Electron Spin Resonance and Molecular Orbital Study of Radicals in Irradiated Fluoro-derivatives

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The low temperature matrix isolation technique coupled with e.s.r. spectrometry was employed to study the radicals produced by low temperature irradiation by a ^{60}Co source of a number of fluoro and fluoro-chloro derivatives including chloroformyl- and fluoroformyl-perfluoropolyethers, trichlorofluoromethane, 1,1,2-trichloro-1,2,2-trifluoroethane, and perfluoro-1-methyldecalin (PFMD). The major radiolysis process in the acyl chloride is thought to be dissociative electron capture with formation of acyl radicals; the splitting of the C–O bonds in the chains is also inferred from the identification of RR'CF· and RCF_2· species. In the acyl fluoride direct splitting of the COF group is also assumed to take place in order to explain the higher relative yield (with respect to the acyl chloride) of RCF_2·. The irradiation of PFMD yields RR'CF· and RCF_2· at low temperature and the 1-perfluoro-1-methyldecalin-8a-yl radical after warming above 160—180 K. This radical has a spectrum which is consistent with an average planar configuration at C-8a. By irradiation of $CFCl_3$ and $CF_2ClCFCl_2$ (thiourea clathrate) ·$CFCl_2$ and $CF_2Cl\dot{C}FCl$ were obtained; the structure and conformation of these radicals have been investigated by the CNDO/2 MO method.

FLUORINE-CONTAINING radicals have been subject to an increasing number of studies in recent years because of their importance as reactive intermediates in synthetic chemistry and also because of the theoretical interest of their e.s.r. and structural properties.[1] For e.s.r. investigations, the radicals are most often produced in fluid media by u.v. photolysis of reaction mixtures, or in solid polycrystalline matrices by γ-irradiation.[1c] The latter technique leads to spectra of greater complexity but has the advantage of allowing the determination of the anisotropies of α- and β-fluorine hyperfine couplings; furthermore the possibility of trapping unstable paramagnetic intermediates is enhanced. We have applied the low temperature matrix isolation technique to the e.s.r. study of radical intermediates from the radiolysis at 77 K of a number of fluoro- and chloro-fluoro-derivatives containing functional groups which are of interest both from the radiation chemistry and e.s.r. standpoints. These comprise the formylpolyethers AF and AC, perfluoro-1-methyldecalin (mixture of isomers) (PFMD), trichlorofluoromethane, and 1,1,2-trichloro-1,2,2-trifluoroethane. AF and AC belong to a class of compounds which has not yet been investigated with respect to their radiolytic behaviour; furthermore they are considered to be potential sources of fluoroacyls, a class of radicals of which only two examples have been reported in the literature.[2]

$CF_3O[CF_2CF(CF_3)O]_{2.5}CF_2CFO$
AF

$CF_3O[CF_2CF(CF_3)O]_{2.5}CF_2CClO$
AC

The radiolysis of PFMD was the subject of an early investigation by McKenzie[3] which was primarily concerned with the analysis of the stable radiolysis end-products; nothing is known about the nature of free radical intermediates. An important point regarding this compound is the formation of free radicals at the bridgehead sites C-4a and -8a, which poses interesting problems relating to the competition between electronic and strain factors in determining the geometry of the free valence centres. The chloro-fluoro-derivatives were thought to be of interest because of the possibility of studying the effect of α- and β-chlorine substitution on the structure and conformation of radicals with one and two α-fluorine atoms. This part of the investigation was carried out with the help of MO calculations to the CNDO/2 level of approximation;[4] furthermore, the advantage was taken, from the solid state technique, to determine α-fluorine and α-chlorine hyperfine anisotropies in one of the species identified.

EXPERIMENTAL

The fluoro-chloro-derivatives and perfluoro-1-methyldecalin were commercially available products. The acyl chloride AC was prepared by chlorination with $SOCl_2$ of a particular fraction of the photo-oxidation of perfluoropropene.[5] The acyl fluoride AF was obtained from the acyl chloride by fluorination with potassium fluoride. These compounds are oligomers of variable chain length with an average number of $[CF_2CF(CF_3)O]$ units equal to 2.5. γ-Irradiation, sample preparation, and e.s.r. measurements have been described elsewhere.[6] Computer programs from QCPE and standard bond angles and distances were employed for the CNDO/2 calculations.

