High Resolution Fluorine-coupled ^{13}C Nuclear Magnetic Resonance Spectra of Substituted Pentafluorobenzenes. Theoretical and Empirical Correlations of J_{CF}

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The high resolution ^{19}F and ^{19}F-coupled ^{13}C n.m.r. spectra of several substituted pentafluorobenzenes, C_6F_5X (X = H, F, NH_2, NO_2, Cl, Br, CH=CH_2, OCH_3, CH_3, I, CN, OH, and CHO), have been completely analysed, and all the signs and magnitudes of the ^{13}C–^{19}F coupling constants determined. INDO MO calculations of $^nJ_{FF}$ and $^nJ_{CF}$ have been performed, and comparisons are made with the experimental values. The calculations include the Fermi contact, orbital, and spin–dipolar contributions to the coupling and are shown to reproduce the substituent effects upon $^nJ_{FF}$. The calculations of $^nJ_{CF}$ values are less successful. $^1J_{C(4)F(4)}$ correlates well with σ_p whereas the correlation of the other $^1J_{CF}$ values is less successful. No improvement in the correlations occur with a dual parameter equation. All the couplings, $^nJ_{CF}$, that show a sufficient variation with the substituent change are successfully correlated with a three parameter equation involving *F*, *R*, and *Q*. In particular $^2J_{C(1)F(2)}$ and $^3J_{C(2)F(6)}$, in close proximity to the substituent, are successfully correlated by this equation.

SUBSTITUENT effects upon chemical shifts in aromatic systems have been rather extensively investigated.[1] In particular ^{19}F chemical shifts are continuing to be used to investigate the transmission of electronic effects through aromatic systems by several groups of workers.[2-4] More recently the use of ^{13}C chemical shifts have received widespread attention and many useful correlations have been noted.[5] On the contrary substituent effects upon coupling constants have received less attention although a great deal of information exists for proton–proton,[1] proton–fluorine, and fluorine–fluorine coupling constants.[6] The possibility of using couplings to carbon atoms within the aromatic framework of the molecule to investigate substituent effects has been rather neglected. Although several early papers had reported the effects of substituents upon proton–carbon couplings in these systems, it is only recently that a thorough investigation was presented for the monosubstituted benzenes.[7] For fluorine–carbon coupling constants, however, very few studies have been reported.[8,9]

In order to clarify the situation carbon–fluorine coupling constants (J_{CF}) in several substituted pentafluorobenzenes have been determined and are reported here. This system is the fluorine analogue of the monosubstituted benzene system and as such allows the widest investigation possible. Substituent effects upon fluorine–fluorine coupling constants (J_{FF}) in these and related systems have received much attention.[6] In particular these effects have been shown to be additive[10,11] and various correlations with Hammett substituent parameters have been reported.[10,12,13] The importance of orbital and spin–dipolar contributions in

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the calculation, by MO theory, of J_{FF} values has been exemplified for hexafluorobenzene, and amino- and nitro-pentafluorobenzenes,[14] but a thorough investigation of the calculation of these J_{FF} values has not hitherto been presented. We report here such an investigation with calculations of both these and J_{CF} values in substituted pentafluorobenzenes by the use of INDO MO theory.

EXPERIMENTAL

The samples used in the present study were purchased from Bristol Organics Limited and were used without further purification. Liquid samples were made up as solutions (75%, v/v) in [$^2H_6$]acetone (20%, v/v) containing tetramethylsilane (5%, v/v); solids were made up as saturated solutions in acetone–Me_4Si (4 : 1, v/v). Samples were degassed by four freeze–pump–thaw cycles and sealed under vacuum in 5 and 10 mm sample tubes.

TABLE 1

^{19}F Chemical shift differences [a] and J_{FF} values [b] for the substituted pentafluorobenzenes C_6F_5X

X	J_{23}	J_{24}	J_{25}	J_{26}	J_{34}	J_{35}	$\delta_{2,6}$	$\delta_{3,5}$	δ_4	R.m.s. error	Ref.
H	−20.57	1.21	8.78	−2.04	−18.75	−1.23	2 238.72	0.00	737.16	0.007	*c*
F	−20.27	−3.01	3.86	−3.01	−20.27	−3.01	0.00	0.00	0.00	0.029	*c*
NH_2	−20.52	−7.33	5.13	4.64	−20.75	−2.40	1 150.12	849.55	0.00	0.013	*d—g*
NO_2	−21.24	5.40	6.68	−9.98	−19.94	−0.37	1 224.78	0.00	1 134.77	0.041	*e, h*
Cl	−20.63	0.47	5.99	−5.29	−19.77	−1.96	1 954.62	0.00	493.94	0.019	*d—f, i*
Br	−21.47	1.22	6.28	−5.30	−19.62	−1.65	2 647.79	0.00	561.71	0.017	*d—f, j*
$CH=CH_2$	−20.47	1.37	8.22	−2.20	−19.66	−2.00	1 898.57	0.00	644.71	0.008	*k*
OCH_3	−20.44	−3.20	4.65	−0.44	−20.62	−3.36	685.99	59.67	0.00	0.020	*l*
CH_3 [q]	−20.89	−0.06	8.55	−0.63	−19.43	−2.27	1 969.39	0.00	428.32	0.037	*e, m, n*
I	−22.91	1.97	7.28	−4.72	−19.46	−1.25	3 822.85	0.00	654.20	0.011	*e, f, j, l, o,*
CN	−20.12	5.88	8.05	−7.85	−19.47	0.28	2 504.20	0.00	1 481.34	0.019	*d—f, m*
OH	−20.65	−5.73	4.40	2.24	−20.75	−3.19	700.28	477.95	0.00	0.016	*d, f, p*
CHO [r]	−20.18	6.46	9.49	−4.82	−19.13	−1.11	1 588.13	0.00	1 535.31	0.012	*n*

