first part can be reasonably estimated by a minimal basis set, even though the full process is not described satisfactorily. The extended 4-31G basis, on the other hand, handles both parts well.

Since use of the extended basis involves considerable computation, it cannot easily be applied to larger organic molecules. Under these circumstances the STO-3G basis, the simpler of the two minimal basis sets, should be valuable in estimating bond separation energies. These may then be used in conjunction with more accurately known energies for the parents to predict stabilities of large organic molecules.

Acknowledgment. This research was supported in part by National Science Foundation Grant No. GP-9338.

Appendix

Table V reports the optimum valence shell ζ values used in this study. For computational efficiency, these were calculated using the LEMAO-4G representation. Previous work has shown such ζ's to be systematically close to the 6-Gaussian values.[9] The ζ's for all nonequivalent atoms (with the exception that hydrogen atoms attached to the same heavy atom are given the same ζ) were varied in steps of 0.01 until the total energy was minimized. Two to three optimization cycles on the complete set result in ζ's accurate to 0.003 or better. Final runs were then made with the LEMAO-6G basis using these ζ values.

---

(9) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, in press.

On Fluorine-19 Hyperfine Splittings in the Electron Spin Resonance Spectra of Fluorinated Aromatic Free Radicals. II. Triphenylmethyl Radicals[1]

Shrikant V. Kulkarni and Charles Trapp[2]

Contribution from the Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616, and the Department of Chemistry, University of Louisville, Louisville, Kentucky 40208. *Received October 20, 1969*

Abstract: The electron spin resonance spectra of symmetrically fluorinated triphenylmethyl radicals have been obtained. The fluorine-19 hyperfine interactions have been correlated with the spin densities on the fluorine atoms calculated by an approximate MO method with the use of the two-parameter equation, $a_F = Q_{CF}{}^F\rho_C{}^\pi + Q_{FC}{}^F\rho_F{}^\pi$. The estimated values of the parameters are $Q_{CF}{}^F = -85$ and $Q_{FC}{}^F = 1043$ G. These values of the parameters are consistent to within 8% in correlating all the experimental data not only on the series of fluorinated triphenylmethyl radicals but also on another series of fluorinated aromatic radicals (see following article, part III[1b]). The estimated maximum uncertainty in the parameters is about 20%. Contrary to what has been generally assumed, the results of this investigation suggest that in aromatic radicals a_F and $\rho_C{}^\pi$ can have opposite signs. Evidence for a direct interaction between *o*-fluorine atoms and spin density on the methyl carbon atom is presented.

McConnell's relationship,[3] $a_H = Q_{CH}{}^H\rho_C{}^\pi$, has successfully related the observed proton hyperfine splittings, a_H, in the electron spin resonance (esr) spectra of aromatic hydrocarbon radicals, to the spin densities, $\rho_C{}^\pi$, in the π-electron system on the contiguous carbon atoms. $Q_{CH}{}^H$ is a proportionality constant generally determined from experiment, but which can also be calculated approximately from theory.[3] Fluorine-19, which occurs in 100% natural abundance, is a nucleus similar to the proton in magnetic moment and spin. Until recently there have been only a few esr studies on fluorinated aromatic free radicals. The results of these early esr investigations,[4–7] as well as some early nuclear magnetic resonance (nmr) studies,[8,9] indicated that the simple linear relationship

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

analogous to McConnells' relationship for protons may not be adequate to describe the data on fluorinated compounds.

In order to explain their nmr results on a series of fluorine-substituted aminotroponiminates, Eaton, *et al.*,[8,9] proposed a modified relationship, which we will write as

$$a_F = Q_{CF}{}^F\rho_C{}^\pi + Q_{FC}{}^F\rho_F{}^\pi \tag{2}$$

---

[1] (a) Part I has been published as a communication: S. V. Kulkarni and C. Trapp, *J. Amer. Chem. Soc.*, **91**, 191 (1969). (b) Part III: S. V. Kulkarni and C. Trapp, *ibid.*, **92**, 4809 (1970). (c) This work was presented in part at the Symposium on Fluorine-Containing Free Radicals held during the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 8–12, 1969. (d) Details of this work may be found in the thesis of S. V. Kulkarni, submitted in partial fulfillment of the requirements for the Ph.D. degree, to the graduate school of Illinois Institute of Technology, Chicago, Ill., June 1969.

[2] Address correspondence to this author at the Department of Chemistry, University of Louisville.

[3] (a) H. M. McConnell, *J. Chem. Phys.*, **24**, 632, 764 (1956); (b) H. S. Jarrett, *ibid.*, **25**, 1289 (1956).

[4] D. H. Anderson, P. J. Frank, and H. S. Gutowsky, *ibid.*, **32**, 196 (1960).

[5] A. H. Maki and D. H. Geske, *J. Amer. Chem. Soc.*, **83**, 1852 (1961).

[6] A. Carrington, A. Hudson, and H. C. Longuet-Higgins, *Mol. Phys.*, **9**, 377 (1965).

[7] M. Kaplan, J. R. Bolton, and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 955 (1965).

[8] D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Mol. Phys.*, **5**, 407 (1962).

[9] D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L. Cairns, *J. Amer. Chem. Soc.*, **84**, 4100 (1962).

ρ_F^π is the spin density in the π-electron system of the fluorine atom under consideration. Q_{FC}^F represents the effective polarization of the s orbitals on the fluorine atom resulting from the spin density ρ_F^π. Equation 2 seems more realistic than eq 1 in that it allows for conjugation of the fluorine atom orbitals with the π electrons in the aromatic ring. Nevertheless, there has been considerable controversy as to whether or not eq 2 fits the data sufficiently better than eq 1 to justify its use. More general relationships than eq 2 have also been proposed.[10]

A number of additional studies of fluorinated aromatic free radicals have recently appeared in the literature.[1a,11-18] Some authors[14,15] tend to prefer eq 1 as an adequate representation of their results, whereas others[1a,16,17] seem to prefer eq 2. This question is not easily settled in an unambiguous manner, primarily because of the difficulty in measuring or estimating the rather small values of ρ_F^π. Previously no even moderately consistent set of parameters, applicable to more than one type of compound, has been found for use in eq 2. In this paper we describe our experimental results on a number of symmetrically fluorinated triphenylmethyl radicals, as well as some calculations of ρ_F^π's, which lead to a reasonably consistent set of parameters, Q_{CF}^F and Q_{FC}^F. In the following paper (part III)[1b] we describe the experimental results on a series of symmetrically fluorinated benzophenone anion radicals and show that the parameters obtained for the triphenylmethyl radicals apply rather well to this series of compounds also.

