The Effects of α -Halogen Substitution on the Configuration of Alkyl Radicals in Solution by Electron Spin Resonance

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The e.s.r. spectra of a variety of alkyl radicals with α -halogen substituents have been examined in solution. The configurations of α -halogen substituted ethyl and β , β , β -trifluoroethyl radicals are correlated with the hyperfine splittings of α -methyl protons and α -trifluoromethyl fluorines, respectively. For an α -fluorine substituent, electronegativity plays an important role in determining the pyramidal configuration of the radical center, whereas size appears to be a more important factor with chlorine and bromine in promoting a less pyramidal configuration at the radical center. Two α -halogen substituents have a disproportionately greater effect than one halogen in influencing the configuration at the radical site. The *g*-factors of fluoroalkyl radicals are qualitatively analyzed in order to discuss possible mechanisms of β -fluorine hyperfine interactions and the effect of trifluoromethyl substitution on the configuration of the radical site.

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On a examiné les spectres r.p.e. d'un certain nombre de radicaux alkyles possédant des substituants halogènes en position α . Les configurations des radicaux éthyles substitués en α par des hydrogènes et les radicaux β , β , β -trifluoroéthyles sont reliées respectivement avec les couplages hyperfins des groupes α -méthyles et α -trifluorométhyles. Dans le cas d'un substituant fluor en α , l'électronégativité joue un rôle important sur la configuration pyramidale du centre radicalaire; toutefois dans le cas du chlore et du brome, il apparait que la grosseur est un facteur plus important pour promouvoir un centre radicalaire ayant une configuration moins pyramidale. Deux substituants halogènes en position α ont un effet proportionnellement beaucoup plus grand qu'un halogène en vue d'influencer la configuration du site radicalaire. Les facteurs g des radicaux fluoroalkyles sont analysés qualitativement en vue de pouvoir discuter des mécanismes possibles d'interactions hyperfines des hydrogènes en β et l'effet de la substitution d'un groupe trifluorométhyle sur la configuration du site radicalaire.

[Traduit par le journal]

Introduction in states the conformations of free radicals can be ten

directly affected by steric interactions imposed by α -substituents (1). A notable example is provided by the change in the stable conformation 1 of the *n*-propyl radical to 2 in the *t*-amyl analog by replacement of the two α -protons with methyl groups (1*d*).



For the *n*-propyl radical, e.s.r. studies in the solid state at $4 \,^{\circ}$ K are in accord with deductions of its conformation in solution at higher temperatures (1). Conformations of alkyl radicals

in solution are based on the magnitude and the temperature dependence of the β -proton hyperfine splittings together with the selective variations in the spectral linewidths (1b-f).

Substitution in the α -position of alkyl radicals may also exert a conformational change in free radicals by altering the configuration at the radical site. For example, the decrease in the extent of bridging in α, α -difluoro- β -chloroethyl radical **3** compared to the conformationally frozen β -chloroethyl radical **4** has been ascribed



to an increasingly pyramidal configuration at the radical center (1i, 2).

The measurement of ¹³C splittings represents

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the best approach for determining the configuration at the α -carbon in simple alkyl radicals by e.s.r. Thus, Fessenden and Schuler have quantitatively estimated the degree of bending in the series of fluorinated methyl radicals CH_nF_{3-n} from ¹³C hyperfine splittings (3). Due to problems associated with routine determination of ¹³C splittings, however, it is desirable to utilize additional probes such as the more readily measurable α -proton, fluorine, chlorine, methyl proton, and trifluoromethyl fluorine h.f.s. to determine the configuration of radical sites in alkyl radicals (4, 5). In this paper we wish to discuss several methods for deducing the configurations of halogenated alkyl radicals from the isotropic e.s.r. parameters.

Results and Discussion

Proton Hyperfine Splittings of α -Methyl Groups On the basis of the α -hydrogen and α -methyl proton hyperfine coupling constants, $a_{\rm H}^{\alpha}$ and $a_{\rm CH_3}$, of a series of alkyl radicals: methyl, ethyl, *i*-propyl, and *t*-butyl, Fessenden and Schuler concluded that $a_{\rm CH_3}$ can be correlated by the expression (1*a*)

$$[1] a_{CH_3} = Q_H^{CH_3} \rho_{\alpha}$$

 $Q_{\rm H}^{\rm CH_3}$ is a constant with a value of 29.30 G and ρ_{α} , the spin density at the α -carbon is given by eq. 2,

[2]
$$\rho_{\alpha} = (1 - 0.081)^n$$

where *n* is the number of α -methyl groups. Equation 2 implies that each α -methyl group withdraws about 8% of the spin density from the carbon center. A relationship given in eq. 3 which is applicable more generally to alkyl radicals with nonpolar or monopolar substituents has been developed by Fischer employing this concept (6).

$$[3] \qquad \qquad \rho_{\alpha} = \prod_{i=1}^{3} \left[1 - \Delta(X_i)\right]$$

 $\Delta(X_i)$ is a parameter which measures the spinwithdrawing influence of an α -substituent denoted as X_i . A series of $\Delta(X_i)$ values has been derived for various substituents by an iterative procedure from experimentally measured values of a_{CH_3} , although no values have been recorded heretofore for any halogen substituent.

The hyperfine splitting constants and g-factors for a series of α -haloalkyl radicals are listed in Table 1. The values of a_{CH_3} are independent of temperature between -40 and -130 °C, and they have been used to determine $\Delta(X_i)$ for fluorine, chlorine, and bromine substituents.

