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 $\sigma_R°$ 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 $\sigma_R°$ 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.

---

[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]

M. G. Hogben, R. S. Gay, A. J. Oliver, J. A. J. Thompson, and W. A. G. Graham

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada. *Received March 2, 1968*

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, $\sigma_R°$ 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.

---

[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.

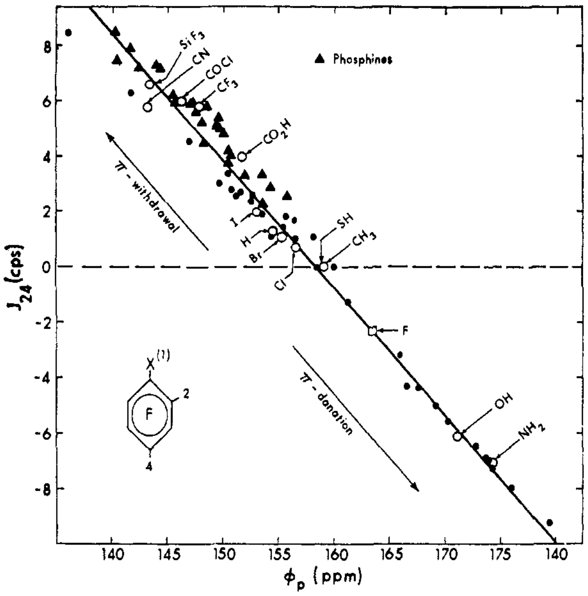


Figure 1. The relationship of the *o*–*p*-fluorine coupling constant (J_{24}) to the chemical shift of the *p*-fluorine (ϕ_p) for 73 C_6F_5–X compounds. The ϕ_p scale is based on C_6F_6 = 163.0 ppm upfield from $CFCl_3$. The π donor–acceptor effect of the substituent, X, is indicated, and the common substituents labeled. For the point representing fluorine itself as substituent, see ref 9. Closed triangles represent the 29 compounds with phosphorus as substituent atom.

The pentafluorothiophenoxy derivatives were prepared by the reaction of the appropriate organometallic halide with pentafluorothiophenol. The other new compounds were further members of the series of pentafluorophenoxy- and pentafluoroaniline derivatives of paper I and were prepared in the same way.

Pentafluoro-N,N-dimethylaniline was prepared by refluxing pentafluoroaniline with aqueous formic acid and aqueous formaldehyde after the manner of Allen, Burdon, and Tatlow.[3]

Results and Discussion

Values of J_{24} and ϕ_p for 73 pentafluorophenyl derivatives[1,4–8] have been examined in this study; the nmr parameters for 56 of these compounds have been measured in this laboratory. The positions of compounds on the J_{24}–ϕ_p plot can be related to the π donor–acceptor properties of the substituent as indicated in Figure 1. Closer examination of the relationship reveals a marked separation of compounds depending on whether a first-row element is bonded to the pentafluorophenyl ring, or whether the substituent is attached through an element from the second or third period. This may be clearly seen for substituents involving main groups V, VI, and VII. The separation is evidently due to the absence of vacant d orbitals in the valence shell of first-row elements. Hence amines, as represented by the NH_2 group, act as π donors, while phosphines show weak to strong acceptor properties; donation of the phosphorus lone pair to the C_6F_5 ring is apparently more than countered by a π (p→d) withdrawal of electrons from the ring. Similarly, the π (p→p) donation that causes the OH group to be a strong donor is counterbalanced in C_6F_5SH by donation of ring π electrons to the vacant 3d orbitals of sulfur. Thus, the SH group shows a net π effect close to zero, while other SR derivatives have slight π-acceptor properties. The halogen substituents also show this effect. The point representing fluorine itself[9] is well separated from the other halogens.

One notable exception to this trend of separation of first and later row substituents is found in the case of CF_3 and SiF_3; here, CF_3 appears to be almost as strong a π acceptor as SiF_3, and the points lie relatively close on the J_{24}–ϕ_p plot. The unusual π-acceptor property of CF_3 has been previously noted. A σ_R value of +0.14 has been given[10] to CF_3 which places it among the strongest π acceptor substituents, in good agreement with the present study. The π acceptor character of CF_3 has been explained in terms of no-bond resonance forms.[11] An alternative description in molecular orbital terms[12] makes use of vacant σ* antibonding orbitals of the C–F bonds which are presumably lowered in energy by the highly electronegative fluorine atoms.

