The Structural Dependence of the Inductive Effect. Part IV.[1] The Calculation of Vicinal Substituent Effects upon ^{19}F Shielding in Freely-rotating Fluoroethanes and Higher Fluoroalkanes

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The calculational procedure applied previously to geminal and directly bonded substituent effects upon n.m.r. shielding is extended to account for the influence of vicinal substituents. The agreement with experiment is good (±3·4 p.p.m.) for situations where there is rotational averaging between conformations of equal energy, but in other cases conformational preference causes significant deviations.

ATTEMPTS to rationalise the shielding of fluorine nuclei in aliphatic fluorocarbons have not generally been successful. Substituted methanes have been discussed recently by us, but the effects of vicinal substituents in fluoroethanes and higher alkanes are not understood. Feeney, Sutcliffe, and Walker [2] have suggested that the variations observed in the chemical shift of the fluorine nuclei in compounds of the type $CF_3 \cdot CXYZ$ can be accounted for by variations in the magnitude of the van der Waals fields due to the groups X, Y, and Z; the approach is reasonably successful for situations where X, Y, and Z are halogens, but breaks down completely when one or more is hydrogen. A similar situation arises if the approach of Schaefer and his co-workers [3] is adopted, and attempts are made to correlate the shielding with the empirical parameter $Q = \alpha_i I_i / r_i^3$ (α_i = polarisability of a substituent i, I_i is the first ionisation potential, and r_i is the average distance of the substituent i from the fluorine nucleus). Emsley and Phillips [4] discussed the shielding of fluorine nuclei in a variety of halogenated ethanes in which separate rotational isomers have been ' frozen out,' [5,6] and have shown that the suggested origin of the substituent effects in changes in van der Waals fields is almost certainly incorrect.

It has been possible however to rationalise the effects of CH_3 and CF_3 groups upon ^{19}F shielding in molecules of the type CF_3R, CF_2R_2, and CFR_3 (R = CH_3 or CF_3) in terms of the new theory of inductive effects; [7] since almost all ^{19}F chemical shifts of compounds of the type $CF_3 \cdot CXYZ$ lie within the limits of the shifts of $CF_3 \cdot CF_3$ (+63 p.p.m. from $CFCl_3$) and CF_3CH_3 (+91 p.p.m. from $CFCl_3$) it seems possible that the theory can be extended to cover the effects of substituents which are vicinal to the observed nucleus.

The data have been taken from references 4 and 8. Chemical shifts are taken from ambient-temperature spectra except where indicated, and all shifts are referred to $CFCl_3$.

RESULTS AND DISCUSSION

Consider a molecule $C^1(abF) \cdot C^2(efg)$, in which the substituents a, b, e, f, and g are as yet unspecified and

the shielding of the F nucleus is to be observed. We adopt the approach described previously, and suggest that the shielding of the fluorine nucleus is proportional to the difference in the effective electronegativities of F and the C to which it is directly bonded. The effective electronegativities are Huggins values which are modified by a variety of mutual interactions between all groups in the molecule. In addition to interactions discussed previously [7] we must consider those due to the groups e, f, and g. The new perturbations may be symbolised as follows: (i) ' Primary vicinal interactions.' These express the direct perturbation upon the electronegativity of a substituent by vicinal delocalisation [9] between it and the perturbing group. The degree of vicinal delocalisation is a cosine function of the dihedral angle between the two species [9] [this perturbation between two groups i and j may be written as equation (1)].

$$P_{v1}^{ij} = k_{v1}^{ij} E_i E_j \cos \theta_{ij} \qquad (1)$$

(ii) ' Secondary vicinal interactions.' These are analogous to the secondary geminal interactions discussed earlier [7] and express the perturbation to the electronegativity of a group caused by vicinal delocalisation between two other groups. A cosine variation is again to be expected [the perturbation may be written as equation (2)]. This is felt by groups other than i and j,

$$P_{v2}^{ij} = k_{v2}^{ij} E_i E_j \cos \theta_{ij} \qquad (2)$$

and it is necessary to differentiate between a perturbation upon C(1) (P_{v2}^{ij}) and upon the substituents bonded to it (a, b, and F, $P_{v2'}^{ij}$).