The series of symmetrically fluorinated triphenylmethyl radicals was chosen for the initial study because this system has a number of inherent advantages. Firstly, the symmetrically fluorinated radicals were expected to give relatively simple spectra (no more complicated than triphenylmethyl itself), and thus fairly accurate values of the hyperfine splittings (hfs) could be obtained. Secondly, all these radicals are neutral odd-alternant radicals, hence there was no need to consider any possible effects on the hfs resulting from uncompensated charges. The odd-alternant property of these radicals is useful in that negative spin densities are likely to occur as well as positive spin densities, and thus the set of parameters obtained should be more reliable than if the system had contained only positive spin densities. Also from the point of view of the molecular orbital calculations of spin densities, the odd electron in these radicals occupies a nonbonding orbital which is considerably removed energetically from the other filled molecular orbitals. As a result, small perturbations introduced due to fluorine substitution[1a,8,15] do not cause scrambling of the energy levels.

During the course of our investigations, three studies on fluorine-substituted triphenylmethyl radicals were published in the literature.[13,15,16] Except for the radical tris(*p*-fluorophenyl)methyl, there is no overlap between these data and ours. These previous studies were primarily on unsymmetrically fluorinated radicals and the data obtained were not in themselves sufficient to obtain a consistent set of parameters for eq. 2

Experimental Section

All eight triphenylmethyl radicals (Table I) were prepared from the corresponding carbinols. Three of the carbinols were generously supplied by Professor Robert Filler. The rest were made by Grignard reactions or by using *n*-butyllithium and diethyl carbonate on suitable halogenated benzenes. Details of the procedure can be found elsewhere.[1d] The carbinols were converted to the corresponding triarylmethyl radicals by generation and subsequent reduction of the carbonium ions.[11]

Table I. Observed Hyperfine Splitting Constants[a] in Fluorine-[b] Substituted Triphenylmethyl Radicals in Toluene

Radicals	a_p	a_m	a_o
Triphenylmethyl	2.745	1.105	2.53
Tris(4-fluorophenyl)methyl	$\underline{6.26}$	1.102	2.61
Tris(2,6-difluorophenyl)methyl	2.60	1.06	2.11
Tris(3,5-difluorophenyl)methyl	2.52	$\underline{1.67}$	2.14
Tris(pentafluorophenyl)methyl[c]	$\underline{6.80}$	$\underline{1.61}$	$\underline{2.76}$
Tris(4-methyltetrafluorophenyl)-methyl	2.73	$\underline{1.65}$	$\underline{2.60}$
Tris(4-methoxytetrafluorophenyl)-methyl	0.190	$\underline{1.57}$	$\underline{2.53}$
Tris(4-trifluoromethyltetrafluoro-phenyl)methyl	2.825	$\underline{1.83}$	$\underline{2.72}$

[a] All the hyperfine splitting constants in gauss. [b] Fluorine hyperfine splittings are underlined. [c] Reference 11.

A search for appropriate reagents for the preparation of the desired carbonium ion and its reduction to the radical led to the use of trifluoroacetic acid and chromium(II) perchlorate. Moodie, *et al.*,[19] have reported the use of a trifluoroacetic acid and trifluoroacetic anhydride solvent system in their nmr studies of triarylcarbonium ions. Chromium(II) was preferred as a reducingg agent rather than titanium(III), as previously reported for the completely fluorinated triphenylmethyl radical,[11] because of their relative reduction potentials.[20] Since chromium(II) is easily oxidized by atmospheric oxygen, the solution of chromium(II) perchlorate was kept under a layer of light oil and was dispensed directly into the carbonium-ion-containing solutions. Perchlorate was chosen as counterion because it is a poor nucleophilic agent. This procedure has been found to be a most general procedure for the preparation of radicals of this type. Specific details of the procedure for the preparation of the various radicals may be found elsewhere.[1d]

Electron spin resonance spectra of all the radicals were obtained on a Varian Associates Model V-4502-12 X-band spectrometer using 100-kc field modulation and a 9-in. electromagnet. A Varian Associates Model V-4533 cylindrical cavity was used for all the measurements. The samples were contained in cylindrical quartz sample tubes. Highly accurate measurements of the *g* values of the radicals were not made, and thus are not reported here individually. In all cases, however, the *g* values were found to be within 0.1% of the free-electron *g* value. Various spectra of the same radical were obtained using different modulation amplitudes and different radical concentrations in order to get maximum

---

(10) A. Hinchliffe and J. N. Murrell, *Mol. Phys.*, **14**, 147 (1968).

(11) C. Trapp, C. S. Wang, and R. Filler, *J. Chem. Phys.*, **45**, 3472 (1966).

(12) J. K. Brown and W. G. Williams, *Trans. Faraday Soc.*, **64**, 298 (1968).

(13) A. H. Maki, R. D. Allendoerfer, J. C. Danner, and R. T. Keys, *J. Amer. Chem. Soc.*, **90**, 4225 (1968).

(14) P. H. H. Fischer and H. Zimmermann, *Can. J. Chem.*, **46**, 3847 (1968).

(15) J. Sinclair and D. Kivelson, *J. Amer. Chem. Soc.*, **91**, 1088 (1969).

(16) R. D. Allendoerfer and A. H. Maki, *ibid.*, **91**, 1088 (1969).

(17) W. G. Espersen and R. W. Kreilick, *Mol. Phys.*, **16**, 577 (1969).

(18) W. E. Geiger, Jr., and W. M. Gulick, Jr., *J. Amer. Chem. Soc.*, **91**, 4657 (1969).

(19) R. B. Moodie, T. M. Connor, and R. Stewart, *Can. J. Chem.*, **37**, 1402 (1959).

(20) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1962.

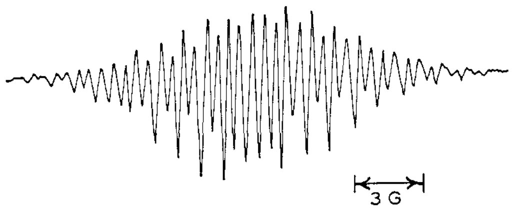

Figure 1. The esr first-derivative spectrum of tris(2,6-difluorophenyl)methyl radical–F_6 in toluene solution at room temperature.

