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¹⁹F contact interaction shifts: effects of fluorine conjugation[†]

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¹⁹F contact interaction constants for a series of ortho-, meta- and parasubstituted fluorobenzenes have been derived from isotropic hyperfine contact interaction shifts on appropriate N-substituted nickel (II) aminotroponeimineates. It is shown that the simple proportionality between proton contact interaction constants, a_i , and $p\pi$ spin densities of adjacent carbon atoms, ρ_i , of aromatic C–H fragments ($a_i = Q\rho_i$) does not hold for aromatic C–F fragments. Instead, there is an important $\pi\pi$ contribution to ¹⁹F contact interaction constants in fluoroaromatics which results from π -bonding between fluorine and the aromatic system. A self-consistent analysis of ¹⁹F contact interaction constants in fluoroaromatics is given in terms of C–F π -bond orders.

1. INTRODUCTION

Spin density distributions in paramagnetic molecules can be obtained from the nucleus-electron isotropic hyperfine contact interaction [1]. Two experimental approaches are available for the determination of the contact interaction constants, a_i , of a paramagnetic species. One approach is from the hyperfine splittings of EPR spectroscopy [2]. Contact interaction constants also may be derived from the contact shifts observed under certain conditions in the NMR spectra of paramagnetic species. The EPR approach has up to the present been more generally applied; in order that contact shifts be observed in NMR either or both the conditions

$$T_1^{-1} \gg a_i,$$
$$T_e^{-1} \gg a_i.$$

must be satisfied [3]. In the above inequalities, T_1 is the electron spin relaxation time, and T_e is the characteristic exchange time for the paramagnetic species. However, when it is applicable the NMR approach has the great advantage over EPR in that the sign of a contact interaction constant is given by the direction of the contact shift (high field or low field). In the EPR experiment, signs of contact interaction constants are indeterminate. We have recently been engaged in studies of some paramagnetic chelates where the above conditions are satisfied [4, 5, 6].

However, even after the contact interaction constant is obtained, the very difficult problem of translating this experimental quantity into a reliable spin density remains. And indeed, the most significant advances in our understanding of the electronic structures of molecules in the past five years have come about as a result of the experimental and theoretical efforts to establish quantitative connections between contact interaction constants and spin density distributions [7].

† Contribution No. 742.

McConnell [1] in 1956 postulated that for an aromatic C-H fragment there was a simple proportionality between the spin density centred on carbon, ρ_{c} , and the proton-electron contact interaction constant given by

$$a_{\rm H} = Q \rho_{\rm C}.\tag{1}$$

Subsequent experimental and theoretical work has established that, to a good approximation, Q for the C-H fragment is -22.5 gauss [8]. The minus sign for Q comes about as a result of the indirect π - σ mechanism that places a negative spin density on the hydrogen atom if the carbon $p\pi$ spin density is positive.

Experimental and theoretical studies, however, concur in assigning a value of about +27 gauss to the proportionality constant between the contact interaction constant of the hydrogen atoms of the methyl group and the spin density on the adjacent carbon atom for an aromatic \dot{C} -CH₃ fragment [9]. The positive sign for Q here comes about because an unpaired electron on the aromatic carbon atom can be delocalized directly into the 1s orbitals of the hydrogen atoms [9, 10] of the methyl group by the well-known hyperconjugative mechanism. The appropriate values of Q for other bonding situations have not yet been established with any certainty.

In the present study we will present some results on the relationship between fluorine contact interaction constants and carbon $p\pi$ spin densities in fluoroaromatics. These results are pertinent to the question of possible conjugation between the fluorine and the ring. Double bond character for X-F bonds has been widely postulated [11], but the physical evidence for its existence has been somewhat ambiguous.

2. Experimental

A general procedure for the synthesis of N,N'-disubstituted 1-amino-7imino-1,3,5-cycloheptatrienes (aminotroponeimines) has been published [12]. The isomeric fluorophenyl derivatives described in this report were prepared similarly from the reaction of the appropriate fluoroaniline (two equivalents) with 5,5,6,6-tetrafluoro-1,3-cycloheptadiene (one equivalent) and triethylamine (four equivalents) in refluxing methanol.