RESULTS

The e.s.r. spectra of immobilized, randomly oriented fluoroalkyls with two α-fluorine nuclei result from the superimposition of triplets of various splittings depending on the orientation of the radicals respect to the magnetic field direction. Strong features are expected to appear resulting from the principal values of the hyperfine tensors $A_{max.}^{F\alpha}$, $A_2^{F\alpha}$, and $A_3^{F\alpha}$; as $A_{max.}^{F\alpha}$ is usually in the range 150—250 G, a distinctive feature of the spectrum is the presence of two wing peaks with an overall splitting of 2 $A_{max.}^{F\alpha}$, *ca.* 400 G, symmetrically disposed about the central line which is about ten times more intense.[7,8] When only one α-F is present, the main features of the spectrum result from the superimposition of doublets with splittings again corresponding to the three principal $A^{F\alpha}$ values. If $A_2^{F\alpha} = A_3^{F\alpha}$ (axial symmetry), the spectrum may appear as a triplet with an overall splitting of roughly the magnitude of $A_{max.}^{F\alpha}$. β-Fluorine atoms, when present, are expected to show up as fine structure in the main features. The low temperature (*ca.* 85 K) spectrum of the acyl fluoride (Figure 1A) shows parallel features for both $RCF_2\cdot$ ($A_{max.}^{F\alpha}$ *ca.* 23 G) and $RR'CF\cdot$ ($A_{max.}^{F\alpha}$ *ca.* 200 G) radicals. Fine structure, thought to be a triplet of *ca.* 50 G, is distinguishable in the parallel features of $RR'CF\cdot$; this structure is probably generated by α-CF_2 or α-CF_3 groups, the latter being locked in an orientation where only one of the C–F bond lies close to the nodal plane [radicals of type $R(CF_3)CF\cdot$, $RCF_2(R')CF\cdot$]. On warming at 150 K the $M_{I\pm1}$ peaks also show a doublet splitting of *ca.* 35 G which suggests that part of these radicals might have the formula $RR'CFCF_2\cdot$. At 150 K the magnitude of $A_{max.}^{F}$ for $RCF_2\cdot$ is *ca.* 37 G smaller than at 85 K; this reversible change can be related to a decrease of the degree of deviation from planarity of the radical centre caused by the increase of the temperature. The e.s.r. spectrum of the acyl chloride (Figure 1B) closely resembles that of the acyl fluoride except in two important respects: (a) the wing peaks at ±230 G are considerably less intense, thus indicating a smaller relative abundance of the $RCF_2\cdot$ species and (b) the central peak can only to a minor extent be accounted for in terms of A_2 and A_3 contributions and is therefore considered diagnostic of the presence of another species. The asymmetry of this part of the spectrum is suggestive of an anisotropic *g* factor; furthermore the barely resolved structure reveals the presence of weakly interacting β-F atoms. This may be due to acyl-type radicals which in AC are expected to be formed through the dissociative electron capture reaction $RCF_2COCl + e^- \longrightarrow RCF_2\dot{C}O + Cl^-$.

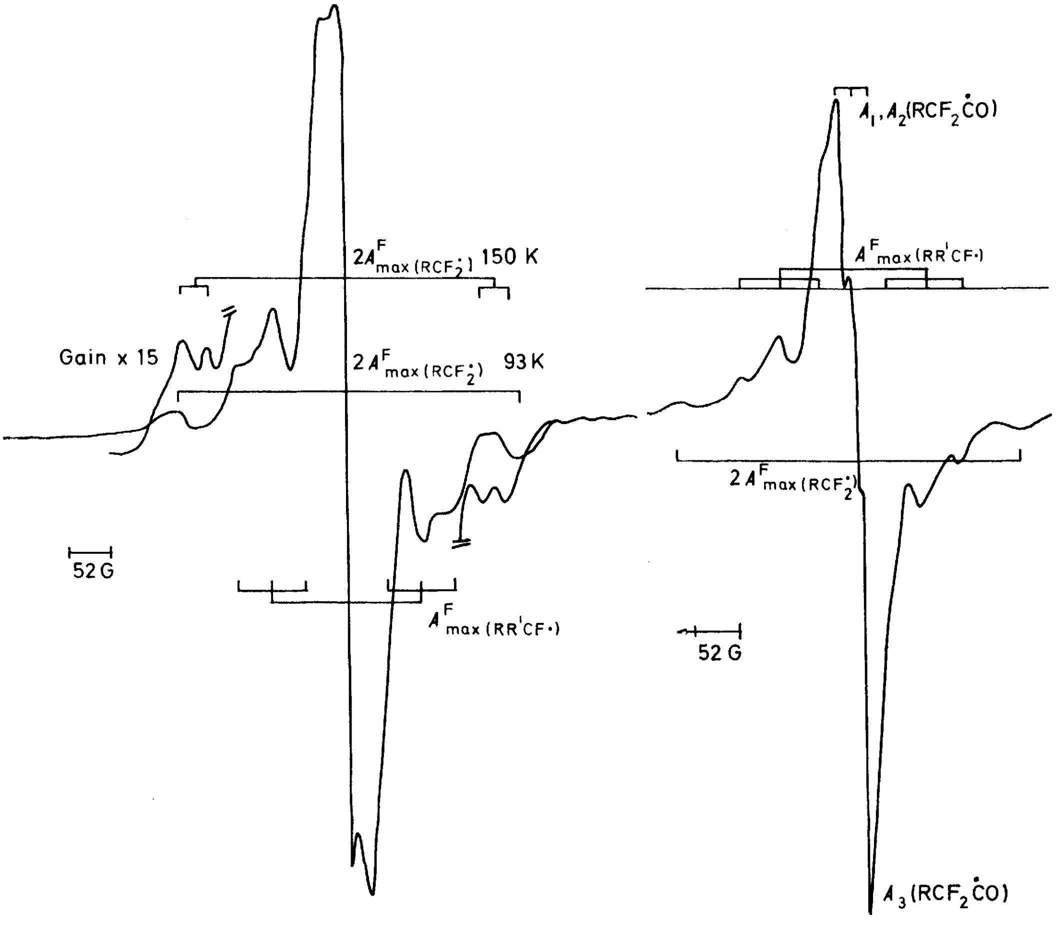
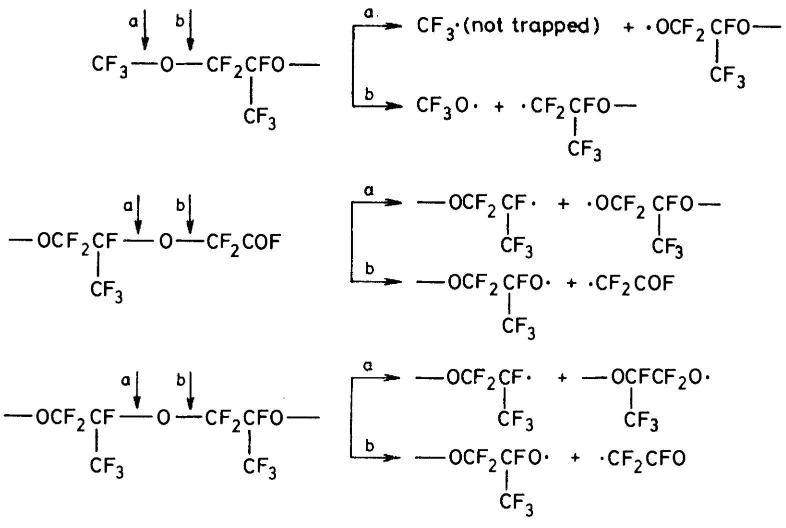


