

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 85, NUMBER 18

SEPTEMBER 20, 1963

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION NO. 867 FROM THE CENTRAL RESEARCH DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., EXPERIMENTAL STATION WILMINGTON 98, DEL.]

Fluorine-19 Contact Interaction Shifts: The CF_3 , OCF_3 , SCF_3 , SF_5 , and SO_2CF_3 Groups

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RECEIVED MAY 4, 1963

Previous studies of F^{19} contact interaction shifts in the fluoroaromatics have been extended to compounds containing the CF_3 , OCF_3 , SCF_3 , SF_5 , and SO_2CF_3 groups. For the purpose of these experiments, suitably substituted Ni(II) aminotroponimineates have been prepared. Results have been expressed in terms of a parameter Q_F , which represents the fluorine hyperfine coupling (in gauss) for unit spin in the carbon $p\pi$ -orbital at the point of attachment of the substituent group. Significant contact shifts have been observed in all the compounds examined. The n.m.r. method allows the sign of the hyperfine coupling to be determined, and both positive and negative Q -values have been obtained. The results are discussed in terms of the possible spin delocalization and spin polarization mechanisms which can lead to unpaired electron density at the fluorine nucleus.

Introduction

The measurement of hyperfine coupling constants in the e.p.r. spectra of free radicals¹ and more recently the observation of contact interaction shifts in the n.m.r. spectra of free radicals^{2a} and of paramagnetic chelates^{2b,2c} have led to the concept of a spin density distribution in a paramagnetic molecule. The two types of experimental observation are both manifestations of the same physical phenomenon, namely, the I-S coupling of nuclear and electron spins, but the n.m.r. method, where applicable, has certain advantages. In particular, it leads directly to the sign of each hyperfine coupling constant, and it is capable of detecting small spin densities in complex molecules.

In order that a contact shift may be observed for a given nucleus, it is necessary that there should be a finite possibility of finding the unpaired electron at the nucleus. This will only be the case if the orbital containing the spin has some of the character of an s-orbital centered on that nucleus. The contact shifts observed are therefore closely related to the chemical bonding of the atom. Thus far only four bonding situations have been studied in any detail. They are: (a) The case of a hydrogen atom bonded to an sp^2 -carbon in an aromatic molecule: This is particularly straightforward since for the hydrogen atom only the 1s-orbital need be considered. It was proposed by McConnell^{3a} and by Bersohn^{3b} that the important mechanism is one of π - σ correlation and the theory has been developed extensively by McConnell and Chesnut.⁴ The important result is that the hyperfine coupling is directly proportional to the spin density on the carbon, *i.e.*

$$a_H = Q_H \rho_C \quad (1)$$

where Q_H is a constant which has a negative sign.

(1) For a recent review see S. I. Weissman, *Ann. Rev. Phys. Chem.*, **13**, 151 (1961).

(2) (a) T. H. Brown, D. H. Anderson, and H. S. Gutowsky, *J. Chem. Phys.*, **33**, 720 (1960); (b) A. Forman, J. N. Murrell, and L. E. Orgel, *ibid.*, **31**, 1129 (1959); (c) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *ibid.*, **37**, 347 (1962).

(3) (a) H. M. McConnell, *ibid.*, **24**, 764 (1956); (b) R. Bersohn, *ibid.*, **24**, 1066 (1956).

(4) H. M. McConnell and D. B. Chesnut, *ibid.*, **28**, 107 (1958).

(b) The case of a methyl group attached to an sp^2 carbon: Here the symmetry of the methyl group molecular orbitals is such as to allow spin to be transferred directly to a hydrogen 1s-orbital by hyperconjugation, and it has been shown by Bolton, Carrington, and McLachlan⁵ that at least for certain anthracene ions the hyperconjugative effect dominates any spin polarization⁶ effect. Once again the coupling constant may be related to the carbon spin density by an equation similar to 1, *i.e.*

$$a_{\text{CH}_3} = Q_{\text{CH}_3} \rho_C \quad (2)$$

but in this case Q_{CH_3} is positive and is not a true constant. Different values of Q are obtained for different positions of substitution of the methyl group,⁷ and these may be interpreted as reflecting varying degrees of hyperconjugation.

(c) The case of a fluorine atom attached to an sp^2 -carbon^{7,8}: Here both a spin polarization and a conjugation effect have been shown to be important. The former is independent of the position of substitution, but the latter has been found to vary linearly with the C-F π -bond order.

(d) C^{13} in an aromatic ring⁹: In this case also contributions from spin centered on the atom itself and from spin on neighboring atoms must be considered.

It was the purpose of the present study to obtain hyperfine coupling constants for fluorine atoms in several more complex chemical environments than those previously studied. In view of examples (c) and (d) above, it seemed probable that two or more mechanisms

(5) G. R. Bolton, A. Carrington, and A. D. McLachlan, *Mol. Phys.*, **5**, 31 (1962).

(6) Delocalization of unpaired electrons involves mixing of orbitals of the same symmetry. Spin polarization refers to exchange interactions between electrons in orbitals of different symmetries. The two effects have been discussed by D. A. Levy and L. E. Orgel, *Mol. Phys.*, **3**, 583 (1960).

