It is interesting to compare the observed ^{7}Li high-resolution nmr line width of methyllithium in diethyl ether with the natural line width predicted in Figure 1. The former varies from about 3.5 Hz below −50° to about 0.7 Hz at 0° and higher.[6] The latter is 0.1 Hz or less at all temperatures measured (−35° to 38°). Clearly the line broadening is not dominated by spin relaxation. The major factor is probably unresolved lithium–proton scalar coupling as proposed. The decrease in broadening on warming to 0° is consistent with a dissociative process enabling intermolecular exchange.

Correlations between Carbon-13 and Boron-11 Chemical Shifts. III. Pairwise Interaction Parameters[1]

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Abstract: ^{11}B chemical shifts for a variety of tetracoordinate boron resonance nuclei are shown to be pairwise additive with respect to attached substituent groups as has been observed for ^{13}C shifts of tetracoordinate carbon resonance nuclei. Assuming ^{11}B and ^{13}C shifts to be generally pairwise additive for tetracoordinate resonance nuclei, a total of 13 common ^{11}B and ^{13}C pairwise additivity parameters is obtained which are shown to be linearly related. The slope of the linear equation relating the ^{13}C and ^{11}B pairwise parameters is quantitatively accounted for by a consideration of the ratio of the paramagnetic contribution to the chemical shift for BH_4^- and CH_4. The chemical shifts of the hydroxy-substituted hydroborate intermediates, $BH_n(OH)_{4-n}^-$, with $n = 1$–3, are predicted as an example of the potential utility of the correlation. Finally, in view of the correlation between the pairwise parameters, a prediction is made concerning possible similarities in the chemistry of BH_3CO and its isoelectronic carbon analog, CH_3CO^+.

Nmr studies involving ^{13}C and ^{11}B nuclei have long been hampered by features unfavorable toward magnetic resonance measurements.[3] Recently, however, advances in instrumentation, such as field-frequency stabilization techniques[4–7] and pulsed and Fourier-transform nmr spectroscopy,[8] have been increasing the number and application of nmr studies of these nuclei, especially for ^{13}C. In view of this, linear correlations in chemical shift or chemical shift parameters between these two nuclei would be expected to have considerable utility as an empirical tool. In addition, such correlations would imply closely related theoretical interpretations of the chemical shift for these nuclei, thus providing checkpoints for the testing of chemical shift theories.

One linear correlation in chemical shift between these two nuclei has been reported.[9] For ^{13}C shifts in alkanes and the corresponding ^{11}B shifts in the isoelectronic amine–boranes, the equation relating the ^{13}C and ^{11}B shifts was found to be

$$\delta_{^{13}\mathrm{C}} = 1.44\delta_{^{11}\mathrm{B}} + 86.0 \qquad (1)$$

where ^{13}C shifts are in ppm from benzene and ^{11}B shifts are ppm from boron trifluoride diethyl etherate. The average deviation for some ten observed ^{13}C shifts calculated from the observed ^{11}B shifts by this equation was 1.96 ppm (in chemical shift) out of a range in ^{13}C shifts of 50 ppm. Other studies[1a,10,11] have further emphasized the close relationships existing between ^{13}C and ^{11}B chemical shifts, although these have been limited mainly to saturated hydrocarbons and analogous boron–nitrogen compounds.

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(1) (a) Previous paper in this series: J. M. Purser and B. F. Spielvogel, *Inorg. Chem.*, 7, 2157 (1968); (b) presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

(2) (a) Author to whom correspondence should be addressed at Duke University; (b) PRF Predoctoral Fellow, 1969, University of North Carolina.

(3) ^{13}C has low natural abundance (1.1%), long values of relaxation time, and a poor natural sensitivity (μ = 0.70220 nuclear magneton). Although ^{11}B has the higher natural abundance of the two boron isotopes and has a somewhat higher natural sensitivity (μ = 2.688 nuclear magnetons) than ^{13}C, line broadening is observed for ^{11}B ($I = {}^3/_2$) because of its quadrupole moment. See J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, Elmsford, N. Y., 1966, pp 970 and 980.

(4) D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 2228 (1967).

(5) F. J. Weigert and J. D. Roberts, *ibid.*, **89**, 2967 (1967).

(6) G. E. Maciel, P. D. Ellis, and D. C. Hofer, *J. Phys. Chem.*, 71, 2160 (1967).

(7) G. E. Hall, *Annu. Rev. NMR Spectrosc.*, 1, 227 (1968).

(8) T. C. Farrar, *Anal. Chem.*, **42**, 109A (1970).

(9) B. F. Spielvogel and J. M. Purser, *J. Amer. Chem. Soc.*, **89**, 5294 (1967).

(10) B. F. Spielvogel and J. M. Purser, *Chem. Commun.*, 386 (1968).

(11) H. Nöth and H. Vahrenkamp, *Chem. Ber.*, **99**, 1049 (1966). These authors plotted ^{13}C shifts in substituted methanes, CH_3X, *vs.* ^{11}B shifts of the anions BX_4^-, where X = H, Me, NMe_2, OMe, and F. The plot was reasonably linear for the first three substituents but deviated significantly in the case of OMe and F. However, in a plot of the ^{13}C shifts of CX_4 *vs.* the ^{11}B shifts of BX_4^-, where X = H, Me, or OMe, a linear relationship existed but the matter was not further pursued.

In this paper, a linear correlation is presented between ^{13}C and ^{11}B pairwise interaction parameters for tetracoordinate carbon[12] and boron compounds. The ^{13}C and ^{11}B pairwise parameters, associated with a variety of substituent groups attached to the resonance nucleus, closely reproduce the observed ^{13}C and ^{11}B chemical shift in tetracoordinate compounds. Furthermore, it is shown that the slope of the equation relating the ^{11}B and ^{13}C pairwise parameters may be accounted for by the relative paramagnetic shielding of ^{11}B and ^{13}C nuclei in isoelectronic tetracoordinate compounds. An example of the utility of the correlation between the pairwise parameters to boron chemistry is given. Finally, in view of the correlation in chemical shift parameters, some predictions are made concerning relationships in the chemistry of certain tetracoordinate boron and carbon compounds.

Chemical Shift Considerations

Much more attention has been given to theoretical calculations of ^{13}C chemical shifts[13] than to ^{11}B chemical shifts.[14] ^{11}B shifts have most often been considered in a qualitative manner with the distinction made that ^{11}B resonances of tetrahedrally coordinated boron in simple molecules and ions are generally found in the upper half of the chemical shift range, whereas ^{11}B resonances of three-coordinate boron compounds occur at lower fields.[15]

A useful attempt to qualitatively relate ^{11}B shifts to the nature of the substituent group has been carried out by Nöth and Vahrenkamp.[11] These authors clearly show that in three-coordinate boron compounds the ^{11}B shift is dependent upon the type and number of substituent groups but does not obey any linearly additive relationship with respect to the substituents. Although these authors did not extensively consider substituent effects for tetracoordinate boron compounds, examination of Figure 1 again reveals striking similarities in the substituent effect on the resonances of ^{11}B and ^{13}C nuclei in tetracoordinate compounds. The ^{11}B chemical shift values used for Figure 1b are listed in Table I, and the ^{13}C values for Figure 1a are those of Lauterbur.[16] Although the boron and carbon compounds considered in Figure 1 are not strictly analogous, the effect on the chemical shift of consecutive replacement of hydrogen by halogen on the units is noteworthy. Substituent effects on ^{13}C and ^{11}B shifts are considered in the next two sections.

