species, 51015-91-9; V, 51015-77-1; V-coordinated species, 51015-92-0; VI, 51015-94-2; VI-coordinated species, 51015-96-4; VII, 51051-50-4; VII-coordinated species, 51051-51-5; VIII, 51051-53-7; VIII-coordinated species, 51051-54-8; IX, 51016-00-3; IX-coordinated species, 51016-02-5; $(CH_3)_3NBH_2I$, 25741-81-5; $(CH_3)_2NCH_2CO_2H$, 1118-68-9; $(CH_3)_4N^+(CH_3)_2NCH_2CO_2^-$, 28333-38-2; ethyl 2-dimethylaminoisobutyrate, 51015-89-5; diborane, 19287-45-7; 3-dimethylaminopropionic acid, 6300-04-5.

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# Boron-11 and Fluorine-19 Nuclear Magnetic Resonance Pairwise Interaction Parameters. Application to Donor-Acceptor Interactions in Boron Trihalide Adducts[1]

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$^{11}B$ and $^{19}F$ chemical shifts and $^{11}B-^{19}F$ coupling constants of boron trihalide adducts fit Malinowsky's criteria of "pairwise additivity." Hard and soft donor atoms give rise to very different donor-halogen pairwise interaction parameters. These are of use in determining the donor atom in an adduct when the Lewis base involved has more than one potential donor site. Various correlations of pairwise parameters, including those involving different central nuclei, appear promising.

## Introduction

In several types of compounds, chemical shifts of nuclei other than protons have been shown to be pairwise additive with respect to the substituent groups,[2] and the same is true for several cases of coupling constants between directly bonded atoms.[2] Thus the chemical shift (or spin-spin coupling) can be expressed as $\delta = \Sigma\eta_{i,j}$ where $\eta_{i,j}$ is a parameter associated with substituents i and j and independent of all other substituents. The sum is taken over all substituents about a central atom, excluding the nucleus observed in the nmr experiment. Thus in the case of a complex $D\cdot BF_2Cl$

$$\delta_{^{11}B} = \eta_{F,F} + 2\eta_{F,Cl} + \eta_{D,Cl} + 2\eta_{D,F}$$

$$\delta_{^{19}F} = \eta'_{F,Cl} + \eta'_{D,Cl} + \eta'_{D,F}$$

$$J_{^{11}B-^{19}F} = \eta''_{F,Cl} + \eta''_{D,Cl} + \eta''_{D,F}$$

where $\eta$ is different in each of the above equations. Pairwise additivity has been demonstrated for $^{19}F$, $^{11}B$, $^{13}C$, $^{27}Al$, $^{93}Nb$, and other chemical shifts and for directly bonded couplings $J_{C-F}$, $J_{Si-H}$, $J_{Sn-H}$, and other systems.[3,4]

We have shown that pairwise additivity rules apply to the $^{11}B$ and $^{19}F$ chemical shifts and $^{11}B-^{19}F$ coupling constants of the mixed tetrahaloborate anions.[3a] Our recent studies of mixed boron trihalide adducts[5-7] have provided nmr data which seemed to involve certain irregularities. It turns out that these data can be correlated by pairwise additivity parameters though not by direct additivity parameters and that a few seeming irregularities in chemical shift are a result of trends in the pairwise parameters. Thus we report here the extension of our calculations of pairwise interaction parameters in tetrahaloborate anions to our nmr data on mixed boron trihalide adducts.

## Experimental Section

Calculations were based on chemical shifts and coupling constants given in Table I (see paragraph at end of paper regarding supplementary material). These data were collected from a number of studies carried out in this laboratory. The data were used to calculate the sets of pairwise parameters for (i) $^{19}F$ chemical shifts, (ii) $^{11}B$ chemical shifts, and (iii) $^{11}B-^{19}F$ coupling constants, shown in Tables II-IV, respectively. The calculations were carried out on a Burroughs B5500 computer using a least-squares fitting routine. When the resulting pairwise parameters were used to recalculate the original nmr parameters, deviations between calculated and observed parameters were small (Table I). Standard deviations between observed and calculated parameters were as follows: (i) $^{19}F$ chemical shift, ±0.44 ppm in a range of 85.5 ppm; (ii) $^{11}B$ chemical shift, ±0.67 ppm in a range of 139 ppm; (iii) $^{11}B-^{19}F$ coupling constant, ±0.72 Hz in a range of 113.6 Hz. These deviations are similar to those reported by Spielvogel and Purser.[3b]

Since the halogen-halogen pairwise parameters for the neutral adducts are almost identical with those determined previously for the tetrahaloborate anions,[3a] the values for these parameters given in Tables II-IV are those calculated from the complete data set including both the neutral adducts and the tetrahaloborate anions.

