The Structural Dependence of the Inductive Effect. Part V.[1] Effects of Vicinal Substituents on the Shielding of Fluorine-19 Nuclei in Saturated Compounds of Fixed Conformation, and in Fluoro-olefins and *ortho*-substituted Fluorobenzenes

By **L. Phillips** * and **V. Wray**, Organic Chemistry Department, Imperial College of Science and Technology, London SW7 2AY

The model previously developed for the calculation of chemical shifts in conformationally averaged aliphatic systems is extended to rigid systems and some trends are discussed. A successful extension to include π-electronic interactions allows the accurate calculation of shielding differences in a variety of mixed halogenofluoro-olefins and in *ortho*-halogenofluorobenzenes.

We have shown that it is possible to calculate the effects of vicinal substituent changes on ^{19}F nuclear shielding in a variety of freely rotating situations,[1] using a recently described theory.[2-4] The method successfully accounts for the fact that replacing a substituent, which is vicinal to fluorine, by a more electronegative group causes an increased shielding of the ^{19}F nucleus; this is in apparent opposition to the expected inductive effect and is a consequence of interactions involving other groups present in the molecule.

Agreement with experiment is poor when conformational preferences are in evidence, and it will be instructive to examine ^{19}F shielding in rigid systems which are conformationally unambiguous. Several systems lend themselves to such examination, such as fluorinated carbohydrates [5,6] and fluorinated cycloalkanes.[7,8] It will also be relevant to consider fluoro-olefins and fluorobenzenes as special examples of conformationally rigid systems.

The most successful approach so far developed for understanding vicinal interactions has been that of Emsley [7] and of Sutcliffe and his co-workers,[8] who use an electric field theory of vicinal substituent effects. When a halogen substituent X (which is vicinal to fluorine) is changed for another halogen it is assumed that the electric field at the ^{19}F nucleus due to the permanent dipole of the C–X bond does not alter significantly. The van der Waals field due to time-dependent dipoles associated with X does vary however, and is assumed to be the dominant factor in controlling the shielding of the ^{19}F nucleus. The difference caused in the shielding of such a fluorine by this change in its environment is assumed to be proportional to the change in the van der Waals field, $\langle E^2\rangle$, according to equation (1).

$$\Delta^{\mathrm{X1}}_{\mathrm{X2}} = -B\Delta\langle E^2\rangle \qquad (1)$$

$\Delta\langle E^2\rangle$ may be calculated by an established approximate procedure [9] and the constant B is usually estimated empirically, although observation of the pressure dependence of ^{19}F shielding in gaseous samples may lead to an independent assessment of its value.[10] Satisfactory results have been obtained in a variety of situations,[7,8] but it is becoming increasingly apparent that

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[1] L. Phillips and V. Wray, preceding paper.

[2] L. Phillips and V. Wray, *J. Chem. Soc.* (*B*), 1971, 2068.

[3] L. Phillips and V. Wray, *J. Chem. Soc.* (*B*), 1971, 2074.

[4] L. Phillips and V. Wray, *J.C.S. Perkin II*, 1972, 214.

[5] L. Phillips and V. Wray, *J. Chem. Soc.* (*B*), 1971, 1618.

[6] L. D. Hall and J. F. Manville, *Chem. Comm.*, 1968, 37; L. D. Hall ,R. N. Johnson, J. Adamson, and A. B. Foster, *Canad. J. Chem.*, 1971, **49**, 118.

[7] J. W. Emsley, *Mol. Phys.*, 1965, **9**, 381.

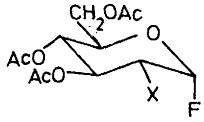
[8] J. Feeney, L. H. Sutcliffe, and S. M. Walker, *Mol. Phys.*, 1966, **11**, 117, 129, 137, 145.

[9] N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Mol. Phys.*, 1964, **8**, 133.

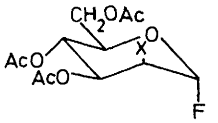
[10] H. J. Bernstein, A. D. Buckingham, and W. T. Raynes, *J. Chem. Phys.*, 1962, **36**, 3481.

the method has serious shortcomings. For example, although there are good grounds for supposing that the value of B will vary with the type of bond in which the fluorine is situated and will depend for example upon its double-bond character,[8,9] it is necessary to change arbitrarily the value of B in closely related systems in order to achieve satisfactory agreement with experiment.[7,11]

