

Fluorine Hyperfine Interaction in Aromatic Anion Radicals

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The relation between the fluorine hyperfine splittings in about 20 fluorine substituted aromatic radicals and the π spin densities calculated according to McLachlan's method is analysed with an expression of the type

$$a^F = Q_{FF}^F Q_{FF}^{\pi} + Q_{CC}^F Q_{CC}^{\pi} + (Q_{CF}^F + Q_{FC}^F) Q_{CF}^{\pi}.$$

For the Q factors the following values are obtained:

$$Q_{FF}^F = 931 \text{ gauss}; \quad Q_{CC}^F = 86.6 \text{ gauss} \quad \text{and} \quad (Q_{FC}^F + Q_{CF}^F) = 345 \text{ gauss}.$$

Two simpler expressions with one and two parameters respectively are also tested.

A theoretical estimate is made for the values of the Q factors and the results are compared with the values obtained semi-empirically.

I. Introduction

During the early stages of ESR investigation of free radicals, the number of fluorine containing species was limited to a few π -type species, the fluoranil semiquinone¹, the p-fluoronitrobenzene anion², and the 4-fluoroacetophenone anion³. In recent years a considerable literature on fluorinated π -type radicals has appeared for ionic and neutral species. The former include the fluorinated nitrobenzene anions⁴⁻⁸, several difluorinated nitrobenzene anion radicals^{7, 8}, the 2,7-difluorofluorenone ketyl⁹, several mono- and difluorinated benzophenone anions¹⁰, the 2,5-difluoro-1,4-benzo- and 2,3-difluoro-1,4-naphtho-semiquinones¹¹, and several fluorinated nitrophenol anions⁸. Amongst the neutral radicals are di-(p-fluorophenyl)-nitroxide¹², mono- and poly-fluorinated nitrobenzene radicals resulting from pro-

ton addition during photolysis^{5, 13}, penta-fluoro-nitrosobenzene radical¹³, and tri-(fluorophenyl)-methyl radicals¹⁴.

During the course of these investigations various spin-polarisation parameters expressing experimentally observed fluorine coupling constants as a function of fluorine and/or carbon spin densities have been proposed, but no set of parameters applicable to a larger group of compounds has been found. We intended to see if such a set of parameters, either in a one- two-, or even three-constant formulation could be found empirically from known coupling constants and π -spin densities calculated via McLachlan's approximate SCF method¹⁵. We will show that it is possible to give such formulations: it appears however to be very difficult to decide unambiguously on a best set of parameters.

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¹ P. H. ANDERSON, P. J. FRANK, and H. S. GUTOWSKI, J. Chem. Phys. **32**, 196 [1960].

² A. H. MAKI and D. H. GESKE, J. Am. Chem. Soc. **83**, 1852 [1961].

³ P. H. RIEGER and G. K. FRAENKEL, J. Chem. Phys. **37**, 2811 [1962].

⁴ P. B. AYSCOUGH, F. P. SARGENT, and R. WILSON, J. Chem. Soc. **1903**, 5418.

⁵ A. CARRINGTON, A. ANDERSON, and H. C. LONGUET-HIGGINS, Mol. Phys. **9**, 377 [1965].

⁶ A. CARRINGTON, A. HUDSON, and G. R. LUCKHURST, Proc. Roy. Soc. London **A 284**, 382 [1965].

⁷ M. KAPLAN, J. R. BOLTON, and G. K. FRAENKEL, J. Chem. Phys. **42**, 955 [1965].

⁸ P. H. H. FISCHER and H. ZIMMERMANN, Can. J. Chem. **46**, 3847 [1968].

⁹ R. DEHL and G. K. FRAENKEL, J. Chem. Phys. **39**, 1793 [1963].

¹⁰ P. H. H. FISCHER and H. ZIMMERMANN, Z. Naturforsch. **23 a**, 1339 [1968].

¹¹ P. H. H. FISCHER and H. ZIMMERMANN, Z. Naturforsch.

¹² P. H. H. FISCHER and F. A. NEUGEBAUER, Z. Naturforsch. **19 a**, 1513 [1964]; **21 b**, 1035 [1966].

¹³ J. K. BROWN and W. G. WILLIAMS, Trans. Faraday Soc. **64**, 298 [1968].

¹⁴ J. SINCLAIRE and D. KIVELSON, J. Am. Chem. Soc. **90**, 5074 [1968].

¹⁵ During the course of this work a paper of A. HINCHCLIFFE and J. N. MURREL on this topic, Mol. Phys. **14**, 147 [1968], appeared.



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The most general way of expressing the fluorine hyperfine coupling constants a^F in terms of π -electron spin density is the general form of the McConnell equation, that is

$$a^F = Q^F \varrho^\pi \quad (1)$$

where Q^F is the hyperfine coupling matrix and ϱ^π is the normalized π -spin density matrix, both 2×2 matrices in the case of a hypothetical C—F fragment. The recent interest in fluorine hyperfine interaction has resulted in a variety of relations and Q factors to express fluorine coupling constants, mainly in aromatic systems. ANDERSON et al.¹ and MAKI and GESKE² have proposed a simple relationship of the form

$$a^F = Q_{CC}^F \varrho_{CC}^\pi \quad (2)$$

with a value of Q_{CC}^F of the order of 60 gauss. This equation is formally equivalent to the MCCONNELL equation¹⁶ for the C—H fragment, although the physical situation is different because of the extension of the π -electron system onto the fluorine atom under consideration.

