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Electron spin resonance spectra of an irradiated single crystal of difluoromalonamide and hyperfine tensors of α -fluorine couplings

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The principal values of the ¹⁹F hyperfine tensor for the \cdot CF(CONH₂)₂ radical in a γ -irradiated single crystal of diffuoromalonamide have been determined to be 200, -1, -10 g perpendicular to the radical plane, parallel to the C-F bond, and perpendicular to the C-F bond in the radical plane, respectively. The deviation from axial symmetry of the hyperfine tensor is discussed in comparison with that in other related compounds and it is concluded that the spin polarization of $2p\sigma$ electrons in the C-F bond plays an important role. The polarization factors, Q_{CF}^{F} and Q_{FC}^{F} , for the $2p\sigma$ electrons have been estimated to be -45 and +233 G so as to account for the hyperfine tensors of a series of compounds.

1. INTRODUCTION

A fluorine atom possesses a nuclear spin of $\frac{1}{2}$ like hydrogen and the magnitudes of the magnetic moments are similar. It might be expected that fluorine hyperfine couplings would be similar to those of hydrogen. However, it was found from single crystal analyses of some irradiated fluorine-containing compounds [1, 2] that the hyperfine tensors of the α -fluorine couplings have an entirely different nature from those of α hydrogen. The main cause of the difference comes from the mixing of the half-filled orbital with the fluorine $2p\pi$ orbital, resulting in a considerable amount of spin density in F_{2pπ}.

Since the hyperfine tensors for α fluorine were first determined by Lontz and Gordy [1] in \cdot CF₂CONH₂ and by Cook *et al.* [2] in \cdot CHFCONH₂, a few more have been added, the results being summarized in table 1. As seen from the table, there are fairly large varieties in the principal values. For example, \cdot CF₂CONH₂ in trifluoroacetamide has an axially symmetric hyperfine tensor[‡] indicating that the predominant contribution to the hyperfine anisotropy arises from the spin density in F_{2pπ}. On the other hand, \cdot CHFCONH₂ in monofluoroacetamide exhibits slight deviation from axial symmetry. Cook *et al.* [2] have ascribed the deviation to the minor contribution from the anisotropic interaction of a fluorine nucleus with the major spin density in the carbon $2p\pi$ orbital (C_{2pπ}) and with the polarized spin density in the fluorine $2p\sigma$ orbital (F_{2p\sigma}). Much larger deviation from axial

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[‡] Although Lontz and Gordy [1] gave an axially symmetric tensor, Rogers and Kispert [3] found a tensor slightly deviated from axial symmetry as listed in table 1. Toriyama and Iwasaki [7] also studied this radical in connection with the peroxy radical \cdot OOCF₂CONH₂ and found no evidence for deviation from axial symmetry.

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symmetry has been observed by Rogers and Whiffen [6] for $-OOCCF_2CFCOO^-$ in perfluorosodiumsuccinate. Kaplan *et al.* [8] have pointed out that there might be unexamined and unexplained complications in the anisotropy of the α -fluorine hyperfine couplings of these compounds.

Table 1. Hyperfine tensors of α -fluorine couplings determined from single crystal analyses.

In order to elucidate the cause of the large variety of deviations from axial symmetry, we have studied the $CF(CONH_2)_2$ radical in an irradiated single crystal of difluoromalonamide as the most typical example having only one α fluorine, for which simple two-line spectra are expected. From our results together with other data it was found that the spin density in $F_{2p\sigma}$ plays an important role in determining the deviation from axial symmetry, and that Q factors for the spin polarization of the $2p\sigma$ electrons in the C-F bond are obtainable to account for all the data.

2. EXPERIMENTAL

Difluoromalonamide was prepared by introducing dry gaseous ammonia into a diethyl ether solution of diethyl difluoromalonate. The melting point of the sample thus obtained is 206°c. Single crystals were grown from aqueous solutions by slow evaporation at room temperature. From the angular dependence of the E.S.R. spectra it was found that the crystal has orthorhombic symmetry. The experimental coordinate axes were chosen so as to make them parallel to the crystallographic axes. The appearance of the single crystal used and the experimental axes X, Y and Z are shown in figure 1. The radicals were formed by irradiation of the crystal at room temperature with ⁶⁰Co γ -rays. The total dose was about 1×10^7 R at a dose rate of 2×10^5 R/hour.