The availability of nmr data is limited by various unfavorable features of some of the adduct systems, including low solubility, rapid decomposition, rapid halogen redistribution, and unfavorable halogen-redistribution equilibria giving near-zero amounts of certain mixed adducts. Also it was not possible to resolve splittings due to $^{11}B-^{19}F$ coupling in several series of oxygen-donor adducts. Thus each of Tables II-IV gives pairwise interaction parameters for a different group of compounds. Due to a combination of several unfavorable factors little information is available on iodine-containing adducts.

## Results

**$^{19}F$ Chemical Shift Parameters.** The donor-halogen parameters for the adducts of oxygen donors and trimethylamine ("hard donors"[8]) show a pronounced decrease in the order $\eta_{D,F} > \eta_{D,Cl} > \eta_{D,Br}$ whereas the reverse order is found for the "soft" donors[8] $Me_2S$ and $Me_3P$ (Table II), as well as the soft donor $Me_3PS$. [We are aware of the

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(1) Presented in part at the 56th Canadian Chemical Conference, Montreal, June 1973.

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

(3) (a) J. S. Hartman and G. J. Schrobilgen, *Inorg. Chem.*, 11, 940 (1972); (b) B. F. Spielvogel and J. M. Purser, *J. Amer. Chem. Soc.*, 93, 4418 (1971).

(4) (a) E. R. Malinowski, *J. Amer. Chem. Soc.*, 91, 4701 (1969); (b) E. R. Malinowski and T. Vladimiroff, *ibid.*, 86, 3575 (1964); (c) T. Vladimiroff and E. R. Malinowski, *J. Chem. Phys.*, 42, 444 (1965); (d) R. G. Kidd and H. G. Spinney, *J. Amer. Chem. Soc.*, 95, 88 (1973); *Inorg. Chem.*, 12, 1967 (1973).

(5) M. J. Bula, D. E. Hamilton, and J. S. Hartman, *J. Chem. Soc., Dalton Trans.*, 1405 (1972).

(6) B. Benton-Jones, M. E. A. Davidson, J. S. Hartman, J. J. Klassen, and J. M. Miller, *J. Chem. Soc., Dalton Trans.*, 2603 (1972).

(7) M. J. Bula and J. S. Hartman, *J. Chem. Soc., Dalton Trans.*, 1047 (1973).

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**Table II.** Pairwise Substituent Parameters for $^{19}$F Chemical Shifts[a]

| Class of donor | Donor | $\eta_{D,F}$ | $\eta_{D,Cl}$ | $\eta_{D,Br}$ |
|---|---|---|---|---|
| Nitrogen donors | $Me_3N$ | 56.45 | 50.59 | 47.12 |
| | 4-Me(py) | 45.48 | 43.67 | 41.86 |
| | $CH_3CN$ | 45.60 | 43.70 | |
| Oxygen donors | $Me_2O$ | 53.78 | 42.46 | 38.69 |
| | MeOEt | 52.66 | 42.31 | |
| | Acetone | 48.84 | 39.80 | |
| | MeOAc | 49.37 | 40.33 | 36.74 |
| | EtOAc | 49.27 | 40.21 | 37.56 |
| | $Me_3PO$ | 47.24 | 36.95 | |
| | tmu | 49.46 | 37.41 | |
| | DMAC | 48.96 | 39.37 | |
| | MeC(O)SMe | 48.78 | 39.49 | 36.84 |
| Soft donors | $Me_3P$ | 43.32 | 51.41 | 55.29 |
| | $Me_2S$ | 43.96 | 45.91 | |
| | $Me_3PS$ | 33.84 | 33.10 | |
| | MeC(S)OMe | 41.2 | | |
| Halogen–halogen interactions | $F^-$ | 50.77 | 36.47 | 31.08 |
| | $Cl^-$ | 36.47 | 31.36 | 28.26 |
| | $Br^-$ | 31.08 | 28.26 | 26.23 |

[a] Chemical shifts in ppm to high field of internal $CFCl_3$.