It is possible to envisage ' tertiary ' interactions such as those between C(2) and its substituents e, f, and g which result in a perturbation to the electronegativity of the substituents upon C(1) (a, b, and F). It is felt that these will, however, be negligible and they will not be considered in the treatment that follows.

With the terminology outlined above and previously,[7] it is now possible to extend the treatment to the present situation; following equation (17) of ref. 7 the shielding of fluorine in the molecule $C^1(abF) \cdot C^2(efg)$ can be written

[1] Part III, L. Phillips and V. Wray, preceding paper.
[2] J. Feeney, L. H. Sutcliffe, and S. M. Walker, *Mol. Phys.*, 1966, **11**, 117.
[3] F. Hruska, H. M. Hutton, and T. Schaefer, *Canad. J. Chem.*, 1965, **43**, 2392.
[4] J. W. Emsley and L. Phillips, ' Progress in Nuclear Magnetic Resonance Spectroscopy,' ed. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, vol. 7, Pergamon Press, Oxford, 1971, p. 95.

[5] R. A. Newmark and C. H. Sederholm, *J. Chem. Phys.*, 1963, **39**, 3131.
[6] R. A. Newmark and C. H. Sederholm, *J. Chem. Phys.*, 1965, **43**, 602.
[7] L. Phillips and V. Wray, *J. Chem. Soc. (B)*, 1971, 2068.
[8] F. J. Weigert, M. B. Winstead, J. I. Garrels, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 7359.
[9] J. A. Pople and D. P. Santry, *Mol. Phys.*, 1963, **7**, 269.

explicitly. If there is free rotation about the C(1)–C(2) bond and all conformations are equally probable then the terms involving cosines of dihedral angles vanish and the equation becomes (3).

$$\sigma = \sigma_0 + k'\{E_C(1 + k_1^{Ca}E_a + k_2^{Cb}E_b + k_3^{CC}E_C) + \\ E_F(-1 + k_5^{aF}E_a + k_6^{bF}E_b + k_7^{CF}E_C) + E_C(k_8^{Cb}E_b + \\ k_9^{Ca}E_a) + E_b k_{10}^{ba}E_a + E_c[k_{11}^{eC}E_e + k_{12}^{fC}E_f + k_{13}^{gC}E_g]\} \quad (3)$$

The constants k_1–k_{10} have the same significance as before but k_{11}, k_{12}, and k_{13} are new and describe the net

an expression (4) can be written for the chemical shift from $CFCl_3$.

$$\Delta_{Cab\,F\cdot Cefg}^{CFCl_3} = 154\cdot12\ (9\cdot45 - E_a - E_b - E_C) - \\ 771\cdot08 - k'k^{ab}E_aE_b - k'k^{bC}E_bE_C - k'k^{aC}E_aE_C - \\ K(E_e + E_f + E_g) \quad (4)$$

The first situation which lends itself to examination is when $a = b = F$, and $e = f = g = Z$. In this case all conformations are equally populated and equal distortion of bond angles will ensure that in any conformation the

TABLE 1

Comparison of observed and calculated ^{19}F chemical shifts in CF_3-compounds where there is rotational averaging between conformations of equal energy