The method and some of its shortcomings have been recently discussed,[12] but some additional factors have emerged from our recent interest in fluorinated carbohydrates[5] which indicates that the approach may not even qualitatively explain certain observations. For example, in the series of 2-X-substituted-α-glycosyl fluorides (I) the effect of changing X from fluorine to iodine causes an 11·7 p.p.m. deshielding of the α-fluorine; in 2-X-substituted-α-mannosyl fluorides (II) however the corresponding change is 26·5 p.p.m. (6). In compounds of type (I) the groups X and F are significantly closer together than in compounds of type (II), and the change in the van der Waals field on going from X = F to I will be correspondingly smaller by a factor of *ca.* 1·22. Thus, if it is assumed that the 11·7 p.p.m. variation observed on changing X = F to I in (I) is wholly due to the change in the van der Waals field arising from X, the theory would predict a change of 14·3 p.p.m. on going from 2-deoxy-2-fluoromannosyl fluoride (II; X = F) to the 2-iodo-analogue (II; X = I); in fact the observed change is 26·5 p.p.m. Furthermore, the electric field theory predicts that the α-fluorine in the iodo-derivative of (II; X = I) should be shielded compared with the analogous glucose derivative (I; X = I) by approximately 6 p.p.m. {using values for B and the parameters required for the calculation of $\Delta\langle E^2\rangle$ [equation (1)] obtained from references 6 and 8}. In fact it is *deshielded* by some 28 p.p.m., and the method predicts neither the magnitude nor sign of the observed shielding change.



(I)



(II)

It is clearly necessary to re-evaluate the van der Waals theory of chemical shifts in the light of these observations, and it will also be desirable to re-examine the effect of substituents in fluoro-olefins and *ortho*-substituents in fluorobenzenes upon the shielding of the fluorine nucleus. In such compounds, it is not possible to calculate the substituent chemical shift (s.c.s.) due to the vicinal substituent either by simple π molecular orbital theory[13,14] or by more advanced methods.[15] An '*ortho*' effect apparently exists, which has been explained by Boden, Emsley, Feeney, and Sutcliffe[9] in terms of the variations of van der Waals fields due to the substituents; any alternative treatment must also be applicable to this situation.

It has not so far been pointed out that for a range of substituents a quite precisely linear correlation exists between *ortho*-group s.c.s. and those due to the 2-substituents in 2-deoxy-2-X-mannosyl fluorides (II). A similar correlation also exists between either of these parameters and the corresponding s.c.s. in both *cis*- and *trans*-fluoro-olefins, and the relationships are shown in Figure 1. Clearly, the observed shielding effects may have a common origin which the van der Waals field approach does not satisfactorily explain; for example a *trans*-s.c.s. in a fluoro-olefin is larger than the corresponding *cis*-s.c.s.[16]

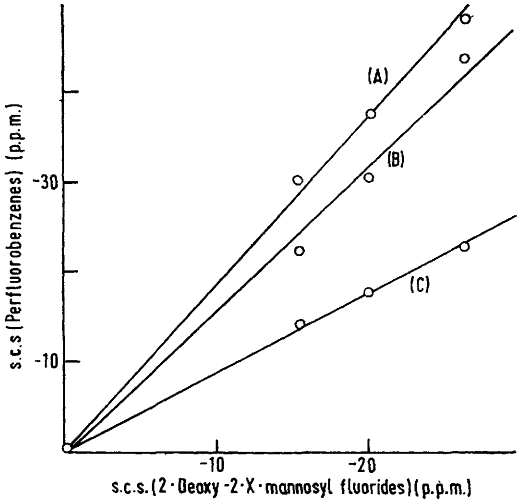


FIGURE 1 Plots of the s.c.s. of 2-deoxy-2-X-mannosyl fluoride against the corresponding s.c.s. of the *ortho*-fluorine in monosubstituted perfluorobenzenes (B) and of *trans* (A) and *cis* (C) CF_2:CFX

It was decided to examine the possibility of extending the inductive theory developed in previous Parts of this series,[1-4] to such situations in an attempt to provide a satisfactory overall explanation of the observed trends.

CALCULATION AND DISCUSSION

Saturated Systems.—In principle, it should be possible to make use of the equations developed previously[1] to calculate the effect of vicinal substituents upon the shielding of ^{19}F and other nuclei in molecules of fixed conformation. In practice, the number of data available is at present too small to allow for the evaluation of the various interaction constants arising from vicinal delocalisation[1] and to provide a realistic test of the method.

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[11] J. Homer and D. Callaghan, *J. Chem. Soc.* (*B*), 1969, 247; J. Homer and D. Callaghan, *J. Chem. Soc.* (*B*), 1970, 1573.

[12] J. W. Emsley and L. Phillips, *Progr. N.M.R. Spectroscopy*, 1971, **7**, 91.

[13] M. Karplus and T. P. Das, *J. Chem. Phys.*, 1961, **34**, 1683.

[14] F. Prosser and L. Goodman, *J. Chem. Phys.*, 1963, **38**, 374.

[15] J. W. Emsley, *J. Chem. Soc.* (*A*), 1968, 2018.