[a] The ^{19}F chemical shift differences and J_{FF} values are in Hz. The lowest frequency ^{19}F signal is arbitrarily taken as zero. [b] The relative signs and magnitudes of J_{26} and J_{35} for X = Cl and Br were determined by double irradiation [8] while the signs for the remaining members were taken from the literature. [c] Ref. 16. [d] W. B. Moniz, E. Lustig, and E. A. Hansen, *J. Chem. Phys.*, 1969, **51**, 4666. [e] R. Fields, J. Lee, and D. J. Mowthorpe, *J. Chem. Soc.* (*B*), 1968, 308. [f] E. A. Cohen, A. J. R. Bourn, and S. L. Manatt, *J. Magnetic Resonance*, 1969, **1**, 436. [g] L. C. Duncan and G. H. Cady, *Inorg. Chem.*, 1964, **3**, 1045. [h] A. Peake and L. F. Thomas, *Chem. Comm.*, 1966, 529. [i] P. Bladon, D. W. A. Sharp, and J. W. Winfield, *Spectrochim. Acta*, 1964, **20**, 1033. [j] M. A. Cooper, *Org. Magnetic Resonance*, 1969, **1**, 363. [k] M. I. Bruce, *J. Chem. Soc.* (*A*), 1968, 1459. [l] I. J. Lawrenson and R. G. Jones, *J. Chem. Soc.* (*B*), 1967, 797. [m] Ref. 12. [n] R. R. Dean and W. McFarlane, *J. Chem. Soc.* (*B*), 1969, 509. [o] W. B. Moniz and E. Lustig, *J. Chem. Phys.*, 1967, **46**, 366. [p] A. J. Dale, *Spectrochim. Acta*, 1971, **27A**, 81. [q] $|^4J_{FH}|$ 2.28, $|^5J_{FH}|$ 0.25, and $|^6J_{FH}|$ 1.38 Hz. [r] $^4J_{FH}$ 1.05, $^5J_{FH}$ −1.34, and $^6J_{FH}$ 0.21 Hz.

All spectra were recorded, as described previously,[15,16] on a Varian XL-100-12 spectrometer system; homonuclear ^{19}F decoupling was carried out with the Gyrocode® accessory. All iterative refinements were run with a program based upon LAOCOON III.

Fermi contact, orbital, and spin–dipolar contributions to the fluorine–fluorine and carbon–fluorine couplings were calculated by self-consistent perturbation theory,[17-19] at the INDO level of approximation,[20] using the program originally developed by Blizzard and Santry.[18] Standard geometries [19,21] were used with an aromatic carbon–fluorine bond length of 1.34 Å.

Substituent conformations were such as to optimise substituent–ring conjugation with the plane of the substituent group in the plane of the aromatic ring. For pentafluoroanisole calculations were performed on the conformation with a C–H bond of the methyl group at a dihedral angle of 180° with the C–O bond; for pentafluorophenol the O–H bond was placed in the plane of the ring.

All computations were carried out in single-precision on a PDP-10 computer.

Spectral Analysis.—The fluorine spectra of all the compounds presented here have been analysed before and in several cases the signs of the couplings have been unambiguously assigned. A general solution of the AA′XX′Z spectrum has been presented previously [22] which shows that there are normally eight possible solutions to this system which depend upon the relative magnitudes and signs of $J_{AA'}$ and $J_{XX'}$. Two tickling experiments suffice to determine unambiguously the correct solution. In the present case the signs and relative magnitudes of these couplings were determined from comparison with the literature or from tickling experiments.[22] In all cases, however, the correct solution of the eight possibilities was the one with the lowest r.m.s. error. Thus the determination of frequencies in the Fourier transform mode of operation shows distinct advantages over the continuous wave mode of operation for these compounds in that frequencies are sufficiently precise,[23] provided there are enough data points, that the tickling experiments would have been unnecessary. The results of these analyses are shown in Table 1.