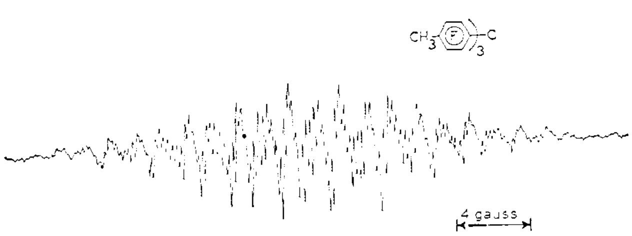

Figure 2. The esr first-derivative spectrum of tris(4-methyltetrafluorophenyl)methyl radical–F_{12} in toluene solution at room temperature.

possible resolution. In general the spectra obtained were very well resolved.

In some cases it was possible to obtain the values of the hfs constants directly from the spectra but computer simulation of the spectra was usually carried out. A SESRS[21] program routine for simulation of the esr spectra was adapted for use on an IBM Model 7094 computer and a Calcomp plotter. The final assignments for the hfs constants were based on the comparison of the experimental and computed spectra. The splitting constants were determined to within 1–3 % depending upon the magnitude of the constants.

Results

Triphenylmethyl Radical. A highly resolved spectrum of triphenylmethyl radical in toluene was obtained in which 120 hfs lines out of a possible 196 lines were observed. The spectrum compared favorably with that reported by Chestnut and Sloan.[22] Our values for the splitting constants (Table I) are only slightly different from those reported previously,[13,22–24] but we felt that it was worthwhile to obtain the spectrum of the parent compound of the series on the same apparatus used for the fluorinated triphenylmethyl radicals. An unequivocal assignment of the observed hfs constants to the ring positions was made by studying the esr spectra of a series of symmetrically deuterated triphenylmethyl radicals.[25]

Tris(pentafluorophenyl)methyl–F_{15} Radical. The esr spectrum of this radical in toluene solution at room temperature was very similar to the spectrum of the radical in benzene solution reported previously by Trapp, *et al.*[11] The simulated spectrum confirmed the values for the hfs constants (Table I) reported previously.[11] A variable temperature study of the spectrum did not show any markedly noticeable changes in the spectrum, except at low temperatures near the melting point of toluene.

Tris(4-fluorophenyl)methyl–F_3 radical. The spectrum of this radical has been observed previously by Sinclair and Kivelson[15] and Maki, *et al.*[16] Our values for the hfs constants are 3–4 % lower than their values on the average. The difference is only slightly larger than the expected experimental error, and thus may not be significant.

Tris(2,6-difluorophenyl)methyl–F_6 Radical. Our preliminary results on this radical have been previously reported.[1a] The esr spectrum of the radical in toluene solution at room temperature is shown in Figure 1. The value of the hfs constants could only be determined by computer simulation. The hfs splitting constants determined for this radical are given in Table I. We note that these values do not compare well with the hfs constants determined by Allendoerfer and Maki[16] on the (*o*-fluorophenyl)diphenylmethyl radical. In particular their *o*-fluorine splitting of 1.35 G is considerably below ours. It is possible that the unsymmetrical nature of the latter radical has resulted in a spin distribution which is considerably different. On the other hand, the complex nature of the spectrum in this unsymmetrical molecule could possibly have resulted in an incorrect determination of the constants.

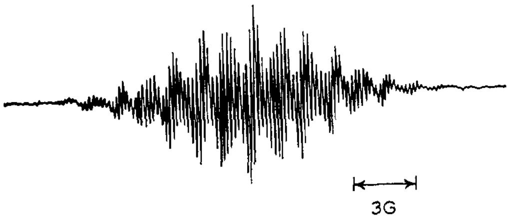

Figure 3. The esr first-derivative spectrum of tris(4-methoxytetrafluorophenyl)methyl radical–F_{12} in toluene solution at room temperature.

Tris(3,5-difluorophenyl)methyl–F_6 Radical. Considerable difficulty was encountered in obtaining a well-resolved spectrum of this radical even at lower temperatures. The splitting constants could only be obtained from a computer simulation of the spectrum. The results are presented in Table I. No figure containing the spectrum is presented here, since the experimental spectra obtained were too long and narrow to be reduced to a meaningful figure. Esr data on this radical have not been reported previously.

Tris(4-methyltetrafluorophenyl)methyl–F_{12} Radical. The esr spectrum of this radical has not been observed before. Figure 2 shows a highly resolved spectrum of the radical in toluene solution at room temperature.

Tris(4-methoxytetrafluorophenyl)methyl–F_{12} Radical. A highly resolved spectrum of this radical is presented in Figure 3. The nine protons of the methoxy group were assigned a hyperfine splitting constant of 0.190 G. A computer simulation of the spectrum was not necessary to determine the hfs constants given in Table I. The esr spectrum of this radical has not been reported previously.

Tris(4-trifluoromethyltetrafluorophenyl)methyl–F_{21} Radical. This compound was found to be a very stable radical which exhibited a resonance in the solid state similar to that reported on the tris(pentafluorophenyl)methyl radical.[11] The esr spectrum in toluene solution at room temperature is shown in Figure 4. The spectrum of this radical has also not been observed previously.

---

[21] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **38**, 1999 (1963). We thank Professor A. H. Maki for providing us with a copy of the SESRS program.

[22] D. B. Chestnut and G. J. Sloan, *ibid.*, **33**, 637 (1960).

[23] P. B. Ayscough, A. P. McCann, and R. Wilson, *Proc. Chem. Soc., London*, 16 (1961).

[24] J. S. Hyde, *J. Chem. Phys.*, 43, 1806 (1965).

[25] S. V. Kulkarni and C. Trapp, in preparation.

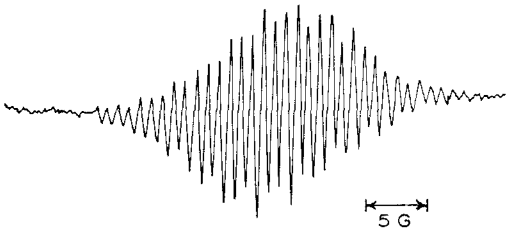

Figure 4. The esr first-derivative spectrum of tris(4-trifluoromethyltetrafluorophenyl)methyl radical–F_{21} in toluene solution at room temperature.

