

The Structural Dependence of the Inductive Effect. Part VII.¹ Effects of 1-Substituents upon Geminal Proton-Fluorine Spin-Spin Coupling Constants ($^2J_{\text{FH}}$)

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A detailed empirical analysis has been made of the nature of 1-substituent effects upon $^2J_{\text{FH}}$ in situations where the nuclei are bonded to carbon and to silicon. The non-additivity of such effects is explained in terms utilised previously by us in connection with nuclear shielding and a useful, simple, expression is given which enables $^2J_{\text{HF}}$ to be calculated in terms of the Huggins electronegativities of the substituents.

CONSIDERABLE attention has been given recently to theoretical and empirical descriptions of $^2J_{\text{HH}}$ in a variety of systems. Sternhell has reviewed the subject comprehensively,² and a successful theoretical rationalisation has been given by Pople and Bothner-By.³ More

recently, Maciel and his co-workers have made use of Finite Perturbation Theory⁴ to calculate $^2J_{\text{HH}}$ in a wide variety of systems,⁵⁻⁸ and several empirical analyses have also appeared.⁹⁻¹³

In contrast, relatively little attention has been paid

¹ Part VI, L. Phillips and V. Wray, *J.C.S. Perkin II*, 1972, 536.

² S. Sternhell, *Quart. Rev.*, 1969, **23**, 236.

³ J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, 1965, **42**, 1339.

⁴ J. A. Pople, J. W. McIver, and N. S. Ostlund, *J. Chem. Phys.*, 1968, **49**, 2965.

⁵ G. E. Maciel, J. W. McIver, N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, 1970, **92**, 4151, 4497.

⁶ P. D. Ellis and G. E. Maciel, *J. Amer. Chem. Soc.*, 1970, **92**, 5829.

⁷ P. D. Ellis and G. E. Maciel, *Mol. Phys.*, 1971, **20**, 433.

⁸ G. E. Maciel and K. D. Summerhays, *J. Amer. Chem. Soc.*, 1971, **93**, 520.

⁹ M. J. Lacey, C. G. Macdonald, A. Pross, J. S. Shannon, and S. Sternhell, *Austral. J. Chem.*, 1970, **23**, 1421.

¹⁰ P. J. Chivers and T. A. Crabb, *Tetrahedron*, 1970, **26**, 3389.

¹¹ P. J. Halls, R. A. Y. Jones, A. R. Katritzky, M. Snarey, and D. L. Trepanier, *J. Chem. Soc. (B)*, 1971, 1320.

¹² G. Swaelens, M. Anteunis, and T. Tavernier, *Bull. Soc. chim. belges*, 1970, **79**, 441.

¹³ M. Anteunis, G. Swaelens, and J. Gelan, *Tetrahedron*, 1971, **27**, 1917.

to ${}^2J_{\text{HF}}$ although there have been several attempts^{10,14-16} to calculate this parameter for simple situations using both Finite Perturbation Theory⁴ and the 'Sum Over States' method.¹⁷ The various methods give widely varying results for even the simplest of molecules, CH_3F , depending upon the form of the wavefunctions utilised, and only the results of Ditchfield and Snyder¹⁴ are in reasonable agreement with experimental data. All calculations are in accord with the earlier suggestion by Pople¹⁸ that the Fermi-contact mechanism dominates the coupling, and the calculated contribution of 17% of the observed total arising from the spin-orbital mechanism has been verified by later work.¹⁴ There has as yet been no theoretical study of the influence of substituents upon ${}^2J_{\text{HF}}$, and the empirical descriptions of the observed trends are rather imprecise.

Arison *et al.*¹⁹ have studied the effect upon ${}^2J_{\text{HF}}$ of varying the substituent X in compounds of the type CHF_2X , and have shown that the magnitude of this parameter increases markedly with increase in electronegativity of X. Substituent effects are non-additive however, as may be seen from the fact that successive replacement of hydrogen in CFH_3 by fluorine causes a non-linear increase in ${}^2J_{\text{HF}}$:

${}^2J_{\text{HF}}$	CH_3F ²⁰	CH_2F_2 ²¹	CHF_3 ²²
	46.3	50.4	79.7

Frankiss²³ observed that in compounds of the type SiHFXY , ${}^2J_{\text{HF}}$ also increases with increase in the electronegativity of the substituents X and Y and thereby deduced that the sign of the coupling must be the same as in the analogous carbon compounds. He commented, however, that the situation is by no means simple since substituent effects are not additive.