The Halogens. To show that the ordering of substituents in the J_{24}–ϕ_p relationship was dependent upon resonance rather than inductive effects, it was found helpful to use Hammett–Taft functions as supporting evidence.[1] The order of π-donor strengths in the halogens, F > Cl > Br > I, agrees with their positions on the J_{24}–ϕ_p plot. However, in the case of substituents which may involve partial multiple bonding to the ring (*i.e.*, back-donation of π electrons in addition to the σ bond), the $\sigma_R{}^\circ$ values will not necessarily be the same for systems other than disubstituted benzenes. Thus, although the ordering of the four halogens among themselves according to π-donor strength is the same in both phenyl and pentafluorophenyl systems, their positions relative to substituents with negligible π effects (CH_3 and H) are not. In the phenyl series, the halogens are essentially weak π donors, with $\sigma_R{}^\circ$ values becoming more negative in the series H < I < CH_3 < Br < Cl < F; this is the same order found by Taft in ^{19}F nmr studies on monofluorophenyl derivatives.[13] However, halogens as substituents on the pentafluorophenyl ring appear to be much weaker π donors; the order of π-donor strength is I < H < Br < Cl < CH_3 < F, so that with the exception of fluorine they might be considered π acceptors. *The different character of the halogens in the C_6H_5X systems seem to relate to the polarity of the ring–halogen σ bond.* In the halobenzenes, this bond will be rather highly polar with the halogen atom negative. This polarity will favor the transfer or back-donation of halogen lone-pair electrons to the benzene ring so that the halogens will appear as π donors.[14] In the penta-

---

(3) J. G. Allen, J. Burdon, and J. C. Tatlow, *J. Chem. Soc.*, 6329 (1965).

(4) P. L. Timms, D. D. Stump, R. A. Kent, and J. L. Margrave, *J. Am. Chem. Soc.*, **88**, 940 (1966); R. B. Johannesen, F. E. Brinkman, and T. D. Coyle, *J. Phys. Chem.*, 72, 660 (1968).

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

(6) N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Mol. Phys.*, **8**, 133 (1964).

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

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

(9) The position of the fluorine point is based on the measured chemical shift, ϕ_p = 163.0 ppm, which leads to a predicted J_{24} value of −2.0 cps.

(10) R. W. Taft, *J. Am. Chem. Soc.*, **79**, 1045 (1957).

(11) J. D. Roberts, R. L. Webb, and E. A. McElhill, *ibid.*, 72, 408 (1950).

(12) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **6**, 1213 (1967).

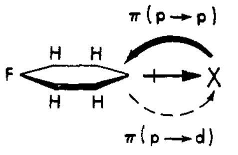
(13) R. W. Taft, E. Price, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 709, 3146 (1963).

Table I. *p*-Fluorine Chemical Shifts (ϕ_p) and the *o*–*p*-Fluorine Coupling Constant (J_{24}) of Several Pentafluorophenylphosphines

