the G–C complex is partially dissociated and that a binary Zn–C complex is formed. Additional experiments would have to be carried out before a full interpretation of the effect of $ZnCl_2$ can be given.

G–U and C–U. By considering Figures 8(2, 4, 9), and 8(3, 4, 10) and recalling that zinc does not interact with uridine, we propose that in equimolar mixtures Zn–G–U and Zn–C–U only binary complexes Zn–G and Zn–C, respectively, are formed.

Acknowledgment. The authors are deeply indebted to Dr. E. D. Becker for his helpful comments on the manuscript.

Electron Spin Resonance Studies of Substituted Triphenylmethyl Radicals[1a]

J. Sinclair and D. Kivelson[1b]

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Abstract: The esr spectra of some substituted triphenylmethyl radicals in dilute liquid solution have been examined and the isotropic hyperfine splittings and *g* values were determined. Line-width studies at different temperatures and in various solvents were made on halogen-substituted radicals, and experimental evidence was obtained which indicated that nuclear quadrupole relaxation was the dominant line-broadening mechanism. The effect of substituent groups on the unpaired spin distribution, as determined by proton and C^{13} splittings, was found to be very slight. The fluorine π-spin density does not seem to contribute much to the isotropic splitting a_F, and the data could be fitted to the equation $a_F = Q_{eff}\rho_c^\pi$ where $Q_{eff} = 57$ G and ρ_c^π is the spin density on the carbon adjacent to the fluorine. This value of *Q* can be understood on the basis of existing theory. Chlorine hyperfine splittings, about 0.1 of the magnitude of the corresponding proton splittings, were observed. The effect of substituents on the isotropic *g* value was examined and correlated with the expected dependence on spin–orbit coupling.

The electron spin resonance spectra of the triphenylmethyl (TPM) radical and some substituted triphenylmethyl radicals in liquid solution have been reported by several workers.[2–5] Isoptropic proton and C^{13} hyperfine splitting constants, determined from these spectra, have been used to estimate spin densities.

In this work several substituted triphenylmethyl radicals have been prepared and their esr spectra in dilute solutions have been obtained. Besides obtaining information on the effect of the substituent on the unpaired spin distribution, one is able to examine hyperfine splittings arising from the substituents (halogen atoms, methyl groups, etc.), to study the line widths and from these to obtain information about the relaxation mechanisms, and to study the effect of the substituents on the *g* values of the radicals.

Although the esr spectra of these radicals are very complicated because of the large number of magnetic nuclei interacting with the unpaired electron, these compounds are useful in a study such as this because many different substituted radicals may be easily prepared, the compounds are relatively stable and easy to handle, the lines are very narrow (~0.070 G) and, therefore, small effects in coupling constants and line widths can be observed.

Experimental Section

The radicals were prepared by the method of Gomberg.[6,7] The solvents were of reagent grade and used without further purification. The apparatus used for preparing and handling the samples is described elsewhere.[8] The concentrations of the solutions were decreased until the effects of spin–spin exchange were eliminated. The concentrations were probably in the range 3×10^{-3} to 1×10^{-4} *M*.

The spectra were taken with a Varian X-band spectrometer employing 100-kc modulation and a Fieldial control unit. Temperatures were regulated and measured with the Varian variable temperature apparatus. The magnetic field strengths were measured with a Harvey-Wells Model G-502 nmr probe; the radiofrequencies of the probe were measured with a Beckman Model 6146 electronic counter. The *g* values were determined by placing the unknown into one chamber of a dual cavity and a standard in the other. The two signals were detected separately and displayed simultaneously on a dual-channel recorder. The primary standard used in *g* value measurements was *p*-benzosemiquinone negative ion ($g = 2.00468 \pm 0.00002$).[9] Since this radical is relatively unstable, dilute solutions of diphenylpicrylhydrazyl (DPPH) in toluene were used as a secondary standard ($g = 2.00359 \pm 0.00005$).[10]

The splitting constants were determined by comparing computer simulated spectra with the observed spectra. The simulated spectra were calculated with trial values of the hyperfine splitting constants, Lorentzian line shapes, and a single mean line width ΔH. The splitting constants were determined to about 3%.

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(1) (a) Supported in part by the National Science Foundation and the National Institutes of Health; (b) Alfred P. Sloan Fellow.

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(8) J. Sinclair, Ph.D. Thesis, University of California, Los Angeles, 1965.

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Table I. Observed Hyperfine Splitting Constants for Substituted Triphenylmethyl Radicals

Substituent	a_p[a]	a_o	a_m	$a_{C^{13}}$	a_{subst}	Ref
Unsubstituted[b]	2.78	2.53	1.11	26		1, 2, 4
3 *p*-Fluorines	...	2.70	1.13	24.5	6.50	*c*
3 *m*-Fluorines	2.85	2.64	1.09	...	1.56	*c*
3 *p*-Chlorines	...	2.55	1.14	...	0.21	5,*c*
3 *p*-Methoxy groups	...	2.89	1.05	22.9[c]	0.34	5
3 *p*-Nitro groups	...	2.50	1.14	...	0.66	3
1 *p*-Chlorine	2.75	2.53	1.14	...	0.21	*c*
2 *p*-Chlorines	2.75	2.55	1.14	...	0.21	*c*
1 *p*-Iodine	2.8	2.6	1.1	...	.	*c*
1 *p*-Fluorine	2.84	2.61	1.15	...	6.45	*c*
1 *o*-Methyl group	2.8	2.5	1.1	...	2.2	5
1 *p*-Methyl group	2.84	2.62	1.15	...	3.05	*c*
Tris(pentafluorophenyl)methyl[d]	6.80	2.76	1.61	118	...	*e*

[a] Values for the splitting constants are given in gauss. [b] The values obtained in this work for unsubstituted TPM are $a_p = 2.77$, $a_o = 2.53$, $a_m = 1.11$. [c] This work. [d] The values given here are for *para*-, *meta*-, and *ortho*-substituted fluorines. [e] C. Trapp, C. S. Wang, and R. Filler, *J. Chem. Phys.*, **45**, 3472 (1966).