[16] T. Schaefer, F. Hruska, and H. M. Hutton, *Canad. J. Chem.*, 1967, **45**, 3143.

For molecules such as 2-deoxy-2-X-glycosyl fluorides,[6] the corresponding mannosyl derivatives,[6] and some substituted cyclohexyl fluorides [7] for which data are available, the s.c.s. (referred to X = F) will be given by an expression which reduces to (2).

$$\Delta^{F}_{X} = K_1E_F{}^2 - K_2E_FE_X + K_3 \qquad (2)$$

The constants K_1, K_2, and K_3 are complex and their values depend upon the nature of the ring structure, the substituent groups in the vicinity of X and F, and the geometrical relationship between X and F. For X = halogen or oxygen (but not hydrogen) K_1 is equal to K_2 and equation (2) becomes (3).

$$\Delta^{F}_{X} = K_1E_F(E_F - E_X) + K_3 \qquad (3)$$

This linear relationship between Δ^{F}_{X} and $E_F - E_X$ is demonstrated for five such series in Figure 2. Whereas these observations in no way justify the form of the general equation derived previously [1] they do indicate that the observed shielding changes may indeed arise from structurally dependent inductive effects.

A potentially more tractible situation occurs with fluoroethane derivatives in which the conformational equilibrium has been ' frozen out ' and the spectra of the individual conformers are available. There is only a limited amount of data for such situations [17] but expressions may be derived [1] which should be capable of rationalising the observed trends. For example, in the fixed conformation of the molecule $CF_2X{\cdot}Cabc$, (III), the difference in shielding between the two fluorines should be calculable since the only terms in the shielding expressions for the two fluorines which differ are the angularly dependent primary and secondary vicinal delocalisation interaction.[1] The chemical shift between F1 and F2 will be given by equation (4) following the terminology defined previously.[1]

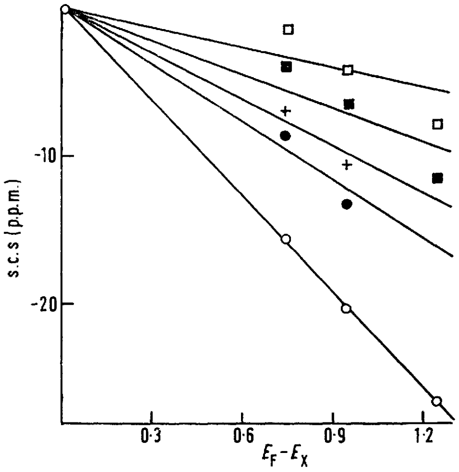
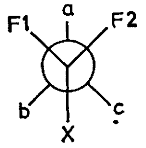


FIGURE 2 Plots of the s.c.s. values of 2-deoxy-2-X-mannosyl fluorides (○), 2-X-α- (■) and β-2-deoxyglycosyl fluorides (■), and axial (●) and equatorial (+) monosubstituted perfluorocyclohexane (fluorine vicinal to substituent) against $E_F - E_X$



(III)

$$\Delta^{F1}_{F2} = E_FE_ck^{Fc}_{v1}(\cos 180° - \cos 60°) + E_FE_bk^{Fb}_{v1}(\cos 60° - \cos 180°) + E_FE_bk^{Fb}_{v2}(\cos 180° - \cos 60°) + E_FE_ck^{Fc}_{v2}(\cos 60° - \cos 180°) \qquad (4)$$

If b and c are halogens, then $k^{Fc}_{v1} = k^{Fb}_{v1}$ and $k^{Fc}_{v2} = k^{Fb}_{v2}$; equation (4) simplifies to (5).

$$\Delta^{F1}_{F2} = 3/2(k_{v2} - k_{v1})E_F(E_c - E_b) \qquad (5)$$

There are insufficient data to verify this relationship, but examination of that which is available (Table A2 of ref. 12) does suggest that when c and b have electronegatives of comparable magnitude then Δ is small (0—3 p.p.m. for c = Cl, b = Br) and when c and b have widely differing electronegativities Δ is large (4 p.p.m. for c = F, b = Cl; 10 p.p.m. for c = F, b = H).

For these molecules and similar fluorohalogenoethanes it is not possible to derive values of k_{v1} and k_{v2} which are of general use and enable successful chemical shift calculations to be performed. This may of course occur because the theory is incorrect and the observed shielding changes arise from causes other than the inductive effect. Alternatively however, small deviations from the assumed perfect geometry will cause marked deviations of the theoretically calculated chemical shifts from those which are observed, because of the cosine dependence of the vicinal delocalisation terms. If this is so, and the appropriate constants were to be calculable from other data on more rigidly defined systems (*e.g.* fluorosteroids) then the calculational procedure would provide a useful method for studying such distortions for molecules in solution or in the liquid phase.

