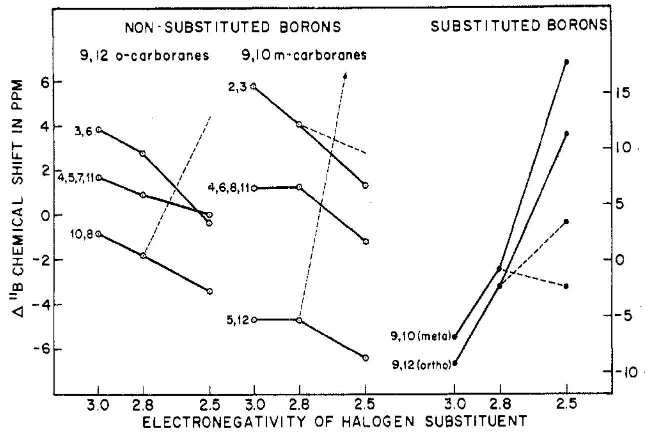

Figure 2. The change in chemical shift of the nonsubstituted and halogen-substituted borons for 9,12-dihalo-*o*-carboranes and 9,10-dihalo-*m*-carboranes relative to the shift of the equivalent boron in the parent *o*- or *m*-carborane plotted against halogen electronegativity. Positive Δ corresponds to an upfield shift. The scale on the left side refers to the nonsubstituted borons and that on the right to the substituted borons. Dashed lines refer to the Δ shift values calculated from the shifts reported by Stanko, *et al.*,[2] using their assignments.

and recent work by Hart and Lipscomb[10] all indicate that ^{11}B nmr chemical shifts depend in a very regular manner on the halogen and site of substitution. Although replacement of hydrogen by chlorine results in deshielding of the substituted boron, as expected by Stanko, *et al.*, replacement of hydrogen by iodine results in a strong shielding of the substituted boron. The effect of substitution of bromine for hydrogen is usually a small deshielding. The effects can be understood[4,11] in terms of the combination of the effect of the halogen electronegativity on the size of the boron 2p orbital and the anisotropic magnetic susceptibility of the halogen atom.

As noted by Hart and Lipscomb[10] the shift of the substituted boron in disubstituted carboranes is almost independent of the position of substitution of the other halogen. We have noted that the shifts of the unsubstituted borons in dihalodecaboranes are predictable on the basis of the additive contributions from each substituent.[9] Because the title compound shows shielding of the substituted boron relative to *o*-carborane and that the effect should extend to dihalogenated compounds, we suggest that the correlations we have observed for the halodecaborane(14) series,[4] the 6,9-bis(dimethyl sulfide) diligando halodecaborane series[8] and the dihalodecaborane series[9] may be extended to the *o*- and *m*-carborane series.

It would seem that Stanko, *et al.*, were unable to interpret their 23-kOe spectra without resorting to proton decoupling, so they did not have the benefit of the information contained in the multiplicities of the lines. Therefore, they assumed that in all cases the halogen-substituted boron would be the most deshielded boron. In all of the cases that we have observed, the change in ^{11}B chemical shift of the substituted boron on going from bromine to iodine substitution (12-18.5 ppm) is larger by a factor of 2-3 than that observed on going from chlorine to bromine substitution (6-8 ppm). Our experience suggests, therefore, that the peak assigned to B(9), B(12) (24.0 ppm) by Stanko, *et al.*, in the spectrum of 9,12-diiodo-*o*-carborane should be reassigned to B(8), B(10) in order to conform with the above generalization. For the same reason, the chemical shifts of 9,10-diiodo-*m*-carborane were reassigned as follows: B(5), B(10) (22.4 ppm), B(2), B(6) (36.9 ppm), and B(9), B(10) (38.4 ppm).

