Chemical Shifts and Coupling Constants in Pentafluorophenyl Derivatives. I. Correlations of Chemical Shifts, Coupling Constants, and π-Electronic Interactions[1]

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Abstract: The fluorine chemical shifts and coupling constants of 61 pentafluorophenyl derivatives with widely varied substituents are examined. It is found that two of the *meta* coupling constants form good straight line relationships with the chemical shift of the *p*-fluorine and it is argued that these relationships are mainly dependent upon the π-electron donor or acceptor character of the substituent.

Nuclear magnetic resonance (nmr) has proved a useful method in furthering the understanding of electronic interaction between the benzene ring and its substituents. The chemical shifts of *p*- and *m*-carbon nuclei[2-5] and of other nuclei (protons,[2] fluorine,[6-8] and boron[9]) attached to the benzene ring at these positions have been related to π-electron charge densities.

The increasing availability of pentafluorophenyl derivatives has led us to explore the possibility that nmr parameters of the pentafluorophenyl group might be correlated with the electronic interaction at the bond between substituent and ring. It was anticipated that coupling constants among the fluorine atoms, as well as their chemical shifts, would reflect changes in the ring-substituent interaction.

This paper elaborates upon our previous communication[10] which outlined (a) an empirical coupling constant–chemical shift relation, (b) a proposal that this relation differentiated between π-donor and π-acceptor substituents, and (c) the application of this proposal to certain phosphine complexes. Paper II of this series examines the results of this work in terms of bonding within the series of organometallic compounds studied.

Experimental Section

Materials. All pentafluorophenyl reagents used in this work were obtained from Imperial Smelting Corporation. The boron halides and $CFCl_3$ were obtained from Matheson of Canada Ltd., and other chemicals from the usual commercial sources. The boron halide and hydrogen chloride complexes of $C_6F_5P(C_6H_5)_2$ and C_6F_5CN were prepared using the conventional high vacuum technique by distilling an excess of the gas directly into the nmr tube containing a degassed benzene solution of the pentafluorophenyl compound and hexafluorobenzene. In the case of $C_6F_5P(C_6H_5)_2 \cdot BCl_3$, the nmr spectra were recorded immediately upon warming since the complex crystallized within a few hours. The crystalline complex was isolated and recrystallized from methylene chloride.

Anal. Calcd for $C_{18}H_{10}BCl_3F_5P$: C, 46.1; H, 2.2. Found: C, 46.8; H, 2.3.

The crystalline complex was insufficiently soluble to produce an adequate spectrum, although very small peaks of the correct chemical shift were sufficient to distinguish the compound from the HCl adduct of the phosphine.

The C_6F_5CN complexes with BF_3, BCl_3, and BBr_3 were not isolated or characterized due to dissociation of the adducts. For this reason, some caution is necessary in interpreting the spectra of the C_6F_5CN complexes. All other new compounds prepared were characterized either by elemental or by mass spectral analysis.

The various phosphines and their complexes were prepared in this laboratory by reaction of pentafluorophenyllithium and the appropriate phosphorus chloride and subsequent reaction with the metal carbonyl.[11] The various pentafluorophenyltin compounds were prepared in this laboratory by the reaction of pentafluorophenyllithium with the appropriate halotin compound.[12] The pentafluorophenoxy and pentafluoroaniline derivatives were also prepared in this laboratory by the reaction of the appropriate organometallic halide with pentafluorophenol or its sodium salt, and with N-lithiopentafluoroaniline.[13]

Nmr Measurements. The ^{19}F spectra were obtained at either 56.4 Mcps or 94.1 Mcps using Varian HA spectrometers. Signals more than 2000 cps from the reference were observed by disabling the manual oscillator and substituting a Hewlett Packard 241 A oscillator. Hexafluorobenzene was used as internal reference and chemical shifts are presented relative to $CFCl_3$ by adding 163.0 ppm (see Discussion) to the chemical shift from C_6F_6. The temperature of measurement was *ca.* 30°. The spectra were taken from 20 to 30% (v/v or w/w) solutions in benzene except for some of the complexes, especially those of the metal carbonyls, which were sparingly soluble and were measured as saturated solutions.

Nmr Analysis. The pentafluorophenyl system was treated as an AA'KXX' system. The first-order spectrum of the *p*-fluorine is analyzed initially yielding J_{24} and J_{34}, and J_{14} as well if the substituent atom has a magnetic moment (*e.g.*, phosphorus). The numbering sequence is clockwise around the benzene ring with the substituent at 1 and the *o*-fluorines at 2 and 6. The value of J_{34} thus obtained may then be used to separate the two overlapping parts of the *m*-fluorine spectrum. The result is the upfield half of an AA'XX' system which is analyzed after the manner of Grant, Hirst, and Gutowsky[14] yielding J_{23}, J_{25}, J_{35}, and J_{26}. The low-field half, the *ortho* spectrum, is then computed with J_{12} equal to zero and thence by inspection J_{12} can be determined. The couplings J_{12}, J_{13}, and J_{14} and any coupling to nuclei bonded to the substituent atom can safely be considered first-order interactions. Figures 1 and 2 exemplify spectra of *p*- and *m*-fluorines.

Figure 3 shows how the *ortho* spectrum is derived and also the steps involved in determining J_{12}. Figure 3a shows the half-spectrum of the AA'XX' system as derived from the *meta* spectrum. Figure 3b shows the computed *ortho* spectrum, achieved by adding the J_{24} coupling. The observed *ortho* spectrum for $C_6F_5P(C_6H_5)_2$

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[1] Taken in part from the Ph.D. thesis of M. G. Hogben, University of Alberta, Dec 1967.

[2] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

[3] P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838 (1961).

[4] G. B. Savitsky, *J. Phys. Chem.*, **67**, 2723 (1963).

[5] G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.*, **42**, 2427 (1965).

[6] R. W. Taft and J. W. Rakshys, Jr., *J. Am. Chem. Soc.*, **87**, 4387 (1965), and other references cited therein.

[7] V. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Mol. Phys.*, **8**, 133 (1964).

[8] I. J. Lawrenson, *J. Chem. Soc.*, 117 (1965).

[9] H. C. Beachell and D. W. Beistel, *Inorg. Chem.*, **3**, 1028 (1964).

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

[11] R. S. Gay and W. A. G. Graham, to be published.

[12] J. A. J. Thompson and W. A. G. Graham, *Inorg. Chem.*, **6**, 1875 (1967).

[13] A. J. Oliver and W. A. G. Graham, to be published.

[14] D. M. Grant, R. C. Hirst, and H. S. Gutowsky, *J. Chem. Phys.*, **38**, 470 (1963).

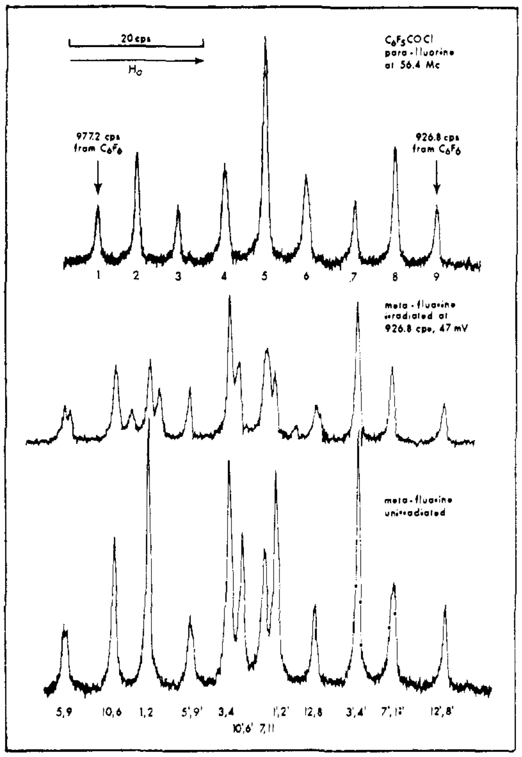

Figure 1. The *para* and *meta* spectra of C_6F_5COCl, showing the effect of double irradiation on the *meta* spectrum.