The analysis of the ^{13}C spectra presented no difficulties. As previously [15,16] we assumed that the ^{13}C isotope effects upon the J_{FF} values could be neglected; thus the values for

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[23] L. Ernst and D. N. Lincoln, *J. Magnetic Resonance*, 1974, **16**, 190.

the ^{12}C isotopomer were used throughout. The signs of the carbon–fluorine couplings were evident from the spectral analysis or were deduced from a comparison with those of hexafluorobenzene.[16] In all the latter cases substituent effects upon the couplings were insufficient to cause a sign change. It was necessary to consider the ^{13}C isotope effect upon the fluorine chemical shifts during the analysis of the spectra of carbon atoms 2(6) and 3(5). Thus in most cases the isotope shift differences between fluorine atoms 3 and 5, and 2 and 6 could be determined from the final iterations for carbon atoms 2 and 3, respectively.

The values of J_{CF} are given in Table 2; Table 3 shows the isotope shift differences determined from the same analyses. The data for penta- and hexa-fluorobenzene have been reported previously[16] but are included here for convenience.

TABLE 2

J_{CF} Values (Hz) for the substituted[a] pentafluorobenzenes C_6F_5X

	C(1)				C(2)					
X	^2J	^3J	^4J	R.m.s.	^1J	^2J	$^3J(4)$	$^3J(6)$	^4J	R.m.s.
H	23.44	0.50	3.56	0.012	−248.09	11.22	3.78	12.32	4.25	0.037
F	13.73	3.19	5.21	0.029	−251.13	13.73	3.19	3.19	5.21	0.029
NH_2	14.52	2.10	3.29	0.012	−238.90	13.23	3.29	7.21	4.21	0.019
NO_2	*b*	*b*	*b*		−262.12	14.06	3.79	2.30	4.92	0.023
Cl	19.44	1.07	5.14	0.025	−249.91	12.85	3.31	3.18	4.77	0.020
Br	23.02	0.00	5.10	0.010	−247.71	12.54	3.47	4.07	4.68	0.040
$CH{=}CH_2$	13.95	0.79	4.26	0.026	−250.41	11.49	3.35	7.89	4.32	0.032
OCH_3	12.51	1.75	4.49	0.026	−247.70	12.00	3.36	5.22	4.48	0.009
CH_3	19.49	0.86	3.94	0.014	−244.66	11.02	3.61	8.76	4.26	0.026
I	28.44	1.44	4.75	0.004	−244.58	11.96	3.59	6.15	4.48	0.007
CN	*b*	*b*	*b*		−260.00	13.04	4.29	4.98	4.03	0.025
OH	14.27	2.38	4.08	0.012	−242.76	12.78	3.24	5.25	4.57	0.026
CHO[c]	10.21	1.86	3.83	0.023	−261.33	11.47	4.12	6.69	4.32	0.023

	C(3)						C(4)			
	^1J	$^2J(2)$	$^2J(4)$	^3J	^4J	R.m.s.	^1J	^2J	^3J	R.m.s.
H	−249.76	16.67	12.86	1.41	5.21	0.039	−252.89	13.39	5.17	0.037
F	−251.13	13.73	13.73	3.19	5.21	0.029	−251.13	13.73	3.19	0.029
NH_2	−245.42	14.65	13.38	3.58	4.71	0.015	−241.64	13.94	4.30	0.021
NO_2	−255.29	15.39	13.41	1.82	5.31	0.045	−261.95	13.42	4.26	0.038
Cl	−252.51	16.24	13.43	2.48	5.24	0.034	−254.34	13.63	4.18	0.034
Br	−253.53	17.29	13.36	2.17	5.24	0.027	−254.61	13.56	4.40	0.032
$CH{=}CH_2$	−249.37	17.30	12.88	2.22	5.13	0.017	−253.75	13.67	5.09	0.015
OCH_3	−248.67	14.97	13.21	3.66	5.03	0.033	−248.21	13.84	3.95	0.020
CH_3	−248.70	17.47	12.76	2.06	5.09	0.016	−250.03	13.54	5.19	0.018
I	−254.66	18.83	13.24	1.69	5.21	0.019	−254.84	13.57	4.79	0.029
CN	−253.59	15.01	13.32	1.97	5.11	0.027	−262.85	13.33	4.94	0.015
OH	−247.48	14.57	13.44	3.72	4.96	0.024	−245.10	13.33	3.82	0.020
CHO[c]	−252.90	16.16	12.98	1.33	5.28	0.024	−261.22	13.46	5.29	0.022

[a] The substituted carbon is designated C(1). [b] The signal for this carbon was broad and could not be analysed. [c] $|^2J_{CH}|$ 27.33, $|^3J_{CH}|$ 1.78, $|^4J_{CH}|$ 1.34, and $|^5J_{CH}|$ 0.00 Hz.