N,N'-di(p-fluorophenyl) aminotroponeimine was isolated in 74.5 per cent crude yield as the red-orange crystalline base, m.p. 113–114° after four crystallizations from methanol.

Anal. Calcd. for $C_{19}H_{14}N_2F_2$: C, 74.0; H, 4.58; N, 9.09. Found: C, 74.2; H, 4.58; N, 9.43.

The nickel chelate was prepared by heating an ethanol solution of the ligand with aqueous ammoniacal nickel chloride. After two crystallizations from methylene chloride-methanol, the chelate had m.p. 245-246°.

Anal. Calcd. for $C_{38}H_{26}N_4F_4Ni$: C, 67.8; H, 3.89; N, 8.33. Found: C, 67.8; H, 4.27; N, 8.30.

N,N'-di(*m*-fluorophenyl) aminotroponeimine was prepared similarly (49.5 per cent crude yield), but it proved more convenient to isolate and characterize it as the mono-hydrochloride. Several crystallizations from isopropanol-methanol gave yellow-orange needles, mp. 219.2–220°.

Anal. Calcd. for $C_{19}H_{15}N_2F_2Cl$: C, 66·2; H, 4·39; N, 8·13. Found: C, 66·1; H, 4·48; N, 7·98. The nickel chelate, prepared as described above, melts at $189-190^{\circ}$ after two crystallizations.

Anal. Calcd. for $C_{38}H_{26}N_4F_4Ni$: C, 67.9; H, 3.89; N, 8.33. Found: C, 68.3; H, 3.94; N, 8.58.

N,N'-di(o-fluorophenyl) aminotroponeimine was similarly isolated and characterized as the hydrochloride (93 per cent crude yield). Three crystallizations from isopropanol-methanol gave long yellow needles, m.p. 214–216°.

> Anal. Calcd. for $C_{19}H_{15}N_2F_2Cl$: C, 66·2; H, 4·39; N, 8·13. Found: C, 66·4; H, 4·57; N, 7·78.

The nickel chelate crystallized from methylene chloride-methanol as dark red microcrystals, m.p. 239-240°.

Anal. Calcd. for $C_{38}H_{26}N_4F_4Ni$: C, 67.9; H, 3.89; N, 8.33. Found: C, 67.7; H, 3.96; N, 8.21.

The NMR spectra were obtained in CDCl_3 using a Varian spectrometer operating at 40 Mc/s. The solutions were internally referenced to eliminate bulk susceptibility effects. The proton spectra were calibrated with respect to tetramethylsilane, and the fluorine spectra with respect to 1,2-difluorotetrachloroethane. The usual side-band modulation method of measurement was used. The contact shifts were obtained from the difference in resonance frequency between resonances of corresponding nuclei (¹H or ¹⁹F) of the Ni chelate and the Zn chelate or ligand. Temperatures in the range -80° c to $+60^{\circ}$ c were obtained by enclosing the sample in a Dewar flask through which flowed a stream of pre-cooled or pre-heated nitrogen. The temperature was measured by a thermocouple with an accuracy of about $\pm 0.5^{\circ}$. The range of temperature measurements on the ortho compound was restricted by limited solubility.

3. Results and discussion

¹⁹F hyperfine splittings have been observed by EPR in two paramagnetic species. Anderson *et al.* [13] observed a value for $a_{\rm F}$ of 4.14 gauss for the tetrafluoro-*p*-benzosemiquinone radical. A value of $|Q_{\rm CF}| \simeq 40$ gauss was obtained from the assumed expression

$$a_{\mathbf{F}} \cong Q_{\mathbf{CF}} \rho_{\mathbf{C}},\tag{2}$$

the above value for $a_{\rm F}$, and the value of $\rho_{\rm C}$ observed in the tetrahydro-*p*-benzosemiquinone radical. This latter assumption was necessitated because $\rho_{\rm C}$ for tetrafluoro-*p*-benzosemiquinone was not known independently. Although the sign of $Q_{\rm CF}$ was not determinable from the EPR experiment, Anderson and coworkers [13] assumed that the dominant electron-nucleus interaction mechanism for the Č-F fragment was the same π - σ mechanism established for Č-H fragments and on this basis assigned to $Q_{\rm CF}$ a minus sign.