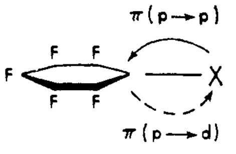
	$\phi_p{}^a$	$J_{24}{}^b$	Ref^c		$\phi_p{}^a$	$J_{24}{}^b$	Ref^c
C_6F_5–POF_2	140.2	8.6	1	$(C_6F_5)_2POF$	141.5	7.9	1
C_6F_5–$P(C_6H_5)_2HCl$	140.4	7.5	1	$(C_6F_5)_2PCl$	147.5	5.6	1,8
C_6F_5–$P(C_6H_5)_2BCl_3$	143.8	7.3	1	$(C_6F_5)_2P(C_6H_5)Mo(CO)_5$	148.1	5.2	1
C_6F_5–PCl_2	145.4	6.2	1, 8	$(C_6F_5)_2PC_6H_5$	150.5	4.2	1
C_6F_5–$P(C_6H_5)_2O$	147.3	5.9	1	$(C_6F_5)_2PH$	150.5	3.8	8
C_6F_5–PF_2	147.4	5.9	8	$(C_6F_5)_2PN(CH_3)_2$	152.1	3.3	8
C_6F_5–$P(C_6H_5)_2S$	148.6	5.8	1				
C_6F_5–$PCl\ N(CH_3)_2$	149.6	5.4	8				
C_6F_5–$P(C_6H_5)_2W(CO)_5$	149.2	5.2	1				
$\{C_6F_5P(C_6H_5)_2\}_2PdCl_2$	149.2	5.1	1				
C_6F_5–$P(C_6H_5)_2Fe(CO)_4$	149.5	5.0	1	$(C_6F_5)_3PO$	142.4	7.2	1
C_6F_5–$P(C_6H_5)_2Cr(CO)_5$	149.5	5.0	1	$(C_6F_5)_3PS$	144.3	7.2	1
C_6F_5–$P(C_6H_5)_2Mo(CO)_5$	150.0	4.8	1	$(C_6F_5)_3PF_2$	146.0	6.0	1
C_6F_5–$P(C_6H_5)_2$	150.6	4.0	1	$(C_6F_5)_3P$	147.7	4.5	1
C_6F_5–$P(CH_2CH_3)_2$	153.5	3.3	8				
C_6F_5–$P(CH_3)_2$	154.2	2.9	1, 8				
C_6F_5–PH_2	153.7	2.3	8				
C_6F_5–$P[N(CH_3)_2]_2$	155.7	2.6	8				

^{a} In parts per million (ppm), based on the scale C_6F_6 = 163.0 ppm upfield from $CFCl_3$. ^{b} In cycles per second (cps). ^{c} Values from ref 8 have been adjusted as described in ref 1.

fluorophenyl system, however, the relatively high electronegativity of the C_6F_5 group[15] will diminish the polarity of the ring–substituent σ bond, and the tendency of the halogen to donate its lone pairs to the ring will be correspondingly reduced. Fluorine still appears as a π donor but in the other halogens where vacant valence-shell d orbitals are available, the balance is shifted to a net π-acceptor property; schematically, the proposed bonding might be represented as in I and II, where the symbol ↔ denotes a strong polarity in the σ bond.



I



II

A matter of very great interest in coordination chemistry is the nature of halogen–metal interaction. Recently, two groups have made use of fluorine chemical shifts of fluorophenyl substituents on a metal atom to gauge this interaction, with interesting although sometimes different results.[16,17] In a series of square-planar platinum(II) complexes of the type *trans*-[Pt(X)-$C_6F_5(PEt_3)_2$] (where X = Cl, Br, I, CH_3) it was concluded that the halogens were π acceptors relative to methyl, the order of increasing π-acceptor strength being CH_3 < Cl < Br < I.[16] On the other hand, using fluorine shifts of the corresponding monofluorophenyl-platinum(II) complexes, Parshall concluded that chlorine, bromine, and iodine were π donors.[17,18]

Recalling that chlorine, bromine, and iodine appear to be π acceptors in the C_6F_5X system,[1] but π donors in the FC_6H_4X system of Taft,[13] it now seems possible to reconcile these apparently opposed conclusions as to halogen–metal π interaction. For the monofluorophenyl case, σ-bond polarities in the ring–Pt–X system are such as to enhance back-donation. The more electronegative pentafluorophenyl group, on the other hand, alters polarity in the σ-bond system so as to reduce back donation from Pt to C_6F_5 and from X to Pt. This is clearly a simplified approach to an otherwise complicated bonding situation. The conclusion here would be that halogen ligands may serve as either π acceptors or π donors depending upon the circumstances. For example, it has recently been suggested on the basis of infrared studies that halogen in the pentacarbonylmanganese halides, $XMn(CO)_5$, is a π donor.[19] In this case the polarity of the X–Mn σ bond is such as to promote the π-donor character of the halogen.

The Phosphines. The over-all positions of all 29 derivatives of phosphorus are shown in Figure 1. In general they range from weak π acceptors to strong π acceptors. Table I gives the J_{24} and ϕ_p values for each derivative and with reference to this table the following results are of interest.