(7) D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4100 (1962).

(8) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Mol. Phys.*, **5**, 407 (1962).

(9) (a) A. D. McLachlan, H. H. Dearman, and R. Lefebvre, *J. Chem. Phys.*, **33**, 65 (1960); (b) M. Karplus and G. K. Fraenkel, *ibid.*, **35**, 1312 (1961).

TABLE I

N,N'-DISUBSTITUTED 1-AMINO-7-AMINO-1,3,5-CYCLOHEPTADIENES

\bar{R}	X	Formula	M.p., °C.	Ligand analyses, %					
				Carbon		Hydrogen		Nitrogen	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
CF ₃ C ₆ H ₄ - (<i>m</i>)	H	C ₂₁ H ₁₄ F ₆ N ₂	84-85	61.8	61.6	3.46	3.70	^a	
CF ₃ C ₆ H ₄ - (<i>p</i>)	H	C ₂₁ H ₁₄ F ₆ N ₂	142-143.2	61.8	62.2	3.46	3.58	6.86	7.00
CF ₃ OC ₆ H ₄ - (<i>m</i>)	H	C ₂₁ H ₁₄ F ₆ N ₂ O ₂ ·HCl	205-206.4	52.9	53.3	3.17	2.59	5.87	6.15
CF ₃ OC ₆ H ₄ - (<i>p</i>)	H	C ₂₁ H ₁₄ F ₆ N ₂ O ₂ ·HCl	238-239	52.9	52.5	3.17	2.56	5.87	6.05
CF ₃ SC ₆ H ₄ - (<i>m</i>)	H	C ₂₁ H ₁₄ F ₆ N ₂ S ₂ ·HCl	174-176	49.6	49.4	2.97	3.26	5.50	5.45
CF ₃ SC ₆ H ₄ - (<i>p</i>)	H	C ₂₁ H ₁₄ F ₆ N ₂ S ₂ ·HCl	207-209.4	49.6	49.5	2.97	3.01	5.50	5.48
CF ₃ SO ₂ C ₆ H ₄ - (<i>m</i>)	H	C ₂₁ H ₁₄ F ₆ N ₂ O ₄ S ₂ ·HCl	191.5-193.5	44.0	44.5	2.64	2.89	4.90	5.30
SF ₅ C ₆ H ₄ - (<i>m</i>)	H	C ₁₉ H ₁₄ F ₁₀ N ₂ S ₂ ·HCl	204.6-207.5	40.7	40.9	2.70	2.69	5.00	5.17
					41.0		2.63		
SF ₅ C ₆ H ₄ - (<i>p</i>)	H	C ₁₉ H ₁₄ F ₁₀ N ₂ S ₂	130-131.6	43.5	43.9	2.69	2.89	5.35	5.42
C ₂ H ₅	SF ₅ C ₆ H ₄ N=N- (<i>m</i>)	C ₁₇ H ₁₉ F ₆ N ₄ S	Oil ^b
C ₂ H ₅	SF ₅ C ₆ H ₄ N=N- (<i>p</i>)	C ₁₇ H ₁₉ F ₆ N ₄ S	117-119	50.2	50.6	4.72	4.81	13.8	14.1
					50.5		4.60		
CF ₃ C ₆ H ₄ - (<i>m</i>)	H	C ₄₂ H ₂₆ F ₁₂ N ₄ Ni	100-101	57.7	58.3	3.00	3.25	6.42	6.69
CF ₃ C ₆ H ₄ - (<i>p</i>)	H	C ₄₂ H ₂₆ F ₁₂ N ₄ Ni	262-263	57.7	58.0	3.00	3.05	6.42	6.72
CF ₃ OC ₆ H ₄ - (<i>m</i>)	H	C ₄₂ H ₂₆ F ₁₂ N ₄ O ₄ Ni	123-125	53.8	54.3	2.80	3.28	5.98	6.27
CF ₃ OC ₆ H ₄ - (<i>p</i>)	H	C ₄₂ H ₂₆ F ₁₂ N ₄ O ₄ Ni	187.5-189	53.8	54.1	2.80	3.08	5.98	6.06
CF ₃ SC ₆ H ₄ - (<i>m</i>)	H	C ₄₂ H ₂₆ F ₁₂ N ₄ S ₄ Ni	130.8-132.2	50.4	50.0	2.61	2.45	5.59	5.86
CF ₃ SC ₆ H ₄ - (<i>m</i>)	H	C ₄₂ H ₂₆ F ₁₂ N ₄ S ₄ Ni	197.5-199.5	50.4	50.2	2.61	2.69	5.59	5.63
CF ₃ SO ₂ C ₆ H ₄ - (<i>m</i>)	H	C ₄₂ H ₂₆ F ₁₂ N ₄ O ₈ S ₄ Ni	103-105	44.7	45.0	2.32	2.53	4.96	5.09
SF ₅ C ₆ H ₄ - (<i>m</i>)	H	C ₃₈ H ₂₆ F ₂₀ N ₄ S ₄ Ni	171.8-173.5	41.3	41.5	2.37	2.63	5.07	5.16
SF ₅ C ₆ H ₄ - (<i>p</i>)	H	C ₃₈ H ₂₆ F ₂₀ N ₄ S ₄ Ni	335-336	41.3	41.6	2.37	2.58	5.07	5.57
C ₂ H ₅	SF ₅ C ₆ H ₄ N=N- (<i>m</i>)	C ₃₄ H ₃₆ F ₁₀ N ₈ S ₂ Ni	219-221	47.0	47.4	4.17	4.09	12.9	13.2
		C ₃₄ H ₃₆ F ₁₀ N ₈ S ₂ Zn	240-241.5	46.6	47.2	4.14	4.02	12.8	13.0
C ₂ H ₅	SF ₅ C ₆ H ₄ N=N- (<i>p</i>)	C ₃₄ H ₃₆ F ₁₀ N ₈ S ₂ Ni	219-224	47.0	47.3	4.17	4.23	12.9	13.3

