The Structural Dependence of the Inductive Effect. Part III.[1a] The Calculation of Geminal Substituent Effects upon ^1H and ^{13}C Chemical Shifts, and Directly-bonded Substituent Effects upon ^{13}C, ^{11}B, ^{31}P, and ^{119}Sn Shielding

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The calculational procedure applied in Part I to ^{19}F shielding is extended to other nuclei. Substituent effects caused by directly bonded interactions are allowed for, in addition to geminal effects.

The method enables the chemical shifts of ^1H, ^{13}C, ^{11}B, and ^{31}P nuclei in a variety of situations to be calculated (from suitable references), and successfully explains deviations from additivity of substituent effects. An important exception is noted for the case of ^{119}Sn shielding in some mixed halides of Sn^{IV}.

In Part I [1b] we described a method of calculating the chemical shifts of ^{19}F nuclei, in a variety of molecules, from an arbitrary reference. The method is based upon the assumption that the dominant contribution to shielding of ^{19}F lies in the paramagnetic term of Ramsey's equation,[2] and that changes in this term may be related to changes in the ionic character of the bond of which the

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[1] (*a*) Part II, L. Phillips and V. Wray, *J. Chem. Soc.* (*B*), 1971, 2074; (*b*) *ibid.*, 2068.

[2] N. F. Ramsey, *Phys. Rev.*, 1950, **78**, 699; 1952, **86**, 243.

fluorine is part.[3] It is generally accepted[4] that the paramagnetic term is the more important for nuclei in atoms which have *p*, *d*, or *f* electrons, and so the method should be equally applicable to other nuclei such as ^{13}C, ^{31}P, ^{11}B, or ^{119}Sn.

It is supposed that ^{1}H shielding has little or no dependence upon the paramagnetic term, and that diamagnetic contributions are all important.[5] In spite of this, it is observed that substituent effects upon ^{1}H shielding are frequently paralleled by such effects upon ^{13}C or ^{19}F shielding, *e.g.*, in the case of *para*-substituted benzenes.[6] Such parallels have not been generally discussed in the case of aliphatic derivatives, but this may be because of the complexity of the situation. However, inductive effects do play an important part in deciding the chemical shifts of protons[5] as the diamagnetic term depends upon the 1*s* electron density at the H atom which is dependent upon the inductive powers of substituents. It is therefore valid to examine the applicability of the approach developed previously[1] to the case of ^{1}H shielding as well as to the shielding of other nuclei.

RESULTS AND DISCUSSION

Geminal Substituent Effects upon ^{1}H *Shielding*.—By analogy with equation (23) in Part I[1b] the ^{1}H chemical shift between two molecules C(abd)–H and C(efg)–H will be given by equation (1), where the various terms

$$\Delta = k'\{(k_\alpha E_{\mathrm{C}} + k_\beta E_{\mathrm{H}})(E_{\mathrm{a}} + E_{\mathrm{b}} + E_{\mathrm{d}} - E_{\mathrm{e}} - E_{\mathrm{f}} - E_{\mathrm{g}}) + k^{\mathrm{ab}}E_{\mathrm{a}}E_{\mathrm{b}} + k^{\mathrm{ad}}E_{\mathrm{a}}E_{\mathrm{d}} + k^{\mathrm{bd}}E_{\mathrm{b}}E_{\mathrm{d}} - k^{\mathrm{fg}}E_{\mathrm{f}}E_{\mathrm{g}} - k^{\mathrm{eg}}E_{\mathrm{e}}E_{\mathrm{g}} - k^{\mathrm{ef}}E_{\mathrm{e}}E_{\mathrm{f}}\} \quad (1)$$

have the same significance as before[1] but the constants refer specifically to ^{1}H resonance.

For a series of molecules of the type C(abX)–H where a and b remain constant and X is varied, the chemical shift of any member referred to the case where X = I * is given by equation (2) where $K_1 = k'(k_\alpha E_{\mathrm{C}} + k_\beta E_{\mathrm{H}})$

$$\Delta^{\mathrm{CabI}H}_{\mathrm{CabX}H} = (E_{\mathrm{I}} - E_{\mathrm{X}})[K_1 + K_2(E_{\mathrm{a}} + E_{\mathrm{b}})] \quad (2)$$

and $K_2 = k'k^{\mathrm{aX}}(E_{\mathrm{b}} + E_{\mathrm{a}}) = k'k^{\mathrm{bX}}\ (E_{\mathrm{b}} + E_{\mathrm{a}})$.