Results

The hyperfine constants for various substituted triphenylmethyl radicals are given in Table I; the *g* values are given in Table II.

Table II. Data on *g* Values for the Substituted Triphenylmethyl Radicals

Substituent	*g* value[a]	λ_{sub}, cm^{-1}	$\delta g \times 10^4$ [b]	$\rho/\Delta E \times 10^7$
H	2.00266	...	...	...
1 *p*-Fluorine	2.00275	λ_F 271	0.9	5.0 ± 3
3 *p*-Fluorines	2.00302	λ_F 271	3.6	6.7 ± 1
3 *m*-Fluorines	2.00260	λ_F 271	−0.6	−1.1 ± 1
1 *p*-Chlorine	2.00298	λ_{Cl} 587	3.2	8.2 ± 1.3
2 *p*-Chlorines	2.00319	λ_{Cl} 587	5.3	7.0 ± 0.7
3 *p*-Chlorines	2.00332	λ_{Cl} 587	6.6	5.7 ± 0.4
1 *p*-Iodine	2.00328	λ_I 5060	6.2	1.9 ± 0.2
1 *p*-Methyl	2.00267	λ_C 28	0.1	5.4[c]
1 *m*-Chlorine	2.00252	λ_{Cl} 587	−1.4	−3.6 ± 1.2

[a] Error estimated at ±0.00005. [b] $\delta g = g_s - g_{TPM}$, where g_s is the *g* value of the substituted triphenylmethyl, and g_{TPM} is the *g* value for triphenylmethyl. [c] Very uncertain.

The tri(*p*-methoxyphenyl)methyl radical was prepared with 61% C^{13} in the central position. Figure 1 gives the esr spectrum of a 3×10^{-3} *M* toluene solution of the C^{13}-enriched compound as a function of temperature. The traces show that the two outer groups of lines, those due to the C^{13} species in 61% abundance, broaden with decreasing temperature while the central group, which arises from the C^{12} species, sharpens. This can be understood by noting that as the temperature of the solution is decreased the viscosity increases and the molecular tumbling motion is slowed; the anisotropic dipolar interaction of the electron with the C^{13} nucleus becomes an effective spin relaxation path. Since C^{12} has zero nuclear moment this relaxation mechanism is not operative in the C^{12} species. The sharpening of the C^{12} lines at lower temperatures is due to the decrease of the spin–spin exchange with the decrease of the radical–radical collision rate.[11,12]

An examination of a resolved spectrum of the C^{13}-enriched species reveals that the high-field components have slightly larger line widths than do the corresponding low-field components. In analogy with the results of Mackor and de Boer[13] this would indicate that the C^{13} nuclear hyperfine splitting is positive for this radical. This sign is in agreement with the calculations of Karplus and Fraenkel.[14]

The esr spectrum of tri(*p*-fluorophenyl)methyl in ether at −25° is shown in Figure 2a. Figure 2b gives a computer reconstructed spectrum. This radical was also prepared with 61% C^{13} in the central position. Examination of corresponding high- and low-field lines of the C^{13} spectrum revealed that the high-field lines were broader; therefore, $a_c > 0$.

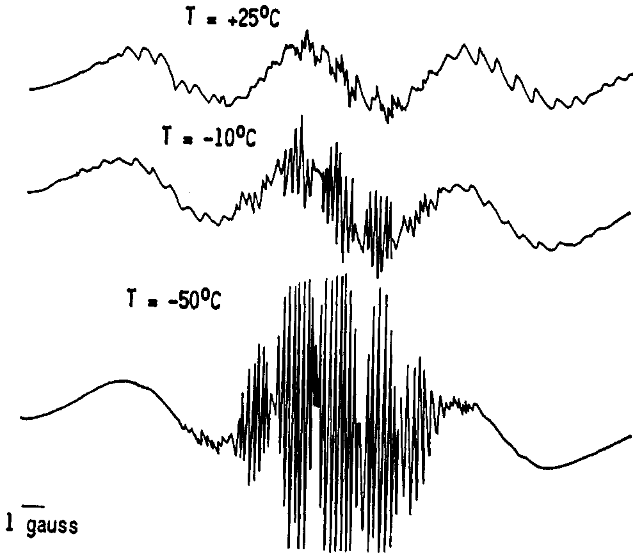

Figure 1. Resolution of the esr spectrum of tri(*p*-methoxylphenyl)-methyl-C^{13} in toluene solution as a function of temperature.

From the asymmetry of the observed spectrum of the C^{13} species relative to that of the C^{12} spectrum, the second-order shift in the C^{13} spectrum was observed to be 0.13 ± 0.05 G to lower fields, while the calculated shift, assuming $a_c = 24.5$ G, is 0.092 to lower fields.

p-Chlorophenyldiphenylmethyl was prepared in order to examine the effect of chlorine atoms on the unpaired spin distribution, and to determine whether or not isotropic chlorine hyperfine splittings could be resolved.