The work of EATON and coworkers^{17, 18} indicated, however, that Eq. (2) might be inadequate, and they, as well as other workers^{5, 7, 13, 19} proposed an equation of the type

$$a^F = Q_{FF}^F \varrho_{FF}^\pi + Q_{CC}^F \varrho_{CC}^\pi, \quad (3)$$

Q_{FF}^F of Eq. (3) is equivalent to Q_{FC}^F , and Q_{CC}^F of (3) to Q_{CF}^F of previous works.

This type of equation is equivalent to the KARPUS-FRAENKEL²⁰ type of equation used to relate carbon-13 and nitrogen-14 coupling constants with spin densities. KAPLAN et al.⁷, CARRINGTON et al.⁵, and BROWN and WILLIAMS¹³ note that Eq. (3) will reduce to an equation of type (2) if the ratio of π -spin densities in fluorine and neighboring carbon atom, $\varrho_{FF}^\pi/\varrho_{CC}^\pi$, is nearly constant. This does, however, make it difficult to interpret the Q values. However, $\varrho_{FF}^\pi/\varrho_{CC}^\pi$ is not constant, at least when considering a larger number of compounds. A comparison of the various Q_{FF} 's and Q_{CC} 's obtained to date, indicates that there is no single consistent set of parameters expressing a^F . This is discussed in detail by KAPLAN and coworkers⁷.

A third type of relation between measured a^F values and spin densities has been suggested first by SCHASTNEV and ZHIDOMIROV²¹, later by HINCHCLIFFE and MURRELL¹⁵. These authors suggested an equation of the type

$$a^F = Q_{FF}^F \varrho_{FF}^\pi + Q_{CC}^F \varrho_{CC}^\pi + (Q_{CF}^F + Q_{FC}^F) \varrho_{CF}^\pi \quad (4)$$

which differs from Eq. (3) in that a third term ($Q_{CF}^F + Q_{FC}^F$) is introduced, which takes into consideration the polarisation introduced by the overlap spin density ϱ_{CF}^π . A difference exists between the equations suggested by SCHASTNEV and ZHIDOMIROV and by HINCHCLIFFE and MURRELL in that the former workers use $\varrho_{CF}^\pi = (\varrho_{CC}^\pi \varrho_{FF}^\pi)^{1/2}$. This special relationship will only be valid under the condition that a single Slater determinant is used for the ground state wave function.

In the following Table 1, the varying Q 's obtained to date are compiled for comparison.

Q_{FF}^F	Q_{CC}^F	$(Q_{CF}^F + Q_{FC}^F)$	Ref.
	± 40		1
	± 47.5		2
+ 848 ^a	— 147 ^a		18
+ 371 ^b	— 37.5 ^b		7
+ 1393	— 147		19
+ 580	— 83		17
	+ 50 ^c		5
	+ 62 ^c		13
— 143 to + 3086 ^d	— 18 to — 620 ^d	+ 56 to + 595 ^d	21
+ 200 ^e	— 11 to — 19 ^f	— 43 to — 68 ^f	15

^a Para and meta positions fitted.

^b Same data as ¹⁸, but ortho and para positions fitted.

^c Value cited is Q_{eff} .

^d Value varies with hybridization.

^e This value appears to be erroneously quoted as 200 gauss instead of 200 MHz.

^f Value depends on particular model used.

Table 1. Fluorine σ - π Interaction Parameters (in gauss).

II. Molecular Orbital Calculations

The π -electron spin densities have been calculated via the usual Hückel LCAO method, and an approximation to configuration interaction has been introduced via MCLACHLAN's method²², with the parameter $\lambda = 1.2$.

¹⁶ H. M. MCCONNELL, J. Chem. Phys. **24**, 633, 764 [1965] and other papers.

¹⁷ D. R. EATON, A. D. JOSEY, W. D. PHILLIPS, R. E. BENSON, and T. L. CAIRNS, J. Am. Chem. Soc. **84**, 4100 [1962].

¹⁸ D. R. EATON, A. D. JOSEY, W. D. PHILLIPS, and R. E. BENSON, Mol. Phys. **5**, 407 [1962].

¹⁹ R. J. COOK, J. R. ROWLANDS, and D. H. WHIFFEN, Mol. Phys. **7**, 31 [1964].

²⁰ M. KARPUS and G. K. FRAENKEL, J. Chem. Phys. **35**, 1312 [1961].

²¹ P. V. SCHASTNEV and G. M. ZHIDOMIROV, Zh. Strukt. Khim. **5**, 839 [1964].

²² A. D. MCLACHLAN, Mol. Phys. **3**, 233 [1960].

In the above method two types of integrals are required. These integrals are defined by the equations

$$\alpha_r = \alpha_C + h_r \beta_{CC} \text{ and } \beta_{rs} = k_{rs} \beta_{CC} \quad (5)$$

where α_r is the Coulomb integral for atom r , α_C the Coulomb integral for carbon, β_{CC} the resonance integral for carbon, and β_{rs} the resonance integral for the bond $r-s$. h_r and k_{rs} are empirical quantities. As diverse classes of compounds were studied, a large number of h_r and k_{rs} is required. For the nitro group, the parameters already successfully employed by RIEGER and FRAENKEL³ were used, namely $h_0 = 1.4$, $h_N = 2.2$, $k_{CN} = 1.2$, and $k_{NO} = 1.67$. The assumptions made and the reasons for the choice of these particular $-\text{NO}_2$ group parameters have been discussed by these authors³. For the benzophenones, values of $h_0 = 1.5$, $k_{CO} = 1.6$, and $k_{CC'} = 0.9$ were found to give acceptable agreement between calculated and experimentally measured proton coupling. $k_{CC'}$ refers to the exchange integral between ring carbon and carbonyl-group carbon. For the OH group in the nitrophenols $h_0 = 1.5$ and $k_{CO} = 1.6$ were employed, and no distinction was made between nitro-group oxygens, due to internal hydrogen bonding, for instance.