Figure 1. Sketch of the appearance of the single crystal used and the experimental coordinate axes.

The E.S.R. spectra were measured with a Japan Electron Optics Model JES-3BS spectrometer operated at 9.4 and 24 GHz at room temperature. The spectra were recorded as a second derivative representation with the 80 Hz and The signal of Mn²⁺ in ZnS was used as a marker for 100 kHz double modulation. the magnetic field. The resonance position and the hyperfine splittings of Mn²⁺ were calibrated using the signal of DPPH and a side-band technique of the proton magnetic resonance. The angular dependence of the spectra were measured at $2-10^{\circ}$ intervals by rotating the crystal about the X, Y and Z axes. Other special crystal orientations such that the magnetic fields are in the plane perpendicular to the direction of the maximum principal value of the hyperfine tensor or in the plane including the maximum and minimum principal values were also investigated to determine the smaller two principal values and their signs relative to the maximum principal value. The final data were derived from the spectra measured at 24 GHz, since the forbidden transitions arising from the nuclear Zeeman interaction were To interpret the principal directions of the hyperfine more clearly observed. tensor the g tensor was also determined.

Some other measurements with crystals irradiated at 77°K were also carried out.

3. INTERPRETATION OF THE SPECTRA

3.1. Method of analysis

In analysing the fluorine hyperfine couplings, the nuclear Zeeman interaction is not neglected since the maximum principal value is very large while the minimum is often extremely small, and in addition the problem of choosing the relative signs of the principal values has to be considered [2]. The spin hamiltonian for such a system is:

$$\mathscr{H} = \beta \mathsf{HgS} + \mathsf{SAI}/g_0 \beta - g_N \beta_N \mathsf{HI}, \tag{1}$$

the solution of which has already been given by a number of workers [9-11]. In our treatment slightly different and more convenient formulations were made for the hyperfine splittings and the transition probabilities. These are easily derived from the formulations already given by other workers [9-11].

The hyperfine splittings d_+ and d_- for the outer and inner doublets, one of which is the so-called forbidden transition due to the nuclear Zeeman interaction, are given by:

$$d_{\pm} = (A_{+} \pm A_{-})/2, \tag{2}$$

where

$$A_{\pm}^{2} = \tilde{\mathbf{h}}\tilde{\mathbf{L}}(\mathbf{A}_{0} \pm w\mathbf{E})^{2}\mathbf{L}\mathbf{h},\tag{3}$$

$$w = 2g_{\rm N}\beta_{\rm N}H,\tag{4}$$

 A_0 is the hyperfine tensor in the principal coordinate system, **E** the unit tensor, **L** the transformation matrix from the principal to the experimental coordinate system (that is, the matrix consisting of the direction cosines of the principal axes with respect to the experimental coordinates) and **h** the unit vector along the magnetic field. The intensities of the inner and outer doublets are given by:

$$I_{\pm} = \left| d_{\pm}^2 - w^2 \right| / A_{+} A_{-} = \left| d_{\pm}^2 - w^2 \right| / (d_{+}^2 - d_{-}^2).$$
(5)

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When $|\mathbf{A}_0|_i \ll w$ or $|\mathbf{A}_0|_i \gg w$, the intensity of the forbidden transition becomes very small and the splittings of the arrowed transition tend to the following expressions:

For $|\mathbf{A}_0|_i \ll w$:

$$d_{-} \rightarrow A = \tilde{\mathbf{h}} \tilde{\mathbf{L}} \mathbf{A}_0 \mathbf{L} \mathbf{h} = \tilde{\mathbf{h}} \mathbf{A}_X \mathbf{h}.$$
 (6)