Pairwise Additivity of Chemical Shifts. The correlation of chemical shifts by additivity of pairwise interaction parameters was first suggested by Lauterbur[17] to account for ^{13}C shifts in substituted methanes, but no quantitative data were presented. Malinowski and coworkers[12] later demonstrated, using pairwise additivity parameters, that the ^{13}C shifts in 47 substituted methanes could be closely reproduced, obtaining a standard deviation of 1.9 ppm out of a range in chemical shift of 230 ppm. The rule of pairwise additivity for a tetracoordinate resonance nucleus is simply $\delta_{(1,2,3,4)} = \Sigma\eta_{i,j}$, where $\delta_{(1,2,3,4)}$ is the chemical shift of the resonance nucleus in a series of molecules containing substituents 1, 2, 3, and 4 in chemically equivalent positions with respect to the resonance nucleus. In addition, in certain types of compounds, the chemical shifts[18] of fluorine-19, boron-11, and hydrogen-1, as well as shifts[19] of aluminum-27, have also been shown to obey pairwise additivity rules. A theoretical justification of the pairwise additivity rule applied to chemical shifts has been presented by Vladimiroff and Malinowski.[18] According to these authors, pairwise contributions arise because the wave function of each substituent group suffers a linear correction due to the presence of each neighboring substituent group.

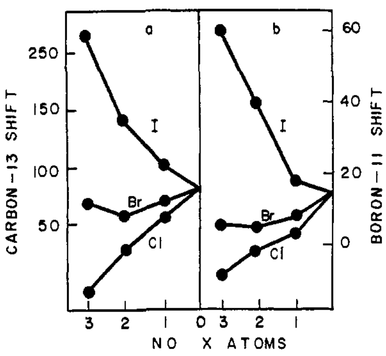

Figure 1. (a) A plot of ^{13}C chemical shifts (parts per million relative to benzene) *vs.* the number of X (halogen) substituents in $CH_{4-n}X_n$, where n = 0–3. Data are taken from ref 16 except for CH_4, from ref 23. (b) A plot of ^{11}B chemical shifts (parts per million relative to $BF_3 \cdot Et_2O$) *vs.* the number of X (halogen) substituents in $(C_2H_5)_3NBH_{3-n}X_n$, where n = 0–3. The chemical shifts are taken from Table I.

Table I. ^{11}B Chemical Shifts for Some Halogen-Substituted Triethylamine-Boranes[a]

X[b]	Et_3NBH_2X[c]	Et_3NBHX_2[d]	Et_3NBX_3[e]
Cl	2.6	−2.55	−10.0
Br	7.6	4.4	5.1
I	17.6	39.4	59.8

[a] In parts per million upfield from $BF_3 \cdot (C_2H_5)_2O$. [b] X = substituent attached to boron. For X = H, the shift of Et_3NBH_3 is +14.3: C. W. Heitsch, *Inorg. Chem.*, **4**, 1019 (1965). [c] Values are from J. N. G. Faulks, N. N. Greenwood, and J. H. Morris, *J. Inorg. Nucl. Chem.*, **29**, 329 (1967). These values were converted to the $BF_3 \cdot (C_2H_5)_2O$ standard by the approximate conversion $\delta_{BF_3 \cdot (C_2H_5)_2O} = \delta_{B(OCH_3)_3} - 17.4$ as given in ref 3, p 973. [d] Calculated values using ^{11}B pairwise parameters as determined in this study; observed values not available. [e] P. N. Gates, E. J. McLauchlan, and E. F. Mooney, *Spectrochim. Acta*, **21**, 1445 (1965).

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(12) ^{13}C pairwise parameters as determined by E. R. Malinowski, T. Vladimiroff, and R. F. Tavares, *J. Phys. Chem.*, 70, 2046 (1966).

(13) For a recent review of ^{13}C nmr spectroscopy, see E. F. Mooney and P. H. Winson, *Annu. Rev. NMR Spectrosc.*, **2**, 153 (1969).

(14) For a recent review of ^{11}B nmr spectroscopy, see W. R. Henderson and E. F. Mooney, *ibid.*, **2**, 219 (1969); see also G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969. Although the latter reference is concerned primarily with the polyhedral boron hydrides and carboranes, it also lists all other available ^{11}B chemical shifts.

(15) P. C. Lauterbur in "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press, New York, N. Y., 1962, p 477; see also ref 11.

(16) P. C. Lauterbur, *Ann. N. Y. Acad. Sci.*, 70, 841 (1958).

(17) Reference 15, p 492.

(18) T. Vladimiroff and E. R. Malinowski, *J. Chem. Phys.*, **46**, 1830 (1967).

(19) E. R. Malinowski, *J. Amer. Chem. Soc.*, **91**, 4701 (1969).

Table II. Comparison between Observed ^{11}B Chemical Shifts and Values Calculated by Pairwise Additivity

Compd or ion	Approx anal[b]			Nonapprox anal	
	Obsd[a]	Calcd[b]	Diff	Calcd	Diff
$B(C_2H_5)_4^-$	16.6[c]	16.6	0.0	16.0	0.0
$(CH_3)_3NB(C_2H_5)_3$	−4.3[c]	−4.8	−0.5	−4.7	−0.4
$(CH_3)_3NBF(C_2H_5)_2$	−10.3[c]	−9.3	1.0	−9.4	0.9
$(CH_3)_3NBF_2(C_2H_5)$	−6.7[c]	−7.7	−1.0	−7.6	−0.9
$(CH_3)_3NBF_3$	0.3[d]	0.2	0.1	0.6	0.3
$(C_2H_5)_3NBF_3$	−0.2[e]	0.2	0.4	−0.2	0.0[l]
BF_4^-	1.8[f]	1.8	0.0	1.8	0.0[l]
$(CH_3)_3NBCl(C_2H_5)_2$	−11.7[c]	−11.4	0.3	−11.4	0.3
$(CH_3)_3NBCl_2(C_2H_5)$	−12.4[c]	−12.7	−0.3	−12.6	−0.2
$(CH_3)_3NBCl_3$	−8.9[d]	−8.7	0.2	−8.4	0.5
$(C_2H_5)_3NBCl_3$	−10.0[e]	−8.7	1.3	−10.0	0.0[l]
BCl_4^-	−6.6[g]	−7.3	−0.7	−6.8	−0.2
BH_4^-	38.2[g]	38.4	0.2	38.4	0.2
$(CH_3)_3NBH_3$	8.3[d]	11.0	+2.5	7.5	−0.8
$(C_2H_5)_3NBH_3$	14.3[e]	11.0	−3.3	14.3	0.0[l]
$H_2B[N(CH_3)_3]_2^+$	−2.9[h]	−1.0	1.9	−2.1	0.8
$H_2B[N(CH_3)_2(C_2H_5)]_2^+$	−1.4[g]	−1.0	0.4	*j*	
$H_2B[N(CH_3)(C_2H_5)_2]_2^+$	0.6[h]	−1.0	−1.6	*j*	
$(C_2H_5)_3NBH_2Cl$	2.6[i]	4.0	1.4	3.0	0.4
$[(CH_3)_3N]_2BHCl^+$	−0.1[h]	−2.9	−2.8	−0.9	−0.8
$(C_2H_5)_3NBBr_3$	5.1[e]	4.6	−0.5	5.1	0.0[l]
$(CH_3)_3NBBr_3$	5.2[d]	4.6	−0.6	5.2	0.0[l]
$(C_2H_5)_3NBH_2Br$	7.6[i]	7.6	0.0	7.6	0.0[l]
$[(CH_3)_3N]_2BHBr^+$	−5.2[h]	−5.1	0.1	−5.2	0.0[l]
BBr_4^-	23.9[g]	24.4	0.5	*k*	