We have observed interesting variations in ${}^2J_{\text{HF}}$ as a result of substituent changes in several related series of molecules (see later), and decided to examine the possibility of obtaining a generally applicable qualitative picture of substituent effects upon this parameter.

EXPERIMENTAL AND RESULTS

Monofluoro-, difluoro-, bromofluoro-, chlorofluoro-, and 1-fluoro-1-methyl-acetamides, -*N*-methylacetamides, and -*NN*-dimethylacetamides were prepared by the standard procedure from the appropriate methyl or ethyl ester and amine. Many of the compounds are new, and the details of synthesis will be described elsewhere.¹⁹ ${}^{19}\text{F}$ and ${}^1\text{H}$ N.m.r. spectra were recorded with a Varian HA-100 spectrometer operating in field-frequency locked mode. Dilute solutions (*ca.* 5% w/v) of each compound in deuteriochloroform were studied at normal probe temperature (31 °C) and line positions were measured, in spectra recorded using 100 Hz sweep width, with a frequency counter. The

¹⁴ R. Ditchfield and L. C. Snyder, *J. Chem. Phys.*, 1972, **56**, 5823.

¹⁵ H. Nakatsuji, I. Morishima, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Japan*, 1971, **44**, 2010.

¹⁶ A. D. C. Towl and K. Schaumberg, *Mol. Phys.*, 1971, **22**, 49.

¹⁷ Y. Kato and A. Saika, *J. Chem. Phys.*, 1967, **46**, 1975.

¹⁸ J. A. Pople, *Mol. Phys.*, 1958, **1**, 216.

¹⁹ B. H. Arison, T. Y. Shen, and N. R. Trenner, *J. Chem. Soc.*, 1962, 3828.

values of ${}^2J_{\text{HF}}$ were taken directly from the spectra, which are first-order in nature, and are reported in Table 1.

TABLE 1

Values of ${}^2J_{\text{HF}}$ for the substituted acetamides, *N*-methylacetamides, and *NN*-dimethylacetamides

X	${}^2J_{\text{HF}}$ (calc.)/ Hz	XCHF·	XCHF·	XCHF·
		CONH ₂	CONHMe	CONMe ₂
		J/Hz	J/Hz	J/Hz
H	46.6	46.5	47.0	47.0
Me	48.4	49.6	50.6	49.6
Br	49.9	51.0	51.3	
Cl	50.8	51.6	51.8	51.4
F	54.1	55.2	53.4	54.6

DISCUSSION

We have made a compilation of coupling constants involving fluorine which will be published elsewhere,²⁴ and in order that our data may be discussed in context we list in Table 2 values taken from this work for typical

TABLE 2

Typical values of ${}^2J_{\text{HF}}$ in molecules XYCHF

X	Y	${}^2J_{\text{HF}}$ /Hz	Ref.
F	F	79.5	22
F	OR	69—75	24
F	Cl	63	<i>a</i>
F	SO_2CF_3	69.5	<i>b</i>
F	$\text{P}(\text{OMe})\text{CF}_3$	50.4	<i>c</i>
F	R	52—62	24
Cl	Cl	53.5	<i>a</i>
R	OR	50—57	24
R	NR_2 , NO_2	42—54	24
R	Cl	47—53	24
R	SR, S^{VI}	43—49	24
R	Br	48—52	24
F	H	50.4	21
R	I	47—48	24
H	SF_5	46	<i>d</i>
Cl	Si^{IV}	46—48	24
R	R	43—55	24
R	PCl_2	46.7	<i>e</i>
R	H	45—50	24
R	Si^{IV}	43—46	24
R	Ge^{IV}	45—46	24
H	H	46.3	20
H	SiMe_3	46.8	<i>f</i>

R = alkyl or substituted alkyl.