The unusually small value of the proton h.f.s. in CH_3CF_2 ($a_H = 13.99$ G) is striking for an α -methyl group in comparison with those in other alkyl radicals (23-26 G). Two factors may be considered for this unusual observation: (a) the bond polarization by an α -fluorine substituent, and (b) the configuration of the methyl group relative to the half-filled orbital at C_{α} . It is unlikely that bond polarization plays an important role since a single α -fluorine is insufficient to cause a proportional reduction on a_{CH_3} , and the value of the methyl splitting in CH₃CHF (24.48 G), is similar to that in the ethyl radical (26.99 G). We suggest that the pyramidal geometry at the α -carbon is the most important factor in causing the unusually small h.f.s. of the α -methyl proton in CH₃CF₂^{\cdot}. The INDO-MO method² was used to determine the stable configuration at C_{α} and the conformation of both CH_3CHF and CH_3CF_2 by optimizing the calculated proton and fluorine h.f.s. to the experimental values. Interestingly, the geometry resulting from the optimization listed in Table 2 is close to the minimized total energy. Furthermore, the geometries of best fit at C_{α} for CH₃CHF and CH₃CF₂ are almost the same as those obtained experimentally and theoretically for H_2CF and HCF_2 , respectively (3, 7). This result implies that the configuration of the radical center is affected very little on replacement of a hydrogen by a methyl group.

INDO results of CH_3CF_2 in Table 2 also indicate that bond polarization does not contribute significantly to the small α -methyl proton h.f.s. since the methyl splitting increases substantially from 14.35 to 25.64 G simply by constraining the radical site in CH_3CF_2 to a planar configuration. Furthermore, nonplanarity is also

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²An INDO program obtained from QCPE, Indiana University, has been converted for the CDC 6600. In spite of the approximations involved, the semiempirical INDO method has been shown to predict the geometry of fluorinated methyl radicals fairly reliably in comparison with those involving *ab initio* calculations (7).

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	T	Hyperfine splitting (G)						
Radical	Т (°С)	$\langle g angle$	a _x ^α	$a_{\rm H}{}^{\alpha}$	$a_{\rm H}{}^{\beta}$	ρ_{α}^{*}	φ† (deg)	Mode of generation‡
CH ₃ CH ₂	-113	2.00260		22.37	26.99	0.919	0	P. S
CH ₃ CHF	-106	2.00366	59.21	17.31	24.48	0.836	10	́Р
CH_3CF_2	-78	2.00361	94.01		13.99	0.478	25	H. S
CH ₃ CCl ₂	-108	2.00727	4.34		19.70	0.672	12	Ś
CH ₃ CHBr	- 77	2.00751	< 0.2	20.47	24.71	0.843	0	Р
$(CH_3)_2CH$	-113	2.00267		22.12	24.75	0.845	0	P, S
$(CH_3)_2CF$	-48	2.00360	60.85		21.11	0.721	14	Ĥ
(CH ₃) ₂ CCl§			2.3		22.3	0.761	0	
(CH ₃) ₂ CCH ₃	-113	2.00270		_	22.93	0.776	0	P, S

TABLE 1.	Electron spin resonance	parameters of α -hal	ogen substituted ethyl radicals
	•	*	

*From eq. 1. †From eq. 7 and $\Delta(H) = 0.0$, $\Delta(CH_3) = 0.081$, $\Delta(F) = 0.024$, $\Delta(CI) = 0.099$. ‡P = t-butyl perester, S = halogen abstraction by R_3S_i , H = hydrogen abstraction by t-BuO or CF₃O. §Reference 4b.

TABLE 2.	Conformational dependence of electron spin resonance parameters in α -fluorina	ted
	ethyl radicals by INDO-MO	

CH_3CH_2		CH	I₃CHF	CH	CH_3CF_2		
Structural and e.s.r. parameters*	H_1 H_2 H_3	H ₂ H ₂ H ₃	$H_{2}^{H_{1}}F$	$F \xrightarrow{H_1} F \xrightarrow{H_2} F \xrightarrow{H_3}$	$F_{H_2}^{H_1}F_{H_3}$		
∠ C _β C _α H _α	120	120	121				
$\angle C_{\beta}C_{\alpha}F_{\alpha}$		120	119	120	115		
$\angle H_{\alpha}C_{\alpha}H_{\alpha}$	120						
$\angle H_{\alpha}C_{\alpha}F_{\alpha}$		120	119				
$\angle F_{\alpha}C_{\alpha}F_{\alpha}$		·		120	106		
$r(C_{\alpha}-C_{\beta})$	1.40	1.52	1.52	1.50	1.51		
$a_{\rm H_1}$	53.41	51.02	52.28	49.90	37.21		
$a_{\rm H_2}$	14.69	13.70	11.10	13.51	2.92		
$a_{\mathrm{H}_{2}}$	14.69	14.11	13.64	13.51	2.92		
$\frac{1}{3}(\ddot{a}_{H_1} + a_{H_2} + a_{H_3})$	27.60	26.28	25.67	25.64	14.35		
$\frac{1}{2}(a_{\rm H_2} + a_{\rm H_2})/a_{\rm H_1}$	0.27	0.27	0.24	0.27	0.078		
$a_{\rm H}^{\alpha}$	-20.36	-20.76	-18.58				
$a_{\rm F}{}^{\alpha}$		58.55	61.95	49.89	93.69		
a_{13C}^{α}	39.9	38.12	44.56	36.86	142.50		
a_{13C}^{β}	-12.4	-11.88	-11.22	-11.80	0.89		
Total energy (a.u.)		-43.0290	-43.0303	-68.7258	- 68.7374		

