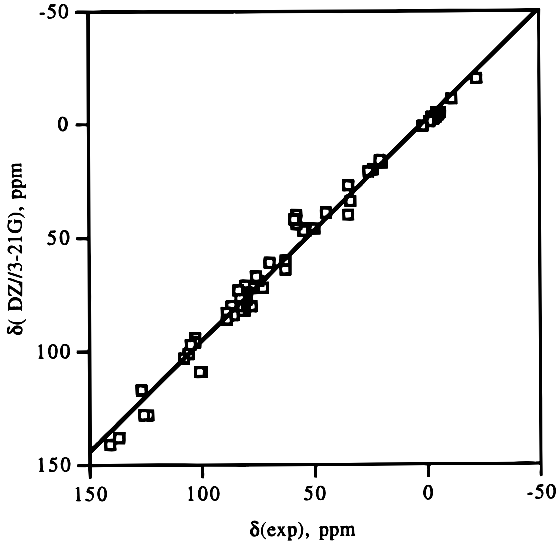

Figure 3. ^{13}C NMR chemical shift comparisons between experimental and IGLO(DZ//3-21G) calculated values for all the compounds in Table 1; $\delta(\mathrm{DZ//3\text{-}21G}) = 0.976\delta(\mathrm{exp}) - 1.908$ ($r^2 = 0.986$).

The IGLO and GIAO results are summarized in Table 1. The small geometry differences between optimization procedures carried out at the 3-21G and 6-31G* levels did not cause significant changes in IGLO calculated chemical shifts. Calculations were carried out, variously, on Multiflow-Trace, Alliant FX/2800 and SUN 4/280, and SPARC station Model 10 computers. The Gaussian-94 code was used on the SDSC Cray C90.

Results and Discussion

The ab-initio/IGLO/NMR and ab-initio/GIAO/NMR calculated ^{13}C NMR chemical shifts for a considerable number of carboranes (Figure 1), given in Table 1, are compared with the corresponding experimentally observed chemical shifts in Figures 2−4. The linear correlation between the IGLO/NMR//ab-initio calculated ^{13}C NMR chemical shifts and the corresponding experimentally obtained chemical shifts are very good. From the findings in this study, ^{13}C IGLO/NMR calculations carried out at the DZ level on 6-31G* optimized geometries (and even on geometries optimized at the 3-21G level of theory)

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(10) (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.; 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, Inc.: Pittsburgh, PA.; (b) GAUSSIAN-92: Gaussian 92, Revision F.4; Frisch, M. J., Trucks, G. W., Head-Gordon, M., Gill, P. M. W., Wong, M. W., Foresman, J. B., Johnson, B. G., Schlegel, H. B., Robb, M. A., Replogle, E. S., Gomperts, R., Andres, J. L., Raghavachari, K., Binkley, J. S., Gonzalez, C., Martin, R. L., Fox, D. J., Defrees, D. J., Baker, J., Stewart, J. J. P., Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1992. (c) GAUSSIAN 94, Revision C.2; Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T., Petersson, G. A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Cioslowski, J., Stefanov, B. B., Nanayakkara, A., Challacombe, M., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M. W., Andres, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. J., Binkley, J. S., Defrees, D. J., Baker, J., Stewart, J. P., Head-Gordon, M., Gonzalez, C., Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1995. (d) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

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

(12) Ceulemans, A.; Goijens, G.; Nguyen, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 9395−9396.

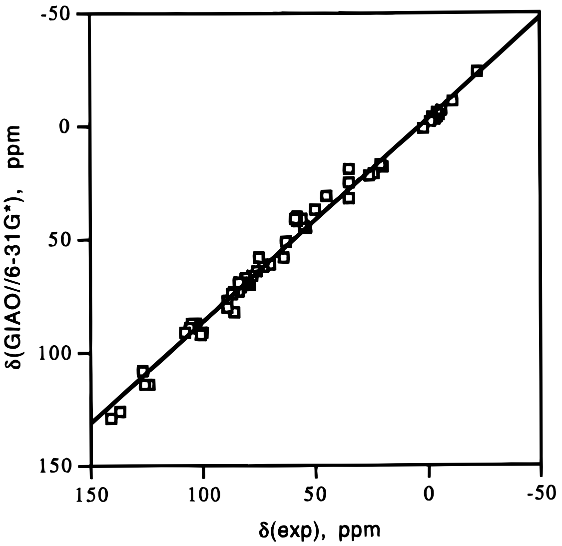

Figure 4. ^{13}C NMR chemical shift comparisons between experimental and GIAO(6-31G*//6-31G*) calculated values for all the compounds in Table 1; δ(6-31G*//6-31G*) = 0.893δ(exp) − 2.554 (r^2 = 0.991).

of carboranes provide a reasonable estimate of where to expect the experimental ^{13}C chemical shift within the approximately 180-ppm range (δ = ca. +150 to ca. −30) in which the reported δ(^{13}C) values are normally found. Considering that the calculations were carried out at these modest DZ//3-21G (IGLO//Gaussian-geometry-optimized) and DZ//6-31G* levels of theory it is satisfying that the slope of each derived relationship [δ-(DZ//3-21G) = 0.976δ(exp) − 1.908 (r^2 = 0.986); δ(DZ//6-31G*) = 0.941δ(exp) − 1.897 (r^2 = 0.990)] is not far from unity, the intercept not far from the ideal value of nil, and the r^2 value close to unity. Similar results are found with the application of the GIAO/NMR method to the same compounds.

When the splendid ^{13}C δ(IGLO)/δ(exp) and ^{13}C δ(GIAO)/δ(exp) correlations are considered alongside previously very acceptable ^{11}B δ(IGLO)/δ(exp) correlations among carborane compounds, it is clear that this calculational combination should significantly add to the confidence level in the assignment of specific polyhedral geometries for any newly discovered carborane compounds.

Acknowledgment. The authors wish to thank the NSF, CHE-9222375, for partial support of this project. M.D., J.J., and J.A. also thank the MBRS-NIH program for partial support and California State University, Sacramento, CA, for access to the Multiflow Trace (NSF Grant CHE-8822716) minisupercomputer facilities. We also wish to thank M. Schindler for permission to use the IGLO program designed by W. Kutzelnigg and M. Schindler, and M. Barfield for helpful discussions concerning NMR calculational methods. We wish to thank the NSF for a grant that helped to purchase the 300-MHz NMR instrument used in the present study. We are grateful to the San Diego Supercomputer Facility for the use of Gaussian-94 on the Cray C90.

JA954089Y