Within the phosphines, there can be distinguished a number of smaller series in which relative positions can be explained in terms of π bonding. The J_{24}–ϕ_p plot has already been shown to illustrate the bonding in the series consisting of pentafluorophenyldiphenylphosphine and its metal carbonyl and boron trichloride adducts.[20a] These compounds increase in withdrawal

---

(14) This viewpoint is similar to the synergic mechanism attributed to the metal–ligand bond in coordination chemistry: *cf.* F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1966, p 728.

(15) For references concerning electronegativity values for C_6F_5, *cf.* J. A. J. Thompson and W. A. G. Graham, *Inorg. Chem.*, **6**, 1875 (1967).

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

(17) G. W. Parshall, *J. Am. Chem. Soc.*, **86**, 5367 (1964); **88**, 704 (1966).

(18) Although the over-all trend of π donor or acceptor character can be inferred from Parshall's method, the significance of small trends within the series should not be overrated. The π-acceptor parameter is obtained as the difference between two fluorine chemical shifts, and for CH_3, Cl, Br, and I covers a range of only 0.2 ppm. This is comparable to the variation that solvent effects can introduce, a fact which is apparent when the π-acceptor parameter is calculated from Parshall's results in cyclohexane; the results are: CN, 0.86; $C_6H_5C{\equiv}C$, 0.4; C_6H_5, 0.2; SCN (or NCS), 0.1; *p*-FC_6H_5 and CH_3, 0.0; OCN (or NCO), Cl, Br, and I, −0.3. Thus the precise ordering of the halogens is different in cyclohexane than in acetone, although in both solvents they appear to be π donors to platinum in the monofluorophenyl systems.

(19) W. A. Graham, *Inorg. Chem.*, 7, 315 (1968).

(20) (a) M. G. Hogben, R. S. Gay, and W. A. G. Graham, *J. Am. Chem. Soc.*, **88**, 3457 (1966). (b) We thank a referee for pointing out that the P–B bond pair can act in a similar way to the P lone pair and hence back donation to the ring is reduced though not necessarily eliminated.

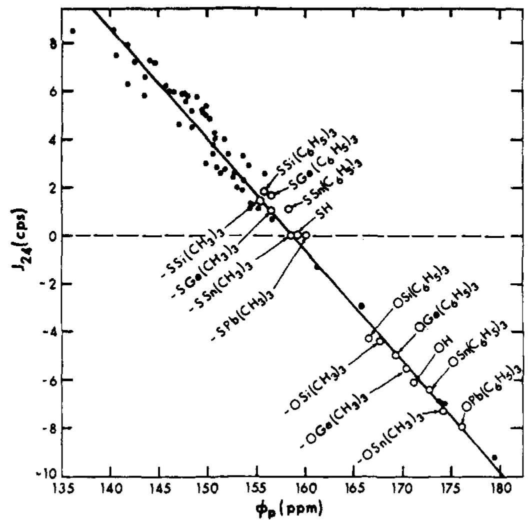


Figure 2. The J_{24}–ϕ_p relationship for methyl and phenyl, oxygen and sulfur derivatives of group IV.

of electrons from the pentafluorophenyl ring in that order. Since the PR_2 group is a π acceptor, in contrast to the NR_2 group which is shown to be a π donor, one may presume that the π (p→p) donation of the lone pair is outweighed by the π acceptance of phosphorus d orbitals. However, when phosphorus is complexed with BCl_3 no lone pair is available[20b] for donation to the pentafluorophenyl ring with the result that π (p→d) bonding is the principal effect. The intermediate π-acceptor property of the metal carbonyl derivative can be rationalized by the competition between the filled metal d orbitals and the benzenoid π electrons for access to the vacant d orbitals of phosphorus. The π (p→d) bond in this compound is therefore not as strong as in the BCl_3 complex in which, of course, there is no such competition.[20b]

The results given here show further that when the lone pair on phosphorus is removed by bonding to oxygen or sulfur, the result is again a withdrawal of electrons from the pentafluorophenyl ring which is stronger than that in the metal carbonyl adduct but weaker than in the boron trichloride adduct. It can also be seen that removal of the lone pair in the formation of the phosphonium chloride causes a more complete withdrawal of electrons from the C_6F_5 group than in the boron trichloride adduct. Hence among pentafluorophenyldiphenylphosphine derivatives, $C_6F_5P(C_6H_5)_2X$, the π-acceptor character of the phosphorus atom increases along the series: [free phosphine] < $Mo(CO)_5 \sim Cr(CO)_5 \sim Fe(CO)_4 \sim W(CO)_5 < S < O < BCl_3 < H^+Cl^-$, which presumably reflects decreasing back-donation by the complexed group.

