Communications to the Editor

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

Sir:

The relationship,[1] $a_{\rm H} = Q^{\rm H}\rho_{\rm C}^{\pi}$, 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

$$a_{\rm F} = Q_{\rm eff}{}^{\rm F}\rho_{\rm C}{}^{\pi} \qquad (1)$$

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

$$a_{\rm F} = Q_{\rm CF}{}^{\rm F}\rho_{\rm C}{}^{\pi} + (S^{\rm F} + Q_{\rm FC}{}^{\rm F})\rho_{\rm F}{}^{\pi} \qquad (2)$$

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 $a_{\rm F}$ 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, $a_{\rm F}/a_{\rm H}$, 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 $a_{\rm H}$(*para*) and $a_{\rm H}$(*meta*) are almost the same as the unsubstituted radical. In addition $a_{\rm F}$(*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		$a_{\rm F}/a_{\rm H}$
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 $a_{\rm F}/a_{\rm H}$(*para*) and $a_{\rm F}/a_{\rm H}$(*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 $a_{\rm F}/a_{\rm H}$(*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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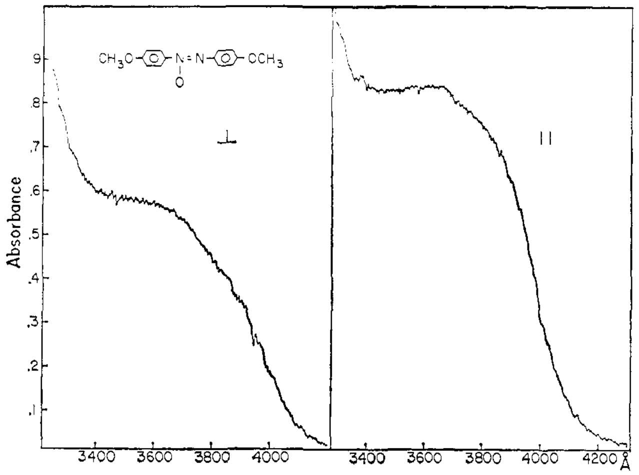

Figure 1. Polarized absorption spectra of 1×10^{-2} *M* *p*-azoxyanisole in the oriented nematic phase of *p*-(*p*'-ethoxybenzoxy)-phenyl butyl carbonate. The electric vector of light is polarized parallel and perpendicular to the long axis of the solvent molecules. Solvent begins to absorb appreciably at λ 3400 Å for || orientation and λ 3250 Å for ⊥ orientation.

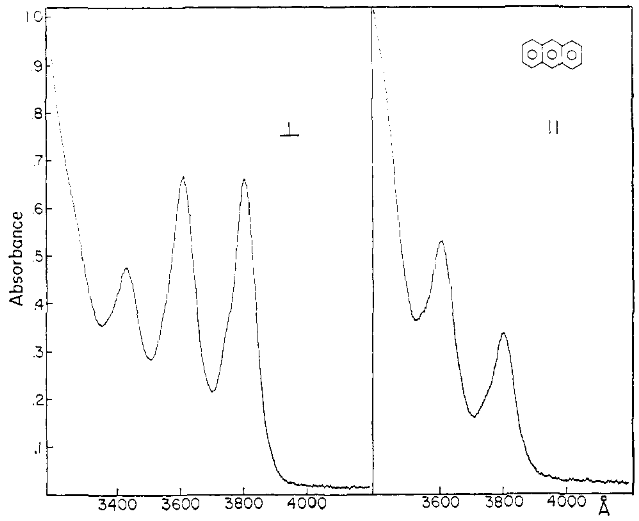

Figure 3. Polarized absorption spectra of a 1.7×10^{-2} *M* nematic solution of anthracene. The intense polarized short-wavelength band is due to the liquid crystal solvent. In the parallel spectrum, long-axis absorption by the solvent obscures the third band maximum of anthracene.

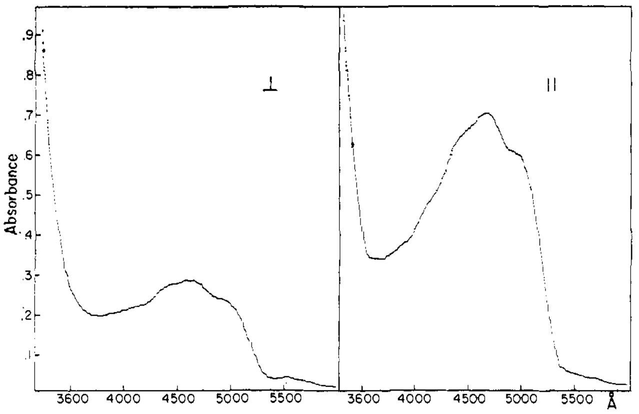

Figure 2. Polarized absorption spectra of 7×10^{-3} *M* β-carotene in nematic solvent. In the right-hand spectrum the electric vector of light is parallel, and in the left-hand spectrum perpendicular to the long axis of the solvent molecules.

