Additivity of Substituent Effects upon Proton–Fluorine Coupling Constants in Polysubstituted Fluorobenzenes

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Substituent effects upon J_{FH} values in polysubstituted fluorobenzenes are demonstrated to be additive for the substituents F, Cl, Br, I, NO_2, NMe_2, and OMe. An evaluation of the substituent constants by a regression analysis allows the accurate calculation of 230 J_{FH} values in 70 compounds. The consequences of this analysis for the resolution of the ambiguities in the assignment of $^3J_{FH}$ and $^4J_{FH}$ values, and of the sign of $^5J_{FH}$ in many reported J_{FH} values are discussed. The variation of the substituent constants with substituent electronegativity, E_X, are considered and an assessment of the literature reports of the correlation of J_{FH} with E_X is made.

THE characteristic ranges of *ortho*-, *meta*-, and *para*-proton–proton coupling constants and the additivity of substituent effects in polysubstituted benzenes is well established [1-6] and has been used for a number of years

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[1] S. Castellano and R. Kostelnik, *Tetrahedron Letters*, 1967, 5211.

[2] K. Hayamizu and O. Yamamoto, *J. Mol. Spectroscopy*, 1968, **25**, 422.

[3] D. G. de Kowalewski and S. Castellano, *Mol. Phys.*, 1969, **16**, 567.

[4] T. Schaefer, G. Kotowycz, H. M. Hutton, and J. W. Lee, *Canad. J. Chem.*, 1968, **46**, 2532.

[5] J. M. Read, R. W. Crecely, R. S. Butler, J. E. Loemker, and J. H. Goldstein, *Tetrahedron Letters*, 1968, 1215.

[6] J. E. Loemker, J. M. Read, and J. H. Goldstein, *J. Phys. Chem.*, 1968, **71**, 991.

in structural determinations. The additivity of substituent effects upon fluorine–fluorine coupling constants has been established in a wide variety of polysubstituted benzenes,[7] even though there is a considerable overlap of the magnitudes of the *meta*- and *para*-couplings.

Although a large amount of data exists for proton–fluorine coupling constants, J_{FH}, an additivity relationship has not yet been established for highly substituted benzenes; only one paper[8] deals, in any detail, with the empirical calculation of these J values in di- and tri-substituted benzenes by the use of such a scheme. More substituent constants (and hence more J values) are needed in order to describe the effects of substituents upon heteronuclear than upon homonuclear J values; thus, in the homonuclear case, six constants are required for each substituent (two for *ortho*-, three for *meta*-, and one for *para*-), while, in the heteronuclear case, ten constants are required for each substituent (four for *ortho*-, four for *meta*-; and two for *para*-J). This fact, together with the distribution of such J values in a large number of references, accounts for the sparsity in the number of attempts to establish such a relationship.

TABLE 1

Substituent constants,[a] $\Delta J^{\mathrm{X}}_{\mathrm{FH}}$ and unperturbed couplings, ${}^{n}J^{\mathrm{H\ Benzene}}_{\mathrm{FH}}$