[a] In parts per million relative to $BF_3 \cdot (C_2H_5)_2O$. When more than one shift has been reported, the value measured with respect to $BF_3 \cdot (C_2H_5)_2O$ has been used. If only a shift measured from $B(OCH_3)_3$ were available, the approximate conversion (ref 3, p 973) $\delta_{BF_3 \cdot (C_2H_5)_2O} = \delta_{B(OCH_3)_3} - 17.4$ was used. [b] All amines are treated as NR_3. [c] Reference 11. [d] D. E. Young, H. E. McAchran, and S. G. Shore, *J. Amer. Chem. Soc.*, **88**, 4392 (1966). [e] Footnote *e* of Table I. [f] T. P. Onak, N. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959). [g] R. J. Thompson and J. C. Davis, *Inorg. Chem.*, **4**, 1466 (1965). [h] N. E. Miller and E. L. Muetterties, *J. Amer. Chem. Soc.*, **86**, 1036 (1964). [i] Footnote *c* of Table I. [j] Omitted from analysis. [k] Omitted from this analysis for reasons discussed in text. [l] Not used in determination of average deviation. The number of compounds with chemical shifts available is equal to the number of parameters to be determined.

Recently, Litchman and Grant[20] presented a formulation of ^{13}C chemical shifts for halogenated methanes in terms of substituent parameters representing both the direct effect of a substituent group and the effect of pair interactions among the substituent groups. Using a valence-bond formalism, these authors discussed the direct and pairwise interaction parameters in relation to charge polarization, the steric effect of the halogen substituents on the effective orbital radii, and deviations from the classical bond structure. Lack of extensive ^{11}B chemical shift data prevents a similar formulation for boron compounds, and in the next section, the more concise formulation of chemical shifts in terms of pairwise parameters is employed.

Correlation of ^{11}B Chemical Shifts by Pairwise Additivity. In view of the close relationships observed in previous studies between the chemical shifts of tetracoordinate ^{13}C and ^{11}B resonance nuclei, the goal of the present study was to determine if chemical shifts of tetracoordinate ^{11}B resonance nuclei could be correlated by pairwise additivity and, if so, to compare the resulting pairwise parameters with their ^{13}C counterparts. Although correlation of ^{11}B shifts by pairwise additivity has been reported,[18] the study was limited to tricoordinate boron compounds. The correlation by Malinowski, *et al.*,[12] of ^{13}C shifts by pairwise additivity dealt with substituted methanes containing in addition to H the substituent groups Cl, Br, I, CH_3, C_6H_5, CO_2H, OH, and CN. However, many of the boron analogs of these substituted methanes have not yet been prepared or would be categorized as unstable intermediates. Thus, it is not possible to test the rule of pairwise additivity of ^{11}B shifts on a group of boron compounds completely analogous to the carbon compounds considered by Malinowski.

One of the most common types of tetracoordinate boron compounds is the molecular boron Lewis acid–base adduct. Accordingly, in the following analysis of ^{11}B shifts by pairwise additivity, data on a large number of amine adducts of boron Lewis acids are used, although data on some anionic and cationic boron derivatives are included. The specific ^{11}B shifts (literature values) used in this study are listed in Table II. Two approaches to the treatment of these shifts by pairwise additivity were used. The first approach recognizes the existence of a rather large number of known (substituted) borane adducts with the common Lewis bases, trimethylamine and triethylamine, but generally the ^{11}B shift is available for only one of the amine derivatives. Where data are available for both trimethylamine and triethylamine derivatives, the difference in shift often is small, usually a few parts per million, as may be seen in Table II. Thus, in the first approach, all amine substituents were formulated as simply NR_3. The analysis was carried out by expressing the observed shifts in terms of the pairwise additivity parameters and then solving the resulting simultaneous equations by computer using a program[21] for the solution of simultaneous equations and subsequent least-squares analysis to

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(20) W. M. Litchman and D. M. Grant, *J. Amer. Chem. Soc.* 90, 1400 (1968).

(21) Program kindly provided by Professors C. N. Reilley and T. R. Ridgeway, University of North Carolina, Chapel Hill, N. C.

Table III. Pairwise Interaction Parameters for ^{11}B Chemical Shifts in Tetracoordinate Boron Compounds[a]

	Pairwise parameter, $\eta_{i,j}$		
Substituents	Approx anal[b]	Nonapprox anal	
H, H	6.39		6.40
H, Br	4.05		4.52
Br, Br	4.08		6.27[c]
NR_3, NR_3	3.50	$R = CH_3$	7.17
C_2H_5, C_2H_5	2.77		2.77
H, Cl	2.38		3.05
F, F	0.30		0.30
F, NR_3	−0.23	$R = CH_3$	−0.10
		$R = C_2H_5$	−0.37
Cl, Cl	−1.22		−1.13
F, C_2H_5	−1.59		−1.69
Cl, NR_3	−1.68	$R = CH_3$	−1.66
		$R = C_2H_5$	−2.20
Cl, C_2H_5	−1.90		−1.94
Br, NR_3	−2.54	$R = CH_3$	−4.53
		$R = C_2H_5$	−4.57
H, NR_3	−2.73	$R = CH_3$	−3.91
		$R = C_2H_5$	−1.63
C_2H_5, NR_3	−4.34	$R = CH_3$	−4.33

[a] Parts per million from $BF_3 \cdot (C_2H_5)_2O$. [b] All amine substituents are treated as NR_3. [c] Shift of BBr_4^- is omitted in the analysis for reasons discussed in the text.

yield best parameter values. The pairwise parameters obtained are listed in Table III under the column head Approx anal. Using these pairwise parameters, chemical shifts were calculated and compared with the observed values and the results tabulated in Table II under the column head Approx anal. The average deviation of calculated values from the observed values was 0.9 ppm out of a range of ^{11}B shifts of some 50 ppm. The usually reported error in measurement of ^{11}B shifts is ±0.5 ppm.