The choice of the fluorine parameters appears to be quite critical. The spin density distribution at all the positions, excepting fluorine and neighboring carbon, is quite insensitive to changes in the h_F and k_{CF} parameters, while Q_{FF}^F does however vary considerably. A certain range of parameters has been suggested in recent studies^{18, 19, 5, 23, 24}.

An independent measurement of π -spin density on the fluorine nucleus is desirable to make a choice of preferred parameters. For only one compound, the anion of 3,5-difluoro-nitrobenzene⁷, such an estimate is available from linewidth data. As a consequence, KAPLAN et al.'s⁷ values of $h_F = 2.25$ and $k_{CF} = 0.72$, with no auxiliary inductive parameter for the carbon adjacent to the fluorine, were preferentially used for all calculations, as these parameters reproduce the π -spin density of the fluorines in the above compound quite admirably. Besides these values of $h_F = 2.25$ and $k_{CF} = 0.72$, we also used the sets $h_F = 1.6$, $k_{CF} = 0.72$, and $h_F = 1.6$, $k_{CF} = 0.85$, denoted by a, b and c respectively. These

parameters are within the range of values usually recommended for the F atom in a C-F bond. It appears that both an increase in the value of k_{CF} and a decrease in the value of h_F give an increase in the spin density Q_{FF}^F and a decrease in Q_{CC}^F .

The calculated spin densities for the first set of parameters and the experimentally determined spin densities are given in Table 2. It must be born in mind that not all of the experimental spin densities are unambiguously determined, rather are they based on consistency arguments and spin distribution behaviour in similar species.

A rather good agreement between experimentally determined and calculated Q_{CC}^F is found for the C-H fragments.

III. Fluorine Splitting

a) Initially an attempt was made to see whether the fluorine hyperfine coupling constant a^F of the compounds described in Section III could be adequately explained by a linear relationship of the type

$$a^F = Q_{\text{eff}}^F Q_{CC}^F. \quad (6)$$

A reasonable fit can only be achieved if all coupling constants have the same sign as the spin density at the respective fluorines and adjacent carbon atoms. Using the method of orthogonal vectors²⁵, a least square fit of the 15 a^F to the calculated spin densities Q_{CC}^F gave a best value of $Q_{\text{eff}}^F = +54.5$ gauss, in agreement with the value of $+57$ gauss found by SINCLAIR and KIVELSON¹⁹ and the value of ~ 50 gauss of CARRINGTON et al.⁵, and other workers. The calculated a^F are given in Table 2. Figure 1 shows a plot of experimentally found fluorine coupling vs. calculated a^F 's, with the line of slope 1 representing perfect correlation. The dots represent constants employed in the least squares analysis, while the squares refer to other data not included in the fit. These are the anions of 2,3-difluoro-1,4-naphthoquinone (16) and 2,5-difluorobenzoquinone (17)¹¹, of fluoranil (18)¹, of 2,7-difluorofluorenone (19)⁹, as well as a neutral radical, di-(p-fluorophenyl)nitroxide (20)¹². The coupling constants are reasonably well reproduced for some compounds, the overall agreement of a^F (calc.) and a^F (exptl.) is however not impressive.

²³ Y. I'HAYA, J. Am. Chem. Soc. **81**, 6120 [1959].

²⁴ A. STREITWIESER, MO-Theory for Organic Chemists, J. Wiley and Sons, Inc., New York 1961.

²⁵ B. VENKATARAMAN, B. G. SEGAL, and G. K. FRAENKEL, J. Chem. Phys. **30**, 1006 [1959].

Anion Radical	Position	Spin Density		Experiment (a)
		Hückel	McLachlan	
3-Fluoro-nitrobenzene	1	.03962	.00677	.
	2	.11106	.14888	.14219
	3	.00437	-.04534	
	4	.12020	.16216	.16498
	5	.00522	-.04615	(-) .04262(b)
	6	.10105	.13276	.13333
	7 (N)	.22697	.24105	
	8, 9 (O)	.19559	.20166	
	10 (F)	.00032	-.00343	
2-Fluoro-nitrobenzene	2	.09516	.11890	
	10 (F)	.00693	.00429	
4-Fluoro-nitrobenzene	4	.11803	.15542	
	10 (F)	.00857	.00659	
3,5-Difluoro-nitrobenzene	3, 5	.09463	-.04384	
	10, 11 (F)	.00034	-.00334	
2,5-Difluoro-nitrobenzene	2	.09293	.11485	
	5	.00128	-.05124	
	10 (F ₅)	0.0009	-.00367	
	11 (F ₂)	.00677	.00446	
2,4-Difluoro-nitrobenzene	2	.09567	.12128	
	4	.11871	.15647	
	10 (F ₂)	.00685	.00434	
	11 (F ₄)	.00850	.00661	
	1	.08090	.09144	
	2	.02396	-.01545	
4-Fluoro-2-nitrophenol	3	.12478	.18086	.14810
	4	.00000	-.05566	
	5	.12466	.16691	.16414
	6	.02435	-.02117	(-) .02110(b)
	7 (N)	.22527	.25083	
	8, 9 (O)	.18556	.20115	
	10 (O)	.02497	.00392	
	11 (F)	.00000	-.00398	
	5	.11704	.15475	
5-Fluoro-2-nitrophenol	11 (F)	.00824	.00665	
6-Fluoro-2-nitrophenol	6	.02271	-.02058	
	11 (F)	.00162	-.00244	
4,4'-Difluoro-benzophenone	1	.04032	.01897	
	2	.07696	.10268	.11561
	3	.00281	-.03615	(-) .04051(b)
	4	.09342	.12555	
	13 (CO)	.24759	.28641	
	14 (O)	.15337	.14760	
	15 (F)	.00625	.00571	
4-Fluoro-benzophenone	4	.08674	.11604	
	15 (F)	.00588	.00498	
3,3'-Difluoro-benzophenone	3	.00516	-.03095	
	15 (F)	.00035	-.00233	
2-Fluoro-benzophenone	2	.06360	.07872	
	15 (F)	.00433	.00289	