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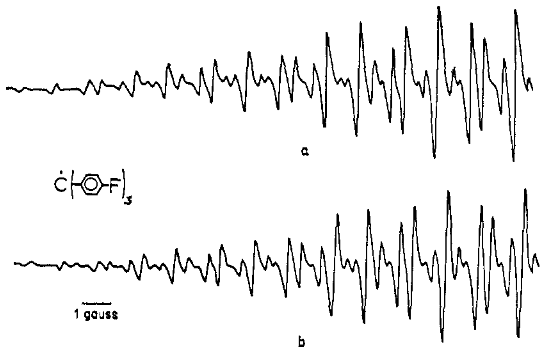

Figure 2. One-half of the experimental (a) and reconstructed (b) esr spectra of an ether solution of tri(*p*-fluorophenyl)methyl at $T = 25°$, $\Delta H = 0.08$ G; $a_o = 2.70$; $a_m = 1.13$; $a_F = 6.50$.

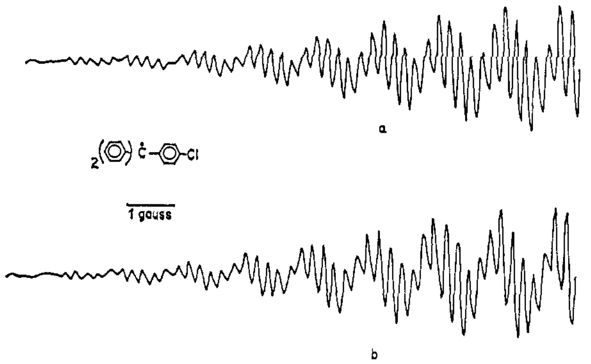

Figure 3. One-half of the experimental (a) and reconstructed (b) esr spectra of *p*-chlorodiphenylmethyl in ether solution at $T = -50°$, $\Delta H = 0.12$ G; $a_p = 2.75$; $a_o = 2.53$; $a_m = 1.14$; $a_{Cl} = 0.21$.

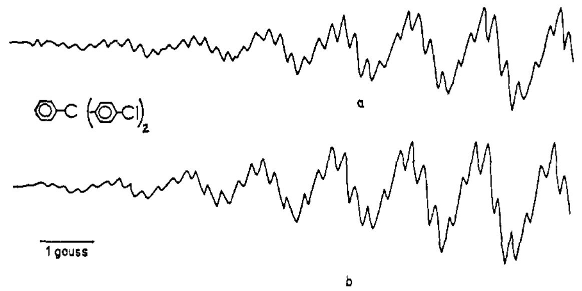

Figure 4. One-half of the experimental (a) and reconstructed (b) esr spectra of the di(*p*-chlorophenyl)phenylmethyl in ether solution at $T = -20°$, $\Delta H = 0.18$ G; $a_p = 2.75$; $a_o = 2.55$; $a_m = 1.14$; $a_{Cl} = 0.21$.

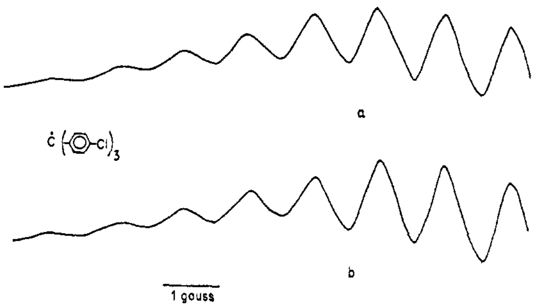

Figure 5. One-half of the experimental (a) and reconstructed (b) esr spectra of the tri(*p*-chlorophenyl)methyl in toluene solution at room temperature, $\Delta H = 0.21$ G; $a_o = 2.55$; $a_m = 1.14$; $a_{Cl} = 0.21$.

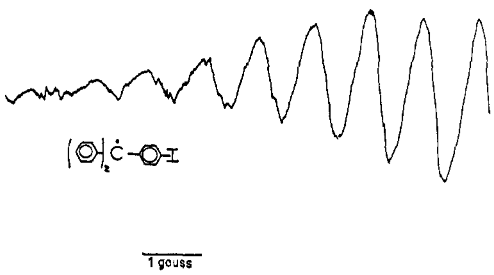

Figure 6. The observed esr spectrum of *p*-iodophenyldiphenylmethyl in ether solution at $T = 60°$.

Chlorine-35 (75% abundance) has a nuclear spin of $^{3}/_{2}$ and a nuclear moment of 0.821 nuclear magneton, while Cl^{37} (25% abundance) has a spin of $^{3}/_{2}$ and a nuclear moment of 0.683 nuclear magneton; thus, each chlorine nucleus would further split each line of the esr spectrum into four additional components. The difference in the splitting due to the two chlorine isotopes could not be resolved. Figure 3a gives one-half of the observed spectrum in ether solution at −50°, while Figure 3b gives a reconstructed spectrum. As the temperature of an ether solution of this radical is lowered, the lines increase in width until at approximately −90° the 0.21-G line separation is smeared out. This broadening effect was also observed in toluene and benzyl ether solutions, except in these solutions the temperatures at which the lines smear out were higher than that for the ether solution (−40° for toluene and +40° for benzyl ether). These effects are discussed elsewhere.[8]

Di(*p*-chlorophenyl)phenylmethyl was prepared in order to determine whether or not chlorine hyperfine splittings could be observed, and to examine the effect of viscosity and temperature on the resolution of the spectrum. Figure 4 gives the experimental and reconstructed spectra. The 0.18-G line width used in the reconstructed spectra is considerably larger than the 0.12-G line width used for the monochloro compound. As in the monochloro case, the resolution of the spectra in ether and toluene solutions of this radical decreased as the temperature was lowered. The temperatures at which resolution was lost are −50° for ether solutions and 0° for toluene solutions.