^a Calcd.: F, 27.9. Found: F, 28.1. ^b Characterized as zinc chelate.

would be involved in each case. The experiments were therefore designed along the following lines.

First, the proton n.m.r. spectra of a paramagnetic chelate and of its corresponding ligand or zinc chelate were measured, and the hyperfine coupling constants a_{H_i} for protons attached to sp²-carbons calculated from the differences in the resonance frequencies of corresponding protons in the paramagnetic and diamagnetic compounds. The signs of a_{H_i} are obtained immediately from the direction of the shift (high field or low field).

Second, the spin densities ρ_i in the carbon p π -orbitals were calculated using eq. 1. This is possible because the simplicity of bonding case (a) allows only the σ - π correlation mechanism to operate and Q_H is a good constant. A value of -22.5 gauss was used throughout.¹⁰

Third, the spin densities obtained in this way were used to estimate the p π spin density at the position of substitution of the fluorine-containing group X. For reasons described below, it is believed that these estimated spin densities are correct to $\pm 5\%$.

Fourth, the F¹⁹ n.m.r. spectra of the diamagnetic and paramagnetic compounds were measured and from the contact shift the sign and magnitude of the hyperfine coupling constant a_{F_i} were obtained.

Fifth, a_F and ρ_C were used to define a parameter Q_X according to the equation

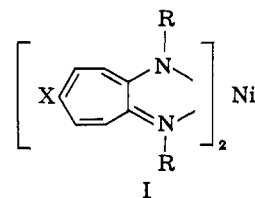
$$a_{F_i} = Q_X \rho_{C_i}$$

Finally, wherever possible, the procedure was repeated for one or more different positions of substitution of X.

An experiment along these lines thus provides information on the magnitude, the sign, and the variation with position of substitution of the parameter Q . This enables some deductions to be made regarding the

relative importance of spin polarization and spin delocalization effects in the various bonding situations.

The Ni(II) aminotroponimineates of structure I provide a very suitable system for contact-shift studies of this kind.



These compounds can be synthesized with different groups R and X. In the present instance, compounds were prepared with substituent R containing CF₃, OCF₃, SCF₃, SO₂CF₃, and SF₅ groups substituted on a phenyl ring and substituent X containing the SF₅ substituted on a phenyl azo group. In all cases there exists in solution a rapid equilibrium between square, planar, diamagnetic molecules, and tetrahedral paramagnetic molecules.¹¹ It is this rapid equilibrium which gives rise to the short electronic relaxation time which is an essential condition for the observation of sharp-line n.m.r. spectra.^{2,11}

Experimental

Earlier papers^{2,12} have described a general procedure for the synthesis of N,N'-disubstituted aminotroponimineates, and the preparation of several derivatives was described in detail. In general, 5,5,6,6-tetrafluoro-1,3-cycloheptadiene is treated with two equivalents of a primary aromatic or aliphatic amine and with four equivalents of triethylamine as hydrogen fluoride acceptor in refluxing methanol solution. A period of 2-4 hr. is usually sufficient for the reaction to be completed. Often, the highly colored products separate from solution during the

(11) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963).

(12) W. R. Brasen, H. E. Holmquist, and R. E. Benson, *ibid.*, **83**, 3125 (1961).

(10) S. I. Weissman, T. R. Tuttle, and E. de Boer, *J. Phys. Chem.*, **61**, 28 (1957).

reflux period. The preparation of the fluorine-substituted derivatives of this paper is illustrated by the following example.

N,N'-Di-(*p*-trifluoromethylphenyl)-aminotroponeimine.—A solution of 4.03 g. (0.025 mole) of *p*-aminobenzotrifluoride, 5.8 g. (0.06 mole) of triethylamine, and 2.13 g. (0.0125 mole) of 5,5,6,6-tetrafluoro-1,3-cycloheptadiene in 25 ml. of methanol was refluxed 6 hr., cooled, and poured on cracked ice. The orange oil which formed did not crystallize. The aqueous layer was poured off, and the oil was washed several times with water by decantation. Trituration of the oil with a small amount of methanol caused crystallization, and filtration gave 2 g. (40%) of the orange aminotroponeimine. Several crystallizations from chloroform-methanol yielded orange prisms, m.p. 142–143.2°.