 $r(C_{\alpha}-H_{\alpha}) = 1.08$ Å, $r(C_{\beta}-H_{\beta}) = 1.08$ Å, $r(C_{\alpha}-F_{\alpha}) = 1.35$ Å, $C_{\beta} = tetrahedral;$ angles in degrees, bond lengths in Å, and h.f.s. in G.

reflected in the rather high barrier to rotation about the C_{α} --C_{β} bond in CH₃CF₂ (2.2 kcal mol^{-1}), in contrast to the essentially free rotation of the methyl groups in the alkyl analogs, such as ethyl, isopropyl, and t-butyl radicals (1a-e, 5).

Since eqs. 1 and 3 have not been tested for any α -halogen substituted ethyl radicals, we have calculated values of $\Delta(F)$ for α -fluoroethyl radicals from the observed values of a_{CH_3} , and found them to vary from 0.091 to 0.279 for $CH_3\dot{C}HF$ and $CH_3\dot{C}F_2$, respectively. The variation is not unexpected because the value of hand, was obtained from INDO calculated

 a_{CH_3} , which results largely from a hyperconjugative interaction in radicals of the π -type (8), will be proportional to the spin density at the α -carbon, ρ_{α} , only if the half-filled orbital has the same amount of p-character. Two factors may be considered for this variation: (a) the effect of bond polarization by an α -fluorine substituent on the value of $Q_{\rm H}^{\rm CH_3}$ and (b) the change in p-character induced by an increase in the pyramidal configuration at the radical site by successive replacement of hydrogen by fluorine.

A unique value of $\Delta(F) = 0.024$, on the other

values of a_{CH_3} for both $CH_3\dot{C}HF$ and $CH_3\dot{C}F_2$ in hypothetical planar configurations by using eqs. 1 and 3, and a value of $Q_{\rm H}^{\rm CH_3} = 29.30 \, {\rm G}.$ The same values of $Q_{\rm H}^{\rm CH_3} = 29.30 \,\rm G$ obtained for CH₃ĊH₂, CH₃ĊHF, and CH₃ĊF₂, when they are all constrained to the same planar configurations, suggests that the hyperfine splitting produced by a (full) electron in a pure p-orbital on freely rotating methyl protons is the same for an α -fluorinated ethyl as well as for an ethyl radical. The latter may not be unexpected, since the extent of mixing between the p-orbital and a CH₃ group orbital of the correct symmetry will depend upon the energy difference between the two. Indeed, the energy of a p-orbital at a planar carbon center to which one fluorine is attached (*i.e.*, the half-filled molecular orbital energy =-0.3890 a.u. from an INDO calculation) is about the same as that (-0.3811 a.u.) for a p-orbital on carbon to which two fluorines are bonded. Thus, the assumption that there is a constant energy separation between the halffilled p-orbital and the methyl group orbital may be a reasonable one for planar α -fluoroalkyl radicals, as it has been suggested by Fessenden and Schuler (1a) for alkyl radicals. Furthermore, the unusually small value of $\Delta(F)$ is consistent with the high electronegativity of the fluorine atom, which presumably makes a smaller contribution in the canonical structure 6 to the total wave function for the radical with X = F compared to CH₃.

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$$\dot{c}$$
- $\ddot{x} \leftrightarrow \dot{c}$ - \dot{x}

The excellent agreement between the experimental results and the INDO calculations suggests that the reduction in the value of the methyl splitting in CH_3CF_2 is mainly due to the change in the configuration of the methyl group relative to the half-filled orbital at the pyramidal radical center. It also suggests that a quantitative correlation between the observed value of a_{CH_3} and the configuration at the radical site may be more generally applicable to other radicals.

If θ describes the dihedral angle between the β -CH bond and the p-orbital at the carbon radical center, the hyperfine splitting constant for the β -proton is given by eq. 4 (9), where *A* and *B* are constants.

$$[4] a_{\rm H}^{\ \beta} = A + B\cos^2\theta$$



For planar radicals, the β -proton h.f.s. arises largely from a hyperconjugative interaction (*i.e.*, *A* is negligible in comparison with *B* in eq. 4),



where X = H, CH_3 , Cl, F, Br and the ratio R of the hyperfine splitting constants for $H_{2,3}$ and H_1 in 7 will be a constant and independent of the α -substituents. According to eq. 5, a constant value of R = 0.25 is expected if $A \ll B$. Indeed, the

[5]
$$R = \frac{\frac{1}{2}(a_{H_2} + a_{H_3})}{a_{H_1}}$$
$$= \frac{A + B\cos^2 120^{\circ}}{A + B\cos^2 0^{\circ}}$$
$$= \frac{A + \frac{1}{4}B}{A + B}$$

calculated ratio of 0.27 for $\frac{1}{2}(a_{H_2} + a_{H_3})/a_{H_1}$ in Table 2 is the same for the ethyl radical as well as for α -fluoro and α, α -difluoroethyl radicals in a hypothetical planar configuration. On the other hand, the ratio of the calculated hyperfine splitting constants for H_{2,3} and H₁ as well as the methyl proton h.f.s., a_{CH_3} , are strongly dependent on the degree of bending at the radical center as shown in Table 3 and Fig. 1. By analogy, we assume that related radicals have values for *R* which are also mainly determined by the degree of bending at the radical site.