In order to show correlations which we feel are typical of all the series mentioned, we have plotted the chemical shifts of the borons in the various dihalocarboranes relative to the shifts of the equivalent borons in the unsubstituted parent compounds *vs.* the electronegativity of the appropriate halogen (Figure 2). All differences are derived from the values reported by Stanko, *et al.* The solid lines represent our assignments and the dashed lines represent the assignments by Stanko, *et al.* Although the reassignments have not been made on the basis of direct evidence, the solid lines closely parallel the trends previously noted for the decaborane(14) series[4] and the diligando decaborane(14) series.[8] That the parallel extends to sites far removed from the site of substitution suggests that even in the carborane series, the nonbonded halogen electrons are delocalized into the cage. The effect of that delocalization is an alternating variation in the charge density which results in a variation in the size of the boron 2p orbitals and the associated paramagnetic contribution to the chemical shift.[11]

Acknowledgments. Financial support by the Sarah Mellon Scaife Foundation is greatly appreciated, as is the use of the Nmr Facilities for Biomedical Studies which is supported by National Institutes of Health Grant No. RR 00292 and administered by the MPC Corp., Pittsburgh, Pa.

Registry No. 8-Iodo-*o*-carborane, 26375-71-3.

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[9] R. F. Sprecher and B. E. Aufderheide, *Inorg. Chem.*, 13, 2287 (1974).

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[11] (a) F. P. Boer, R. A. Hegstrom, M. D. Newton, J. A. Potenza, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 88, 5340 (1966); (b) M. Karplus and J. A. Pople, *J. Chem. Phys.*, 38, 2803 (1963); (c) J. A. Pople, *Mol. Phys.*, 7, 301 (1964); (d) B. V. Cheney and D. M. Grant, *J. Amer. Chem. Soc.*, 89, 5319 (1967).

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Boron-11 Nuclear Magnetic Resonance Chemical Shift Additivity in Halogenated Decaboranes

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A quantitative approach to the study of boron-11 chemical shifts has been hampered by the small chemical shift range compared to J_{B-H} and the boron-11 line width, a large number of commonly used standards, and a general lack of understanding of boron chemical shifts. The primary contribution to changes in boron chemical shift, however, is generally understood to be the paramagnetic shielding term σ_p[1] although attempts have been made to correlate with the diamagnetic term σ_d[2] and ring currents.[3] Here we show

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(1) (a) F. P. Boer, R. A. Hegstrom, M. D. Newton, J. A. Potenza, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 88, 5340 (1966); (b) M. Karplus and J. A. Pople, *J. Chem. Phys.*, 38, 2803 (1963); (c) C. J. Jameson and H. S. Gutowsky, *ibid.*, 40, 1714 (1964); (d) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969; (e) B. F. Spielvogel and J. M. Purser, *J. Amer. Chem. Soc.*, 93, 4418 (1971).

(2) E. A. Laws, R. M. Stevens, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 94, 4467 (1972).

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Table I. ^{11}B Chemical Shifts (ppm) for Dihalogen-Substituted Decaborane(14) Isomers as 0.1 *M* Solutions in CH_2Cl_2 Referenced by External Replacement to 0.1 *M* TMB in CH_2Cl_2

	B_1	B_2	B_3	B_4	B_5	B_6	B_7	B_8	B_9	B_{10}
Decaborane(14)	6.2	54.2	6.2	54.2	17.7	7.8	17.7	17.7	7.8	17.7
2,4-Dichlorodecaborane(14)	4.3	38.2	4.3	38.2	17.8	12.6	17.8	17.8	12.6	17.8
1,2-Dichlorodecaborane(14)	−4.2	38.4	4.0	53.1	. . .[a]	10.2	. . .	. . .	13.7	. . .
1,3-Dichlorodecaborane(14)	−5.5	51.1	−5.5	51.1	16.2	12.6	16.2	16.2	12.6	16.2
2-Chloro-9-bromodecaborane(14)	7.3	39.7	7.3	52.1	16.6	8.9	16.6	20.0	9.6	20.0
1-Chloro-6-bromodecaborane(14)	−2.7	49.9	7.1	55.3	20.2	9.5	17.2	15.0	10.6	17.7
2,4-Diiododecaborane(14)	3.5	64.4	3.5	64.4	17.7	9.2	17.7	17.7	9.2	17.7
1,2-Diiododecaborane(14)	15.8	61.0	3.1	50.8	. . .	8.6	. . .	. . .	9.6	. . .

[a] Indicates the shift could not be assigned.

that the changes in the ^{11}B nmr chemical shifts on halogen substitution of decaborane are additive parameters which can be used to predict chemical shifts in dihalogenated decaboranes.

