The Structure of Ketyl Radicals. II. An Electron Spin Resonance Study of Spin Delocalization into Perfluorinated Alkyl Side Chains[1]

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Abstract: Esr spectra have been observed for the ketyl radical anions of hexafluoroacetone, perfluorodiethyl ketone, and perfluorocyclobutanone; each ketyl was generated by *in situ* electrolysis *in vacuo*. The fluorine hyperfine splittings are large and show the expected second-order splittings. Extensive molecular orbital calculations have been carried out on these molecules using the INDO formalism. The calculated fluorine 2s spin densities correlate very well with the observed relative fluorine hyperfine splittings. Both experimental observations and theoretical calculations indicate that the β-fluorine hyperfine splittings obey an approximate $\cos^2\theta$ dependence where θ is the dihedral angle. The molecular orbital calculations further indicate that the spin transfer to the fluorine 2s orbitals proceeds *via* transfer to the fluorine 2p orbitals. It is clearly shown that fluorine hyperfine splittings should *not* be found to be proportional to the π spin density on the adjacent π center.

The mechanism of electron-spin delocalization into saturated alkyl side chains has been a subject of considerable experimental and theoretical interest.[4–7] However, only recently has any interest been expressed in the mechanism of spin delocalization into perfluorinated alkyl side chains.[8–12] Most authors agree that a direct across-space interaction of the nonbonding 2p orbitals of fluorine with the $2p_z$ orbitals of the π system is an important factor in the mechanism of spin delocalization; nevertheless, little is known about the details of this mechanism.

By analogy with alkyl proton hyperfine splittings, it is tempting to apply an equation of the type

$$a_\beta^{F} = B_X \cos^2\theta\rho_X^{\pi} \qquad (1)$$

where ρ_X^{π} is the π spin density on atom X adjacent to a perfluorinated side chain. a_β^{F} is the isotropic β-fluorine hyperfine splitting and B_X is a constant. Morokuma[13] has shown that eq 1 does apply to the hexafluoroacetone ketyl. However, it is of interest to examine whether or not eq 1 is generally applicable to radicals containing perfluorinated side chains.

To provide a test of eq 1 we have investigated a series of perfluorinated ketyl radicals. Because the unpaired electron is expected to be located primarily in the π orbitals of the carbonyl fragment, the spin densities on this fragment should not vary much from one ketyl to another. Thus any changes in the fluorine hyperfine splittings (hfs) should reflect changes in the interaction of the perfluorinated alkyl group with the π system.

The radicals which we have examined are the hexafluoroacetone anion (HFA), the perfluorocyclobutanone anion (PFCB), and the perfluorodiethyl ketone anion (PFDK). In a preliminary communication[14] (part I of this series) we reported our conclusions concerning the structure of HFA. Janzen, *et al.*, have previously reported results for both HFA and PFCB.[12]

Experimental Section

The fluorinated ketyls were generated electrolytically *in situ* in a vacuum electrolysis cell;[15] tetra-*n*-butylammonium perchlorate (Southwestern Analytical Chemicals) was used as the supporting electrolyte. The esr spectra were recorded on a Varian E-3 spectrometer using the Wurster's Blue radical[16] to calibrate the field sweeps. An extremely careful analysis of the esr spectrum of the Wurster's Blue radical in absolute ethanol yields the following hyperfine splitting constants (G): $a^{N} = 7.051 \pm 0.007$, $a_{CH_3}^{H} = 6.773 \pm 0.005$, $a_{CH}^{H} = 1.989 \pm 0.009$; the *g* factor is 2.003015 ± 0.000012,[17] corrected for second-order shifts.[18] We use this radical for calibration purposes since it is stable *in vacuo* and has many lines spread out over ~100 G.