For $|\mathbf{A}_0|_i \gg w$:

$$d_{+}^{2} \rightarrow \alpha^{2} = \tilde{\mathbf{h}} \tilde{\mathbf{L}} \mathbf{A}_{0}^{2} \mathbf{L} \mathbf{h} = \tilde{\mathbf{h}} \mathbf{A}_{X}^{2} \mathbf{h}, \tag{7}$$

where \mathbf{A}_X is the hyperfine tensor in the experimental coordinate system. Equations (6) and (7) are the familiar expressions for the usual cases where the nuclear Zeeman interaction can be neglected. In our case, the observed splittings cannot be directly fitted by equation (6) or (7). It is, however, easily verified that the correct splittings d_+ and d_- have the following relations with A and α :

$$A = d_{-}d_{+}/w, \tag{8}$$

$$\alpha^2 = d_+^2 - (w^2 - d_-^2). \tag{9}$$

A or α^2 is a linear function of the six independent elements of the tensor A_X or A_{X^2} , although d_{\pm} expressed by equation (2) is not a linear function. Therefore, if the observed splittings corresponding to d_{-} or d_{+} can be modified into the physical quantity corresponding to A or α^2 , the simple least squares method for linear functions is applicable to determine the six elements of A_X or A_X^2 from a number of observations. In order to modify the observed splittings into A or α^2 by using equation (8) or (9), one has to know the splittings for the forbidden transition, that is, d_{-} if d_{+} is observed and d_{+} if d_{-} is observed. Therefore, if the approximate values of the hyperfine tensor are known, the separations of the forbidden transition calculated from equation (2) may be used for this modification of the observed The least squares treatment of these modified quantities will give more quantities. accurate values for the hyperfine tensor from which the more reliable separations of the forbidden transition may be calculated. The successive modification using the least squares results will refine the values of the hyperfine tensor and the iteration procedure will be terminated when the self-consistent results are obtained.

In order to get the first approximate values, one may fit the observed splitting directly to the expression given by equation (6) or (7)—in other words, one may start with the unmodified splitting values. The computer programme was made to handle the splittings corresponding to d_+ or/and d_- .

3.2. Hyperfine tensor

When the magnetic field is applied along the X, Y or Z axis, the spectra at 24 GHz consist of two lines with equal intensity, indicating the existence of only one coupling nucleus with spin $\frac{1}{2}$. When the magnetic field lies in the XY, YZ or ZX plane other than in the canonical direction X, Y or Z, two sets of two lines were observed, indicating the orthorhombic symmetry of the trapping sites of the radicals. The typical spectra measured in the ZX plane are indicated in figure 2. The hyperfine coupling of the two line spectrum is extremely anisotropic and the splitting value in the ZX plane extends from zero to about 200 G. This must be clearly due to the α -fluorine coupling and the radical formed must be $\cdot CF(CONH_2)_2$.



Figure 2. Typical E.S.R. spectra of a single crystal of CF₂(CONH₂)₂ irradiated at room temperature. The spectra were measured at 24.08 GHz. The magnetic fields were applied (a) along the Z direction; (b) at 45°; (c) at 50°; (d) at 60° from the Z axis in the ZX plane; (e) along the X direction.

When the splitting approaches 25 G, that is the condition of the fluorine nuclear resonance, the satellite lines due to the nuclear spin flip were observed and then the resonance lines for the radical site with the smaller coupling value consist of the inner and outer doublets as shown in figure 2 (c). The separations of the inner doublet ranged from 0 to 8.5 G indicating that the smaller principal values are less than 25 G. The observed angular dependence of the inner and outer doublets is plotted in figure 3.