A similar increase in π withdrawal is found when pentafluorophenylphosphorus difluoride is oxidized to the corresponding oxyfluoride. Again, when the lone pair in tris(pentafluorophenyl)phosphine is donated to oxygen or sulfur, an increase in π withdrawal from the benzene ring is found. The lone pair is also effectively removed when the phosphorus expands its coordination to five in the compound tris(pentafluorophenyl)phosphorus difluoride. Thus π withdrawal from C_6F_5 increases along the series: $(C_6F_5)_3P < (C_6F_5)_3PF_2 < (C_6F_5)_3PS < (C_6F_5)_3PO$.

Table I also reveals an order of increasing π-acceptor power of X in the series C_6F_5X which is consistent with the above considerations: $P[N(CH_3)_2]_2 < P(CH_3)_2 < P(C_2H_5)_2 < P(C_6H_5)_2 < P(C_6F_5)_2 < PF_2 < PCl_2$.

Group IV Derivatives of Oxygen and Sulfur. Figure 2 and Table II give the ϕ_p and J_{24} values for compounds of the series: C_6F_5–XMR_3, where X is oxygen or sulfur, M is Si, Ge, Sn, or Pb, and R is methyl or phenyl. The separation of sulfur compounds from the analogous oxygen compounds has already been attributed to back-donation of ring π electrons to the vacant d orbitals of sulfur; this reduces the net π-donor strength of sulfur substituents in general to almost zero. The lone pairs on sulfur and oxygen have two possible modes of bonding: they can interact with the pentafluorophenyl group causing an increase in π-electron density in the ring, or with the group IV metal, when possible, decreasing ring π-electron density. Thus, the two competing bonding possibilities will have opposite effects on the pentafluorophenyl ring, which provides a means of estimating the extent of π bonding of oxygen or sulfur to the group IV element.

The observed order of the group IV elements is the same in both oxygen and sulfur series, and indicates that the tendency to form π bonds with oxygen (or sulfur) decreases in the series Si > Ge > Sn > Pb. A possible explanation of this would be that the overlap between the group IV vacant d orbital and the group VI lone pairs is strongest for silicon and decreases to lead. Attempts to prepare the trimethylcarbon (*t*-butyl) derivatives have not been successful. These points would be extremely valuable since they would represent cases in which double bond formation by the group IV element was possible only with the benzene ring. The points for the phenol and thiophenol are available, however, and their positions within the two series are of some interest. The phenol derivative is midway between germanium and tin, which would indicate that while silicon and germanium are π acceptors, tin and lead are π donors relative to hydrogen. These estimates of the π-acceptor properties of the group IV metals are in general accord with conclusions drawn from base strength measurements.[21–23] The electron-donating properties of tin and lead were explained in terms of electronegativities and inductive effects. However, in the light of this study, it may well be possible that tin and lead are exhibiting π-donor properties.

For the sulfur compounds, the thiophenol is close to tin and lead (Figure 2) and silicon and germanium again act as π acceptors. Thus the π-acceptor properties of germanium are much stronger with sulfur than with oxygen, which also agrees with the previous studies of C–D stretching frequencies in mixtures of base and deuteriochloroform.[23]

The Pentafluoroaniline Derivatives. The J_{24} and ϕ_p values of several pentafluoroaniline derivatives are presented here with results that are relevant to the question of nitrogen–silicon π bonding.[24–28] The planar

---

(21) R. West, R. H. Baney, and D. C. Powell, *J. Am. Chem. Soc.*, **82**, 6269 (1960).

(22) N. A. Matwiyoff and R. S. Drago, *J. Organometal. Chem.* (Amsterdam), **3**, 393 (1965).

(23) E. W. Abel, D. A. Armitage, and D. B. Brady, *Trans. Faraday Soc.*, 3459 (1967).