We have recently determined the boron-11 chemical shifts for all monochloro-, monobromo-, and monoiododecaborane ($B_{10}H_{14}$) isomers.[4] Chemical shifts were compared to those of the parent decaborane(14) and found to depend in a regular manner upon the halogen and the site of substitution. Shielding of the unsubstituted borons was generally found to be in the order $\sigma(\mathrm{Cl}) > \sigma(\mathrm{Br}) > \sigma(\mathrm{I})$ which is that expected to result from overlap between the 2s,p orbitals on boron and the *n*s,p orbitals on the halogen in the order $\mathrm{Cl} > \mathrm{Br} > \mathrm{I}$ and subsequent donation of electron density from the halogen nonbonding orbitals to the boron cage. Increasing electron density of the cage orbitals produces a decrease in the $\langle r^{-3}\rangle_{2p}$,[1a,b,c] a decrease in σ_p, and therefore increased shielding. The contribution of the two halogen substituents to $\langle r^{-3}\rangle_{2p}$ and σ_p might be expected to be the sum of each halogen contribution considered separately, providing that one halogen does not significantly interfere with the overlap of the other and that the decaborane(14) cage is sufficiently electron deficient to accept the expected electron donation from both halogens.

The magnetic anisotropy of the halogen substituent and the induced paramagnetic shielding are the major factors contributing to the chemical shift of the halogenated boron, causing the iodinated boron resonance to shift more than 16 ppm upfield from that of the parent B-H. The neighbor anisotropy screening may produce a significant shift for the halogenated boron but is expected to produce only a small shift contribution to the nonhalogenated borons because of the R^{-3} and angle dependence in the equation

$$\Delta\sigma = \Delta\chi(1 - 3\cos^2\theta)/3R^3$$

where $\Delta\chi$ is the magnetic susceptibility of the halogen, θ is the angle from the bond axis, and R is the halogen-boron distance. The general shift trend mentioned earlier for nonsubstituted borons of $\sigma(\mathrm{Cl}) > \sigma(\mathrm{Br}) > \sigma(\mathrm{I})$ is opposite in direction to that expected to result from the magnetic anisotropy of the halogens.[5] The relatively large shifts observed for borons in parts of the cage remote from the halogen and the apparent alternation of chemical shift direction also do not support a large anisotropy contribution but can be understood in terms of the change in paramagnetic shielding term with changing boron 2p orbital size.

The 120 ^{11}B chemical shifts determined for the monohalodecaboranes provide a very complete basis for the prediction of chemical shifts in the disubstituted compounds. We have found that the change in chemical shift of the monohalogenated decaboranes relative to the equivalent boron in decaborane (Δ shift) is additive and can be used to directly predict the chemical shifts for dihalogenated decaboranes (Table I). For example, the Δ shift produced at B_5 on substitution of chlorine for hydrogen at B_1 and the Δ shift of B_5 observed for 2-chlorodecaborane(14) can be used to preduct the shift of B_5 in 1,2-dichlorodecaborane(14). Care must be taken to use the correct numbering system for the monosubstituted compounds being used to predict the shifts of a disubstituted compound. At least-squares fit of the observed Δ shifts for the compounds listed in Table I is plotted (Figure 1) against those shifts calculated from the equation