FIGURE 1 E.s.r. spectra of the fluoroformyl perfluoropolyether (A) and the corresponding chloroformyl compound AC (B) recorded at 85 K after γ-irradiation at 77 K. The parallel features of $RCF_2\cdot$ radicals in spectrum A showing the doublet splitting of *ca.* 36 G were recorded at 153 K

This tentative interpretation (Figure 1B) is based on two triplets of 18 and 14 G centred at *g* 2.000 and 2.005, respectively. The magnitude of the β-F couplings and the average *g* value are consistent with the observations made by Kochi and Krusic on the perfluoroacetyl radical in solution.[2]

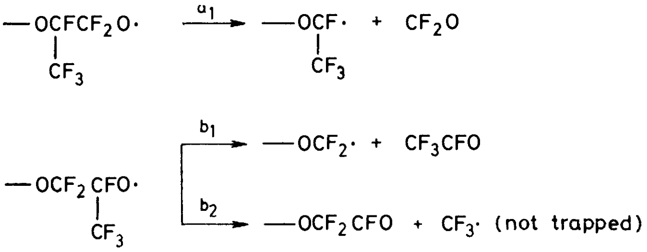
On warming at 150 K, the overall spectrum disappears in a few minutes without showing the changes expected from the decarbonylation reaction $RCF_2\dot{C}O \longrightarrow RCF_2\cdot + CO$. This implies that the $RCF_2\dot{C}O$ radicals are stable at this temperature or decompose slowly compared with radical decay by coupling. This is consistent with the observation that perfluoropropionyl and perfluoroacetyl radical decompose at a significant rate only above 170 and 190 K, respectively.[2] Dissociative electron capture by the acyl fluoride, $RCF_2COF + e^- \longrightarrow RCF_2\dot{C}O + F^-$, is probably less favoured because of the greater strength of the C–F relative to the C–Cl bond. In this compound, the direct loss of the COF group (a well known photolytic process [9]) may become predominant thus leading to a greater relative abundance of $RCF_2\cdot$ species. $RCF_2\cdot$ and $RR'CF\cdot$ species can also arise from C–C, C–F, or C–O bond scission in the main chains. However the absence of tertiary radicals $RR'R''C\cdot$, whose formation is energetically favoured, suggests that C–F bond scission may be of minor importance. On the other hand inspection of AF and AC shows that $RR'CFCF_2\cdot$ radicals cannot be formed by C–C but rather by C–O bond rupture. Therefore we have based the tentative Scheme 1 on this mechanism which is consistent with the e.s.r. results.