In some instances, it proved more convenient to isolate the N,N'-disubstituted aminotroponeimines as the hydrochlorides, since the free bases did not crystallize readily. The following preparation illustrates this procedure.

N,N'-Di-(*m*-trifluoromethoxyphenyl)-aminotroponeimine Hydrochloride.—A solution of 3.54 g. (0.02 mole) of *m*-trifluoromethoxyaniline, 4.5 g. of triethylamine, and 1.66 g. (0.01 mole) of tetrafluorocycloheptadiene in 20 ml. of methanol was heated at reflux for 6 hr. and allowed to cool slowly. No crystalline product separated, and the orange solution was poured on ice. Since the resulting heavy orange oil also failed to crystallize, it was taken up in ether and dried with anhydrous sodium sulfate. The ethereal solution was decanted and saturated with anhydrous hydrogen chloride. The yellow crystalline hydrochloride was collected, dried *in vacuo*, and weighed 3.37 g. (71%). Three crystallizations from isopropyl alcohol gave bright yellow, N,N'-(*m*-trifluoromethoxyphenyl)-aminotroponeimine hydrochloride, m.p. 205–206.4°.

The preparation of nickel chelates of the aminoimines is readily accomplished in several ways. A satisfactory procedure for the fluorine-substituted compounds described here involves reaction of two equivalents of the ligand with one equivalent of nickel(II) acetate tetrahydrate in boiling ethanol solution. When the ligands were not easily soluble in ethanol, enough benzene or chloroform was added to effect complete solubility. The reaction appeared to be complete after about 45 min. The products were washed with water, dried, and recrystallized from mixtures of methylene chloride and methanol. Analytical results for the new nickel(II) aminotroponeimineates (and parent ligands) discussed in this paper are presented in Table I. The proton resonances of the chelates generally were so widely spaced because of contact-interaction shifts that the n.m.r. spectra alone were usually sufficient to determine whether or not a desired chelate had been formed.

¹H n.m.r. spectra were obtained in CDCl₃ or CS₂ solutions using standard Varian equipment operating either at 40 Mc./sec. or 60 Mc./sec. ¹⁹F spectra were similarly obtained at 40 Mc./sec. or 56.4 Mc./sec. The analysis of nickel(II) aminotroponeimineate spectra has been discussed in detail previously.² Assignment of the different resonances is based on the direction of the shifts as predicted by simple valence bond structures, the relative spectral intensities, intercomparison between structurally similar compounds, and the observation of spin-spin (I-I) structure. In the present series of compounds there are no significant ambiguities in the assignments. Calibration was effected by the usual audiomodulation technique using as internal calibrants tetramethylsilane for the proton spectra and 1,2-difluoro-1,1,2,2-tetrachloroethane for the fluorine spectra (Freon 112).

The contact shifts are defined as the difference in resonance frequency of nuclei with the same chemical environment in paramagnetic and diamagnetic compounds. It may be assumed that the Zn(II) aminotroponeimineates will be structurally very similar to the tetrahedral Ni(II) compounds. In practice it has been found that both the proton and fluorine resonance frequencies of the Zn chelates are the same to within a few cycles as those of the ligands. Either the ligand or the zinc chelate may therefore be conveniently used as a reference. The choice of reference has been indicated in Table II.

Results

The contact interaction shift of the *i*th proton ($\Delta H_i/H$) is given by

$$\frac{\Delta H_i}{H} = \left(\frac{\Delta f_i}{f} \right) = -a_{H_i} \frac{\gamma_e}{\gamma_H} \frac{g\beta S(S+1)}{2SkT[\exp(\Delta F/kT) + 3]} \quad (3)$$

In eq. 3, ΔH_i and Δf_i are the shifts in resonance field and frequency, respectively, a_{H_i} is the hyperfine coupling constant of the *i*th proton, γ_e and γ_H are the magnetogyric ratios for the electron and for the proton, and ΔF is the free energy difference for the diamagnetic \rightleftharpoons paramagnetic equilibrium which exists in these chelate solutions.¹³ It is apparent that the right-

hand side of this equation contains two unknowns, a_{H_i} and ΔF , so that contact-shift measurements over a range of temperatures are necessary to determine both absolutely. An analogous expression can be written for the fluorine contact shifts by replacing a_{H_i} by a_{F_i} and γ_H by γ_F . It follows therefore that

$$\left(\frac{\Delta f_i}{f} \right)_F \left(\frac{f}{\Delta f_i} \right)_H = \frac{a_{F_i} \gamma_H}{a_{H_i} \gamma_F} \quad (4)$$