Equation (2) predicts that a plot of $\Delta^{\mathrm{I}}_{\mathrm{X}}$ against $(E_{\mathrm{I}} - E_{\mathrm{X}})$ should be linear, and have a slope which depends upon the sum of the electronegativities of the groups a and b. This is demonstrated in Figure 1 for the series C*H*$_3$X, CH$_3$·C*H*$_2$X, and (CH$_3$)$_2$C*H*X. The chemical shifts of the relevant protons in these series are listed in Table 1, together with the slopes of the lines drawn in Figure 1. According to equation (2), these slopes *S* are related by equation (3).

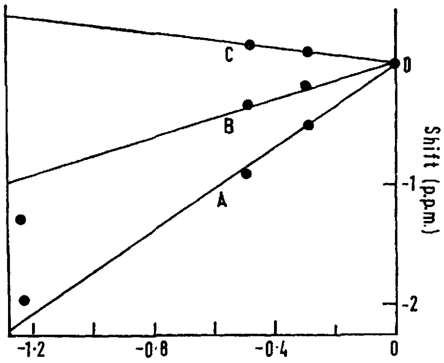

FIGURE 1 Substituent chemical shifts, referred to X = I, for the series A, CH$_3$X; B, CH$_3$·CH$_2$X; and C, (CH$_3$)$_2$CHX plotted against the Huggins electronegativity difference, $(E_{\mathrm{I}} - E_{\mathrm{X}})$.

$$S = K_1 + K_2(E_{\mathrm{a}} + E_{\mathrm{b}}) \quad (3)$$

A plot of *S* against $(E_{\mathrm{a}} + E_{\mathrm{b}})$ is linear and yields the values of constants K_1 and K_2; $K_1 = -12{\cdot}96$ p.p.m./Huggins unit and $K_2 = 2{\cdot}56$ p.p.m./(Huggins unit)^2. Equation (2) therefore takes the form (4). Equation (4)

$$\Delta^{\mathrm{I}}_{\mathrm{X}} = (E_{\mathrm{I}} - E_{\mathrm{X}})[+12{\cdot}96 - 2{\cdot}56(E_{\mathrm{a}} + E_{\mathrm{b}})] \quad (4)$$

enables the substituent chemical shifts in the series CH$_3$X, CH$_3$·CH$_2$X, and (CH$_3$)$_2$CHX to be calculated to within 0·17 p.p.m. (r.m.s.) of their reported values averaged from four compilations;[7] a comparison of observed and calculated substituent chemical shifts (referred to X = I) is given in Table 1.

TABLE 1

Observed and calculated substituent chemical shifts (referred to X = 1) for the series CH$_3$X, CH$_3$·CH$_2$X, and (CH$_3$)$_2$CHX

Compound type	Slope from Figure 1	F		Cl		Br	
		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
C*H*$_3$X	+1·68	−1·94	−2·13	−0·89	−0·85	−0·52	−0·51
CH$_3$·C*H*$_2$X	+0·74	−1·29	−0·84	−0·37	−0·34	−0·21	−0·20
(CH$_3$)$_2$C*H*X	−0·36			+0·14	+0·18	+0·09	+0·11

The form of equation (4) correctly predicts that a plot of $\Delta^{\mathrm{I}}_{\mathrm{X}}$ against $(E_{\mathrm{I}} - E_{\mathrm{X}})$ may have either positive or negative slope depending upon $(E_{\mathrm{a}} + E_{\mathrm{b}})$ and will have

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* In the earlier work[1b] the compound in which X = F was chosen as the reference point; because of the non-availability of suitable compounds and the lack of a convenient compilation of ^{1}H chemical shifts, it is necessary to choose X = I as the reference for ^{1}H shielding.

[3] A. Saika and C. P. Slichter, *J. Chem. Phys.*, 1954, **22**, 26.

[4] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, ' High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon Press, Oxford, 1966, vol. 1, p. 151.

[5] Ref. 4, p. 130.

[6] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, 1961, **35**, 731.