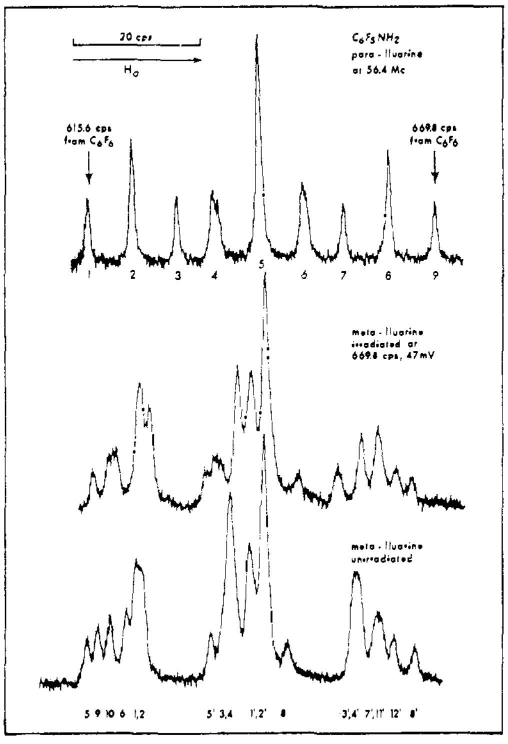

Figure 2. The *para* and *meta* spectra of $C_6F_5NH_2$, showing the effect of double irradiation on the *meta* spectrum.

is shown in Figure 3c. The coupling of the *o*-fluorine to phosphorus (J_{12} = 39 cps) causes the spectrum to show two overlapping multiplets, each the same as Figure 3b. When the phosphine is complexed to a metal carbonyl in the compound $C_6F_5P(C_6H_5)_2Mo(CO)_5$, J_{12} decreases to less than 2 cps. Comparing Figure 3d with Figure 3b, we find that only the two innermost lines in Figure 3d are derived from single transitions. Since these give no indication of splitting, J_{12} is taken to be less than this peak width (2 cps).

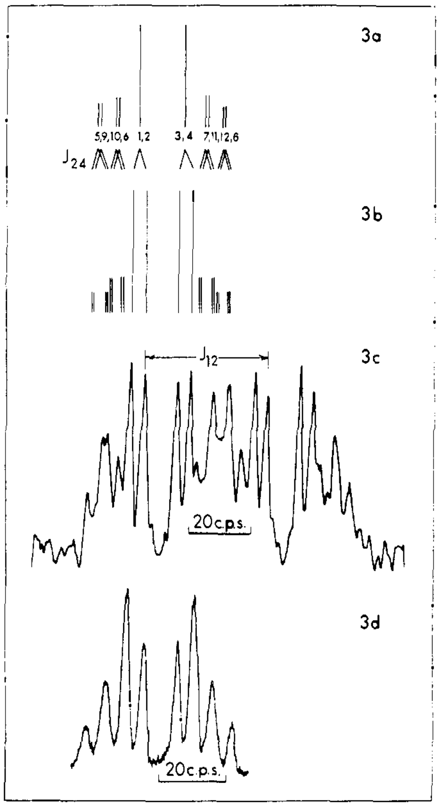

Figure 3. (a) Half-spectrum of AA'XX'derived from *meta* spectrum. (b) Theoretical *ortho* spectrum, J_{12} = 0. (c) Observed *ortho* spectrum of $C_6F_5P(C_6H_5)_2$. (d) Observed *ortho* spectrum of $C_6F_5P(C_6H_5)_2Mo(CO)_5$.

The correctness of the analysis was verified by comparison with the results given by the TWOSUM computer program.[15] The program gives a listing of all transitions together with the energy levels associated with each transition. For a given set of chemical shifts and coupling constants, spectra were computed with different signs of J_{24}. The resulting sets of spectra were identical in appearance although a given line was derived from different energy levels in the two cases, as shown in Table I. With reference to Figure 1, irradiating C_6F_5COCl at a frequency corresponding to line 9 in the *para* spectrum produced three lines in place of the original singlets 1,2 and 1',2' in the *meta* spectrum. The computed spectrum showed that when J_{24} was of the opposite sign to J_{23}, the two energy levels (7 and 17) involved in line 9 of the *para* spectrum are also found in the *meta* spectrum at lines 1,2 and 1',2', as designated by the symbol b in Table I. Had J_{24} been of same sign as J_{23}, line 9 would have involved energy levels 1 and 4 and the lines 3,4 and 3',4' would then have been affected (case a). This latter possibility was in fact found to be the case for $C_6F_5NH_2$ (Figure 2) and it was concluded that J_{24} was of different sign in $C_6F_5NH_2$ than in C_6F_5COCl.

Lines 1,2 and 1',2' in the *meta* spectrum are each comprised of two transitions. One of these did not have an energy level derived from line 9 in the *para* spectrum and remained unaffected. The affected transition caused two small peaks to appear on either side of the original.

Results and Discussion

A summary of data on 61 C_6F_5–X compounds from this[16] and other work[7,8,17–22] is presented in Table II.

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(15) A FORTRAN IV program by G. R. Demaré, J. S. Martin, and F. W. Birss, University of Alberta, based on NMRIT and NMREN by R. C. Ferguson and D. W. Marquardt, *J. Chem. Phys.*, 41, 2087 (1964).

(16) To avoid excessive length in Table II, only single values, averaged where necessary, are given. For values determined in this work, but shown as part of an average in Table II, see ref 1.

(17) P. Bladon, D. W. A. Sharp, and J. M. Winfield, *Spectrochim. Acta*, 20, 1033 (1964).

(18) M. G. Barlow, M. Green, R. N. Haszeldine, and H. G. Higson, *J. Chem. Soc., B*, 1025 (1966).

Table I. Energy Levels Computed for Transitions in the *p*- and *m*-Fluorine Spectra of Pentafluorobenzoyl Chloride[a]

	Line[b] *para* spectrum	Energy levels for each transition: J_{24} same sign as J_{23}	Energy levels for each transition: J_{24} opposite sign to J_{23}
↓	1	29–32	16–26
	2	24–30, 25–31	24–30, 25–31
	3	16–26	29–32
	4	19–27, 18–28	6–14, 5–15
H_0	5	11–20, 13–22, 10–21 12–23	10–21, 12–23, 11–20 13–22
	6	6–14, 5–15	19–27, 18–28
	7	7–17	1–4
	8	2–8, 3–9	2–8, 3–9
	9	1–4 (a)	7–17 (b)

	meta spectrum		For both cases of sign
↓	5,9		9–21, 23–30
	10,6		22–31, 8–20
	1,2	(b)	17–27, 27–32
	5′,9′		3–10, 12–24
	3,4	(a)	4–14, 14–26
	10′,6′		13–25, 2–11
H_0	7,11		9–22, 20–30
	1′,2′	(b)	19–29, 7–19
	12,8		21–31, 8–23
	3′,4′	(a)	6–16, 1–6
	7′,11′		3–13, 11–24
	12′,8′		10–25, 2–12

[a] Symbols a and b refer to energy levels common to both *para* and *meta* spectra, depending on the sign of J_{24} (see text). [b] The same numbering of lines is also used in Figures 1 and 2. Primed numbers refer to lines in the upfield half of the *meta* spectrum which result from coupling to the *p*-fluorine.

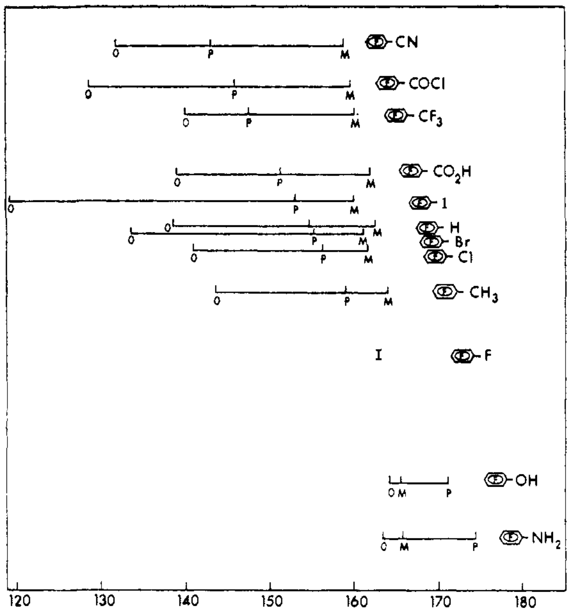

Figure 4. The chemical shifts of the *o*-, *p*-, and *m*-fluorines for the common organic substituents.