HFA was obtained from Pierce Chemical Co. and PFCB was a gift from Dr. D. C. England at Du Pont. Both HFA and PFCB were used as received. PFDK was synthesized following a patented procedure of Wiley.[19]

Hyperfine splitting constants were computed from experimental line positions using a least-squares fit with corrections for second-order shifts.[20]

An INDO molecular orbital computer program was obtained from the Quantum Chemistry Program Exchange, Indiana University, and modified for use on a Control Data 6600 computer. All spin densities were computed "with projection." We find that without annihilation of the contaminating quartet states the spin densities are generally quite a bit larger.[21]

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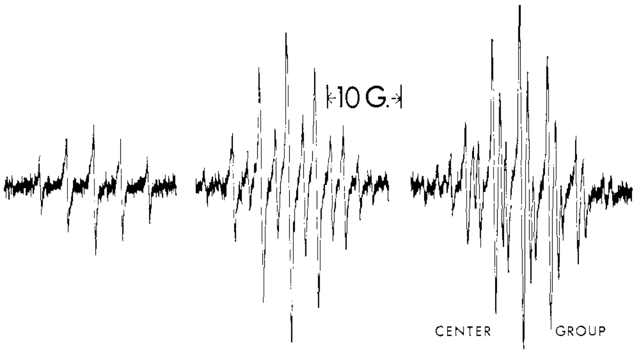

Figure 1. Low-field half of the first-derivative esr spectrum of the perfluorodiethyl ketone radical anion.

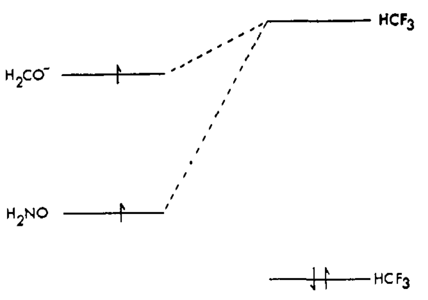

Figure 2. Highest occupied and lowest unoccupied orbital energies for CF_3H, H_2CO^-, and H_2NO as calculated from INDO molecular orbital theory. The energy levels are drawn to scale. Data are taken from ref 13.

Results

The HFA fluorine hfs has been reported previously as $a^F = 34.7 \pm 0.2$ G in acetonitrile.[12a] We find $a^F = 34.94 \pm 0.05$ G in acetonitrile at 23°. This hfs is *temperature independent* within ±0.1 G down to −30°. In methylene chloride $a^F = 34.77 \pm 0.08$ G.

The fluorine hfs's for PFCB have also been reported previously as $a_\beta{}^F = 82.9 \pm 0.3$ G and $a_\gamma{}^F = 37.3 \pm 0.2$ G in acetonitrile.[12c] We find $a_\beta{}^F = 84.4 \pm 0.1$ G and $a_\gamma{}^F = 38.0 \pm 0.1$ G. These differ somewhat from those reported previously. In addition, we are able to resolve all of the expected second-order line components. Thus the spectrum is not anomalous in this regard as had previously been surmised.[12c] It is not clear why all second-order splittings were not observed before except that our experimental setup involves a vacuum electrolysis cell. It is thus possible to remove all traces of oxygen from the solvent.

Figure 1 illustrates the low-field half of the esr spectrum of PFDK in acetonitrile. The signal-to-noise ratio is such that the weak outside lines are not observed. Second-order splitting is again observed. The expected intensity ratio of the second-order lines is 1:3:2 for four equivalent fluorines; this is what is observed in Figure 1. Each main group is split into a septet by the six equivalent fluorines of the trifluoromethyl groups. The fluorine hfs's are $a_\beta{}^F = 58.50 \pm 0.08$ G and $a_\gamma{}^F = 3.88 \pm 0.08$ G. These hfs's are *temperature independent* within ±0.1 G down to −10°.

Discussion

Fluorine atoms are very sensitive to any slight unpairing of electrons in the fluorine 2s orbitals. (It has been estimated that one unpaired electron in a fluorine 2s orbital would give rise to an isotropic hyperfine splitting of ~17,000 G.[22]) In spite of this, fluorine hfs's are rarely larger than a few hundred gauss. Hence, the magnitudes of fluorine 2s spin densities are very small. This presents a stringent challenge to existing valence theories to be able to account for such small effects.

In part I[14] we compared the fluorine hfs's for HFA and its isoelectronic analog bis(trifluoromethyl) nitroxide (TFNO). The ratio of the fluorine hfs's is 4.2; such a ratio cannot be explained in terms of gross structural differences, as the ^{13}C and ^{14}N hfs's indicate that both molecules are close to planar. A "charge effect" would seem to be eliminated since the fluorine hfs's in both HFA and TFNO[23] are relatively insensitive to large changes in the dielectric constant of the solvent.