[7] Ref. 4, p. 672; L. M. Jackman and S. Sternhell, ' Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon Press, Oxford, 1969, p. 164; J. A. Pople, W. G. Schneider, and H. J. Bernstein, ' High Resolution Nuclear Magnetic Resonance,' McGraw-Hill, London, 1959, p. 277; D. Chapman and P. D. Magnus, ' Introduction to Practical High Resolution Nuclear Magnetic Resonance Spectroscopy,' Academic Press, London, 1966, p. 73.

zero slope when $(E_a + E_b) \simeq 5{\cdot}1$ Huggins units. This is exactly analogous to the results obtained for similar series of fluorinated compounds by use of ^{19}F resonance,[1b] in which the corresponding value of $(E_a + E_b)$ is 5·8 Huggins units. The difference between the ^1H and ^{19}F values may be real, but probably arises in part from the fact that fewer series are conveniently available for ^1H studies and the determination is therefore less precise.

Calculations of Chemical Shifts from CH_4.—The ^1H chemical shift between the indicated protons in any two molecules of the type C(abd)–H and C(efg)–H can be calculated from equation (1) if the various interaction constants such as $k'k^{ab}$, $k'k^{eg}$, *etc.*, are known: $k'(k_\alpha E_C + k_\beta E_H)$ has been evaluated above as 12·96, and the other constants may be deduced empirically as described earlier.[1b] For 13 compounds of the type CH_nX_m (where X = halogen) the experimental results can be calculated to a satisfactory degree of accuracy ($\pm 0{\cdot}18$ p.p.m.) by use of the following values: $k'k^{XX} = kk^{HH} = -1{\cdot}94$; $k'k^{HF} = -2{\cdot}17$; $k'k^{HCl} = -2{\cdot}04$; $k'k^{HBr} = -1{\cdot}99$; and $k'k^{HI} = -1{\cdot}82$. Table 2 compares observed and calculated chemical shifts for these compounds, referred to CH_4, and shows that the method is successful in accounting for the deviations from additivity observed on successive replacement of H by halogen in a series of the type CH_nX_m (Table 3). Another interesting feature is the observed behaviour of the proton chemical shift in a series of the type CH_nX_m where *n* and *m* remain constant and the nature of X is changed. For CH_3X, the chemical shifts lie in the expected order of electronegativities of X, with increased shielding in the order F < Cl < Br < I < H (Table 4). For CHX_3 however, the shifts do *not* lie in the expected order but occur, in order of increased shielding, as Cl < Br < F < I < H (Table 5). In each case the observed trend is correctly predicted.

TABLE 2

Comparison of observed and calculated ^1H chemical shifts for a variety of halogenomethanes

Compound	Δ obs./p.p.m.[a]	Δ calc./p.p.m.
CH_4	0	0
CH_3Cl	−2·82	−2·82
CH_2Cl_2	−5·10	−5·27
$CHCl_3$	−7·01	−7·37
CH_3Br	−2·45	−2·67
CH_2Br_2	−4·71	−4·90
$CHBr_3$	−6·95	−6·69
CH_3I	−1·93	−1·99
CH_2I_2	−3·67	−3·82
CHI_3	−4·68	−4·80
CH_3F	−3·87	−3·57
CH_2F_2	−5·22	−5·48
CHF_3	−6·02	−5·74

[a] Ref. 7.

TABLE 3

$$CH_4 \longrightarrow CH_3Cl \longrightarrow CH_2Cl_2 \longrightarrow CHCl_3$$

	$CH_4 \rightarrow CH_3Cl$	$CH_3Cl \rightarrow CH_2Cl_2$	$CH_2Cl_2 \rightarrow CHCl_3$
Δ obs.	−2·82	−2·28	−1·91
Δ calc.	−2·82	−2·45	−2·10

TABLE 4

	CH_3F	CH_3Cl	CH_3Br	CH_3I	CH_4
Δ obs.	−3·87	−2·82	−2·45	−1·93	0
Δ calc.	−3·57	−2·82	−2·67	−1·99	0

TABLE 5

	$CHCl_3$	$CHBr_3$	CHF_3	CHI_3	CH_4
Δ obs.	−7·01	−6·59	−6·02	−4·68	0
Δ calc.	−7·37	−6·69	−5·74	−4·80	0

For substituent groups bonded to the α-C atom by sp^3 carbon, the interaction constants $k'k^{CH}$ and $k'k^{CC}$ can be obtained as described previously,[1b] and for the series CH_4, $CH_3{\cdot}CH_3$, $(CH_3)_2CH_2$, and $(CH_3)_3CH$ values of $k'k^{HH} = -1{\cdot}94$, $k'k^{HC} = -2{\cdot}04$, and $k'k^{CC} = -2{\cdot}09$ enable satisfactory calculation of shielding to be carried out, as shown in Table 6.