A comparison of values from different sources is complicated by variations due to conditions of measurement. Reported values of J_{23} and J_{34} vary in some instances over a 1-cps range (the experimental error is usually given as 0.2 cps); the range for other smaller coupling constants is proportionately less. Chemical shifts are more sensitive to conditions, and values differing by as much as 2 ppm have been reported by various workers.

One factor involved in the variation of reported chemical shifts is the choice of reference. Although ^{19}F chemical shifts have commonly been measured by using trichlorofluoromethane as reference and solvent, hexafluorobenzene has been found in this work to be a preferred reference and benzene a more suitable solvent.[23a] A recent quantitative approach to solvent effects on fluorine chemical shifts[23b] supports this and shows that if $CFCl_3$ is used as a universal reference, measured chemical shifts may differ by 2–3 ppm depending upon choice of solvent. However, if $CFCl_3$ is used for aliphatic compounds and C_6F_6 for aromatic compounds, variations are reduced to 0.5 ppm or lower. We have found these uncertainties to be of the same magnitude as the differences encountered in Table II. The chemical shift of hexafluorobenzene relative to trichlorofluoromethane has been reported at values ranging from 162.23[7] to 163.9 ppm.[21] In our work, concentrations in the range 20–30% w/w or v/v (approximately 10 mol %) were used, this being effectively the lowest concentration at which *both* chemical shifts and coupling constants could be conveniently measured. We have used the value 163.0 for conversion to the $CFCl_3$ scale. Under similar conditions, other workers[8] have found 162.9 ppm.

The results of an investigation of concentration effects on chemical shift are summarized in Table III, in which differences between measurements at 10 mol % and values obtained by extrapolation to infinite dilution are compared for nine compounds. The differences are small, and even for those substituents such as OH and NH_2 where association might be expected, are less than the standard deviations of the correlations presented below. The coupling constant, J_{24}, for these nine compounds changed by less than 0.1 cps in the same range of concentrations.

To correlate data from the various sources in Table II, we have adjusted the reported chemical shifts in two cases. Boden, *et al.*, used C_6F_6 as reference,[7] but expressed their results relative to $CFCl_3$ by adding 162.23 ppm. To bring these into line with our scale (C_6F_6 = 163.0), 0.77 ppm was added to each shift. Barlow, *et al.*,[18] measured chemical shifts in 50% solutions using internal $CFCl_3$ or external CF_3CO_2H as reference. Comparing the four compounds of their work that were also analyzed in this work, it was found that the chemical shifts averaged 1.4 ppm higher. This discrepancy, no doubt due to concentration effects, was accounted for by subtracting 1.4 ppm from all chemical shifts from that source. Although it is realized that solvent effects change the chemical shifts of the *o*-,

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(19) P. L. Timms, D. D. Stump, R. A. Kent, and J. L. Margrave, *J. Am. Chem. Soc.*, **88**, 940 (1966).

(20) J. Cooke, M. Green, and F. G. A. Stone, *J. Chem. Soc.*, *A*, 170 (1968).

(21) F. J. Hopton, A. J. Rest, D. T. Rosevear, and F. G. A. Stone, *ibid.*, 1326 (1966).

(22) R. B. Johannesen, F. E. Brinkman, and T. D. Coyle, *J. Phys. Chem.*, **72**, 660 (1968).

(23) (a) Our preference for C_6F_6 results from (a) the proximity of its chemical shift to those of pentafluorophenyl compounds generally; (b) the high concentration of fluorine nuclei it provides; and (c) its single sharp resonance. Trichlorofluoromethane, in view of its low fluorine content, must be used in such high concentration that it becomes, for practical purposes, the solvent; moreover, it gives rise to a rather broad signal with definite shoulders. (b) J. W. Emsley and L. Phillips, *Mol. Phys.*, **11**, 437 (1966).

Table II. ^{19}F Chemical Shifts and Coupling Constants of Pentafluorophenyl Compounds