Maki and Geske [14] obtained a value of $a_{\rm F}$ from analysis of the EPR spectrum of the *p*-fluoronitrobenzene anion radical. Here it was noted that $a_{\rm H}$ for the ortho and meta hydrogen atoms were essentially unchanged from the values observed in the parent nitrobenzene anion radical, so the assumption was made that the para carbon spin densities were the same for the two radicals. Using these two experimental quantities and equation (2), a value of $|Q_{\rm CF}| = 47.5$ gauss was obtained.

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In previous work [4, 5] we have employed proton contact interaction shifts to determine spin density distributions in substituted nickel (II) aminotroponeimineates. As an example of the spectra of these chelates, the ¹H spectrum of



¹H spectrum of nickel (II) N,N'-di(m-fluorophenyl) aminotroponeimineate.

nickel (II) N, N'-di(m-fluorophenyl) aminotroponeimineate is shown in the figure above. These chelates exist in rapidly interconverting singlet and triplet forms. Proton contact interaction shifts are given by the expression [6]

$$\left(\frac{\Delta H}{H}\right)_{i} = -a_{i}\frac{\gamma_{e}}{\gamma_{H}}\frac{g\beta S\left(S+1\right)}{2SkT\left[\exp\left\{-\frac{(\Delta E - T\Delta S)}{kT}\right\} + 3\right]}.$$
(3)

Both a_i , ΔE and ΔS can, therefore, be obtained if the spectra are measured at different temperatures. The spin densities at sp² carbon atoms with directly bonded hydrogen atoms are then obtained from

$$a_{\rm H} = \mathcal{Q}\rho_{\rm C},\tag{4}$$

with Q = -22.5 gauss.

The ¹H and ¹⁹F spectra of the Ni(II) chelates of ortho, meta and para N,N'-di(fluorophenyl) aminotroponeimineates have been observed and contact shifts were obtained by comparison with the corresponding diamagnetic zinc chelate or with the ligand. Previous work [6] has shown that the proton spectra of the ligand and zinc chelate are virtually identical. This seems also be be true for the ¹⁹F spectra of the ligand and zinc chelate of N,N'-di(fluorophenyl) aminotroponeimines, despite the fact that large fluorine chemical shifts are generally encountered in diamagnetic fluorine-containing compounds. Table 1 gives the experimental data for the *p*-fluorophenyl compounds. Columns 11 and 12 show that either the ligand or the zinc chelate may be used as a reference for the contact shifts, and the last two columns show that the temperature dependences of the fluorine resonance and of the proton resonances are identical

$ \Delta f$	Zn Chelate ref.	1.150	1.135	1.157	1.237	1.258	1.243	resonances.
Ratio $\Delta f_{ m F}$	Ligand ref.	1.135	1.128	1.141	1.197	1.168	1.085	nce for proton
Zn A.T.	F	+ 2076	+ 2057	+ 2050	+ 2041	+ 2033	+ 2029	rnal refere
Ş	F	+2061	+2052	+ 2042	+2031	+ 2019	+ 2016	ed as inter
esonance	Meta		- 290					was use
Ligand r	Ortho		- 282					hylsilane
	7-ring		- 270					Tetramet
	Ъ	+ 895	+1189	+1491	+1679	+1838	+1927	lution.
	Meta	- 650	- 553	- 457	- 386	- 335		CDC1 ₃ sc
ces, c.p.s.	Ortho	+ 85	0	- 108	- 189	- 222		Ic/s in C
e resonanc	×	+ 2444	+1779	+1033	+561	+ 244		d at 40 N
Ni chelato	β	- 1297	-1035	- 753	- 564	-425	- 352	measured
	σ	+1705	+1231	+ 687	+ 343	+116	- 105	ctra were
	T°C	+ 50	+26	0	- 20	-40	- 60	The spe

1,2-diffuorotetrachloroethane was used as internal reference for fluorine resonances. ¹⁹F shifts for the zinc aminotroponeimineate are listed in column 12. Temperature dependences of ratios of fluorine contact shifts to contact shifts of the H_{β} proton are listed in columns 13 and 14.