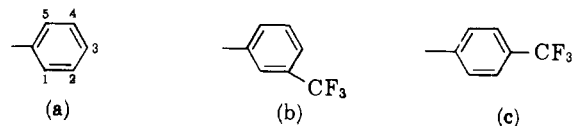
Also since $a_{H_i} = Q_H \rho_{C_i}$ and the parameter Q_F is defined by the equation $a_{F_i} = Q_F \rho_{C_i}$ it follows that

$$Q_{F_i} = Q_H \cdot \frac{\gamma_{F_i}}{\gamma_{H_i}} \left(\frac{\Delta f}{f} \right)_{F_i} \left(\frac{f}{\Delta f} \right)_{H_i} \quad (5)$$

where $(f/\Delta f)_{H_i}$ is the proton shift at the position of substitution of the fluorine-containing group. This latter quantity is not directly measurable but if the proton shift at a second position *j* is measured, then

$$(\Delta f/f)_{H_j} = (\Delta f/f)_{H_i} \cdot (\rho_i/\rho_j) \quad (6)$$

Q_{F_i} can then be found from eq. 5 and 6 if the relative spin densities in the $p\pi$ -orbitals at *i* and *j* are known. It is convenient to use the β -position of the seven-membered ring as a reference position throughout. The ratios ρ_i/ρ_j are estimated from the measured proton contact shifts in a series of compounds. Thus consider for example the compounds with the substituents R



In compound b the negative spin at position 2 arises from the polarization effects of the positive spin at positions 1 and 3 and the negative spin at position 4 from that of the positive spins at 3 and 5. Position 3 is common to both these effects. The negative spin at 2 can therefore differ from the measured value at 4 by an amount that is not greater than the measured difference in spin density between 1 and 5. The spin densities at positions 1, 2, 4, and 5 of compound c may be compared with those at the corresponding positions in compound a. By a similar argument the spin density at position 3 of compound c cannot differ from that at position 3 of compound a by more than the observed differences at positions 1, 2, 4, and 5. In general, the variation in spin densities at corresponding positions in a series of compounds such as this has been found to be of the order of 5% or less and it is therefore estimated that the maximum error in the ratios ρ_i/ρ_j used in eq. 6 is around 5%. The experimental shifts $(\Delta f_i)_H$ and $(\Delta f_i)_F$ can be measured to a much greater precision than this, and the magnetogyric ratios γ_e , γ_H , and γ_F are also accurately known. For Q_H a value of -22.5 gauss was taken, and this also has an uncertainty of around 5%. It may therefore be concluded that the parameters Q_{F_i} may be in error to the extent of $\pm 10\%$.

In Table II the observed proton and fluorine contact shifts, the relative spin densities at the positions of proton substitution, the estimated spin densities at the positions of fluorine substitution, and the derived values of Q_F are presented. Data on two other compounds, the Ni(II) N,N'-diethyl- γ -(*p*-fluorophenylazo)- and N,N'-diphenylaminotroponeimineates are also included for comparison. A typical proton spectrum of a para-

(13) In this paper, and others from this laboratory, the convention has been adopted that the sum of the spin densities, as calculated from eq. 3 and 1, equals the total number of unpaired electrons in the molecule, *i.e.*, $\Sigma \rho = 2S$ where $S = 1$ for a triplet molecule. This has led to the introduction of a factor of $2S$ in the denominator of the expression on the right-hand side of equation 3. As a result, the a_{H_i} of equation 3 is actually greater than the hyperfine spacing which would be observed in an e.p.r. spectrum by a factor of $2S$.

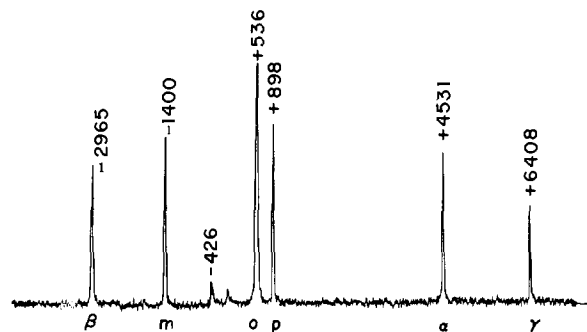


Fig. 1.— H^1 spectrum of Ni(II) N,N' -di-(*m*-trifluoromethoxyphenyl)-aminotroponimineate; solvent, $CDCl_3$; 60 Mc./sec.

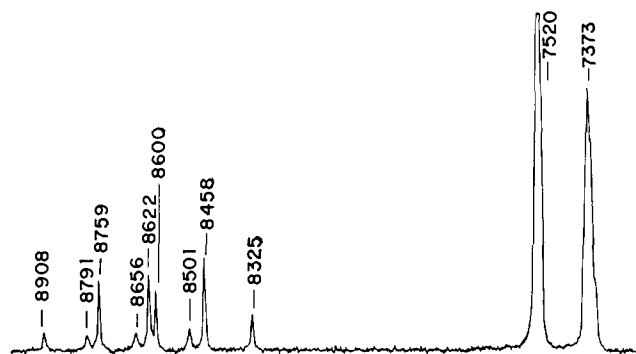


Fig. 2.— F^{19} spectrum of Ni(II) N,N' -di-(*m*-pentafluorosulfo-phenyl)-aminotroponimineate; solvent, $CDCl_3$; 56.4 Mc./sec.