Fluoro-olefins and Fluorobenzenes.—It has been pointed out above that a parallel exists between vicinal s.c.s. values in saturated systems and in olefins and fluorobenzenes; the case of the olefins is particularly suitable for study, since data are available for a significant number of mixed halogenofluoro-olefins.[12,18] It is probable that π-electronic interactions play a significant part in determining shielding in such situations, but from a consideration of the linear correlations

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[17] R. R. Dean and J. Lee, *Trans. Faraday Soc.*, 1969, **65**, 1; J. D. Roberts, F. J. Weigert, M. B. Winstead, and J. I. Garrels, *J. Amer. Chem. Soc.*, 1970, **92**, 7359.

[18] J. Renben and A. Demiel, *J. Chem. Phys.*, 1966, **44**, 2216; C. G. Moreland and W. S. Brey, *J. Chem. Phys.*, 1966, **45**, 805.

depicted in Figure 1 it must be concluded that such π effects parallel the σ-electronic interactions. It may therefore be possible to treat both σ- and π-electronic effects upon ^{19}F shielding by the method described earlier.[1]

In Part IV of this series [1] equation (1) was derived for the shielding of fluorine in the molecule CFab•Cefg. For a fluoro-olefin CFa:Cbd the shielding may be deduced in a similar way, if it is assumed that groups a, b, and d which interact by conjugation with the π system perturb the electronegativity of F and C in an analogous way to their perturbations which occur *via* the σ systems. If this is the case, then all terms in the equation will have the same form as before (the constants being modified in value to accommodate the π term) except for the constants describing vicinal delocalisation. The degree of delocalisation between two vicinally situated groups arising from orbitals of σ symmetry varies with the cosine of the dihedral angle between them,[19] hence the bond order between two *cis*-groups is of opposite sign to that between two *trans*-groups; for an analogous interaction *via* the orbitals of π symmetry however, there will be no such variation and the corresponding vicinal perturbation constants for both a *cis* and *trans* relationship will have the same sign.

On this basis we may write the expression for the shielding in the fluoro-olefin CFa:Cbd [equation (6)] (d is *cis* to F).

$$\begin{aligned}\sigma_\mathrm{F} = \sigma_0 + k'[&E_\mathrm{C}(1 + k_1^{\mathrm{Ca}}E_\mathrm{a} + k_2^{\mathrm{CC}}E_\mathrm{C}) + E_\mathrm{F}(-1 + \\ &k_3^{\mathrm{Fa}}E_\mathrm{a} + k_4^{\mathrm{FC}}E_\mathrm{C}) + E_\mathrm{C}k_5^{\mathrm{Ca}}E_\mathrm{a} + E_\mathrm{C}\{(k_{\mathrm{g1}}^{\mathrm{Cb}} + \\ &k_{\mathrm{D2}}^{\mathrm{Cb}} - k_{\mathrm{g2'}}^{\mathrm{Cb}})E_\mathrm{b} + (k_{\mathrm{g1}}^{\mathrm{Cd}} + k_{\mathrm{D2}}^{\mathrm{Cd}} - k_{\mathrm{g2'}}^{\mathrm{Cd}})E_\mathrm{d}\} + \\ &E_\mathrm{F}\{(k_{\mathrm{v2}\sigma}^{\mathrm{Fb}} - k_{\mathrm{v1}\sigma}^{\mathrm{Fb}})\cos\theta_{\mathrm{Fb}}E_\mathrm{b} + (k_{\mathrm{v2}\sigma}^{\mathrm{Fd}} - \\ &k_{\mathrm{v1}\sigma}^{\mathrm{Fd}})\cos\theta_{\mathrm{Fd}}E_\mathrm{d}\} + E_\mathrm{a}\{(k_{\mathrm{v2}\sigma}^{\mathrm{ab}} - k_{\mathrm{v2'}\sigma}^{\mathrm{ab}})\cos\theta_{\mathrm{ab}}E_\mathrm{b} + \\ &(k_{\mathrm{v2}\sigma}^{\mathrm{ad}} - k_{\mathrm{v2'}\sigma}^{\mathrm{ad}})\cos\theta_{\mathrm{ad}}E_\mathrm{d}\} + \\ &E_\mathrm{F}\{(k_{\mathrm{v2}\pi}^{\mathrm{Fb}} - k_{\mathrm{v1}\pi}^{\mathrm{Fb}})E_\mathrm{b} + (k_{\mathrm{v2}\pi}^{\mathrm{Fd}} - k_{\mathrm{v1}\pi}^{\mathrm{Fd}})E_\mathrm{d}\} + \\ &E_\mathrm{a}\{(k_{\mathrm{v2}\pi}^{\mathrm{ab}} - k_{\mathrm{v2'}\pi}^{\mathrm{Fb}})E_\mathrm{b} + (k_{\mathrm{v2}\pi}^{\mathrm{ad}} - k_{\mathrm{v2'}\pi}^{\mathrm{Fd}})E_\mathrm{d}\} + \\ &E_\mathrm{b}k_{\mathrm{g2'}}^{\mathrm{bd}}E_\mathrm{d}]\end{aligned} \tag{6}$$