TABLE 3

^{19}F Isotope shift differences[a] obtained directly from the spectral analyses

X	$\Delta_{5.3}$	$\Delta_{6.3}$
H		
F	2.20	2.20
NH_2	1.89	1.70
NO_2		1.94
Cl	1.88	1.75
Br	1.92	1.77
$CH{=}CH_2$	1.96	
OCH_3	1.86	
CH_3	1.98	
I	1.97	1.71
CN		1.87
OH	1.83	1.81
CHO	1.94	1.84

[a] The isotope shift differences between the shifts of fluorines 5 and 3, $\Delta_{5.3}$, and fluorines 6 and 3, $\Delta_{6.3}$, were obtained in the analyses of the spectra of carbon nuclei 2 and 3, respectively, and are in Hz.

DISCUSSION

Ramsey[24] was the first to show that the coupling between nuclear spins in a randomly tumbling molecule could be explained by interactions *via* the electrons in the molecule. He demonstrated that three types of interaction occur between the magnetic moment due to the nuclear spin and the electrons: (a) a Fermi contact interaction with the electron spin, (b) an orbital interaction with the magnetic field due to the orbital motion of the electron, and (c) a dipolar interaction with the electron spin.

Various methods have been developed for the calculation of these terms but the most efficient appears to be that developed by Blizzard and Santry[18] following the work of Pople and his co-workers.[17] The latter have calculated the Fermi contact term by finite perturbation theory where a perturbation was inserted during the calculation of the self-consistent field wavefunctions for the molecule. Excited wavefunctions need not be calculated and the desired features of the electron–electron repulsion were included to the same level of approximation in both the perturbed and unperturbed wavefunctions. This method, however, is particularly time consuming and thus precludes the calculation of the other two terms. By the use of a different mathematical approach Blizzard and Santry[18] have used SCF perturbation theory, working within the INDO framework,

[24] N. F. Ramsey, *Phys. Rev.*, 1953, **91**, 303.

to calculate all three terms. The first-order perturbation to the molecular orbital coefficient matrix is calculated directly from the unperturbed coefficient matrix (obtained from a zero-order INDO calculation) by matrix multiplication rather than diagonalization. This considerably speeds up computation and reduces errors that could occur with Pople's approach when small differences between large numbers are calculated.

At the INDO level of approximation of MO theory the above approach leads to an expression for the coupling between nuclei A and B (J_{AB}) of the form (1)

$$J_{AB} = a_{AB}J_C + b_{AB}(J_O + J_D) \qquad (1)$$

where J_C, J_O, and J_D are respectively the contact, orbital, and dipolar contributions calculated by the theory omitting the integral products $a_{AB} = s_A^2(O)\,s_B^2(O)$ and $b_{AB} = \langle r^{-3}\rangle_A \langle r^{-3}\rangle_B$. Thus it is necessary to know the values of the nuclear valence shell *s*-electron densities [$s^2(O)$] and the expectation value of r^{-3} for the valence shell *p*-orbitals ($\langle r^{-3}\rangle$).

INDO MO Calculations of $^nJ_{FF}$.—Initially the values of $s^2(O)$ and $\langle r^{-3}\rangle$ for fluorine, optimized previously[16] for the fluorobenzenes ($C_6H_nF_{6-n}$), were used. These reproduced the couplings well, with a correlation of the calculated couplings, J_{FF}^{calc}, against the experimental couplings J_{FF}^{obs}, of slope 1.05, intercept 0.74 Hz, correlation coefficient 0.982 and r.m.s. error 2.21 Hz. For completeness the present data were combined with the previous fluorobenzene data and the values of $s^2(O)$ and $\langle r^{-3}\rangle$ for fluorine reoptimized for the available 80 couplings. These values of 13.310 and 5.514 a.u. respectively are very close to those obtained previously for the fluorobenzene data (13.373 and 5.687 a.u.). The couplings calculated with these values are given in Table 4 and the correlation for all the data, substituted pentafluorobenzenes and fluorobenzene data,[16] of J_{FF}^{calc} against J_{FF}^{obs}, of slope 0.979, intercept 0.294, correlation coefficient 0.982 and r.m.s. error 2.23 Hz, is shown in the Figure.

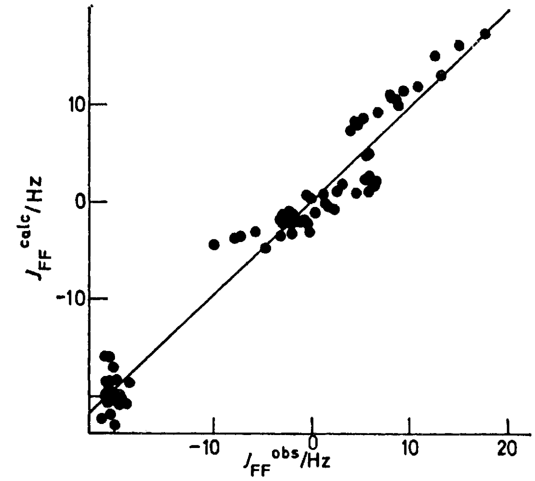
TABLE 4

INDO MO Calculations of the Fermi contact C,[a] orbital, and spin-dipolar O + D[b] contributions to $^nJ_{FF}^{calc}$ for C_6F_5X