	Chemical shifts[a]			Coupling constants[b]									
Compd	ϕ_o	ϕ_p	ϕ_m	$\pm J_{24}$	$\mp J_{34}$	$\mp J_{23}$	$\pm J_{25}$	$\mp J_{35}$	$\mp J_{26}$	J_{12}	J_{13}	J_{14}	Source[c]
$C_6F_5POF_2$	128.7	140.2	157.6	8.6	19.9	21.5	9.0	0	9.4	1.0	9.5	3.5	A
$C_6F_5CNBCl_3$	128.1	136.0	156.4	8.5	20.4	18.4	7.2	1.0	10.1				A
$(C_6F_5)_2POF$	131.5	141.5	158.2	7.9	20.9	22.3	8.8	0	7.4	...	7.0	3.0	A
$C_6F_5P(C_6H_5)_2HCl$	125.6	140.4	156.6	7.5	20.1	22.6	8.2	0	8.5	13.0	4.0	2.7	A
$C_6F_5P(C_6H_5)_2BCl_3$	120.4	143.8	158.7	7.3	20.3	23.4	9.0	0	9.2	14.0	2.7	3.1	A
$(C_6F_5)_3PO$	132.6	142.4	158.5	7.2	20.8	...	...	...	...	...	...	3.0	A
$(C_6H_5)_3PS$	132.2	144.3	159.0	7.2	20.8	...	...	...	...	...	...	3.2	A
$C_6H_5SiF_3$	125.3	143.4	159.8	6.6	...	...	...	...	...				GH
$C_6F_5CNBF_3$	131.3	141.6	158.3	6.3	20.2	19.4	7.8	0.1	8.5				A
$C_6F_5PCl_2$	130.2	145.4	159.8	6.2	19.6	22.3	9.7	0.4	6.8	63.2	0.9	1.1	AJ
C_6H_5COCl	130.8	146.1	160.0	6.0	19.1	20.6	8.5	0	7.6				A
$(C_6F_5)_3PF_2$	132.4	146.0	159.4	6.0	19.7	21.9	7.5	0	7.7	...	10.3	3.6	A
$C_6F_5PF_2$	138.7	147.4	162.1	5.9	18.6	21.6	9.9	0	4.8	43.6	2.5	2.1	J
$C_6H_5PO(C_6H_5)_2$	128.8	147.3	160.1	5.9	20.6	23.4	9.2	0	5.1	2.0	3.4	2.3	A
$C_6F_5PS(C_6H_5)_2$	128.1	148.6	160.1	5.8	20.8	23.4	8.7	0.6	5.9	0	3.8	3.0	A
C_6F_5CN	132.0	143.2	158.9	5.8	18.7	19.5	8.3	0	7.9				A
$C_6F_5CF_3$	140.2	147.8	160.3	5.8	20.0	20.2	8.4	0	7.6				AC
$(C_6F_5)_2PCl$	128.8	147.5	160.3	5.6	19.4	22.1	9.1	0.2	5.7	38.7	1.5	1.8	AJ
$C_6F_5PClN(CH_3)_2$	127.6	149.6	161.1	5.4	19.8	22.2	8.7	1.2	6.1	51.0	1.7	1.3	J
$(C_6F_5)_2P(C_6H_5)Mo(CO)_5$	127.4	148.1	159.1	5.2	20.4	22.3	7.2	0	6.6	5.0	1.3	1.4	A
$C_6F_5P(C_6H_5)_2W(CO)_5$	124.4	149.2	159.3	5.2	20.6	23.7	9.2	0	3.3	0	1.3	1.9	A
$[C_6F_5P(C_6H_5)_2]_2PdCl_2$	124.7	149.2	161.1	5.1	20.4	23.5	8.3	0	6.7	...	0	0	A
$C_6F_5P(C_6H_5)_2Fe(CO)_4$	124.3	149.5	159.4	5.0	20.9	23.4	8.7	0	6.8	0	1.1	1.8	A
$C_6F_5P(C_6H_5)_2Cr(CO)_5$	124.1	149.5	159.5	5.0	20.8	23.7	8.9	0	6.3	0	0.9	1.7	A
$C_6F_5P(C_6H_5)_2Mo(CO)_5$	124.3	150.0	159.5	4.8	20.4	23.0	8.6	1.0	6.2	0	0.9	1.6	A
$C_6F_5CNBBr_3$	135.4	146.9	159.2	4.6	21.0	22.6	8.0	0	8.5				A
$(C_6F_5)_3P$	130.6	147.7	159.8	4.5	20.5	...	...	...	...	...	...	...	A
$(C_6F_5)_2PC_6H_5$	129.2	150.5	160.8	4.2	20.1	23.5	9.3	0	4.6	31.1	1.1	0	A
$C_6F_5CO_2H$	139.2	151.6	162.1	4.0	20.1	21.5	8.6	1.2	5.1				A
$C_6F_5P(C_6H_5)_2$	127.7	150.6	161.0	4.0	20.9	24.1	9.4	1.5	4.5	38.9	0.6	0.6	A
$(C_6F_5)_2PH$	128.6	150.5	160.4	3.8	19.4	20.3	7.1	2.4	6.5	12.3	1.6	0	J
$(C_6F_5)_3SnMn(CO)_5$	120.5	150.4	160.9	3.4	19.5	...	...	...	...				A
$(C_6F_5)_2PN(CH_3)_2$	134.2	152.1	161.3	3.3	19.8	23.9	9.2	1.2	4.4	29.0	3.0	1.7	J
$C_6F_5P(CH_2CH_3)_2$	130.9	153.5	162.9	3.3	20.2	23.7	9.8	1.7	4.0	35.8	1.0	0.8	J
$(C_6F_5)_2Sn(C_6H_5)_2$	119.4	149.6	159.3	3.0	19.2	24.7	10.3	0	6.8				A
$C_8F_5P(CH_3)_2$	132.0	154.2	163.0	2.9	19.8	23.2	9.4	1.8	3.6	30.1	1.7	0	AJ
$(C_6F_5)_2Sn(C_6H_5)Mn(CO)_5$	119.4	150.7	159.7	2.8	19.4	26.3	10.6	0	7.0				A
$(C_6F_5)_2Sn[Mn(CO)_5]_2$	117.5	151.6	160.4	2.7	19.6	29.2	8.6	0	7.6				A
$C_6F_5Sn(C_6H_5)_3$	117.9	151.2	159.9	2.6	19.2	22.6	9.8	1.1	6.9				A
$C_6F_5Sn(C_6H_5)_2Mn(CO)_5$	117.2	152.6	160.1	2.6	19.2	21.3	8.3	1.1	7.3				A
$C_6F_5P[N(CH_3)]_2$	138.8	155.7	162.7	2.6	20.2	26.0	9.6	2.8	3.3	5.0	6.6	2.6	J
$[C_6F_5SFe(CO)_3]_2$	127.0	152.5	159.8	2.4	21.2	24.1	8.2	3.6	3.6				E
$C_6F_5PH_2$	128.7	153.7	161.6	2.3	19.4	23.2	9.4	1.5	3.6	3.9	1.3	0	J
C_6F_5I	119.5	153.0	160.1	2.0	19.8	23.0	7.2	1.3	5.1				CD
$C_6F_5Sn(CH_3)_3$	123.0	153.5	161.4	1.9	19.1	26.7	12.0	1.5	6.5				D
C_6F_5H	138.7	154.3	162.6	1.3	18.4	20.0	8.6	1.1	2.2				A
$C_6F_5HgCH_3$	122.6	154.2	160.7	1.1	19.5	28.3	11.6	1.6	6.6				D
C_6F_5Br	133.2	155.2	161.0	1.1	19.9	21.6	6.3	1.6	5.5				ACD
C_6F_5Cl	141.0	156.5	161.7	0.7	19.5	20.6	6.3	2.0	5.3				CDF
C_6F_5SH	137.5	159.1	162.3	0	20.2	22.2	7.6	0	3.0				A
$C_6F_5CH_3$	143.9	159.1	164.4	0	18.9	20.4	8.6	0.4	1.9				AC
$C_6F_5SFe(CO)_2(C_5H_5)$	132.2	159.3	164.3	0	21.2	25.0	8.2	1.4	1.4				E
$C_6F_5OSi(C_6H_5)_3$	156.2	166.5	165.0	−4.3	21.6	...	...	...	...				A
$C_6F_5OSi(CH_3)_3$	158.7	167.6	165.1	−4.4	21.0	...	...	...	...				A
$C_6F_5OGe(C_6H_5)_3$	157.0	169.2	166.3	−5.0	21.6	...	...	...	...				A
C_6F_5OH	164.4	171.2	165.8	−6.1	21.1	21.0	4.4	2.8	−3.4				D
$C_6F_5OSn(C_6H_5)_3$	160.4	172.8	168.8	−6.4	21.9	...	...	...	...				A
$C_6F_5NHCH_3$	162.6	173.8	165.9	−6.9	21.6	21.1	4.5	2.3	−3.9				D
$C_6F_5NHSi(CH_3)_3$	158.9	174.1	165.7	−7.0	21.4	21.5	4.6	2.7	−3.3				A
$C_6F_5NH_2$	163.3	174.3	165.8	−7.0	20.4	20.2	5.1	2.3	−4.6				AC
$C_6F_5OPb(C_6H_5)_3$	161.3	176.1	168.2	−8.0	22.2	25.2	6.0	0	−5.5				A

[a] Chemical shifts of *o*-, *p*-, and *m*-fluorines in parts per million (ppm). The ϕ scale is based here on C_6F_6 = 163.0 ppm upfield from $CFCl_3$.

[b] The coupling constants are in cycles per second (cps). Numbering is clockwise around the ring with the substituent at 1 and the *o*-fluorines at 2 and 6. The signs are based on the result of ref 26 and 27a in combination with results from this work. The value 0 is given for unresolved coupling constants. The resolution was generally approximately 0.2 cps. Due to line overlap the resolution limit for J_{12} was approximately 2 cps. The symbol .... means that analysis was not attempted. This is generally found for coupling constants derived from the *meta* spectrum which was sometimes broadened (*e.g.*, for compounds with two or three pentafluorophenyl groups, spectra were usually broadened, probably by inter-ring coupling). The couplings to phosphorus in the various phosphines are arranged under columns J_{12}, J_{13}, J_{14}. Couplings to other substituent atoms are not presented. [c] The data have been compiled from the following sources: A, this work; C, ref 8; D, ref 7; E, ref 20; F, ref 17; G, ref 22, H, ref 19; J, ref 18.

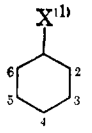

Table III. The Differences Between Chemical Shifts of Nine C_6F_5-X Compounds Measured at ~10 mol % from Their Extrapolated Value at Infinite Dilution[a]

X	*ortho*	*para*	*meta*
CN	0.07	0.18	0.08
CF_3	0.08	0.02	−0.03
I	0.08	0.03	0
Br	0.06	0.01	0
H	0.06	−0.03	−0.02
Cl	0.01	0	0
CH_3	0.03	−0.05	0.05
OH	0.01	0.32	0.04
NH_2	0	−0.10	−0.08

[a] Negative values indicate a downfield shift with increased dilution. Differences are given in parts per million (ppm). The value at infinite dilution was extrapolated from the chemical shifts measured at ~20, 10, 5, and 2.5 mol % in benzene to which 1% w/w hexafluorobenzene had been added.