Spin Density Calculations

The unpaired spin density in a free radical can be defined as the difference between the charge density of electrons of α spin and electrons of β spin at a given atomic position in the molecule. Thus, for purposes of calculation it is convenient to assume that the unpaired electron has α spin. Of the various approaches to the calculation of spin densities, reviewed recently by Hall and Amos,[26] the McLachlan perturbation approximation to self-consistent field theory[27] has been found to be the best method, overall, from the point of view of convenience and accuracy.[13,28] The perturbation method is based on known self-consistent orbitals and neglect of the exchange integral of bonds. McLachlan[27] also found that Hückel orbitals could be used in place of the self-consistent orbitals without introducing appreciable error. All the calculations reported here have been based on Hückel orbitals. The spin densities were calculated from the equation

$$\rho_r = |\psi_{or}|^2 + \sum_{i=1}^{occ}[|\psi_{ir}'|^2 - |\psi_{ir}|^2] \qquad (3)$$

where $\psi_1, \psi_2, \ldots, \psi_n$ are ordinary Hückel orbitals and $\psi_1, \psi_2, \ldots, \psi_n$ are calculated with β_{rs} unchanged, but where $\alpha_r = 2\lambda C_{or}{}^2\beta$.

The determination of the parameters, $Q_{CF}{}^F$ and $Q_{FC}{}^F$, by fitting the experimental data to eq 2 requires a reasonably accurate method of estimating $\rho_C{}^\pi$ and $\rho_F{}^\pi$. We have used the following procedure in determination of $\rho_C{}^\pi$ and $\rho_F{}^\pi$. Firstly, we attempted to fit the data on the proton splittings in triphenylmethyl, itself, as closely as we possibly could. $\rho_C{}^\pi$ for the ring positions in triphenylmethyl was determined from the experimental a_H's with the use of McConnell's relationship. As described in more detail below, it was possible to obtain almost an exact fit to the data on triphenylmethyl by the adjustment of the coulomb and resonance parameters associated with the methyl carbon atom, and also the empirical parameter, λ, in the McLachlan-type spin density calculations. Thus, in a sense, the positions in triphenylmethyl which were to be fluorine substituted were forced to fit the experimental spin densities. The exact values of the magnitudes of the parameters employed to accomplish this are not likely to be highly significant in themselves. Their real significance is that, since fluorine substitution is known to produce little change in the spin density distribution in the aromatic rings, they should also provide accurate values for the spin densities at carbon positions which are fluorine substituted in the fluorinated radicals. The same values of the coulomb and resonance parameters of the methyl carbon atom and the SCF parameter, λ, which were found to reproduce accurately the experimental spin densities in triphenylmethyl itself, were employed in the calculations on the fluorinated radicals. As expected, it is found in these calculations that fluorine substitution does not alter very much the calculated spin densities in the ring. The calculated values of $\rho_C{}^\pi$ can be checked experimentally at unsubstituted ring positions in the fluorinated radicals by comparing the experimental proton hfs constants with the values calculated with McConnell's relationship. The calculated and experimental carbon spin densities, $\rho_C{}^\pi$, at the proton position agree very well. In fact, it was generally possible to predict the direction of the small change in $\rho_C{}^\pi$ at the proton positions resulting from fluorine substitution. The proton splittings, thus, served as a check upon the accuracy of the spin density calculations. Consequently, we believe that it was not necessary to be overly concerned about the meaning of the particular values employed for the parameters.

The accuracy of the calculated values of $\rho_F{}^\pi$ cannot, of course, be checked by direct comparison with experiment, as is the case with $\rho_C{}^\pi$ at proton positions. Indeed, the use of McLachlan's semiempirical MO method for the calculation of spin densities at heteroatoms such as fluorine is somewhat questionable. Certainly the values obtained will not be highly accurate; however, the fact that the calculated values of $\rho_C{}^\pi$ in the incompletely fluorinated radicals agree to within 2–3% of the experimental values implies that the error in $\rho_F{}^\pi$ is probably not much worse than 30%. This conclusion is based on the fact that the calculated spin densities add up to unity and that the ratio, $\rho_C{}^\pi/\rho_F{}^\pi$, is not much greater than ten. In the following paragraphs more details of the spin density calculations employed in the interpretation of the data are presented.

Triphenylmethyl Radical. In all the Hückel and McLachlan calculations previously found in the literature, the value of the coulomb integral of the methyl carbon atom was taken to be the same as that of the other carbon atoms in the molecule. This results in equal spin densities at the *ortho* and *para* carbon atoms, which is contrary to the experimental observation. We have shown recently[28] that surprisingly good agreement with experiment can be obtained if the methyl carbon atom in triphenylmethyl is treated as a heteroatom in the McLachlan calculation. The coulomb integral is then

$$\alpha_{Me} = \alpha_0 + h_{Me}\beta_0 \qquad (4)$$

The sign of h_{Me} is determined by electronegativity considerations,[28] and its magnitude is determined by varying h_{Me} to obtain the best agreement with experiment. The value of h_{Me} thus obtained was −0.9. It is interesting to note that a similar value of h_{Me} for the methyl carbon atom in the benzyl radical was also found[28] to give good agreement with the data on that radical. This leads us to believe that our procedure of fitting the data may have some real validity; perhaps even the magnitude of parameter employed may have some meaning. However, as discussed above, the validity of the results of the calculations of carbon

---

(26) C. G. Hall and A. T. Amos, *Advan. At. Mol. Phys.*, 1, 36 (1965).
(27) A. D. McLachlan, *Mol. Phys.*, 3, 233 (1960).
(28) S. V. Kulkarni and C. Trapp, *ibid.*, 17, 209 (1969).