magnetic Ni(II) aminotroponimineate is shown in Fig. 1. Figure 2 shows the F^{19} spectrum of the Ni(II) di-(*m*-pentafluorosulfo-phenyl)-aminotroponimineate. This is typical of the AB_4 pattern expected for the SF_5 group and can be readily analyzed. Similar spectra were obtained for all the diamagnetic SF_5 compounds and for the other *m*- SF_5 substituted Ni chelates. However the two paramagnetic *p*- SF_5 compounds at room temperature show only incompletely resolved spectra. It appears that in these compounds the contact shifts oppose the normal chemical shifts between the basal and apical fluorines so that at room temperature all five fluorines are almost equivalent. However, contact shifts are temperature dependent as shown by eq. 3, whereas chemical shifts are relatively insensitive to temperature changes, so that in principle an analyzable spectrum can be obtained by varying the temperature. A series of traces of the Ni(II) N,N' -diethyl- γ -(pentafluorosulfo-phenylazo)-aminotroponimineate F^{19} spectrum at different temperatures is shown in Fig. 3. The transition from a single line toward the normal AB_4 spectrum is clearly visible, but the limited solubility at low temperatures complicates the analysis of the part of the spectrum arising from the single apical fluorine. For this reason the Q -values given for the apical fluorines of these two compounds in Table II are less certain than the rest of the data.

It may be noted from the above that although the derivation of absolute values of spin densities from this type of contact shift measurement requires temperature studies, values of Q_F can be obtained from room temperature measurements alone.

Discussion

From the results of Table II, it is apparent that in all the cases considered sufficient spin has reached the fluorine nucleus to produce a significant contact shift. An estimation of the amount of unpaired spin in the fluorine atomic p-orbital may be obtained by comparison of the present results with the hyperfine splitting

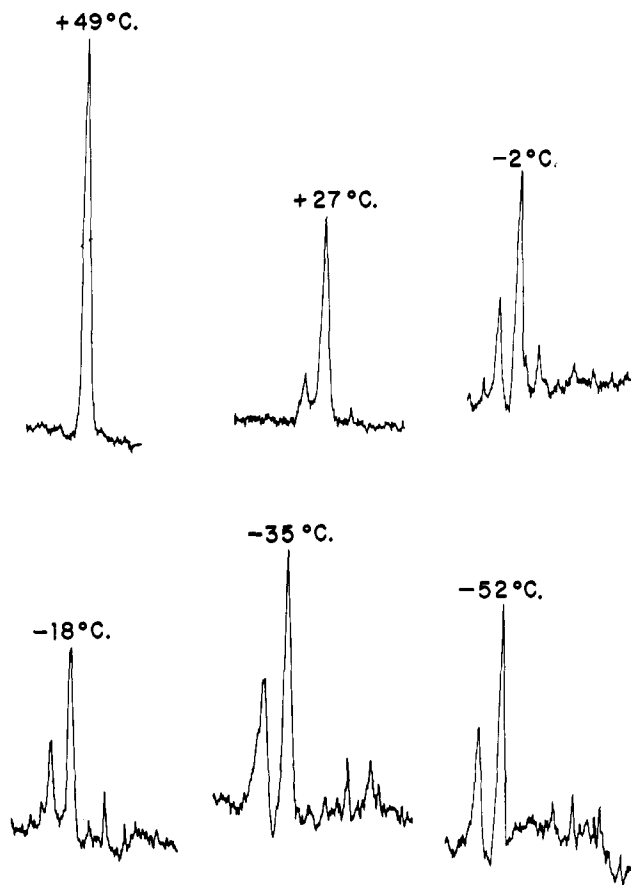
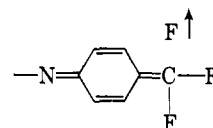


Fig. 3.—Temperature dependence of the F^{19} spectrum of Ni(II) N,N' -diethyl- γ -(*p*-pentafluorosulfo-phenylazo)-aminotroponimineate; solvent, $CDCl_3$; 56.4 Mc./sec.

of the free fluorine atom (1077 gauss).¹⁴ Thus, for the *p*- CF_3 group the observed Q -value of +38.4 gauss implies that a unit spin on the *para* carbon would produce a fluorine hyperfine splitting of 38.4 gauss. Effectively therefore $38.4/1077 = 3.6\%$ of the spin has been transferred to the fluorine. However in the above case the actual spin density at the *para* carbon is $\sim +0.01$ so that the spin on the fluorine is $\sim +0.0004$. For the other groups with smaller Q -values, the amount of spin involved will be correspondingly lower. It is apparent therefore that contact shift measurements provide a sensitive method of detecting small effects and conversely that mechanisms such as hyperconjugation, which may produce a pronounced contact shift, are not necessarily energetically significant.

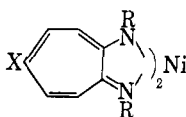
From these data it is also possible to make some tentative suggestions regarding the mechanisms by which spin reaches the fluorine nucleus. Thus the Q -values of +38.4 gauss and +9.0 gauss for a CF_3 group attached to a phenyl ring at the *para* and *meta* positions, respectively, may be compared with the corresponding values for a CH_3 group of +27.7 gauss and +8.3 gauss. This suggests that the CF_3 group is capable of hyperconjugation similar to that of a CH_3 group with the effect being strongest for the *para* substituted derivative for which resonance structures of the type



can be written. Such a structure places spin in what

(14) H. E. Radford, V. W. Hughes, and V. Beltran-Lopez, *Phys. Rev.*, **123**, 153 (1961).

