the magnetic field strength (*i.e.*, "sweeping" the spectrum from the high-mass end to the low-mass end) and admitting acetone into the source after the sample signals had been obtained. The spectrum was then matched to an electron beam generated spectrum of perfluorotributylamine using the acetone signals as indices. In some cases, the mass instead was calculated using mass separation distances for sample peaks and for the p and p + 1 signals of acetone and the distance between voltage markers in the two regions of the spectrum.

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Boron-11 Nuclear Magnetic Resonance Shift Assignments for 8-Iodo-1,2-dicarbadodecaborane(12) and Related Compounds

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Preliminary ^{11}B chemical shift assignments have been made for 1,2-dicarbadodecaborane(12)[1] (*o*-carborane) and several halogenated derivatives.[2] These assignments have been made primarily on the basis of molecular symmetry and chemical evidence. Because of the characteristic small chemical shift range of carboranes, $J_{\text{B-H}}$ is often of a magnitude comparable to the chemical shifts and proton decoupling has been extensively used to simplify the spectra. The ^{11}B–^{11}B nmr double-resonance technique,[3,4] combined with off-resonance proton decoupling and the dispersion of chemical shifts available at 60 kOe has enabled us to assign all of the ^{11}B chemical shifts for 8-iodo-*o*-carborane.[5]

An *o*-carborane[6] substituted in the 8 position has C_s symmetry, with its one symmetry plane passing through B(3), B(6), B(8), and B(10). The spectrum therefore should consist of three doublets of relative area 1 for B(3), B(6), and B(10) and an area 1 singlet for the substituted B(8) and three doublets of area 2 for the three symmetry-equivalent pairs, B(4), B(7); B(5), B(11); and B(9), B(12).

The 80.2-MHz ^{11}B nmr spectrum of 8-iodo-*o*-carborane (Figure 1) shows resonances attributable to nine boron atoms. A singlet of relative area 1 is evident as the most shielded boron and three doublets of area 2 and two doublets of area 1 are readily discerned. On partial decoupling of the protons,

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(5) 8-Iodo-*o*-carborane was prepared by condensation of 2-iodo-6,9-[S(CH₃)₂]₂B₁₀H₁₁ with methyl propiolate followed by decarbomethoxylation with potassium *tert*-butoxide.

(6) Detailed drawings and numbering schemes for *o*- and *m*-carboranes can be found in R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970.
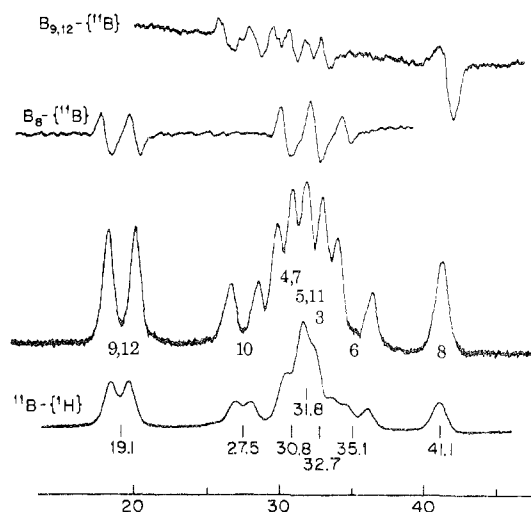

Figure 1. ^{11}B nmr assignments and double-resonance experiments for 8-iodo-*o*-carborane. The bottom scale and chemical shifts are in ppm from trimethyl borate. In the lowest spectrum ^{11}B–{^{1}H} indicates that the ^{11}B spectrum was observed with partial ^{1}H decoupling. The top two traces resulted from the ^{11}B–^{11}B double-resonance experiments. That boron which was observed is denoted as B$_n$.

with a concomitant decrease in the doublet spacing, one of the lines splits into two resonances to reveal the hidden doublet at 32.7 ppm.

The singlet at 41.1 ppm relative to trimethyl borate[7] is assigned to B(8). Three ^{11}B–^{11}B double-resonance experiments[3] were performed to identify the remaining resonances. The intensity of the B(8) resonance was monitored as a second radiofrequency field was swept through the rest of the spectrum. The singlet B(8) resonance showed coupling to the two-boron doublet at 19.1 ppm, the two-boron doublet at 30.8 ppm, and the hidden one-boron doublet at 32.7 ppm. We expect B(8) to be coupled to B(9), B(12); B(4), B(7); and B(3); therefore we assign the hidden doublet at 32.7 ppm to B(3). The two-boron doublet at 19.1 ppm must be either B(9), B(12) or B(4), B(7). We found it to be coupled to the two-boron doublet at 30.8 ppm, the two-boron doublet at 31.8 ppm, the one-boron doublet at 27.5 ppm, and the singlet B(8). The resonance at 19.1 ppm cannot be due to B(4), B(7) because the only unique borons which should be coupled to B(4), B(7) are B(8) and B(3), both of which have already been assigned to resonances other than that at 27.5 ppm. Therefore, we assign the resonance at 19.1 ppm to B(9), B(12). The one-boron doublet at 27.5 ppm, to which B(9), B(12) is coupled, we assign to B(10). The remaining one-boron doublet at 35.1 ppm must be assigned to B(6). Of the pair of two-boron doublets which remain to be assigned, the one at 30.8 ppm is assigned to B(4), B(7) because it is coupled to B(8) and the one at 31.8 ppm is assigned to B(5), B(11). To confirm these assignments, a third experiment was performed which showed B(10) to be coupled to B(9), B(12); B(5), B(11); and B(6) as expected.

The shift of B(8) in the title compound (41.1 ppm) is in such strong contrast to the shifts of the iodinated boron atoms in 9,12-diiodo-*o*-carborane (24.0 ppm) and 9,10-diiodo-*m*-carborane (22.4 ppm) reported by Stanko, *et al.*,[2] that we were led to examine their assignments in detail. Our experience with the halodecaborane(14) series,[4] their 6,9-bis(dimethyl sulfide) diligando derivatives,[8] and dihalodecaboranes[9]

(7) Chemical shifts were taken on a 0.1 *M* sample of 8-iodo-*o*-carborane in methylene chloride and referenced by replacement to a 0.1 *M* sample of trimethyl borate in methylene chloride.

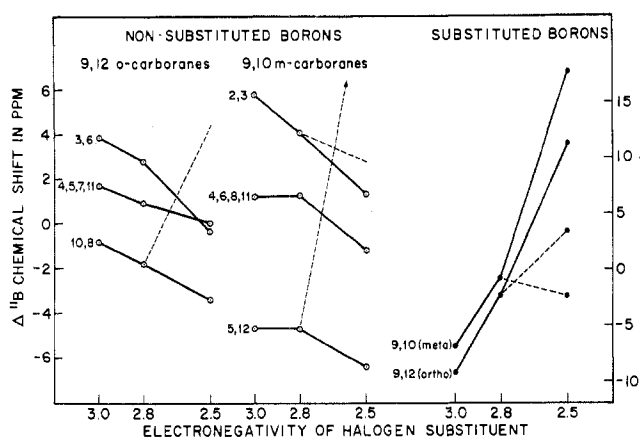(8) B. E. Aufderheide and R. F. Sprecher, unpublished results.

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]

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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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