^a G. Levi and M. Chalaya, *Compt. rend.*, 1967, **264(B)**, 857.
^b R. A. Mitsch and J. E. Robertson, *J. Heterocyclic Chem.*, 1965, **2**, 152. ^c H. Goldwhite, R. N. Haszeldine, and D. G. Rowsell, *Chem. Comm.*, 1965, 83. ^d H. J. Emeleus and B. W. Tattershall, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1823. ^e J. Dyer and J. Lee, *J. Chem. Soc. (B)*, 1970, 409. ^f G. A. Olah and G. D. Mateescu, *J. Amer. Chem. Soc.*, 1971, **93**, 781.

ranges of ${}^2J_{\text{HF}}$ observed in a wide variety of molecules of the type XYCHF. It is apparent that, qualitatively at least, ${}^2J_{\text{HF}}$ does increase with increase in the electronegativity of the groups X and Y; the Figure illustrates this in a plot of the data of Table 2 against the sum of the Huggins electronegativities of the groups X and Y (for composite groups, the electronegativity of the atom bonded to the coupling fragment is used). The data

²⁰ T. R. Krugh and R. A. Bernheim, *J. Chem. Phys.*, 1970, **52**, 4942.

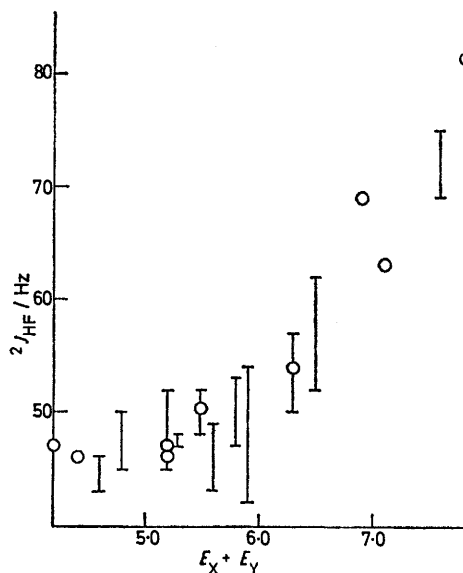
²¹ M. Barfield and J. D. Baldeschwieler, *J. Chem. Phys.*, 1964, **41**, 2633.

²² S. G. Frankiss, *J. Phys. Chem.*, 1963, **67**, 752.

²³ S. G. Frankiss, *J. Phys. Chem.*, 1967, **71**, 3418.

²⁴ J. W. Emsley, L. Phillips, and V. Wray, *Progr. N.M.R. Spectroscopy*, in the press.

suggest that β -substituent effects (*i.e.* from groups vicinal to the coupling H and F nuclei) must be significant for if one of the substituents is an alkyl group (and the other remains constant) the observed value of ${}^2J_{\text{HF}}$ may vary considerably as a result of structural variation within that group.

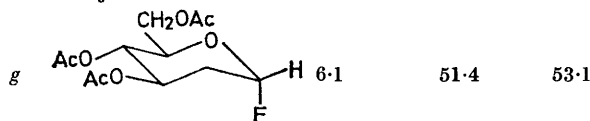


If a range of compounds is chosen with the object of minimising such β -effects (*i.e.* the substituents are single atoms or simple groups such as CH_3 or OCH_3), the correlation is still non-linear and curves markedly with apparent discontinuities. Table 3 lists data for such a series of molecules.

TABLE 3

Values of ${}^2J_{\text{HF}}$ (Hz) in specific molecules; experimental results and values calculated by using equation (3)

Ref.	Structure	$E_X + E_Y$ *	${}^2J_{\text{HF}}$ obs.	${}^2J_{\text{HF}}$ calc.
22	CHF_3	7.8	79.5	76.8
a	CHF_2OMe	7.4	74.4	68.7
b	CHF_2Cl	7.05	63.0	64.6
c	CHF_2Me	6.5	57.2	55.7
b	CHFCl_2	6.3	53.6	57.2
21	CH_2F_2	6.1	50.4	49.2
d	$\text{CHFCl}\cdot\text{CHCl}_2$	5.75	49.0	51.8
e	CHFBrMe	5.55	50.5	50.7
f	$\text{MeCHF}\cdot\text{CH}_2\text{I}$	5.2	48.0	48.9
c	MeCH_2F	4.8	47.5	46.8
20	CFH_3	4.4	46.3	46.1



* The values for the electronegativities were taken as follows: F 3.90, OR 3.40, Cl 3.15, Br 2.95, C 2.60, H 2.20 (M. L. Huggins, *J. Amer. Chem. Soc.*, 1953, **75**, 4123).

^a Footnote b, Table 2. ^b Footnote a, Table 2. ^c D. D. Elleman, L. C. Brown, and D. Williams, *J. Mol. Spectroscopy*, 1961, **7**, 303. ^d R. R. Dean and J. Lee, *Trans. Faraday Soc.*, 1968, **64**, 1409. ^e J. W. Coomber and E. Whittle, *J. Chem. Soc.*, 1965, 6661. ^f G. Olah, J. M. Bollinger, and J. Brinich, *J. Amer. Chem. Soc.*, 1968, **90**, 2587. ^g L. D. Hall and J. F. Manville, *Chem. and Ind.*, 1967, 468.