netic fields (~20 kG) and then freeze in the resulting order. In addition, spectra must be corrected for anisotropic light scattering by the frozen liquid crystal solvent. We wish to describe a new method for measuring polarizations of electronic bands; this technique uses nematic liquid crystals as an orienting host and thereby avoids the aforementioned experimental difficulties. The present communication describes our initial measurements of band polarizations for selected organic molecules and transition metal complexes.

Solutions were prepared by dissolving 0.5 mg or less of solute in 100 mg of the nematic phase of *p*-(*p*'-ethoxybenzoxy)phenyl butyl carbonate.[3,4] Although this liquid crystal melts to the mesomorphic state at 54°, it can exist in a super-cooled nematic state for a considerable period of time; thus all measurements were made at ambient temperatures. Absorption spectra were taken with a Cary 14 spectrophotometer equipped with polarizing filters. The cells used in this study consisted of two quartz plates held in a stainless steel body and separated by a 0.005-cm Teflon spacer. The liquid crystal solution was oriented by simply rubbing the quartz plates in one direction before introducing the sample. As Chatelain first demonstrated,[5] this procedure is generally sufficient to achieve uniform alignment of the long axis of the liquid crystal molecules in the direction of rubbing.

It can be shown that the observed polarization data are related to the extinction coefficients along molecule-fixed axes, ϵ_x, ϵ_y, ϵ_z, in the following way.[6]

$$\epsilon_{\parallel} - \epsilon_{\perp} = S_{xx}\epsilon_x + S_{yy}\epsilon_y + S_{zz}\epsilon_z \qquad (1)$$

The quantities $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are the extinction coefficients measured with the electric vector of light parallel and perpendicular respectively, to the direction of alignment of the long axis of the liquid crystals; S_{ii} are parameters which describe the orientation of the solute in the liquid crystal matrix and are defined as

$$S_{ii} = \left\langle \frac{3\cos^2\theta_i - 1}{2} \right\rangle_{\text{average}}$$

where θ_i is the angle which the *i*th molecular axis makes with the long axis of the liquid crystal.

From the considerable amount of data which have been accumulated about orientation factors S_{ii} from liquid crystal nmr studies,[7] we have concluded that several useful generalizations can be made. Solute molecules align in the best packing arrangement; *e.g.*, planar molecules orient their long axis parallel to the alignment of the liquid crystal molecules. Thus, for all planar molecules which have been studied, S_{xx} for the long axis is positive, indicating parallel orientation, and S_{zz} for the axis out of plane is negative. The sign of S_{yy} is not as certain but for most long, planar molecules is negative.

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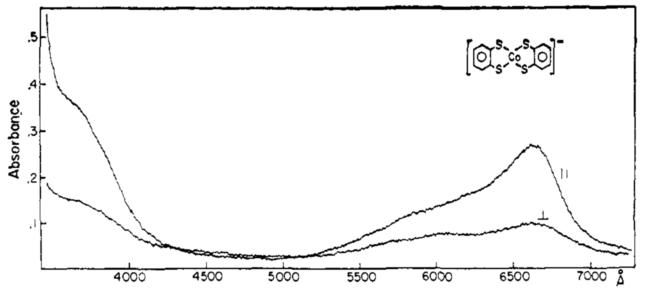

Figure 4. Polarized spectra of 8 × 10^{-3} *M* nematic solution of *n*-tetrabutylammonium bis(benzene-1,2-dithiolato)cobaltate. The electric vector of light is polarized parallel and perpendicular to the long axis of the solvent molecules.

Figures 1 and 2 show that $(\epsilon_{\parallel} - \epsilon_{\perp})$ is positive for the long-wavelength absorption bands of β-carotene and *p*-azoxyanisole. On the basis of eq 1 and the above discussion, we interpret this to mean that the electronic transitions in question are polarized along the long molecular axis $(\epsilon_x \gg \epsilon_y, \epsilon_z)$. This interpretation is in accord with other experiments.[2,8–10] As shown in Figure 3, $(\epsilon_{\parallel} - \epsilon_{\perp})$ for the lowest energy band system in anthracene is negative. Since ϵ_z for anthracene is expected to be nearly zero, the data indicate short-axis (*y*) polarization. Again, our interpretation agrees with previous work.[11–13] Thus it may be concluded that in the spectra studied here our generalizations concerning solute orientation are valid and that the technique is capable of reliable polarization information.