Table 2. Calculated and Experimental Spin Densities. Only one nitrobenzene, nitrophenol, and benzophenone are given completely, in all other cases only the pertinent Q_{FF}^{π} and Q_{CC}^{π} is given. Complete data are available upon request. (a) Experimental Q_{CC}^{π} with $Q_{CC}^H = -23.7$ gauss. (b) Signs not experimentally determined.

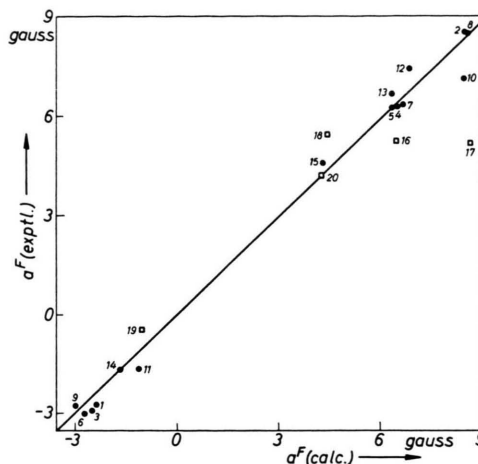


Fig. 1. Correlation Diagram of Calculated and Experimental a^F using Eq. (2).

b) An attempt was then made to ascertain whether the experimental data could be understood in terms of a more complex equation. Firstly, an equation of the type (3) was tried, i. e. an explanation of experimental fluorine coupling constants in terms of two spin polarisation parameters Q_{FF}^F and Q_{CC}^F . Again using the method of orthogonal vectors, the least squares analysis of the a^F (exptl.) and the McLachlan spin densities gave best values of $Q_{FF}^F = +146$ gauss and $Q_{CC}^F = +48.1$ gauss.

The calculated and experimental results are presented in Fig. 2 and in Table 3, where the two contributions from Q_{FF}^{π} and Q_{CC}^{π} are separately shown.

We note that the correlation diagram (Fig. 2)

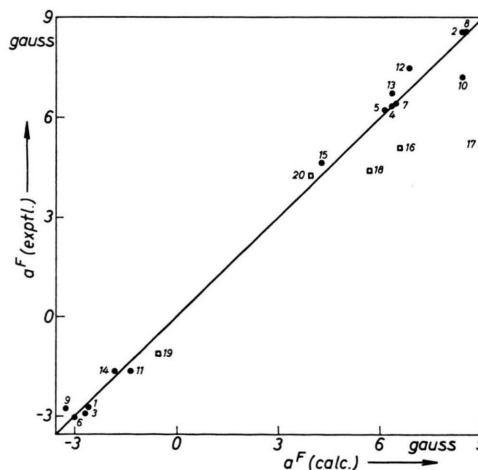


Fig. 2. Correlation Diagram of Calculated and Experimental a^F using Eq. (3).

Radical	a^F (gauss) Calc. ^a	Exptl.	Position in Fig. 2
3,5-Difluoro- nitrobenzene	-2.39	-2.73 ^b	1
4-Fluoronitro benzene	8.47	8.61 ^b	2
3-Fluoronitro benzene	-2.47	-2.92	3
2-Fluoronitro- benzene	6.48	6.36	4
2,5-Difluoro- nitrobenzene	6.26	6.24 (2)	5
	-2.79	-3.03 (5)	6
2,4-Difluoro- nitrobenzene	6.61	6.40 (2)	7
	8.53	8.59 (4)	8
4-Fluoro-2- nitrophenol	-3.03	-2.74 ^h	9
3-Fluoro-6- nitrophenol	8.43	7.21 ^h	10
2-Fluoro-6- nitrophenol	-1.12	-1.63 ^h	11
4,4'-Difluoro- benzophenone	6.84	7.50 ⁱ	12
4-Fluorobenzo- phenone	6.32	6.73 ⁱ	13
3,3'-Difluoro- benzophenone	-1.67	-1.65 ⁱ	14
2-Fluorobenzo- phenone	4.29	4.63 ⁱ	15
2,3-Difluoro-1,4- naphthoquinone	6.47	5.31 ^{c, d}	16
2,5-Difluorobenzo- quinone	8.63	5.24 ^{c, d}	17
Fluoranyl	5.51	4.41 ^{c, e}	18
2,7-Difluoro- fluorenone	-0.46	-1.11 ^{c, f}	19
Di-(p-fluorophenyl) nitroxide	4.24	4.25 ^{c, g}	20

^a Calculated using McLachlan spin densities and $Q_{\text{eff}} = +54.5$ gauss.

^b Data from ref. 7.

^c Not included in least squares fit.

^d Data from ref. 11.