TABLE II



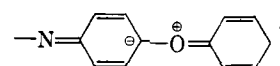
X	R	Position	Contact shift, c.p.s.	Relative spin density ^c	Q _i , gauss	X	R	Position	Contact shift, c.p.s.	Relative spin density ^c	Q _i , gauss
H		α	+4758	-1.953		H		α	+5471	-1.903	
		β	-2436	1.000				β	-2873	1.000	
		γ	+6564	-2.695				γ	+7516	-2.614	
(Ligand)		ortho	+870	-0.357				ortho	+1320	-0.459	
		meta	-906	+ .372				ortho'	+875	- .304	
		para	+1230	- .505		(Ligand)		meta	-1173	+ .408	
			+2261	-1.903				para	+1543	- .537	
H		α	-1188	1.000				CF ₃	-137	(+ .362)	-2.8
		β	+3180	-2.677					+3499	-1.882	
(Ligand)		γ	+407	-0.343		H		α	-1859	1.000	
		ortho	-464	+ .391				β	+5009	-2.694	
		meta	-1130	(- .524)	+38.4			γ	+627	-0.337	
		CF ₃	+3077	-1.926		(Ligand)		ortho	-746	+ .401	
			-1598	1.000				meta	-1378	(- .524)	+29.9
H		α	+4228	-2.646				SF ₅ (basal)	-131	(- .524)	-2.7
		β	+623	-0.390				SF ₅ (apex)	+5148	-1.911	
(Ligand)		γ	+574	- .359		H		β	-2694	1.000	
		ortho	-622	+ .389				γ	+7068	-2.624	
		ortho'	+837	- .524				ortho	+1064	-0.395	
		meta	+258	(+ .380)	+9.0	(Zn chelate)		ortho'	+986	- .366	
		para	+2484	-1.944				meta	-1050	+ .390	
H		β	-1278	1.000				para	+1423	- .528	
		γ	+3423	-2.678				SF ₅ (basal)	-110	(+ .390)	-2.2
(Zn chelate)		ortho	+443	-0.347				SF ₅ (apex)	-45	(+ .390)	-0.9
		meta	-489	+ .383					+5206	-1.739	
		CF ₃	-46	(- .524)	+1.5	F		α	-2994	1.000	
			+4940	-1.933				β	-8706	+2.908	
H			-2556	1.000		(Ligand)		CH ₂	-791	+0.264	
		α	+6817	-2.668				CH ₃	+1216	- .406	
		β	+966	-0.378				ortho	-303	+ .101	
		γ	-970	+ .379				meta	-3433	(- .462)	+52.6
		ortho	+1344	- .526				F	+4746	+1.701	
		meta	-266	(+ .379)	-5.8	F ₅ S		α	-2790	1.000	
		para	+4592	-1.893				β	-8421	+3.018	
		CF ₂	-2426	1.000		(Ligand)		CH ₂	-828	+0.297	
			+6489	-2.675				CH ₃	+1244	- .446	
(Zn chelate)		α	+837	-0.345				ortho	-402	+ .144	
		β	-952	+ .392				meta	-1333	(- .467)	+21.6
		ortho	-246	(- .524)	+4.1			SF ₅ (basal)	-30	(- .467)	+0.5
		meta	+4139	-1.933				SF ₅ (apex)	+4786	-1.722	
		para	-2141	1.000				α	-2779	1.000	
		CF ₃	+5594	-2.613				β	-8501	+3.059	
(Zn chelate)			+777	-0.363				CH ₂	-832	+0.299	
		α	-828	+ .387				CH ₃	+1234	- .444	
		β	+1097	- .512				ortho	+1223	- .440	
		γ	-204	(+ .387)	-5.2			ortho'	-371	+ .134	
		ortho						meta	+1315	- .473	
		meta						para	+124	(+ .134)	+7.1
		para						SF ₅ (basal)	+26	(+ .134)	+1.5
		CF ₃						SF ₅ (apex)			

^a 40 Mc./sec. data; all other shifts at 60 Mc./sec. ^b CS₂ solution; all others in CDCl₃. ^c Estimated relative spin densities in parentheses.

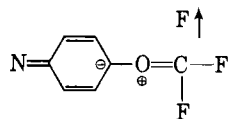
is predominantly a fluorine 2p-orbital, but it must be assumed that this orbital has sufficient 2s-character to produce the observed density at the nucleus. It may be noted that, as for the CH₃ group,⁵ the positive sign of *Q* is not in itself sufficient to distinguish between a spin polarization and a spin delocalization mechanism since polarization through two bonds also leads to positive spin at the fluorine. The marked difference between the *meta* and *para* *Q*'s is, however, readily under-

standable if the delocalization mechanism is predominant but difficult to account for by a polarization effect.