Table II. Calculated Spin Densities for Fluorinated Triphenylmethyl Radicals[a,b]

Compound	ρ_1	ρ_4	ρ_{10}	ρ_{16}	ρ_{19}	ρ_{20}	ρ_{23}	ρ_{29}
Triphenylmethyl								
Hückel molecular orbital	0.0765	0.0017	0.0697	0.0	0.298			
Approximate SCF; McLachlan								
$\lambda = 1.2$	0.1026	−0.0333	0.0947	−0.018	0.378			
$\lambda = 1.6$	0.1103	−0.0449	0.1027	−0.0301	0.4127			
Tris(4-fluorophenyl)methyl								
Hückel molecular orbital	0.0751	0.0007	0.0702	0.0132	0.2987	0.0036		
Approximate SCF; McLachlan								
$\lambda = 1.2$	0.0995	−0.0337	0.0966	−0.0206	0.3837	0.0028		
$\lambda = 1.6$	0.1065	−0.0443	0.1030	−0.0331	0.4205	0.0024		
Tris(2,6-difluorophenyl)methyl								
Hückel molecular orbital	0.0788	0.0025	0.0682	0.0117	0.2887			0.0032
Approximate SCF; McLachlan								
$\lambda = 1.2$	0.1060	−0.0315	0.0922	−0.0224	0.3694			0.0025
$\lambda = 1.6$	0.1146	−0.0428	0.1001	−0.0348	0.4035			0.0022
Tris(3,5-difluorophenyl)methyl								
Hückel molecular orbital	0.0740	0.0017	0.0704	0.0147	0.3010		0.0001	
Approximate SCF; McLachlan								
$\lambda = 1.2$	0.0988	−0.0319	0.0959	−0.0207	0.3829		−0.0015	
$\lambda = 1.6$	0.1058	−0.0430	0.1041	−0.0300	0.4183		−0.0020	
Tris(pentafluorophenyl)methyl								
Hückel molecular orbital	0.0742	0.0012	0.0694	0.0105	0.2928	0.0034	0.0006	0.0032
Approximate SCF; McLachlan								
$\lambda = 1.2$	0.0996	−0.0323	0.0955	−0.0245	0.3796	0.0029	−0.0014	0.0026
$\lambda = 1.6$	0.1072	−0.0434	0.1042	−0.0374	0.4165	0.0025	−0.0019	0.0024
Tris(4-methyltetrafluorophenyl)methyl								
Hückel molecular orbital	0.0742	0.0011	0.06953	0.0104	0.2933	0.0032	0.0001	0.0032
Approximate SCF; McLachlan								
$\lambda = 1.2$	0.0996	−0.0325	0.0958	−0.0248	0.3803	0.0009	−0.0014	0.0026
$\lambda = 1.6$	0.1071	−0.0436	0.1044	−0.0377	0.4173	0.0026	−0.0020	0.0024
Tris(4-methoxytetrafluorophenyl)methyl								
Hückel molecular orbital	0.0743	0.0013	0.0694	0.0106	0.2928	0.0029[c] (0.00002)	0.0001	0.0032
Approximate SCF; McLachlan								
$\lambda = 1.2$	0.0999	−0.0321	0.0954	−0.0243	0.3791	0.0024 (0.00003)	−0.0014	0.0027
$\lambda = 1.6$	0.1076	−0.0433	0.1040	−0.0371	0.4157	0.0022 (0.00003)	−0.0019	0.0024
Tris(4-trifluoromethyltetrafluorophenyl)methyl								
Hückel molecular orbital	0.0736	0.0008	0.0694	0.0099	0.2927	0.0053	0.00004	0.0032
Approximate SCF; McLachlan								
$\lambda = 1.2$	0.0983	−0.0328	0.0961	−0.0254	0.3815	0.0042	−0.0014	0.0027
$\lambda = 1.6$	0.1059	−0.0445	0.1048	−0.0387	0.4194	0.0048	−0.0020	0.0024

[a] See Figure 5 for labeling of positions. [b] In all these calculations methyl carbon was treated as a heteroatom with $h_{\mathrm{Me}} = -0.9$ and $k_{\mathrm{C-Me}} = 0.9$, which corresponds to about 30° twist. [c] The term in parentheses is the spin density on the $-CH_3$ group treated as a heteroatom; the other term is the spin density on the oxygen atom of the methoxy group.

spin densities in the fluorinated radicals does not depend upon whether or not the exact magnitude of the parameter, h_{Me}, has an independent significance.

The resonance integral between the methyl carbon atom and the adjacent ring carbon atom was also changed from the standard value by use of the equation

$$\beta_{\mathrm{C-Me}} = k_{\mathrm{C-Me}}\beta_0 \qquad (5)$$

Triphenylmethyl is believed to have a propeller-like structure rather than a planar structure. The effect of twisting the rings was incorporated into the calculations by choosing $k_{\mathrm{C-Me}} = \cos \phi\beta_0$, where ϕ is the angle of twist.[29] The value chosen for $k_{\mathrm{C-Me}}$, and which gave good agreement with experiment, was 0.9. The calculated spin densities were not strongly dependent upon the value chosen for this parameter.

With the above values of α_{Me} and $\beta_{\mathrm{C-Me}}$, it was found that the best agreement with experiment was obtained with a value of 1.6 for the empirical parameter λ in the McLachlan calculations. Normally a value of 1.2 is chosen for λ, but different values of λ have been employed previously to fit experimental data.[27,30] The results of the calculations on triphenylmethyl for both values of λ are presented in Table II. The numbering of the ring positions for these calculations is given in Figure 5.

Fluorinated Radicals. Heteroatoms were incorporated into the calculations in the same manner as described above for the methyl carbon atom (eq 4 and 5). The electronegativity of fluorine suggests that h_{F} should be approximately 3. Carrington, *et al.*,[6] have used $h_{\mathrm{F}} = 1.60$ and $k_{\mathrm{C-F}} = 0.7$. However, Eaton, *et al.*,[8] have used the values $h_{\mathrm{F}} = 2.5$ and $k_{\mathrm{C-F}} = 0.619$. These authors arrived at the values of the empirical parameters by the consideration of the ionization potentials of the heteroatoms, employing the relationship $\alpha_{\mathrm{X}} = \alpha_{\mathrm{C}} - E_{\mathrm{C}} + E_{\mathrm{X}}$. Resonance integrals were estimated from $\beta_{\mathrm{C-X}} = (S_{\mathrm{C-X}}/S_{\mathrm{C-C}}) \cdot \beta_{\mathrm{C-C}}$. No systematic variation of the parameters h_{F} and $k_{\mathrm{C-F}}$ in our calculations was attempted. To do so would have increased by at least an order of magnitude the already large number of calculations required. However, a few slightly different values of the param-

---

(29) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

(30) C. L. Talcott and R. J. Meyers, *Mol. Phys.*, **12**, 549 (1967).