In the second approach, no approximation for the amines was used, and the analysis of the ^{11}B shifts by pairwise additivity again carried out. The resulting pairwise parameters are listed in Table III under the column head Nonapprox anal. Calculated values of the chemical shifts using these parameters were obtained and compared with the observed chemical shifts; the results are listed in Table II, under the column head Nonapprox anal. In this latter approach, the difference between calculated and observed chemical shifts is found to be zero for a number of compounds, but this is simply a result of the availability of only the same number of shifts as parameters to be determined in these cases. Not including these zero deviations, the average deviation of calculated chemical shifts from the observed values was 0.4 ppm out of a range of ^{11}B shifts of some 50 ppm.

The above results clearly demonstrate that pairwise additivity closely correlates the observed ^{11}B shifts in the compounds considered, even in the approximate case where all amine substituents were treated as NR_3. Considering that the shifts were measured in cationic, anionic, and neutral boron species in a variety of different solvents and usually against external standards also indicates that influences from these effects must not be large. Although the primary objective of this study was to determine if ^{11}B shifts in tetracoordinate compounds were pairwise additive and to compare the resulting parameters with their ^{13}C counterparts, it should be noted that these ^{11}B pairwise parameters should be useful in predicting unmeasured ^{11}B chemical shifts.

Correlation of ^{11}B and ^{13}C Pairwise Parameters

Using Approximate ^{11}B Pairwise Parameters. If the ^{11}B pairwise parameters found in Table III are compared with the ^{13}C parameters determined by Malinowski, *et al.*,[12] only four parameters common to both nuclei are found. To compare as many common pairwise parameters as possible, the assumption was made that in general ^{11}B and ^{13}C shifts in tetracoordinate compounds would be pairwise additive and additional ^{11}B and ^{13}C parameters were evaluated on this basis. Thus, η_{CH_3,CH_3} for ^{11}B was evaluated from the shift of the tetramethylborate anion;[22] $\delta_{B(CH_3)_4^-} = 20.5$ ppm, yielding $\eta_{CH_3,CH_3} = 3.42$ ppm. This value could then be compared with the known ^{13}C value.[12] Likewise, pairwise parameters common to both nuclei but not determined in either this or the ^{13}C study[12] could be evaluated. For example, $\eta_{H,N(CH_3)_2}$ for ^{13}C was evaluated using the chemical shift of trimethylamine,[23] $\delta_{CH_3N(CH_3)_2} = 81.2$ ppm and the ^{13}C $\eta_{H,H}$ value[12] of 22.53 ppm, giving a value of 4.54 ppm for η_{H,NMe_2}. The ^{11}B parameter was evaluated from the shift of the dimethylaminotrihydroborate anion, $\delta_{H_3BNMe_2^-} = 14.7$ ppm,[24] and the $\eta_{H,H}$ value of 6.39 ppm (Table III), giving a value of −1.49 ppm for η_{H,NMe_2}. In this manner, 9 additional common pairwise parameters were obtained, resulting in a total of 13 for comparison. All 13 common parameters and shift data used in their evaluation are listed in Table IV. To some extent, lack of ^{11}B and ^{13}C chemical shift data prevents compilation of a more extensive list of common pairwise parameters. An additional factor is the difference in chemical stability for many analogous boron and carbon systems. For example, *cf.* CH_3OH *vs.* its unstable boron analog, BH_3OH^-; $B(OH)_4^-$ *vs.* its unstable carbon analog, $C(OH)_4$.

Fitting the 13 common pairwise parameters in Table IV to a linear relationship by a least-squares analysis yields the following equation (correlation coefficient of 0.99).

$$(\eta_{i,j})_{^{11}B} = 0.398(\eta_{i,j})_{^{13}C} - 3.12 \qquad (2)$$

Using this equation, values for the ^{11}B pairwise parameters were calculated from the ^{13}C values and the results displayed in Table IV. The average deviation of the calculated ^{11}B values from the original values is 0.67 ppm in chemical shift out of a range of ^{11}B parameter values of about 24 ppm. The calculated $\eta_{Br,Br}$ shows a very large deviation (+2.94 ppm) from the observed value. Although this large deviation may be real and theoretically meaningful, the possibility exists that the true shift of the BBr_4^- anion used in the evaluation of $\eta_{Br,Br}$, may not yet have been measured. The ^{11}B shifts of the anions BCl_4^-, BBr_4^-, and BI_4^- have been shown by Thompson and Davis[22] to be dependent upon the concentration of added halide ion in accord with the following equilibrium

$$BX_3 + X^- \rightleftharpoons BX_4^-$$

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(22) R. J. Thompson and J. C. Davis, *Inorg. Chem.*, **4**, 1466 (1965).

(23) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).

(24) P. C. Keller, *J. Amer. Chem. Soc.*, **91**, 1231 (1969).

Table IV. Comparison of ^{11}B and ^{13}C Pairwise Interaction Parameters; Approximate ^{11}B Parameters Used

					$\eta_{Br,Br}$ omitted	
Substituents	$(\eta_{i,j})_{^{13}C}$[a]	$(\eta_{i,j})_{^{11}B}$[b]	$(\eta_{i,j})_{^{11}B}$(calcd)[c]	Diff	$(\eta_{i,j})_{^{11}B}$(calcd)[d]	Diff
H, NR_3	1.77[e]	−2.73	−2.42	0.31	−2.31	0.42
H, $N(CH_3)_2$	4.54[f]	−1.49[j]	−1.32	0.17	−1.18	0.31
Cl, Cl	5.19	−1.22	−1.06	0.16	−0.92	0.30
OCH_3, OCH_3	8.19[g]	−0.48[k]	0.14	0.62	0.30	0.78
C_6H_5, C_6H_5	9.77[h]	1.13[l]	0.77	−0.36	0.95	−0.18
H, Cl	11.57	2.38	1.48	−0.90	1.68	−0.70
C_2H_5, C_2H_5	15.11[i]	2.77	2.89	0.12	3.12	0.35
CH_3, CH_3	16.45	3.42[m]	3.43	0.01	3.67	0.25
H, Br	15.20	4.05	2.93	−1.12	3.16	−0.89
Br, Br	25.49	4.08	7.02	2.94		
H, H	22.53	6.39	5.85	−0.54	6.15	−0.24
H, I	27.17	9.03[n]	7.69	−1.34	8.04	−0.99
I, I	61.22	21.33[o]	21.25	−0.08	21.92	0.59

