Communications to the Editor

On Fluorine-19 Hyperfine Splittings in the Electron Spin Resonance Spectra of Fluorinated Aromatic Free Radicals

Sir:

The relationship,[1] $a_H = Q^H\rho_C^\pi$, adequately describes the hyperfine splittings observed in the esr spectra of aromatic hydrocarbon free radicals. Since fluorine is an atom with a nucleus similar to a proton in magnetic moment and spin, it is of interest to determine whether a similar relationship

$$a_F = Q_{eff}^F\rho_C^\pi \qquad (1)$$

will hold for fluorine-substituted aromatic radicals. Theory[2,3] seems to suggest that a more general relationship, such as

$$a_F = Q_{CF}^F\rho_C^\pi + (S^F + Q_{FC}^F)\rho_F^\pi \qquad (2)$$

is required.

The relatively small amount of presently available experimental data of fluorinated aromatic radicals[4-6] indicates that eq 1 may be adequate, at least in an approximate manner. This implies that the additional terms in the extended relationship for a_F are negligible or are proportional to the first term. However, the observed hyperfine splittings[7] in the neutral radical, tris(pentafluorophenyl)methyl, seem to be an important exception. The ratios of the fluorine hfs in this radical to the hydrogen hfs in triphenylmethyl at equivalent ring positions are not, even approximately, a constant. These results seem to demonstrate that eq 1 is inadequate, since all the available data indicate that fluorine substitution does not significantly alter the spin densitites in the aromatic rings. It has been suggested,[6] however, that the apparent discrepancies in the observed ratios, a_F/a_H, may be due to gross structural differences in the two radicals. This would manifest itself by a deviation in the configuration about the methyl carbon atom from planarity and a change in the spin densities in the rings.

In order to test this supposition, we have obtained the esr spectra of tris(2,6-difluorophenyl)methyl, which is the triphenylmethyl radical fluorinated in all the *ortho* positions but no others. The data are presented in Table I. The splitting constants were determined by computer simulation of the spectra and are accurate to about 3%. The spectra were taken on a standard Varian V-4502-12 epr spectrometer in toluene solution at room temperature. Structural factors, which could cause deviations in planarity and, perhaps, changes in spin densities in the ring positions, are similar in this radical and in the completely fluorinated radical. We see, however, that a_H(*para*) and a_H(*meta*) are almost the same as the unsubstituted radical. In addition a_F(*ortho*) is close to (but perhaps significantly different from) the value in the completely fluorinated radical.

Table I. Hyperfine Splitting Constants of the Triarylmethyl Radicals Discussed in the Text[a]

Radical	Position		a_F/a_H
Triphenylmethyl[b]	*ortho*	2.53	
	meta	1.11	
	para	2.77	
Tris(pentafluorophenyl)methyl[c]	*ortho*	2.76	1.09
	meta	1.61	1.45
	para	6.80	2.45
Tris(2,6-difluorophenyl)methyl[d]	*ortho*	2.11	0.83
	meta	1.06	
	para	2.61	

[a] All constants are in gauss. [b] D. B. Chestnut and G. J. Sloan, *J. Chem. Phys.*, **33**, 637 (1960). [c] Reference 7. [d] This work.

By comparing the data on the three radicals (triphenylmethyl, the completely fluorinated triphenylmethyl, and the *ortho*-fluorinated triphenylmethyl), we can conclude that structural effects caused by fluorine substitution in the *ortho* position do not change significantly the spin densities at the *para* and *meta* positions. Thus the lack of constancy in the observed ratios a_F/a_H(*para*) and a_F/a_H(*meta*) still require an explanation. The explicit inclusion of the second term in eq 2 would appear to be an adequate explanation. However, the problem of the anomalously low value of a_F/a_H(*ortho*) may not be explicable even on this basis. Allendoerfer and Maki[8] have suggested that a direct interaction between the methyl carbon atom and the *o*-fluorine nuclei is likely. Other possibilities are the inclusion of off-diagonal spin density matrix elements.[3]

We conclude from the data presented above that eq 1 is not sufficient to describe fluorine hfs in aromatic radicals, and that the whole question of the nature of fluorine splitting constants must still be considered open.

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Polarized Electronic Spectroscopy of Molecules Oriented by a Nematic Liquid Crystal[1]

Sir:

Very recent work has demonstrated that polarization data for electronic absorption bands may be obtained by orienting the molecules of interest in cholesteric liquid crystals.[2] In order to achieve uniform alignment in a cholesteric host, it is necessary to use large mag-

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