**Table III.** Pairwise Substituent Parameters for $^{11}$B Chemical Shifts[a]

| Donor | Source | $\eta_{D,F}$ | $\eta_{D,Cl}$ | $\eta_{D,Br}$ | $\eta_{D,I}$ |
|---|---|---|---|---|---|
| $Me_3N$ | *b* | 2.15 | 1.34 | 0.02 | −0.48 |
| $Me_2O$ | *b* | 2.58 | 0.62 | 0.41 | |
| tmu | *b* | 2.95 | 2.00 | | |
| $Me_2S$ | *b* | 1.76 | 2.34 | 3.07 | 5.05 |
| $F^-$ | *b* | 3.31 | 2.23 | | |
| $Cl^-$ | *b* | 2.23 | 1.71 | 3.49 | 8.78 |
| $Br^-$ | *b* | | 3.49 | 6.94 | 13.91 |
| $I^-$ | *b* | | 8.78 | 13.91 | 24.28 |
| Pyridine | *c* | 3.0 | 1.8 | 1.6 | 1.8 |
| 4-Methylpyridine | *c* | 3.0 | 1.8 | 1.7 | |
| $Me_3P$ | *c* | 2.5 | 3.4 | 4.0 | |
| $(C_6H_5)_2CO$ | *c* | 2.4 | 1.1 | 2.7 | |
| Dimethylformamide | *c* | 2.9 | 1.6 | 2.2 | |
| $MeCO_2Et$ | *c* | 2.7 | 0.2 | 2.4 | |
| $EtCO_2Et$ | *c* | 2.9 | 1.3 | | |
| *i*-$PrCO_2Et$ | *c* | 2.9 | −1.0 | | |
| $ClCH_2CO_2Et$ | *c* | 2.6 | −0.3 | −8.8 | |
| $Cl_2CHCO_2Et$ | *c* | 2.3 | −9.9 | −11.6 | |
| $Cl_3CCO_2Et$ | *c* | 2.0 | −11.3 | −13.6 | |
| $BrCH_2CO_2Et$ | *c* | 2.4 | −2.1 | −3.5 | |
| $Br_2CHCO_2Et$ | *c* | 2.3 | −8.8 | −7.0 | |

[a] Chemical shifts: ppm to high field of external $(MeO)_3B$. [b] From the mixed-adduct data in Table I. [c] From previous studies $BX_3$ adducts (Table XI, pp 280–282, in ref 12).

**Table IV.** Pairwise Substituent Parameters for $^{11}$B–$^{19}$F Coupling Constants[a]

| Class of donor | Donor | $\eta_{D,F}$ | $\eta_{D,Cl}$ | $\eta_{D,Br}$ |
|---|---|---|---|---|
| Nitrogen donors | $Me_3N$ | 8.65 | 19.79 | 26.09 |
| | 4-Me(py) | 6.12 | 18.24 | 22.38 |
| Ether donors | $Me_2O$ | −0.93 | 13.9 | 19.59 |
| | MeOEt | −1.73 | 14.83 | |
| Carbonyl donors | MeC(O)SMe | −2.28 | 16.48 | 22.02 |
| | DMAC | −1.03 | 15.53 | |
| | tmu | −1.78 | 16.08 | |
| Soft donors | $Me_3P$ | 26.26 | 35.04 | 37.88 |
| | $Me_2S$ | 13.00 | 30.4 | |
| | $Me_3PS$ | 15.30 | 34.6 | |
| Halogen–halogen terms | $F^-$ | −0.71 | 13.89 | 19.27 |
| | $Cl^-$ | 13.89 | 26.33 | 32.43 |
| | $Br^-$ | 19.27 | 32.43 | 37.14 |

[a] In hertz; relative signs, only, are given.

present Drago–Pearson controversy surrounding "hard" and "soft" acid–base theory, and in this paper the terms are used in a purely qualitative sense, for the lack of another such simple term. We have been unable to establish significant correlations with Drago's quantitative *E* and *C* parameters.] Donors which are intermediate between hard and soft such as 4-methylpyridine show smaller variations in the parameters over the series from fluorine to bromine. While the pairwise parameters for oxygen donors show considerable variation, the *differences* between $\eta_{D,F}$ and $\eta_{D,Cl}$ and (where data are available) between $\eta_{D,Cl}$ and $\eta_{D,Br}$ remain fairly constant. These oxygen-donor differences are distinct from the differences observed in these terms when any other atom is donor. Thus the pairwise parameters provide an indication of the donor site, which is consistent with the already established oxygen donation in tetramethylurea[9] and dimethylacetamide.[10] Oxygen donation is also indicated in MeC(O)SMe in accord with other evidence from this laboratory.[11] Ether donors have significantly different values of $\eta_{D,X}$ than carbonyl donors; only the *differences* in $\eta_{D,X}$ as X is changed remain essentially the same for both types of oxygen donors. The similarity of the $Me_3PO$ adduct pairwise parameters to those of the carbonyl donors is not surprising since doubly bonded oxygen is the donor in both cases.