^e Data from ref. 1 and using $h_O = 1.5$, $k_{CO} = 1.6$, $h_{CC'} = -0.15$.

^f Data from ref. 9 and using $h_O = 1.6$, $k_{CO} = 1.5$, $k_{CC'} = 1.2$, $h_{C'} = 0.16$.

^g Data from ref. 12 and using $h_O = 1.4$, $h_N = 2.2$, $k_{CN} = 1.2$, $k_{NO} = 1.67$.

^h Data from ref. 8.

ⁱ Data from ref. 11.

Table 3. Calculated ^{19}F Coupling Constants Using $a^F = Q_{\text{eff}} \varrho_{\text{CC}}^{\pi}$ with $Q_{\text{eff}} = 54.5$ gauss.

shows only a slightly improved fit over the correlation using one constant only, no improvement for the coupling constants not included in the least squares analysis. An investigation of Table 3 shows that the contribution of the term $Q_{\text{FF}}^F \varrho_{\text{FF}}^{\pi}$ is roughly 5 to 20% of that of the term $Q_{\text{CC}}^F \varrho_{\text{CC}}^{\pi}$, explaining

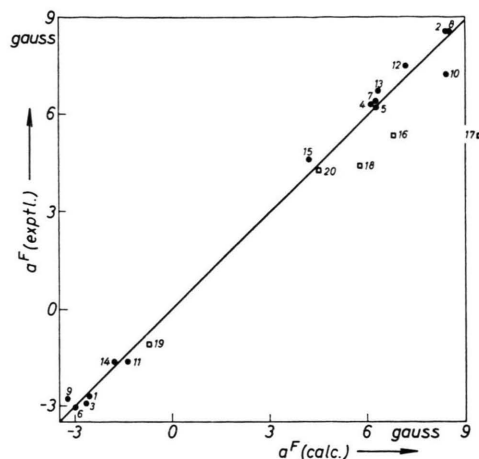


Fig. 3. Correlation Diagram of Calculated and Experimental a^F using Eq. (4).

the similarity of the constants in the one- and two-constant least square fit.

The coupling constant is to a large extent determined by the carbon π -spin density, the contribution from the fluorine π -spin density being only a correction. Furthermore, Q_{FF}^F is critically dependent on the spin density $\varrho_{\text{FF}}^{\pi}$, as shown by least squares fits to spin densities and coupling constants where $\varrho_{\text{FF}}^{\pi}$ was intentionally altered. Thus, halving the spin density $\varrho_{\text{FF}}^{\pi}$ results in a Q_{FF}^F roughly twice as large, with only a very small change being observed in Q_{CC}^F , that is $Q_{\text{FF}}^F \varrho_{\text{FF}}^{\pi} \cong K$, a constant factor. Since there is no independent check on the spin densities given in Table 2 with the exception of the anion of 3,5-difluoronitrobenzene⁷ it is difficult to assess the theoretical significance of the numerical values for Q_{FF}^F and Q_{CC}^F . Spin polarisation parameters derived using Hückel or SCF spin densities, say, will be numerically different. Nevertheless the above values may serve as a useful guide for the size of fluorine couplings to be expected, when McLachlan spin densities are employed and when no gross structural anomalies or other factors falsify the results.

c) Lastly an attempt was made to explain fluorine coupling constants by the general form of the McConnell equation. This equation, when considering only the fluorine atom from which a splitting is observed and its neighboring carbon atom, will be

$$a^F = Q_{\text{FF}}^F \varrho_{\text{FF}}^{\pi} + Q_{\text{CC}}^F \varrho_{\text{CC}}^{\pi} + (Q_{\text{CF}}^F + Q_{\text{FC}}^F) \varrho_{\text{CF}}^{\pi} \quad (7)$$

Again using the same 15 experimental coupling constants and spin densities as before, in addition

Radical	a^F (gauss)				Position in Fig. 3
	Calc. ^b		Total	Exptl.	
3,5-Difluoronitrobenzene	— 0.49	— 2.11	— 2.60	— 2.73	1
4-Fluoronitrobenzene	.96	7.48	8.44	8.61	2
3-Fluoronitrobenzene	— .50	— 2.18	— 2.68	— 2.92	3
2-Fluoronitrobenzene	.63	5.72	6.35	6.36	4
2,5-Difluoronitrobenzene	.65	5.52	6.17	6.24 (2)	5
	— .54	— 2.46	— 3.00	— 3.03 (5)	6
2,4-Difluoronitrobenzene	.63	5.83	6.46	6.40 (2)	7
	.97	7.53	8.50	8.59 (4)	8
4-Fluoro-2-nitrophenol	— .58	— 2.68	— 3.26	— 2.74	9
3-Fluoro-6-nitrophenol	.97	7.44	8.41	7.21	10
2-Fluoro-6-nitrophenol	— .36	— .99	— 1.35	— 1.63	11
4,4'-Difluorobenzophenone	.83	6.04	6.87	7.50	12
4-Fluorobenzophenone	.73	5.58	6.36	6.73	13
3,3'-Difluorobenzophenone	— .34	— 1.49	— 1.83	— 1.65	14
2-Fluorobenzophenone	.42	3.79	4.21	4.63	15
2,3-Difluoro-1,4-naphthoquinone	.89	5.71	6.60	5.31	16
2,5-Difluorobenzquinone	1.40	7.62	9.02	5.24	17
Fluoranyl	.82	4.86	5.68	4.41	18
2,7-Difluorofluorenone	— .13	— .41	— .54	— 1.11	19
Di-(p-fluorophenyl)nitroxide	.18	3.74	3.92	4.25	20

^a Same data and MO calculations as in Table 2.