For bent radicals, Fessenden and Schuler quantitatively estimated the degree of bending at radical site for fluoromethyl radicals from the observed α ¹³C splitting using eq. 6,

[6]
$$a_{\rm C}(\phi) = a_{\rm C}(0) + 1190(2\tan^2 \phi)$$

where ϕ is the angle between a C—F bond and a plane normal to the three-fold symmetry axis, and $a_{\rm C}(0)$ is the ¹³C splitting of a planar methyl radical and equal to 30 G (3). The term 2 tan² ϕ

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TABLE 3.	Conformational dependence of the β -proton hyperfine splitting
	for α, α -difluoroethyl radical by INDO-MO*

/ FC_F / C_C_F	
$\begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} $	R
106 115 14.35 37.21 2.92	0.078
109 116 15.81 39.70 3.87	0.097
112 117 17.34 42.21 4.91	0.116
116 118 19.76 45.87 6.71	0.146
120 120 25.64 49.90 13.51	0.271

 $r(C_{\beta}-H_{\beta}) = 1.08 \text{ Å}, r(C_{\alpha}-F_{\alpha}) = 1.35 \text{ Å}, r(C_{\alpha}-C_{\beta}) = 1.51 \text{ Å}, C_{\beta} \text{ is tetrahedral.}$



FIG. 1. Electron spin resonance parameters of CH₃CF₂ as a function of the configuration at the radical as determined by INDO-MO: (*a*) β -proton h.f.s., (*b*) ratio of β -proton splittings, (*c*) difference in the total energy relative to the optimized structure with \angle FCF = 106° and \angle CCF = 115°.

corresponds to the s-character of the orbital containing the unpaired electron, suggesting that the spin density at the α -carbon atom is reduced from ρ_{α} to $\rho_{\alpha}(1 - 2\tan^2 \phi)$ where the term $(1 - 2\tan^2 \phi)$ corresponds to the p-character of the orbital containing the unpaired electron. A set of modified equations which correlate a_{CH_3} with the spin density at the α -carbon atom for bent radicals can be obtained from the corresponding eqs. 1 and 3.

[1]
$$a_{CH_3} = Q_H^{CH_3} \rho_{\alpha}$$

where $Q_H^{CH_3} = 29.30 \text{ G}$

[7]
$$\rho_{\alpha} = (1 - 2 \tan^2 \phi) \prod_{i=1}^{3} [1 - \Delta(X_i)]$$

where $\Delta(X_i)$ is a parameter which measures the spin-withdrawing influence of an α substituent X_i on a planar radical configuration, namely via bond polarization. For bent radicals, the spin density at α -carbon depends on bond polarization as well as the angle of bending exerted by α -substituents.

In Table 1, ρ_{α} was calculated from eq. 1 and the observed value of a_{CH_3} , ϕ was obtained from ρ_{α} by the use of eq. 7.

Fluorine Hyperfine Splittings for the α -Tri-

fluoromethyl Group (a_{CF2})

Fessenden and Schuler obtained eq. 1 with $Q_{\rm H}^{\rm CH_3} = 29.30$ G and $\Delta(\rm CH_3) = 0.081$ by using an iterative procedure from the experimentally observed value of $a_{\rm CH_3}$ for ethyl, isopropyl, and *t*-butyl radicals (1*a*). In Table 4, we have summarized the e.s.r. parameters of a series of radicals which result from the successive replacement of a hydrogen atom in the methyl radical with a trifluoromethyl group, namely CF₃CH₂, (CF₃)₂CH, and (CF₃)₃C. The value of $a_{\rm CF_3}$ are temperature independent in the range of -40 to -130 °C for CF₃CH₂ and (CF₃)₂CH.³

There is some current disagreement as to the effect which successive replacement of a hydrogen by a methyl group has on the configuration of alkyl radicals. In the series: ethyl, *i*-propyl, and *t*-butyl radicals, and especially for $C(CH_3)_3$, an argument based on the magnitude and the sign of the temperature dependence of ¹³C splitting has suggested that the *t*-butyl radical is non-planar (10). However, Symons, Ingold, and

³The temperature dependence of the β -fluorine h.f.s. of (CF₃)₃C has not been studied (4*c*), but it is not unreasonable to assume that this β -fluorine h.f.s. is temperature independent.

	_			а	F ^β		
Radical	Т (°С)	$\langle g angle$	$a_{\rm H}{}^{\alpha}$ (G)	Exptl.	Calcd.†	$\Delta a_{\rm F}^{\rm p}$ (G)‡	ρ_{α}^{*}
CH ₃	-113	2.00262	22.88				1
CF_3CH_2	-113	2.00234	23.77	29.61	29.43	0.18	0.778
$(CF_3)_2CH$	-113	2.00221	24.61	22.64	22.90	-0.26	0.605
(CF ₃) ₃ C§	- 60	2.0015		17.9	17.81	0.09	0.471

TABLE 4. Electron spin resonance parameters of α -trifluoromethyl substituted methyl radicals

 $a_{F}^{\beta} (calcd) = 37.83 \text{ G} \times \rho_{\alpha}.$ $\Delta a_{F}^{\beta} = a_{F}^{\beta} (exptl) - a_{F}^{\beta} (calcd).$ §Taken from ref. 4c.

