primary quantum yield for decomposition. A second partition, dependent on both wavelength and temperature, determines the fraction of excited radicals formed. We cannot at present offer a less diffuse rationalization.

Possible differences in the photochemistry of the *cis* and *trans* forms of nitrites have been considered.[20] The tentative conclusion from the present work is that the primary dissociative yield is the same for both rotamers in the banded region. Isopropyl nitrite is 76% *trans* at 25° in the gas phase.[21] The extinction coefficients of the two forms are not known, but Tarte concluded from examination of band contours that $\epsilon_{trans} < \epsilon_{cis}$ for a given band.[22] It is unlikely that the two forms absorb the same relative fractions of light at the three different wavelengths. Since the observed primary yield is the same at the three wavelengths (Table II), probably the primary dissociative yields of the two forms are the same.

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Electron–Nuclear Double Resonance in Solutions. II. Substituent Effects in Triphenylmethyl Radicals

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Abstract: The electron–nuclear double resonance (ENDOR) spectra of a series of six methyl- and fluorine-substituted triphenylmethyl radicals have been observed and measured. ENDOR of the protons was observed at −70° in toluene solution. No fluorine ENDOR was detected in the fluorinated radicals, and possible reasons for the lack of signals are advanced. Fluorine coupling constants were assigned from the electron spin resonance spectra. Fluorine and methyl substitution in *meta* and *para* positions is found to have little effect on the spin density distribution, whereas the large effect of *ortho* substitution is consistent with a sterically induced twisting of the substituted ring from the plane of the four central carbon atoms. Deviations of *ortho*-methyl proton and fluorine coupling constants from the values expected on the basis of a simple π-electron model is ascribed to a direct interaction between orbitals of the substituent and the π orbital of the central carbon atom which contains a large positive spin density.

The effect of substituents on the properties of triarylmethyl radicals and carbonium ions has long been a subject of considerable interest to organic and theoretical chemists. Substituents affect the stability of the carbonium ions in sulfuric acid[2] and their optical absorption spectra.[3] The dissociation constants of the various hexaarylethenes and the stability of the corresponding triarylmethyl radicals are also affected.[4,5] Attempts to justify this behavior through valence bond and molecular orbital theory have been frustrated largely by lack of knowledge of the conformation of the phenyl rings about the central carbon atom.[6,7] It seems clear from electron spin resonance (esr) and nuclear magnetic resonance (nmr) data that the rings of the triphenylmethyl radical and its carbonium ion are equivalent in solution. Thus, as in the crystal,[8] the rings are probably twisted by the same amount into a propeller conformation with the three carbon–phenyl bonds forming a plane. When a ring substituent is added to the carbonium ion, Kurland, *et al.*,[9] have shown from nmr studies that the rings are no longer magnetically equivalent. Until recently, esr spectra of many of the substituted triarylmethyl radicals have been too complex to interpret, but electron–nuclear double resonance (ENDOR) studies of these systems has led to straightforward interpretation of the proton hyperfine splittings.[10-12]

In this communication, we report on the results of ENDOR and esr measurements on a series of methyl- and fluorine-substituted triphenylmethyl radicals. Cor-

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relation of hyperfine data with theoretical models requires a relation between the hyperfine coupling constant of a particular nucleus and the spin density distribution in the molecule. McConnell has proposed a linear relationship between the proton coupling constant, a_{H}, and the atomic orbital spin density on the contiguous carbon atom, $\rho_{\mathrm{C}}{}^{\pi}$

$$a_{\mathrm{H}} = Q^{\mathrm{H}}\rho_{\mathrm{C}}{}^{\pi}$$

which is applicable to aromatic radicals.[13] Attempts have been made to extend this useful equation to other systems such as methyl protons and fluorine nuclei in aromatic radicals. Although a similar relation appears to hold for methyl protons,[14-16] the extension of a linear relationship to fluorine nuclei has been the subject of considerable controversy.[17-23] Recently, Hinchliffe and Murrell[23] have had some success in calculating fluorine hyperfine interactions. Their calculations support the contention that a simple linear relation is not a useful approximation for fluorine. Apart from the difficulties inherent in *a priori* calculations of coupling constants, the validity of any relationship is difficult to test because very few aromatic fluorocarbon radicals have been studied, and of these most contain heteroatoms which make the molecular orbital calculation of spin densities rather uncertain. Trapp and coworkers have recently measured the esr of tris(pentafluorophenyl)methyl radical[24] which would provide an ideal example if it is assumed that the spin density distribution is unaltered from the triphenylmethyl radical. Trapp observed large variations in the ratio $a_{\mathrm{F}}/a_{\mathrm{H}}$ for corresponding positions which implies either the failure of a simple linear relationship, or a severe perturbation on the spin density distribution upon fluorine substitution. We have prepared three triphenylmethyl radicals which are substituted only in the *ortho*, *meta*, or *para* position in order to assess the effect of fluorine substitution on the spin density distribution. Because of the loss of symmetry on partial fluorine substitution, the esr spectra become too complex for interpretation, but a combination of esr and ENDOR spectroscopy enables the coupling constants to be measured and assigned with little ambiguity. Solution ENDOR of $^{19}\mathrm{F}$ has not been reported previously, so it is of interest also to compare the relative ENDOR enhancements and line shapes of fluorine nuclei and protons.

