distributions,[32] its application to the theoretical calculations of vicinal coupling constants appears very alluring. Because of the strong similarity of behavior of all other coupling constants in the series of N-substituted pyridines and monosubstituted benzenes, the experimental correlations of these parameters with the nature of the substituent will be discussed in a forthcoming paper dealing with the latter series of compounds.

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The Nuclear Magnetic Resonance Spectra of Fluorobenzenes. II. The Effect of Substituents on the *meta* and *para* Fluorine–Fluorine Coupling Constants[1a]

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Abstract: A breakdown of the *meta* and *para* F–F couplings in fluorobenzenes on the basis of additive substituent contributions enables both the magnitude and sign of any such F–F coupling to be calculated from the substituent contributions given here. The agreement between the calculated and observed couplings is, in general, within the experimental error of the latter and in those cases where the signs are known these are reproduced precisely. These couplings vary from *ca.* +5 to +18 cps for the *para* coupling and from *ca.* −20 to +20 cps for the *meta* coupling. The substituent contributions show a linear dependence on the Hammett σ value of the substituent, in contrast to the analogous H–H couplings, and also, more surprisingly, the substituent contributions change sign in going from *ortho–ortho* to *ortho–para* positions. These trends, and the contrast between FF and (FH and H–H) couplings, are shown to be due to the π electron contribution to the F–F couplings.

Proton–proton couplings in aromatic systems are known to fall within characteristic ranges depending on the orientation of the coupled protons; *e.g.*, Emsley, *et al.*, quote J_{ortho} = 7.0–9.2 cps, J_{meta} = 1.1–3.1 cps, and J_{para} = 0.0–0.7 cps.[2] These characteristic values have been used extensively in structural determinations for a number of years. The analogous proton–fluorine couplings may also be used in this manner although as the characteristic ranges of the *ortho* and *meta* couplings overlap considerably (Emsley, *et al.*, quote J_{ortho} = 6.2–10.1 cps, J_{meta} = 6.2–8.3 cps, and J_{para} = 2.1–2.3 cps),[3] these only distinguish the *para* couplings.

However, the analogous fluorine–fluorine couplings, for which there are a large amount of data in the literature,[4–6] cannot be used at all to obtain structural information. Previous workers[2,7] in this field have attempted to define characteristic ranges of values of these couplings, but, as more data became available, these "ranges" overlap so considerably as to be of little use to the structural chemist.

The *ortho* F–F couplings are virtually constant (*ca.* −19 to −21 cps)[3,7] and independent of the substituents and we will not consider them further. However, this small range of values means that the determination of the negative sign of this coupling in a few compounds[1,8] may be safely extrapolated to all *ortho* F–F couplings. We use this assumption and adjust all the relative sign data reported to agree with this. In contrast, the *para* and particularly the *meta* F–F couplings show amazingly large variations. We shall show that it is possible to obtain *para* F–F couplings ranging from +5 to +18 cps and *meta* couplings from −20 to +24 cps. The range of values for the *meta* coupling overlaps those of both the *ortho* and *para* couplings and is so large that the concept of characteristic values becomes too vague to be meaningful. We shall show that it is possible to interpret all the existing data on the basis of a simple scheme which considers the effects of substituents on these couplings explicitly. Furthermore, in many compounds, the sign of the *meta* coupling has not been determined. The scheme presented here predicts the signs of these couplings. In the cases subsequently reported,[9,10] these predictions were confirmed. Pre-

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(1) (a) Part I: R. J. Abraham, D. B. Macdonald, and E. S. Pepper, *J. Chem. Soc., Sect. B*, 835 (1967); (b) Mellon Institute Visiting Fellow, 1966–1967; The University of Liverpool, Liverpool, England; (c) Mellon Institute; (d) Smith, Kline and French Laboratories Ltd.

(2) J. W. Emsley, J. Freeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, Ltd., Oxford, 1966, p 770.

(3) See ref 2, p 903.

(4) N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Mol. Phys.*, **8**, 131 (1964).

(5) I. J. Lawrenson, *J. Chem. Soc.*, 1117 (1965).

(6) J. Homer and L. F. Thomas, *ibid.*, 141 (1965).

(7) E. Lustig and P. Diehl, *J. Chem. Phys.*, **44**, 2974 (1966).

(8) L. Snyder and E. W. Anderson, *ibid.*, **42**, 3336 (1965).

(9) W. B. Moniz and E. Lustig, *ibid.*, **46**, 366 (1967).