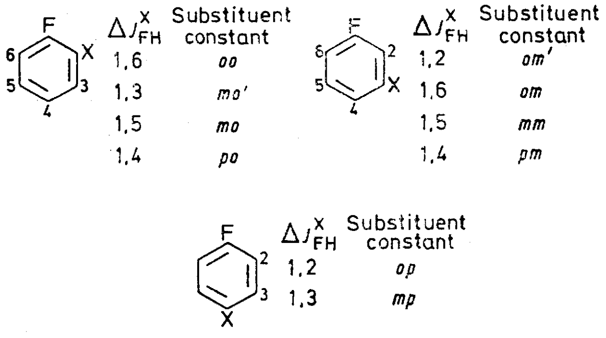
	$\Delta J^{\mathrm{X}}_{\mathrm{FH}}$/Hz										
X	*oo*	*mo′*	*mo*	*po*	*om*	*om′*	*mm*	*pm*	*op*	*mp*	E_{X}[b]
F	1.713(27)	2.319(27)	−0.745(29)	−0.863(31)	0.355(29)	−0.258(34)	1.124(29)	−0.570(38)	−0.564(43)	−1.429(43)	3.90
Cl	0.474(9)	1.978(8)	−0.507(3)	−0.481(8)	0.015(10)	−0.191(3)	0.771(10)	−0.275(6)	−0.459(8)	−0.772(6)	3.15
Br	−0.021(9)	1.379(8)	−0.494(3)	−0.365(5)	−0.263(10)	−0.237(2)	0.624(10)	−0.270(4)	−0.341(7)	−0.630(8)	2.95
I	−0.742(6)	0.645(6)	−0.412(2)	−0.233(3)	−0.538(7)	−0.137(2)	0.360(4)	−0.215(5)	−0.434(3)	−0.417(4)	2.65
NO_2	2.293(7)	1.886(7)	−0.851(4)	−0.638(2)	−0.164(2)	−0.847(3)	0.164(2)	−0.233(1)	−0.758(8)	−0.941(9)	3.35
NMe_2	3.899(3)	3.636(3)	−0.354(8)	−0.517(3)	3.636(3)	−0.266(7)	1.820(3)	−0.211(3)			3.05
OMe	2.599(3)	2.869(3)	−0.445(9)	−0.684(3)	2.300(3)	−0.043(9)	1.487(3)	−0.244(3)	−1.019(1)	−0.720(1)	3.50
r[c]	0.48	0.48	0.67	0.98	0.18	0.13	0.31	0.72	0.68	1.00	

n	${}^{n}J^{\mathrm{H}}_{\mathrm{FH}}$ Benzene/Hz
3	8.819
4	5.520
5	−0.297

[a] The number of times each parameter appeared in the analysis is in parentheses. [b] Substituent electronegativity.[2] [c] Correlation coefficient for the correlation of the substituent constants with E_{X}. In each case only constants determined from more than one measurement were used.

A recent collection of fluorine–coupling constant data[9] enables us to interpret much of the existing data in terms of a simple additivity scheme. This scheme allows us to predict the sign of ${}^{5}J_{\mathrm{FH}}$ in cases where this was not determined and to assign J_{FH} values to specific nuclei, where ambiguities, in the literature, existed for polysubstituted compounds.

Determination of Substituent Constants.—In order to interpret the large number of experimental J_{FH} values it is necessary to define a substituent constant as the change that occurs in the value of the J_{FH} upon substitution of a proton by a substituent X (*i.e.* $\Delta J^{\mathrm{X}}_{\mathrm{FH}} = J^{\mathrm{X\ Benzene}}_{\mathrm{FH}} - J^{\mathrm{H\ Benzene}}_{\mathrm{FH}}$). Thus the substituent constants shown in the Scheme are necessary for any substituent, where the first letter of the constant refers to the orientation of the coupled nuclei and the second refers to the orientation of the substituent and the coupled fluorine (the apostrophe distinguishes the case where the substituent is on the same side of the molecule as the proton). The calculated coupling, ${}^{n}J^{\mathrm{Calc}}_{\mathrm{FH}}$ is then given by equation (1).



SCHEME Substituent constants

$$ {}^{n}J^{\mathrm{Calc}}_{\mathrm{FH}} = {}^{n}J^{\mathrm{H\ Benzene}}_{\mathrm{FH}} + \sum_{i=1}^{4} \Delta J^{\mathrm{X}}_{\mathrm{FH}} \qquad (1) $$

Previously a limited number of these substituent constants were determined by the use of the experimental J_{FH} values in fluorobenzene and the appropriate monosubstituted fluorobenzene.[8] This procedure, however, does not allow substituent constants to be determined for substituents in which data for the appropriate monosubstituted fluorobenzenes are unavailable; it also places undue emphasis on the fluorobenzene data.