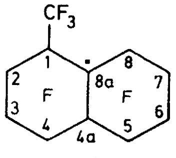
SCHEME 1

Fluoroalkoxyl radicals are expected to undergo fast β-scission during irradiation at 77 K according to routes a_1, b_1, and b_2 in Scheme 2. According to Scheme 2, the greater relative abundance of $RR'CF\cdot$ relative to $RCF_2\cdot$ species in the irradiated acyl chloride is explained by a predominance of type a and/or b_1 scissions relative to the others.

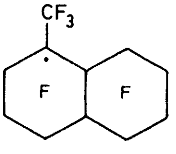
Perfluoro-1-*methyldecalin* (PFMD).—The e.s.r. spectrum of PFMD irradiated at 77 K shows clearly the parallel features of $RR'CF\cdot$ and $RCF_2\cdot$ radicals with $A_{\text{max.}}^{F}$ *ca.* 170 and 220 G, respectively (Figure 2A). On warming above 160 K, these features disappear irreversibly, ultimately leaving a new signal which persists for days in the liquid state at room temperature (Figure 2B). This change takes place in a temperature range (170—180 K) where diffusional motion of radicals is important and is accompanied by a drastic decrease of the overall radical population. The presence of $RR'CF\cdot$ and $RCF_2\cdot$ species strongly suggests that C–C bond scission with ring opening is of major importance in the radiolysis mechanism. This conclusion is consistent with the observation by McKenzie [3] of a large radiolytic yield for a polymeric material in the liquid state radiolysis of perfluorodecalin (PFD) (G_{polymers} 1.4, G_{PFD} 1.7); in fact ring opening followed by biradical coupling is a reasonable mechanism for ' polymer ' formation in this saturated compound. The major component in the spectrum in Figure 2B, which consists of three doublets of 63.1, 46.9, 29.2 G (Figure 2C), is considered diagnostic of the presence of the perfluoro-1-methyldecalin-8a-yl radical (I).



SCHEME 2



(I)



(II)

According to this interpretation, the largest splitting is assigned to the F atom at C-4a, since it is nearly eclipsed with respect to the axis of the unpaired electron orbital; the other doublets arise from two of the three F atoms at C-1 and -8, one of which must be close to the nodal plane so that it only contributes to the experimental linewidth. A second minor component in the spectrum of Figure 2A is revealed at first glance by the two shoulders, whose relative intensity changes somewhat with the experimental conditions; according to the computer simulations (Figures

2E and F), this component might be generated by the perfluoro-1-methyldecalin-1-yl radical (II) with $a_{8a}{}^{F}$ 61.2, $a_2{}^{F}$ 38.7, $a_2{}^{F}$ 21.2, and $a_{CF_3}{}^{F}$ 16.9 G.

The relative abundance of this radical is estimated to be *ca.* 30%. The origin of radical (I) [and (II)] is not clear. Because of the poor resolution of the initial spectrum, it is not possible to ascertain whether it is formed during irradiation at 77 K or by post-irradiation fluorine atom abstractions by RR′CF· and RCF_2· radicals. It seems evident anyway that its greater yield, as inferred from the final spectrum, is due to its exceptional inertness toward the decay by coupling rather than to its relative tendency to formation by radiolysis. The inertness toward coupling is likely to arise from steric hindrance and therefore it is expected to be strongly influenced by the number and type of substituents around the free valence centre; on this basis the lack of observation of the perfluoro-1-methyldecalin-4a-yl radical, which is expected to have the same tendency to formation as (I), would be explained in terms of a lower stability toward coupling. The magnitude of the β-fluorine splittings in radical (I) is suggestive of an average planar configuration at C-8a; this is inferred from the fact that the $a_{8a}{}^{F}$ coupling, for which a dihedral angle of *ca.* 0° can safely be assumed, is satisfactorily reproduced ($a_{exp.}{}^{F}$ 63.1, $a_{calc.}{}^{F}$ 59 G) by equation (1) which is based on the