Amine nitrogen seems to be very different in its interactions from pyridine or nitrile nitrogen. The differences might be attributed to the effects of the π cloud of multiply bonded nitrogen, which tends to enhance the soft character of nitrogen bases.

**$^{11}$B Chemical Shift Parameters.** As with the $^{19}$F parameters, the $^{11}$B parameters for the hard donors ($Me_3N$, $Me_2O$, $F^-$) decrease in the order $\eta_{D,F} > \eta_{D,Cl} > \eta_{D,Br}$ while for the soft donors ($Me_2S$, $Br^-$, $I^-$) the order is reversed (Table III). $^{11}$B chemical shifts are available for few series of mixed adducts. However $^{11}$B chemical shifts are available for many unmixed boron trihalide adducts[12] and can be used to calculate donor–halogen pairwise terms, using the halogen–halogen pairwise terms of Table III. A selection of donor–halogen terms calculated in this manner, included in Table III, is less reliable because (i) a variety of solvents and references were used and (ii) the number of chemical shift values available is no greater than the number of pairwise terms calculated. Nevertheless a similar pattern emerges. The $Me_3P$ adduct parameters show the same trend as the parameters of the other soft donors $Me_2S$, $Br^-$, and $I^-$. Pyridine and 4-methylpyridine show the behavior expected of bases intermediate on the hard–soft scale; *i.e.*, there is little change over the series $\eta_{D,F}$, $\eta_{D,Cl}$, $\eta_{D,Br}$. Carbonyl donors give irregular patterns.

**$^{11}$B–$^{19}$F Coupling Constant Parameters.** Trends in the coupling constant pairwise parameters (Table IV) differ from those in the chemical shift parameters in that both hard and soft donors give donor–halogen parameters which increase in the order $\eta_{D,F} < \eta_{D,Cl} < \eta_{D,Br}$. The parameters are much larger for the soft donors $Me_2S$, $Me_3PS$, and especially $Me_3P$ than for the hard donors. The oxygen donors all give similar donor–halogen parameters, with however, a distinct difference between ether oxygen and carbonyl oxygen.

The oxygen donor–fluorine parameters are small and

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(9) J. S. Hartman and G. J. Schrobilgen, *Can. J. Chem.*, **50**, 713 (1973); **51**, 99 (1973).

(10) S. J. Kuhn and J. S. McIntyre, *Can. J. Chem.*, **43**, 375 (1965).

(11) M. J. Bula, J. S. Hartman, and C. V. Raman, submitted for publication.

(12) W. G. Henderson and E. F. Mooney, *Annu. Rev. NMR (Nucl. Magn. Resonance) Spectrosc.*, **2**, 219 (1969); see Table XI.

opposite in sign to all the other donor-halogen parameters. Only the fluorine-fluorine parameter is of the same sign. This provides another test for oxygen donation, which further confirms oxygen donation in tetramethylurea,[9] dimethylacetamide,[10] and MeC(O)SMe[11] adducts.

The two nitrogen donors $Me_3N$ and 4-methylpyridine give similar donor-halogen parameters. The same is true for the two sulfur donors $Me_2S$ and $Me_3PS$. Thus the coupling constant parameters seem to approach closer to a generalized donor atom-halogen interaction.

## Discussion

**Pairwise Interaction Parameters as an Empirical Tool in Nmr Studies of Adducts.** Nmr parameters can be summarized in a much more condensed form by using the pairwise interaction parameters. Errors are small, with the parameters showing little sensitivity to the size of the data set. The pairwise parameters can be used to predict chemical shifts and coupling constants; some trends are simplified and some apparent anomalies disappear when the data are expressed in terms of pairwise parameters. Thus $^{11}B$ chemical shifts of the $Me_2S$ adducts are to high field of those of the corresponding $Me_2O$ and $Me_3N$ adducts, except for the $BF_3$ adduct. While a plausible explanation can be given in terms of the weakness of the donor-acceptor bond in $Me_2S \cdot BF_3$[7], it is now apparent that the observed shifts can be accounted for more simply in terms of opposite trends in the series $\eta_{D,F}$, $\eta_{D,Cl}$, $\eta_{D,Br}$ for $Me_2S$ and the hard donors.