[a] Parts per million from benzene; unless noted otherwise, values are those determined by Malinowski, *et al.*[12] Other values have been determined from chemical shifts listed in the footnotes, assuming the shifts to be pairwise additive. [b] Parts per million from $BF_3\cdot(C_2H_5)_2O$; unless noted otherwise, values are those from this work as listed in Table III, under Approx anal. Other values have been determined from chemical shifts listed in the footnotes, assuming pairwise additivity. [c] Values calculated by the equation relating ^{13}C and ^{11}B $\eta_{i,j}$ as determined by least squares: $(\eta_{i,j})_{^{11}B} = 0.398\,(\eta_{i,j})_{^{13}C} - 3.12$. [d] Values calculated by the equation relating ^{13}C and ^{11}B $\eta_{i,j}$ ($\eta_{Br,Br}$ omitted, see text) as determined by least squares: $(\eta_{i,j})_{^{11}B} = 0.408(\eta_{i,j})_{^{13}C} - 3.03$. [e] From $\delta_{(CH_3)_4N^+} = 72.9$ ppm[23] and $\eta_{H,H} = 22.53$ ppm.[12] [f] From $\delta_{(CH_3)_3N} = 81.2$ ppm[23] and $\eta_{H,H} = 22.53$ ppm.[12] [g] From $\delta_{CH_3OCH_3} = 69.3$ ppm,[23] $\delta^*_{CH_2(OCH_3)_2} = 33.0$ ppm,[16] and $\eta_{H,H} = 22.53$ ppm.[12] [h] From $\delta^*_{CH_2(C_2H_5)} = 86.5$ ppm (R. M. Pearson, Ph.D. Thesis, University of California, Davis, 1965, p 15), $\eta_{H,H} = 22.53$ ppm,[12] and $\eta_{H,C_6H_5} = 13.54$ ppm.[12] [i] From $\delta^*_{C(C_2H_5)_4} = 90.66$ ppm, calculated from the chemical shift parameters of D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, **86**, 1984 (1964). [j] From $\delta_{H_3BNMe_2^-} = 14.7$ ppm[24] and $\eta_{H,H} = 6.39$ (Table III, this work). [k] From $\delta_{B(OCH_3)_4^-} = -2.9$ ppm (footnote *f* of Table II). [l] From $\delta_{B(C_6H_5)_4^-} = 6.8$ ppm (footnote *g* of Table II). [m] From $\delta_{B(CH_3)_4^-} = 20.5$ ppm (footnote *g* of Table II). [n] From shifts of Et_3NBH_2I and Et_3NBI_3 (values reported in Table I), $\delta_{BI_4^-} = 128.0$ ppm (footnote *g* of Table II), and $\eta_{H,H}$ and η_{H,NR_3} values in Table III under the heading Approx anal. [o] From $\delta_{BI_4^-} = 128.0$ ppm (footnote *g* of Table II).

For example, the ^{11}B chemical shift of BI_4^- was measured using a mixture of BI_3 and tetrabutylammonium iodide in methylene chloride.[22] The shift varied from about +66 ppm (for approximately equal weights of the two reactants) up to a limiting shift of +127.5 ppm as more of the quaternary ammonium iodide was dissolved in the solution. In the case of the BBr_4^- anion, a limiting shift of +24.1 was obtained when excess pyridinium bromide was added to pyridinium tetrabromoborate dissolved in nitrobenzene. However, boron tribromide and nitrobenzene have been shown to form a strong adduct,[25] and an equilibrium of the following type may be involved.

$$C_6H_5NO_2 + BBr_4^- \rightleftharpoons BBr_3\cdot C_6H_5NO_2 + Br^-$$

Landesman and Williams[26] have measured the ^{11}B shifts of $CsBBr_4$ in nitrobenzene and reported a value of +26 ppm, but suggested that the actual shift might be higher since a higher concentration of bromide ion might give more BBr_4^- in equilibrium with BBr_3 or its nitrobenzene adduct according to the above equilibrium.

If the $\eta_{Br,Br}$ parameter is omitted, the following equation is obtained (least-squares analysis) for the remaining 12 common parameters.

$$(\eta_{i,j})_{^{11}B} = 0.408(\eta_{i,j})_{^{13}C} - 3.03 \qquad (3)$$

Calculated values of the ^{11}B parameters using this equation and differences from the original values are listed in the last two columns of Table IV. The average deviation of calculated values from the original values is 0.50 ppm. Figure 2 shows a plot of the ^{13}C *vs.* ^{11}B pairwise parameters (with $\eta_{Br,Br}$ omitted). It may also be observed from Figure 2 or the data in Table IV that, with or without $\eta_{Br,Br}$, the larger deviations in the correlation occur with $\eta_{H,Cl}$, $\eta_{H,Br}$, and $\eta_{H,I}$. To determine if the use in the correlation of the approximate ^{11}B pairwise parameters were responsible for these deviations, the correlation was carried out using the nonapproximate parameters as described in the next section.

Use of Nonapproximate ^{11}B Pairwise Parameters. Comparison of the values of the approximate and nonapproximate ^{11}B pairwise parameters in Table III reveals that appreciable differences exist among some of the parameters. Although these differences are obviously partly the result of employing an approximation (NR_3 for all amines), it should be noted that in the analysis of the ^{11}B shifts using the nonapproximate pairwise parameters, the shift of BBr_4^- was omitted[27] (Table II) for the reason discussed previously in the text. This change would also be expected to contribute to some readjustment of the nonapproximate ^{11}B parameter values.

The 13 $\eta_{i,j}$ ^{13}C parameters as listed in Table IV were then correlated with their ^{11}B counterparts using the nonapproximate ^{11}B parameter values (Table III), and the results are presented in Table V. The least-squares determined line is

$$(\eta_{i,j})_{^{11}B} = 0.408(\eta_{i,j})_{^{13}C} - 3.15 \qquad (4)$$

The average deviation of calculated ^{11}B parameter values from the original values using this equation is 0.61 ppm out of a range of parameter values of 25 ppm.

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(25) (a) H. C. Brown and R. R. Holmes, *J. Amer. Chem. Soc.*, **78**, 2173 (1956); (b) E. F. Mooney, M. A. Qaseem, and P. H. Winson, *J. Chem. Soc. B*, 224 (1968).

(26) H. Landesman and R. E. Williams, *J. Amer. Chem. Soc.*, **83**, 2663 (1961).

(27) Interestingly, the value obtained for $\eta_{Br,Br}$, 6.27, by omitting the shift of BBr_4^- would give a calculated shift for BBr_4^- of 37.6 ppm, some 12–14 ppm higher than reported values.[22,26]

Table V. Comparison of ^{11}B and ^{13}C Pairwise Interaction Parameters: Nonapproximate ^{11}B Parameters Used

Substituents	$(\eta_{i,j})_{^{11}B}$[a]	Calcd $(\eta)_{i,j}{}_{^{11}B}$[b]	Diff
H, $N(CH_3)_3$	−3.91	−2.43	1.48
H, N $(CH_3)_2$	−1.49[c]	−1.29	0.20
Cl, Cl	−1.13	−1.03	0.10
OCH_3, OCH_3	−0.48[c]	0.19	0.67
C_6H_5, C_6H_5	1.13[c]	0.84	−0.29
H, Cl	3.05	1.57	−1.48
C_2H_5, C_2H_5	2.77	3.01	0.24
CH_3, CH_3	3.42[c]	3.56	0.14
H, Br	4.52	3.05	−1.47
Br, Br	6.27	7.24	0.97
H, H	6.40	6.04	−0.36
H, I	7.90[d]	7.93	0.03
I, I	21.33[c]	21.83	0.50

[a] Parts per million from $BF_3 \cdot (C_2H_5)_2O$. Unless noted otherwise, values are from Table III, under heading Nonapprox anal. [b] Values calculated by the equation relating the ^{13}C $\eta_{i,j}$ (values as listed in Table IV) and ^{11}B $\eta_{i,j}$ values as determined by least-squares analysis, $(\eta_{ij})_{^{11}B} = 0.408(\eta_{i,j})_{^{13}C} - 3.15$. [c] Value of ^{11}B η_{ij} from Table IV. [d] Evaluated from the same shifts as found in Table IV, footnote *n*, except for the use of nonapproximate $\eta_{H.NET_3} = 1.63$ ppm. The resulting $\eta_{H.I}$ parameter is thus 1.13 ppm lower than that found in Table IV.