The esr spectrum of tri(*p*-chlorophenyl)methyl was first examined in toluene solution by Judeikis and Kivelson.[5] The experimental and reconstructed spectra are shown in Figure 5. The line width of 0.21 G is greater than that for the dichloro compound.

The esr spectrum of *p*-iodophenyldiphenylmethyl at −60° in ether solution is given in Figure 6. Iodine has a nuclear spin of $^{5}/_{2}$ and a nuclear moment of 2.79 nuclear magnetons. Consequently, each hyperfine line should be split into six lines due to the interaction with this atom. From the observed line widths one can put an upper limit on a_I of about 0.035 G; this assumes the entire line width is due to unresolved hyperfine splittings. As the temperature of an ether solution was increased from −70° the lines broadened. Since the line widths did not seem to vary with increased dilution, the line breadth was not due to spin–spin exchange. Other relaxation mechanisms will be discussed below.

p-Tolyldiphenylmethyl was examined and its esr spectrum was found to consist of about 170 lines with a mean line width of 0.075 G. The methyl splitting, a_{CH_3}, was determined to be 3.05 G; thus, Q_{CH_3} equals 26 G, where $Q_{CH_3} = (a_{CH_3}/\rho_c^\pi)$, and ρ_c^π is the *p*-carbon spin density in unsubstituted triphenylmethyl.[4,5] Other workers report values for Q_{CH_3} in the range 25–28 G.[15]

Discussion of Fluorine Splittings

Considerable interest has focused recently on the interpretation of isotropic fluorine hyperfine splitting constants in fluorine-substituted free radicals.[16–23] The fluorine nucleus has a nuclear spin of $^1/_2$ and a nuclear moment of 2.627 nuclear magnetons; thus, it is very similar in its magnetic properties to a proton with $I = {}^1/_2$ and $\mu = 2.793$ nuclear magnetons. Maki and Geske[16] have suggested that isotropic fluorine splittings in organic radicals obey an equation of the form

$$a_F = Q_{eff}{}^F \rho_c \tag{1}$$

where ρ_c^π is the π-electron spin density on the carbon adjacent to the fluorine and $Q_{eff}{}^F$ is a constant on the order of 55 G. This equation is of the same form as the expression used to relate proton hyperfine splittings, a_H, to ρ_c with a $Q_{CH}{}^H$ equal to -23 G.[17] From the data in Table I it can be seen that for substituted triphenylmethyl radicals the proton splitting constants, and hence the spin densities, ρ_c^π, adjacent to the protons are not appreciably affected by substitution at other positions. Consequently, it is reasonable to assume that the value of ρ_c^π adjacent to a fluorine has approximately the same value when a proton is substituted for the fluorine. In Table III the observed splitting constants, ρ_c^π's, and $Q_{eff}{}^F$'s determined for various radicals are presented. A least-squares fit of the a_F *vs.* ρ_c^π data suggests a value of about 57 G for $Q_{eff}{}^F$. Since the signs of some of the splittings are not known we have assumed that a_F has the same sign as ρ_c^π; we have also neglected the data for N,N′-di(*m*-fluorophenyl)aminotroponeimineatenickel(II). These procedures will be discussed below.

Since the fluorine atom is capable of π-bonding with the adjacent carbon atom, we must consider the possibility of finding unpaired π-electron density directly on the fluorine; this, of course, does not occur with a proton. A suitable expression for a_F might be[18–24]

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

where $Q_{CF}{}^F$ and $Q_{FC}{}^F$ are the polarizations of the σ bond joining the carbon and fluorine by the unpaired electron densities on the carbon (ρ_c^π) and fluorine (ρ_F^π), respectively, and S^F represents the polarization of the fluorine 1s orbital by the spin on the fluorine. Equation 2 is similar to the expression proposed by Karplus and Fraenkel for isotropic C^{13} splittings.[14]

The attempts to fit the observed esr data on isotropic fluorine splittings to eq 2 have been discussed and criticized by Fraenkel, *et al.*[18] The conclusion that these authors reached is that there is no consistent set of parameters which will reproduce the observed splittings. One difficulty lies in the inability to make accurate estimates of ρ_F^π, the π-spin density on the fluorine atom.