Figure 4 represents the first measurement of the polarizations of the lowest allowed bands in planar inorganic complexes of the monoanionic bis(benzenedithiolato)-metalate system. Both the 15,200- and 27,800-cm^{-1} bands in the $Co(bdt)_2^-$ complex are long-axis polarized. We have also measured the 25,400-cm^{-1} band in $Cu(bdt)_2^-$ and find it similarly polarized. These results provide strong support for a recent theoretical analysis[14] of the electronic structures of these complexes in which the bands are assigned to L → M charge-transfer transitions. For example, the assignment of the 25,400-cm^{-1} band in $Cu(bdt)_2^-$ as $b_{2u}L \rightarrow b_{1g}d\sigma^*$ is consistent with the *x* polarization.

As the above examples show, electronic spectroscopy in oriented nematic liquids provides a quick, simple method for obtaining band polarizations for both inorganic and organic molecules. The method perhaps will be most useful in studying intense bands, because it is not always possible to find a suitable host in single crystal work. We are presently investigating several representative metal complexes to test further the range of applicability of this technique.

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Magnetism and Structure of $[Cr_4(OH)_6(en)_6]^{6+}$ [1]

Sir:

The structure of Pfeiffer's cation,[2] $[Cr_4(OH)_6(en)_6]^{6+}$, has been a subject of recent interest. In an interpretation of magnetic susceptibility measurements on $[Cr_4(OH)_6(en)_6]I_6 \cdot 4H_2O$ from room temperature to liquid nitrogen temperature (77°K), Wentworth and Saillant[3] logically assumed that the arrangement of the four metals in the tetrameric complex is the same as in Werner's optically active inorganic ion,[4] $Co[(OH)_2Co(NH_3)_4]_3^{6+}$, namely, three metal(III) atoms surrounding a central metal(III) to form a trigonal planar array. Later it was pointed out[5] that a tetrahedral $[Cr(III)]_4$ unit is in better accord with the observed temperature dependence of the magnetic susceptibility than is the "Werner structure."

We have made magnetic susceptibility measurements on $[Cr_4(OH)_6(en)_6]I_6 \cdot 4H_2O$ and $[Cr_4(OH)_6(en)_6](N_3)_6 \cdot 4H_2O$ down to 4.2°K using a vibrating sample magnetometer with liquid helium dewar and found that neither of the above models is adequate over the wider temperature range. Theoretical curves[5] of μ_{eff}^2 *vs. T* for the tetrahedral and trigonal planar models are compared in Figure 1 with the experimental results for $[Cr_4(OH)_6(en)_6](N_3)_6 \cdot 4H_2O$. The calculated curve for trigonal planar structure is clearly in complete variance with experiment. And the theoretical curve for tetrahedral structure falls well below the experimental points starting at about 80°K.

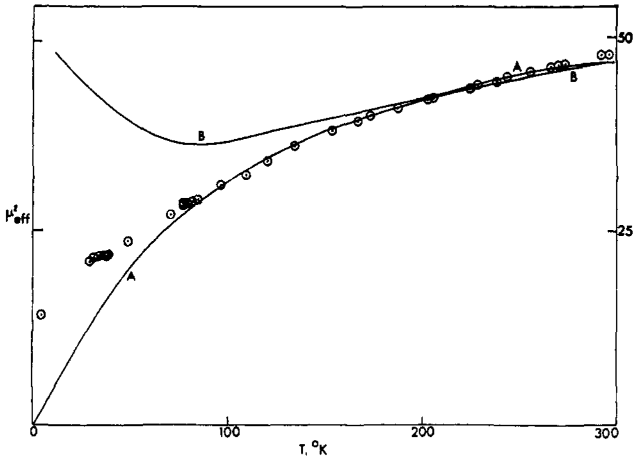

Figure 1. Plots of μ_{eff}^2 *vs. T:* (A) theoretical curve for a tetrahedral model with *S* = 3/2, *g* = 2.00, *J* = −10*k;* (B) theoretical curve for a trigonal planar model with *S* = 3/2, *g* = 2.00, *J* = −5*k;* (⊙) observed data for $[Cr_4(OH)_6(en)_6](N_3)_6 \cdot 4H_2O$.

We have resolved this question by determining the crystal and molecular structure of $[Cr_4(OH)_6(en)_6](N_3)_6 \cdot 4H_2O$. The structure was determined by conventional heavy-atom methods from data obtained from Cu Kα radiation and a Datex-automated General Electric

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