	$^3J_{23}$			$^4J_{24}$			$^5J_{25}$			$^4J_{26}$			$^3J_{34}$			$^4J_{35}$		
X	C	O + D	J_{FF}^{calc}	C	O + D	J_{FF}^{calc}	C	O + D	J_{FF}^{calc}	C	O + D	J_{FF}^{calc}	C	O + D	J_{FF}^{calc}	C	O + D	J_{FF}^{calc}
H	−14.20	−5.53	−19.73	−3.07	3.91	0.85	4.28	5.74	10.02	−5.03	1.93	−3.10	−13.79	−6.61	−20.40	−4.78	2.85	−1.93
F	−15.46	−6.42	−21.87	−5.05	2.69	−2.36	3.36	4.15	7.51	−5.05	2.69	−2.36	−15.46	−6.42	−21.87	−5.05	4.15	−0.90
NH_2	−13.34	−6.14	−19.48	−3.83	0.51	−3.32	3.46	5.25	8.71	−3.84	5.02	1.18	−13.56	−6.01	−19.56	−4.39	3.43	−0.96
NO_2	−15.84	−6.29	−22.13	−4.64	7.09	2.44	3.81	5.49	9.30	−4.39	0.16	−4.23	−15.84	−6.83	−22.67	−5.38	−3.25	−2.13
$CH=CH_2$	−12.98	−5.32	−18.30	−3.52	3.57	0.05	3.96	6.82	10.78	−4.16	2.02	−2.14	−12.41	−5.79	−18.20	−4.58	3.30	−1.28
OCH_3	−14.02	−6.01	−20.03	−4.77	1.49	−3.27	3.31	4.75	8.05	−3.12	3.84	0.72	−14.32	−6.20	−20.52	−4.59	1.51	−3.08
CN	−14.48	−5.66	−20.14	−3.31	4.58	1.27	4.37	6.74	11.11	−4.49	1.04	−3.45	−14.18	−6.58	−20.77	−4.67	3.58	−1.09
OH	−14.29	−6.19	−20.48	−4.37	1.11	−3.25	3.35	4.79	8.15	−4.75	4.15	−0.61	−14.40	−6.21	−20.61	−4.64	3.07	−1.57
CHO	−14.28	−5.26	−19.54	−3.31	5.16	1.86	4.39	7.23	11.62	−4.53	0.02	−4.52	−13.78	−6.34	−20.11	−4.93	3.10	−1.83
CH_3	−14.11	−5.54	−19.65	−2.95	3.35	0.40	4.14	6.53	10.68	−4.11	2.34	−1.77	−13.35	−6.44	−19.79	−4.54	3.30	−1.24

[a] The Fermi contact contribution is denoted by C and was calculated with $s^2(O)$ 13.310 a.u. [b] The combined orbital and spin–dipolar contributions are denoted by O + D and were calculated with $\langle r^{-3}\rangle$ 5.514 a.u.

The present calculations confirm the observations of Brown and Davies[14] that the orbital and spin–dipolar terms make significant contributions to all the fluorine–fluorine coupling constants. For the longer range four and five bond couplings the orbital and spin–dipolar contributions are of the same order of magnitude as those of the Fermi-contact contribution, while for the three bond couplings they account for *ca.* 25—30% of the total calculated coupling. The calculations are particularly encouraging in that the relative order and the magnitude of the couplings in any particular compound are correctly predicted. Also the signs are reproduced, except in the cases with couplings near zero.



Correlation of $^nJ_{FF}^{calc}$, from INDO MO theory, with $^nJ_{FF}^{obs}$

TABLE 5

Correlation of individual J_{FF}^{calc} with J_{FF}^{obs}

Coupling	Range	Slope	Intercept	R.m.s. error	Correlation coefficient
23	1.12	1.13	2.99	1.14	0.333
24	13.79	0.44	−0.58	0.79	0.945
25	5.63	0.66	5.11	0.44	0.959
26	14.44	0.38	−1.11	1.09	0.851
34	2.00	0.24	−15.67	1.29	0.139
35	3.64	−5.58	−1.50	0.71	0.103

Substituent effects on particular couplings are reproduced correctly (correlation coefficient >0.85, Table 5) for $^4J_{24}$, $^5J_{25}$, and $^4J_{26}$ which have ranges >5 Hz, although the calculated ranges of the couplings are underestimated. No correlations would be meaningful for $^3J_{23}$ and $^3J_{34}$ as the ranges involved are too small and in aromatic compounds $^3J_{FF}$ values are known to be more susceptible to solvent effects than the longer range J_{FF} values.[10,25] Although the range of $^4J_{35}$ is not appreciably smaller than $^5J_{25}$ it is poorly correlated. The reason for this probably lies in the inability of the

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[25] E. A. Cohen, A. J. R. Bourn, and S. L. Manatt, *J. Magnetic Resonance*, 1969, **1**, 436; M. A. Cooper, *Org. Magnetic Resonance*, 1969, **1**, 363.