Table III. Observed Fluorine Splitting Constants and Carbon Spin Densities for Various Fluorine-Substituted π-Free Radicals

Compound	ρ_c^π [a]	a_F, G	Q_{eff},[b] G	Ref
Tri(*p*-fluorophenyl)-methyl	0.117	6.50[a]	55.5	*d*
Tri(*m*-fluorophenyl)-methyl	−0.047	1.56[a]	33.9	*d*
p-Fluoronitrobenzene negative ion	0.170	8.41[a]	49.5	16
Monofluoroacetamide	0.975[c]	+56.3[a]	+57.3	*e*
m-Fluoronitrobenzene negative ion	−0.045	3.0[a]	64.7	*f*
N,N′-Di(*p*-fluoro-phenyl)aminotro-poneimineate	0.0107	+0.526[a]	+47.3	*g*
p-Fluoroacetophenone	0.078	3.78[a]	48.6	*h*
Tetrafluorobenzosemi-quinone ion	0.100	4.41[a]	44.1	*i*
N,N′-Di(*m*-Fluoro-phenyl)aminotropone-imineate	−0.0081	−0.033[b]	+4.0	*g*
γ-(*p*-Fluorophenyl)azo-aminotropone-imineate	0.0096	+0.505[b]	+52.6	*j*
3,5-Difluoronitro-benzene negative ion	−0.045	−2.73[b]	+60.5	*k*

[a] The spin densities were determined by assuming that fluorine substitution has not changed the π density on the adjacent carbon. ρ_c^π is thus a_H/Q_{CH} with $Q_{CH} = -23.7$ G. [b] The signs of the numbers are assumed to be unknown unless it is explicitly written. All values are in gauss. [c] This value was obtained from the proton splitting. [d] This work. [e] D. Wiffen, R. Cook, and J. Rowland, *Mol. Phys.*, **7**, 31 (1963). [f] R. Wilson, P. Asycough, and F. Sargent, *J. Chem. Soc.*, 5418 (1963). [g] D. Baton, J. Josey, W. Phillips, and R. Benson, *Mol. Phys.*, **5**, 407 (1962). [h] M. Das and G. Fraenkel, *J. Chem. Phys.*, 1350 (1965). [i] D. Anderson, D. Frank, and H. Gutowsky, *ibid.*, **32**, 196 (1960). [j] W. Phillips, D. Eaton, D. Josey, R. Benson, and T. Cairns, *J. Amer. Chem. Soc.*, **84**, 4100 (1962). [k] G. Fraenkel, M. Kaplan, and J. Bolton, *J. Chem. Phys.*, **42**, 955 (1965).

From this, and previous work, the main facts about fluorine splittings that have emerged are (1) substitution of a fluorine atom for a hydrogen atom in an organic radical produces only slight perturbations on the unpaired electron distribution; (2) there is an approximately linear proportionality between a_F and ρ_c^π, where ρ_c^π is measured in the hydrogen-substituted radical; (3) the sign of the proportionality constant, $Q_{eff}{}^F$, is positive. This last fact has been demonstrated in at least four cases: in the work of Phillips, *et al.*,[19,20] where nmr contact shifts in fluorophenyl-substituted aminotroponeimineates were examined; in the line-width analysis in 2,5-difluoronitrobenzene negative ion;[18] in the work of Fessenden and Schuler who found a_F and a_c to be of the same sign in fluorinated methyl radicals;[21] and finally, in the work presented here. We have looked carefully at the esr spectra of the *p*-fluorophenyldiphenylmethyl radical in benzyl ether at 0° and noted that the high-field components were slightly broader than the corresponding low-field components. The contribution to the traceless part of the hyperfine interaction, and hence to the line broading, probably depends much more on the spin density ρ_F^π than on π_c^π.[22]

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(16) A. Maki and D. Geske, *J. Amer. Chem. Soc.*, **83**, 1852 (1961).
(17) H. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).
(18) See Table III, footnote *k*.
(19) See Table III, footnote *g*.
(20) See Table III, footnote *j*.
(21) R. Fessenden and R. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965).
(22) See Table III, footnote *e*.
(23) A. Carrington, A. Hudson, and H. Longuet-Higgins, *Mol. Phys.*, **9**, 377 (1965).
(24) See Table III, footnote *i*.

The line widths can then be analyzed in the same manner as that developed by Mackor and deBoer,[13] and from this analysis we conclude that $a_F > 0$ for *p*-fluorophenyldiphenylmethyl.

By comparing eq 1 and 2 we see that Q_{eff}^F may be written as

$$Q_{eff}^F = Q_{CF}^F + (\rho_F^\pi/\rho_c^\pi)Q' \qquad (3)$$

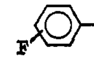
where $Q' = Q_{FC}^F + S^F$. Q_{CF}^F is interpreted as the parameter which measures the polarization of the σ-bonding orbitals by the unpaired spin density on the adjacent carbon atom. The value of the corresponding constant in the CH case is well established at -23 G.[17] The values of Q_{CX}^X for atoms other than X equal to H have been reported in the literature. Stone and Maki[25] give $Q_{CN}^N = -2$ G for *p*-azine ions, Gulick and Geske give $Q_{CO}^O = -16.7$ G in the *p*-benzosemiquinone negative ion,[26] and Karplus and Fraenkel give $Q_{CC'}^{C'} = -13.9$ G.[14]

In principle Q_{CF}^F could be obtained from a plot of measured values of Q_{eff}^F *vs.* ρ_F^π/ρ_c^π for a series of fluorine-substituted compounds; however, ρ_F^π/ρ_c^π is an exceedingly difficult quantity to obtain. Theoretical estimates of ρ_F^π/ρ_c^π were made for a number of compounds. The results are listed in Table IV. The McLachlan approximate SCF method[27] was used with the Hückel heteroatom parameters $\gamma_{CF} = \beta_{CF}/\beta_{cc} = 0.619$ and $h_F = (\alpha_F - \alpha_c)/\beta_{cc} = 2.5$, 1.7, and 1.1.[18,19,27,28] A least-squares treatment gives $Q_{CF}^F = +37.5$, $+54.0$, and $+45.5$ G for $h_F = 2.5$, 1.7, and 1.1, respectively. It is hard to assess the reliability of these predictions in view of the crude manner in which ρ_F^π/ρ_c^π was obtained.