Let $(k_{\mathrm{g1}}^{\mathrm{Cb}} + k_{\mathrm{D2}}^{\mathrm{Cb}} - k_{\mathrm{g2'}}^{\mathrm{Cb}}) = k_6^{\mathrm{Cb}}$; $(k_{\mathrm{g1}}^{\mathrm{Cd}} + k_{\mathrm{D2}}^{\mathrm{Cd}} - k_{\mathrm{g2'}}^{\mathrm{Cd}}) = k_7^{\mathrm{Cd}}$; $(k_{\mathrm{v2}}^{\mathrm{Fb}} - k_{\mathrm{v1}}^{\mathrm{Fb}}) = k_8^{\mathrm{Fb}}$; $(k_{\mathrm{v2}}^{\mathrm{Fd}} - k_{\mathrm{v1}}^{\mathrm{Fd}}) = k_9^{\mathrm{Fd}}$; $(k_{\mathrm{v2}}^{\mathrm{ab}} - k_{\mathrm{v2'}}^{\mathrm{ab}}) = k_{10}^{\mathrm{ab}}$; $(k_{\mathrm{v2}}^{\mathrm{ad}} - k_{\mathrm{v2'}}^{\mathrm{ad}}) = k_{11}^{\mathrm{ad}}$; $\theta_{\mathrm{Fb}} = 180°$; $\theta_{\mathrm{Fd}} = 0°$, $\theta_{\mathrm{ab}} = 0°$ and $\theta_{\mathrm{ad}} = 180°$.

If a, b, and d are halogens then $k_8^{\mathrm{Fb}} = k_9^{\mathrm{Fd}} = k_{\mathrm{v1}}^{\mathrm{XX}}$, $k_{10}^{\mathrm{ab}} = k_{11}^{\mathrm{ad}} = k_{\mathrm{v2}}^{\mathrm{XX}}$, and $k_6^{\mathrm{Cb}} = k_7^{\mathrm{Cd}}$. Choosing tetrafluoroethylene as reference, the chemical shift of the ^{19}F nucleus in the molecule CFa:Cbd may be written as (7) (d is *cis* to F).

$$\begin{aligned}\Delta_{\mathrm{CaF:Cbd}}^{\mathrm{C_2F_4}} = k'[&(k_1^{\mathrm{CX}}E_\mathrm{C} + k_3^{\mathrm{XX}}E_\mathrm{F} + k_5^{\mathrm{CX}}E_\mathrm{C})E_\mathrm{F} + \\ &2k_6^{\mathrm{CX}}E_\mathrm{C}E_\mathrm{F} + 2(k_{\mathrm{v1}\pi}^{\mathrm{XX}} - k_{\mathrm{v2}\pi}^{\mathrm{XX}})E_\mathrm{F}^2 - (k_1^{\mathrm{CX}}E_\mathrm{C} + \\ &k_3^{\mathrm{XX}}E_\mathrm{F} + k_5^{\mathrm{CX}}E_\mathrm{C})E_\mathrm{a} - (E_\mathrm{b} + E_\mathrm{d})(k_6^{\mathrm{CX}}E_\mathrm{C} + \\ &k_{\mathrm{v1}\pi}^{\mathrm{XX}}E_\mathrm{F} + k_{\mathrm{v2}\pi}^{\mathrm{XX}}E_\mathrm{a}) + (E_\mathrm{d} - E_\mathrm{b})(k_{\mathrm{v2}\sigma}^{\mathrm{XX}}E_\mathrm{a} + \\ &k_{\mathrm{v1}\sigma}^{\mathrm{XX}}E_\mathrm{F}) + k_{12}(E_\mathrm{F}^2 - E_\mathrm{b}E_\mathrm{d})]\end{aligned} \tag{7}$$

More simply, this equation takes the form (8).