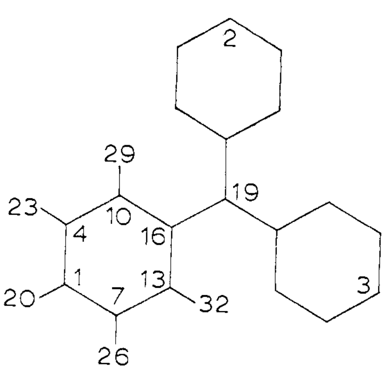

Figure 5. Numbering system for atomic positions in the triarylmethyl radicals discussed in the text.

eters were tried. ρ_F^π was more strongly affected by these variations than ρ_C^π. The parameters suggested by Eaton, *et al.*,[8] provide the best correlation of the data and are also inherently most reasonable. The calculations reported in Table II employed their[8] values of the parameters. We do not believe that the general conclusions of this work would be affected by the choice of h_F and k_{CF} within reasonable limits, though the magnitudes of $Q_{CF}{}^F$ and $Q_{FC}{}^F$ determined would be affected.

Some of the fluorinated radicals studied here also contained a methyl group, a methoxy group, and a trifluoromethyl group. Streitwieser's values[31] were used for methyl ($h_{CH_3} = 3.0$, $k_{C-CH_3} = 0.7$) and the so-called heteroatom model was employed. Streitwieser's values[31] were also used for the methoxy group ($h_O = 2.7$, $k_{C-O} = 0.6$, $k_{O-CH_3} = 0.3$, and $h_{CH_3} = 3.0$). No estimates of the values for the parameters h and k for the trifluoromethyl group could be found in the literature. Huheey[32] has reported the group electronegativities for a number of substituent groups. The group electronegativity value for CF$_3$ on the Pauling scale is $\chi_{CF_3}{}^P = 3.46$, that for fluorine is $\chi_F{}^P = 3.0$. This suggested a value of 2.88 for h_{CF_3}. Similarly, k_{C-CF_3} could be estimated to be 0.7. These values were employed here.

The results of the spin density calculations are presented in Table II.

Discussion

Eaton, *et al.*,[8,9] suggested the use of eq 2 to explain their nmr results on the Ni(II) chelates of *o*-, *m*-, and *p*-N,N′-difluorophenylaminotroponiminates. They obtained the contact interaction constants for the various nuclei by comparison of the chemical shifts with the corresponding diamagnetic zinc chelates. This method gives both the signs and magnitudes of the hyperfine splitting constants. When they attempted to employ eq 1 to interpret their data they found that $Q_{eff}{}^F$ varied widely depending on the position of the substituted fluorine. The fact that $Q_{eff}{}^F$ turned out to be positive also suggested that eq 1 may not be adequate.

In their employment of eq 2, Eaton, *et al.*, argued that since the spin density on the fluorine orbitals results from conjugation of fluorine orbitals with the 2pπ orbitals of the aromatic framework, the spin density on fluorine should be related to the double bond character of the C–F bond. Consequently, they set $\rho_F{}^\pi = AP_{CF}\rho_C{}^\pi$, where P_{CF} is the bond order and A is a proportionality constant. They obtained reasonable agreement with experiment with $AQ_{FC}{}^F = +848$ G and $Q_{CF}{}^F = 147$ G. P_{CF} was obtained by a simple Hückel molecular orbital treatment. Kaplan, *et al.*,[7] repeated the calculations of Eaton, *et al.*, and concluded that the C–F bond order used by Eaton, *et al.*, might have been in considerable error. Also, whereas Eaton, *et al.*, rather arbitrarily used the *para* and *meta* positions to obtain the parameters of eq 2, Kaplan, *et al.*, suggested that use of the *para* and *ortho* positions should also be considered. Substantially different values of the parameters were then obtained. Kaplan, *et al.*, found that neither set of parameters adequately fit the data on other radicals. These and other considerations led to a reemphasis on the use of eq 1 by several groups of workers[6,7,12,14,15] with a $Q_{eff}{}^F$ value in the neighborhood of +40 to +60 G.

There are, however, a number of difficulties associated with the use of eq 1 in place of eq 2 or some other more appropriate expression. A survey of fluorine hyperfine constants and comparison with corresponding proton splittings shows that the $Q_{eff}{}^F$ values range from 12.4 G for (*o*-fluorophenyl)diphenylmethyl radical[16] to 77.4 gauss for 6-fluoro,2-nitrophenol.[14] What is more critical, and which is fully evident for the first time from this work, is that even for the fluorinated radicals of the same series, such as the fluorine-substituted triphenylmethyl radicals, the $Q_{eff}{}^F$ values are found to be highly dependent on the position of the substituent. The appropriate data are collected in Table III. In addition there is an implication in the use of eq 1 that $Q_{eff}{}^F$ is somewhat analogous to McConnell's Q^H for protons. This would lead us to believe that, perhaps, $Q_{eff}{}^F$ should be negative, whereas in fact, it can be positive.

The next logical step was to determine to what extent eq 2 can be used to fit the data. Table I contains the experimental splitting constants and Table II has the corresponding spin densities which were calculated in the manner described in the preceding section. A set of $Q_{CF}{}^F$ and $Q_{FC}{}^F$ can be calculated from any two fluorine-substituted radicals, or from only one radical if it is substituted in more than one position. It was hoped that a good set of parameters would be able to fit all the fluorine hfs on all the substituted triphenylmethyls to within, say, 10%.

From the observed a_F/a_H ratios in the series of fluorinated triphenylmethyl radicals (Table III) it is apparent that the *o*-fluorine constants are generally smaller than expected. In fact, they are often considerably smaller than the corresponding proton splittings, and they do not seem to be at all uniform from one radical to another. A possible reason for this could be found in the stereochemistry of the *o*-fluorine atoms which may be in a position to interact directly with the spin on the methyl carbon atom.[1a,16] It seems not unreasonable to attribute the anomalous *ortho* splittings to this direct interaction. Bearing this in mind, only the observed *para* and *meta* splittings, with corresponding calculated spin densities, were used to evaluate $Q_{CF}{}^F$ and $Q_{FC}{}^F$ in eq 2.

There are a number of slightly different procedures which can be used to determine the parameters in eq 2.

---

(31) A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, **82**, 4123 (1960).

(32) J. E. Huheey, *J. Phys. Chem.*, **69**, 3284 (1965).