The slope of the line is the same as that of eq 3, and the intercepts differ by only 0.12 ppm.

In this analysis, the calculated $\eta_{Br,Br}$ (from the ^{13}C parameter) is 0.97 ppm above the $\eta_{Br,Br}$ used in the correlation and would result in a calculated shift of +43.4 ppm from the standard for BBr_4^-. Again the calculated $\eta_{H,Cl}$ and $\eta_{H,Br}$ exhibit large deviations (close to −1.5 ppm), although the calculated value for $\eta_{H,I}$ agrees quite well with its original value in this instance. The calculated $\eta_{H,N(CH_3)_3}$, however, exhibits a large deviation of +1.48 ppm. Although additional chemical shift data on compounds containing these sustituents are clearly desirable to further check the ^{11}B and ^{13}C pairwise parameters used in the correlation and to check the above results, the observation may be made that significant solvent effects on the ^{13}C resonances of substituted methanes containing the substituents Cl, Br, and I in combination with H have been observed. Thus Becconsall and Hampson[28] have reported a solvent shift of over 7.7 ppm on the ^{13}C resonance of CH_3I in going from neat CH_3I to dilute solutions in $(CH_3)_4Si$. A solvent effect of 3.6 ppm on the shift of CH_3Br has been reported.[23] Likewise, Lichter and Roberts[29] have recently reported a solvent effect on the ^{13}C shift of chloroform. They reported a variation of over 4 ppm and observed a linear correlation between the ^{13}C shift and proton shift in the same solvent. These authors suggested that the solvent effect arises from changes in the average distance of the bonding electrons in the chloroform carbon–hydrogen bond as a result of intermolecular association. Finally, it may be noted that in the study of Malinowski, *et al.*,[12] some of the largest deviations between the observed ^{13}C shifts and those calculated by pairwise additivity occurred in compounds containing both hydrogen and bromine substituents. For example, the differences between observed and calculated values for CH_3Br was −6.1; $CHBr_3$, 4.0; and $CH_3C^*H_2Br$, −3.5 ppm. Thus it may well be that the deviations from linearity noted for $\eta_{H,Cl}$, $\eta_{H,Br}$, $\eta_{H,I}$ (and η_{H,NMe_3}) may be traced to enhanced solvent effects on ^{11}B and ^{13}C shifts in compounds containing these substituents, possibly operating through the mechanism suggested above by Lichter and Roberts.[29] In addition, differences in solvent dependency of ^{11}B and ^{13}C shifts might be expected because of charge differences between isoelectronic boron and carbon systems. Investigations of solvent effects on ^{11}B shifts as well as additional studies on ^{13}C shifts would be desirable. Although many additional studies and more chemical shift data are clearly needed to elucidate some of the finer details of the correlation, the basic correlation between the pairwise parameters considered has been well established.

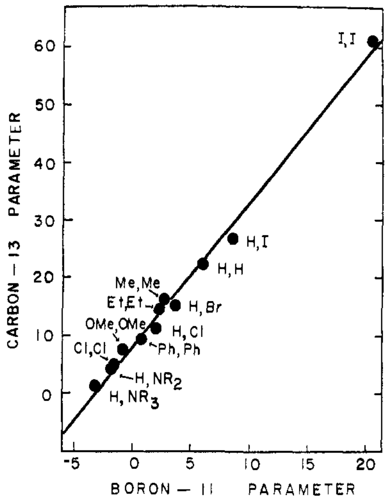

Figure 2. A plot of the carbon-13 pairwise parameters (in parts per million relative to benzene) *vs.* their analogous boron-11 pairwise parameters (parts per million relative to $BF_3 \cdot Et_2O$). The line represents the least-squares fit for all common parameters (Table IV) except $\eta_{Br,Br}$.

Theoretical Considerations

Although the intercepts of the equation relating the ^{11}B and ^{13}C pairwise parameters are dependent upon the choice of chemical shift reference standards, the slope of the equation should be related to the relative shielding of the ^{11}B and ^{13}C nuclei with respect to common pairwise substituents. As the linearly related pairwise parameters can be used to calculate chemical shifts, it would be equally appropriate to discuss a linear correlation between ^{11}B and ^{13}C shifts in isoelectronic compounds with the same slope as found in the correlation between the pairwise parameters. Thus, in the following consideration, attention will be focused upon the relative shielding of ^{11}B and ^{13}C nuclei in isoelectronic tetracoordinate compounds.

From the general theory of chemical shifts by Ramsey,[30] Saika and Slichter[31] suggested that the screening expression could be divided into three contributions

$$\sigma = \sigma_d + \sigma_p + \sigma'$$

where σ_d is the diamagnetic contribution for the atom

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(28) J. K. Becconsall and P. Hampson, *Mol. Phys.*, 10, 21 (1965).

(29) R. L. Lichter and J. D. Roberts, *J. Phys. Chem.*, 74, 912 (1970).

(30) (a) N. F. Ramsey, *Phys. Rev.*, 78, 699 (1950); (b) *ibid.*, 86, 243 (1952).

(31) A. Saika and C. P. Slichter, *J. Chem. Phys.*, 22, 26 (1954).

under consideration, σ_p is the paramagnetic term, and σ' is a term which includes screening contributions from all other atoms in the molecule. Contributions from this last term, σ', are the result of anisotropy in the magnetic susceptibility of remote groups in the molecule.[32] As recently pointed out by Cheney and Grant,[33] this remote anisotropic term describes a field effect, affecting both protons and heavy nuclei alike when positioned in an equivalent spatial configuration; thus influences of this type in ^{13}C (and ^{11}B) nmr must be no larger than approximately the range of such effects found in proton magnetic resonance. For heavier nuclei, Cheney and Grant[33] concluded that σ' at most comprises only a few per cent of the total chemical shift range. Contributions from σ' will therefore be neglected in this section. Likewise, it has been shown that for ^{13}C and heavier nuclei, changes in the diamagnetic term, σ_d, must be small and are usually neglected in calculating chemical shifts.[33,34] The paramagnetic term is therefore the dominant term in the theory of chemical shift for heavy nuclei, and considerable attention has been directed toward the evaluation of this term using quantum mechanical treatments.

One study, particularly pertinent to this work, has been carried out by Jameson and Gutowsky,[34c] These authors showed that the range of chemical shift values for various nuclei could be correlated with the atomic number of the nuclei. Explicit expressions were derived for the paramagnetic contribution to the nuclear magnetic shielding in both the valence-bond and the LCAO–MO framework, and the dependence of the range of chemical shift with atomic number was rationalized in terms of the paramagnetic contribution to the chemical shift.