TABLE 6

Observed and calculated ^1H chemical shifts for a series of hydrocarbons

Compound	Δ obs./p.p.m.	Δ calc./p.p.m.
CH_4	0	0
CH_3CH_3	−0·65	−0·65 *
$(CH_3)_2CH_2$	−1·12	−1·12
$(CH_3)_3CH$	−1·33	−1·33 *

* The exact agreement for these values arises from the use of these data to calculate $k'k^{CH_3-H}$ and $k'k^{CH_3-CH_3}$.

It is apparent that the method of calculation[1b] for geminal substituent effects upon ^{19}F shielding is equally applicable to ^1H shielding.

Geminal Substituent Effects upon ^{13}C *Shielding*.—The methods applied[1b] to the calculation of ^{19}F chemical shifts and ^1H chemical shifts (above) should also be applicable to ^{13}C shielding. Thus, the differences in the shielding of ^{13}C nuclei in the $^{13}CH_3$ groups of a series of molecules C(abX)–CH_3 should be calculable by an equation similar to (2) in which the constants K_1 and K_2 refer specifically to ^{13}C. Data for three such series[8] are shown in Table 7, together with values calculated by use of equation (5). The numerical constants were

$$\Delta^{CabICH_3}_{CabXCH_3} = (E_I - E_X)[15{\cdot}74 - 5{\cdot}66(E_a + E_b)] \quad (5)$$

obtained as described previously, and the substituent chemical shifts shown in Table 7 agree with experimental results to within $\pm 0{\cdot}25$ p.p.m. (r.m.s.).

TABLE 7

Observed and calculated substituent chemical shifts (referred to X = I) for the series $CH_3{\cdot}CH_2X$, $(CH_3)_2CHX$, and $(CH_3)_3CX$

Compound	X	Δ obs./p.p.m.[a]	Δ calc./p.p.m.
$CH_3{\cdot}CH_2X$	I	0	0
	Br	2·9	2·8
	Cl	4·7	4·6
$(CH_3)_2CHX$	I	0	0
	Br	3·8	3·4
	Cl	5·0	5·7
$(CH_3)_3CX$	I	0	0
	Br	4·1	4·1
	Cl	7·0	6·9

[a] Ref. 8.

Equation (5) shows that the slope of a plot of Δcalc. against $(E_I - E_X)$ becomes zero when $(E_a + E_b) = 2{\cdot}78$.

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[8] P. C. Lauterbur, *Ann. New York Acad. Sci.*, 1958, **70**, 841.

For compounds other than those containing C–metal bonds, this is not possible to realise in practice; the minimum value for $(E_a + E_b)$ occurs when $a = b = H$ at 4·40 Huggins units. Unlike ^1H and ^{19}F shielding, replacement of geminal halogen substituent by a less electronegative halogen should always result in a deshielding of the ^{13}C nucleus in a CH_3 group, but it is not possible to predict what the behaviour of ^{13}C in some other situation (*e.g.*, $^{13}CF_3$) will be.

The number of ^{13}C data available for consideration is limited, but the results are encouraging.

Directly-bonded Substituent Effects.—The shielding of a nucleus in a multivalent atom presents a somewhat different problem from those considered so far. Suitable cases for examination are ^{13}C, ^{11}B, ^{31}P, and ^{119}Sn nuclei in series of compounds in which the substituents directly bonded to the central atom (C, B, P, or Sn) are changed.