$$\begin{aligned}\Delta_{\mathrm{CaF:Cbd}}^{\mathrm{C_2F_4}} = K_1 - E_\mathrm{a}[&K_2 - K_3(E_\mathrm{b} + E_\mathrm{d}) + K_4(E_\mathrm{d} - \\ &E_\mathrm{b})] - K_5(E_\mathrm{b} + E_\mathrm{d}) + K_6(E_\mathrm{d} - E_\mathrm{b}) + \\ &k_{12}(E_\mathrm{F}^2 - E_\mathrm{b}E_\mathrm{d})\end{aligned} \tag{8}$$

where $K_1 = k'\{(k_1^{\mathrm{CX}}E_\mathrm{C} + k_3^{\mathrm{XX}}E_\mathrm{F} + k_5^{\mathrm{CX}}E_\mathrm{C})E_\mathrm{F} + 2k_6^{\mathrm{CX}}E_\mathrm{C}E_\mathrm{F} + 2(k_{\mathrm{v1}\pi}^{\mathrm{XX}} - k_{\mathrm{v2}\pi}^{\mathrm{XX}})\}E_\mathrm{F}^2$; $K_2 = k'(k_1^{\mathrm{CX}}E_\mathrm{C} + k_3^{\mathrm{XX}}E_\mathrm{F} + k_5^{\mathrm{CX}}E_\mathrm{C})$; $K_3 = k'k_{\mathrm{v2}\pi}^{\mathrm{XX}}$; $K_4 = k'k_{\mathrm{v2}\sigma}^{\mathrm{XX}}$; $K_5 = k'(k_6^{\mathrm{CX}}E_\mathrm{C} + k_{\mathrm{v1}\pi}^{\mathrm{XX}}E_\mathrm{F})$; $K_6 = k'k_{\mathrm{v1}\sigma}^{\mathrm{XX}}E_\mathrm{F}$; and $k_{12} = k'k_{\mathrm{g2'}}^{\mathrm{XX}}$.

For the compounds in which the group a is fluorine, *i.e.* CF1F2:Cbd, equation (8) may be used to predict the difference in chemical shift between F1 and F2 [equation (9)] (d is *cis* to F1).

$$\Delta_{\mathrm{F2}}^{\mathrm{F1}} = 2K_6(E_\mathrm{d} - E_\mathrm{b}) \tag{9}$$

For compounds of this type, a plot of $\Delta_{\mathrm{F2}}^{\mathrm{F1}}$ against $(E_\mathrm{d} - E_\mathrm{b})$ should therefore be linear and of slope $2K_6$.

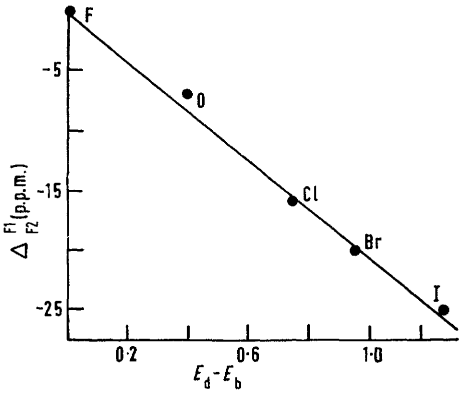

FIGURE 3 Plot of $\Delta_{\mathrm{F2}}^{\mathrm{F1}}$ against $(E_\mathrm{d} - E_\mathrm{b})$ for CF_2:CFX compounds

This is shown in Figure 3, and yields a value of $K_6 = -10{\cdot}12$ p.p.m./Huggins unit of electronegativity.

The sum of the chemical shifts (from C_2F_4) of these two fluorines is given by (10).

$$\begin{aligned}\Delta_{\mathrm{F1}}^{\mathrm{C_2F_4}} + \Delta_{\mathrm{F2}}^{\mathrm{C_2F_4}} = (2K_1 - 2K_2E_\mathrm{F}) + (2K_3E_\mathrm{F} - \\ 2K_5)(E_\mathrm{b} + E_\mathrm{d}) - 2K_4E_\mathrm{F}(E_\mathrm{b} - E_\mathrm{d}) + \\ 2k_{12}(E_\mathrm{F}^2 - E_\mathrm{b}E_\mathrm{d})\end{aligned} \tag{10}$$

K_4 and k_{12} both represent secondary interactions occurring in the σ-electronic system, and may be small. If this is so, a plot of $(\Delta_{\mathrm{F1}}^{\mathrm{C_2F_4}} + \Delta_{\mathrm{F2}}^{\mathrm{C_2F_4}})$ against $(E_\mathrm{b} + E_\mathrm{d})$ should be linear with slope $2(K_3E_\mathrm{F} - K_5)$ and intercept $2(K_1 - K_2E_\mathrm{F})$. This is shown in Figure 4, thereby verifying that the terms involving K_4 and k_{12} are negligible and yielding values of the slope of 60·34 p.p.m./Huggins unit and intercept —467·79 p.p.m.