In the present treatment these shortcomings are overcome by assuming additivity and also by treating the values for the ' unperturbed ' molecule (${}^{n}J^{\mathrm{H\ Benzene}}_{\mathrm{FH}}$) as unknowns. The test of this assumption is the correspondence of the experimental and calculated J_{FH} values. Thus we are able to write down a set of m linear equations with y unknowns where m is the number of experimental J_{FH} values available and y is the number of substituent

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[7] R. J. Abraham, D. B. Macdonald, and E. S. Pepper, *J. Amer. Chem. Soc.*, 1968, **90**, 147.

[8] J. E. Loemker, K. M. Pryse, J. M. Read, and J. H. Goldstein, *Canad. J. Chem.*, 1969, **47**, 209.

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

TABLE 2

Experimental and calculated J_{FH}/Hz in polysubstituted fluorobenzenes

Compound	Ref.	Exp J_{FH}	Calc J_{FH}
1	*a*	9.18	8.82
		5.76	5.52
		0.35	−0.30
2	*b*	8.06	7.84
		−1.40	−1.16
		4.53	4.77
		10.85	10.53
3	*c*	9.23	9.17
		−0.86	−0.87
		6.46	6.64
		8.19	8.56
4	*d*	8.03	8.25
		4.18	4.09
5	*e*	−2.07	−1.73
		5.70	5.90
		9.95	10.27
		6.87	7.09
		−2.51	−2.02
6	*f*	6.24	6.41
		3.26	3.35
		9.69	9.97
		10.36	10.89
		−2.00	−1.73
		8.71	8.96
		8.17	8.61
		7.64	8.00
		5.03	5.21
7	*g*	9.12	8.92
		−1.68	−1.44
8	*a*	4.46	4.47
		9.81	9.71
		−2.70	−2.59
		8.15	8.22
9	*h*	−2.46	−2.30
		10.43	10.63
		5.60	5.67
		8.61	8.35
10	*i*	9.98	10.07
		6.79	6.79
		−2.64	−3.16
11	*j*	9.64	9.29
		5.01	5.01
		−0.85	−0.78
		7.62	7.50
12	*j*	8.63	8.83
		9.02	8.63
		6.30	6.29
		−0.47	−0.57
13	*j*	4.79	4.75
		8.48	8.36
14	*k*	−2.10	−1.81
15	*j*	8.35	8.38
		7.93	8.17
		5.41	5.52
16	*k*	6.30	6.33
		8.40	8.55
17	*j*	8.61	8.56
		8.69	8.58
		6.45	6.14
		−0.63	−0.57
18	*j*	4.90	4.89
		8.62	8.48
19	*j*	6.13	6.27
		8.54	8.46
		4.33	4.40
20	*j*	8.23	8.23
		3.72	3.60
		5.40	5.47
		4.68	4.71
		7.91	8.02
		7.81	7.99
21	*l*	8.50	8.89
		−2.05	−1.80
22	*k*	−2.20	−2.40
		8.60	8.93
23	*m*	6.40	6.45
		−2.70	−2.87
		7.40	7.45
		10.00	9.73
24	*m*	−2.70	−2.78
		6.80	6.44
		10.70	10.17
		9.30	8.83
25	*j*	9.10	8.80
		4.97	5.03
		−0.52	−0.66
		7.10	6.90
26	*m*	6.20	5.85
		−2.70	−2.86
		7.90	7.59
		10.00	9.45
27	*m*	−2.50	−2.66
		6.30	6.29
		10.30	10.29
		8.40	8.33
28	*j*	6.29	6.17
		−0.24	−0.53
		4.99	5.11
		7.97	8.08
29	*j*	8.14	8.28
		−0.27	−0.51
		5.85	5.88
		8.42	8.68
30	*j*	8.39	8.38
		5.10	5.10
31	*e*	−1.30	−1.10
		6.35	6.23
		7.40	7.82
32	*n*	9.30	9.04
		−1.22	−1.08
		8.00	8.02
33	*m*	9.20	9.17
		7.70	7.80
		−2.70	−2.81
		5.20	5.12
34	*m*	10.10	10.20
		6.00	6.03
		−2.50	−2.53
		7.80	7.61
35	*j*	7.46	7.41
		−0.86	−0.94
		4.61	4.67
		11.40	11.11
36	*j*	8.82	8.65
		−0.53	−0.53
		5.60	5.69
		8.28	7.97
37	*j*	8.13	8.06
		4.71	4.58
38	*k*	6.49	6.46
		3.72	3.73
		10.19	10.35
39	*j*	10.56	10.71
		7.62	7.59
40	*j*	5.80	5.98
		3.49	3.24
		10.59	10.55
		7.91	8.08
		7.48	7.41
		4.34	4.25
41	*j*	8.68	8.42
		5.73	5.70
		7.70	7.80
		11.26	11.47
		8.64	8.53
		−1.58	−1.50
42	*j*	6.36	6.56
		4.11	4.07
		8.43	8.53