Although the analysis of the angular dependence gives a sufficiently accurate principal value (200 G) and the direction of the maximum element, smaller principal values including their signs and directions are hard to determine accurately from these experiments, since the inner doublets were observed only over a limited range. Therefore the other measurements were made in the field directions lying in the plane perpendicular to the direction of the maximum principal value, that is the radical plane for one of the four sites. In this special crystal orientation, the spectra consist of four sets of two lines because of orthorhombic symmetry. One of them shows the small angular variation in the splitting and always consists of an inner doublet. This site should correspond to the radical orientation in which the magnetic field lies in the radical plane. The angular dependence for this site is plotted in figure 4. The maximum (10 G) and minimum splittings (0 G) must give



Figure 3. Angular dependence of the hyperfine splittings for the outer (d_+) and inner (d_-) doublets. The magnetic fields are in the (a) XY; (b) ZX; (c) ZY plane. Circles indicate the observed values. Solid lines are the calculated angular dependence for the sign combination of +200, -10 and 0 c. The dotted lines are for +200, +10 and 0 c.



Figure 4. Angular dependence of the hyperfine splittings in the field directions lying in the plane perpendicular to the direction of the maximum principal value. Circles indicate the observed values. Solid and dotted lines are the calculated angular dependence of the inner (d_{-}) and outer (d_{+}) doublets, respectively.

the smaller two principal values and their directions. The solid and dotted lines are the calculated inner and outer doublets, respectively, for these principal values. The transition probabilities of the outer doublet are calculated to be always less than 0.08 in agreement with observation.

In order to determine the relative sign of the principal value of 10 G, the measurements were also carried out in field directions lying in the plane including the principal values of 200 and 10 G. Figure 5 indicates the splittings of the outer



Figure 5. Angular dependence of the hyperfine splittings for the outer (d_+) and inner (d_-) doublets in the field directions lying in the plane including the largest and smallest principal values. Solid lines are the calculated angular dependence for the sign combination of +200 and -10 G. The dotted line is for +200 and +10 G.

and inner doublets observed in the small angular range from the radical plane. The solid curves represent the calculated angular dependence of the outer and inner doublets assuming the opposite sign for 200 and 10 G, and the dotted line indicates the calculated inner doublet assuming the same sign. The observed angular dependence completely agrees with that calculated for the opposite sign. Thus all the principal values and their directions were determined. The angular dependences in the XY, YZ and ZX planes calculated from these values are shown by the solid curves in figure 3. Good agreement with the observed splittings of the outer and inner doublets was obtained. The choice of the same sign for 200 and 10 G gave disagreement in the angular dependence of the inner doublet as shown by the dotted lines in figure 3. Finally a least squares fitting of all the data was made to determine the most probable principal values and their directions by using a computer programme written for a case in which both inner and outer doublets can be observed. The final results are in table 2.

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Principal values	Direction cosines with respect to XYZ axes [†]			
	l	m	n	
$A_1 = 200 \pm 1 \text{ g}$	0.688	± 0.201	0.698	
$A_2 - 1 \pm 1$ G	0.168	± 0.891	-0.422	
$A_3 - 10 \pm 1$ G	0.706	∓0.408	-0.579	
A ₀ 63		[
$g_1 2 \cdot 0029 \pm 0 \cdot 0002$	0.512	± 0.204	0.835	
$g_2 2 \cdot 0047 \pm 0 \cdot 0002$	0.307	± 0.864	-0.399	
$g_3 2 \cdot 0043 \pm 0 \cdot 0002$	0.803	± 0.460	-0.479	
$g_0 = 2 \cdot 0040$				

 \dagger Direction cosines are given for two of the four sites. For the other two sites the sign of l should be changed to minus.

Table 2. Principal values and the directions of the hyperfine and g tensors in $\dot{CF}(CONH_2)_2$.

3.3. g tensor

The g tensor was also determined from the angular dependences of the spectra. In the case of such a large hyperfine coupling, the second-order shift of the resonance position may not be ignored [12]. For the case of anisotropic hyperfine interaction, the theoretical treatment of the second-order shift has been carried out by Maruani *et al.* [12]. When g anisotropy is small, the centre of the hyperfine lines is given by:

where

$$H_{\rm c} = h\nu/g\beta - \delta^2/4H_{\rm e} \tag{10}$$

$$\delta^2 = (A_1^2 + A_2^2 + A_3^2 - \alpha^2), \tag{11}$$

$$H_{\rm e} = h\nu/g_0\beta, \tag{12}$$

 A_1 , A_2 and A_3 are the principal values of the hyperfine tensor, and α^2 is the same quantity as that given by equation (7). In these equations the nuclear Zeeman term was neglected. However, when only the second-order shift of the resonance position is to be considered, omission of this term gives rise to no serious error, since the shift is appreciable only for small value of α^2 and only the largest principal value, which is very much larger than w, contributes to the shift. Therefore, using equations (10)–(12), corrections for the second-order shift were made in determining the g values from the centre of the hyperfine splittings. The principal values and their directions obtained by a least squares fitting are in table 2.