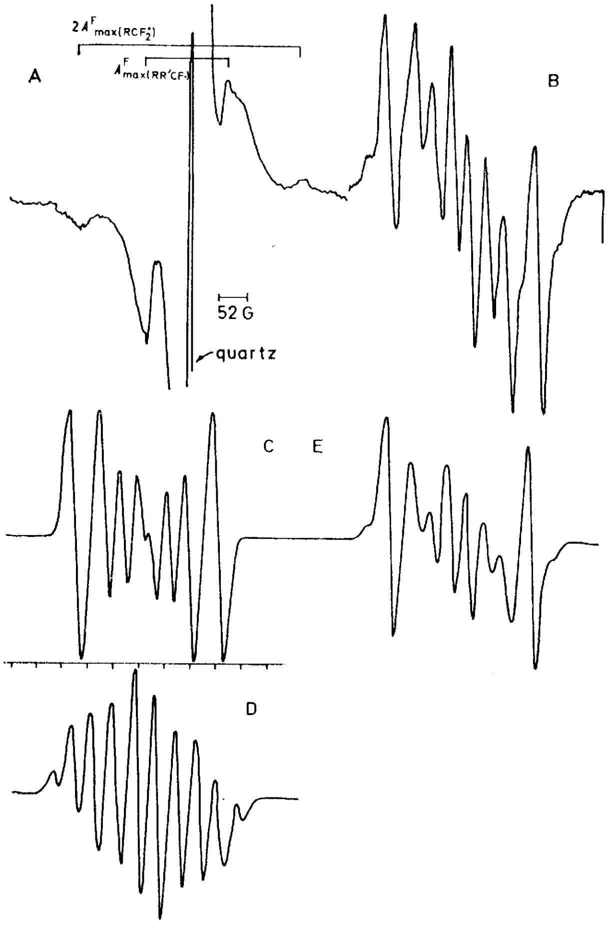


FIGURE 2 E.s.r. spectra of perfluoro-1-methyldecalin recorded at 143 (A) and 298 K (B) after γ-irradiation at 77 K. The computer simulation E was obtained by summation of two patterns C and D for radicals (I) and (II), respectively (see text). Pattern C (70%): *a* (1 F) 63.1, *a* (1 F) 46.9, *a* (1 F) 29.2, L.W. 15 G (Gaussian); pattern D (30%) : *a* (1 F) 61.2, *a* (1 F) 42.1, *a* (1 F) 21.6, *a* (3 F) 16.9 G.

$$a_{\beta}{}^{F} = |-23 + 82\cos^2\theta| \qquad (1)$$

experimental results obtained from approximately planar fluorine-containing radicals.[10] Were the radical (I) strongly pyramidal at C-8a, the $a_{8a}{}^{F}$ coupling would probably not exceed 35—40 G; this is inferred from the decrease of a_F couplings for freely rotating CF_3 groups on going from the near planar $\cdot C(CF_3)_3$ ($a_{CF_3}{}^{F}$ 18.69 G [9]) to the strongly pyramidal $CF_3CF_2\cdot$ ($a_{CF_3}{}^{F}$ 11.35 G [9]).

The application of equation (1) to the other two couplings of 46.9 and 29.2 G in radical (I), yields dihedral angles θ_1 22.6 and θ_2 37°, respectively; these values suggest that the non-interacting fluorine atom may be at C-1. Radical (I), with its planar average configuration, compares interestingly with the decalin-8a-yl radical which also is thought to be planar at C-8a on the basis of its stereochemical behaviour.[11]

The admission of oxygen or of chlorinated hydrocarbons into the liquid sample causes the disappearance of spectrum in Figure 2B. This observation is explained by reactions of types (2) and (3). The reaction with O_2 is slow and no peroxyl radical signal is detected during the decay.

$$CF_3C_{10}F_{15}\cdot + RCl \longrightarrow CF_3C_{10}F_{15}Cl + R\cdot \qquad (2)$$

$$CF_3C_{10}F_{15}\cdot + O_2 \longrightarrow CF_3C_{10}F_{15}O\cdot \qquad (3)$$

Fluoro-chloro-derivatives.—The irradiation of fluoro-chloro-derivatives in the crystalline state leads to formation of radicals by loss of chlorine atoms presumably *via* dissociative electron capture processes, the preferred sites for

$$CF_2ClCFCl_2 \xrightarrow{e^-} CF_2Cl\dot{C}FCl + Cl^- \qquad (4)$$

$$CFCl_3 \xrightarrow{e^-} \dot{C}FCl_2 + Cl^- \qquad (5)$$

C–Cl bond scission being those where the greatest number of chlorine atoms is available [reactions (4) and (5)]. The room temperature e.s.r. spectrum of 1,1,2-trichloro-1,2,2-trifluoroethane as an adduct with thiourea consists of two 1 : 1 : 1 : 1 quartets of 4 and 8 G and two doublets of 65 and 24 G. This hyperfine structure has been attributed to the radical $CF_2Cl\dot{C}FCl$ with a conformation where one of the β-

TABLE 1

Prediction of fluorine and chlorine hyperfine splitting by CNDO/2 MO method. Comparison with experimental results

	a^{F}/G		a^{Cl}/G	
Radical	Calculated	Experimental	Calculated	Experimental
$\cdot CH_2F$	70.2	64.3 [a]		
$(CF_3)_2CF\cdot$	65.3	67.4 [b]		
$\cdot CHF_2$	8.31	84.2 [a]		
$CF_3CF_2\cdot$	84.9	87.26 [b]		
$CF_3\cdot$	140.5	142.4 [a]		
$\cdot CF_2Cl$	92.7	109.8 [c]	16.6	16.1
$\cdot CFCl_2$	84.7	84.5 [c]	9.4	10.6
$\cdot CFClCONH_2$	57.3	50.1 [d]	3.2	3.0
$\cdot CCl_3$			6.8	6.7—7.1 [e]