Fischer have pointed out that the evidence used to deduce the nonplanarity at the radical site is not rigorous (1g, 11). The nearly constant values of the g-factors and the α -proton splittings, as well as the small change of the α ¹³C splittings from 38.34 G in methyl radical to 45.2 G in *t*-butyl radical suggest that the effect of α -methyl substitution on the bending of the radical site is quite small.

The essentially free rotation in the β , β , β -trifluoroethyl radical can be attributed to a low barrier associated with the 6-fold rotation symmetry along the C_{α} — C_{β} bond as a result of planarity at the trigonal α -carbon center (12). There is a small but significant increase in the α -proton h.f.s. in going from CF₃CH₂ to $(CF_3)_2$ CH, but the change is also accompanied by an increase in steric repulsion due to the presence of an additional bulky CF₃ group. It appears unlikely that the configuration of $(CF_3)_2CH$ and $(CF_3)_3C$ could be anything but planar. Since CF_3 is more electronegative than hydrogen, Pauling's argument (13) that substitution of more electronegative groups should increase the bending does not seem to hold for the series of radicals with the structure, $CH_n(CF_3)_{3-n}$.⁴ The effect of electronegativity may be offset by the steric effects of the CF₃ groups in these radicals. A correlation of the fluorine h.f.s. in α -trifluoromethyl groups similar to eq. 1 for α -methyl proton h.f.s. can be obtained by an iterative procedure

$$[8] a_{\rm CF_3} = Q_{\rm F}^{\rm CF_3} \rho_{\alpha}$$

with $Q_{\rm F}^{\rm CF_3} = 37.83 \, {\rm G}$ and $\Delta({\rm CF}_3) = 0.222$. The unique values of $Q_{\rm F}^{\rm CF_3}$ and $\Delta(\rm CF_3)$ indicate that the variations in the p-character of the half-filled orbital are relatively small amongst

the radicals considered here. The latter also implies that α -trifluoromethyl substituents do not dramatically affect the configuration of alkyl radicals. The rather large spin-withdrawing influence of a CF₃ group in which $\Delta(CF_3) =$ 0.222, suggest that structures such as 6 for $X = CF_3$ are relatively unimportant to the total wave-function for the radical.

Due to the intrinsic features of the INDO program (14), the lack of agreement between the calculated and experimental β -fluorine h.f.s. is noteworthy. Nonetheless, a relationship similar to eq. 4 for β -proton splittings (with a negligible $A_{\rm F}$ in comparison with $B_{\rm F}$) has been proposed for the β -fluorine h.f.s. of planar radicals such as 8 (15) and $R' = \left[\frac{1}{2}(a_{F_2} + a_{F_3})/a_{F_1}\right] = 0.25$

$$\Theta$$
] $a_{\rm F}^{\ \ \beta} = B_{\rm F} \cos^2 \theta$

was obtained. Similarly, a dependence of R' on bending will be expected. Indeed, a value for R'



of -3.14/40.4 or -0.078 can be extracted from the results of Meakin and Krusic for the perfluoroethyl radical from their low temperature e.s.r. study (16). The bending at the radical site of perfluoroethyl radical has been supported by INDO calculations (4c), and it is also reflected in the rather high barrier to rotation about the C_{α} — C_{β} bond (16) (2.85 kcal mol⁻¹). Accordingly, eqs. 7 and 8 can be used to correlate $a_{\rm CF_3}$ with the spin density at the α -carbon atom for bent β , β , β -trifluoroethyl radicals. The e.s.r. parameters for α -halogen substituted β , β , β trifluoroethyl radicals are given in Table 5, together with values for ρ_{α} and ϕ calculated

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⁴For recent theoretical arguments to the FCF and CF₃CCF₃ bond angles, see ref. 28.

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Radical			$a_{\mathbf{X}}^{\alpha}$	$a_{\rm H}^{\alpha}$	$a_{\rm F}^{\beta}$	0 *	φ* (deg)	Mode of
	(0)	\87	(0)	(0)	(0)	Ρα	(ucg)	generations
CF ₃ CH ₂	-113	2.00234		23.77	29.61	0.778	0	S
CF ₃ CHF	-106	2.00363	66.18	21.47	25.25	0.668	14	Р
CF ₃ CF ₂	- 84	2.00386	87.26		11.36	0.300	29	Р
CF ₃ CHCl [†]	-60		3.7	22.2	23.4	0.619	13	
CF ₃ CCl ₂	-81	2.00797	4.14		18.56	0.491	18	S
(CF ₃) ₂ CH	-113	2.00221		24.61	22.64	0.605	0	Р
(CF ₃) ₂ CF‡	-60	2.0033	67.4		19.2	0.508	15	

TABLE 5. Electron spin resonance parameters of α -halogen substituted β , β , β -trifluoroethyl radicals

*See text. †Taken from ref. 15b. ‡Taken from ref. 4c.

S = halogen abstraction by R_3S_i , P = photolysis of *t*-butyl peresters.





from eqs. 7 and 8. The e.s.r. spectrum of α , β , β , β -tetrafluoroethyl radical is given in Fig. 2.

The Effect of α -Halogen Substitution on the Configuration of Alkyl Radicals

Based on the observed α -chlorine and methyl proton h.f.s., Cooper *et al.* concluded that 2-chloroisopropyl radical is essentially planar (4b). We obtain a value of $\Delta(Cl) = 0.099$ from the observed a_{CH_3} and the use of eqs. 1 and 3. Using this value of $\Delta(Cl)$ and eqs. 1, 7, and 8, we obtained values of ρ_{α} and ϕ for α -chlorinated ethyl and β,β,β -trifluoroethyl radicals which are given in Tables 1 and 5.