3.4. Irradiation at 77°K

When the sample was irradiated at $77^{\circ}\kappa$, the spectra were entirely different from those described in the foregoing section. The spectra measured at the canonical directions show that the radical produced possesses two α -fluorine atoms and accordingly its probable structure is $\cdot CF_2CONH_2$ formed by breakage of the C-C bond rather than the C-F bond. In this case, there are two possibilities, for the breakage of one of the two C-C bonds doubles the number of sites, and the complicated spectra for directions, other than the canonical directions make it difficult to determine the hyperfine tensor. When the temperature was raised, the $\cdot CF_2CONH_2$ radical was unstable at room temperature and its spectrum disappeared, leaving the weak signal due to the $\cdot CF(CONH_2)_2$ radical.

4. DISCUSSION

4.1. Principal directions of the hyperfine and g tensors

Before discussing the deviation of the hyperfine tensor from axial symmetry, it is necessary to assign the principal directions to the radical geometry. Unfortunately, there is no information on the crystal structure of the mother molecule. Consequently the principal directions of the hyperfine tensor were compared with those of the g tensor. Both tensors have nearly the same principal coordinate system as shown in table 2. The minimum g value which is close to the free spin value should be along the axis of $C_{2p\pi}$. The fact that the direction of the maximum principal value of the hyperfine tensor corresponds to that of this g value means that the direction of 200 G is parallel to the $C_{2p\pi}$ orbital and that the main contribution to the hyperfine anisotropy arises from the spin density in $F_{2p\pi}$. This is the same situation as in \cdot CHFCONH₂ where the crystal structure of the mother molecule is available.

The maximum g value is expected to be parallel to the C-F bond, because the excitation of one of the fluorine 2p lone pair electrons to the half-filled orbital would raise the g value in this direction, due to the considerably larger spin-orbit coupling constant (270 cm⁻¹) for fluorine than for carbon (29 cm⁻¹). Since the direction of the intermediate principal value of -1 G is nearly the same as that of the maximum g value, it is attributed to the C-F bond. Consequently the direction of the minimum principal value -10 G is attributed to the direction perpendicular to the C-F bond in the radical plane. This assignment was confirmed by the discussion in the following section. Although in the \cdot CHFCONH₂ case the minimum principal value of the hyperfine tensor is along the C-F bond, the opposite situation occurs in our radical. This result suggests that the minimum direction of the hyperfine tensor of α fluorine may not always be along the C-F bond and the relation of the intermediate and minimum principal values may vary from radical to radical.

4.2. Breakdown of the hyperfine tensor

The deviation from axial symmetry of the hyperfine tensor in our radical resembles in its magnitude the CHFCONH₂ case where the deviation was attributed to polarization of the $2p\sigma$ electrons in the C-F bond. According to Cook *et al.* [2], the anisotropic component of the hyperfine tensor may be expressed by the following equation:

$$\mathbf{B}_{\mathbf{F}} = \mathbf{B}_{\mathbf{C}\pi}\rho_{\mathbf{C}\pi} + \mathbf{B}_{\mathbf{F}\pi}\rho_{\mathbf{F}\pi} + \mathbf{B}_{\mathbf{F}\sigma}\rho_{\mathbf{F}\sigma},\tag{13}$$