^{13}C *Shielding.* In a molecule of the type C(abde), the shielding of the ^{13}C nucleus will be proportional to the sum of the effective electronegativities of the groups a, b, d, and e [equation (6)]. By use of the perturbation

$$\sigma_{^{13}\mathrm{Cabde}} = \sigma_0 + k'[E'_a + E'_b + E'_d + E'_e] \quad (6)$$

method described in Part I[1b] the effective electronegativities can be evaluated and substituted into equation (6). This leads to expression (7). The various

$$\sigma'_{^{13}\mathrm{Cabde}} = \sigma_0 + k'[E_a + E_b + E_d + E_e + E_a(k^{ab}E_b + k^{ad}E_d + k^{ae}E_e + k^{aC}E_C) + E_C(k^{Cb}E_b + k^{Cd}E_d + k^{Ce}E_e) + E_d k^{de}E_e + E_b(k^{bd}E_d + k^{be}E_e)] \quad (7)$$

k's are composite constants[1b] and express the net effect that each interacting group has upon the electronegativity of the others. The problem now is to evaluate the constants; as before it is assumed that the value of k for interaction between two halogens, k^{XX}, is independent of the nature of the halogen and the value of k for the interaction between carbon and halogen, k^{CX}, is also independent of the nature of X. This simplifies equation (7) for the situation in which all substituents are halogens, and the difference in shielding between ^{13}C in such a molecule and a suitable reference such as $^{13}CCl_4$ will be given by equation (8). ($k' +$

$$\Delta^{^{13}\mathrm{CCl}_4}_{^{13}\mathrm{Cabde}} = (k' + k'k^{CX}E_C)(4E_{Cl} - E_a - E_b - E_d - E_e) + k'k^{XX}(6E_{Cl}^2 - E_aE_b - E_aE_d - E_aE_e - E_bE_d - E_bE_e - E_dE_e) \quad (8)$$

$k'k^{CX}E_C$) can be evaluated as a single composite constant, K_1^C, as can $k'k^{XX}$ (K_2^C). With the appropriate value for E_{Cl}, the Huggins electronegativity of chlorine, equation (8) becomes (9). The number of data upon

$$\Delta^{^{13}\mathrm{CCl}_4}_{^{13}\mathrm{Cabde}} = K_1^C\,(12{\cdot}60 - E_a - E_b - E_d - E_e) + K_2^C\,(59{\cdot}52 - E_aE_b - E_aE_d - E_aE_e - E_bE_d - E_dE_e - E_bE_e) \quad (9)$$

which equation (9) can be tested is limited, but an empirical evaluation of the constants yields the results $K_1^C = 612{\cdot}50$, $K_2^C = 50{\cdot}00$. With these values it is possible to calculate the chemical shift from $^{13}CCl_4$ of the ^{13}C nuclei in a variety of mixed halogenocarbons to within experimental error; the results are shown in Table 8.

TABLE 8

Observed and calculated ^{13}C chemical shifts for a variety of fully-halogenated methanes

Compound	Δ obs./p.p.m.[a]	Δ calc./p.p.m.
CCl_4	0	0
CCl_3Br	28	28
CCl_2Br_2	61	58
$CClBr_3$	90	90
CBr_4	124	124
CI_4		355
CF_4		−251

[a] Ref. 8.

The shielding of the ^{13}C in a series of partially halogenated methanes presents some interesting problems. Lauterbur[8] has recorded the data for these compounds, but is unable satisfactorily to account for the observed trends which are shown graphically in Figure 2. Successive chlorination of methane results in a deshielding of the central ^{13}C nucleus, as shown in Table 9; successive bromination causes an initial deshielding, but this

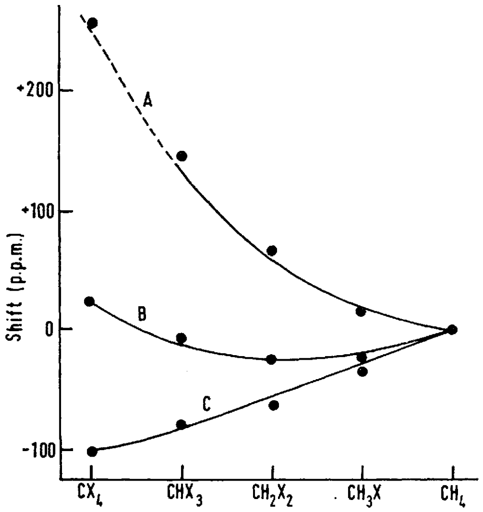

FIGURE 2 Graphs of the observed ^{13}C chemical shifts (lines) and calculated chemical shifts (points) of some substituted methanes CH_xX_{4-x} against the number of substituent atoms; A, X = I; B, X = Br; C, X = Cl

TABLE 9

Observed and calculated ^{13}C substituent chemical shifts for a variety of halogenomethanes referred to CH_4