For the α -bromoethyl radical, Fig. 3, a value of a_{CH_3} equal to 24.71 G is very close to 24.48 G obtained for a_{CH_3} of the α -fluoroethyl radical. However, the smaller electronegativity and the bulkier nature of the bromine atom suggest that the radical is planar or nearly planar. A value of $\Delta(Br) = 0.082$ was calculated on this basis using eqs. 2 and 3.

g-Factors and the Mechanism of β-Fluorine Hyperfine Splittings

There are two principal mechanisms which

have been proposed to account for the interaction between a β -fluorine substituent and an unpaired electron at the radical center. The first involves an interaction between the lowest unoccupied antibonding orbital of the trifluoromethyl group and the half-filled orbital of radical (17). The second mechanism involves a 1–3 homoconjugation between the half-filled p-orbital and the lone-pair p-orbital of the fluorine (18).

The second mechanism can only make a positive contribution to the g-factor since the half-filled orbital at the carbon center is of higher energy than the lone-pair p-orbital of fluorine (19). However, a positive or negative contribution to the g-factor may arise from the first mechanism. The sign of the contribution depends on the difference between $(\varepsilon^0 - \varepsilon^b)$ and $(\varepsilon^0 - \varepsilon^a)$ where ε^0 , ε^b , and ε^a are the half-filled orbital, the highest occupied bonding orbital, and the lowest unoccupied antibonding orbital energies, respectively.

The monotonic decrease in the isotropic g-factor with an increasing number of α -trifluoromethyl substituents shown in Table 4 is in



FIG. 3. Electron spin resonance spectrum of α -bromoethyl radical in cyclopropane solution at -77 °C. The stick spectrum shows the binomial intensity ratios. The proton n.m.r. field markers are in kHz.

striking contrast to the essentially constant g-factors for the hydrocarbon analogs. The trend in g-factors noted above for α -CF₃ substituted alkyl radicals suggests that the second mechanism does not contribute in a major way to the spin-transfer process. The first mechanism has been used to interpret the difference between the large fluorine h.f.s. in hexafluoro-acetone ketyl and the small one in the isoelectronic nitroxide (20c). Thus, the diagram shown in Fig. 4 illustrates that the energy difference between the lowest unoccupied antibonding orbital of the CF₃ group and the half-filled orbital of the carbonyl group is indeed smaller than that in the nitroxide function.

According to the first mechanism, $a_{\rm F}^{\ \beta}$ is approximately inversely proportional to the energy difference between the lowest unoccupied antibonding orbital of the trifluoromethyl group and the half-filled orbital at the radical center. From the observed value of $a_{CF_3} = 22.64 \text{ G}$ for (CF₃)₂CH in comparison with 34.7 G for $(CF_3)_2CO^{-1}$ and 8.26 G for $(CF_3)_2NO$, we conclude that the half-filled orbital of the CH group has an energy close to 0 a.u. (20, 21). Thus, the difference $(\varepsilon^0 - \varepsilon^a) \approx 0.3$ a.u. is expected to be smaller than $(\varepsilon^0 - \varepsilon^b) \approx 0.7$ a.u., and an α -CF₃ group would make a negative contribution to the g-factor if the first mechanism were responsible for the observed β -fluorine h.f.s. Such a conclusion is consistent with the observed monotonic decrease of the g-factors of the radicals resulting from successive replacement of a hydrogen with a CF₃ group. Therefore, we interpret the decrease of the g-factor as a support for a mechanism of spin transfer into the antibonding orbital of the CF₃ group similar to that formulated for hexafluoroacetone ketyl. Such an effect would not be expected in methyl compounds since the highest unoccupied orbital of the methyl group is of higher energy than the level in the trifluoromethyl group due to the smaller electronegativity of the proton. The latter is in accord with the nearly invariant g-factor of the series of alkyl radicals: methyl, ethyl, isopropyl, and *t*-butyl.

On the other hand, the g-factors of ethyl or β , β , β -trifluoroethyl radicals with one α -halogen substituent are always greater than those of the parent radicals as listed in Tables 1 and 5. The larger g-factor in these radicals is consistent with the findings of McConnell and Robertson (22), that in planar π -radicals, the successive substitution of hydrogen by an atom with a lone pair of electrons at a position where the spin density is appreciable, causes a progressive increase in the g-factor. This effect can be attributed to the delocalization of the spin onto the lone pair orbital of the α -halogen atom, which affords a positive contribution to the g-factor



FIG. 4. Highest occupied and lowest unoccupied orbital energies for HCF₃, $H_2C\dot{O}^-$, and $H_2N\dot{O}$ as calculated from INDO-MO. The energy levels are drawn to scale. Data are taken from reference 17*c*. For the energy level of $\dot{C}H$ see text.

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due to the lower energy level of lone pair orbital in comparison with the half-filled orbital at the radical center. When a second halogen atom is introduced, however, there is only a small increase or even a decrease in the g-factor. Evidently as the degree of bending increases due to the introduction of the second α -halogen, the effect of delocalization on to halogen which is associated with a positive contribution to g-factor is increasingly offset by a factor associated with a negative contribution. A similar change in g-factors has been previously noted in the series of $\dot{C}H_nF_{3-n}$ and $\dot{S}iH_nF_{3-n}$ (3, 23).