In spite of the theoretical difficulties cited above, a satisfactory explanation of the large change in fluorine hfs's between HFA and TFNO was provided by Morokuma.[13] He utilized Pople's INDO–MO theory[24] and showed that the unpaired electron on the carbonyl group is delocalized into a vacant antibonding π-type orbital on the CF_3 group in HFA. The delocalization in HFA is greater than in TFNO because the energy of the highest occupied MO for a carbonyl fragment is closer to the energy of the lowest unoccupied π-type orbital on the CF_3 groups than is that for the corresponding nitroxide fragment.

Morokuma demonstrated this by his INDO calculations on the CF_3H, H_2CO^-, and H_2NO molecules.[13] The energies of the highest occupied orbital of the latter two are shown to the left of Figure 2, while the energies of the highest occupied and lowest unoccupied orbitals of CF_3H are shown to the right of Figure 2. Since interaction between two coupled systems is generally proportional to the inverse of the energy separation, one thus expects a larger interaction (and hence greater delocalization) for a CF_3 group interacting with a carbonyl as opposed to the nitroxide. Also electron transfer occurs *into* the antibonding orbital of the CF_3 group. In a sense this is analogous to a "fluoride ion hyperconjugation"[25] mechanism.

Morokuma showed that the ratio of calculated INDO fluorine 2s spin densities for HFA and TFNO is 4.9 compared to 4.2, the ratio of the fluorine hfs's.[13] Similar agreement is found for the ratio of the CF_3 carbon 2s spin density to the ^{13}C hfs ratio and for the carbonyl carbon *vs.* nitrogen 2s spin densities. Thus we have reasonable confidence in extending the INDO calculations to PFCB and PFDK.

The INDO theory predicts a $\cos^2\theta$ dependence of the fluorine hfs for both HFA and TFNO;[13] θ is the dihedral angle between the CF bond and a line perpendicular to the molecular plane defined by the sp² hybridized carbonyl carbon. To an accuracy of four decimal places, for HFA

$$\rho_{2s}{}^F = 0.0024 \cos^2\theta \qquad (2)$$

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[21] This is in agreement with F. G. Herring, W. C. Zin, and M. R. Mustafer, *J. Magn. Resonance*, 2, 9 (1970).

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and for TFNO

$$\rho_{2s}{}^{F} = 0.0005 \cos^2 \theta \qquad (3)$$

If we assume that the fluorine hfs is proportional to $\rho_{2s}{}^{F}$, then[26] for HFA

$$a_{\beta}{}^{F} = 69.9 \cos^2 \theta \qquad (4)$$

and for TFNO

$$a_{\beta}{}^{F} = 16.5 \cos^2 \theta \qquad (5)$$

Thus from eq 1 $B_C\rho_C{}^{\pi} = 69.9$ G and $B_N\rho_N{}^{\pi} = 16.5$ G.

Before discussing the results for PFDK and PFCB, we must consider the important observation that *virtually no temperature dependence* is observed for the fluorine hfs in HFA and PFDK, whereas considerable temperature dependence of the fluorine hfs is observed for TFNO[11] and also for R–NO–C(Me)$_3$, where R = CF_2CF_3 or $CF(CF_3)_2$.[12d] We choose to interpret these results as indicating that the perfluorinated alkyl groups in HFA and PFDK are freely rotating at least within the time scale of the esr experiment (rotation rate $\gg 10^9$ Hz), whereas for TFNO and RNOC(Me)$_3$ the perfluorinated alkyl groups exhibit a hindered rotation. The reason for this different behavior may be that the C–N bond is shorter than the C–C bond. On the other hand, the HFA *vs.* TFNO results might be explained by assuming that HFA is planar but TFNO is slightly nonplanar such that the molecule is rapidly inverting. This would result in a low-inversion vibrational frequency. Higher temperatures would result in a greater degree of nonplanarity; this would cause an increase in a^N (as is observed) and possibly a decrease in a^F (due to decreased overlap with the nitroxide p orbitals). Nevertheless, whatever the explanation is, we must assume free rotation for the perfluorinated groups in HFA and PFDK. This is at variance with the conclusions of Janzen, *et al.*[12d]