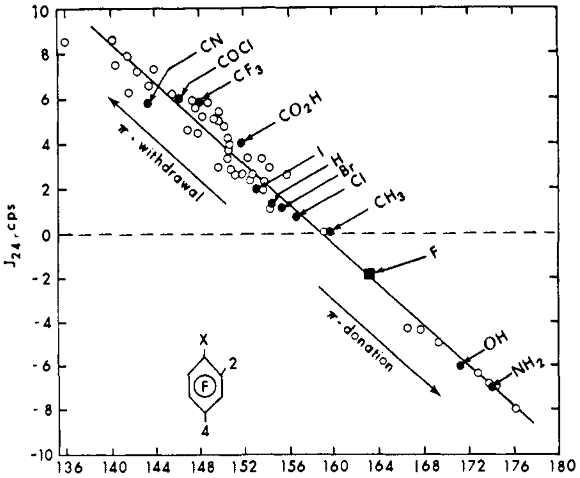

Figure 5. The relationship of the coupling constant between the *o*- and *p*-fluorines (J_{24}) to the chemical shift of the *p*-fluorine (ϕ_p) for all 61 pentafluorophenyl derivatives. The point representing fluorine as substituent is interpolated from the chemical shift of hexafluorobenzene (163 ppm).

p-, and *m*-fluorines in different ways, there seems no other way of accommodating all results measured under different conditions than by the gross assumptions outlined above. Coupling constants, which are less sensitive to concentration changes, were not adjusted for differences in the conditions of measurement. In the statistical analysis, the mean values of chemical shifts and coupling constants were used when more than one source is cited.

A close examination of the results in Table II shows that *o*-fluorine chemical shifts (ϕ_o) fall in the range 117–164 ppm, *m*-fluorine chemical shifts (ϕ_m) in the range 156–169 ppm, and *para* chemical shifts (ϕ_p) in the range 136–176 ppm. These changes are illustrated in Figure 4 for 12 common organic substituents. The *ortho* coupling constants, J_{23} and J_{34}, varied little with substituent. The mean value for J_{23} was 22.7 cps; that for J_{34} was 20.9 cps. No trends were discerned for the only *para* coupling constant, J_{25}, which ranged from 4 to 12 cps. Of the three *meta* coupling constants J_{24}, J_{26}, and J_{35}, the first two showed obvious correlations with the nature of the substituent.

J_{24} *vs.* ϕ_p. It was found that J_{24} formed a straight line relationship with ϕ_p (Figure 5). Since this relationship is the principal concern of this paper, the results of Table II are tabulated in order of decreasing J_{24} values.

The straight line in Figure 5 can be represented algebraically by $J_{24} = -0.453\phi_p + 71.98$, as found by a computerized least-square method. The root-mean-square deviation for a plot of all 61 substituents was 0.69 cps. The goodness of fit of the data to a straight line, as defined by the square of the correlation coefficient $(r_{xy})^2$, for the plot of 61 substituents, was 0.974.[24]

$$(r_{xy})^2 = \frac{(N\sum XY - \sum X \sum Y)^2}{[N\sum X^2 - (\sum X)^2][N\sum Y^2 - (\sum Y)^2]}$$

For the very wide range of substituents measured or plotted from data of other workers, only two points ($CN \cdot BCl_3$, $CN \cdot BF_3$) existed outside 2.2 standard deviations. These two points, however, formed a good straight line when linked with the two similar substituents, CN and $CN \cdot BBr_3$. Values for $(C_6F_5)_3P$ and $(C_6F_5)_3PO$ were measured in this work, and established that the previously reported parameters,[25] inconsistent with the relation proposed here, were incorrect. For groups of similar substituents (as summarized in Table IV) such as the phosphines, benzonitriles, halobenzenes, and the phenoxy derivatives of group IV organometallic compounds, the root-mean-square deviation was close to the experimental error (0.2 cps).

Table IV. Equations Relating J_{24} with the Chemical Shifts of the *p*- and *m*-Fluorines[a]

	a	*c*	$(r_{xy})^2$	RMS
	$J_{24} = a\phi_p + c$			
All compounds (61)	−0.453	71.98	0.974	0.69
Phosphines (28)	−0.390	62.98	0.932	0.42
Halogens (3)	−0.375	59.41	0.995	0.04
Nitriles (4)	−0.359	57.30	0.996	0.08
OMR_3[b] (6)	−0.396	61.89	0.984	0.16
	$J_{24} = a\phi_m + c$			
All compounds (61)	−1.47	239.3	0.84	1.7
Phosphines (28)	−0.86	142.8	0.67	0.9
Halogens (3)	−0.82	133.4	0.98	0.1
Nitriles (4)	−1.27	206.8	0.96	0.3
OMR_3[b] (6)	−0.72	114.2	0.66	0.7
All compounds (61)	$J_{24} = -0.524\phi_p + 0.262\phi_m + 40.69$		0.98	0.65

[a] Figures in parentheses refer to the number of points from which the equation is derived. RMS is the root-mean-square deviation; $(r_{xy})^2$ is the square of the correlation coefficient. [b] Pentafluorophenoxy derivatives in which M = Si, Ge, Sn, Pb and R = C_6H_5 or CH_3.

The sign change was demonstrated by comparing the sign of J_{24} relative to J_{23} for the two compounds pentafluorobenzoyl chloride and pentafluoroaniline. For pentafluorobenozyl chloride, J_{24} and J_{23} were of opposite sign, whereas for pentafluoroaniline J_{24} was

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(24) We report values of $(r_{xy})^2$, which range from 0 to 1 as a completely random scatter of points approaches a perfect straight line, in preference to root-mean-square values, which can be misleading. For example, comparing eq 1 and 2 in Table VI, we find that the points represented by eq 1 approximate much more closely to a straight line (*i.e.*, higher $(r_{xy})^2$ value) than do the points represented by eq 2; the root-mean-square deviation for eq 1 is considerably larger than for eq 2, however.

(25) H. J. Emeléus and J. M. Miller, *J. Inorg. Nucl. Chem.*, **28**, 662 (1966).

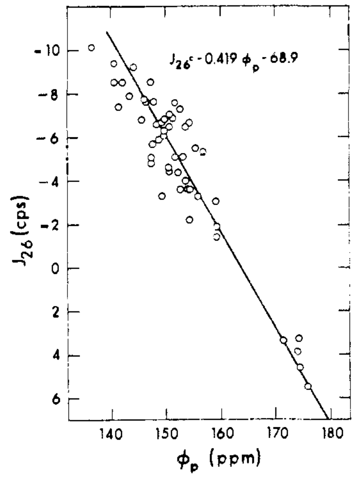

Figure 6. The relationship of the coupling constant between the two *o*-fluorines, J_{26}, and the chemical shift of the *p*-fluorine, ϕ_p.

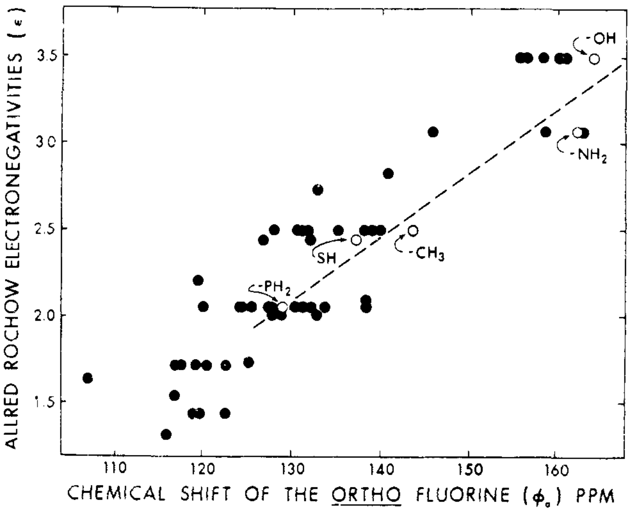

Figure 7. The relationship of the electronegativity of the substituent atom to the chemical shift of the *o*-fluorine.

of the same sign of J_{23}. Since J_{23} remained approximately constant at 20 cps for all 61 derivatives, it was assumed that J_{23} did not change sign. A detailed account of the sign determination has been given in the Experimental Section. These sign designations are consistent with two previous determinations. Snyder and Anderson[26] found that $J_{FF}{}^{meta}$ in hexafluorobenzene, as observed in the nematic liquid crystal, was -4 cps and therefore was of the same sign as $J_{FF}{}^{ortho}$, which was assumed to be negative. Our interpolated value of J_{24} for hexafluorobenzene using Figure 5 is -2.0 cps, the value of J_{24} corresponding to $\phi_p = 163.0$. We presume the very different conditions of measurement have caused this discrepancy.