Conclusion

An equation has been derived to estimate the angle of bending at the radical site due to α -halogen substitution in alkyl radicals which is based on the experimentally observed α -methyl proton or α -trifluoromethyl fluorine hyperfine splitting constants. Two α -fluorine substituents have a disproportionately greater influence on bending than one fluorine, in accord with results calculated by INDO. The effect of an α -chlorine or bromine substituent is akin to that of a methyl group, and suggests that size has an important influence. The effect of an α -trifluoromethyl group on the g-factor has been qualitatively correlated with the energy levels of the CF₃ group. The observed monotonic decrease of the g-factors on successive replacement of an hydrogen atom in the methyl radical by a CF₃ group is consistent with the hyperconjugative mechanism proposed for the β -fluorine splitting. The positive contribution to the g-factor by α -halogen substituents is offset to an increasing extent by the increasing degree of bending at the radical site.

Experimental Section

The modified Varian X-band spectrometer, microwave frequency measurements, light source, and sample tubes are as described previously (1*d*).

To minimize the error in the *g*-value determinations, all measurements were made on spectra recorded on the same day for increasing magnetic field. Perylene cation radical g = 2.00258 (24) was used as standard in the configuration employed. The accuracy of the measurements is estimated as ± 0.00003 . Hyperfine splittings were corrected for second-order shifts and confirmed by computer simulation.

For photolytic reduction of alkyl halides, equal volumes of di-*t*-butyl peroxide and triethylsilane were diluted with sufficient cyclopropane (and ethane) to give a final ratio of approximately 1:1:1:4 (v/v). For the photolysis of acyl peresters, a small amount of the perester

(ca. 100 mg) was dissolved in a relatively large volume (15:1) of cyclopropane or cyclopropane-ethane mixtures. For the photolytic abstraction of hydrogen atom from the fluorohydrocarbons, a solution with a halfvolume of di-t-butyl peroxide or bis-trifluoromethyl peroxide was diluted with cyclopropane or Freon-12 (CF_2Cl_2) to give a final ratio of approximately 1:0.5:4. For the generation of 1,1-difluoroethyl radical from 1,1-difluoroethane, bis-trifluoromethyl peroxide used, since di-t-butyl peroxide under the same conditions did not afford sufficiently high concentrations of radicals for e.s.r. measurements. For the generation of 2-fluoropropyl radical from the photolytic abstraction of hydrogen from 2-fluoropropane, spectra of radicals with good signal-to-noise could only be observed at temperatures higher than -80 °C.

Materials

Di-*t*-butyl peroxide was obtained from Shell Chemical Co., washed with water, dried, passed through an alumina column, and redistilled at reduced pressure prior to use. Triethylsilane was obtained from Columbia Chemicals Co., refluxed over molecular sieve and redistilled prior to use. Bis-trifluoromethyl peroxide was obtained from PCR, Inc. 1,1,1,-trichloroethane (Matheson), 1,1,1trifluoro-2-bromoethane (Perce Chemical Co.), and 1,1,1-trichlorotrifluoroethane, (PCR, Inc.) were washed with water, dried, and redistilled prior to use. Perfluoropropyl bromide was obtained from PCR, Inc. and used as such. 1,1-Difluoroethane (Genetron 152A) and 1,1difluoro-1-chloroethane (Genetron 142B) were obtained from Matheson Co. Perfluoropropionyl chloride was obtained from Pierce Chemical Co.

t-Butyl Hexafluoroisobutyryl Perester was prepared via the acid chloride (25) (n.m.r.: δ 1.31 (s), 4.03 (septet)).

t-Butyl β,β,β *-trifluoro-\alpha-fluoropropionyl* Perester was prepared via the anhydride. (n.m.r.: δ 1.31(s), 5.17 (d × q).

t-Butyl a-fluoropropionyl Perester

Ethyl methanesulfonyl-lactate was prepared by the method of Crossland and Servis (26). Yield 95%, (n.m.r.: δ 1.32 (t), 1.58 (d), 3.07 (s), 4.25 (q), 5.04 (q)). The lactate (20 g) and 12 g anhydrous potassium fluoride in 65 ml of hexamethylphosphoric triamide were heated and stirred at 100 °C over a period of 24 h. The reaction mixture was cooled, diluted with cold water, and extracted with anhydrous ether. The extracts were washed with water, dried over anhydrous magnesium sulfate, and distilled (b.p. = 51 °C at 93 mm). Yield of ethyl α -fluoropropionate, 50% (n.m.r.: δ 1.30 (t), 1.50 (d × d), 4.20 (q), 4.87 (d \times q)). Ethyl α -fluoropropionate (15 g) and 100 ml of 10% potassium hydroxide aqueous solution were stirred at room temperature over a period of 3 h. The reaction mixture was extracted with ether, dried, and distilled (b.p. = 84–85 °C at 54 mm). Yield α -fluoropropionic acid 70% (n.m.r.: (δ 1.62 (d × d), 5.06 (d × q)), t-Butyl-a-fluoropropionyl perester was prepared via the acid chloride (n.m.r.: (δ 1.31 (s), 1.63 (d × d), 5.14 (d × q)). 2-Fluoropropane was prepared by the method of Edgell and Parts (27) via the mesylate (n.m.r.: & 1.32 $(d \times d)$, 4.86 $(d \times \text{septet})$). *t*-Butyl- α -bromopropionyl perester was prepared from α -bromopropionic acid via the acid bromide (n.m.r.: δ 1.33(s), 1.84(d), 4.36(q)).