where $\mathbf{B}_{C\pi}$, $\mathbf{B}_{F\pi}$ and $\mathbf{B}_{F\sigma}$ are the anisotropic hyperfine tensors due to the interactions of a fluorine nucleus with carbon $2p\pi$ ($\rho_{C\pi}=1$), fluorine $2p\pi$ ($\rho_{F\pi}=1$), and fluorine $2p\sigma$ ($\rho_{F\sigma}=1$) electrons, respectively. In equation (13) the contributions from the carbon $2p\sigma$ and the overlap spin density are neglected. From the symmetry requirement, all the tensors have a common principal coordinate system and $\mathbf{B}_{F\pi}$ and $\mathbf{B}_{F\sigma}$ are axially symmetric although $\mathbf{B}_{C\pi}$ is not. The symmetry axis of $\mathbf{B}_{F\pi}$ is along the $F_{2p\pi}$ orbital while that of $\mathbf{B}_{F\sigma}$ is along the C-F bond; the principal values are evaluated to be (1084, -542, -542 G) from the value of $\langle r^{-3} \rangle_{av}$ for a selfconsistent field 2p atomic orbital for neutral fluorine [13]. $\mathbf{B}_{C\pi}$ was calcuated by Cook *et al.* [2] using the method of McConnell and Strathdee [14] with Slater orbitals and a C-F bond length of 1.40 Å. The principal values of $\mathbf{B}_{C\pi}$ are -3 G along the normal to the radical plane, +10 G parallel to the C-F bond, and -7 G perpendicular to the C-F bond in the radical plane.

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If one knew the major spin density in $C_{2p\pi}(\rho_{C\pi})$, one could estimate $\rho_{F\pi}$ and $\rho_{F\sigma}$ from equation (13)[†] using the observed anisotropy. In the ·CHFCONH₂ case, $\rho_{C_{\pi}}$ may be estimated from the hydrogen hyperfine coupling. Bolton [15] suggested that $|Q_{CH}^{H}| = 27$ G implies $\rho_{C\pi} = 0.837$. If one assumes this value of $\rho_{C_{\pi}}$, the observed anisotropy leads to $\rho_{F_{\pi}} = 0.117$ and $\rho_{F_{\pi}} = -0.017$. These estimates are not sensitive to the assumed value for $\rho_{C_{\pi}}$. If one assumes that $\rho_{F_{\pi}}$ is caused by spin delocalization due to the mixing of $F_{2p\pi}$ and the $C_{2p\pi}$ half-filled orbital, the rest of the spin density in the CONH₂ group may be 0.046. However, if $\rho_{C_{\pi}} = 0.8$, then $\rho_{F_{\pi}} = 0.119$, $\rho_{F_{\pi}} = -0.016$, and $\rho_{CONH_2} = 0.081$. Therefore, it may be safe to assume $\rho_{\text{CONH}_2} = 0.05$ to 0.1. Consequently, $\rho_{\text{C}\pi}$ in our radical may be 0.8 to 0.7. Equation (13) leads to $\rho_{F_{\pi}} = 0.127_5$ and $\rho_{F_{\sigma}} = -0.0028$ for $\rho_{C_{\pi}} = 0.8$, and $\rho_{\mathbf{F}_{\pi}} = 0.1277$ and $\rho_{\mathbf{F}_{\pi}} = -0.0018$ for $\rho_{\mathbf{C}_{\pi}} = 0.7$. The value of $\rho_{\mathbf{F}_{\pi}}$ in our radical is very close to that in \cdot CHFCONH₂, but $|\rho_{F\sigma}|$ is very much smaller in our case. However, it should be remembered that we have assigned the intermediate principal value rather than the smallest one to be parallel to the C-F bond. If the same assignment as in \cdot CHFCONH₂ were employed, then $\rho_{F\pi} = 0.122_0(0.122_2)$ and $\rho_{F\sigma} = -0.0139(-0.0129)$ for $\rho_{C\pi} = 0.8(0.7)$ which are very similar to those in Therefore some doubt may exist in the assignment given by \cdot CHFCONH₂. consideration of the g anisotropy. In order to decide this question, first $\rho_{F\pi}$ and $\rho_{F\sigma}$ were estimated similarly for other radicals, assuming the value of $\rho_{C\pi}$ for each to be 0.7 or 0.8. The results are in table 3. The values for $\rho_{F\pi}$ do not vary very much, except in $-OOCCF_2CFCOO^-$, but those for $\rho_{F\sigma}$ vary from -0.002 to -0.4reflecting changes in the deviation from axial symmetry. We now consider the reason for the large variation in $\rho_{F\sigma}$, despite the small variation in $\rho_{C\pi}$ and $\rho_{F\pi}$, which causes the spin density in $F_{2p\sigma}$.