(10) M. G. Hogben, R. S. Gray, and W. A. G. Graham, *J. Am. Chem. Soc.*, **88**, 3457 (1966).

liminary accounts of these results for the *meta* couplings have been given by us[11] and other workers.[12]

Table I. Substituent Constants for *meta* and *para* F–F Couplings[a]

	meta couplings (J_0 = 5.8 cps) Substituent contribution, cps			*para* couplings (J_0 = 18.1 cps) Substituent contribution, cps
Substituent	*ortho–ortho*	*ortho–para*	*meta–meta*	
NH_2	7.2	−8.7	0.5	−2.9
OH	4.7	(−7.7)	−0.8	−3.0
CH_3	0.7	−2.0	(0.1)	−0.3
Ph	(0.6)	(−1.6)	(0.4)	(−0.3)
H	0.0	0.0	0.0	0.0
F	−0.1	−3.8	−0.3	−3.2
Cl	−3.2	−0.4	0.7	−2.0
Br	(−3.4)	(−0.5)	(0.1)	(−2.1)
I	−3.1	(0.5)	(0.7)	(−1.4)
CF_3	−5.5	4.2	2.0	0.0
CN	−5.7	(4.3)	(1.9)	(−0.3)
NO_2	−8.2	5.6	2.3	−0.6

[a] The values in parentheses have been obtained from only one measured coupling constant and are, therefore, not "best fit values."

The Determination of the Substituent Constants

In order to interpret the large amount of experimental data on the *meta* and *para* F–F couplings, it was necessary to make some simplifying assumptions. The basic assumption made here is that the effects of the substituents on the coupling constants are additive. In the case of the *para* couplings, only one parameter is needed to define the influence of the substituent as the four possible substituent positions in *p*-difluorobenzene are all equivalent. Thus on this basis any *para* F–F coupling should be given by adding the substituent contributions to the coupling in *p*-difluorobenzene. For the *meta* coupling the situation is more complex as there are now three different positions in 1,3-difluorobenzene: the 2, 4 or 6, and 5 positions. We define the three substituent constants as *ortho–ortho* (2), *ortho–para* (4 or 6), and *meta–meta* (5), reflecting the positions of the substituent from the coupled F nuclei. Again therefore any *meta* F–F coupling should be given by the coupling in *m*-difluorobenzene plus the additive substituent contributions. It is recognized that this additivity assumption is a "first-order" approximation; however, it will be shown that there is generally good agreement between the observed and calculated couplings. In order to obtain the substituent constants and also the values of the couplings in *m*- and *p*-difluorobenzenes (which have not yet been experimentally determined), all the available couplings were written down following the additivity scheme and the resultant set of *m* linear equations in *r* unknowns solved for the best least-squares fit.

In the case of the *para* couplings this was quite straightforward. All the *para* F–F couplings are positive, the smallest value being found in perfluoro compounds (*e.g.*, +6 cps in hexafluorobenzene); thus no evaluation of the sign was necessary. Also there is much less data available, owing partly to the fact that there is always only one distinct *para* F–F coupling for each molecule. The additivity rule led to the determination of nine variables (eight substituent constants plus J_0, the coupling constant in the reference compound *p*-difluorobenzene) from 28 equations of conditions. These substituent constants are given in Table I and the observed and calculated *para* couplings in Tables II and IV. In addition to these values, couplings involving other substituents were known, but with only one compound for each substituent group. Thus each of these substituent constants is defined by the experimental value of the coupling constants and does not provide a test of the additivity scheme. In these cases the substituent constants are listed in parentheses in Table I and the calculated couplings are not given with the observed couplings in the tables.

The determination of the *meta* F–F substituent constants was much more complex. There are three different substituent constants for each group which trebles the number of unknowns. Also the *meta* couplings can be of either sign and in many of the compounds the sign is not known. Thus it was necessary to start from the few compounds in which the signs were known and predict the signs of the *meta* couplings in all the other compounds. Furthermore in many compounds there is more than one *meta* coupling and these are often not uniquely assigned to the various ^{19}F nuclei. Again this assignment had to be made. Finally, inspection of the available experimental data seemed to indicate that some of the data for the nitro and amino compounds contained large experimental errors (± 1–2 cps). In order not to distort the values of the substituent constants for the remaining groups but at the same time to obtain the large substituent constants for the nitro and amino groups, the following procedure was adopted. The substituent constants for all the groups except nitro and amino (20 variables including J_0, the coupling constant in *m*-difluorobenzene) were obtained from the solution of 49 equations of condition. These values were then inserted into the equations involving the nitro and amino compounds and the six unknown substituent constants evaluated from 24 further equations of condition. These substituent constants are given in Table I and the observed and calculated couplings in Tables III and IV. As with the *para* couplings, these were some more substituent constants which were found in only one compound. These compounds were usually the pentafluorophenyl compounds (Table IV) in which case the determination of the signs of all the *meta* couplings and the assignment of J_{26} and J_{35} is still required. These mostly follow from the values for similar substituent groups (*e.g.*, the values for Br are very similar to Cl). The assignment is given in Table IV and where the value of the coupling has been used to define the substituent constant only the predicted sign of the coupling is given in parentheses. For the hydroxyl and methyl groups, the available data are limited to one or two compounds plus the pentafluorophenyl derivatives. Also in the latter the values of J_{26} and J_{35} are very similar (Table IV). In these cases it was not possible to make an unambiguous assignment of J_{26} and J_{35} although the signs of these follow from a consideration of the remaining substituent contributions; *e.g.*, in pentafluorophenol, J_{26} should be positive and J_{35} negative but J_{26} could be either +2.8 or +3.4 cps (Table IV). Similarly in pentafluorotoluene J_{25} and J_{35} should both be negative but they could be either −0.6 or −1.8 cps. This