$BCl_3$ adducts and $BCl_4^-$ absorb at especially low field in the $^{11}B$ spectrum because the chlorine-chlorine pairwise term is smaller than any of the other halogen-halogen terms, while $BI_3$ adducts and $BI_4^-$ absorb at especially high field because of the especially large iodine-iodine term. The halogen-halogen $^{11}B$ terms generally override the effects of the donor-halogen terms. Thus both the $Me_3N$ and $Me_2S$ series of adducts, which differ greatly in the donor-halogen terms, give the same $^{11}B$ chemical shift ordering, $BCl_3 < BF_3 < BBr_3 < BI_3$. Mooney and coworkers have made attempts to correlate $^{11}B$ complexation shifts with donor-acceptor bond strengths of boron trihalide adducts.[13] From consideration of the pairwise interaction parameters, such a correlation cannot be successful in the general case. Complexation shifts are largely determined by differences between halogen-halogen pairwise parameters for trigonal and tetrahedral boron. This major portion is independent of the donor. The remaining portion arises from donor-halogen pairwise terms in the adduct, which have no counterpart in the free boron trihalides. This portion would be the source of any correlation of $^{11}B$ chemical shifts with donor-acceptor bond strength. However, the donor-halogen pairwise terms either decrease or increase along the series $\eta_{D,F}$, $\eta_{D,Cl}$, $\eta_{D,Br}$, depending on whether the base is hard or soft, whereas relative Lewis acidity follows the same order, $BF_3 < BCl_3 < BBr_3 < BI_3$, for both hard and soft bases.

Shifts in the $^{19}F$ resonance to lower field in the series $D \cdot BF_3$, $D \cdot BF_2X$, $D \cdot BFX_2$ (X = Cl, Br)[5-7] are seen to be largely a result of the halogen-halogen terms decreasing as the halogens change from F to Cl to Br (Table II). When this tendency is counteracted by an especially large increase in the donor-halogen terms from F to Cl to Br, a reversal of the chemical shift trend becomes possible. Such a reversal is almost realized in the $Me_2S \cdot BF_nCl_{3-n}$ series[7] and does indeed occur in the $Me_3P \cdot BF_nBr_{3-n}$ series.[14] Thus the approximately linear relationship between $^{19}F$ chemical shifts and $^{11}B-^{19}F$ coupling constants which has been observed in the boron trihalide adducts of $Me_2O$[5] is a result of similar trends in the $^{19}F$ chemical shift and $^{11}B-^{19}F$ coupling constant pairwise parameters. The increasing deviations from this linear relationship which occur over the series of bases $Me_2O$, $Me_3N$, 4-methylpyridine, and $Me_2S$[5-7] results from the reversal of the trend of $^{19}F$ chemical shift pairwise parameters $\eta_{D,X}$ over the series X = F, Cl, Br as the base changes from hard to soft, with no corresponding reversal in the trend of the coupling constant parameters. Although the linear relationship of chemical shift and coupling constant does remain a useful empirical tool in the study of oxygen-donor adducts,[14,15] more insight can be gained from the use of the pairwise interaction parameters.

It is of interest that the coupling constant pairwise terms are of both positive and negative sign (Table IV). A good fit could not be obtained without this sign change. Note that relative signs only are given. All but the oxygen donor-fluorine and fluorine-fluorine parameters have the same sign which is shown as positive. The few parameters of opposite sign are small, and the coupling constant has this sign only when all of the pairwise terms involved have this sign. Thus only $BF_4^-$ and the oxygen donor-boron trifluoride adducts give opposite-sign coupling constants and these are small. These small $^{11}B-^{19}F$ couplings frequently cannot be resolved due to quadrupole relaxation of boron but can now be calculated to be as follows: $Me_2O \cdot BF_3$, −2.6 Hz; MeOEt·$BF_3$, −4.3 Hz; MeC(O)SMe·$BF_3$, −5.3 Hz; DMAC·$BF_3$, −2.8 Hz; tmu·$BF_3$, −4.3 Hz. The pairwise interaction parameters confirm that the sign of the boron-fluorine coupling constant can be changed by relatively small effects.[16]

**Trends in the Pairwise Parameters. Bonding Implications.** Irregularities in $^{11}B$ chemical shifts of mixed tetrahaloborate anions when fluorine is present (Figure 7 of ref 3a) can be expressed in terms of anomalous halogen-fluorine pairwise parameters. A plot of $^{11}B$ halogen-halogen pairwise parameters against the sum of the halogen electronegativities gives a smooth curve for the nonfluorine parameters, but the two fluorine parameters $\eta_{F,F}$ and $\eta_{F,Cl}$ are anomalously large by electronegativity considerations alone (Figure 1). An extension of this plot to donor-halogen parameters does not give as distinctive a pattern, but it is of interest that all pairwise terms involving fluorine fall within a small range (1.76-3.31 ppm) with little or no apparent dependence on the nature of the nonfluorine substituent. Thus the pairwise additivity rule seems to approach closer to a direct additivity rule when fluorine is involved. This might be related to some multiple bonding in the B-F bond, similar to but attenuated from that which is well-established when fluorine is bonded to trigonal boron.