Table III. Effective Spin-Polarization Constants, $Q_{\text{eff}}{}^{\text{F}}$, and the Ratios of Fluorine and Hydrogen hfs Constants, $|a_{\text{F}}/a_{\text{H}}|$, for Fluorinated Triphenylmethyl Radicals

Compound	a_{F}, G	a_{H}, G	$\rho_{\text{C}}{}^{\pi\ a}$	$Q_{\text{eff}}{}^{\text{F}}$	$\|a_{\text{F}}/a_{\text{H}}\|$	Ref
Tris(4-fluorophenyl)methyl	6.26	2.745	0.116	54.2	2.28	*b*
	6.50	2.78	0.117	55.6	2.34	15
	6.44	2.875	0.120	53.4	2.25	16
Tris(pentafluorophenyl)methyl	6.80 (*p*)	2.745	0.116	58.9	2.48	11, *b*
	1.61 (*m*)	1.11	−0.047	34.6	1.46	11, *b*
	2.76 (*o*)	2.53	0.107	25.9	1.09	11, *b*
Tris(2,6-difluorophenyl)methyl	2.11	2.53	0.107	19.8	0.83	*b*
Tris(3,5-difluorophenyl)methyl	1.67	1.11	−0.047	35.6	1.50	*b*
(*p*-Fluorophenyl)diphenylmethyl	6.34	2.857	0.120	52.7	2.22	16
	6.45	2.78	0.117	55.1	2.32	15
(*o*-Fluorophenyl)diphenylmethyl	1.35	2.609	0.110	12.35	0.52	16
Bis(*m*-fluorophenyl)phenylmethyl	1.55	1.14	−0.048	32.06	1.35	16
Tris(*m*-fluorophenyl)methyl	1.56	1.11	−0.047	33.25	1.40	15
Tris(4-methyltetrafluorophenyl)methyl	2.60 (*o*)	2.53	0.107	24.3	1.03	*b*
	1.65 (*m*)	1.11	−0.047	35.4	1.49	*b*
Tris(4-methoxytetrafluorophenyl)methyl	2.53 (*o*)	2.53	0.107	23.6	1.00	*b*
	1.57 (*m*)	1.11	−0.047	33.4	1.41	*b*
Tris(4-trifluorotetrafluorophenyl)methyl	2.72 (*o*)	2.53	0.107	25.4	1.10	*b*
	1.83 (*m*)	1.11	−0.047	39.2	1.65	*b*

[a] Determined from $a_{\text{H}} = Q_{\text{CH}}{}^{\text{H}}\rho_{\text{C}}{}^{\pi}$ with $Q_{\text{CH}}{}^{\text{H}} = -23.7$ G and a_{H} values from triphenylmethyl. [b] This work.

This results from the fact that there are more experimental data on the series of substituted triphenylmethyls than there are parameters in eq 2. One procedure is to select all the possible combinations of *m*- and *p*-fluorine splittings with corresponding calculated spin densities and then to average the results of the separate pairwise calculations. From the data obtained in this work ten such pairs could be formed, which gave ten sets of *Q* values. These averaged out to $Q_{\text{CF}}{}^{\text{F}}$ and $Q_{\text{FC}}{}^{\text{F}}$ values of −85.1 and +1043 G, respectively. These values were then used to predict the *para* and *meta* splittings in all the radicals. The observed and calculated values as well as the percentage deviations are given in Table IV. The results are found to be surprisingly good and the deviations from the observed splittings are within ±8%. A slight modification to this approach suggests the use of weighted averages for the *Q* values. The pairs of radicals with no *o*-fluorine substituents were arbitrarily assigned a weight of three. On this basis a pair of radicals, tris(4-fluorophenyl)methyl and tris(4-methyltetrafluorophenyl)methyl, was assigned the weight of two. Pairs involving two radicals with *o*-fluorine atoms were assigned a weight of one. This procedure gives $Q_{\text{CF}}{}^{\text{F}} = -83.7$ G and $Q_{\text{FC}}{}^{\text{F}} = +995$ G. With this set of *Q* values the deviations from the experimental values are slightly smaller. Though the values obtained from the weighted averaging procedure are slightly better, the former values, $Q_{\text{CF}}{}^{\text{F}} = -85.1$ G and $Q_{\text{FC}}{}^{\text{F}} = +1043$ G, give somewhat better agreement on an entirely different series of radicals, the benzophenone anion radicals (see the following paper).[1b] For this reason we prefer the former values, although the two sets do not differ much from each other. It is rather difficult to make meaningful estimates of the uncertainties in the calculated values of $Q_{\text{CF}}{}^{\text{F}}$ and $Q_{\text{FC}}{}^{\text{F}}$ in view of the many factors which could affect the magnitudes of the parameters. Assuming that the general approach we have employed is correct, we may estimate that the maximum likely error in the parameters is about 20%.

Table IV. . Calculated Fluorine Splittings in Fluorinated Triphenylmethyl Radicals Using the Two-Parameter Equation[a]

Compound	Fluorine splittings, G Obsd	Calcd	Percentage deviation
Tris(4-fluorophenyl)methyl			
p-Fluorine	6.26	6.56	−5
Tris(3,5-difluorophenyl)methyl			
m-Fluorine	1.67	1.57	+6
Tris(pentafluorophenyl)methyl			
p-Fluorine	6.80	6.51	+4
m-Fluorine	1.61	1.57	−3
Tris(4-methyltetrafluorophenyl)methyl			
m-Fluorine	1.65	1.62	+2
Tris(4-methoxytetrafluorophenyl)methyl			
m-Fluorine	1.57	1.70	−8
Tris(4-trifluoromethyltetrafluorophenyl)methyl			
m-Fluorine	1.83	1.70	+7

[a] Fluorine splittings calculated with $Q_{\text{CF}}{}^{\text{F}} = -85.1$ and $Q_{\text{FC}}{}^{\text{F}} = +1043$ G.