Breslow, Hyde, and coworkers have recently studied the ENDOR spectra of triphenylmethyl radicals with $-\mathrm{CH_2{-}X{-}CH_3}$ substituents ($\mathrm{X} = \mathrm{O, S, CH_2}$)[11,25] and have found evidence that the unsubstituted rings are inequivalent at low temperature when the substituent ($\mathrm{X} = \mathrm{S, CH_2}$) is in an *ortho* position. We have extended the study of this type of radical to include the $-\mathrm{CH_3}$ substituent for which more is known about the hyperfine constant–spin density relationship.

Experimental Section

Five of the radicals, (*o*-fluorophenyl)diphenylmethyl, (*p*-fluorophenyl)diphenylmethyl, bis(*m*-fluorophenyl)phenylmethyl, tris(*p*-fluorophenyl)methyl, and (*p*-tolyl)diphenylmethyl, were prepared from the corresponding carbinols. The carbinols, which were used without purification, and (*o*-tolyl)diphenylmethyl chloride (mp 136.5–137.5°, lit.[4] 137°) were generously supplied by Professor Daniel Kivelson. Details of their preparation are given elsewhere.[26,27] The carbinols were converted to the corresponding triarylmethyl bromides by dissolving the carbinol in concentrated acetic acid and adding sufficient hydrobromic acid to precipitate the bromide following the procedure of Fieser.[28] The procedure gave sufficiently pure triphenylmethyl bromide (mp 151°, lit.[28] 152°) without recrystallization so none was attempted on the small amounts, <100 mg, of the other bromides prepared. The bromide or chloride was then sealed into the sample tube with sufficient silver to reduce it completely. Thoroughly degassed dry toluene was distilled in under vacuum. After about 5 min of agitation the silver and silver halide produced were filtered off through a fritted disk and the portion of the tube containing the solids was removed, giving a stable solution of the free radical. Solutions of the radicals were all yellow. The fluorinated radicals were stable for periods ranging from 1 day to several weeks, with the stability increasing as fluorine substitution decreased. The *o*-tolyl radical was quite stable while the *p*-tolyl compound polymerized to a green material after 1 day, presumably a form of Tschitchibabin's hydrocarbon. The ENDOR and esr investigation of each radical was completed within the first 24 hr after the reduction so no effects of decay or side reactions are apparent in the spectra.

The ENDOR spectra were recorded on the high-power spectrometer constructed in these laboratories and described previously.[12] The esr spectra were taken with a Varian V-4502 spectrometer. Except as noted, each spectrum was recorded at −70° at a concentration of approximately 10^{-3} *M* in hydrocarbon. The concentration was adjusted by distillation of solvent within the sample tube for best resolution.

The procedure employed for obtaining an assignment of coupling constants was generally similar to that described previously.[12] Accurate splitting constants were obtained from the ENDOR spectra. These were assigned to various numbers of protons consistent with the radical being studied. Esr spectra were calculated on an IBM 7040 computer using the modified SESRS program described previously[29] and plotted by a Cal-Comp 470 plotter. The various plots were then compared with the experimental spectrum. Modifications of this procedure in particular cases are described in detail in the next section.

Results

Bis(*m*-fluorophenyl)phenylmethyl. The high-frequency portion of the ENDOR spectrum of this radical is shown in Figure 1. The mirror image of this spectrum occurs below the center frequency of 14.955 MHz which corresponds to the proton Larmor frequency. The observation that each line in the spectrum is symmetrical about a single frequency indicates that no ENDOR effects due to fluorine transitions are present. Fluorine ENDOR transitions would be expected to be

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Table I. Hyperfine Coupling Constants of Triarylmethyl Radicals[a]

Radical	Position[b]							
	ortho	*meta*	*para*	2	3	4	5	6
Triphenylmethyl[c]	2.609	1.143	2.857					
Diphenylmethyl[d]	3.05	1.22	3.05	8.36[e]				
Bis(*m*-fluorophenyl)phenylmethyl	2.538	1.116	2.756	2.623	1.55[f]	2.901	1.116	2.673
(*p*-Fluorophenyl)diphenylmethyl	2.629	1.156	2.892	2.629	1.090	6.34[f]	1.090	2.629
Tris(*p*-fluorophenyl)methyl				2.684	1.113	6.44[f]	1.113	2.684
(*o*-Fluorophenyl)diphenylmethyl	2.859	1.204	3.153	1.35[f]	0.920	2.096	1.047	2.060
Perfluorotriphenylmethyl[g]	2.76[f]	1.61[f]	6.80[f]					
(*p*-Tolyl)diphenylmethyl	2.597	1.136	2.844	2.597	1.136	3.034[e]	1.136	2.597
(*o*-Tolyl)diphenylmethyl	3.044[h]	1.247	3.401[i]	0.677[e]	0.928	1.457	0.928	1.327

[a] Expressed in gauss. Accuracy of values obtained from ENDOR is ±0.005 G unless otherwise indicated. Accuracy of values from esr is about ±0.025 G. [b] See Figure 2 for labeling of atom positions. [c] Data from ref 12. [d] Data from ref 33. [e] Methyl proton splitting. [f] ^{19}F splitting. [g] Data from ref 24. [h] Accuracy ±0.015 G. [i] Accuracy ±0.030 G.