Table 1. NMR spectra of p-fluorophenyl derivatives.

as demanded by equation (3).	Table 2 lists	the spin	densities	for these	three
compounds and also those of the	unsubstituted	phenyl co	ompound	for compa	rison.
Values of ΔE and ΔS are also in	ncluded.				

Compound	ρ _α	ρ_{β}	ρ _γ	Portho	$ ho_{ m meta}$	ρpara	ΔE (cm ⁻¹)	Δ <i>S</i> (e.u.)
Phenyl	+0.0413	-0.0210	+0.0580	+0.00748	-0.00794	+0.0107	1080	10.3
<i>p</i> -fluorophenyl	+0.0408	-0.0210	+0.0560	+0.00729	- 0.00746	—	1722	13.3
<i>m</i> -fluorophenyl	+0.0410	-0.0210	+0.0568	+0.00760	-0.00813	+0.01044	1434	13.0
o-fluorophenyl		-0.0210		+0.00657	- 0.00826	+0.0107	—	
					J	<u> </u>	}	

Table 2. Spin densities.

It is apparent that fluorine substitution has little effect on the spin density distribution on the six- or seven-membered rings, and this conclusion has been substantiated by measurements on a wide range of other compounds [6]. In the ortho and meta fluoro derivatives the spin density at the substituted carbon was therefore assumed equal to that of the corresponding unsubstituted position; in the para fluoro compound a value for $\rho_{\rm C}{}^p$ was taken from the unsubstituted phenyl compound. The fluorine hyperfine splitting constants and the values of Q obtained by assuming these spin densities and using equation (4) are listed in The negative spin density at the meta position arises as a result of spin table 3. correlation effects with the positive spin density appearing at the ortho and para positions. A change in the spin density at the ortho or para position should be reflected by a change of spin density at the meta position. The absence of such variations in the above compounds, therefore, provides valid evidence for the carbon spin densities assumed at the positions of substitution.

Aminotroponeimineate	$a_{ m F}$ (gauss)	ρc	$Q_{\rm CF}$ (gauss) from (equation (2))
p-fluorophenyl m-fluorophenyl o-fluorophenyl	+0.506 - 0.0325 + 0.270	+ 0.0107 - 0.00813 + 0.00657	$ \begin{array}{r} +47.2\\ +4.0\\ +41.1 \end{array} $

Table 3. ¹⁹F contact interaction constants and carbon spin densities for some nickel (II) aminotroponeimineates.

It is to be noted from the results of table 3 that $|Q_{\rm CF}|$ as derived from equation (2) varies widely depending on the position of substitution of fluorine on the phenyl ring. As mentioned earlier, Maki and Geske [14] derived a value for $|Q_{\rm CF}|$ of 47.5 gauss for the *p*-fluoronitrobenzene anion radical. It is probably significant that this value of $|Q_{\rm CF}|$ agrees closely with our value of +47.2 gauss obtained for the *p*-fluorophenyl chelate; in both cases fluorine is substituted at the para position. Signs of contact interaction constants could be determined in the present NMR approach, and the sign $Q_{\rm CF}$ as derived from equation (2) is positive, at least for the three chelates of this study. The variability of $Q_{\rm CF}$ then suggests that equation (2) is quite inadequate in relating fluorine contact interaction shifts to carbon spin densities. The observed positive sign for $Q_{\rm CF}$ indicates that the

nucleus-electron interaction mechanism employed so successfully in C-H fragments cannot be the complete story in C-F.

A contribution to the fluorine contact interaction constant is to be expected for a C-F fragment from the spin density on the carbon atom to which the fluorine atom is bonded. This nucleus-electron interaction should proceed via a π - σ mechanism similar to that found in aromatic C-H fragments and, for positive spin density on the carbon atom, should produce a negative spin density at the fluorine nucleus. It is difficult to make a quantitative estimate of this contribution because of our ignorance of the s-character of the bonding σ -orbital of fluorine, but a value of the order of magnitude of that found for hydrogen is not unreasonable [13].