Our evaluation of the $Q_{\text{CF}}{}^{\text{F}}$ and $Q_{\text{FC}}{}^{\text{F}}$ values has been based on certain assumptions about the signs of the fluorine hfs constants. The signs of the various hyperfine splittings were not determined in this work. It has sometimes been stated in the literature[15] that the signs of a_{F} and $\rho_{\text{C}}{}^{\pi}$ have been shown to be the same. Thus, if $\rho_{\text{C}}{}^{\pi}$ is positive, a_{F} should be positive. This conclusion is based on (1) the work of Eaton, *et al.*,[8,9] previously mentioned, where the sign of a_{F} was experimentally determined and found to be positive at positions of positive $\rho_{\text{C}}{}^{\pi}$, (2) the line width analysis in 3,5-difluoronitrobenzene negative ion,[7] and (3) the work of Cook, *et al.*,[33] on monofluoroacetamide, where once again the sign was experimentally determined. However, we question the general validity of this result. Certainly the work of Eaton, *et al.*, and Cook, *et al.*, has shown it to be true for the particular compounds they studied; but Kaplan, *et al.*,[7] were more cautious in their analysis of their line width data on the 3,5-difluoronitrobenzene negative ion.

(33) R. J. Cook, J. R. Rowlands, and D. H. Whiffen, *Mol. Phys.*, 7, 31 (1963).

If eq 2 is, indeed, applicable to fluorine hyperfine splittings, then there is no reason to assume that a_F and ρ_C^π will have the same sign. In any particular case this will depend always upon the relative magnitudes of ρ_C^π and ρ_F^π. In the case of the monofluoroacetamide radical, ρ_F^π is estimated to be about 15% of ρ_C^π. This indicates that there is a fairly efficient mechanism for transfer of spin density to fluorine. However, the situation in a fluorine-substituted aromatic system is likely to be different. The participation of fluorine orbitals in conjugation with the ring carbon orbitals will probably be relatively much smaller. Indeed, this is just the result obtained in the spin density calculations described in the previous section. On this basis we have taken the *p*-fluorine splitting constants to be negative and the *meta* constants to be positive; thus we have assumed that the first term of eq 2 is the predominant term. This assumption then leads us to the calculated values of Q_{CF}^F and Q_{FC}^F given above, where Q_{CF}^F is found to be negative and Q_{FC}^F is found to be positive. A negative value of Q_{CF}^F is to be expected in analogy with the Q value for protons. A positive value of Q_{FC}^F is consistent with the work of Radford, *et al.*,[34] on atomic fluorine.

The reasonableness of these results tends to support the original assumption about the signs of a_F at the various positions. However, stronger support for the assumption about the signs is given by the fact that all other possibilities for assignment of the signs can be shown to lead to somewhat unreasonable conclusions. There are only two other possible assignments. The first of these is that a_F^p is positive and a_F^m is negative. This assignment would result in one of the following conclusions: (1) Q_{CF}^F is positive and Q_{FC}^F is negative, which is not only inherently unreasonable, but contrary to the data on atomic fluorine, (2) $Q_{FC}^F > 5000$ G, which is also unreasonable and contrary to the data on atomic fluorine, or (3) the true values of ρ_F^π are greater by a factor of about 7 or 8 than our calculated values. This last possibility is difficult to rule out absolutely, but not only does it seem unlikely that the semiempirical calculations employed could be this much in error, but it is also likely that such large values for ρ_F^π would produce significant changes in the spin densities in the rings, which is contrary to the experimental facts.

The second possibility for the signs of a_F^p and a_F^m is that they both, conceivably, could have the same sign. If we assume that both are negative, then we obtain $Q_{CF}^F \cong -164$ G and $Q_{FC}^F \cong +4500$ G. Surprisingly enough, the agreement with experimental data based on these values results in deviations which are only twice as large (~14%) as those obtained with the previously mentioned Q values. However, the magnitude of the latter values, especially $Q_{FC}^F = +4500$ G, seems unreasonably large, and thus we believe they can be discarded. The data on atomic fluorine[34] suggest that $Q_{FC}^F \sim 1000$ G.

The Q values determined in the above manner from the *p*- and *m*-fluorine hfs were used to calculate the *ortho* splittings. As expected, the calculated *ortho* splittings were found to be about equal in magnitude to the *para* splittings. The difference between the observed and calculated values can then be ascribed to the "*ortho* effect."

We have arrived at the somewhat surprising conclusion that in the compounds we have studied, a_F and ρ_C^π have opposite signs. This conclusion is based upon the approximate MO calculations described above. Whether this conclusion is correct or not can only be established definitely by nmr studies of these radicals. We hope to do such studies in the future. However, even if it developed that our assignment of the signs was incorrect, it would still not be possible to escape the conclusion that the one-parameter equation is insufficient to explain the data on fluorine hfs.

In addition to the reasons given previously for our choice of signs of a_F, and the magnitudes of Q_{CF}^F and Q_{FC}^F based on this choice, there are a number of independent reasons for believing that the values of Q_{CF}^F and Q_{FC}^F are very nearly correct. In the following paper (part III),[1b] we have applied the identical MO method and fluorine parameters to an entirely different series of free radicals. This is a series of fluorine-substituted benzophenone anion radicals. It is found that the same set of Q values is able to predict the fluorine hfs constants on these radicals to within ±7%. This result is either extremely fortuitous, which we doubt, since the two types of radicals are so different, or we are forced to conclude that the values of the Q's given are approximately correct and have general validity.

It should also be possible to apply eq 2, with the set of parameters we have determined, to all other fluorine-containing free radicals which have been studied. Unfortunately, spin densities for these radicals have not always been determined or calculated. As an example, however, let us calculate the isotropic contribution to the fluorine hfs constant in the monofluoroacetamide radical, where both ρ_C^π and ρ_F^π are known.[35] With $\rho_C^\pi = +0.837$ and $\rho_F^\pi = +0.119$, we obtained $a_F = +53.5$ G. The experimental value is $+56.4$ G.[33] The agreement with experiment is very good.

In conclusion then, it appears that the two-parameter equation originally suggested by Eaton, *et al.*,[8,9] may be sufficient to correlate the data on fluorinated aromatic free radicals. The more general expression proposed by Hinchliffe and Murrell[10] is probably not necessary, since it would be unreasonable to expect correlation with the data to better than the 7% provided by the two-parameter equation.

Acknowledgments. We wish to thank Dr. J. K. Brown and Professor G. Giacometti for helpful correspondence. We also benefitted from an interesting discussion with Professor J. R. Bolton.

---

(34) H. E. Radford, V. W. Hughes, and V. B. Lopez, *Phys. Rev.*, **123**, 153 (1961).

(35) J. R. Bolton in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1962, Chapter 1, p 46.