4.3. Q factors in polarization of $F_{2p\sigma}$ electrons

The spin density in $F_{2p\sigma}$ may be considered as the sum of two contributions from polarizations due to $\rho_{C\pi}$ and $\rho_{F\pi}$. Therefore, the anisotropic contribution

				1
Radicals	Assumed	Experimental		Calculated
	ρcπ	<i>ρ</i> F π	ρϝσ	<i>ρ</i> F σ
·CF(CONH ₂) ₂	0.70	+0.128	-0.002	-0.003
·CHFCONH ₂	0.80	+0.119	-0.016	-0.015
$\cdot CF_2CONH_2^{\dagger}$	0.70	+0.094	-0.007	-0.018
$\cdot CF_2CONH_2$	0.70	+0.094	-0.015	−0·018
·CF ₂ CONH ₂ §	0.70	+0.113	-0.010	-0.010
·CF ₂ COONH ₄	0.70	+0.106	0.009	-0.013
CF3CFCONH2	0.70	+0.114	-0.010	-0.009
-OOCCFCF2COO-	0.80	+0.054	-0.043	-0.043
·CF ₃	0.70	+0.097	-0.010	-0.016
		l		

† Lontz and Gordy (r.t.) [1].

‡ Rogers and Kispert (r.t.) [3].

§ Rogers and Kispert $(77^{\circ}\kappa)$ [3].

Table 3. Spin densities on $F_{2p\pi}$ and $F_{2p\sigma}$ obtained from a breakdown of the hyperfine tensor, and spin densities on $F_{2p\sigma}$ calculated from the estimated Q factors.

[†] Since the tensors in equation (13) are traceless, one can determine only two unknown parameters among $\rho_{C\pi}$, $\rho_{F\pi}$ and $\rho_{F\sigma}$.

from $\rho_{\mathbf{F}\sigma}$ may be written in the form:

$$\mathbf{B}_{\mathbf{F}\sigma}\rho_{\mathbf{F}\sigma} = \mathbf{Q}_{\mathbf{C}\mathbf{F}}^{\mathbf{F}}\rho_{\mathbf{C}\pi} + \mathbf{Q}_{\mathbf{F}\mathbf{C}}^{\mathbf{F}}\rho_{\mathbf{F}\pi}, \tag{14}$$

where $\mathbf{Q}_{CF}^{\mathbf{F}}$ and $\mathbf{Q}_{FC}^{\mathbf{F}}$ are tensor polarization factors of $F_{2p\sigma}$ electrons due to unit spin density in $C_{2p\pi}$ and $F_{2p\pi}$, respectively. Since $\mathbf{B}_{F\sigma}$ is axially symmetric, the \mathbf{Q} -factor tensors should have principal values of the form (-Q, +2Q, -Q). From the mechanism of the spin polarization, $Q_{CF}^{\mathbf{F}}$ is expected to be negative and $Q_{FC}^{\mathbf{F}}$ positive. Therefore, $\rho_{F\sigma}$ is the difference of two large quantities so that it should be sensitive to small variations in $\rho_{C\pi}$ and $\rho_{F\pi}$. This is the reason for the situation mentioned before.