(24) E. W. Randall, J. J. Elner, and J. J. Zuckerman, *J. Am. Chem. Soc.*, **88**, 622 (1966).

(25) E. A. V. Ebsworth, *Chem. Commun.*, 530 (1966).

Table II. *p*-Fluorine Chemical Shifts (ϕ_p) and the *o*-*p*-Fluorine Coupling Constant (J_{24}) of Series of Group IV Derivatives of Sulfur and Oxygen[a]

	ϕ_p[b]	J_{24}[c]		ϕ_p[b]	J_{24}[c]
C_6F_5-$SSi(CH_3)_3$[d]	155.3	1.4	C_6F_5-$SSi(C_6H_5)_3$[d]	155.7	1.8
C_6F_5-$SGe(CH_3)_3$[d]	156.5	1.0	C_6F_5-$SGe(C_6H_5)_3$[d]	156.5	1.7
C_6F_5-$SSn(CH_3)_3$[d]	158.4	0	C_6F_5-$SSn(C_6H_5)_3$[d]	158.1	1.1
C_6F_5-$SPb(CH_3)_3$[d]	160.0	0			
C_6F_5-SH	159.1	0			
C_6F_5-$OSi(CH_3)_3$	167.6	−4.4	C_6F_5-$OSi(C_6H_5)_3$	166.5	−4.3
C_6F_5-$OGe(CH_3)_3$[d]	170.3	−5.6	C_6F_5-$OGe(C_6H_5)_3$	169.2	−5.0
C_6F_5-$OSn(CH_3)_3$[d]	174.2	−7.3	C_6F_5-$OSn(C_6H_5)_3$	172.8	−6.4
			C_6F_5-$OPb(C_6H_5)_3$	176.1	−8.0
C_6F_5-OH[e]	171.2	−6.1			

[a] Values here are taken from paper I unless otherwise stated. [b] In parts per million (ppm), based on the scale C_6F_6 = 163.0 ppm upfield from $CFCl_3$. [c] In cycles per second (cps). [d] Results of this study, not reported previously. [e] Reference 6.

structure of trisilylamine and the implied sp^2 hybridization of the nitrogen σ bonds has been explained in terms of nitrogen to silicon (p→d) π bonding. This effect on the σ hybridization and geometry of nitrogen was at one time viewed as a necessary consequence of the nitrogen–silicon (p→d) bonding in other silylamines. Thus it was surprising when the value of $J_{^{15}N-H}$ in C_6H_5-$^{15}NHSi(CH_3)_3$, 76 cps, which was expected to increase with increased percentage of s character in the nitrogen σ orbitals, was but little changed from that reported for aniline itself, 78 cps.[24] Double-bond formation between nitrogen and silicon would presumably have resulted in sp^2 hybridization, giving higher $J_{^{15}N-H}$ values, as in the case of the pyridinium ion (variously given as 98.7 and 90.5 cps)[29,30] as opposed to sp^3 hybridization exemplified by the ammonium ion ($J_{^{15}N-H}$ = 73.7, 73.2 cps).[30,31] It was pointed out,[25] however, that a nonplanar geometry does not exclude the possibility of π bonding between the lone pair and silicon d orbitals, which would be possible even in a pyramidal silylamine. It was also suggested that the above argument notwithstanding, the hybridization used in the N–H bond need not change if the silicon gains double-bond character at the expense of the benzene ring alone.[27] In other words, this argument seems to imply that it would not matter to which atom the nitrogen donates its lone pair since the N–H hybridization is dependent only upon the total of the lone-pair donation to both silicon and the benzene ring.

The need for a nonstereochemical means of investigating nitrogen–silicon π bonding has been pointed out;[26] the approach suggested here may fill this need, since it depends only on the electron distribution as experienced by the pentafluorophenyl ring and not upon the geometry of the nitrogen, nor the nature of the remaining N–H bond.