Table IV. Calculated Values of ρ_F^π/ρ_c^π

Compound	ρ_F^π/ρ_c^π		
	$h_F = 2.5$	$h_F = 1.7$	$h_F = 1.1$
Tri(*p*-fluorophenyl)methyl	0.0346	0.0513	0.125
Tri(*m*-fluorophenyl)methyl	0.0443	0.0802	0.141
p-Fluoronitrobenzene negative ion	0.0295	0.0464	0.0840
m-Fluoronitrobenzene negative ion	0.0441	0.0819	0.1401
N,N′-Di(*p*-fluorophenyl)aminotroponeimineate[a]	0.0351	0.1125	1.445
Tetrafluorobenzosemiquinone ion	0.0341	0.0667	...
N,N′-Di(*m*-fluorophenyl)aminotroponeimineate[a]	0.0313	0.941	...

[a] These values were calculated on the fragment



using the nitrogen parameters of $h_N = 1.3$ and $\gamma_{CN} = 0.836$.

These calculations seem to indicate that $|(S^F + Q_{FC}^F)\rho_F^\pi| \ll |\rho_c^\pi Q_{CF}^F|$, that ρ_F^π/ρ_c^π does not vary much from compound to compound, and, consequently, that eq 1 with $Q_{eff}^F = 57$ G is a reasonable approximation for the more detailed relationship, eq 2. It is probably not unreasonable to assume that $(S^F + Q_{FC}^F)$ is similar to the value found for the free fluorine atom, *i.e.*, $+36$ G;[29,30] this correspondence appears to be true for the carbon atom.[14,31] This would imply that $(S_F + Q_{FC}^F)\rho_F^\pi$ is indeed very small in the compounds measured here.

As Table III indicates, the value of Q_{eff}^F for the di(*m*-fluorophenyl)aminotroponeimineate compound is completely out of line with the other values. This result is usually taken as an indication that an equation such as eq 1 is totally inadequate to explain isotropic fluorine splittings. We have calculated the quantity $(\rho_c^\pi)_F/(\rho_c^\pi)_H$, according to the approximate SCF procedure, for the series of fluorine-substituted compounds listed in Table III. $(\rho_c^\pi)_F$ is the spin density at the carbon adjacent to the fluorine, and $(\rho_c^\pi)_H$ is the spin density at this position for the hydrogen-substituted case. (For the aminotroponeimineates the fluorophenylamine fragment was used as a model.) For all the compounds except the di(*m*-fluorophenyl)aminotroponeimineate, this ratio was in the range 0.9–1.0 which indicates that fluorine substitution does not perturb the adjacent carbon spin density. On the other hand, the calculation on the *m*-fluoroaminotroponeimineate gives values considerably less than unity. Thus, the low observed value for Q_{eff}^F may be due to a low value of ρ_c^π. Again, it is difficult to assess the reliability of the predictions of these calculations.

It is interesting to compare the values of Q_{CF}^F, Q_{CN}^N, Q_{CO}^O, Q_{CH}^H, and $Q_{CC'}^{C'}$. The magnetic moment of the oxygen nucleus is negative whereas the moments for the the other nuclei are positive; thus, Q divided by the nuclear moment is negative for H, C, N and positive for O and F. According to the theory of Pople and Santry[32] this is predictable because this quotient depends on the energy differences between the 2s and 2p orbitals; if the difference is great the quotient is positive, as in F and O.

The results of esr measurements on the completely fluorinated triphenylmethyl radical in solution are given in Table I.[33] The values for the *para* and *meta* isotropic fluorine hyperfine splittings are very similar to those obtained in this work. Furthermore, the results on the totally fluorinated radical give a value for the hyperfine splitting of an *o*-fluorine. The discussion above predicts a value of approximately 2.5 for a_F/a_H, but for the *ortho* position the ratio appears to be about 1. This apparent disagreement may arise because of gross structural difference between triphenylmethyl and the totally fluorinated radical. Such structural differences might also explain why the carbon-13 hyperfine interaction is so different in the two radicals: $a_C = 118$ G in the fluorinated radical and $a_C = 45$ G[4] in triphenylmethyl radical. This suggests that the configuration around the methyl carbon might deviate about 10° from planarity in the fluorinated radical.

Chlorine Hyperfine Splittings. Not enough data have been accumulated on isotropic chlorine splittings to discuss them theoretically. The experimental data are presented in Table V. If we assume an equation of the form of eq 1, then