[a] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1965, **43**, 2704. [b] Ref. 4. [c] Ref. 13. [d] L. D. Kispert and F. Myers, *J. Chem. Phys.*, 1972, **56**, 2623. [e] C. Hesse, N. Leroy, and J. Roncin, *Mol. Phys.*, 1971, **22**, 137.

fluorine atoms lies close to the nodal plane of the half-filled orbital (Figure 3). This interpretation has been checked by CNDO/2 calculations. As the CNDO/2 method neglects electron exchange integrals, spin polarization contributions must be introduced through parametric equations of the Karplus–Fraenkel type.[12] By fitting calculated u.s.d.s to the observed fluorine and chlorine splittings for a variety of radicals, equations (6) and (7) have been derived (Table 1) where *n* is the number of chlorine atoms and the ρ terms are CNDO/2 calculated u.s.d.s in the *s* and *p* valence orbitals. In the equation (7), $a_{\text{iso.}}{}^{\text{Cl}}$, the contribution of the u.s.d.s in the chlorine 3*s* and carbon *s* and *p* orbitals which are smaller than the remaining term, have been neglected. The CNDO/2 method, in connection with the above parametric equations, leads to satisfactory agreement between calculated and experimental α-fluorine and -chlorine couplings when it is assumed that the radical centre is pyramidal with a degree of deviation from planarity of *ca.* 5° (Table 2).

$$a_{\text{iso.}}{}^{\text{F}} = (1 + 0.2\text{n})[3 \times 10^4\rho_{2s}{}^{\text{F}} + 765(\rho_{2p_x}{}^{\text{F}} + \rho_{2p_y}{}^{\text{F}} + \rho_{2p_z}{}^{\text{F}}) - 10\rho^{\text{C}}] \quad (6)$$

$$a_{\text{iso.}}{}^{\text{Cl}} = 66(\rho_{3p_x}{}^{\text{Cl}} + \rho_{3p_y}{}^{\text{Cl}} + \rho_{3p_z}{}^{\text{Cl}}) \quad (7)$$

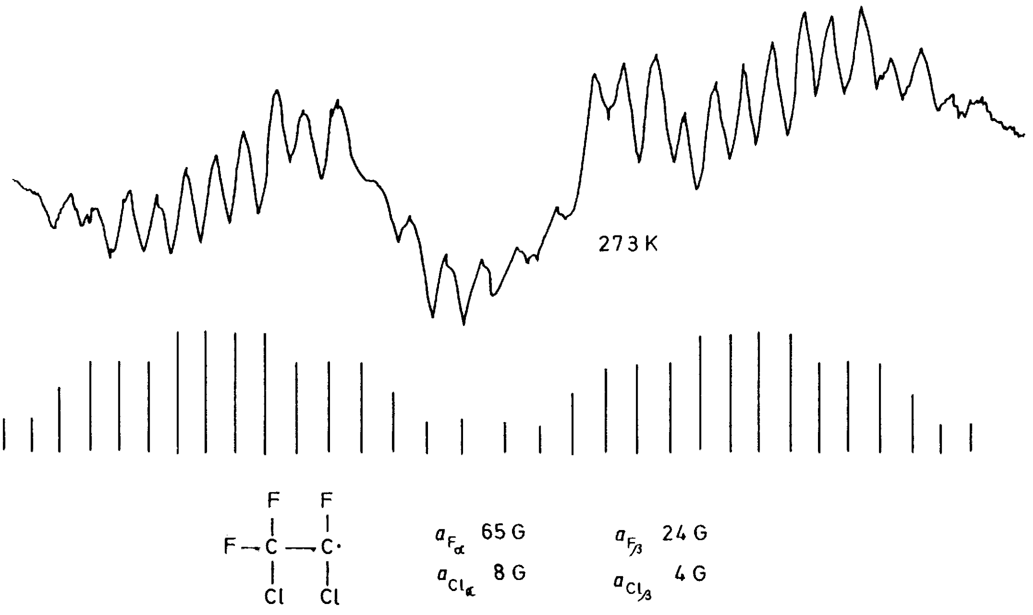
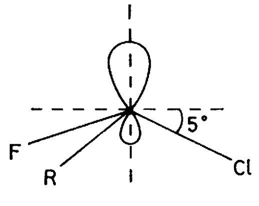


FIGURE 3 E.s.r. spectrum of the thiourea adduct of 1,1,2-trichloro-1,2,2-trifluoroethane recorded at 273 K following γ-irradiation at 77 K

TABLE 2

CNDO/2 Calculations of u.s.d. and fluorine and chlorine couplings (G) for the $CF_2Cl\dot{C}FCl$ radical. The radical centre is assumed to be pyramidal with θ 5°