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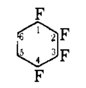
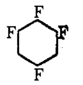
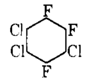
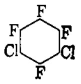
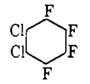
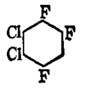
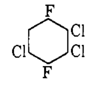
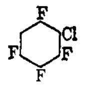
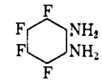
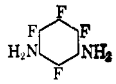
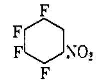
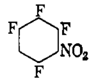
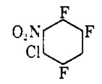
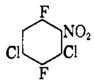
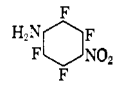
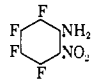
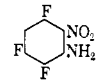
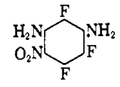
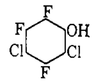
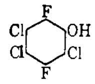
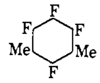
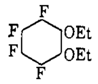
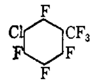
[11] R. J. Abraham, D. B. Macdonald, and E. S. Pepper, *Chem. Commun.*, 542 (1966).

[12] A. Peake and L. F. Thomas, *ibid.*, 529 (1966).

Table II. Observed and Calculated *para* F–F Coupling Constants in Fluorobenzenes

Entry	Compd	Coupling[k]	Ref	Entry	Compd	Coupling	Ref
1		12.0 (11.7)[m]	*a*	2		11.02 (11.7)	*b*
3		9.0 9.05 (9.0)	*c* *d*	4		7.9 7.77 (7.8)	*c* *d*
5		7.4 7.8 (7.6)	*c* *d*	6		+11.2 (11.0)	*f*
7		12.0 (12.2)	*g*	8		9.8 (9.7)	*c*
9		6.2 (6.0)	*h*	10		6.6 (6.0)	*h*
11		11.9 (11.1)	*i*	12		10.4 (11.1)	*i*
13		+11.9(12.4)	*j*	14		14.4 (13.6)	*g*
15		5.3 (8.3)	*h*	16		8.8 (8.3)	*h*
17		+12.8 (11.5)	*l*	18		8.2 (8.6)	*h*
19		8.5 (8.0)	*c*	20		9.8 (9.3)	*c*
21		10.9 (11.0)	*j*	22		6.1 (6.1)	*j*
23		6.0 (6.1)	*j*	24		9.8 (9.7)	*e*

[a] C. Barbier, H. Faucher, D. Gagnaire, and A. Rousseau, *J. Chim. Phys.*, **63**, 283 (1966). [b] E. Lustig and P. Diehl, *J. Chem. Phys.*, **44**, 2974 (1966). [c] P. Bladon, D. W. A. Sharp, and J. M. Winfield, *Spectrochim. Acta*, **20**, 1033 (1964). [d] N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Mol. Phys.*, **8**, 131 (1964). [e] J. J. Burke, private communication. [f] D. F. Evans, *Mol. Phys.*, **6**, 179 (1963). [g] H. S. Gutowsky, C. H. Holm, A. Saika, and G. A. Williams, *J. Am. Chem. Soc.*, **79**, 4596 (1957). [h] J. Homer and L. F. Thomas, *J. Chem. Soc.*, *Sect. B*, 141 (1966). [i] A. Peake, Thesis. [j] L. Cavalli, *J. Chem. Soc.*, *Sect. B*, 384 (1967). [k] The coupling shown is always between the fluorine in the 1 and 4 positions. [l] See ref 8. [m] The calculated coupling constants are given in parentheses.