For compounds in which b = d, equation (8) becomes (11).

$$\Delta_{\mathrm{CaF:Cbd}}^{\mathrm{C_2F_4}} = K_1 - E_\mathrm{a}(K_2 - 2K_3E_\mathrm{b}) - 2K_5E_\mathrm{b} \tag{11}$$

A plot of $\Delta_{\mathrm{CaF:Cbd}}^{\mathrm{C_2F_4}}$ against E_a should therefore be linear and have slope $-(K_2 - 2K_3E_\mathrm{b})$ and intercept $(K_1 - 2K_5E_\mathrm{b})$. Figure 5 shows plots for cases where b = d =

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[19] J. A. Pople and D. P. Santry, *Mol. Phys.*, 1963, **7**, 269.

F, Cl, and Br; these slopes, S, are related by the expression (12).

$$S = -K_2 + 2K_3E_b \qquad (12)$$

A plot of S against E_b (Figure 6) yields values of $K_3 = -16{\cdot}39$ p.p.m./(Huggins unit)^2 and $K_2 = -116{\cdot}56$ p.p.m./Huggins unit.

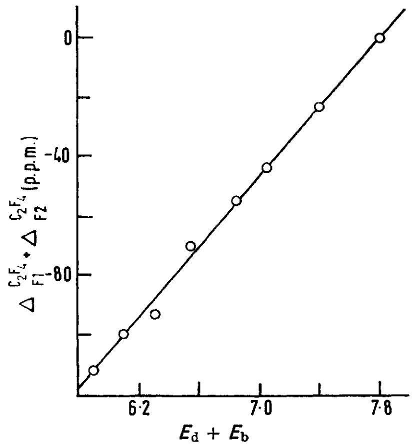


FIGURE 4 Plots of $\Delta^{C_2F_4}_{F1} + \Delta^{C_2F_4}_{F2}$ against $(E_d + E_b)$

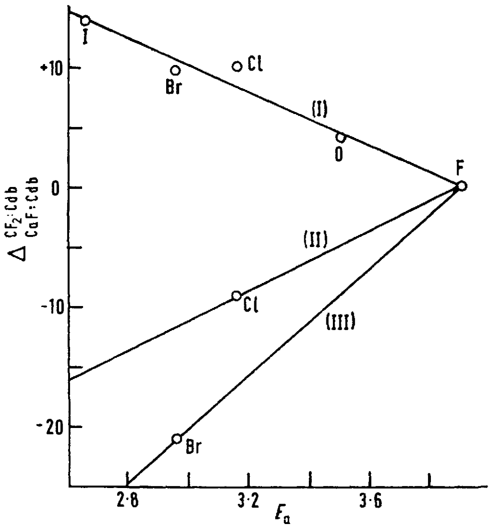


FIGURE 5 Plots of $\Delta^{\mathrm{CF}:\mathrm{Cbd}}_{\mathrm{Ca}F:\mathrm{Cdb}}$ against E_a for (I) b = d = F, (II) b = d = Cl, and (III) b = d = Br

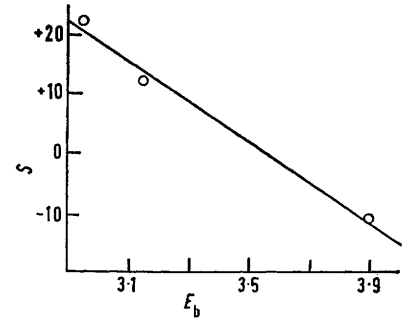


FIGURE 6 Plot of the slopes from Figure 5 against E_b

We now have values, obtained graphically, for $K_6 = -10{\cdot}12$, $K_2 = -116{\cdot}56$, $K_3 = -16{\cdot}39$, K_1 (obtained from the intercept of Figure 4) $= -688{\cdot}47$, and K_5 (obtained from the slope of Figure 4) $= -94{\cdot}09$.

Equation (8) may thus be written down explicitly as (13).

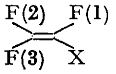
$$\Delta^{C_2F_4}_{CFa:Cbd} = -688{\cdot}47 - E_a\{-116{\cdot}56 + 16{\cdot}39(E_b + E_d)\} + 94{\cdot}09\,(E_b + E_d) + 10{\cdot}12\,(E_b - E_d) \qquad (13)$$

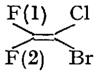
Table 1 shows a comparison between some 23 chemical shifts calculated using equation (13) and their observed values, and the agreement is remarkably good (r.m.s. ±1·3 p.p.m.).