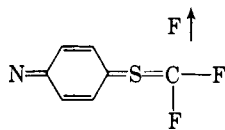
Previous measurements of spin density distributions in these aminotroponimineates² have shown that spin is transmitted through -O- and -S- atoms by structures such as



It seems plausible to suggest therefore that the positive Q 's of the OCF_3 and SCF_3 groups at the *para* position arise from the contribution of structures such as

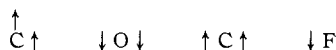


Utilization of the empty d-orbitals of the sulfur atom in the $-\text{SCF}_3$ compound enables additional structures of the type



to be written which may account for the higher Q -value (+4.1 gauss) in the SCF_3 compound than for the OCF_3 compound (+1.5 gauss).¹⁵ A recent study of the F^{19} chemical shifts in trifluoromethoxy and trifluoromethylthio aromatic compounds has also indicated that $-\text{S}-$ is a better conjugating group than $-\text{O}-$ in these compounds by a factor of between two and three.¹⁶ This is in good qualitative agreement with the ratio of the Q -values reported here.

Conjugation of this type does not account for the negative sign of the *meta* Q -values. It is possible in principle that spin polarization through three bonds could produce this negative coupling, *i.e.*



However the magnitude seems rather large for such a long-range effect. It may also be noted that the ratio of the *p*- CF_3 to *p*- OCF_3 Q -values (25.6) is markedly larger than the ratio for the corresponding CH_3 compounds² (7.4). This is indicative that in the *p*- OCF_3 compound there is also a competing mechanism tending to place negative spin at the fluorine. In the

(15) W. A. Sheppard, *J. Am. Chem. Soc.*, **85**, 1314 (1963); pK_a measurements have provided some evidence for d-orbital participation in the bonding of the SCF_3 group.

(16) D. R. Eaton and W. A. Sheppard, *ibid.*, **85**, 1310 (1963).

case of the SO_2CF_3 group, a Q -value is available only for the *meta* compound. The negative sign obtained for this parameter suggests that similar considerations will probably apply to this group. The value obtained (-2.8 gauss) is about half that for the corresponding SCF_3 compound.

The SF_5 compound was of particular interest in view of results recently obtained in a study of the chemical shifts of this group in aromatic compounds.¹⁶ A marked difference was observed in the behavior of the chemical shifts of the basal and apical fluorines, and the present results show that the contact shifts are also very different. The Q -values obtained range from +30 to -2 gauss, and it seems unlikely that they can be accounted for by a single mechanism. The contact shifts are very much larger for the basal fluorines than for the apex fluorine, and it is probable that a direct interaction between these basal fluorines and the aromatic π -system is involved. This again is consistent with the deductions made from the chemical shift measurements. These results may also be compared with the contact shifts of analogous fluorobenzene derivatives which have been interpreted in terms of fluorine double bonding.^{7,8} There is a similarity, especially for the basal fluorines, in that the largest positive Q -values are found at the *para* positions where conjugation effects are expected to be strongest.

Significant F^{19} contact shifts have been observed in all the compounds examined in this study. It appears that both spin delocalization (conjugation) and spin polarization can provide effective mechanisms for transmitting spin density from an aromatic π -system to the F^{19} nucleus. The n.m.r. approach, which enables the signs of the I-S coupling constants to be obtained, in conjunction with measurements on the same group substituted at different positions, seems to provide the best hope of disentangling the various effects; n.m.r. contact shifts differ from the more familiar chemical shifts in that they depend upon spin densities rather than charge densities. However, there is clearly a relationship between the two types of measurement, and a combination of the results from both may well provide a powerful approach to the study of problems of chemical bonding.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER 8, B. C., CANADA]

The Electron Spin Resonance Spectrum of Electrolytically Generated 7,7,8,8-Tetracyanoquinodimethane Radical Anions

By P. H. H. FISCHER¹ AND C. A. McDOWELL

RECEIVED APRIL 24, 1963

The electron spin resonance spectrum of the radical ion of 7,7,8,8-tetracyanoquinodimethane has been observed with all the expected hyperfine components completely resolved. The radical was generated by electrolysis at a platinum wire cathode operating at a potential of -0.1 v. with respect to a saturated calomel electrode. The solvent was a mixture of 80% dimethoxyethane and 20% acetonitrile with tetra-*n*-propylammonium perchlorate as supporting electrolyte. In addition to observing all the 45 lines due to hyperfine interactions caused by four equivalent nitrogen nuclei and four equivalent hydrogen nuclei, several additional lines of weak intensity due to C^{13} hyperfine splitting were found. The analysis of the spectrum leads to the following values for the hyperfine coupling constants for the nitrogen and hydrogen nuclei, namely, $a^N = 1.02$ gauss and $a^H = 1.44$ gauss.

I. Introduction

In the course of our studies of the electron spin resonance spectra of a number of organic radical anions produced by electrolysis, we obtained in the case of many nitrile radical anions results closely similar to those recently reported by Rieger, Bernal, Reinmuth, and Fraenkel.² These authors were unable to obtain

satisfactory results in the case of the anion formed from 7,7,8,8-tetracyanoquinodimethane (TCQN). They found only a single broad line when the TCQN was electrolyzed in acetonitrile solution. We have been able to prepare the radical anion of TCQN without difficulty by electrolysis at a platinum electrode in a

(1) Holder of a National Research Council Studentship, 1960-1963.

(2) P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 683 (1963).