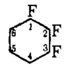
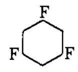
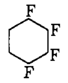
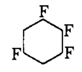
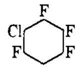
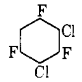
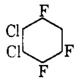
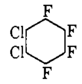
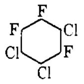
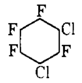
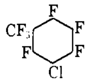
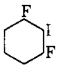
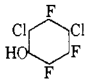
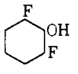
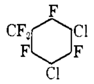
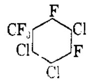
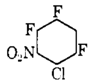
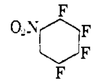
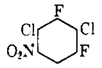
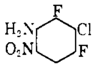
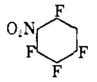
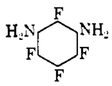
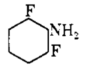
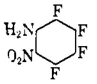
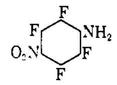
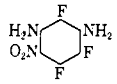
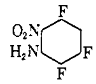
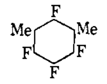
introduces some extra uncertainty into the substituent constants in these cases, but this is not particularly significant.

There are some more measurements of F–F couplings in perfluorophenyl derivatives of phosphorus and other atoms (Sn, Hg, Ni, Pd)[4,10,13] which we have not included in our treatment, mainly because of the limited applicability of such substituent constants. Before we consider the substituent group contributions it is necessary to inspect in detail the observed and calculated couplings.

The Observed and Calculated Coupling Constants. The data for the *para* couplings cover 24 compounds in Table II and seven compounds in Table IV (apart from those which define the substituent contributions) and involve eight unknowns. The root-mean-square deviation of the observed and calculated couplings is *ca.* 0.5 cps over a range of 10 cps. Inspection of Tables II and IV shows also that the additivity rule gives, in general, good agreement with experiment. It is not clear whether the deviations from the rule are systematic or due to experimental error. In the few cases in which the coupling has been measured by a number of authors, there can be a spread of up to *ca.* 1 cps in the value. For example, in pentafluoroaniline J_{25} has been reported as 4 cps[6] (4.9 cps in Table IV). In only one compound (entry 15, Table II) is the difference between the observed and calculated coupling much larger than 1 cps and it is probably significant that the spectrum of this compound was degenerate and difficult to analyze.[6]

(13) F. J. Hopton, A. J. Rest, D. T. Rosevear, and F. G. A. Stone, *J. Chem. Soc.*, *Sect. A*, 1326 (1966).

Table III. Observed and Calculated *meta* F–F Coupling Constants in Fluorobenzenes

Entry	Compd	Coupling[o]	Ref	Entry	Compd	Coupling	Ref
1		+6.42 (+5.7)[p]	*a*	2		+5.84 (+5.5)	*b*
3		+1.4 (+1.8)	*c*	4		J_{13} + 5.74 (+5.4) J_{35} + 1.73 (+1.6)	*d*
5		J_{13} 4.9 (+4.9) J_{35} 1.0 (+1.2) J_{15} 1.3 (−1.6)	*e*	6		1.9 (+1.9)	*f*
7		+2.3 (+2.2)	*g*	8		+1.7 (+2.1) +2.5	*g* *e*
9		0.8 (−0.9)	*e, g*	10		2.3 (−2.0)	*e,g*
11		J_{13} 9.5 (+9.2) J_{15} 4.3 (−4.2) J_{35} 2.3 (+2.7)	*h*	12		+2.3 (+2.7)	*i*
13		1.9 (−2.5)	*e*	14		+10.28 (+10.5)	*a*
15		5.8 (+6.1)	*h*	16		7.5 (+7.1)	*j*
17		+3.8 (+3.9)		18		J_{15} + 10.5 (+7.5) J_{24} + 3.6 (+4.2)	*k*
19		4.2 (+4.5)		20		3.1 (−3.8)	*l*
21		J_{13} +4.9 (+7.3) J_{15} −6.2 (−6.4) J_{35} +10.0 (+11.0)	*k*	22		−6.6 (−6.3)	*k*
23		0 (+0.2)	*m*	24		+12.1 (+13.0)	*i*
25		J_{13} −5.9, 6.4 (−4.5) J_{24} +8.8, 7.7 (+7.9)	*k, m*	26		J_{13} +8.8 (+7.7) J_{46} −9.5 (−9.5)	*k*
27		+3.7 (+2.8)	*k*	28		+8.6 (+8.0)	*k*
29		0 (+0.4)	*n*	30		0.0 (+0.1)	*i*