TABLE 1

Comparison of observed and calculated ^{19}F chemical shifts (from C_2F_4) of halogenofluoro-olefins

Structure *		Observed shift (p.p.m.)	Calculated shift (p.p.m.)
CF_2CF_2		0·0	+1·4
(A) X = Cl	(1)	+10·0	+9·9
	(2)	−30·0	−28·8
	(3)	−14·0	−13·6
(A) X = Br	(1)	+9·7	+12·2
	(2)	−37·5	−36·8
	(3)	−17·4	−17·6
(A) X = I	(1)	+13·8	+15·5
	(2)	−47·7	−48·9
	(3)	−22·5	−23·6
$CF_2{:}CCl_2$		−46·5	−43·8
$CF_2{:}CBr_2$		−55·8	−55·9
(B)	(1)	−50·2	−51·8
	(2)	−49·2	−47·8
(A) X = OCR_3	(1)	+4·2	+6·0
	(2)	−15·3	−14·7
	(3)	−8·2	−6·6
CFBr:CFBr	(*cis*)	−39·7	−40·9
	(*trans*)	−22·0	−21·7
CFCl:CFCl	(*cis*)	−29·9	−29·6
	(*trans*)	−15·40	−14·4
$CFBr{:}CBr_2$		−76·9	−74·8
$CFCl{:}CCl_2$		−55·7	−53·8
		(r.m.s. ±1·3)	

* (A) =


; (B) =


One important result is that the chemical shifts of *cis*- and *trans*-1,2-dibromodifluoroethylene and *cis*- and *trans*-1,2-dichlorodifluoroethylene are correctly predicted. These values were not used in any way to establish the linear correlations from which the constants were derived, and the present calculational procedure is the only one as yet available which correctly calculates the shielding difference between *cis*- and *trans*-isomers; the difference arises because of the cosine dependence of the interaction constant describing vicinal σ delocalisation.

Fluorinated Cyclohexenes and ortho-*Substituted Fluorobenzenes*.—Data are available for the chemical shifts of fluorine in compounds of the type shown in (IV) and (V).

For any such system, of the type CFY:CXY (Y,Y *cis*), expressions for the chemical shift of the fluorine may be obtained from equation (8), which now takes the form (14).

$$\Delta^{\mathrm{C_2F_4}}_{\mathrm{CFY:CXY}} = K_{\mathrm{Y}} + (K_6 - K_5 + K_3E_{\mathrm{Y}})E_{\mathrm{X}} \quad (14)$$

The constant K_{Y} is composite and depends upon the nature of the group Y; it has the same value for all the halogens, but will be different when Y = C or H. For compounds (IV) and (V) the value of the term K_{Y} is unknown and it is not possible to calculate the shifts from C_2F_4; however it should be possible to calculate s.c.s. values, *i.e.* chemical shifts referred to the molecule CFY:CFY, since equation (14) then takes the form (15).

$$\Delta^{\mathrm{CFY:CFY}}_{\mathrm{CFY:CXY}} = (K_6 - K_5 - K_3E_{\mathrm{Y}})(E_{\mathrm{X}} - E_{\mathrm{F}}) \quad (15)$$

The constants K_6, K_5, and K_3 are known. In order to calculate the s.c.s. value for series of type (V) it is necessary to substitute for E_{Y} the Huggins electronegativity of sp^3 hybridised carbon, 2·60. For *ortho*-substituted fluorobenzenes (V) E_{Y} is the Huggins electronegativity of sp^2 hybridised carbon which is not immediately available; however, Klopman[20] quotes values for orbital electronegativities for a variety of atoms including both sp^3 and sp^2 carbon, and from the linear correlation of these values with Huggins electronegativities it is possible to deduce a value of 3·0 ± 0·1 for sp^2 carbon.

Table 2 lists s.c.s. values calculated using equation (15) for some compounds of type (IV) and (V) and for the situation Y = F, *i.e.* compounds of the type CF_2:CFX. Equation (15) therefore correctly predicts that *cis* vicinal ^{19}F s.c.s. values in such situations depend upon the nature of the pair of substituents Y which are *cis* to each other on the opposite side of the double bond to F and X. It allows for the calculation of ^{19}F s.c.s. values due to halogens in *ortho*-substituted fluorobenzenes to a quite surprising degree of accuracy, and offers an attractive alternative to the van der Waals field approach which would predict that such *cis*-s.c.s. values were *independent* of the nature of the two substituents Y.

TABLE 2

Comparison of observed and calculated s.c.s. values in three CFY:CXY systems (Y,Y *cis*)

Compound	X	Observed shift (p.p.m.)	Calculated shift (p.p.m.)
CF_2:CFX	F	0·0	0·0
	Cl	−14·0	−15·0
	Br	−17·4	−19·1
	I	−22·5	−25·1
$\overline{\mathrm{CF_2\cdot[CF_2]_3\cdot CF{:}C}}\mathrm{X}$	F	0·0	0·0
(IV)	Cl	−30·2	−31·0
	Br	−39·4	−39·3
	I	−53·9	−51·7
o-X-Fluorobenzene	F	0·0	0·0
(V)	Cl	−22·1	−26·1
	Br	−30·2	−33·1
	I	−43·6	−43·5

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