In the LCAO–MO formulation, the expression for the paramagnetic term, σ_p, applicable to the ^{13}C and ^{11}B nuclei, as given by Jameson and Gutowsky,[34c] is of the form

$$\sigma_p = -(2/3)(e^2h/m^2c^2)(1/\Delta E)\langle 1/r^3\rangle_{2p}P_u$$

Here, ΔE is the average electronic excitation energy for the molecule or ion, $\langle 1/r^3\rangle_{2p}$ is the mean inverse cube radius of the boron or carbon 2p electrons, and P_u is an expression which may be defined in terms of p-orbital populations (ref 34c contains the detailed expression).

As stated previously, the observed slope in the linear correlation of ^{11}B and ^{13}C pairwise parameters is related to the relative shielding of the ^{11}B and ^{13}C nuclei in isoelectronic tetracoordinate compounds. Thus, the following ratio of paramagnetic contributions is of interest to compare with the observed slope.

$$\frac{(\sigma_p)_{^{11}B}}{(\sigma_p)_{^{13}C}} = \frac{\Delta E_C}{\Delta E_B}\frac{\langle r^3\rangle_{C2p}}{\langle r^3\rangle_{B2p}}\frac{(P_u)_B}{(P_u)_C}$$

Specifically, we choose to evaluate the ratio of the paramagnetic terms in the isoelectronic species tetrahydroborate and methane. For an estimate of the *ratio* in average electronic excitation energies, we use the ratio of the difference in energy between the highest occupied molecular orbital and the lowest unoccupied molecular orbital level, as determined in the SCF–LCAO–MO calculations of Lipscomb and coworkers for CH_4[35] and BH_4^-,[36] $\Delta E_{CH_4}/\Delta E_{BH_4^-} = 1.1859$ au/0.9915 au = 1.196. The average excitation is a difficult term to evaluate and is usually treated empirically.[37] It should be understood that, although the quantities used above are not necessarily accurate estimates of the individual average electronic excitation energies, their ratio might serve as a fairly accurate measure of the ratio in average excitation energies for CH_4 and BH_4^- due to cancellation of errors.

In the study of Jameson and Gutowsky,[34c] the dependence of $\langle 1/r^3\rangle$ with atomic number was estimated from atomic spin–orbit interactions. As pointed out by these authors, this term may also be estimated by using Slater orbitals, but only for the lightest nuclei, since this approximation becomes worse with increasing atomic number. For boron and carbon nuclei, this latter approach should be satisfactory and the ratio of $\langle 1/r^3\rangle$ terms may be obtained[38] using the expression

$$\langle r^3\rangle_{C2p}/\langle r^3\rangle_{B2p} = \zeta_B{}^3/\zeta_C{}^3$$

Although for ζ, a fixed exponent (effective nuclear charge taken from Slater's rules[38]) in the Slater orbital might be used, it is known from molecular orbital calculations that the best exponents for atoms in molecules differ from the free-atom values[39] and may be obtained by optimization of the exponents by a variational method. Thus we use exponents which have been optimized in LCAO–SCF–MO calculations (using a minimum basis set of Slater orbitals) for BH_4^- by Lipscomb and coworkers[36] and for CH_4 by Pitzer[39] and obtain $\langle r^3\rangle_{C2p}$ $\langle r^3\rangle_{B2p}$ = $(1.39/1.76)^3$ = 0.493. As shown in the treatment by Jameson and Gutowsky[40] on the calculation of xenon chemical shifts in the xenon fluorides, the P_u expression[41] in the paramagnetic contribution can be evaluated in terms of orbital populations, obtainable from MO wave-function parameters. From the MO wave functions of BH_4^- [36] and CH_4,[39] the following $(P_u)_{BH_4^-}/(P_u)_{CH_4}$ may be evaluated. For BH_4^-, $p_{xx} = p_{yy} = p_{zz} = 0.359$; $P_u = 0.881$. For methane, $p_{xx} = p_{xx} = p_{xx} = 0.619$; $P_u = 1.28$. Therefore, $(P_u)_{BH_4^-}/(P_u)_{CH_4} = 0.689$.

Using the above three ratios, the ratio of the paramagnetic contribution to the chemical shift for BH_4^- to CH_4 is calculated to be 0.406. This value is in excellent agreement with the observed slopes (eq 2, 0.398; eq 3 and 4, 0.408). One note of caution should be added. In the correlation between the pairwise parameters, no parameters representing substituents with double or triple bonds were compared. Some preliminary data now available indicate that such parameters may show some deviation from the reported linear relationship. With substituents containing double or

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(32) J. A. Pople, *Discuss. Faraday Soc.*, No. 34, 7 (1962).

(33) B. V. Cheney and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 5319 (1967).

(34) (a) J. A. Pople, *Mol. Phys.*, 7, 301 (1963); (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).

(35) W. E. Palke and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2384 (1966).

(36) R. A. Hegstrom, W. E. Palke, and W. N. Lipscomb, *J. Chem. Phys.*, **46**, 920 (1967).

(37) J. A. Pople, *Mol. Phys.*, 7, 301 (1964).

(38) C. A. Coulson, "Valence," 2nd ed, Oxford University Press, London, 1961, p 39.

(39) R. M. Pitzer, *J. Chem. Phys.*, **46**, 4871 (1967).

(40) C. J. Jameson and H. S. Gutowsky, *ibid.*, 40, 2285 (1964).

(41) Reference 34c contains the detailed expression for P_u.

triple bonds, variations in some of the above calculated ratios (particularly the ratio in average excitation energy) may result in deviations from the linear relationship. Further studies are presently underway as well as extensions of these correlations and calculations to other nuclei.

Applications

Hydroborate Intermediates. In this section, a brief example is presented illustrating the potential utility of the ^{11}B pairwise parameters and their correlation with the ^{13}C parameters to provide chemical shift information on unstable boron intermediates. Many investigators have postulated and searched for boron–hydrogen-containing intermediates in the hydrolysis of the tetrahydroborate ion[42] and in the reaction of diborane with aqueous base.[42] Using polarographic techniques, Gardiner and Collat[43] observed an unstable intermediate in the hydrolysis of the tetrahydroborate ion and proposed a reaction scheme involving the BH_3OH^- ion. They also reported ^{11}B nmr evidence[44] for the intermediate, a 1:3:3:1 quartet with a chemical shift of 12.8 ppm from $BF_3 \cdot (C_2H_5)_2O$. No other ^{11}B nmr signals were detected except for that of $B(OH)_4^-$. Based upon stoichiometric observations, Jolly and Schmitt[45] proposed, in addition to BH_4^-, formation of the intermediate, $BH(OH)_3^-$, in the reaction of solid KOH (containing 7% extra water) with B_2H_6 at −30°. Attempts to obtain the ^{11}B nmr spectrum of the $BH(OH)_3^-$ ion by dissolving the $B_2H_6 \cdot KOH$ solid reaction product were unsuccessful; the solution yielded only resonances attributable to $B(OH)_4^-$ and BH_4^-. The possible presence of another unstable intermediate, $BH_2(OH)_2^-$, was also proposed. These authors suggested that ^{11}B nuclear quadrupole relaxation effects could have been responsible for the inability to observe ^{11}B signals of the intermediates.