[a] R. J. Abraham, D. B. Macdonald, and E. S. Pepper, *J. Chem. Soc., Sect. B.*, 835 (1967). [b] R. G. Jones, R. C. Hirst, and H. J. Bernstein, *Can. J. Chem.*, **43**, 683 (1965). [c] C. Barbier, H. Faucher, P. Gagnaire, and A. Rousseau, *J. Chim. Phys.*, **63**, 283 (1966). [d] E. Lustig and P. Diehl, *J. Chem. Phys.*, **44**, 2974 (1966). [e] P. Bladon, D. W. A. Sharp, and J. M. Winfield, *Spectrochim. Acta*, **20**, 1033 (1964). [f] D. F. Evans, *Mol. Phys.*, **6**, 179 (1963). [g] N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Mol. Phys.*, **8**, 131 (1964). [h] J. J. Burke, private communication. [i] R. J. Abraham, D. B. Macdonald, and E. S. Pepper, *Chem. Commun.*, 542 (1966). [j] R. E. Richards and T. Schaefer, *Trans. Faraday Soc.*, **54**, 1443 (1958). [k] A. Peake and L. F. Thomas, *Chem. Commun.*, 529 (1966). [l] H. S. Gutowsky, C. H. Holm, A. Saika, and G. A. Williams, *J. Am. Chem. Soc.*, **79**, 4596 (1957). [m] J. Homer and L. F. Thomas, *J. Chem. Soc., Sect. B*, 141 (1966). [n] L. Cavalli, *ibid.*, 384 (1967). [o] In those compounds for which only one coupling is given, this coupling is always between the F nuclei and the 1 and 3 positions. [p] The calculated coupling constants are given in parentheses.

It would appear therefore that with the available data any deviations from the additivity rule are obscured by the experimental errors.

There are some interesting predictions which arise; in particular the estimated coupling in *p*-difluorobenzene (or any cyano or nitro derivative) should be unusually large (*ca.* 18 cps). This large coupling would explain why the *p*-difluorobenzene spectrum is deceptively simple[14–16] as the couplings between like nuclei in the molecule (H–H *ortho ca.* 8 cps and F–F *ca.* 18 cps) are

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(14) W. G. Paterson and E. J. Wells, *J. Mol. Spectry.*, **14**, 101 (1964).

(15) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).

(16) H. S. Gutowsky, L. H. Meyers, and D. W. McCall, *J. Chem. Phys.*, **23**, 982 (1955).

Table IV. Observed and Calculated *meta* and *para* F–F Couplings in Pentafluorophenyl Compounds

Substituent	*meta* couplings, cps J_{24}	 J_{26}	 J_{35}	*para* couplings, cps J_{35}	Ref
NH_2	6.9 (−7.1)[g]	4.6 (+5.5)	2.6 (−2.4)	4.9 (5.6)	*a*
OH	6.1 (−)	2.8 (+2.6)	3.4 (−2.8)	4.4 (5.5)	*b*
F	−4 (−2.3)	−4 (−2.3)	−4 (−2.3)	+6 (5.3)	*c*
Ph	0	1.5 (−)	1.5 (−)	8.2	*d*
CH_3	~0 (−0.4)	0.6 (−1.4)	1.8 (−)	8.5 (8.2)	*a*
H	1.3 (+1.5)	2.3 (−2.2)	1.2 (−2.0)	8.8 (8.5)	*a*
Cl	1.0 (+1.1)	5.3 (−5.4)	2.0 (−1.3)	6.2 (6.5)	*a, b*
Br	1.1 (+)	5.5 (−)	1.8 (−)	6.4	*a, b*
I	+2.1 (+)	−4.95 (−5.3)	−1.22 (−)	+7.15	*a, e*
CF_3	5.7 (+5.8)	7.6 (−7.7)	<1 (0.0)	8.4 (8.5)	*a*
CN	5.9 (+)	7.8 (−7.9)	<1 (0)	8.2	*a*
NO	+6 (+7.2)	−10.0 (−10.3)	0 (+0.4)	. . . (7.9)	*f*

[a] I. Lawrenson, *J. Chem. Soc.*, 1117 (1965). [b] N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Mol. Phys.*, **8**, 131 (1964). [c] L. Snyder and E. W. Anderson, *J. Chem. Phys.*, **42**, 3336 (1965). [d] L. Cavalli, private communication. [e] W. B. Moniz and E. Lustig, *J. Chem. Phys.*, **46**, 366 (1967). [f] A. Peake and L. F. Thomas, *Chem. Commun.*, 529 (1966). [g] The calculated couplings are given in parentheses except for those substituents for which there is only one measured coupling constant. In these cases only the predicted sign of the coupling is given.

much greater than the differences in the HF couplings (H–F *ortho ca.* 10 cps and H–F *meta ca.* 6 cps[3]). Also with the substituent groups considered here the *para* F–F coupling will always be positive.