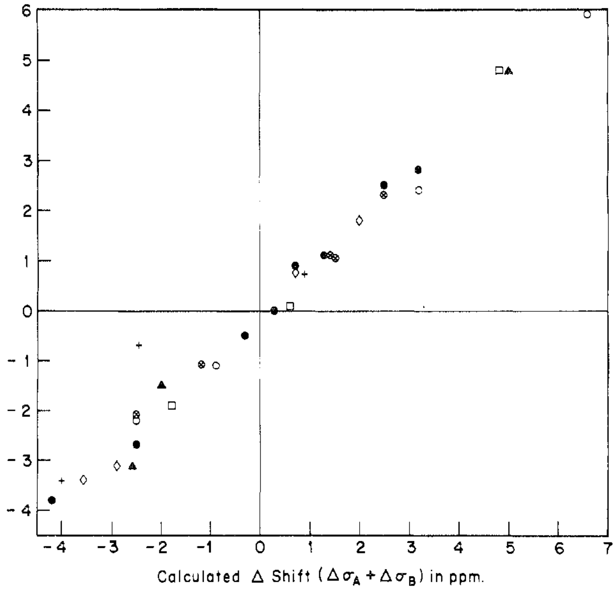

Figure 1. Calculated Δ shift plotted *vs.* observed Δ shift in ppm: □, 2,4-dichlorodecaborane(14); ▲, 1,3-dichlorodecaborane(14); ○, 1,2-dichlorodecaborane(14); ⊕, 2-chloro-9-bromodecaborane(14); ●, 1-chloro-6-bromodecaborane(14); +, 2,4-diiododecaborane(14); ◇, 1,2-diiododecaborane(14). Positive Δ corresponds to upfield shift.

$$\Delta\sigma_C = (0.920 \pm 0.019)[\Delta\sigma_A + \Delta\sigma_B] - (0.047 \pm 0.049)$$

and gives a correlation coefficient[6] of 0.988. $\Delta\sigma_A$ and $\Delta\sigma_B$ are the Δ shifts from the monohalodecaboranes and $\Delta\sigma_C$ is the calculated Δ shift of the dihalodecaborane.

In most cases, chemical shifts were assigned by the ^{11}B-^{11}B double-resonance technique;[4,7] however, in some of the more symmetrically disubstituted decaboranes this was not necessary. All shifts were recorded as approximately 0.1 *M* solutions in methylene chloride, referenced to trimethyl

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(5) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 179.

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borate by external replacement. The samples of 1,2-dichlorodecaborane(14), 2,4-dichlorodecaborane(14), and 1,3-dichlorodecaborane(14) were prepared by addition of 2 equiv of chlorine to 1 equiv of decaborane(14) in methylene chloride in the presence of aluminum chloride. The resulting mixture was then separated by preparative thin-layer chromatography over silica gel.[4] The samples of 1-chloro-9-bromodecaborane(14) and 2-chloro-6-bromodecaborane(14) were prepared by addition of anhydrous hydrogen bromide to a refluxing benzene solution of 1-chloro-6,9-bis(dimethyl sulfide)decaborane and 2-chloro-6,9-bis(methyl sulfide) decaborane, respectively. Both products were also purified by preparative thin-layer chromatography. The samples of 2,4-diiododecaborane(14) and 1,2-diiododecaborane(14) were prepared by heating decaborane in a sealed bulb with 2 equiv of iodine at 115° for 2 days. The products were separated by recrystallization from benzene and preparative thin-layer chromatography over silica gel.

Acknowledgments. Financial support by the Sarah Mellon Scaife Foundation is greatly appreciated, as is the use of the NMR Facilities for Biomedical Studies which is supported by National Institutes of Health Grant No. RR00202 and administered by the MPC Corp., Pittsburgh, Pa.

Registry No. Decaborane(14), 17702-41-9; 2,4-dichlorodecaborane(14), 51933-38-1; 1,2-dichlorodecaborane(14), 51933-39-2; 1,3-dichlorodecaborane(14), 51933-40-5; 2-chloro-9-bromodecaborane(14), 51933-41-6; 1-chloro-6-bromodecaborane(14), 52022-16-9; 2,4-diiododecaborane(14), 23835-60-1; 1,2-diiododecaborane-(14), 51933-42-7; ^{11}B, 14798-13-1.

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Vibrational Spectra of $K_2Zn(CN)_4$, $K_2Cd(CN)_4$, and $K_2Hg(CN)_4$

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Recently Adams and Christopher[1] reported infrared and Raman studies of $K_2Zn(CN)_4$ along with frequency assignments for the vibrational modes. Similar studies have been made in this laboratory for the three isostructural crystals $K_2Zn(CN)_4$, $K_2Cd(CN)_4$, and $K_2Hg(CN)_4$. Most of the vibrational modes have been assigned with certainty from polarized Raman spectra of single crystals or from infrared studies of the powder. This report includes $K_2Zn(CN)_4$ as the frequencies found are slightly different from those reported in ref 1.