It is evident from Figure 3 and Table III that the NH_2 group is a π donor, the result of interaction of the lone pair with the pentafluorophenyl ring. Replacement of hydrogen by a group capable of π bonding with nitrogen should reduce donation to the pentafluorophenyl ring. In the series C_6F_5–N(H)R, π donation by R to the pentafluorophenyl ring increases in the order $B(C_6H_5)_2 < CH_3 \sim Si(CH_3)_3 \sim H < Sn(CH_3)_3$. The expected nitrogen to boron (p→p) π bonding in the boron compound reduces the donation of the lone pair to the pentafluorophenyl ring. Since no change in the J_{24} and ϕ_p values is found when one of the protons of aniline is substituted by either a methyl or trimethylsilyl group, it is concluded from these observations that there is no appreciable π character in the nitrogen–silicon bond in N-trimethylsilylpentafluoroaniline. These results are in contrast to the analogous oxygen and sulfur compounds, which were shown by this and other techniques to involve appreciable double bonding with silicon.

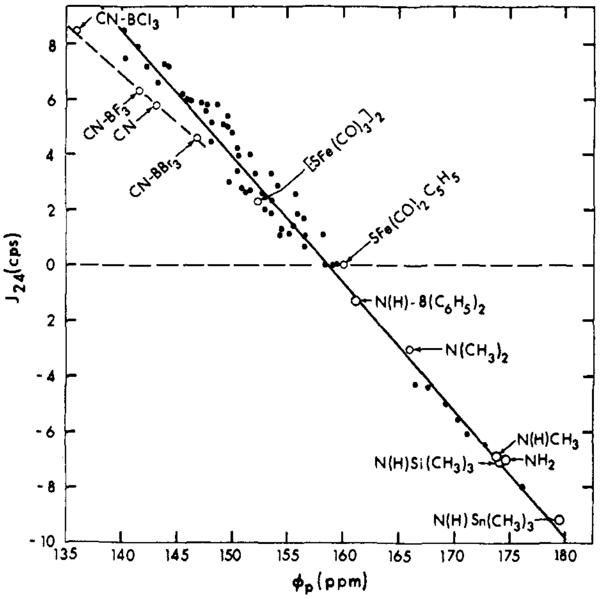


Figure 3. The J_{24}–ϕ_p relationship for cerain pentafluoroaniline, pentafluorobenzonitrile, and thioiron carbonyl derivatives of Table IV.

It is also apparent from Figure 3 that substitution of hydrogen by the trimethyltin group *enhances* π donation to the ring; this is in accord with the decreasing order of π acceptance of the group IV metals as found for oxygen and sulfur and also with the enhanced basicity of methylstannyl amines as found by other techniques.[23]

Although the π-donor character of nitrogen in the NH_2 group is unchanged when one methyl is substi-

---

(26) E. W. Randall and J. J. Zuckerman, *Chem. Commun.*, 732 (1966).

(27) P. G. Perkins, *ibid.*, 268 (1967).

(28) M. G. Hogben, A. J. Oliver, and W. A. G. Graham, *ibid.*, 1183 (1967).

(29) A. J. Brown and E. W. Randall, *Mol. Phys.*, 8, 567 (1964).

(30) G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Am. Chem. Soc.*, 86, 5564 (1964).

(31) J. D. Baldeschwieler, *J. Chem. Phys.*, 36, 152 (1962).

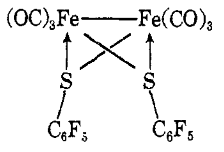
Table III. *p*-Fluorine Chemical Shifts (ϕ_p) and the *o*–*p*-Fluorine Coupling Constant (J_{24}) for Some Pentafluoroaniline and Pentafluorophenyltin Derivatives and Several Other Compounds