The data for the *meta* F–F couplings are both more numerous and more complex than that of the *para* couplings in that the calculated couplings make many predictions as to the signs and assignments of the *meta* couplings. The data excluding the nitro and amino groups gave 49 equations in 20 unknowns with a root-mean-square deviation of observed minus calculated coupling constants of 0.3 cps over a range of couplings from *ca.* −5 to +10 cps. The deviation is well within the experimental error of most of the data so that there is, in general, excellent agreement with the observed data. Furthermore the calculated values reproduce precisely all the available sign determinations on these *meta* F–F couplings. In Table III, this includes entries 1, 2, 3, 4, 7, 8, 12, and 14. In particular the recent determinations of the signs and assignments of the three *meta* couplings in perfluoroiodobenzene obtained from a complete analysis of the spectrum at low magnetic field strengths[9] (Table IV) were predicted precisely by our original substituent parameters[11] based on the absolute values of the couplings in this compound obtained by earlier investigators. The recent experimental determinations of the change in sign of J_{24} in perfluorophenyl compounds on going from perfluoroaniline to perfluorobenzoyl chloride[10] is precisely what would be predicted from Table IV. There are, however, many couplings in Tables III and IV whose signs have yet to be determined and the evaluation of these signs would provide a critical test of the calculated values given here.

For the nitro and amino compounds the experimental data gave rise to 24 equations in six unknowns, with a root-mean-square deviation of the observed from the calculated couplings of *ca.* 1 cps over a range of from *ca.* −10 to +10 cps. Inspection of Tables III and IV shows the generally reasonable agreement with experiment and the calculated values again reproduce all the available sign determinations, even the striking phenomena of couplings of large magnitudes but opposite signs in the same molecule. Furthermore the additivity scheme gives clearly defined assignments and signs of the *meta* couplings in those compounds for which these cannot be found from the analysis. In particular we have changed the admitted tentative assignments given previously for the pentafluorophenyl derivatives[4,5] (Table IV) and also the assignments for entry 26 (Table III).[6] In this molecule the AA′XX′ spectrum gives only the numerical values of the two *meta* couplings. The assignments and signs are not determined.

The differences between the observed and calculated couplings are much larger for the nitro and amino compounds than for the other compounds investigated. Undoubtedly some of these are due as before to experimental error, as shown by the differences in the values of the couplings measured by different investigators or by the same investigator at different times; *e.g.*, in Table III, entry 25, and in Table IV, the perfluoroaniline *meta* couplings have been recently quoted[6] as 8.2, 6, and 4 instead of the values used (6.9, 4.6, and 2.6). However, even allowing for an experimental error of up to 1 cps does not explain some of the differences found; *e.g.*, in Table III, J_{13} in entries 18 and 21 differs by 2–3 cps from the calculated value. Unfortunately with the available data, it is not possible to investigate systematically these differences to find out the extent to which the additivity scheme is an approximation. Finally it is of interest to note that the substituent contributions given predict *meta* F–F couplings ranging from +24.2 cps in 2,6-difluoro-3,5-dinitroaniline to −19.8 cps in 2,6-difluoro-3,5-diaminonitrobenzene.

The Group Substituent Contributions. The preceding sections have shown that to a large extent the question of the effect of substituents on *meta* and *para* F–F couplings has been reduced to the interpretation of the substituent contributions given in Table I. The values given in Table I for the *meta* couplings differ slightly from the less complete set of values reported by us in a preliminary communication,[11] mainly because of the much larger amount of data used here (*ca.* twice as many couplings were included) and also due to the method of processing the data. These values differ somewhat more from a set of substituent constants for F, NH_2, and NO_2 obtained by Peake and Thomas from a limited number of nitro and amino compounds.[12] Again the differences are due solely to the experimental data used, though Peake and Thomas use perfluorobenzene as the base compound rather than *m*-difluorobenzene.

The values of the *meta* F–F substituent contributions

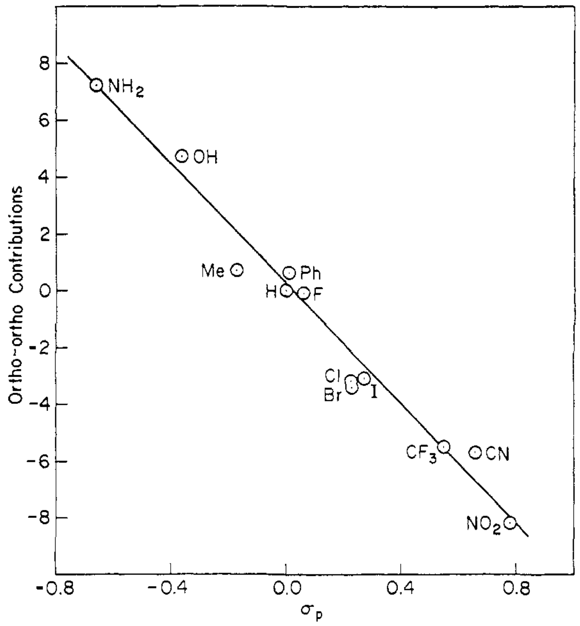

Figure 1.

in Table I are taken from the most complete set of couplings and we consider these the best set to date, although these values will change slightly when more accurate experimental data become available. The *para* F–F substituent contributions have not been reported previously.