^b First number indicates contribution $Q_{FF}^F \varrho_{FF}^{\pi}$, second number $Q_{CC}^F \varrho_{CC}^{\pi}$.

Table 4. Calculated ^{19}F Coupling Constants Using $a^F = Q_{FF}^F \varrho_{FF}^{\pi} + Q_{CC}^F \varrho_{CC}^{\pi}$ with $Q_{FF}^F = +146$ gauss and $Q_{CC}^F = +48.1$ gauss ^a.

Radical	a^F (gauss)						Position in Fig. 4
	Calc. ^b		Total	Exptl.			
3,5-Difluoronitrobenzene	— 3.11	— 3.80	+ 4.34	— 2.57	— 2.73	1	
4-Fluoronitrobenzene	+ 6.14	+ 13.46	— 11.20	+ 8.40	+ 8.61	2	
3-Fluoronitrobenzene	— 3.19	— 3.93	+ 4.49	— 2.63	— 2.92	3	
2-Fluoronitrobenzene	+ 3.99	+ 10.30	— 8.11	+ 6.18	+ 6.36	4	
2,5-Difluoronitrobenzene	+ 4.15	+ 9.95	— 7.80	+ 6.30	+ 6.24	5	
	— 3.42	— 4.44	+ 4.91	— 2.95	— 3.03	6	
2,4-Difluoronitrobenzene	+ 4.40	+ 10.50	— 8.25	+ 6.29	+ 6.40	7	
	+ 6.15	+ 13.55	— 11.24	+ 8.46	+ 8.59	8	
4-Fluoro-2-nitrophenol	— 3.71	— 4.82	+ 5.29	— 3.24	— 2.74	9	
3-Fluoro-6-nitrophenol	+ 6.19	+ 13.40	— 11.15	+ 8.44	+ 7.21	10	
2-Fluoro-6-nitrophenol	— 2.27	— 1.78	+ 2.72	— 1.33	— 1.63	11	
4,4'-Difluorobenzophenone	+ 5.31	+ 10.87	— 9.00	+ 7.19	+ 7.50	12	
4-Fluorobenzophenone	+ 4.64	+ 10.05	— 8.31	+ 6.38	+ 6.73	13	
3,3'-Difluorobenzophenone	— 2.17	— 2.68	+ 3.11	— 1.74	— 1.65	14	
2-Fluorobenzophenone	+ 2.69	+ 6.82	— 5.32	+ 4.19	+ 4.63	15	
2,3-Difluoro-1,4-naphthoquinone	+ 5.69	+ 10.28	— 9.13	+ 6.83	+ 5.31	16	
2,5-Difluorobenzoquinone	+ 8.94	+ 13.72	— 13.22	+ 9.44	+ 5.24	17	
Fluoranyl	+ 5.21	+ 8.76	— 8.18	+ 5.79	+ 4.41	18	
2,7-Difluorofluorenone	— 0.86	— 0.74	+ 0.97	— 0.63	— 1.11	19	
Di-(p-fluorophenyl)nitroxide	+ 1.13	+ 6.74	— 3.45	+ 4.52	+ 4.18	20	

^a Same data and MO calculations as in Tables 2 and 3.

^b Shown are the contributions $Q_{FF}^F \varrho_{FF}^{\pi}$, $Q_{CC}^F \varrho_{CC}^{\pi}$, and $(Q_{FC}^F + Q_{CF}^F) \varrho_{CF}^{\pi}$ in that order.

Table 5. Calculated ^{19}F coupling constants using $a^F = Q_{FF}^F \varrho_{FF}^{\pi} + Q_{CC}^F \varrho_{CC}^{\pi} + (Q_{CF}^F + Q_{FC}^F) \varrho_{CF}^{\pi}$ with $Q_{FF}^F = 931$ gauss, $Q_{CC}^F = 86.6$ gauss and $(Q_{FC}^F + Q_{CF}^F) = 345$ gauss ^a.

No. of Q 's	a)			b)			c)		
	3	2	1	3	2	1	3	2	1
Q_{FF}^F	931	146		74.2	23.4		140	138	
Q_{CC}^F	86.6	48.1	54.5	27.5	42.4	58.7	43.5	48.5	62.4
$(Q_{FC}^F + Q_{CF}^F)$	345			-95.7			-17.1		

Table 6. Spin polarisation parameters, cf. Text.

the overlap spin densities of the 15 C–F bonds, a least squares analysis of the results yielded the values $Q_{FF}^F = 931$ gauss, $Q_{CC}^F = 86.6$ gauss, and $(Q_{FC}^F + Q_{CF}^F) = 345$ gauss. The coupling constants calculated with this three-constant equation and the correlation with experimental values is given in Table 4 and Fig. 3. The three contributions

$$Q_{FF}^F Q_{FF}^{\pi}, Q_{CC}^F Q_{CC}^{\pi} \text{ and } (Q_{FC}^F + Q_{CF}^F) Q_{CF}^{\pi}$$

are separately shown.

The analysis given under a), b), and c) of Table 6 have been performed for the spin densities calculated by employing the parameters

$$\begin{aligned} \text{a) } h_F &= 2.25, & k_{CF} &= 0.72, \\ \text{b) } h_F &= 1.6, & k_{CF} &= 0.72, \\ \text{and c) } h_F &= 1.6, & k_{CF} &= 0.85. \end{aligned}$$

It appears that especially the values for Q_{FF} and $(Q_{CF} + Q_{FC})$ are very sensitive to changes in the parameters h_F and k_{CF} .