R = $-CF_2Cl$

U.s.d. (ρ)						$a_{\text{iso.}}{}^{\text{F}\alpha}$		$a_{\text{iso.}}{}^{\text{Cl}\alpha}$	
F		C		Cl		Calc.	Exp.	Calc.	Exp.
$2s$	0.0001	$2s$	0.0793	$3s$	−0.0010	70.1	65	9.5	8
$2p_x$	0.0042	$2p_x$	0.0591	$3p_x$	−0.0111				
$2p_y$	−0.0014	$2p_y$	−0.0108	$3p_y$	0.0121				
$2p_z$	0.00779	$2p_z$	0.5025	$3p_z$	0.1427				
				$3d_{z^2}$	0.0155				
				$3d_{xz}$	−0.0002				
				$3d_{yz}$	0.0091				
				$3d_{x^2-y^2}$	−0.0002				
				$3d_{xy}$	0.0105				

The energy curve for this configuration, calculated as a function of the orientation of the CF_2Cl group, shows the existence of a minimum when the dihedral angle between the β-C–Cl bond and the axis of the half-filled orbital is *ca.* 210° (Figure 4). This conformation is consistent with the experimental results since it is expected to be characterized

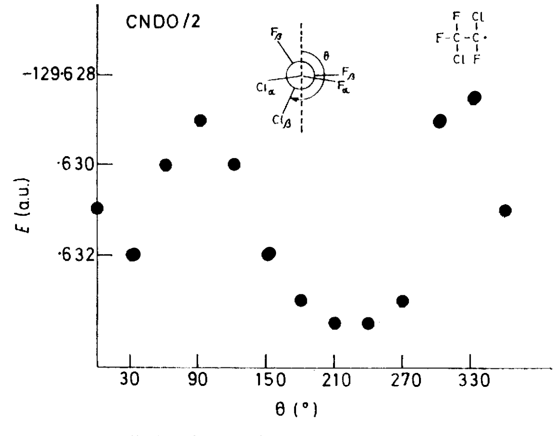


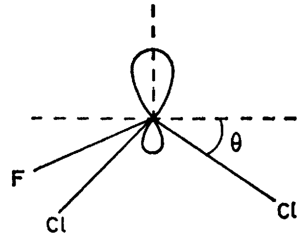
FIGURE 4 CNDO/2MO Calculations on the $\cdot CFClCF_2Cl$ radical as function of the orientation of the CF_2Cl group

by relatively strong magnetic interactions of one chlorine and one fluorine, whilst the remaining fluorine atom should only contribute to the experimental linewidth.

The radical ·$CFCl_2$ has been previously observed by Hudson [13] in the liquid state and the isotropic hyperfine couplings $a_{iso.}^{F}$ 84.5 and $2a_{iso.}^{Cl}$ 10.6 G have been reported.

TABLE 3

The ·$CFCl_2$ radical. CNDO/2 MO Calculations of u.s.d. and of fluorine and chlorine isotropic couplings (G) as a function of the degree of non-planarity θ



θ(°)	U.s.d. C		U.s.d. F		U.s.d. Cl	
15	2s	0.095	2s	0.0003	3s	−0.001
	$2p_x$	−0.011	$2p_x$	0.00	$3p_x$	0.0142
	$2p_y$	−0.030	$2p_y$	−0.002	$3p_y$	0.0189
	$2p_z$	0.53	$2p_z$	0.0779	$3p_z$	0.110

θ(°)	$a_{iso.}^{F}$	$a_{iso.}^{Cl}$	Energy (a.u.)
0	70.0	3.4	−66.935
5	74.4	4.9	−66.937
10	83.3	7.3	−66.940
15	84.6	9.4	−66.942
19.5	81.6	10.9	−66.941
Experimental [13]	84.6	10.5	

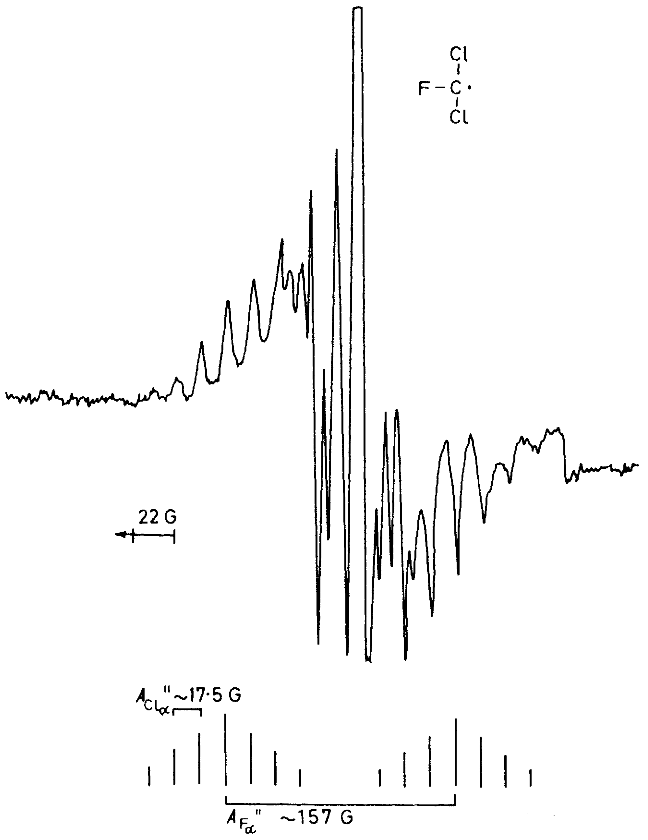


FIGURE 5 E.s.r. spectrum of polycrystalline $CFCl_3$ recorded at 158 K following γ-irradiation at 77 K