Now, if two sets of data on $\rho_{F\sigma}$, $\rho_{C\pi}$ and $\rho_{F\pi}$ are used, one can determine the values of Q_{CF}^{F} and Q_{FC}^{F} . In this case, however, it is to be noted that two sets having largely different $\rho_{F\sigma}$ values should be chosen for obtaining reliable estimates. the values obtained \cdot CHFCONH₂ with Combining for those of $-OOCCFCF_2COO^-$, Q factors were found to be -44 G for Q_{CF}^{F} and 225 G for Q_{FC}^{F} . As expected, Q_{CF}^{F} is negative and Q_{FC}^{F} positive. In order to test the applicability of these values, $\rho_{F\sigma}$ for $\cdot CF(CONH_2)_2$ was calculated by equation (14) using these Q factors together with the values assumed for $\rho_{C\pi}$ and estimated for $\rho_{F_{\pi}}$ from experiment. As previously described, $\rho_{F_{\sigma}}$ in our radical is -0.002 if one assumes that the intermediate principal value is directed along the C-F bond, while it is -0.013 if one assumes that the minimum principal value is along the C-F The calculated $\rho_{F\sigma}$ from the Q factors is -0.004 and is in very good bond. agreement with the value derived from the former assumption. In other words, the values of $\rho_{F\sigma}$ for three different radicals can be interpreted by common Q factors, even though there are fairly large variations in the magnitude of $\rho_{F_{\sigma}}$. This result strongly supports our assignment of the principal directions of the hyperfine tensor.

Finally, using the three sets of data for $CF(CONH_2)_2$, $CHFCONH_2$, and $-OOCCFCF_2COO^-$, the probable values for the Q factors were estimated to be:

$$Q_{\rm CF}^{\rm F} = -45 \pm 5 \,{\rm G}, \quad Q_{\rm FC}^{\rm F} = 233 \pm 30 \,{\rm G}.$$

The uncertainties in these values are due to those in the assumed values for $\rho_{C\pi}$. The values of $\rho_{F\sigma}$ calculated from the above Q factors are listed in the last column of table 3 for a series of radicals. Agreement with the values derived from experiment is fairly good for all the radicals, indicating the validity of equation (14) for a series of compounds.

Thus, the variation in the deviation from axial symmetry of the hyperfine tensor of the α -fluorine couplings, especially in $-OOCCF_2CFCOO^-$, is not surprising and all the data are interpreted by common Q factors for spin polarization of the $2p\sigma$ electrons in the C-F bond. However, the cause of the exceptionally small $\rho_{F\pi}$ in $-OOCCF_2CFCOO^-$ is not clear.

4.4. Isotropic component of the α -F splitting

There have been a number of papers, mainly on solution E.S.R. spectroscopy [8, 16–22], on the isotropic coupling of α -F and spin polarization factors for 2s electrons. Despite many efforts, it is not yet possible to give a satisfactory account of the isotropic splittings of α -F in terms of spin polarization factors. In a series of compounds which have been investigated using single crystals, most of the radicals except \cdot CF₃ give values of Q_{eff} ^F ranging from 70 to 110 G in the expression:

$$a_{\rm F} = Q_{\rm eff} {}^{\rm F} \rho_{\rm C\pi}. \tag{15}$$

This is due to fairly small variations in $K (= \rho_{\mathbf{F}\pi} / \rho_{\mathbf{C}\pi})$ in the more precise expression given by Kaplan *et al.* [8]:

$$a_{\mathbf{F}} = Q_{\mathbf{C}\mathbf{F}'}{}^{\mathbf{F}}\rho_{\mathbf{C}\pi} + (S^{\mathbf{F}} + Q_{\mathbf{F}\mathbf{C}'}{}^{\mathbf{F}})\rho_{\mathbf{F}\pi}$$
(16)

$$= [Q_{CF}'^{F} + K(S^{F} + Q_{FC}'^{F})]\rho_{C\pi}.$$
(17)

In these equations the Q factors of 2s bonding electrons are distinguished by primes from those of $2p\sigma$ electrons. In $-OOCCF_2CFCOO^-$ the K value is half that of other radicals although it gives a similar $Q_{eff}F$. Consequently the difficulty arises in this series of compounds as in the aromatic fluorine-containing radicals. The nature of the isotropic splitting of α -F is still open to question. As for the large deviation of the $Q_{eff}F$ value of $\cdot CF_3$, it may be due to the non-planarity of this radical, as suggested by Fessenden and Schular [23].

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