IV. Theoretical Estimate of Q Parameters

a) General Remarks

We assume that the hyperfine coupling constant for a fluorine atom of a C–F fragment in an aromatic π -type radical may be expressed by the following equation:

$$a^F = Q_{FF}^F Q_{FF}^{\pi} + Q_{CC}^F Q_{CC}^{\pi} + (Q_{CF}^F + Q_{FC}^F) Q_{CF}^{\pi}.$$

This is the equation suggested by SCHASTNEV and ZHIDOMIROV²¹ and later by HINCHCLIFFE and MURRELL¹⁵. Hinchcliffe and Murrell give the general expression for Q_{xy}^F , which we rewrite as

$$Q_{xx}^F = -\frac{16}{3} q_F \beta_F \sum_i \sum_j \frac{\langle \sigma_i p_z(x) | e^2/r_{12} | p_z(y) \sigma_j \rangle}{E_0 - E_k} \cdot \sigma_i(\mathbf{r}_F) \cdot \sigma_j(\mathbf{r}_F). \quad (8)$$

In this expression $p_z(x)$ and $p_z(y)$ are the 2p π atomic orbitals centered at x and y , either C or F. The orbitals σ_i are the doubly-occupied orbitals in the C–F fragment under consideration, and the

orbitals σ_j are unoccupied σ -orbitals of the same fragment. E_0 is the energy of the ground state while E_k is the energy of the respective excited states which one gets by promoting an electron from orbital σ_i to σ_j .

We make the reasonable assumption that the carbon atom is sp^2 -hybridized. If the fluorine bonds in its atomic configuration $(1s)^2(2s)^2(2p)^5$, it can easily be shown that the only non-vanishing contribution to the hyperfine coupling a^F will be due to Rydberg excitations and cannot account for the observed splittings. The bonding F orbital must possess some s-character.

To introduce fluorine s-character into the C–F bonding orbital we assume sp -like hybridization of the fluorine 2s and 2p σ orbitals. Other hybridization is of course conceivable, but the larger overlap with sp hybrids would be in better agreement with the high electronegativity of fluorine. The hybridized orbital participating in the C–F bond will be

$$\sigma_F(B) = N\{(2p_\sigma)_F + \lambda(2s)_F\}$$

$$\text{with } N^{-2} = \{1 + \lambda^2 + 2\lambda \langle (2s)_F | (2p_\sigma)_F \rangle\} \quad (9)$$

while the “lone pair” orbital will have the form

$$\sigma_F(LP) = N\{(2s)_F - \lambda(2p_\sigma)_F\}$$

$$\text{with } N^{-2} = \{1 + \lambda^2 - 2\lambda \langle (2s)_F | (2p_\sigma)_F \rangle\}. \quad (10)$$

Neglecting ionic character of the bond, the bonding and antibonding C–F orbitals will be

$$\sigma_{AB}^B = \frac{\{N(2p_\sigma)_F + N\lambda(2s)_F \pm \sqrt{1/3}(2s)_C \pm \sqrt{2/3}(2p_\sigma)_C\}}{2(1 \pm s)^{1/2}} \quad (11)$$

The ground state function of the C–F fragment, neglecting carbon 1s and 2p σ electrons bonding atoms other than F, as well as the remaining pair of fluorine 2p electrons (which cannot contribute to the splitting anyhow), is written as

$$\psi_0 = |\sigma_{F1s} \bar{\sigma}_{F1s} \sigma_B \bar{\sigma}_B \sigma_{LP} \bar{\sigma}_{LP} \tau_{AB}|. \quad (12)$$

The following are the possible excitations within the C–F fragment

- a) $\sigma_B \rightarrow \sigma_{AB}$,
- b) $\sigma_{F1s} \rightarrow \sigma_{AB}$,
- c) $\sigma_{LP} \rightarrow \sigma_{AB}$,
- d) $\sigma_B \rightarrow \sigma_{Fns}$, ($n > 2$)
- e) $\sigma_{F1s} \rightarrow \sigma_{Fns}$, and
- f) $\sigma_{LP} \rightarrow \sigma_{Fns}$.

Because of the energy denominator $E_0 - E_k$ we expect the excitations d)–f) to make quite small or negligible contributions, the major contribution to the fluorine splitting resulting from the excitations a)–c).

In what follows, an attempt is made to obtain values for the above four spin polarisation parameters.

b) Evaluation of Q 's

Q_{FF}^F , Q_{CC}^F , Q_{CF}^F and Q_{FC}^F are given by Eq. (8) by putting $x=y=F$, etc. Furthermore, we only consider the excitations a) to c), which give the major contributions.

The matrix elements $\langle \sigma_i p_z(x) | e^2/r_{12} | p_z(y) \sigma_{AB} \rangle$ are expanded in terms of atomic orbitals, and the individual homo- and hetero-nuclear exchange integrals evaluated directly using Slater-type orbitals. Their value will of course depend on the degree of hybridization of the fluorine orbitals. The necessary overlap integrals were evaluated using tables of MULLIKEN et al.²⁶

The value of the terms $\sigma_i(\mathbf{r}_F) \cdot \sigma_{AB}(\mathbf{r}_F)$ will of course be critically dependent on the choice of the 1s and 2s functions employed. As Slater atomic orbitals have the tendency to grossly overestimate ψ , especially in the vicinity of $r=0$, we have employed Hartree SCF functions. These values as calculated by WATSON and FREEMAN²⁷ for F^- are

$$\begin{aligned} |1s_0|^2 &= 212.683 \times 10^{24} \text{ cm}^{-3}, \\ |2s_0|^2 &= 10.869 \times 10^{24} \text{ cm}^{-3}. \end{aligned} \quad (14)$$

For a neutral fluorine, however, they should not be vastly different²⁸ and hence will be employed.