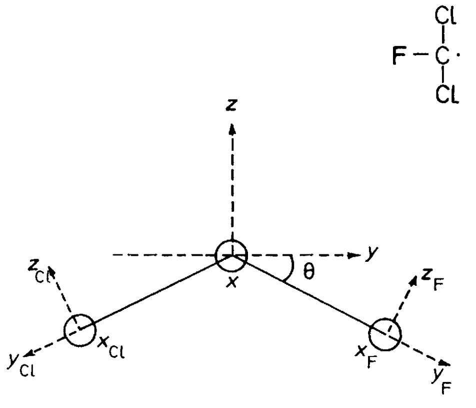


FIGURE 6 Molecular reference axis system for the F and Cl hyperfine tensors in the ·$CFCl_2$ radical

The spectrum obtained by us in the crystalline state is interpreted in terms of hyperfine tensor anisotropy by assuming a fluorine coupling of 157 G and two equivalent chlorine couplings of 17.5 G (Figure 5). For radicals in which the hyperfine coupling tensors do not have the same principal axes, there is not, in general, any orientation of the field for which the hyperfine splittings are stationary and the polycrystalline spectra will not show strong features. When, however, the tensors have nearly parallel axes some stationary behaviour may occur and the corresponding features will be observed. To a first approximation, this seems to be the case of ·$CFCl_2$ radical. The following arguments are based on a molecular reference axis system where the *z* direction corresponds to the axis of the half-filled orbital (Figure 6); furthermore it is assumed that the carbon–halogen bonds make the same angle with the *xy* plane with a definite degree of non-planarity, θ 15°; this configuration was found by the CNDO/2 method to be at the minimum of the energy curve. According to the CNDO/2 method, a major contribution to the anisotropic part of the hyperfine tensors arises from u.s.d. in the p_z orbitals of chlorine and fluorine atoms (Table 3); as a consequence, it is expected that one of the principal values be directed along these orbitals, making an angle of *ca.* 15° with the *z* molecular axis. The second axis should be along the C–halogen bonds and the third perpendicular to these bonds. In this situation, the z reference axis defines a nearly canonical direction for the hyperfine splitting. All the radicals with their z axis oriented along the magnetic field direction will afford fluorine and chlorine couplings close, though not equal, to the principal parallel values, which are the largest ones. Therefore the couplings of 17.5 for chlorine and 157 G for fluorine, detected in the experimental spectrum, correspond to effective principal values which, according to the geometry assumed, are related to the

$$(a_{\text{eff.}}^{\text{F}})^2 = (a_y^{\text{F}})^2\sin^2\theta + (a_z^{\text{F}})^2\cos^2\theta \qquad (8)$$

$$(a_{\text{eff.}}^{\text{Cl}})^2 = (a_y^{\text{Cl}})^2\sin^2\theta + (a_z^{\text{Cl}})^2\cos^2\theta \qquad (9)$$

true parallel principal values by relationships (8) and (9). By adding equations (10) and (11) and by assuming that the

$$a_x^{\text{F}} + a_y^{\text{F}} + a_z^{\text{F}} = 3a_{\text{iso.}}^{\text{F}} = 253.8 \qquad (10)$$

$$a_x^{\text{Cl}} + a_y^{\text{Cl}} + a_z^{\text{Cl}} = 3a_{\text{iso.}}^{\text{Cl}} = 31.5 \qquad (11)$$

hyperfine tensors are nearly, but not rigorously, axial (as suggested by the very low u.s.d. in the p_x and p_y orbitals of Cl and F predicted by the CNDO/2 method), the a_z values are obtained: a_z^{F} 163.6, a_z^{Cl} 18 G. Subtraction of the isotropic couplings $a_{\text{iso.}}^{\text{F}}$ 84.6 and $a_{\text{iso.}}^{\text{Cl}}$ 10.5 G yields the anisotropic components $2B_{\text{F}}$ 79 and $2B_{\text{Cl}}$ 7.5 G. These values, compared with theoretical $2B_0$ values relative to u.s.d. = 1 in a p_z orbital,[14] lead to the experimental u.s.d. in fluorine and chlorine of the $CFCl_2\cdot$ radical $\rho_{2p_z}^{\text{F}}$ 0.073 and $\rho_{3p_z}^{\text{Cl}}$ 0.074.

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