TABLE 2 (*Continued*)

Compound	Ref.	Exp J_{FH}	Calc J_{FH}
43	*k*	8.70	9.08
		6.80	6.98
44	*n*	7.18	7.24
		10.43	10.37
45	*n*	7.10	7.09
		10.22	10.09
46	*o*	10.23	10.21
		7.59	7.69
		7.91	7.98
		9.90	9.81
47	*m*	6.60	6.84
		8.00	7.84
		9.80	9.72
48	*m*	6.20	6.24
		8.00	7.98
		9.30	9.44
49	*m*	5.50	5.51
		9.10	9.16
		8.20	8.19
50	*m*	7.70	7.14
		−2.30	−2.52
		11.80	11.91
51	*m*	6.20	6.55
		−2.60	−2.52
		11.60	11.63
52	*m*	−2.60	−2.46
		5.60	5.81
		11.50	11.36
53	*m*	6.80	6.83
		10.00	10.16
		8.80	8.82
54	*m*	6.80	6.68
		10.40	10.28
		8.50	8.32
55	*m*	−2.30	−2.42
		7.70	7.75
		11.80	11.90
56	*m*	−2.40	−2.31
		7.40	7.61
		11.20	11.41
57	*m*	7.60	7.34
		−2.20	−2.17
		11.00	10.69
58	*p*	7.80	7.80
		4.80	4.80
59	*m*	6.20	6.15
		8.00	7.89
		9.70	9.66
60	*m*	6.20	6.21
		−2.70	−2.68
		10.20	10.33
61	*m*	6.60	6.59
		10.50	10.50
		8.50	8.55
62	*m*	−2.30	−2.34
		6.90	6.84
		10.30	10.28
63	*m*	6.60	6.75
		7.80	7.75
		10.00	9.94
64	*m*	6.80	6.81
		−2.60	−2.69
		10.60	10.61
65	*m*	6.70	6.74
		10.40	10.38
		9.00	9.04
66	*m*	−2.40	−2.46
		7.00	6.99
		10.70	10.77
67	*m*	5.40	5.42
		8.20	8.10
		9.30	9.39
68	*m*	5.50	5.48
		−2.70	−2.63
		10.20	10.06

TABLE 2 (*Continued*)

Compound	Ref.	Exp J_{RF}	Calc J_{RF}
69	*n*	6.20	6.33
		10.50	10.41
		7.80	7.82
70	*m*	−2.30	−2.21
		6.50	6.57
		9.60	9.55