Compound	Δ obs./p.p.m.	Δ calc./p.p.m.
CH_4	0	0
CH_3Cl	−24	−33
CH_2Cl_2	−57	−61
$CHCl_3$	−83	−82
CCl_4	−100	−100
CH_3Br	−16	−21
CH_2Br_2	−25	−25
$CHBr_3$	−13	−9
CBr_4	+24	+24
CH_3I	+17	+18
CH_2I_2	+59	+66
CHI_3	+135	+145
CI_4		+256

changes to a shielding (*cf.* $^{13}CH_4$) for CBr_4 while successive iodination always causes a shielding increase. None of the substituent effects is linear with respect to the number of halogen atoms.

The chemical shift (from $^{13}CH_4$) of each of the examples can however be calculated by use of equation (7) and the empirically derived constants shown in Table 10. The calculated and experimental values are shown in Table 9, and compared graphically in Figure 2 in which the continuous lines are experimental while the points are calculated values. The data in Table 8 can be calculated by using the same constants, and some 17 experimental results have been calculated to within ±5 p.p.m. (r.m.s.) with eight constants. It would be helpful if more experimental data were available, but it has nevertheless been demonstrated that the method of calculation is capable of explaining the behaviour depicted in Figure 2 very satisfactorily by use only of those approximations detailed earlier.[1b]

TABLE 10

Values of empirically derived constants for ^{13}C and ^{11}B shielding

^{13}C		^{11}B	
k'	+2967·89	k'	+1563·32
(p.p.m./Huggins unit)			
$k'k^{CX}$	−905·92	$k'k^{BX}$	−565·01
$k'k^{CH}$	−814·80	$k'k^{BF}$	−593·43
$k'k^{HH}$	−97·57	$k'k^{FF}$	−50·01
$k'k^{XX}$	−50·00	$k'k^{XX}$	−66·00
$k'k^{HCl}$	−69·48	$k'k^{FX}$	−57·70
$k'k^{HBr}$	−68·49		
$k'k^{HI}$	−67·96		
[p.p.m./(Huggins unit)^2]			

^{11}B *Shielding*. The shielding of ^{11}B in molecules of the type BXYZ where X, Y, and Z are halogens, can in principle be calculated by equation (10) which is similar to (7).

$$\sigma_{^{11}BXYZ} = \sigma_0 + k'[(E_X + E_Y + E_Z) + E_X(k^{XY}E_Y + k^{XZ}E_Z + k^{XB}E_B) + E_B(k^{BY}E_Y + k^{BZ}E_Z) + E_Y(k^{YZ}E_Z)] \quad (10)$$

If all interaction constants between B and halogen have the same value, and all halogen–halogen constants are also independent of the nature of the halogen, the chemical shift of a molecule $^{11}BXYZ$ from $^{11}BCl_3$ (arbitrary reference) can be calculated from equation (11)

$$\Delta^{^{11}BCl_3}_{^{11}BXYZ} = K_1^B\,(9{\cdot}45 - E_X - E_Y - E_Z) + K_2^B\,(29{\cdot}76 - E_XE_Y - E_XE_Z - E_YE_Z) \quad (11)$$

in which $K_1^B = (k' + k'k^{BX}E_B)$ and $K_2^B = k'k^{XX}$.

Empirical evaluation of K_1^B and K_2^B (422·00 and −66·00 respectively) enables satisfactory calculations to be performed for a variety of boron halides of this type, *provided that none of the substituents is fluorine*. Table 11 compares calculated and observed[9] values for a variety of such compounds, while Table 12 shows the unsuccessful attempts to calculate chemical shifts for fluorine-containing analogues.

TABLE 11

Observed and calculated ^{11}B chemical shifts for a variety of halogenoboranes, referred to $^{11}BCl_3$ [a]

Compound	Δ obs./p.p.m. [b]	Δ calc./p.p.m. [c]
BCl_3	0	0
$BBrCl_2$	1	1
BBr_2Cl	4	5
BBr_3	8	12
BCl_2I	10	4
$BClI_2$	26	23
BI_3	54	59
BI_2Br	35	38
$BIBr_2$	19	22
BClBrI	14	12

[a] r.m.s. Deviation = ±3 p.p.m. [b] Ref. 9. [c] From equation (12).