There is in addition to the above contact interaction mechanism the possibility of a contribution to $a_{\rm F}$ from spin density centred on a $p\pi$ orbital of fluorine. Spin density would be placed on fluorine as the result of conjugation involving the π -system of the phenyl group and a *p*-orbital centred on fluorine containing an unshared pair of electrons.

The Kekulé structures for the *p*-fluorophenylamino radical are



These structures would place positive spin densities on the nitrogen atom and on the ortho and para positions of the phenyl ring, as is observed. However, fluorine is known to participate in π -bonding, although the extent of such participation is a matter of some controversy [15, 16]. Granting, however, the existence of π -bonding in fluoroaromatics, the structures contribute to the groundstate wave function of the *p*-fluorophenylamino radical. It should be noted



that for a positive carbon spin density, π - σ interaction will produce a negative spin density in the C-F σ -bond at the fluorine nucleus, whereas the resonance effect (structure V and VI) will produce a positive spin density in a $p\pi$ orbital centred on fluorine.

By analogy with the treatment of McLachlan *et al.* [17] and of Karplus and Fraenkel [18] of isotropic ¹³C contact interactions, the ¹⁹F contact interaction constant for a fluoroaromatic should be given as

$$a_{\mathbf{F}} = Q_{\mathbf{CF}}{}^{\mathbf{C}}\rho_{\mathbf{C}} + Q_{\mathbf{FC}}{}^{\mathbf{F}}\rho_{\mathbf{F}},\tag{4}$$

where $\rho_{\rm C}$ and $\rho_{\rm F}$ are, respectively, spin densities centred on carbon and on the fluorine atom attached to the carbon atom. $Q_{\rm CF}{}^{\rm C}$ is the π - σ contribution analogous to that of the aromatic C-H fragment. $Q_{\rm FC}{}^{\rm F}$ is the contribution from π - σ polarization of the 1s and 2s electrons of fluorine by spin density centred on a $2p\pi$ orbital of fluorine.

Unfortunately, estimates of the magnitudes of $\rho_{\rm F}$ are required for the evaluation of $Q_{\rm CF}{}^{\rm C}$ and $Q_{\rm FO}{}^{\rm F}$ from equation (4) and experimental values for $a_{\rm F}$ and $\rho_{\rm C}$ for the three fluoroaminotroponeimineates (table 3). Since the system is non-alternant, negative as well as positive carbon spin densities are expected and the simple LCAO MO approach to the calculation of $\rho_{\rm F}$ is not valid. The valence bond scheme would be more appropriate but structures V or VI are not easily handled in such a calculation.

Spin density is, however, placed on the fluorine atom only as a result of the participation of structures V and VI which give also a partial double bond character to the C-F bond. A plausible assumption would seem to be then, that

$$\rho_{\rm F} = A p_{\rm CF} \rho_{\rm C},\tag{5}$$

where p_{CF} is the double bond order of the C-F bond with values ranging from 0 to 1, and A is a proportionality constant. Values of ρ_{CF} calculated by the procedure outlined in the Appendix are

$$p_{\rm CF}{}^p = 0.229,$$

 $p_{\rm CF}{}^m = 0.178,$
 $p_{\rm CF}{}^o = 0.212.$

Substituting equation (5) into equation (4) we obtain

$$a_{\rm F} = Q_{\rm CF}{}^{\rm C}\rho_{\rm C} + Q_{\rm FC}{}^{\rm F}Ap_{\rm CF}\rho_{\rm C}.$$
(6)

 $Q_{\rm CF}{}^{\rm C}$ and $(Q_{\rm FC}{}^{\rm F}A)$ then can be evaluated from experimental results on any two of the fluorophenylaminotroponeimineates. Using the results for the *p*-fluoro and *m*-fluoro chelates, values of $Q_{\rm CF}{}^{\rm C} = -147$ gauss and $(Q_{\rm FC}{}^{\rm F}A) = +848$ gauss were obtained. Using these values of $Q_{\rm CF}{}^{\rm C}$ and $(Q_{\rm FC}{}^{\rm F}A)$, $a_{\rm F}{}^{\circ}$ is calculated to be +0.22 gauss, in good agreement with the experimental value of +0.27 gauss.