It is tempting to assume that an equation such as eq 1 might apply to PFDK and PFCB. The INDO calculations show that $\rho_C{}^{\pi}$ does not vary much in this series. Thus, the fact that a^F in PFCB exceeds 69.9 G shows that eq 1 is not generally applicable, at least with a constant value of B_C. This should not be surprising, since the substitution of a CF_2 or CF_3 for one of the fluorines in the CF_3 groups of HFA will alter the energy of the CF_3 antibonding orbital and hence change the degree of delocalization. INDO calculations (see later) on both PFDK and PFCB indicate that this is indeed the case.

It is interesting to compare a^F for PFCB and PFDK. If we assume that the FCF bond angle in PFCB is 120° and the molecule is planar with CCC bond angles of 90°, then $\theta = 30°$ and $\cos^2 \theta = {}^3/_4$. For PFDK, $\cos^2 \theta = {}^1/_2$ if the CF_2CF_3 groups are freely rotating. Thus, if only orientation effects were present, we would expect a^F in PFCB and PFDK to be in the ratio of 1.5:1. The observed ratio is 1.44:1. Thus this appears to provide an experimental indication of an approximate $\cos^2 \theta$ dependence for a^F with a small or zero orientation-independent contribution. Indeed, INDO calculations give a ratio of $\rho_{2s}{}^{F} = 1.50:1$, in excellent agreement with experiment. However, the calculations do show that even though $\rho_{2s}{}^{F}$ is almost zero when $\theta = 90°$, there is some deviation from a $\cos^2 \theta$ dependence for $\rho_{2s}{}^{F}$.

The INDO calculations generally give a good overall correlation of calculated $\rho_{2s}{}^{F}$ with the experimental fluorine hfs, as shown in Table I. The only exception is the γ position in PFCB; however, it may be pushing the INDO theory too far to ask for good agreement out to the γ positions!

Table I. Comparison of Experimental Fluorine Hyperfine Splittings for HFA, PFCB, and PFDK with Those Calculated from INDO Theory

Radical	Position	INDO $\rho_{2s}{}^{F}$	a^F, G Exptl	a^F, G Calcd[a]
TFNO	β	0.00024[b]	8.3	8.9
HFA	β	0.00117[b]	34.9	43.6
PFCB	β	0.00221	84.4	82.3
PFCB	γ	0.00035	38.0	13.0
PFDK	β	0.00147[b]	58.5	54.7
PFDK	γ	0.00011[b]	3.9	4.1

[a] Calculated from $a^F = 37{,}200\rho_{2s}{}^{F}$; the γ splittings were omitted from a least-squares fit. [b] Averaged over all orientations of the group.

Conclusions

From this work we conclude that β-fluorine hfs's will in general *not be proportional to the π spin density on the adjacent π center.* Full agreement will be obtained only when all valence electrons are taken into account, as in the INDO theory. This theory does provide an excellent correlation of the data for the fluorine hfs's in the perfluorinated ketyls.

The INDO calculations indicate that the primary mechanism for spin delocalization into a perfluorinated alkyl group is *via* overlap of the fluorine p orbitals with the $2p_z$ orbitals of the π system. This overlap leads to a $\cos^2 \theta$ dependence for $a_{\beta}{}^{F}$; however, the constant of proportionality is expected to vary from one molecule to another.

Acknowledgments. We wish to thank Dr. D. C. England of Du Pont for a generous gift of perfluorocyclobutanone and Dr. D. W. Wiley of Du Pont for details of his patented synthesis of PFDK. Furthermore, we are indebted to the Numerical Analysis Center of the University of Minnesota for a grant of computer time. We would like to thank Dr. Fred Van Catledge for friendly discussions about INDO theory. We also thank Dr. William Gwinn for making available to us a computer program that calculates the Cartesian coordinates of the atoms of a molecule.

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[26] This corresponds to a hfs of ~32,000 G for one electron in a fluorine 2s orbital. This is too large by about a factor of ~2. It is characteristic of the INDO theory that fluorine spin densities are underestimated; however, correlations from one molecule to another are good.