There is some regularity in the $\eta_{D,I}$, $\eta_{D,Br}$, $\eta_{D,Cl}$ series of $^{11}B$ terms for a given donor. It is of interest that both the smallest and the largest pairwise parameters ($\eta_{Me_3N,I}$ and $\eta_{I,I}$) observed, where complete series $\eta_{D,X}$ (X from F to I) are available, involve iodine. Soft-soft interactions give the largest pairwise parameters; soft-hard ones (*e.g.*,

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[13] P. N. Gates, E. J. McLauchlan, and E. F. Mooney, *Spectrochim. Acta*, 21, 1445 (1965).

[14] C. V. Raman, M.Sc. Thesis, Brock University, 1971.

[15] J. S. Hartman and G. J. Schrobilgen, submitted for publication.

[16] R. J. Gillespie, J. S. Hartman, and M. Parekh, *Can. J. Chem.*, 46, 1601 (1968).

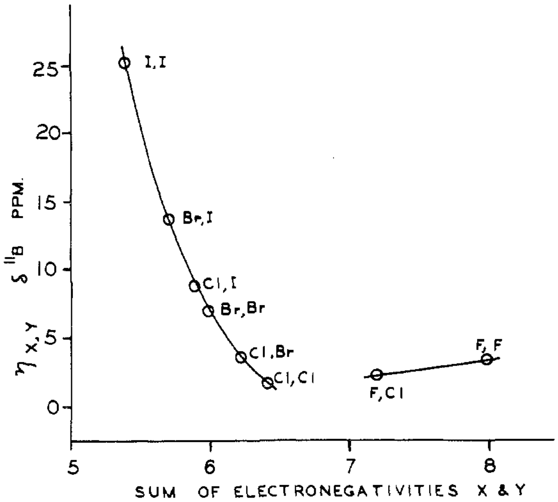

**Figure 1.** Plot of $^{11}$B halogen-halogen chemical shift pairwise additivity parameters, $\eta_{X,Y}$, *vs.* the sum of the halogen electronegativities of X and Y.

$Me_3N$-I) give the smallest ones, while other types including hard-hard are intermediate in magnitude.

Unlike the chemical shift parameters, the coupling constant parameters show a semiquantitative relationship to the sum of the electronegativities of the two interacting atoms (Figure 2). The halogen-halogen parameters fall on a smooth curve, while the donor-halogen parameters, plotted using the simple atomic electronegativity of the donor atom, are displaced, forming an apparently parallel curve.

Perhaps a more significant relationship is shown in Figure 3, namely, the correlation of the coupling constant pairwise additivity parameters with the sum of the van der Waals radii (Pauling) of the two halogens or halogen and donor atom pair being considered. The existence of this apparent through-space or steric effect on the additivity parameters may reflect a geometric influence on the nature of the B-F bond and, hence, on the B-F coupling constant. The deviation of the N-X and P-X parameters from the straight line are such as to indicate a greater steric effect of species such as $Me_3N$ and $Me_3P$ giving the donor atom an effectively larger van der Waals radius, while $Me_2S$ shows the opposite trend; *i.e.*, there is no steric crowding about the sulfur.

The pairwise additivity of coupling constant data has been related by Malinowsky to the presence of multiple bonding in the system. Thus his criteria support the postulate of survival of some multiple bonding in the tetrahedral boron trihalide adducts[3a,5,17] and imply that the Fermi contact term is not dominant[2] for this coupling. Thus the relating of coupling constants in these systems to factors such as "per cent s character" may not be applicable.