The entries in Table I cover most of the common substituent groups and more importantly the variation of the group contribution is large enough to provide information on the mechanism of the F–F couplings. Indeed inspection of the table shows the surprisingly large influence of the substituent on the couplings up to a maximum of 7–8 cps from the *ortho–ortho* and *ortho–para* contributions. As may have been expected, the *meta–meta* contributions are much smaller (−0 to +2 cps) and also, more surprisingly, the substituent contributions to the *para* F–F coupling are small (*ca.* 0 to −3 cps).

The other very striking effect is the change in sign of the *ortho–ortho* and *ortho–para* contributions for the groups which have the largest values. Some indication of the mechanism of the coupling is given by the good linear correlation between the *ortho–ortho* contributions and the Hammett σ_p value[17] (Figure 1). This also explains the linear relationship found between J_{24} in the perfluorophenyl derivatives and the chemical shift of the *p*-fluorine nucleus,[10] as there is a general relationship between fluorine chemical shifts and the Hammett substituent parameters.[18] The *para* F–F couplings would be expected to follow a similar trend. However, the *para* F–F substituent contributions (Table I) do not show any clear correlation with the σ values of the substituents. This is probably due to, in part, the much smaller range of values of the substituent contributions which means that the experimental errors are proportionally much greater than in the *meta* couplings. In view of the recent questioning by Dewar[19] of the basis of the correlations between fluorine chemical shifts and the σ_I and σ_R values of Taft, it was felt that any interpretation of the substituent contributions in terms of these parameters would be of questionable value. What Figure 1 does demonstrate very convincingly is the remarkable difference between the F–F couplings and the analogous H–H couplings. In the latter, there is a roughly linear relationship with the electronegativity of the first atom of the substituent group and the *meta* and *para* couplings in nitrobenzene are virtually identical with those in aniline.[20] In the F–F couplings, this is clearly not the case and the nitro and amino groups are at the opposite ends of the scale. To the extent that the Hammett σ values reflect the perturbation of the π electrons by the substituent groups, the correlation of Figure 1 implies that the *meta* F–F couplings occur *via* the π electrons of the molecules. In order to verify this hypothesis, it is necessary to show that (a) the π electron contribution gives an appreciable coupling and (b) the π electron contribution can explain the observed substituent effects.

The electron contribution to coupling constants was first derived by McConnell, who obtained[21]

$$J_{NN'}(\pi) = \beta^2 Q^2 \eta_{NN'}^2/h\Delta E \qquad (1)$$

where β is the Bohr magneton, Q the hyperfine interaction in gauss of a proton with an electron in a $2p_y$ orbital on the adjacent ring carbon atom, $\eta_{NN'}$ is the π bond order connecting the carbon atoms bonded to N and N′, and ΔE is an effective excitation energy. Evaluating the constants in eq 1 gives

$$J_{NN'}(\pi) = 42.05 a_N^2 \eta_{NN'}^2/\Delta E \qquad (2)$$

where J is in cycles per second, a_N is the hyperfine interaction in units of 1000 Mc/sec, and ΔE is in atomic units.

The average energy approach is known to be approximate as, *e.g.*, eq 2 always predicts positive coupling constants. Recently, Pople and Santry[22] replaced this approximation by a summation over all excited states.

$$J_{NN'}(\pi) = 42.05 a_N^2 \pi_{NN'} \qquad (3)$$

where

$$\pi_{NN'} = \sum_{i}^{\text{occ}} \sum_{j}^{\text{unocc}} C_{iN} C_{iN'} C_{jN} C_{jN'} (\epsilon_i - \epsilon_j)^{-1}$$

is the mutual polarizability of the AO's concerned. This equation as it stands cannot be used with SCF-MO wave functions as the excited states obtained from such programs are virtual excited states obtained by averaging the electron interactions over the occupied states. We were fortunate to have available the SCF-CNDO wave functions of Pople,[23–25] one of the few comprehensive programs of wave functions for large molecules which does not depend on semiempirical estimates of the coulombic and resonance integrals for each substituent group. Thus, we used these more accurate wave functions with the approximate eq 2 rather than the alternative of using much more approximate wave functions with the more precise eq 3.

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(17) H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).
(18) R. W. Taft, *J. Am. Chem. Soc.*, **79**, 1045 (1957).
(19) M. J. S. Dewar and A. P. Marchand, *ibid.*, **88**, 3318 (1966).
(20) S. Castellano, private communication.
(21) H. M. McConnell, *J. Mol. Spectry.*, **1**, 11 (1957).
(22) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).
(23) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965).
(24) J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).
(25) M. Gordon and J. A. Pople, *J. Am. Chem. Soc.*, **89**, 4253 (1967).