The most likely source of a large error in the evaluation of the Q_{xy}^F is the evaluation of the ener-

gies of excitation $E \sigma_i \rightarrow E \sigma_{AB}$. In this work it has been assumed that the excitation energy

$$\Delta E(\sigma_B \rightarrow \sigma_{AB})$$

can be approximately expressed by the exchange integral $\langle \sigma_B \sigma_{AB} | e^2/r_{12} | \sigma_B \sigma_{AB} \rangle$. Again variation with hybridization is expected and observed, the energies all clustering about the value of 13.2 eV. This value does not appear unreasonable. For instance, in molecular hydrogen the triplet state $^3\Sigma_u^+$ is roughly 12 eV above the ground state, and HENNING⁹ has estimated the value of 12.1 eV for the $\sigma_B \rightarrow \sigma_{AB}$ excitation in a C–N bond, using VB methods.

The contribution of the lone pair excitation can be considerable, as conceivably the excitation energy $\sigma_{LP} \rightarrow \sigma_{AB}$ is relatively low. An estimate of the excitation energy by evaluation of an exchange integral gave unrealistically low values, ranging from 0.8 to 4.2 eV. The transition is probably to be found in the ultraviolet region, and for lack of a better value, we have taken a value of 5.3 eV, this energy corresponding to the $A^2\Sigma^+ \rightarrow X^2\Pi$ band system of the CF molecule.

It has been shown for ^{13}C and ^{14}N that K shell polarisation plays an important role. For fluorine also, we consider K shell polarisation, not the Rydberg-type excitations $1s \rightarrow ns$ ($n \geq 3$), which are likely to be very small, but the excitation of 1s electrons to the antibonding sigma orbital σ_{AB} . This excitation energy is estimated from X-ray term values given by SLATER²⁹ as $\Delta E(F_{1s} \rightarrow \sigma_{AB}) \cong 675$ eV. A word of caution here is that the integral $\langle \sigma_{F1s} p_z(F) | e^2/r_{12} | p_z(F) \sigma_{AB} \rangle$ is extremely sensitive to the detailed form of the radical wave functions employed so that it is very difficult to judge the reliability of the contributions of the $1s \rightarrow \sigma_{AB}$ excitation to Q_{FF}^F . One could in fact obtain a negative contribution.

The results of the calculations may be found in Table 7. If we compare our theoretical values with those of Hinchcliffe and Murrell we agree that $(Q_{CF} + Q_{FC})$ is small and negative, that Q_{FF} is positive, and that Q_{CC} is also small and negative.

²⁶ R. S. MULLIKEN, C. A. RIEKE, D. ORLOFF, and H. ORLOFF, J. Chem. Phys. **17**, 1248 [1949].

²⁷ A. J. FREEMAN and R. E. WATSON, Phys. Rev. Letters **6**, 343 [1961].

²⁸ L. C. ALLEN, J. Chem. Phys. **34**, 1156 [1961].

²⁹ J. C. SLATER, Quantum Theory of Atomic Structure, McGraw-Hill, New York 1960.

% s	Q_{FF}^F	Q_{CC}^F	Q_{CF}^F	Q_{FC}^F
10	158.97	— 6.38	.55	— 8.96
20	321.33	— 9.42	.75	— 11.51
30	465.28	— 11.52	.78	— 12.33
40	580.64	— 15.81	.69	— 11.97
50	659.95	— 19.69	.52	— 9.76

Table 7. Estimates of fluorine Q parameters.

V. Conclusions

We note that the agreement between calculated and experimental a^F values is satisfactory when one-, two-, or three-parameter expressions are employed. As is to be expected the agreement increases slightly with increasing number of parameters. We should stress, however, that the Q parameters are obtained from experimentally determined a^F values and spin densities calculated via McLachlan's method adapted for heteronuclear systems. In all probability the McLachlan spin densities for the carbon skeleton are fairly reliable. We are less sure, however, about the very small calculated spin densities of the fluorine atoms. A systematic error in fluorine spin densities will be reflected in a systematic error in the calculated Q parameters. Because of the crudeness of the π -spin density calculation there is no certainty that the semi-empirically determined Q values will agree with theoretical estimates. In fact,

our theoretically calculated Q values do not compare well with the semi-empirical values. They are, however, of the same order of magnitude as those of Hinchcliffe and Murrell. The third set of parameters (Table 6, column c) satisfies the theoretical predictions for Q_{FF} and $(Q_{CF} + Q_{FC})$ quite well if one assumes 10 to 20% S character. In contradiction to the always negative theoretical estimate for Q_{CC} , we find a positive semi-empirical value for this constant. Using our theoretical estimates of the Q 's and the McLachlan spin densities rather poor agreement between $a^F(\text{calc.})$ and $a^F(\text{exptl.})$ is found. We note, however, that a change in fluorine π -spin density by a factor of 2 to 3, which is a small change anyhow and will not affect the overall spin density distribution noticeably, will result in calculated a^F values which are in considerably better agreement with observed ones. Unfortunately, we consider the problem far from being solved. It appears obvious that an improved wave function for the C-F fragment is necessary, and it appears doubtful whether McLachlan's MO method is valid for radical ions with highly electronegative atoms such as F in it. Further work about the interpretation of the Q values is in progress.

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