INDO wavefunction to adequately describe properties of a function situated in a *meta*-position to a substituent; in the case of $^4J_{35}$ both coupled fluorine nuclei are *meta* to the substituent.

INDO MO Calculations of J_{CF}.—For the calculation of $^nJ_{CF}$, values of $s^2(O)$ and $\langle r^{-3}\rangle$ for fluorine and carbon are necessary. The optimized values for fluorine, calculated above, and literature values for carbon[17] were used in these calculations. In agreement with previous calculations[16,18] the orbital and spin–dipolar terms were found to make significant contributions to all couplings. The magnitudes and substituent effects upon the couplings, however, are poorly reproduced; a similar situation was found for these couplings in the fluorobenzenes[16] $C_6H_nF_{6-n}$, and related compounds.[26] The ranges of the couplings are reported in Table 6.

TABLE 6

Observed and INDO MO calculated ranges of $^nJ_{CF}$ in substituted pentafluorobenzenes

Carbon	n	Observed range [a]	Calculated contact term [b]	Range [a] orbital + spin–dipolar terms [c]
1	2	23.44—10.21	−0.60 to −3.54	−3.88 to −7.99
	3	3.19—0.50	5.33—2.04	−1.15 to −1.55
	4	5.21—3.29	2.15—1.26	2.21—1.80
2	1	−238.90 to −262.12	−162.32 to −196.19	−1.77 to −10.52
	2	14.06—11.02	0.07 to −0.99	−4.11 to −4.50
	3 (4)	4.29—3.19	4.81—4.00	−0.60 to −2.02
	3 (6)	12.32—2.30	9.07—3.96	−1.02 to −2.21
	4	5.21—4.03	1.64—0.77	1.85—1.42
3	1	−245.42 to −255.29	−188.00 to −203.88	−2.84 to −4.83
	2 (2)	17.30—13.73	1.54 to −1.05	−4.00 to −4.48
	2 (4)	13.73—12.76	−0.61 to −1.47	−3.84 to −4.15
	3	3.72—1.33	4.91—2.92	−1.42 to −1.64
	4	5.31—4.71	2.31—0.76	2.27 to 1.47
4	1	−241.64 to −262.85	−189.55 to −197.65	−1.60 to −9.54
	2	13.94—13.33	−0.29 to −1.53	−3.76 to −4.56
	3	5.29—3.19	6.99—4.39	−0.59 to −1.99

[a] The ranges are for substituents which could be calculated, namely X = H, F, NH_2, NO_2, CH=CH_2, OCH_3, CN, OH, CHO, and CH_3. [b] The values of $s^2(O)$ for fluorine and carbon used in the calculations were 13.310 and 4.0318 a.u., respectively. [c] The values of $\langle r^{-3}\rangle$ for fluorine and carbon used in the calculations were 5.514 and 1.692 a.u., respectively.

For the longer range couplings (three to five bonds) the signs and the correct order of magnitude of the couplings are predicted. For $^3J_{C(2)F(6)}$ values, which encompass a significant range, the magnitude and substituent changes are predicted, although the change in the coupling is underestimated (the plot of $^3J_{C(2)F(6)}{}^{calc}$ against $^3J_{C(2)F(6)}{}^{obs}$ has slope 0.50, intercept 1.31, correlation coefficient 0.85 and r.m.s. error 0.94). The orbital and spin–dipolar contributions are *ca.* 25% of the Fermi-contact contribution and are of opposite sign. Thus some of the inadequacies in previous calculations[26,27] of the longer range couplings in the fluoronaphthalenes, fluoropyridines, and fluoroquinolines must lie, in part,* in the exclusive use of only the Fermi-contact term.

However, it is evident that, contrary to the experimental data, the two-bond couplings are always predicted to be negative and to be dominated by the orbital and dipolar terms. Inclusion of these latter terms make no improvement in the prediction of the couplings. The difficulties found here appear to be a general feature in the calculation of these couplings and have been noted previously.[16] Similarly, difficulties were encountered with INDO MO calculations of germinal H–H couplings,[29] and thus they may have a common origin. Geminal couplings in general have been shown to be more susceptible to the effects of the change of substituent,[30] solvent,[31] and geometry[32] than other types of coupling constants. However the magnitude of the difference between the calculated and observed couplings indicates that these effects can only be of secondary importance and that the major deficiency lies in the theoretical approach. Weigert and Roberts[8] were able to predict the correct sign of the geminal coupling in fluorobenzene by the use of extended Hückel MO theory to calculate the Fermi-contact contribution by the Pople–Santry formalism. However, the magnitude of the coupling was again underestimated and, as the present work shows, the deficiencies do not lie in the neglect of orbital and spin–dipolar terms.