A recent determination of relative signs and coupling constants has been made on iodopentafluorobenzene using low-field nmr.[27a] Basing the signs on $J_{FF}{}^{ortho}$ as negative, J_{26} and J_{35} were both found to be negative, while the third *meta* coupling constant, J_{24}, was found to be anomalously positive. Since our results show that the sign change of J_{24} occurs for substituents with ϕ_p above 158 ppm, the apparent inconsistency between the sign of J_{24} for iodopentafluorobenzene and hexafluorobenzene is resolved.[27b]

J_{24} *vs.* ϕ_m. The weaker relation between J_{24} and ϕ_m is shown in Table IV. Since the J_{24} values are the same in relationships with ϕ_m and ϕ_p, the equations derived from the same number of points can be compared by their root-mean-square value as well as their $(r_{xy})^2$ value. The root-mean-square value of the ϕ_m series is in each case more than double that for the ϕ_p series.

The last equation in Table IV shows, as expected, that a better correlation exists for a linear combination of ϕ_p and ϕ_m when related to J_{24}. The combination of ϕ_p and ϕ_m found to give the best straight line was $\phi_p - 0.50\phi_m$.

J_{26} *vs.* ϕ_p. In the analysis of the pentafluorophenyl group, the pair of coupling constants J_{26} and J_{35} are indistinguishable. However, the study of iodopentafluorobenzene mentioned above[27a] yielded the unambiguous assignment $|J_{26}| > |J_{35}|$, to which we have adhered. When J_{26} is plotted against ϕ_p, a straight-line relationship is found (Figure 6 and eq 1, Table V). Like the J_{24}–ϕ_p plot, the points with ϕ_p greater than 170 ppm are incorporated into the straight-line relationship by means of a sign change in J_{26} for these points. No trend was discerned for the J_{35} values, which were usually less than 3 cps.

Table V. Equations Derived by Least-Mean-Square Analysis,[a] Relating ϕ_p with Coupling Constants J_{26}, J_{35}, and ϕ_o with the Allred–Rochow Electronegativity, ϵ

Eq no.	Equation	$(r_{xy})^2$	RMS	Pts
1	$\phi_p = -2.38J_{26} + 164.19$	0.84	3.4	61
2	$\phi_p = 5.31J_{35} + 146.90$	0.51	6.0	61
3	$\phi_p = 1.95(J_{35} - J_{26}) + 160.08$	0.88	3.0	61
4	$\phi_p = 2.52(J_{35} + J_{26}) + 167.35$	0.65	5.1	61
5	$\epsilon = 0.0371\phi_o - 2.68$	0.81	0.23	75[b]

[a] $(r_{xy})^2$ is the square of the correlation coefficient, RMS is the root-mean-square deviation, and Pts is the number of points used in the analysis. [b] The extra 14 points are found from chemical shifts in the literature for C_6F_5X where X = $Mn(CO)_5$, BCl_2, BF_2, BCl_2–py, BF_2–py, $B(OH)_2$, C_6H_5, $B(Cl)C_6H_5$, $Ti(C_5H_5)_2C_6H_5$, $Tl(Br)C_6F_5$, $Hg(C_6F_5)$, $Fe(CO)_2C_6H_5$, $Pb(C_6H_5)_3$, and NO_2: ref 29–32.

As shown by Figure 6 and the statistical parameters in Table V, the considerable scatter in the J_{26}–ϕ_p plot reduces its predictive value, in contrast to the J_{24}–ϕ_p, which is sufficiently linear to be applied in the evaluation of substituent effects.

The Electronegativity of the Substituent Atom *vs.* ϕ_o. Figure 7 and eq 5, Table V show that a fair straight-line relationship exists between ϕ_o and ϵ, the electronegativity[28] of the substituent atom bonded directly to the pentafluorophenyl ring. Additional points, including many C_6F_5–metal compounds, have been taken from the literature.[29-32] These results are not

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(26) L. C. Snyder and E. W. Anderson, *J. Chem. Phys.*, 42, 3336 (1965).

(27) (a) W. B. Moniz and E. Lustig, *ibid.*, 46, (1967). (b) A very recent paper (K. Schaumberg, D. Gillies, and H. J. Bernstein, *Can. J. Chem.*, 46, 503 (1968)) reports relative signs for J_{FF} in C_6F_5H. Some of the conclusions, however, are not in accord with the results on C_6F_5I[27a] and C_6F_6,[26] nor with the present work on J_{24} compared with J_{23}.

(28) Using the Allred–Rochow values listed in F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Division, John Wiley & Sons, Inc., New York, N. Y., 1966, p 103.

(29) R. Chambers and T. Chivers, *J. Chem. Soc.*, 3933 (1965).

(30) G. M. Brooke and J. Musgrave, *ibid.*, 1864 (1965).

used elsewhere in this paper since the coupling constants were not reported.

An interesting feature of this plot is that decreasing the electronegativity of the substituent, which presumably increases the over-all charge on the ring, causes a downfield shift in ϕ_o. *ortho* shifts have been previously found to show large deviations to low field as the size of the substituent increases.[2] These anomalous deviations have been described as the "*ortho* effect," and have been attributed to an intramolecular van der Waals effect.[7] The electronegativity relationship presented here is consistent with the above argument in that the largest downfield shifts occur for substituent atoms with lowest electronegativity, which in general will be the largest ones.

Phosphorus–Fluorine Coupling Constants. Other substituent effects on coupling constants can be found in the series of phosphines. The most striking change is shown in the J_{12} values. The J_{12} values in three-coordinate phosphorus compounds fall within the range 30–60 cps, except for the three compounds $C_6F_5PH_2$, $(C_6F_5)_2PH$, and $C_6F_5P[N(CH_3)_2]_2$, which show anomalously low values. However, a marked decrease of coupling occurs when phosphorus expands its coordination. For example, J_{12} for $C_6F_5PF_2$ drops from 44 to 1 cps when the compound is oxidized to $C_6F_5POF_2$. Similarly, J_{12} in $C_6F_5P(C_6H_5)_2$ is 39 cps, but decreases to 2 cps in $C_6F_5PO(C_6H_5)_2$ and to less than 1 cps (not resolved) in $C_6F_5PS(C_6H_5)_2$ and in the metal carbonyl complexes.

The trends of other phosphorus–fluorine coupling constants (J_{13} and J_{14}) mentioned in our previous communication[10] have not been validated by the increased amount of data. It does appear that in general strong electron-withdrawing groups give larger values for J_{13} and J_{14}, but with some exceptions.