(a) Compound	Observed [a] shift (p.p.m.)		Calculated [a] shift (p.p.m.)		Compound	Observed [a] shift (p.p.m.)		Calculated [a] shift (p.p.m.)	
$CF_3\cdot CF_3$ [b]	91		92·2		$CF_3\cdot CH_3$ [b]	63		64	
$CF_3\cdot CCl_2I$	81		77·0		$CF_3\cdot CHBrCl$	76		73·4	
$CF_3\cdot CCl_3$ [b]	82		79·8		$CF_3\cdot CHICl$	79		71·7	
$CF_3\cdot CFClBr$	84	77	82·8	80·8	$CF_3\cdot CHIF$ [b]	85	175	75·9	175
$CF_3\cdot CCl_2F$	85	76·8	83·9	80·4	$CF_3\cdot CF_2H$	88	140	82·8	139·2
$CF_3\cdot CF_2I$	87	67·1	85·3	70·4	$CF_3\cdot CH_2Br$	69		68·1	
$CF_3\cdot CF_2OF$	82	98	90·0	98·7	$CF_3\cdot CH_2Cl$	72		69·2	
$CF_3\cdot CF_2NF_2$	82	120	87·5	107·6	$CF_3\cdot CFHSO_2F$	75		74·7	
$CF_3\cdot CH_2F$	79	241	73·4	241·2	$CF_3\cdot CF_2NCO$	89		87·5	
$CF_3\cdot CF(OF)_2$	77·4	111·9	87·8	109·9					
$CF_3\cdot CF_2\cdot CF_3$ [b]	c	131·5	c	131·5	$CF_3\cdot CHF\cdot CF_3$	76·6	d	75·7	d
$CF_3\cdot CFBr\cdot CF_3$	78	d	79·8	d	$CF_3\cdot CFOFCF_3$	75·6	d	82·8	d
$CF_3\cdot CFI\cdot CF_3$	78	d	78·1	d	$CF_3\cdot CH_2\cdot CF_3$	64		66·2	
$CF_3\cdot CH_2\cdot CH_3$	70		66·2		$CF_3\cdot CHCl\cdot CH_2\cdot Si(CH_3)_3$	77·6		73·4	
$CH_3\cdot CF_2\cdot CH_3$	85		75		$(CF_3)_2CHP(O)(OC_2H_5)_2$	62		65·4	
$(CF_3)_2CBrSBr$	69		71·7		$CF_3\cdot CH_2\cdot CHCl\cdot SiCl_3$	65·1		66·2	
$(CF_3)_2CClSCl$	76		72·8		$CF_3\cdot CH_2\cdot CCl_2\cdot SiCl_3$	59·4		66·2	
$(CF_3)_2CBrOPF_2$	77·8		77·6		$CF_3\cdot CHCl\cdot CH_2\cdot SiCl_3$	77·3		71·5	
$(CF_3)_2ClOPF_2$	74·5		75·9		$CF_3\cdot CHCl\cdot CCl_2\cdot SiCl_3$	65·8		71·5	
$CF_3\cdot CFNF_2\cdot CF_3$	85	113	87·5	107·6	$CF_3\cdot CCl_2\cdot CCl_2\cdot SiCl_3$	69·3		76·7	
$CF_3\cdot CH(OH)\cdot C(CH_3)_2$	71·7		73·4		$CF_3\cdot CClBr\cdot CBrCl_2$ [e]	75·6		75·6	
$CF_3\cdot CH_2\cdot CHClSi(CH_3)_3$	65·5		66·2						
					$(CF_3)_3CF$	190		182·3	

(No. of shifts = 53, r.m.s. = 4·6)

(b) Compound type	No. of compounds	Observed shift range (p.p.m.)	Average observed shift (p.p.m.)	Calculated shift shift (p.p.m.)
$CF_3\cdot CF_2\cdot CR_2$	97	81·1—85	82·8	85
$CF_3\cdot CH_2\cdot CR_3$	5	64—70	65·7	66·2
$CF_3\cdot CF_2\cdot SeR$	12	82—85·4	83·9	84·4
$(CF_3)_2CFSR$	6	74—80	75·4	76·9
$CF_3\cdot C(CR_3)(OR)(NR)$	8	72·3—85	78·3	78·1
$(CF_3)_2CHSR$	8	66—73	70·0	67·5
$CF_3\cdot CF(CR_3)(NR_2)$	5	72·8—79·3	76·8	80·3
$(CF_3)_2C(SR)_2$ or $(CF_3)_2\overline{C\text{-}S\text{-}R\text{-}S}$	4	72—77	74·5	69·0
$(CF_3)_2C(NR_2)_2$ or $(CF_3)_2\overline{CN\text{=}R\text{=}N}$	5	69—84	77·2	75·7
$(CF_3)_2CHNR_2$	2	65—78	72·5	71·0
$CF_3\cdot CFI\cdot CF_2\cdot CR_3$	2	75	75	78·1
$CF_3\cdot CH(OR)\cdot CR_3$	8	72·3—82·4	79·4	73·4

(No. of shifts = 162, r.m.s. = 3·0).