If our data on fluorinated amides XCHFC(O)NR_2 are examined in a similar way by plotting ${}^2J_{\text{HF}}$ (listed in Table 1) *vs.* E_X , a linear graph results. In this situation, one group has been held constant [$\text{X} = \text{CHF}_2$, $\text{Y} = \text{C(O)NR}_2$] while the other is varied and we shall show later that this is a general observation for analogous situations.

It is interesting to note the effect of making the same substituent change in different molecules; in Table 4 the change in the value of ${}^2J_{\text{HF}}$ (Δ^2J_{HF}) which occurs when an alkyl group is replaced by fluorine, is shown for four pairs of molecules. It is apparent that the magnitude of the change in ${}^2J_{\text{HF}}$ on going from XYCHF to ZYCHF depends not only upon the electronegativity difference between X and Z but also upon the nature of the group Y.

TABLE 4

Change in ${}^2J_{\text{HF}}$ (Δ^2J_{HF}) on replacing an alkyl group by fluorine

Structure (1)	${}^2J_{\text{HF}}$ /Hz	Structure (2)	${}^2J_{\text{HF}}$ /Hz	$\Delta^2J_{\text{HF}}[(1)-(2)]$ /Hz
$\text{R}^*\text{CF}_2\text{H}$	57.2	CF_3H	79.5	22.3
$\text{R}^\dagger\text{CClFH}$	49.0	CF_2CH	63.0	14.0
$\text{R}^\ddagger\text{CMeFH}$	48.0	MeCF_2H	57.2	9.2
$\text{R}^*\text{CH}_2\text{F}$	47.5	CH_2F_2	50.4	2.9

$\text{R}^* = \text{Me}$; $\text{R}^\dagger = \text{CHCl}_2$; $\text{R}^\ddagger = \text{CH}_2\text{I}$.

These observations are reminiscent of those made previously concerning substituent effects upon nuclear shielding,²⁵ and the approach used in our analysis of shielding data may easily be applied to the present problem even though the number of analysable data is relatively small.

It is unnecessary to give the method of analysis in detail, since its basis is fully documented elsewhere.^{2,26} Four different series of molecules of the type XYCHF were chosen, with $\text{X} = \text{F}$, Cl , CH_3 , or H , respectively, while the group Y is variable; for each series ${}^2J_{\text{HF}}$ was plotted against the Huggins electronegativity of Y (E_Y) to give satisfactorily linear graphs. Each graph has its own characteristic slope which depends on the group X, and may be defined by equation (1).

$${}^2J_{\text{HF}} = 45.63 + S_X(E_Y - 1.98) \quad (1)$$

In turn, a plot of S_X *vs.* E_X is linear, and may be expressed by equation (2).

$$S_X = 8.45(E_X - 1.98) \quad (2)$$

Substitution of (2) into (1) gives a useful expression (3) for ${}^2J_{\text{HF}}$ in terms of E_X and E_Y . This expression

$${}^2J_{\text{HF}} = 78.76 + 8.45(E_X E_Y) - 16.73(E_X + E_Y) \quad (3)$$

enables ${}^2J_{\text{HF}}$ for the molecules listed in Table 3 to be calculated to a satisfactory degree of precision (± 2.1 Hz r.m.s.); the calculated values are compared with experimental data in Table 3.

We may now examine the relevance of this treatment to our data on fluorinated amides listed in Table 1, by using it to estimate a group electronegativity for

²⁵ L. Phillips and V. Wray, *J. Chem. Soc. (B)*, 1971, 2068.

²⁶ L. Phillips and V. Wray, *J.C.S. Perkin II*, 1972, 214.

C(O)NRR'; a value of 2.5 on the Huggins scale enables the coupling constants, ${}^2J_{\text{HF}}$, in Table 1 to be calculated to a satisfactory degree of precision, as shown in the relevant column of this Table. This is a reasonable figure, since Wells²⁷ gives values of 2.6 for CH₃ and 2.8 for CO₂H.