Interpretation with Respect to Electronic Interactions. In the plot of J_{24} against ϕ_p (Figure 5) the positions of the common organic substituents reveal an empirical relationship involving the electron-donor or -acceptor properties of the substituents. Electron-donating substituents such as NH_2 and OH give high ϕ_p values with large negative J_{24} values. Substituents intermediate in electron donation or acceptance such as H and CH_3 give intermediate ϕ_p values and J_{24} values near zero. Substituents that accept electrons from the benzene ring (*e.g.*, CN, COCl) result in low ϕ_p values with high J_{24} values. Since the theoretical background on substituent effects involves primarily chemical shifts, the following discussion concerns mainly ϕ_p. It is clear from the present work, however, that coupling constants are related to chemical shifts, and thus in parallel fashion to the electronic effects of substituents.[33]

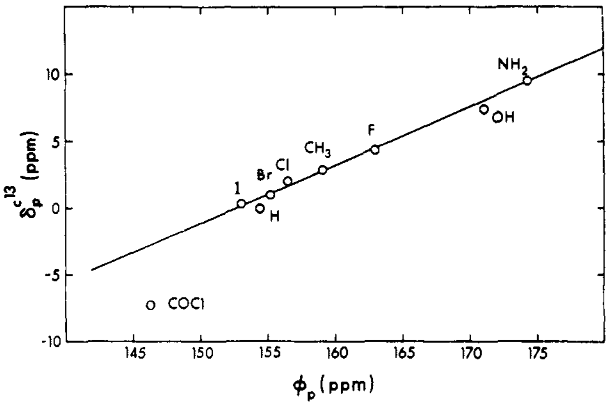

Figure 8. The relationship of the chemical shift of the *p*-fluorine in certain pentafluorophenyl derivatives (ϕ_p) to the chemical shift of the *p*-carbon in corresponding phenyl derivatives ($\delta_p{}^{13C}$).

In the absence of anisotropic and paramagnetic effects, the chemical shift is understood to be a measure of the electron density at the nucleus. Substituent effects on the electronic distribution can therefore be inferred by the chemical shifts of nuclei at different positions in the benzene ring. The classical concept of electronic interactions predicts changes in electron density at the *ortho* and *para* positions when the substituent exhibits resonance effects, whereas changes in electron density at the *meta* position indicate the inductive effect of the substituent. In view of the rapid diminution of inductive effects through the σ-bond framework, *both* inductive and resonance effects are considered to be transmitted to other parts of the benzene ring *via* the π system.[34] Introduction of the resonance effects into the benzene π system is accomplished by extending the π network. However, in order that the inductive effect be transmitted *via* the benzene π system, it is implicit that the substituent inductive effect along the σ bond must polarize the π electrons of the substituted carbon atom.

In a study of considerable relevance for the interpretation of the present results, Spiesecke and Schneider[2] showed that p-^{13}C chemical shifts in monosubstituted benzenes are dependent upon the change in π-electron density at the *p*-carbon arising from the resonance effects of individual substituents. They also concluded that inductive and magnetic anisotropic contributions were negligible. Furthermore, *p*-proton shifts were found to parallel those of the *p*-carbon, implying that the intervening σ bond caused no extraneous effects, since the magnetic field at the hydrogen nucleus still reflected the π-electron distribution at the *p*-carbon. Spiesecke and Schneider also found that inductive effects did not extend to the *meta* positions in these derivatives, since variations in ^{13}C and ^1H shifts were small, uniform, and apparently unrelated to the general electronegativity of the substituent.[35]

Although ^{13}C chemical shifts are not available for the pentafluorophenyl compounds, we have observed that the *p*-fluorine chemical shifts form a straight line relationship with the *p*-carbon shifts from the corresponding phenyl derivatives as shown in Figure 8, im-

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(31) D. E. Fenton, D. G. Gillies, A. G. Massey, and E. W. Randall, *Nature*, **201**, 818 (1964).

(32) R. B. King and M. B. Bisnette, *J. Organometal. Chem.* (Amsterdam), **2**, 38 (1964).

(33) (a) No correlation of fluorine coupling constants with either chemical shift or electron distribution had been reported at the time these results were first communicated.[10] Certain coupling constants in polysubstituted benzenes have now been shown to be predictable by additivity rules.[33b] (b) R. J. Abraham, D. B. Macdonald and E. S. Pepper, *Chem. Commun.*, 542 (1966); A. Peake and L. F. Thomas, *ibid.*, 529 (1966).

(34) We feel that this separation of the over-all ring-substituent interaction into inductive and resonance effects is the most appropriate one for our purposes. It should be noted, however, that another school of thought *defines any* effect which distorts the π system as a resonance effect [R. T. C. Brownlee, A. R. Katritzky, and R. D. Topsom, *J. Am. Chem. Soc.*, **88**, 1413 (1966)].

(35) In contrast, as Taft has shown, the ^{19}F shift in m-C_6H_4F derivatives is uniquely related to the inductive effect of the substituent (*vide infra*).

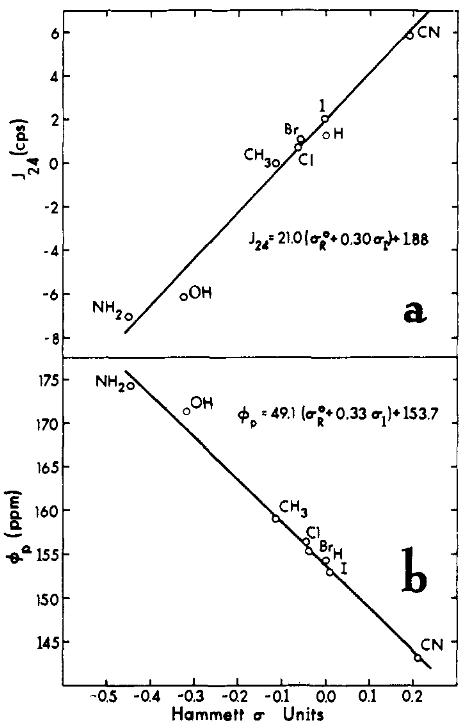

Figure 9. The relationship of J_{24} and ϕ_p to the best combination of the Hammett-Taft parameters $\sigma_R{}^0$ and σ_I.

plying a common basis in the resonance effect. Moreover, previous work on pentafluorophenyl derivatives has shown that the *m*- and *p*-^{19}F shifts can be successfully predicted from the π-electron charge densities and bond orders as calculated by the Hückel molecular orbital method.[7,36] Changes in the π-electron charge density result mainly from the resonance effect of a substituent.

Apart from MO calculations of electron density, the only quantitative treatment of substituent effects has been through the use of Hammett–Taft substituent functions as derived from reactivities. Taft modified the original Hammett substituent function σ, to the form $\sigma = \sigma_R{}^\circ + \sigma_I$ where $\sigma_R{}^\circ$ is the resonance parameter[37] and σ_I the inductive parameter.[38] The following relation[39] was found between these parameters and the ^{19}F chemical shifts of *p*-fluorophenyl derivatives

$$\delta_p{}^F = -29.5\sigma_R{}^\circ - 7.1\sigma_I + 0.60$$

while for the ^{19}F chemical shifts of *m*-fluorophenyl derivatives

$$\delta_m{}^F = -7.1\sigma_I + 0.60$$

The seemingly fortuitous agreement in the σ_I coefficients and constants in these two equations made it possible to define a quantity $\delta_p{}^F - \delta_m{}^F$, which was dependent upon *only* the resonance parameter. Although this means of gauging resonance effects has been derived for conventional organic substituents, it has recently led to interesting conclusions in a study of bonding in fluorophenylplatinum derivatives,[40] where its general applicability was assumed; the latter study was a stimulus for the present work.

An advantage of the pentafluorophenyl system is that both *para* and *meta* chemical shifts can be determined from a single sample; this necessarily means that both parameters have been extracted from identical chemical environments. This is of course not the case in the monofluoro derivatives, where the bonding throughout the molecule is somewhat different for the *para* and *meta* compounds. The presence of additional information in the form of readily available coupling constants is a further advantage of the pentafluorophenyl group.

It is of obvious interest to relate the pentafluorophenyl nmr parameters to $\sigma_R{}^\circ$ and σ_I values. Although the latter have been derived from disubstituted benzenes, and therefore apply more correctly to the monofluorophenyl system,[39] we may trust that interactions with the substituents will not be dissimilar in the two cases. For example, relative $\sigma_R{}^\circ$ values of the halogens on C_6F_5 may well differ slightly from those on FC_6H_4, as we later propose. Some general comments on the validity of correlating nmr and chemical reactivity parameters are given in ref 2, p 737. Even with the foregoing reservations, the correlations should indicate which effect, inductive or resonance, predominates.