^{11}B chemical shifts for the stepwise hydrolysis intermediates BH_3OH^-, $BH_2(OH)_2^-$, and $BH(OH)_3^-$ can now be calculated using ^{11}B pairwise parameters and the correlation between the ^{13}C and ^{11}B parameters. In addition to checking a predicted shift for BH_3OH^- with that reported,[44] the predicted shifts of $BH_2(OH)_2^-$ and $BH(OH)_3^-$ reveal an additional complicating factor (besides probable quadrupolar broadening effects) for observing ^{11}B shifts of these intermediates.

To calculate ^{11}B shifts of the intermediates, the values of the parameters $\eta_{H,H}$, $\eta_{OH,OH}$, and $\eta_{H,OH}$ are required. The $\eta_{H,H}$ was evaluated in this work (Table III) and an $\eta_{OH,OH}$ value of −0.2 ppm may be calculated from the reported shift[46] for $B(OH)_4^-$ of −1.3 ppm. From the ^{13}C value[12] of 4.08 ppm for $\eta_{H,OH}$, the value of the analogous ^{11}B parameter, using the linear relationship between the pairwise parameters (eq 3), is calculated to be −1.28 ppm. The following shifts in ppm from $BF_3 \cdot (C_2H_5)_2O$ can then be calculated.

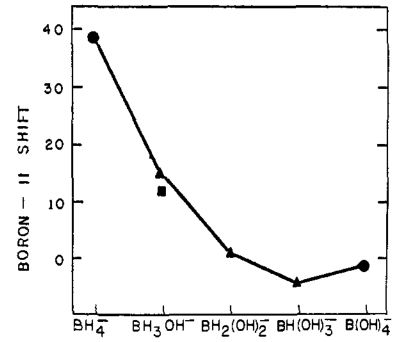

Figure 3. A plot of ^{11}B chemical shifts (parts per million relative to $BF_3 \cdot Et_2O$) for hydroxy-substituted hydroborates: observed values, ●; predicted for the intermediates, ▲; observed for BH_3OH^- (ref 44), ■.

$$\delta_{BH_3(OH)^-} = 3\eta_{H,H} + 3\eta_{H,OH} = 15.3$$

$$\delta_{BH_2(OH)_2^-} = \eta_{H,H} + 4\eta_{H,OH} + \eta_{OH,OH} = 1.0$$

$$\delta_{BH(OH)_3^-} = 3\eta_{H,OH} + 3\eta_{OH,OH} = -4.4$$

Figure 3, in which all pertinent chemical shifts are plotted, emphasizes the closeness of the predicted shifts of $BH_2(OH)_2^-$ and $BH(OH)_3^-$ to the shifts of the final hydrolysis product, $B(OH)_4^-$, the predicted shifts being only a few ppm above and below that of $B(OH)_4^-$. Figure 3 also stresses that not all of the chemicals shifts of the intermediates would necessarily be expected to lie between the shift of tetrahydroborate and that of the final hydrolysis product, $B(OH)_4^-$. If the intermediates $BH_2(OH)_2^-$ and $BH(OH)_3^-$ were present in low concentration, their detection by ^{11}B nmr might well be obscured by a very large $B(OH)_4^-$ signal. Also, spin coupling of boron with hydrogen would result in multiplicity of the signals for the intermediates, further reducing the possibility of detection as well as causing some overlapping with the large $B(OH)_4^-$ signal. Thus, in view of the above factors, coupled with quadrupolar broadening effects, detection of $BH_2(OH)_2^-$ and $BH(OH)_3^-$ by ^{11}B nmr would be difficult. On the other hand, prior information as to approximately where the signals might occur would increase the possibility of detection by ^{11}B nmr.

Figure 3 also shows that the ^{11}B chemical shift found by Gardiner and Collat[44] for the proposed intermediate, BH_3OH^-, is in the region predicted for BH_3OH^-, thus lending further credence to the existence of this species.

Further Work and Some Predictions. The linear correlation between the ^{11}B and ^{13}C pairwise parameters, allowing the transfer of chemical shift information between these two nuclei, has the potential to facilitate studies on analogous boron and carbon compounds. As a test of the utility of the correlation and its applicability to tetracoordinate boron and carbon compounds possessing substituents with double and triple bonds, studies have been initiated into isoelectronic boron and carbon systems containing such substituents.

One system of interest is that of BH_3CO and its isoelectronic carbon analog, the acetyl cation, CH_3CO^+.

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(42) For a recent review concerning the hydrolysis of metal hydroborates, see B. D. James and M. G. H. Wallbridge, *Progr. Inorg. Chem.*, 11, 115 (1970).

(43) J. A. Gardiner and J. W. Collat, *J. Amer. Chem. Soc.*, 87, 1692 (1965).

(44) J. A. Gardiner and J. W. Collat, *ibid.*, 86, 3165 (1964).

(45) W. L. Jolly and T. Schmitt, *ibid.*, 88, 4282 (1966).

(46) (a) J. C. Carter and R. W. Parry, *ibid.*, 87, 2354 (1965); (b) R. W. Parry, C. E. Nordman, J. C. Carter, and G. TerHaar, *Advan. Chem. Ser.*, No. 32, 302 (1964).

The chemistry of BH_3CO has been pursued by Parry and coworkers[46,47] in terms of an isoelectronic BH_3 *vs.* O analogy, suggesting that BH_3CO and CO_2 might exhibit certain chemical similarities. As a result of this analogy,[46,47] the anions $BH_2CONRR'^-$ (where R and R′ are either H or CH_3) and $BH_3CO_2^{2-}$ have been characterized, and evidence also has been presented for a $H_3COC(O)BH_3^-$ anion.

From an nmr point of view, to obtain ^{11}B pairwise parameters for comparison with the analogous ^{13}C parameters, chemical shift data for BH_3CO and the above boron anions would be compared with those of the isoelectronic carbon analogs. However, comparison in such a manner of the ^{11}B and ^{13}C nmr data for these analogous systems also suggests some chemical similarities. The acetyl cation, CH_3CO^+, would be expected to be quite susceptible to nucleophilic attack on the carbonyl carbon by a species X^- to form CH_3COX. A similar attack on BH_3CO may be postulated[48] which would result in anionic derivatives of formula BH_3COX^-. Thus, analogous to the organic compounds of formula CH_3COX, where X = halide, H, R, OR, OC(O)R, NR_2, etc., would be a series of isoelectronic anionic boron analogs. Work in these laboratories[49] strongly suggests a series of such anions of formula H_3BCOX^- in addition to those already characterized,[46,47] existing as both stable entities or as unstable intermediates.

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(47) L. J. Malone and R. W. Parry, *Inorg. Chem.*, 6, 817 (1967).

(48) Recent nonempirical SCF-MO calculations in BH_3CO [D. R. Armstrong and P. G. Perkins, *J. Chem. Soc. A*, 1044 (1969)] indicate that the carbon in BH_3CO is quite strongly positive (0.423 unit).

(49) B. F. Spielvogel, J. A. Knight, and C. S. Moreland, manuscript in preparation.