Semi-empirical Correlations of $^nJ_{CF}$.—The limited usefulness of the theoretical calculations of $^nJ_{CF}$ dictates the investigation of semi-empirical correlations of these with the various Hammett substituent parameters if the influence of the substituent effects is to be understood. This influence would be expected to be more complex than that upon the shifts, as $^nJ_{CF}$ arises from the interation of the carbon and fluorine nuclei, both of which are influenced by the substituent. Only $^1J_{CF}$ would be

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* Several of the experimental assignments reported in ref. 26, particularly for the fluoronaphthalenes, are in error[28] and this would lead to difficulties in the comparison with the calculated couplings.

[26] D. Doddrell, M. Barfield, W. Adcock, M. Aurangzeb, and D. Jordan, *J.C.S. Perkin II*, 1976, 402.

[27] R. L. Lichter and R. E. Wasylishen, *J. Amer. Chem. Soc.*, 1975, **97**, 1808.

[28] L. Ernst, personal communication. For correct assignment see L. Ernst, *Z. Naturforsch.*, 1975, **30b**, 788; *J. Magnetic Resonance*, 1975, **20**, 544.

[29] M. Barfield and D. M. Grant, *Adv. Magnetic Resonance*, 1965, **1**, 149; J. Murrell, *Progr. N.M.R. Spectroscopy*, 1971, **6**, 1; ref. 1.

[30] M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, 1963, **85**, 1899; J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, 1965, **42**, 1339.

[31] M. Barfield and M. D. Johnston, *Chem. Rev.*, 1973, **73**, 53.

[32] G. E. Màciel, J. W. McIver, N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, 1970, **92**, 4151.

expected to show any simple one-parameter correlations, as the ^{19}F shifts have been shown[38] to correlate well with the attached-carbon chemical shifts in the case of C(4), less well for C(2), and rather poorly for C(3). The correlations of $^1J_{CF}$ for C(2) and C(4) with σ_p, and C(3) with σ_m, are shown in Table 7. The σ_p values for CHO and CH=CH$_2$ were unavailable from the literature and were calculated as 0.62 and 0.11 (±0.16), respectively, from the linear plot of the *para*-carbon chemical shifts [C(4)] against σ_p. The good correlation for C(4) is in keeping with the results of previous studies for *para*-substituted fluorobenzenes[8,9] where the increasing ability to withdraw electrons from the π-systems by a substituent leads to more negative $^1J_{CF}$ values. The poorer correlation for C(2) shows that further effects due to the proximity of the substituent are present. For C(3) the range of couplings is somewhat more limited, but again additional effects appear to be present.

TABLE 7

Correlations of $^1J_{CF}$ with σ_p or σ_m [a]

$^1J_{CF}$	Hammett parameter	Slope	Intercept	R.m.s. error	Correlation coefficient	No. of points used in correlation [b]
$^1J_{C(2)F(2)}$	σ_p	−15.82	−248.24	2.99	−0.918	13
$^1J_{C(3)F(3)}$	σ_m	−10.72	−248.32	1.47	−0.901	11
$^1J_{C(4)F(4)}$	σ_p	−14.93	−251.67	0.99	−0.989	13

[a] σ_p and σ_m are taken from ref. 35, except for those for CHO and CH=CH$_2$; see text. [b] All points were used in the correlations, except that σ_m values for CHO and CH=CH$_2$ were not available.

TABLE 8

Correlation of $^nJ_{CF}$ [a] with equation (3) [b] for C$_6$F$_5$X

Carbon	Coupling	Coefficients *a*	*b*	*c*	J_0	R.m.s. error	*R* [c]	Range of *J*
1	^2J	−9.700	−15.183	6.165	7.637	1.18	0.977	18.23
	^3J	1.653	0.293	−0.602	1.900	0.56	0.781	3.19
	^4J	1.319	−1.143	0.259	3.013	0.38	0.823	1.92
2	^1J	−10.043	−23.306	2.647	−253.806	1.41	0.981	22.43
	^2J	2.347	−0.739	−0.321	11.711	0.54	0.815	3.04
	$^3J(4)$	−0.128	1.063	−0.010	3.870	0.17	0.867	1.10
	$^3J(6)$	−7.947	3.693	0.254	10.215	0.99	0.928	10.02
	^4J	0.661	−0.345	−0.046	4.186	0.25	0.646	1.18
3	^1J	−4.450	−1.692	−1.072	−247.049	0.65	0.976	9.87
	$^2J(2)$	−1.918	−0.911	1.091	14.705	0.77	0.836	5.10
	$^2J(4)$	0.685	−0.622	−0.019	12.817	0.12	0.888	0.97
	^3J	0.707	−2.157	−0.239	2.099	0.24	0.958	2.39
	^4J	0.124	0.230	0.036	5.041	0.09	0.834	0.57
4	^1J	−6.181	−15.070	−0.452	−251.869	0.60	0.995	21.21
	^2J	0.089	−0.541	−0.036	13.529	0.04	0.973	0.61
	^3J	−1.240	1.474	0.142	5.121	0.28	0.877	2.10

[a] All the couplings apart from those for X = CH=CH$_2$, *i.e.* points for 10 substituents, were used in the correlations to C(1) while points for 12 substituents were used in the remaining correlations. [b] *F* and *R* values are from ref. 35 while *Q* values are from ref. 34. [c] Correlation coefficients are for the correlation of the observed couplings with the couplings calculated using equation (3).