Equations 1 and 2 in Table VI are the pentafluorophenyl analogs of the Taft equations mentioned above. Similar equations have already been derived by Lawrenson.[8,41] We now add a third equation (eq 3, Table VI) relating J_{24} to these functions as shown also in Figure 9. It should be noted that J_{24} relates best to almost the same combinations of the Taft functions as does ϕ_p: $\sigma_R{}^\circ + 0.33\sigma_I$ for ϕ_p *vs.* $\sigma_R{}^\circ + 0.30\sigma_I$ for J_{24}. It can also be seen that ϕ_m forms a poorer relationship (as shown by a lower $(r_{xy})^2$ value) although the root-mean-square value is smaller, a result of the smaller range of ϕ_m values found. In contrast to the monofluorophenyl case, the coefficients of the σ_I terms are not the same for ϕ_p as for ϕ_m. *Subtraction therefore does not eliminate* σ_I, and the use of ϕ_p–ϕ_m as a criterion of resonance interaction of C_6F_5 compounds[18,21] has

Table VI. Equations Relating Nmr Parameters with Hammett–Taft Functions[a]

Eq no.	Equation	$(r_{xy})^2$	RMS	Pts
1	$\phi_p = -49.05\sigma_R{}^\circ - 16.00\sigma_I + 153.72$	0.99	0.91	8
2	$\phi_m = -9.36\sigma_R{}^\circ - 6.91\sigma_I + 162.71$	0.93	0.65	8
3	$J_{24} = 21.00\sigma_R{}^\circ + 6.21\sigma_I + 1.88$	0.98	0.56	8
4	$\phi_p = -52.28\sigma_R{}^\circ + 148.74$	0.85	3.6	8
5	$\phi_p = -22.24\sigma_p + 159.47$	0.91	2.6	11
6	$\phi_m = -8.31\sigma_I + 164.64$	0.54	1.5	11
7	$\phi_m = -8.58\sigma_m + 164.29$	0.76	1.1	11
8	$J_{24} = 22.26\sigma_R{}^\circ + 3.81$	0.87	1.5	8
9	$J_{24} = 10.04\sigma_p - 0.49$	0.91	1.2	11
10	$\phi_p = -34.41\sigma_p + 22.92\sigma_m + 155.51$	0.97	1.5	11
11	$\phi_m = -4.85\sigma_p - 1.06\sigma_m + 163.10$	0.88	0.7	11
12	$J_{24} = 16.44\sigma_p - 12.06\sigma_m + 1.59$	0.99	0.4	11

[a] $(r_{xy})^2$ is the square of the correlation coefficient. RMS is the root-mean-square deviation.

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(36) F. Prosser and L. Goodman, *J. Chem. Phys.*, **38**, 374 (1963); G. L. Caldow, *Mol. Phys.*, **11**, 71 (1966).

(37) R. W. Taft, *et al.*, *J. Am. Chem. Soc.*, **81**, 5343, 5352 (1959).

(38) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, Chapter 13.

(39) R. W. Taft, E. Price, I. R. Fox, K. K. Anderson, I. C. Lewis, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 709, 3146 (1963).

(40) G. W. Parshall, *ibid.*, **88**, 804 (1966).

(41) A different choice of chemical shift values (Table II), due to averaging results and standardizing conditions of measurements, has led to slightly different coefficients in our equations.

little theoretical justification. Some improvement may result from the use of ϕ_p–ϕ_m however, since the difference in shifts eliminates errors such as those due to nonstandardization of the reference and varying bulk susceptibilities of the solvents. As can be seen from eq 1 and 3 of Table VI the coefficient of the resonance parameters is considerably larger than that of the inductive parameter. It is not surprising then that ϕ_p and J_{24} can separately be related to $\sigma_R{}^\circ$ alone, giving reasonable straight lines as shown by eq 4 and 8. *This is the algebraic way of saying that both ϕ_p and J_{24} are sensitive mainly to resonance interactions.*

As shown by eq 1, 2, and 3 in Table VI, the nmr parameter most affected by the inductive function σ_I is ϕ_m. However, the plot of ϕ_m with σ_I (eq 6) is too poor a fit to a straight line to be useful. While the Taft functions $\sigma_R{}^\circ$ and σ_I have been related in this way, it is interesting to find that the original Hammett functions, σ_{para} and σ_{meta}, can be related both separately and in combination to the three nmr parameters (eq 5, 7, 9, 10, 11, 12 of Table VI). The $(r_{xy})^2$ values are in each case comparable to those found for the Taft function.

Further support for the π donor–acceptor relationship of Figure 5 is found in the order of the halogens in the J_{24}–ϕ_p plot. The halogens are well separated, with fluorine nearest the established π donors (NH_2) and iodine nearest the established π acceptors (CN). This confirms that the ordering is mainly dependent upon resonance effects. Examination of σ_I values ($NH_2 < I < Cl < F < CN$)[42] shows that an appreciable inductive contribution would cause the halogens to close up in the J_{24}–ϕ_p plot, leading to a complete inversion of the observed order if inductive effects became dominant.

In conclusion, the values of J_{24} and ϕ_p as found from the pentafluorophenyl group seem to provide a useful guide to electronic behavior within a larger molecule, in particular, the π-electron interaction. It should be possible to use this guide to elucidate the bonding in a variety of systems. In the following paper, its use is demonstrated with reference to phosphines, group IV organometallic derivatives of pentafluorophenol, pentafluorothiophenol, and pentafluoroaniline.

Acknowledgment. We thank Dr. J. S. Martin for helpful discussions. This research was supported in part by the Defence Research Board of Canada, Grant 9530-49. M. G. H. thanks the National Research Council of Canada for a studentship.

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(42) R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958)

Chemical Shifts and Coupling Constants in Pentafluorophenyl Derivatives. II. Application to a Study of Bonding in Selected Compounds[1,2]

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Abstract: The π interactions within molecules containing the pentafluorophenyl group are examined using the J_{24}–ϕ_p relationship as proposed in the preceding paper. The following series, selected from the 73 pentafluorophenyl compounds studied, are discussed: pentafluorophenylphosphines and some of their complexes including metal carbonyl derivatives; compounds of the type $C_6F_5XMR_3$, where X = O or S, M = Si, Ge, Sn, or Pb, and R = CH_3 or C_6H_5; and of the type C_6H_5NHR where R = $B(C_6H_5)_2$, CH_3, H, $Si(CH_3)_3$, or $Sn(CH_3)_3$. Estimates of (p→d) π bonding between group IV elements and oxygen, sulfur, and nitrogen are given. The influence of σ-bond polarity upon back donation by halogens is considered.

In paper I of this series, an approach to the study of π bonding was outlined based on the linear relation of J_{24}, the coupling constant between the *o*- and *p*-fluorine atoms of the pentafluorophenyl group, to ϕ_p, the chemical shift of the *p*-fluorine.[1] The straight line correlation is of interest in itself, and hopefully will contribute to a further understanding of fluorine coupling mechanisms. Within the J_{24}–ϕ_p relationship, the positions of common organic substituents are such that π-acceptor groups occur at low ϕ_p values and high J_{24} values, whereas π-donor groups occur at high ϕ_p values and large negative J_{24} values. This empirical observation was shown to have theoretical support by reference to the Hammett–Taft reactivity parameters, $\sigma_R{}^\circ$ and σ_I, and to earlier MO calculations of π-electron densities on the *p*-carbon. It appeared that the inductive contribution from the substituent–pentafluorobenzene bond to the J_{24}–ϕ_p values was small in comparison to the resonance effect originating from the π interactions of the substituent.

Experimental Section

Details of the nmr analysis and the conditions of measurement have been given previously.[1] The coupling constant concerned in this paper, J_{24}, is easily identified as the minor triplet in the *p*-fluorine multiplet and since this is normally a first-order interaction, its value is simply determined. The chemical shift was taken as the center of the multiplet. The J_{24}–ϕ_p values for 12 compounds not previously reported are presented.

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(1) Part I: M. G. Hogben and W. A. G. Graham, *J. Am. Chem. Soc.*, **91**, 283 (1969).

(2) Taken in part from the Ph.D. thesis of M. G. Hogben, University of Alberta, 1967.