Compounds: 1, fluorobenzene; 2, 1,2-difluorobenzene; 3, 1,3-difluorobenzene; 4, 1,4-difluorobenzene; 5, 1,2,3-trifluorobenzene; 6; 1,2,4-trifluorobenzene; 7, 1,3,5-trifluorobenzene; 8, 1,2,3,4-tetrafluorobenzene; 9, 1,2,3,5-tetrafluorobenzene; 10, pentafluorobenzene; 11, 1-chloro-2-fluorobenzene; 12, 1-chloro-3-fluorobenzene; 13, 1-chloro-4-fluorobenzene; 14, 1,2,4,5-tetrachloro-3-fluorobenzene; 15, 1,2-dichloro-4-fluorobenzene; 16, 1,2,4-trichloro-3,6-difluorobenzene; 17, 1-bromo-3-fluorobenzene; 18, 1-bromo-4-fluorobenzene; 19, 1,3-dibromo-4-fluorobenzene; 20, 1-bromo-2,5-difluorobenzene; 21, 1-bromo-2,4,6-trifluorobenzene; 22, 1,3-dichloro-2,4,6-trifluorobenzene; 23, 1-chloro-2,3,4,5-tetrafluorobenzene; 24, 1-chloro-2,3,4,6-tetrafluorobenzene; 25, 1-bromo-2-fluorobenzene; 26, 1-bromo-2,3,4,5-tetrafluorobenzene; 27, 1-bromo-2,3,4,6-tetrafluorobenzene; 28, 1-fluoro-2-iodobenzene; 29, 1-fluoro-3-iodobenzene; 30, 1-fluoro-4-iodobenzene; 31, 1,3-difluoro-2-iodobenzene; 32, 1,3-difluoro-5-iodobenzene; 33, 1,2,3,4-tetrafluoro-5-iodobenzene; 34, 1,2,3,5-tetrafluoro-4-iodobenzene; 35, 1-fluoro-2-nitrobenzene; 36, 1-fluoro-3-nitrobenzene; 37, 1-fluoro-4-nitrobenzene; 38, 1-fluoro-2,4-dinitrobenzene; 39, 1,3-difluoro-4,6-dinitrobenzene; 40, 1,4-difluoro-2-nitrobenzene; 41, 1,3-difluoro-4-nitrobenzene; 42, 1-chloro-2-fluoro-4-nitrobenzene; 43, 1,2-dibromo-4,5-difluoro-3-nitrobenzene; 44, 1-chloro-5-fluoro-2,4-dinitrobenzene; 45, 1-bromo-5-fluoro-2,4-dinitrobenzene; 46, 1-bromo-2-chloro-4,5-difluorobenzene; 47, 1-chloro-3-*NN*-dimethylamino-2,4,5-trifluorobenzene; 48, 1-bromo-3-*NN*-dimethylamino-2,4,5-trifluorobenzene; 49, 1-*NN*-dimethylamino-2,5,6-trifluoro-3-iodobenzene; 50, 1-chloro-4-*NN*-dimethylamino-2,3,5-trifluorobenzene; 51, 1-bromo-4-*NN*-dimethylamino-2,3,5-trifluorobenzene; 52, 1-*NN*-dimethylamino-2,3,6-trifluoro-4-iodobenzene; 53, 1-chloro-2-*NN*-dimethylamino-3,4,6-trifluorobenzene; 54, 1-bromo-2-*NN*-dimethylamino-3,4,6-trifluorobenzene; 55, 1-chloro-4-*NN*-dimethylamino-2,3,6-trifluorobenzene; 56, 1-bromo-4-*NN*-dimethylamino-2,3,6-trifluorobenzene; 57, 1-*NN*-dimethylamino-2,3,5-trifluoro-4-iodobenzene; 58, 1-fluoro-4-methoxybenzene; 59, 1-bromo-2,4,5-trifluoro-3-methoxybenzene; 60, 1-bromo-2,3,5-trifluoro-4-methoxybenzene; 61, 1-bromo-3,4,6-trifluoro-2-methoxybenzene; 62, 1-bromo-2,3,6-trifluoro-4-methoxybenzene; 63, 1-chloro-2,4,5-trifluoro-3-methoxybenzene; 64, 1-chloro-2,3,5-trifluoro-4-methoxybenzene; 65, 1-chloro-3,4,6-trifluoro-2-methoxybenzene; 66, 1-chloro-2,3,6-trifluoro-4-methoxybenzene; 67, 2,4,5-trifluoro-1-iodo-3-methoxybenzene; 68, 2,3,5-trifluoro-1-iodo-4-methoxybenzene; 69, 3,4,6-trifluoro-1-iodo-2-methoxybenzene; 70, 2,3,6-trifluoro-1-iodo-4-methoxybenzene.