[a] Chemical shifts are to be read for each group in a compound from left to right. Positive values are to high field of $CFCl_3$. [b] Compound used in the calculation of an interaction constant. [c] Chemical shift in Table 2. [d] Chemical shift in Table 3. [e] Average shift of all recorded conformer shifts (not at ambient temperature). [f] Shift not calculated as k^{HX} not known.

effect upon the electronegativities of F and C(1) of interactions between the groups e, f, and g and C(1) and C(2). The difference in shielding between the fluorine in this molecule and in a halogenated fluoromethane reference may now be deduced, and by making the assumptions about equality of certain constants described earlier [1,7]

dihedral angles are 60 or 180°. Substitution of the known values of certain parameters [7] into equation (4) ($E_a = E_b = E_F = 3\cdot90$; $E_C = 2\cdot60$; $k'k^{ab} = 25\cdot91$) gives expression (5).

$$\Delta_{CF_3\cdot CZ_3}^{CFCl_3} = -523\cdot40 - 20\cdot28k'k^{FC} - 3KE_Z \quad (5)$$

Three suitable compounds are available for examination, namely those in which $Z = H$, Cl, or F, *i.e.*, $CF_3 \cdot CH_3$, $CF_3 \cdot CCl_3$, and $CF_3 \cdot CF_3$. The chemical shifts of these compounds (from $CFCl_3$) are listed in Table 1, and enable values of $k'k^{FC}$ ($= -27 \cdot 16$) and K ($= -5 \cdot 54$) to be deduced.

Provided that angular distortion is not too great, it should now be possible to calculate the chemical shift from $CFCl_3$ of the fluorine nuclei in any compound $CF_3 \cdot CXYZ$ by use of expression (6). (In this situation,

$$\Delta^{CFCl_3}_{CF_3 \cdot CXYZ} = 27 \cdot 40 + 5 \cdot 54(E_X + E_Y + E_Z) \quad (6)$$

all conformations are equally populated.)

The chemical shifts of CF_3 groups in 204 compounds of this type have been calculated from equation (6) and are compared with experimentally observed values in Tables 1(a) and (b). The agreement is very good, and the r.m.s. deviation (3·3 p.p.m.) is within experimental error due to solvent effects, referencing procedures, and temperature variation. For composite substituents such as ⁻NR₂, ⁻SR, *etc.*, the Huggins electronegativity of the atom bonded to C(2) (N, S) is used, and the method is applicable to a wide variety of such situations.

It is possible to envisage other situations in which molecular symmetry dictates equal population of con-

formers. A collection of these data are in Table 2, and the chemical shifts are calculated from equations (4) or (7) and compared with experimental results. For these

TABLE 2

Comparison of observed and calculated ¹⁹F chemical shifts in compounds where there is rotational averaging between conformations of equal energy

Compound	Observed shift (p.p.m.)	Calculated shift (p.p.m.)
$CF_2H \cdot CH_3$	110	111·0
$CF_2H \cdot CF_3$	140	139·2
$CFH_2 \cdot CH_3$	213	213
$CF_3 \cdot CFBr \cdot CF_3$	144	143·7
$CF_3 \cdot CFI \cdot CF_3$	147	147·6
$CF_3 \cdot CFH \cdot CF_3$	214·7	211·0
$CF_3 \cdot CFOF \cdot CF_3$	137·4	137·4
$CF_2Cl \cdot CH_3$	47	50·9
$CF_2Cl \cdot CCl_3$	65·1	66·7
$CF_2Br \cdot CH_3$	37	47·4
$CF_2OF \cdot CCl_3$	91·6	86·3

(No. of shifts = 11, r.m.s. = 3·9).