TABLE 5

Observed and calculated values [equation (4)] of ${}^2J_{\text{HF}}$ in compounds of the type XYSiHF

Compound *	${}^2J_{\text{HF}}^{\text{SI}}$ obs./Hz	Ref.	${}^2J_{\text{HF}}^{\text{SI}}$ calc./Hz
SiF ₃ H	96.2	a	98.1
SiF ₃ HSH	75.2	b	70.0
SiF ₂ HMe	67.5	23	70.0
(MeSiFH) ₂ O	68.2	23	65.4
GeH ₃ ·SiF ₃ H	54.5	c	57.0
SiH ₃ ·SiF ₃ H	53.0	d	54.9
SiH ₃ ·SiH ₂ ·SiF ₂ H	53.2	e	54.9
SiF ₂ H·SiF ₂ H	52.0	d	54.9
SiF ₂ SH·SiF ₂ H	54.9	b	54.9
Me ₂ SiFH	52.1	23	55.2
SiH ₃ ·SiFHCl	51.5	d	50.5
SiH ₃ ·SiFH ₂	43.2	f	44.9
SiFH ₂ ·SiFH ₂	45.0	d	44.9

* The values for the electronegativities of Si, S, and Ge were taken as 1.90, 2.60, and 2.00, respectively (F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 2nd edn., Interscience, New York, 1966, p. 103).

^a R. B. Johanneson, *J. Chem. Phys.*, 1967, **47**, 3088. ^b K. G. Sharp and J. L. Margrave, *Inorg. Chem.*, 1969, **8**, 2655. ^c D. Solan and P. L. Timms, *Inorg. Chem.*, 1968, **7**, 2157. ^d J. E. Drake and N. P. C. Westwood, *J. Chem. Soc. (A)*, 1971, 3300. ^e J. E. Drake, N. Goddard, and N. P. C. Westwood, *J. Chem. Soc. (A)*, 1971, 3305. ^f J. E. Drake and N. Goddard, *J. Chem. Soc. (A)*, 1970, 2587.

The form of equation (3) leads to some interesting conclusions; for a series of compounds XYCHF in which the group X is held constant and has an electro-

negativity of 1.98, changing the nature of group Y should have no observable effect upon ${}^2J_{\text{HF}}$, which should stay constant at *ca.* 45.6 Hz. Moreover, if $E_X < 1.98$ then ${}^2J_{\text{HF}}$ should *increase* with a *decrease* in the electronegativity of Y. There is, in fact, some evidence to support this suggestion for when the group X is Si^{IV} ($E_X = 1.90$) the value of ${}^2J_{\text{HF}}$ for molecules in which Y = Cl, CH₃, or H actually *does* increase slightly in this order rather than decrease. (For Et₃SiCHFCl, ${}^2J_{\text{HF}} = 45.5$; ²⁸ for Cl₃SiCFHMe, ${}^2J_{\text{HF}} = 46.0$; ²⁹ and for Me₃SiCH₂F, ${}^2J_{\text{HF}} = 46.8$ Hz.³⁰)

It was mentioned earlier that Frankiss²³ has observed a similarity in the effects of substituents upon ${}^2J_{\text{HF}}$ when both nuclei are bonded to carbon or silicon. Table 5 lists values of ${}^2J_{\text{HF}}$ in compounds of the type XYSiHF, and by using the same procedure as outlined above for XYCHF it is possible to derive equation (4), which may be used to calculate ${}^2J_{\text{HF}}$ for the compounds in Table 5 to a satisfactory degree of precision (r.m.s. ± 2.4 Hz).

$${}^2J_{\text{HF}}^{\text{SI}} = 49.08 + 7.85(E_X E_Y) - 9.03(E_X + E_Y) \quad (4)$$

In summary, we now understand (qualitatively at least) the effects upon ${}^2J_{\text{HF}}$ of substituents directly bonded to the same atom as the H and F nuclei. It is inevitable however that there are anomalies and these probably arise from the influence of substituents which are upon adjacent atoms in the molecule, *i.e.* β or γ effects; this question will be examined elsewhere.

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²⁷ P. R. Wells, *Progr. Phys. Org. Chem.*, 1968, 111.

²⁸ D. Seyferth and K. V. Darragh, *J. Org. Chem.*, 1970, **35**, 1297.

²⁹ J. Dyer and J. Lee, *Spectrochim. Acta*, 1970, **26A**, 1045.

³⁰ E. S. Alexander, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *J. Chem. Soc. (A)*, 1970, 2285.