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$$a_{\mathrm{Cl}} = Q_{\mathrm{eff}}{}^{\mathrm{Cl}}\rho_{\mathrm{c}}{}^{\pi} \tag{4}$$

and we can write

$$\frac{a_{\mathrm{F}}}{a_{\mathrm{Cl}}} = \frac{\gamma_{\mathrm{F}}|S(0)|_{\mathrm{F}}{}^2\rho_{\mathrm{F}}{}^{\mathrm{S}}}{\gamma_{\mathrm{Cl}}|S(0)|_{\mathrm{Cl}}{}^2\rho_{\mathrm{Cl}}{}^{\mathrm{S}}} \tag{5}$$

where ρ^{s} is the unpaired spin population in the corresponding s orbital, *e.g.*, 2s for fluorine and 3s for chlorine. γ_{F} and γ_{Cl} are the gyromagnetic ratios of the fluorine and chlorine nuclei, respectively, $|S(0)|_{\mathrm{F}}{}^2$ is the probability of an electron in a 2s fluorine orbital being found at the nucleus, and $|S(0)|_{\mathrm{Cl}}{}^2$ is the corresponding quantity for the chlorine 3s orbital. We can readily evaluate this ratio[34] as

$$\frac{a_{\mathrm{F}}}{a_{\mathrm{Cl}}} = 10.3(\rho_{\mathrm{F}}{}^{\mathrm{s}}/\rho_{\mathrm{Cl}}{}^{\mathrm{s}}) \tag{6}$$

This result, along with the data in Table V, indicates that $(\rho_{\mathrm{F}}{}^{\mathrm{s}}/\rho_{\mathrm{Cl}}{}^{\mathrm{s}})$ is in the range 1.5–3.0.

Table V. Observed Chlorine Hyperfine Splitting Constants and Carbon Spin Densities for Various Chlorine-Substituted Free Radicals

Compound	a_{Cl}, G	$\rho_c{}^{\pi a}$	$Q_{\mathrm{eff}}{}^{\mathrm{Cl}}$, G	$a_{\mathrm{F}}/a_{\mathrm{Cl}}$
Chloroacetic acid radical[b]	3.7	0.875	4.2	15.2
p-Chloronitrobenzene negative ion[c]	0.24	0.170	1.4	35
p-Chlorophenyl-diphenylmethyl	0.21	0.117	1.2	31

[a] Obtained from proton splittings of $Q_{\mathrm{CH}}{}^{\mathrm{H}} = -23$ G, assuming $\rho_{\mathrm{c}}{}^{\pi}$ is unchanged by chlorine substitution. [b] R. Norman and W. Dixon, 6th International Symposium on Free Radicals, Cambridge, 1964. [c] See Table III, footnote *f*.

Chlorine Line Widths. The resolution of the esr spectra of the *p*-chloro-substituted triphenylmethyl radicals is strongly dependent on the viscosity and temperature of the solutions in which the spectra are taken. The apparent line widths are approximately additive with each additional *p*-chlorine atom and are more or less proportional to η/T, where η is the viscosity. These widths are discussed more fully elsewhere,[8] but it appears likely that the principal relaxation process depends upon the modulation of the nuclear quadrupole moment by Brownian motion. Both chlorine and iodine have quadrupole moments. The tumbling of the molecule in liquid solution produces a time-varying interaction between the local electric fields and the quadrupole moments which induces relaxation of the nuclear spin states with a relaxation time T_{N}. Since the nuclear spins are coupled to the electron spin through the hyperfine term, a, it is possible that the relaxing nucleus will affect the lifetime of the electronic spin state, and hence the esr line widths. If $aT_{\mathrm{N}} \gg 1$, resolvable hyperfine splittings of the halogen should be observed, and the esr line widths should be approximately $T_{\mathrm{N}}{}^{-1}$, *i.e.*, proportional to η/T. This is observed for the chlorine-substituted compounds. If $aT_{\mathrm{N}} \ll 1$, the nucleus relaxes so rapidly that the electron sees only an average of the nuclear spin states, and, therefore, no hyperfine splittings are observed. The esr line widths are then approximately a^2T_{N} and are proportional to T/η. For the iodine-substituted compounds this behavior was observed. Because of the large quadrupole moment of the iodine nucleus, it relaxes very rapidly and no iodine splittings can be observed. These ideas may also explain the observation that chlorine splittings are observed in only a few of the cases in which chlorine-substituted radicals have been studied.

***g* Values.** The g values of free radicals differ from that of a free electron spin ($g = 2.0023$) because of a combination of spin–orbit and orbital Zeeman interactions.[35] The spin–orbit coupling constant, λ_i, for the *i*th atom increases with increasing atomic number. The shift in isotropic g values, δg, due to the substitution of a heavy atom for a proton in an aromatic ring is approximately[8]

$$\delta g = \frac{2}{3}\sum_i \frac{\lambda_i \rho_i}{\Delta E_i} \tag{7}$$

where ρ_i is the unpolarized (Hückel) spin density on the substituted heavy atom and ΔE_i is the energy gap between the ground state π orbital and a nonbonding orbital on the substituent atom. In deriving this equation it has been assumed that this nonbonding orbital is a p-type orbital, that it is the only important excited orbital for the unpaired electron, and that spin polarization effects can be neglected.

Table II lists the isotropic g values, spin–orbit coupling constants λ, shifts in g values, δg, due to the substituted groups, and values of $\rho_i/\Delta E$ calculated by means of eq 7. If eq 7 is valid, $(\rho_i/\Delta E)$ should be the same for the singly and triply substituted *p*-fluorotriphenylmethyl radicals; to within experimental error this appears to be true. However, $\rho_i/\Delta E$ should have the same value for the singly, doubly, and triply chlorine substituted triphenylmethyls; the discrepancies lie slightly outside the experimental error. Blois, *et al.*,[9] found a very nearly linear relation between g and λ for the tetrahalogenated *p*-benzosemiquinone ions. This suggests that the various halogens in equivalent positions have similar values of $\rho_i/\Delta E$. In our data, the *p*-iodo compound has an anomalously low value of $\rho_i/\Delta E$.