calculations in propane and higher alkanes it is necessary to evaluate $k'k^{HC}$ ($= -31 \cdot 19$) and $k'k^{CC}$ ($= -24 \cdot 88$) and an additional equation (7) can be derived. All other

$$\Delta^{CFCl_3}_{Cklm \cdot CFa \cdot Oefg} = 154 \cdot 12 (9 \cdot 45 - E_a - 2E_C) - 771 \cdot 08 - 2k'k^{aC}E_aE_C - k'k^{CC}E_CE_C - K(E_e + E_f + E_g + E_k + E_l + E_m) \quad (7)$$

TABLE 3

Comparison of observed and calculated ¹⁹F chemical shifts in compounds where there may be conformational preference

(a) Compound	Observed shift [a] (p.p.m.)			Calculated shift [a] (p.p.m.)			Compound	Observed shift [a] (p.p.m.)		Calculated shift [a] (p.p.m.)	
$CF_2Cl \cdot CHFBr$	67	*f*		64·5	*f*		$CF_2Br \cdot CF_2Br$	63·4		70·4	
$CF_2Cl \cdot CHFCl$	68	*f*		65·6	*f*		$CF_2H \cdot CF_2H$	138		129·8	
$CF_2Cl \cdot CFCl_2$	67·9	72·5		70·9	76·2		$CF_2H \cdot CF_2OF$	136·4	99	137·0	89·3
$CF_2Cl \cdot CFClSO_2Cl$	60			66·9			$(CF_2NF_2)_2$	117		102·8	
$CF_2Cl \cdot CF_2Cl$	71·6			75·0			$CFCl_2 \cdot CFH_2$	72·8	216	61·6	232·9
$CF_2Cl \cdot CF_2OF$	69·3	96		77·0	94·6		$CFCl_2 \cdot CF_2OF$	71·8	93·7	78·1	90·4
$CF_2Cl \cdot CF_2I$	67·0	59·6		72·3	66·3		$CFCl_2 \cdot CFCl_2$	67·8		72·1	
$CF_2Br \cdot CHBrCl$ [e]	64·6			56·8			$CFCl_2 \cdot CCl_2Br$ [e]	71·6		66·9	
$CF_2Br \cdot CH_2Cl$	54·5			52·7			$CFCl_2 \cdot CBr_2Cl$ [e]	70·0		65·7	
$CF_2Br \cdot CCl_2Br$	60·6			62·1			$CFClBr \cdot CBr_2Cl$	67·3		65·6	
$CF_2Br \cdot CHFCl$	63·5	*f*		62·1	*f*		$CFClBr \cdot CCl_2Br$ [e]	69·3		66·7	
$CF_2Br \cdot CHFBr$	61·0	*f*		61·0	*f*		$CFBr_2 \cdot CBr_2Cl$ [e]	65·8		59·9	
$CF_2Br \cdot CFBrCl$ [e]	62·3	72·1		66·3	75·5		$CFH_2 \cdot CH_2 \cdot SiCl_3$	209		210·5	
$CF_2Br \cdot CFBr_2$ [e]	70·6	82·8		65·2	77·9		$CFH_2 \cdot CFHBr$	220	*f*	226·6	*f*
$CF_3 \cdot CF_2 \cdot CF_2Cl$	*c* 125·6	*c*	*c* 127·3	*c*			$CF_2Cl \cdot CF_2 \cdot CCl_3$	*c* 122		*c* 114·9	
$CF_3 \cdot CF_2 \cdot CF_2I$	*c* 117·7	60	*c* 124·6	63·2			$CF_2Cl \cdot CF_2 \cdot CF_2Cl$	*c* 119·4		*c* 123·2	
$CF_3 \cdot CF_2 \cdot CF_2 \cdot OF$	*c* 127	93·9	*c* 129·3	91·5			$CF_2Cl \cdot CF_2 \cdot CH_2F$	*c* 122	240	*c* 108·5	234·0
$CF_3 \cdot CF_2 \cdot CF_2 \cdot NF_2$	*c* 116·7	127·2	*c* 126·8	100·4			$CF_2Cl \cdot CF_2C(O)F$	*c* [b]		*c*	
$CF_3 \cdot CF_2 \cdot CF_2H$	*c* 134	138	*c* 122·1	132·0			$CF_2Br \cdot CF_2 \cdot CH_2F$	*c* 119	241	*c* 106·9	234·0
$CF_3 \cdot CF_2 \cdot CFH_2$	*c* 128	244	*c* 112·7	234			$CF_2H \cdot CF_2 \cdot CH_2F$	*c* 128	245	*c* 103·2	234·0
$CF_3 \cdot CHF \cdot CH_2I$	80	193	75·6	185·2			$CF_2H \cdot CF_2 \cdot CHFBr$	*c* 129·5	*f*	*c* 107·4	*f*
$CF_3 \cdot CFI \cdot CF_2Cl$	71	116	63	78·1	143·4	65·1	$CF_2H \cdot CF_2 \cdot CHFCl$	*c* 134	*f*	*c* 108·5	*f*
$CF_3 \cdot CF(NF_2) \cdot CF_2OF$	72·8	167·2	86·1	80·3	140·2	86·8	$CF_2H \cdot CF_2 \cdot CF_2H$	*c* 136	139	*c* 112·7	132·0
$CF_3 \cdot CH_2 \cdot CHFI$	66	144·8		66·2	149·0		$CFH_2 \cdot [CH_2]_4 \cdot CH_3$	219		215·2	
$CF_3 \cdot CFCl \cdot CCl_2CF_3$	82	119	81	80·9	126·7	76·7	$CFH_2 \cdot CH_2 \cdot O \cdot CF_2 \cdot CH(CF_3)_2$	227	64	220·2	68·4
$(CF_3CF_2)_2CF \cdot [CF_2]_2 \cdot CF_3$	189·9		160·6								
$(CF_3)_2CF \cdot CF(CF_3)_2$	189·8		167·8				$(CF_3)_2CF \cdot [CF_2]_2 \cdot CF_3$	185		167·8	