The spin polarization mechanism gives a value of a_H of 30 gauss, which is much too small to make any significant contribution to the proton–proton coupling constant.[21] When the hydrogen is replaced by fluorine, there is now an additional mechanism involving the direct mixing of the carbon and fluorine $2p_y$ atomic orbitals.[26,27]

Furthermore, McConnell has pointed out[21] that the anisotropic part of the hyperfine interaction will need to be included in the evaluation of coupling constants for nuclei other than hydrogen. The only fluorine-containing radical for which all the hyperfine interactions are known is the $CHF\cdot CO\cdot NH_2$ radical produced by irradiated fluoracetamide.[26] The isotropic hyperfine interaction of 158 Mc/sec is made up of +479 Mc/sec from the direct mixing of the carbon and fluorine $2p_y$ AO's and −321 Mc/sec from the spin polarization mechanism.[26] The anisotropic part has one large coupling perpendicular to the radical plane of +500 Mc/sec. The correct value of a_F to use in eq 2 can only be estimated at present. The effects of substituents on the F–F coupling would be expected to occur largely *via* the direct mixing mechanism and this would suggest a value of a_F of *ca.* 500 Mc/sec. This value of a_F combined with a reasonable value of ΔE of 7 ev and the maximum value of $\eta_{NN'}$ of 1 gives a π contribution to the F–F coupling from eq 2 of 50 cps. Thus, this mechanism can give rise to substantial couplings. Inclusion of the large anisotropic contribution would presumably increase this value. We will take a value of $42.05a_F^2/\Delta E$ equal to 100 cps in the following discussion. However, this value needs to be calculated by a comprehensive theoretical treatment to substantiate fully this mechanism.

Incorporating this value into eq 2 together with the values of $\eta_{NN'}$ obtained from the SCF–CNDO wave functions gives π contributions to the F–F couplings in *m*- and *p*-difluorobenzene of 0.02 and 10.3 cps, respectively. Comparison with the experimental values of +5.8 and +18.1 cps (Table I) shows that the π contribution is a significant one, particularly for the *para* coupling, but that this is not the only mechanism involved. This is not surprising as F–F couplings over four and five bonds in saturated systems are well known and often quite large.[2]

In order to estimate the effects of substituents, we compare the bond orders for the *meta* F–F coupling for two substituents—the amino and cyano groups which are at opposite ends of the scale (Table I).

The values of the bond orders between the carbon $2p_y$ AO's for *m*-difluorobenzene, 2,6-difluoroaniline, 2,4-difluoroaniline, 2,6-difluorobenzonitrile, and 2,4-difluorobenzonitrile are 0.98, 5.23, −3.98, −0.22, and 1.68 ($\times 10^{-2}$). These values reproduce precisely the order of the F–F coupling constants in these molecules. Introduction of an amino group *ortho–ortho* to the fluorine nuclei in *m*-difluorobenzene increases the coupling from +5.8 to +13.0 cps, whereas *ortho–para* substitution decreases the coupling to −2.9 cps. In contrast, the cyano group has the opposite effect: *ortho–ortho* substitution decreases the coupling to +0.1 cps and *ortho–para* substitution increases the coupling to +10.1 cps (*cf.* Table I). The use of eq 2 involves the square of the bond order which does not now give the correct order, because the value for 2,4-difluoroaniline becomes more positive than *m*-difluorobenzene. Furthermore, the calculated coupling becomes very small (<1 cps).

Alternatively, we may apply eq 2 directly to the $2p_y$ AO's of the coupled fluorine nuclei, as in this case the bond orders are all positive. This gives for the above molecules $\eta_{NN'}{}^2$ values of 4.9, 8.8, 1.4, 2.9, and 7.4 ($\times 10^{-6}$). Again, the order of the substituent effects is reproduced precisely.

It would appear that for small changes in the bond order, such as we are considering, it would be more appropriate to use the bond order rather than the bond order squared to correlate with coupling constants.

However, we are not intending here to give an *ab initio* calculation of the coupling constants in these molecules, but merely to demonstrate that the original hypothesis of the F–F couplings occurring *via* the π electrons of the molecules can give a substantial effect which reproduces precisely the observed substituent effects. This explains also the basic differences between F–F couplings and F–H and H–H couplings in these molecules as the latter operate predominately through the σ electron system of the molecules. Thus, their dependence on the substituents is quite different, depending mainly on the electronegativity of the substituent,[28] rather than on the Hammett σ value. Also, the magnitude of this dependence is much smaller, being of the order of *ca.* 2 cps for H–H couplings.[28] This electronegativity effect could still be operating in the F–F couplings, but at the moment the experimental errors in the measured coupling constants obtained here are too large to consider this in detail.

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