In order to assess the importance of mesomeric, inductive, and field effects, all the couplings have been correlated, by the method of least squares, to a dual parameter equation of the form (2). In keeping with previous

$$^nJ_{CF} = J_0 + a\sigma_I + b\sigma_p \qquad (2)$$

work[7] σ_I is assumed to take into account not only through-bond inductive effects, but also field and π-inductive effects, while σ_p has been shown to be a good measure of the mesomeric interactions of the substituent.[33] The resulting correlations are in general poor and point to the complex nature of substituent effects upon $^nJ_{CF}$. For $^1J_{CF}$ there is little improvement in the correlations for C(2) and C(3) with the two-parameter equation as compared to those with the simple one parameter correlation above. In particular, substituent effects upon $^2J_{C(1)F(2)}$, which has a large range of values (15.93 Hz), are poorly correlated which suggest that there is a special effect due to the proximity of the coupled nuclei to the substituent. This type of anomalous effect is particularly well known and has been termed the '*ortho*-effect' in connection with chemical shift correlations.[34] A three parameter empirical equation which successfully rationalises the effect of substituents upon carbon, proton, and fluorine chemical shifts in many aromatic and olefinic systems has been reported recently by Smith and Proulx.[34]

A similar equation of the form (3) is used here to

$$^nJ_{CF} = J_0 + aF + bR + cQ \qquad (3)$$

correlate the $^nJ_{CF}$ values. The *F* and *R* values are those of Swain and Lupton[35] and were used here in the hope that they reflect the field and resonance effects of the substituent. *Q* is the substituent parameter of Schaefer *et al.*[36] defined as P/Ir^3, where *P* is the polarizability of

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[33] I. R. Ager, L. Phillips, T. J. Tewson, and V. Wray, *J.C.S. Perkin II*, 1972, 1979.

[34] W. B. Smith and T. W. Proulx, *Org. Magnetic Resonance*, 1976, **8**, 567.

[35] C. G. Swain and E. C. Lupton, *J. Amer. Chem. Soc.*, 1968, **90**, 4328.

[36] F. Hruska, H. M. Hutton, and T. Schaefer, *Canad. J. Chem.*, 1965, **43**, 2392.

the substituent, I is the ionization potential, and r is the C–X bond length. Q, as well as a similar parameter defined by Sutcliffe *et al.*,[37] has been successfully used to rationalize shift changes in situations where the '*ortho*-effect' is operative. The coefficients of equation (3), determined by the linear least squares procedure, are reported in Table 8. Good correlations were obtained for all cases in which the substituent causes a large variation (>6 Hz) in $^nJ_{CF}$. In particular, the substituent effects upon $^2J_{C(1)F(2)}$ are successfully correlated, and those for $^1J_{C(2)F(2)}$ and $^1J_{C(3)F(3)}$ improved. Similarly the effects upon $^3J_{C(2)F(6)}$ are reasonably well reproduced.

The similarity of substituent effects upon the ^{13}C shifts of *para*-substituted fluorobenzenes and those of substituted pentafluorobenzenes[38] suggests that correlations may exist between couplings in the monosubstituted fluorobenzenes[8] and the corresponding couplings reported here. That such correlations do exist is apparent, but the reliability of the previous data is somewhat open to question in the light of our recent work.[16,39] Thus these correlations have not been pursued here.

Thus, in summary, theoretical calculations successfully reproduce the magnitudes, signs, and substituent dependence of $^nJ_{FF}$. Less success is achieved for $^nJ_{CF}$ and attempts to correlate substituent effects upon these couplings using Hammett and related parameters was appropriate. It has been shown that substituent effects upon $^nJ_{CF}$ are more complex than those upon ^{13}C chemical shifts. Only the $^1J_{C(4)F(4)}$ values are satisfactorily correlated by σ_p. Dual parameter equations do not improve the correlations as effects due to the proximity of the substituent are apparent. A three parameter equation involving F, R, and Q successfully correlates substituent effects upon all $^nJ_{CF}$ values that show a sufficiently large variation with substituent change.

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[38] J. M. Briggs and E. W. Randall, *J.C.S. Perkin II*, 1973, 1789.

[39] L. Ernst, D. N. Lincoln, and V. Wray, *J. Magnetic Resonance*, 1976, **21**, 115.