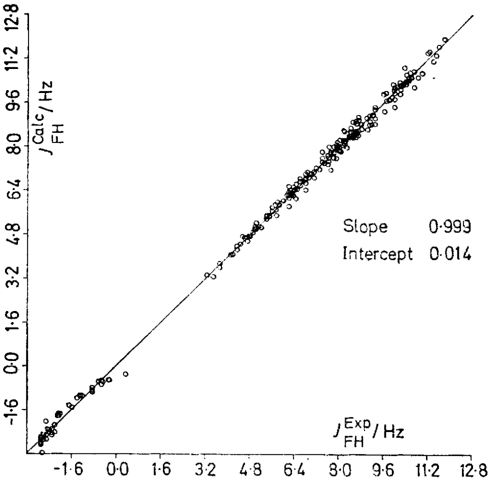
[a] V. Wray and L. Ernst, unpublished results. [b] L. Ernst, D. N. Lincoln, and V. Wray, *J. Magnetic Resonance*, 1976, **21**, 115. [c] D. B. Macdonald, *Chem. Comm.*, 1967, 686. [d] J. E. Loemker, J. M. Read, and J. H. Goldstein, *J. Mol. Spectroscopy*, 1969, **5**, 284. [e] R. J. Abraham and M. A. Cooper, *J. Chem. Soc.* (*B*), 1968, 1094; R. J. Abraham, D. B. Macdonald, and E. S. Pepper, *ibid.*, 1967, 835. [f] R. J. Abraham, M. A. Cooper, and D. B. Macdonald, *Chem. Comm.*, 1968, 1285. [g] V. Wray and D. N. Lincoln, *J. Magnetic Resonance*, 1975, **18**, 374. [h] E. Lustig and P. Diehl, *J. Chem. Phys.*, 1966, **44**, 2974. [i] K. Schaumburg, D. Gillies, and H. J. Bernstein, *Canad. J. Chem.*, 1968, **46**, 503. [j] J. E. Loemker, K. M. Pryse, J. M. Read, and J. H. Goldstein, *Canad. J. Chem.*, 1969, **47**, 209. [k] H .S. Gutowsky, C. H. Holm, A. Saika, and G. A. Williams, *J. Amer. Chem. Soc.*, 1957, **79** 4596. [l] R. G. Jones and R. L. Williams, *Spectrochim. Acta*, 1967, **23A**, 15. [m] J. Burdon, D. R. King, and J. C. Tatlow, *Tetrahedron*, 1966, **22**, 2541. [n] H. M. Hutton, B. Richardson, and T. Schaefer, *Canad. J. Chem.*, 1967, **45**, 1795. [o] E. Lustig, D. N. Lincoln, and V. Wray, *J. Magnetic Resonance*, 1976, **21**, 509. [p] N. Muller and D. T. Carr, *J. Phys. Chem.*, 1963, **67**, 112. Couplings are listed in increasing positional order, *e.g.* for compound 12 the *J* values are in the order 23, 24, 25, 26, 34, 35, 36, 45, 46, and 56.

constants plus the three ' unperturbed ' J_{FH} values and solve for the best least-squares fit.[10]

Initially the *ortho-* and *meta-*J_{FH} values which were ambiguous and those *para-*J_{FH} values whose sign had not been determined were left out. Then these J_{FH} values were assigned and included in the final analysis. Of the 73 compounds available for analysis, three gave calculated J_{FH} values that were not predicted by additivity. These compounds, 1,3-difluoro-2,4,6-trinitrobenzene,[11] 1-*NN*-dimethylamino-3,5,6-trifluoro-2-iodobenzene,[12] and 3,4,6-trifluoro-1-methoxy-2-nitrobenzene [13] were excluded from the final computation.