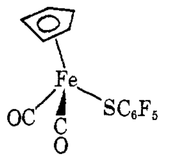
	ϕ_p[a]	J_{24}[b]	Ref
C_6F_5–N(H)B$(C_6H_5)_2$	161.2	−1.3	*c*
C_6F_5–N$(CH_3)_2$	166.2	−3.1	*c*
C_6F_5–N(H)CH_3	173.8	−6.9	6
C_6F_5–N(H)Si$(CH_3)_3$	174.1	−7.0	1
C_6F_5–NH_2	174.3	−7.0	1, 5
C_6F_5–N(H)Sn$(CH_3)_3$	179.5	−9.2	*c*
$(C_6F_5)_3$–SnMn$(CO)_5$	150.4	3.4	1
$(C_6F_5)_2$–Sn$(C_6H_5)_2$	149.6	3.0	1
$(C_6F_5)_2$–Sn(C_6H_5)Mn$(CO)_5$	150.7	2.8	1
$(C_6F_5)_2$–Sn$[Mn(CO)_5]_2$	151.6	2.7	1
C_6F_5–Sn$(C_6H_5)_3$	151.2	2.6	1
C_6F_5–Sn$(C_6H_5)_2$Mn$(CO)_5$	152.6	2.6	1
C_6F_5–Sn$(CH_3)_3$	153.5	1.9	6
$[C_6F_5–SFe(CO)_3]_2$	152.5	2.4	34
C_6F_5–SFe$(CO)_2C_5H_5$	159.3	0	34
C_6F_5–$CNBCl_3$	136.0	8.5	1
C_6F_5–$CNBF_3$	141.6	6.3	1
C_6F_5–CN	143.2	5.8	1
C_6F_5–$CNBBr_3$	146.9	4.6	1

[a] In parts per million (ppm), based on the scale C_6F_6 = 163.0 ppm upfield from $CFCl_3$. [b] In cycles per second (cps). [c] Results from this study, not reported previously.

tuted for a hydrogen, the position of the dimethylamino group indicates a considerable reduction in π donation to the ring. Thus can be explained by the inhibition of resonance caused by steric interaction between the methyl groups and the *o*-fluorines, an effect which has been previously noted[3, 32] in this compound.

Tin Compounds. A series of pentafluorophenyltin compounds[33] was studied. As can be seen in Table III the range of values for ϕ_p and J_{24} was not large, and an extensive discussion of the bonding is perhaps not justified. However, it is apparent that in the change from Sn–C_6H_5 to Sn–Mn$(CO)_5$, the acceptor strength of the tin atom decreases. This is consistent with the view that the tin–manganese bond is multiple in character, involving donation of electron density from filled 3d manganese orbitals to vacant 5d orbitals of tin.[19, 34]


III


IV

Two Pentafluorothiophenoxy Derivatives of Iron Carbonyl. Table III gives the J_{24} and ϕ_p values for compounds III and IV, which have been studied by Stone, *et al.*[35] Comparing their positions on the J_{24}–ϕ_p plot in Figure 3, we find that the dimeric compound, III, with bridging sulfur, shows the strongest withdrawal effect of all sulfur compounds examined (see Figure 2), whereas the monomer, IV, shows a negligible net π effect and is comparable to pentafluorothiophenol. This can be explained if it is assumed that the lone pair on sulfur in IV that normally interacts with the benzene ring has been donated to the other iron atom in III. Hence the benzene ring experiences primarily the (p→d) π withdrawal of the sulfur without its accompanying (p→p) π-donor character. This is analogous to the arguments applied in the phosphine series.

The Pentafluorobenzonitrile Complexes. It has been mentioned earlier that the CN group is a strong acceptor. The lone pair on nitrogen can be donated to Lewis acids, in particular boron trihalides. The results of Table III and Figure 3 show that complexing pentafluorobenzonitrile with BF_3 increases the π withdrawal of the CN group. When BCl_3, a stronger Lewis acid than BF_3, is complexed, the π withdrawal of the CN group is further increased. However, complexing pentafluorobenzonitrile with BBr_3, an even stronger Lewis acid, gives the anomalous result of decreasing the π acceptor properly to below that of the CN group itself.

As mentioned in the preceding paper,[2] the benzonitrile complexes were not isolated or fully characterized. Caution should therefore be applied in interpreting this interesting behavior. However, the spectra showed the presence of only one pentafluorophenyl species with the sharpest peaks found in the course of this study.

Acknowledgment. We thank the Defence Research Board of Canada for support of this work under Grant No. 9530-49. We wish to thank the National Research Council of Canada for studentships to M. G. H., R. S. G., and J. A. J. T.

---

(32) J. Burdon, *Tetrahedron*, **21**, 1101 (1965).

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

(34) W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *ibid.*, **5**, 2217 (1966).

(35) J. Cooke, M. Green, and F. G. A. Stone, *J. Chem. Soc.*, *A*, 170 (1968). We are grateful to Professor Stone for making available in advance of publication the results of his work on these interesting derivatives.