While too great a quantitative significance should not be attached to these derived values of $Q_{\rm CF}{}^{\rm C}$ and $(Q_{\rm FC}{}^{\rm F}A)$, they nevertheless are reasonable. A negative sign is given to $Q_{\rm CF}{}^{\rm C}$ and it would appear to be of the right order of magnitude [13]. $(Q_{\rm FC}{}^{\rm F}A)$ is given a positive sign, and, if the proportionality constant A is of the order unity, $Q_{\rm FC}{}^{\rm F}$ is close to the hyperfine splitting of 1077 gauss obtained recently for the free fluorine atom [19]. It may also be concluded from these results that there is a significant amount of double bonding between the fluorine and the phenyl π -system. This conclusion is consistent with the results of a recent theoretical investigation of Karplus and Das [21] on the NMR chemical shifts of fluorobenzenes. It would seem, though, that measurements of contact interaction constants provide the most direct experimental method of demonstrating conjugative effects of this kind.

In addition, the results on ¹⁹F contact shifts in fluoroaromatics suggest a more general conclusion regarding the employment of contact shifts of atoms or groups bonded to $p\pi$ systems to probe spin density distributions on the $p\pi$ system. If the atom or group being used as probe participates to any extent in π -bonding, a simple proportionality between contact shift and spin density (equation (1)) cannot be expected to exist; instead, treatments such as that for carbon [17, 18] and the above for fluorine must be employed. For example, we have examined ¹H contact shifts of CH₃ groups of methyl-substituted aromatics (attached to the appropriate nickel (II) aminotroponeimineate) and have found [22], using equation (1), variations in apparent values of Q_{CH_3} of more than a factor of three. Such effects will of course require detailed analysis, but should be extremely useful in elucidating effects such as hyperconjugation and halogen conjugation.

Appendix

Simple LCAO MO calculations were carried out on the *p*-fluoro fragment



as well as on the *m*-fluoro and *o*-fluoro derivatives. The problem was considered to be one consisting of nine $p\pi$ electrons. Coulomb integrals were estimated from

$$\alpha_{\rm X} = \alpha_{\rm C} - E(C) + E({\rm X}),\tag{7}$$

where α_{C} is the Coulomb integral of carbon, E(C) is the ionization potential of carbon, and E(X) is the ionization potential of the atom for which an α_{X} is desired. Resonance integrals were estimated from

$$\beta_{\mathrm{C-X}} = \frac{S_{\mathrm{C-X}}}{S_{\mathrm{C-C}}} \beta_{\mathrm{C-C}},\tag{8}$$

where β is a resonance integral and S is an overlap integral. Overlap integrals were evaluated from the tables of Mulliken *et al.* [20] and a value of $\beta_{C-C} = -3 \text{ ev}$ was assumed [16]. Resonance and Coulomb integrals employed in the calculations are given below.

$$\begin{aligned} \alpha_{\rm C} &= \alpha_{\rm C}, & \beta_{\rm CC} = \beta_{\rm CC}, \\ \alpha_{\rm N} &= \alpha_{\rm C} + 1 \cdot 3\beta_{\rm CC}, & \beta_{\rm CN} = 0 \cdot 836\beta_{\rm CC}, \\ \alpha_{\rm F} &= \alpha_{\rm C} + 2 \cdot 5\beta_{\rm CC}, & \beta_{\rm CF} = 0 \cdot 619\beta_{\rm CC}. \end{aligned}$$

Solutions of the secular equations for eigenvalues and eigenvectors were carried out by Mr. D. W. Marquardt of the du Pont Engineering Research Laboratory. π -bond orders were evaluated from

$$p_{ij} = \sum_{\mathbf{r}} n_{\mathbf{r}} C_{ir} C_{rj}, \tag{9}$$

where the summation is over occupied orbitals, n_r is the number of electrons in the *r*th orbital and the C's are coefficients of the eigenvectors.

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