RESULTS AND DISCUSSION

The substituent constants of F, Cl, Br, I, NO_2, NMe_2, and OMe, calculated by the regression analysis, are given in Table 1; the observed J_{FH} values and those calculated with the aid of the substituent constants (Table 1) are compared in Table 2 and the Figure. A total of 230 J_{FH} values from 70 compounds have been analysed.



Correlation of experimental and calculated J_{FH} values

Inspection of Table 2 and the Figure indicates that the additivity scheme gives good agreement between the experimental and calculated J_{FH} values with a r.m.s. error of 0.19 Hz over a range of 14.5 Hz. The small r.m.s. deviation and random distribution of the points suggest that any systematic error arising from the additivity scheme is small and could well be accounted for by experimental uncertainties. Solvent studies on fluorobenzene and some polysubstituted derivatives [14] have shown that changes of up to 0.9 Hz can be expected in $^3J_{FH}$ with smaller changes in $^4J_{FH}$ and $^5J_{FH}$; reports on the same compound by different authors also show that similar variations can occur.[9]

Statistically, 5% of the J_{FH} values would be expected to have errors greater than two standard deviations if the errors are random,[15] and this is found to be the case here. One of these is $^5J_{FH}$ in fluorobenzene. Thus the use of this J_{FH} as a starting parameter for the derivation of substituent constants must lead to serious errors in all the calculated values of $^5J_{FH}$ as can be seen in the results of Loemker *et al.*[8] for these $^5J_{FH}$ values. An error in the reported sign of this $^5J_{FH}$ is unlikely as it has been subjected to careful analyses.[16-18] The non-addivity of the J_{FH} values in the three compounds noted above remain inexplicable.

A practical application of the analysis is that it allows the unambiguous assignment of $^3J_{FH}$ in compounds 27, 34, 53—55, 61, 65, and 69, and of $^4J_{FH}$ in compounds 26, 33, 47—49, 59, 63, and 67. Similarly the ambiguity in the sign of $^5J_{FH}$ for compounds 14, 21—24, 26, 27, 33, 34, 50—52, 60, 62, 64, 66, and 68 is resolved; it turns out to be negative. Even though the sign of the small $^5J_{FH}$ in fluorobenzene is incorrectly calculated, its value is shown to be the most positive of all the known $^5J_{FH}$ values.

There are several papers [14,19-21] dealing with the correlation of J_{FH} and substituent electronegativity (E_X). As substituent effects are shown here to be additive these relationships should be evident as correlations between the substituent constants and E_X. The results of these correlations (Table 1) indicate that only *po* and *mp* correlate well with E_X; if the errors in the substituent constants [estimated from (r.m.s.)/$\sqrt{(n-1)}$ where n is the number of times the parameter appeared in the analysis (Table 1)] are taken into account then poorer correlations are obtained for *mo*, *pm*, and *op*. The correlations of *po* and *pm*, and hence $^5J_{FH}$ with E_X have been pointed out previously,[19,21] while the correlation of *mp* and hence $^4J_{FH}$, with a substituent *para* to F, and E_X was surmised by Loemker *et al.*[19] from three results but is here clearly demonstrated. The non-linear correlations of the other substituent constants clearly indicates that the use [19,21] of a limited number of substituents can lead to fortuitous linear correlations. Similarly the deviations from a linear correlation of $^4J_{FH}$ with $^3J_{FH}$ in *para*-substituted fluorobenzenes are accounted for by the irregular correlation of *op* with *mp*

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and are not caused solely by solvent effects as suspected previously.[14]

In conclusion we have demonstrated the applicability of an additivity scheme for substituent effects upon J_{FH} in polysubstituted fluorobenzenes, which clarifies ambiguities regarding the assignment and sign of several J_{FH} values. The correlations of the substituent constants with E_X enables one to assess previous correlations of J_{FH} with E_X.

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