Experimental Section

$K_2Zn(CN)_4$ and $K_2Cd(CN)_4$ are readily prepared from the nitrates by first precipitating the dicyanides, washing, and adding a stoichiometric amount of KCN. $K_2Hg(CN)_4$ is prepared from stock $Hg(CN)_2$ and KCN. Single crystals of 1-2 mm size were grown by slow evaporation of aqueous solutions. The crystals grew as rather irregular octahedra. The faces were imperfect; however, they gave good polarized Raman spectra. The spectra were improved by immersing the crystal in chlorobenzene as a medium for matching the refractive index of the crystal to minimize reflection defects.

The Raman spectra were observed on a Cary 82 and the infrared spectra on a Perkin-Elmer 521, a Beckman IR-11, and a Cary 14.

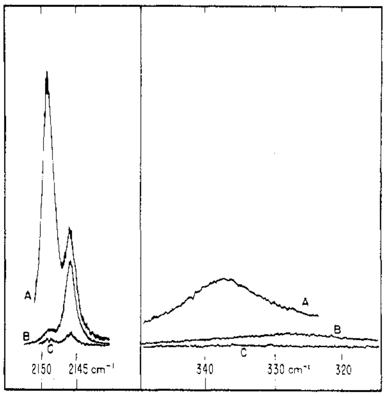

Figure 1. Raman spectrum of a single crystal of $K_2Hg(CN)_4$ immersed in chlorobenzene: A, $[110]\ [[1\bar{1}0]\ [1\bar{1}0]^s]\ [001]$, A_{1g}, F_{2g}; B, $[110]\ [[1\bar{1}0]\ [110]^s]\ [001]$, E_g; C, $[110]\ [[001]\ [1\bar{1}0]^s]\ [001]$, F_{2g}. Slit: 1 cm^{-1} for 2100-cm^{-1} region; 2 cm^{-1} for 300-cm^{-1} region. Gain: 20,000 counts/sec (except as noted in figure).

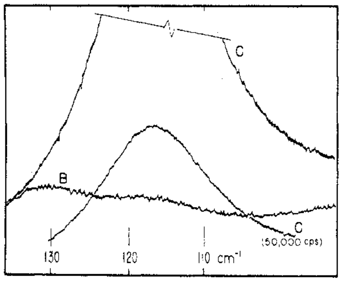

Figure 2. Raman spectrum of a single crystal of $K_2Hg(CN)_4$ immersed in chlorobenzene. Slit: 2 cm^{-1}; see Figure 1 for gain and polarization.

Selection Rules

Adams and Christopher[1] have given the factor group analysis for these crystals which are cubic, F_{d3m} $(O_h{}^7)$, $Z = 8$. There are two formula units per primitive unit cell. The correlation table has been given before[1,2] and is not shown here. There are three Raman-active symmetries: A_{1g} $(x^2 + y^2 + z^2)$, E_g $(x^2 + y^2 - 2z^2; x^2 - y^2)$, and F_{2g} (xy, yz, zx). These three symmetries can be distinguished with one crystal orientation. For example the crystal can be mounted with its [110] axis along the incoming laser beam and its [001] axis along the exiting Raman beam. The incoming laser beam polarization can be rotated through 90° with a polarization rotator to give orientation of $[1\bar{1}0]$ or [001] for the polarization of the incoming beam. The exiting Raman beam passed through a polarization analyzer and a scrambler. We then have the following selection rules, using Swanson's notation[3] for the polarizations

$[110]\ [[1\bar{1}0]\ [1\bar{1}0]^s]\ [001]$ A_{1g}, F_{2g}

$[110]\ [[1\bar{1}0]\ [110]^s]\ [001]$ E_g

$[110]\ [[001]\ [110]^s]\ [001]$ F_{2g}

Results and Discussion

As an example of the Raman spectra, in Figures 1 and 2 are shown part of the spectra for a crystal of $K_2Hg(CN)_4$ mounted with [110] along the incoming beam and [001] along the exiting Raman beam. This crystal was immersed in chlorobenzene to reduce scattering from imperfections and tilted faces. In Figure 1 it is readily apparent that there

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