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- (a) R. W. FESSENDEN and R. H. SCHULER. J. Chem. Phys. 39, 2147 (1963); (b) R. W. FESSENDEN. J. Chim. Phys. 61, 1570 (1964); (c) J. K. KOCHI and P. J. KRUSIC. Chem. Soc. Spec. Publ. 24, 147 (1970); (d) P. J. KRUSIC and J. K. KOCHI. J. Am. Chem. Soc. 93, 846 (1971); (e) P. J. KRUSIC, P. MEAKIN, and J. P. JESSON. J. Phys. Chem. 75, 3438 (1971); (f) K. S. CHEN, D. J. EDGE, and J. K. KOCHI. J. Am. Chem. Soc. 95, 7036 (1973); (g) D. GRILLER and K. U. INGOLD. J. Am. Chem. Soc. 95, 6459 (1973); (h) F. J. ADRIAN, E. L. COCHRAN, and V. A. BOWERS. J. Chem. Phys. 59 3946 (1973); (i) K. S. CHEN, P. J. KRUSIC, and J. K. KOCHI. J. Phys. Chem. In press.
- K. S. CHEN, D. Y. H. TANG, L. K. MONTGOMERY, and J. K. KOCHI. J. Am. Chem. Soc. 96, 2201 (1974).
- R. W. FESSENDEN and R. H. SCHULER. J. Chem. Phys. 43, 2704 (1965).
- (a) A. J. DOBBS, B. C. GILBERT, and R. O. C. NOR-MAN. J. Chem. Soc. A, 124 (1971); (b) J. COOPER, A. HUDSON, and R. A. JACKSON. Mol. Phys. 23, 209 (1972); (c) R. V. LLOYD and M. T. ROGERS. J. Am. Chem. Soc. 95, 1512 (1973).
- K. S. CHEN and J. K. KOCHI. Chem. Phys. Lett. 23, 233 (1973); J. Am. Chem. Soc. 96, 794 (1974).
- H. FISCHER. Z. Naturforsch. 19a, 866 (1964); 20a, 428 (1965).
- -7. (a) K. MOROKUMA, L. PEDERSON, and M. KARPLUS.
 J. Chem. Phys. 48, 4801 (1968); (b) D. L. BEVERIDGE,
 P. A. DOBOSH, and J. A. POPLE. J. Chem. Phys. 48, 4802 (1968).
- 8. A. D. MCLACHLAN. Mol. Phys. 1, 233 (1958).
- 9. C. HELLER and H. M. MCCONNELL. J. Chem. Phys. 32, 1535 (1960).
- D. E. WOOD, L. F. WILLIAMS, R. F. SPRECHER, and W. A. LATHAN, J. Am. Chem. Soc. 94, 6241 (1972).
- 11. (a) M. C. R. SYMONS. Tetrahedron Lett. 207 (1973);

(b) H. PAUL and H. FISCHER. Helv. Chim. Acta, 15, 1575 (1973).

- (a) A. J. BOWLES, A. HUDSON, and R. A. JACKSON. Chem. Phys. Lett. 5, 552 (1970); (b) D. J. EDGE and J. K. KOCHI. J. Am. Chem. Soc. 94, 6485 (1972).
- 13. L. PAULING. J. Chem. Phys. 51, 2767 (1969).
- 14. G. R. UNDERWOOD. Private communication.
- (a) M. IWASAKI. Fluorine Chem. Rev. 5, 1 (1971); (b)
 A. HUDSON and K. D. J. ROOT. Adv. Magn. Reson. 5, 1 (1971).
- P. MEAKIN and P. J. KRUSIC. J. Am. Chem. Soc. 95, 8185 (1973).
- 17. (a) M. J. S. DEWAR. Hyperconjugation. Ronald Press, New York, N.Y. 1962. p. 159; (b) W. R. KNOLLE and J. R. BOLTON. J. Am. Chem. Soc. 91, 5411 (1969); (c) К. МОГОКИМА. J. Am. Chem. Soc. 91, 5412 (1969).
- 18. W. A. SHEPPARD. J. Am. Chem. Soc. 87, 2410 (1965).
- 19. A. J. STONE. Proc. R. Soc. Ser. A, 271, 424 (1963);
- Mol. Phys. 6, 509 (1963); 7, 311 (1964).
 20. E. G. JANZEN and J. L. GERLOCK. J. Phys. Chem. 71, 4577 (1967).
- 21. W. D. BLACKLEY and R. R. REINHARD. J. Am. Chem. Soc. 87, 802 (1965).
- 22. H. M. MCCONNELL and R. E. ROBERTSON. J. Phys. Chem. 61, 1018 (1957).
- 23. M. V. MERRITT and R. W. FESSENDEN. J. Chem. Phys. 56, 2353 (1972).
- 24. B. G. SEGAL, M. KAPLAN, and G. K. FRAENKEL. J. Chem. Phys. 43, 4191 (1965).
- 25. P. D. BARTLETT and R. R. HIATT. J. Am. Chem. Soc. 80, 1398 (1958).
- R. K. CROSSLAND and K. L. SERVIS. J. Org. Chem. 35, 3195 (1970).
- 27. W. F. EDGELL and L. PARTS. J. Am. Chem. Soc. 77, 4899 (1955).
- R. C. BINGHAM and M. J. S. DEWAR. J. Am. Chem. Soc. 95, 7182 (1973). P. KOLLMAN. J. Am. Chem. Soc. 96, 4363 (1974).

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