All three groups of pairwise interaction parameters (Tables II-IV) show striking differences between the donor-halogen parameters of the hard and soft donors. This provides further indications that the electronic structure of the adduct changes significantly as the donor changes from hard to soft. This is consistent with suggestions of additional interaction across the donor-acceptor bond in adducts of a soft donor, $Me_2S$, with heavier halogen-boron trihalide adducts.[7]

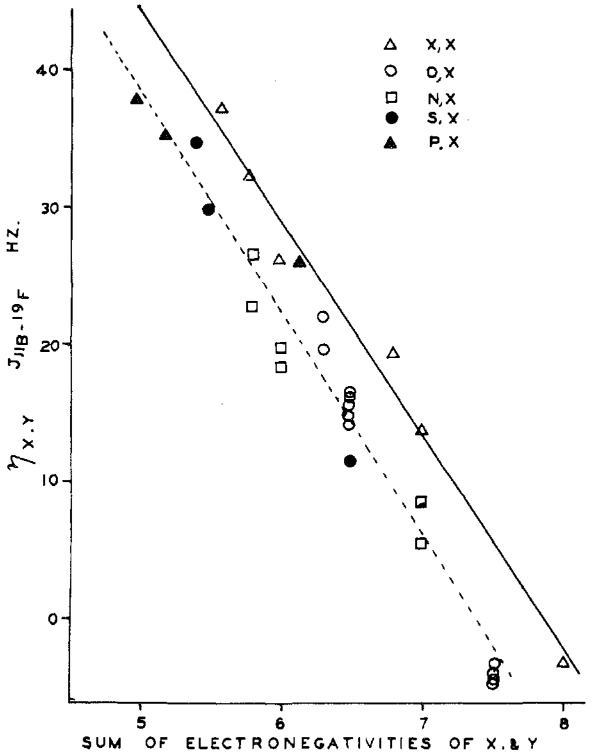

**Figure 2.** $J_{^{11}B-^{19}F}$ pairwise interaction parameters, $\eta_{X,Y}$, *vs.* the sum of the electronegativities of X and Y: —, halogen-halogen curve; ----, donor-halogen curve.

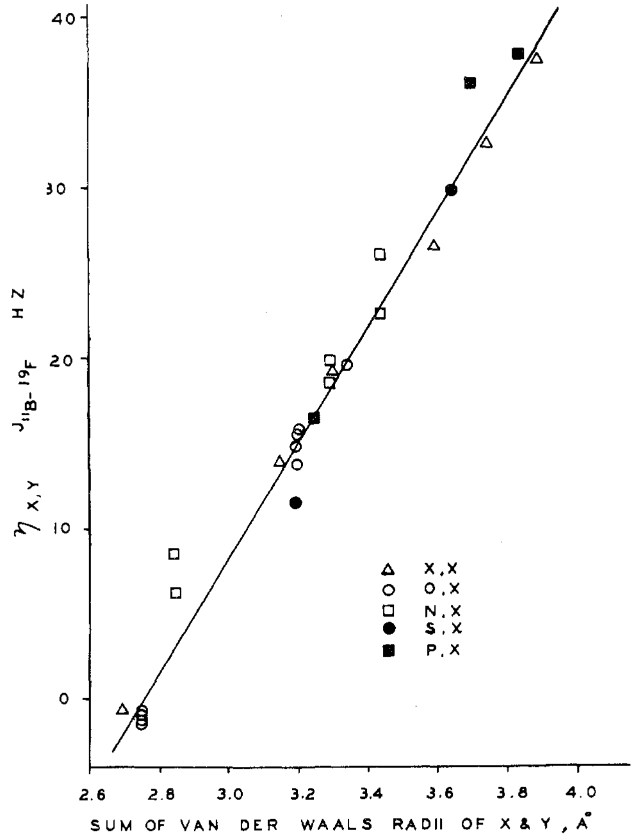

**Figure 3.** $J_{^{11}B-^{19}F}$ pairwise interaction parameters, $\eta_{X,Y}$, *vs.* the sum of the van der Waals radii of X and Y.

The possibility of correlating pairwise interaction parameters about different central atoms is of interest. Unfortunately no donor-halogen parameters seem to be available for other central atoms, but some comparison of halogen-halogen parameters can be made. $^{19}$F chemical shift and

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(17) D. G. Brown, R. S. Drago, and T. F. Bolles, *J. Amer. Chem. Soc.*, 90, 5706 (1968).

$^{29}Si$-$^{19}F$ coupling constant pairwise parameters have recently been reported for the mixed tetrahalosilanes.[18] The chemical shift parameters are plotted against the corresponding boron compound parameters in Figure 4. Separate straight lines are formed by the fluorine-containing and nonfluorine-containing parameters. The difference between the two lines corresponds to about 4 ppm in either the boron or the silicon compound parameters. This seems to confirm that fluorine has anomalous effects when compared to the other halogens. The anomaly is probably related to different degrees of multiple bonding from fluorine to boron and to silicon. The results obtained would be consistent with better fluorine-to-central-atom multiple bonding in the boron compounds than in the corresponding silicon compounds, consistent with the better correspondence in orbital sizes in the boron case.