Equation 7 predicts that if the unpolarized (Hückel) spin density vanishes then $\delta g = 0$. This appears to be true even if spin polarization is taken into account according to the McLachlan SCF theory.[8] The Hückel spin density at a *m*-carbon in triphenylmethyl is zero; therefore, the Hückel spin density on a halogen attached to a *m*-carbon most likely is very close to zero. Consequently, we would expect $\delta g = 0$ for *m*-halotriphenylmethyls. But the data on the *m*-fluoro- and *m*-chloro-substituted triphenylmethyls appears to yield negative values for δg. This suggests that δg is proportional to the total spin density, unpolarized and polarized, since the total spin density at the *meta* position is negative.

The g value reported for the totally fluorinated triphenylmethyl is 2.0033.[33] With this result we can calculate $\rho/\Delta E$ for an *o*-fluorine by means of eq 7 if the values given in Table II for the $\rho/\Delta E$ of the *m*- and *p*-fluorines are used. The result for an *o*-fluorine is $\rho/\Delta E = +3.3 \times 10^{-7}$. The positive sign for this quantity is expected since the unpaired electron density on the fluorine would be expected to have the same sign as the unpaired density on the adjacent carbon. The magnitude of $\rho/\Delta E$ for the *o*-fluorine is less than

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those for the *p*-fluorines. This may be an indication that the unpaired electron density at the *o*-carbon is appreciably less than in normal triphenylmethyl. This could possibly explain the low value for the *o*-fluorine hyperfine splitting observed in the completely fluorinated triphenylmethyl.

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Electron Spin Resonance and Polarographic Studies of the Anion Radicals of Heterocyclic Amine N-Oxides[1]

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Abstract: Polarograms of 30 heterocyclic amine N-oxides were recorded in dimethylformamide at about 25°. Electron spin resonance (esr) spectra of radical anions formed during controlled-potential electrolysis at the potential corresponding to the first reduction wave were observed for 16 of the oxides. The hydrogen (a_H) and nitrogen (a_N) hyperfine coupling constants were determined by the method of spectral simulation. With 4-cyano- and 4-nitropyridine N-oxide anion radicals, deuterium substitution was used to confirm the analysis. HMO calculations with the McLachlan modification, where the necessary parameters were chosen to give agreement with the a_H's of pyrazine di-N-oxide, 4-cyanopyridine N-oxide, and pyrazine mono-N-oxide, yielded the following linear relations between calculated spin density, ρ, and experimental coupling constant for the compounds studied: $a_H = -25.7\rho_C$ and $a_N = 42.6\rho_N - 6.7(\rho_C + \rho_C') - 19.0\rho_O$. Also, using fewer parameters, a_N was satisfactorily expressed by $a_N = 41.9\rho_N - 2.1$. In addition, esr spectra of the anion radicals of pyridine N-oxide and its 2,6-dideuterio derivative were observed during electrolysis in liquid ammonia. The comparison of the a_H's and a_N so observed with the calculated values using the equations given above was in a good agreement. Also the polarographic data were analyzed in terms of radical stability and were related to the esr results as follows. The peak height of the ac polarogram and the half-wave potential ($E_{1/2}$) of the first reduction wave are approximately linearly related to the radical stability. Moreover, the $E_{1/2}$ is in linear relation with the lowest vacant MO energy (ϵ_{LV}) and also with the Hammett σ value of a series of substituted pyridine N-oxides. Thus, $E_{1/2} = 2.75\epsilon_{LV} - 0.77$ and $-E_{1/2} = 1.08\,\sigma - 2.19$. The results are compared with those of related compounds reported in the literature.

The physicochemical nature and molecular interaction ability of heterocyclic amine N-oxides such as pyridine N-oxide, quinoline N-oxide, etc. have been studied from experimental and theoretical points of view.[2,3] These studies, however, have been mainly limited to the neutral amine N-oxides with the exceptions of the anion radicals of pyridine N-oxide[4] and 4-nitropyridine N-oxide[5] and the neutral radical[6] produced from 4-hydroxyaminoquinoline N-oxide, whose esr spectra were reported. There has been no systematic study of the nature of the anion radicals of the tertiary amine N-oxides.

In the course of the polarographic studies of heterocyclic amine N-oxides, it has been shown[7] that anion radicals may be produced by the reduction method of controlled-potential electrolysis in nonaqueous solvents. In the case of compounds such as 4-cyano- and 4-nitropyridine N-oxides, the produced anion radicals were relatively stable. As an extension of these studies, we report the esr spectra and their interpretations of the anion radicals of some heterocyclic amine N-oxides obtained by the above technique. Also the polarographic data recorded in dimethylformamide (DMF) are related to the esr results, and the half-wave reduction potential ($E_{1/2}$) is related linearly to the lowest vacant MO (LVMO) energy and also to the Hammett σ constant.

Previous Hückel MO (HMO) and antisymmetrized MO calculations of some basic heterocyclic amine N-oxides used to interpret the electronic spectra, dipole moments, etc. have suggested[8] that the character of intramolecular charge transfer from the oxygen to the rest of the π system is determined by the LVMO, which may be occupied by an electron to produce an anion radical. This suggested that the above calculations would be very useful in analyzing the hyperfine coupling (hfc) constants of the esr spectra reported here, and, conversely, the information obtained during the present study would be a valuable check on the previous MO calculations.

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