(No. of shifts = 78, r.m.s. = 10·8)

(b) Compound type	No. of compounds	Observed shift range (p.p.m.)	Average observed shift (p.p.m.)	Calculated shift (p.p.m.
$CF_2Br \cdot CF_2 \cdot CR_3$	3	62—66·7	64·9	68·5
$CF_2Cl \cdot CR_2 \cdot CR_3$	6	59·2—71·2	66·6	72·0
$CF_2H \cdot CF_2 \cdot CR_3$	4	137—139	138·3	132·0
$CF_3 \cdot CF_2 \cdot CF_2 \cdot CR_3$	56	119—130	126·1	124·3
$R_3C \cdot CF_2 \cdot CF_2 \cdot CF_2 \cdot CR_3$	27	116·6—129	123·2	117·1
$RCH_2 \cdot CFH \cdot CH_2R$	6	148·5—190·0	180·63	158·9

(No. of shifts = 102, r.m.s. = 9·9).

For footnotes see Table 1.

constants have been established previously, and the agreement with experiment is of the usual precision.

In many situations, the conformations arising from rotation about the C(1)–C(2) bond will be of different energies. For ethane derivatives the barrier to rotation is sufficiently low to ensure that, at room temperature, there is rapid rotation and a Boltzmann distribution between the different possible conformers; the observed spectrum is the weighted average of the spectra due to the different isomers. For such a situation the approximations leading to equation (4) will not hold, *i.e.*, the cosine terms expressing vicinal interactions will not average to zero. It must be expected therefore that when the chemical shifts of ^{19}F in such molecules are calculated by use of equation (4) they will show larger than usual discrepancies from the observed values. It will be instructive to examine the situation, however, in order to observe the importance of the cosine-dependent terms, and Table 3(a) and (b) compares calculated and observed chemical shifts for a variety of weighted-average situations. The overall r.m.s. deviation is large (10·8 p.p.m.) and indicates that conformational preference in rotation about a C–C bond may be responsible for chemical-shift variations of ± 7 p.p.m. If the angularly dependent terms were to be elucidated, then this would present a powerful tool for studying conformational effects in fluorinated systems.