Our tetrahedral-boron $^{11}B$ chemical shift parameters correlate well with corresponding tetrahedral-carbon parameters,[3b] tetrahedral-$^{27}Al$ parameters,[4a] and trigonal-boron parameters,[2] as can be shown by smooth-curve plots. A previously noted anomaly of the $^{13}C$ Br,Br parameter[3b] recurs in our work. Unfortunately no pairwise terms involving fluorine are available for the $^{13}C$ or $^{27}Al$ systems.

Adequate interpretation of trends in pairwise parameters awaits the availability of more data. Nevertheless it seems that corresponding parameters relating to different central nuclei can be related to differences in bonding, so that the parameters should be of value in chemical bonding studies as well as of empirical use.

**Acknowledgments.** We wish to thank the National Research Council of Canada for financial support and McMaster University for use of heteronuclear nmr facilities.

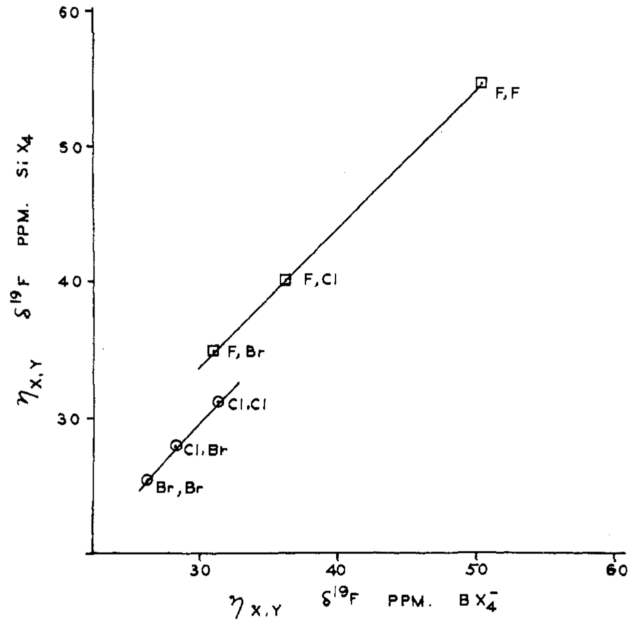

**Figure 4.** $\delta\ ^{19}F$ pairwise interaction parameters for $SiX_4$ species *vs.* $BX_4^-$ species.

**Registry No.** $BCl_3$, 10294-34-5; $BF_3$, 7637-07-2; $BBr_3$, 10294-33-4; $BI_3$, 13517-10-7; $^{11}B$, 14798-13-1.

**Supplementary Material Available.** Table I, showing observed and calculated chemical shifts and coupling constants, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche referring to code number INORG-74-1467.

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# Structural Diagnosis of Chloroaluminate Compounds by Chlorine-35 Nuclear Quadrupole Resonance Spectroscopy

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The $^{35}Cl$ nqr spectra at room temperature are reported for chloroaluminate groups in $Te_4(AlCl_4)_2$, $ICl_2AlCl_4$, $Bi_5(AlCl_4)_3$, $Co(AlCl_4)_2$, $Hg_3(AlCl_4)_2$, and $Te_4(Al_2Cl_7)_2$. These and the literature data for $NaAlCl_4$, $GaAlCl_4$, and $SCl_3AlCl_4$ are compared for known and probable structures. The transitions of relatively free $AlCl_4^-$ groups in "ionic" compounds are found to average 10.6–11.3 MHz with a range of ≤1 MHz for the individual compounds. Strong coordination of $AlCl_4^-$ to the cation (*e.g.*, $Co^{2+}$, $Hg_3^{2+}$) or the formation of $Al_2Cl_7^-$ anions is reflected in an elongation of the bridging aluminum-chlorine bonds and in appreciable increases in both the range and the average frequency of the chlorine transitions. The effects of bridging on the halogen nqr transitions are considered and compared with those for the aluminum and gallium halide dimers $M_2X_6$.

## Introduction

The need for a convenient method for determining the identity and bonding character of the anions in chloroaluminate compounds that is quicker than an X-ray study has been made more apparent by the increased utilization of $AlCl_4^-$ anions in compounds with unusual cations. The problem was brought to a head by the recent preparation of a series of apparently ionic tetrachloroaluminate compounds of some polyhalogen cations[1] which had particularly unfavorable properties for crystallographic study. The classical technique of infrared spectroscopy is inconclusive (and hence misleading) in some practical situations, for example,

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[1] D. J. Merryman, P. A. Edwards, J. D. Corbett, and R. E. McCarley, *Chem. Commun.*, 779 (1970).