TABLE 12

Observed and calculated ^{11}B chemical shifts for a variety of fluorohalogenoboranes, referred to BCl_3

Compound	Δ obs./ p.p.m. [a]	Δ calc./ p.p.m. [b]	Δ calc./ p.p.m. [c]
BCl_3	0	0	0
$BFCl_2$	16	−4	16
BF_2Cl	25	29	29
BF_3	38	98	40
$BFBr_2$	17	−18	14
BF_2Br	28	10	23
BFI_2		−30	21
BF_2I		−17	15
BFICl		−25	10
BFIBr		−27	15
BFClBr	16	−12	14

[a] Ref. 9. [b] From equation (12). [c] From equation (13).

The reason for the breakdown of equation (11) when applied to fluorine-containing compounds probably lies in the well established tendency[10] of fluorine to 'back-donate' electrons from its filled $2p$ orbital into the empty boron $2p$ orbital of appropriate symmetry. This has the consequence of giving to the B–F bond more π-bond character than have the other B–halogen bonds, and the values of $k'k^{BF}$, $k'k^{FF}$, and $k'k^{FX}$ will not be the same as for the other halogens. The general expression (12) for a chemical shift from $^{11}BCl_3$ can be deduced from equations (10) and (11).

$$\Delta^{BCl_3}_{BXYZ} = 2023{\cdot}74 - \{k'(E_X + E_Y + E_Z) + k'k^{XY}E_XE_Y + k'k^{XZ}E_XE_Z + k'k^{YZ}E_YE_Z + k'k^{BX}E_BE_X + k'k^{BY}E_BE_Y + k'k^{BZ}E_BE_Z\} \quad (12)$$

Empirical evaluation of the constants in equation (12) gives the values shown in Table 10, and enables the chemical shifts of compounds containing fluorine to be calculated to the same degree of precision as those in Table 11; these results are shown in the relevant column in Table 12. Equation (12) can also be used to calculate the data in Table 11 and yields the same results. Sixteen chemical shifts have therefore been calculated by use of the six constants listed in Table 10, and comparison with the experimental results verifies the validity of the treatment. Table 12 also lists calculated chemical shifts

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[9] W. G. Henderson and E. F. Mooney, 'Annual Review of NMR Spectroscopy,' ed. E. F. Mooney, Academic Press, London, 1969, vol. 2, p. 271.

[10] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Interscience, New York, 1966, 2nd edn., p. 256.

for $^{11}BF_2I$, $^{11}BFI_2$, $^{11}BFICl$, and $^{11}BFIBr$ for which experimental results are not available.

^{31}P *Shielding*. In order to demonstrate the extension of the theory to ^{31}P shielding two convenient series of molecules are available, namely $(CF_3)_2PX$ [11] and PX_3 [12, 13] where X = halogen.

The shielding of ^{31}P will be given by an equation exactly analogous to equation (10) in which all constants refer specifically to ^{31}P resonance and the terms E_B are replaced by E_P. By use of the same approximations as before, the chemical shift of any member of a series of the type P(RR)–X (X = halogen) referred to the compound in which X = F will be given by equation (13).

$$\Delta^{^{31}P\mathrm{RRF}}_{^{31}P\mathrm{RRX}} = (k' + 2k'k^{\mathrm{RX}}E_{\mathrm{R}} + k'k^{\mathrm{PX}}E_{\mathrm{P}})(E_{\mathrm{F}} - E_{\mathrm{X}}) \quad (13)$$

A plot of the left-hand side of equation (13) against $(E_F - E_X)$ is linear as required by this equation and has slope —98·1 p.p.m./Huggins unit.

For the series PX_3, the chemical shift of any compound referred to X = F will be given by equation (14).

$$\Delta^{^{31}P\mathrm{F}_3}_{^{31}P\mathrm{X}_3} = 3(k' + k'k^{\mathrm{PX}}E_{\mathrm{P}})(E_{\mathrm{F}} - E_{\mathrm{X}}) + 3k'k^{\mathrm{XX}}(E_{\mathrm{F}}^2 - E_{\mathrm{X}}^2) \quad (14)$$

Empirical evaluation of $(k' + k'k^{PX}E_P)$ and $k'k^{XX}$ yields the values 429·50 and —69·00 respectively, and enables the chemical shifts from PF_3 of PCl_3, PBr_3, and PI_3 to be calculated to within ±5 p.p.m. (r.m.s.) of their observed values as shown in Table 13.

TABLE 13

Observed and calculated ^{31}P chemical shifts for PX_3 (X = halogen)

Compound	Δ obs./p.p.m. [a]	Δ calc./p.p.m.
PF_3	0	0
PCl_3	−122	−129
PBr_3	−130	−124
PI_3	−81	−84

[a] Ref. 12.

It is noteworthy that the present calculations rationalise the anomalous order of shielding in this series (decreasing in the order F, I, Cl, Br) as being a consequence of an inductive effect which is modified by geminal delocalisation between the substituents.

Previous workers (*e.g.*, Gutowsky and McCall [13]) suggest that an inductive mechanism cannot explain these observations and that the reasons for the anomaly lie in the opposing effects of ionic and double-bond character of the P–X bonds which vary with the nature of X. The present work suggests that only the ionic character of the P–X bonds change with X and that double-bond character (P=X) remain constant.

^{119}Sn *Shielding*. The shielding of the central ^{119}Sn nucleus in a variety of mixed Sn^{IV} halides [15] has been studied. The substituent effects upon this shielding are remarkably additive; chemical shifts from $^{119}SnCl_4$ of 14 such compounds containing various numbers of atoms of Cl, Br, and I can be calculated to within experimental error by adding +121 p.p.m. for each Br atom which replaces Cl and +396 p.p.m. for each I atom which replaces Cl (*e.g.*, the chemical shift of $^{119}SnClBr_2I$ from $^{119}SnCl_4$ is calculated to be 2 × 121 + 396 = 638 p.p.m. and is observed to be 639 p.p.m.).

Similar additivity of substituent effects upon the ^{19}F shielding of fluorine bonded to Sn has been observed [15] and in Part II [1a] it was suggested that for this type of compound the indirect geminal interaction constants between substituents [the constants such as k^{ab} *etc.*, in equation (7)] were negligible. This must also be true for the case of ^{119}Sn shielding in the mixed Sn^{IV} halides, hence the observed additivity. For compounds of the type Sn WXYZ, where W, X, Y, or Z may be Cl, Br, or I the ^{119}Sn chemical shift from $SnCl_4$ should then be given by an expression (15) analogous to (8) in which all interaction constants k^{XX} are zero.

$$\Delta^{^{119}Sn\mathrm{Cl}_4}_{^{119}Sn\mathrm{WXYZ}} = (k' + k'k^{\mathrm{SnX}}E_{\mathrm{Sn}})(4E_{\mathrm{Cl}} - E_{\mathrm{W}} - E_{\mathrm{X}} - E_{\mathrm{Y}} - E_{\mathrm{Z}}) \quad (15)$$

Equation (15) predicts that the observed shielding increments on changing Cl for Br or I should be directly proportional to the difference in electronegativity between Cl and Br or Cl and I. This is not the case, and such an assumption does not lead to agreement of calculated chemical shifts with observed values.

The apparent breakdown of the theory probably arises from the assumption that the directly-bonded interaction constants k^{SnCl}, k^{SnBr}, and k^{SnI} have the same value, which leads to the form of equation (15) expressed above. Differences in these values would indicate that the double-bond nature of the Sn–X bond varies with the nature of X in addition to its ionic character. It may be that there is sufficient overlap between filled 5*p* orbitals on I with vacant 5*d* orbitals on Sn to cause significant π-bonding. These interactions would not be important for Cl or Br because the energy differences between their respective orbitals and the Sn 5*d* are too large for significant overlap to occur.

Conclusion.—A wide variety of n.m.r. shielding data have been rationalised by the inductive theory previously described.[1] The method clearly indicates the occurrence of the high degree of double bond character in B–F bonds, which is well established; it also indicates that such interactions are not significant for P^{III}–halogen bonds but may be important for bonds between Sn^{IV} and I.

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[11] K. J. Packer, *J. Chem. Soc.*, 1963, 960.

[12] N. Muller, P. C. Lauterbur, and J. Goldenson, *J. Amer. Chem. Soc.*, 1956, **78**, 3557.

[13] H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, 1954, **22**, 162.

[14] J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, 1961, **83**, 326.

[15] P. A. W. Dean and D. F. Evans, *J. Chem. Soc.* (*A*), 1968, 1154.