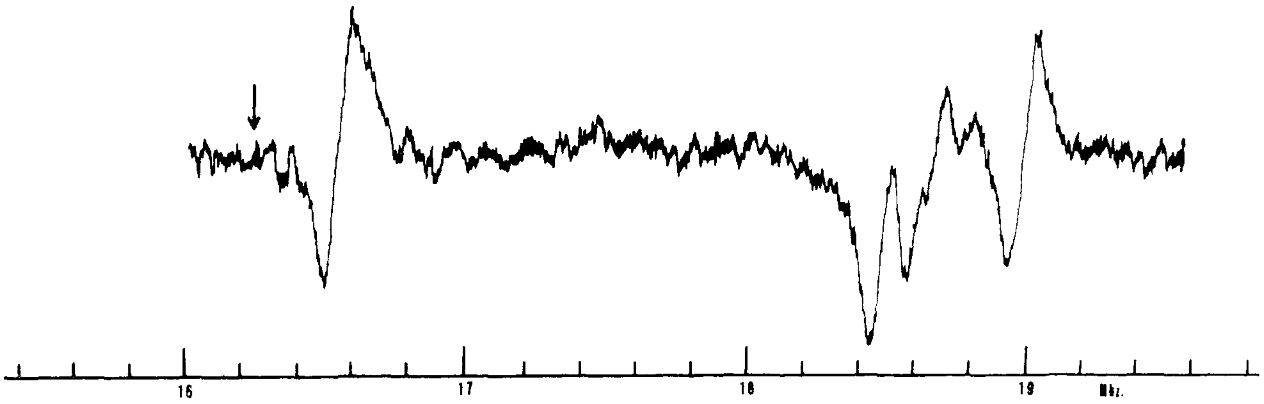

Figure 1. High-frequency half of the ENDOR spectrum of bis(*m*-fluorophenyl)phenylmethyl. The vertical arrow indicates the expected position of a ^{19}F ENDOR signal.

mirrored about the ^{19}F Larmor frequency of 14.068 MHz. In the region where *meta*-proton couplings are expected by analogy with the triphenylmethyl spectrum (16–17 MHz), only a single line is observed, although it is somewhat broad and unsymmetrical. Thus, the four *meta* protons of the substituted and unsubstituted rings must be equivalent to within the linewidth resolution of *ca.* 120 kHz. In the region in which the *ortho*- and *para*-proton ENDOR is expected (18–20 MHz), four lines are observed, the second of which is a barely resolved doublet. The most likely assignment of the coupling constants to ring positions is arrived at from the observation that the ratio a_p/a_o for triphenylmethyl is 1.10,[12] and it seems unlikely that fluorine substitution in the *meta* position will greatly alter this ratio. Thus, the first line should correspond to an *ortho* proton, and the highest frequency line to a *para* proton. Ratios of 1.094 and 1.087 are obtained for a_p/a_o if the first and third lines are assigned to one type of ring, and the second (doublet) and fourth are assigned to the other type. On the basis of the greater combined intensity of the second and fourth ENDOR enhancements, and the doubling of the second, we assign this pair to the fluorine-substituted rings. The doubling of the *ortho*-proton ENDOR is a result of the unsymmetrical fluorine substitution. The triplet pattern from the two equivalent fluorine nuclei can be determined easily from the wings of the esr spectrum. Kurland, *et al.*,[9] have observed that the fluorines are not quite equivalent in the nmr spectrum of the bis(*m*-fluorophenyl)phenylmethyl carbonium ion at low temperature. Our esr spectrum of the free radical shows no signs of this inequivalence, however.

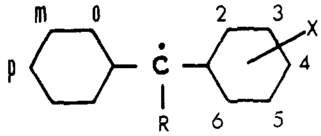

Figure 2. Labeling system for the atom positions of the substituted triphenylmethyls.

Our assignments of the hyperfine coupling constants are given in Table I, and we feel quite confident of them except that our assignment of the 2- and 6-proton coupling constants is arbitrary. The labeling of the atom positions which pertain to Table I is given in Figure 2. Several esr spectra were calculated based on this and several other assignments of the coupling constants observed by ENDOR in the 18–20-MHz region, and only the assignment given above and in Table I leads to detailed agreement between the observed and computed spectra.

(*p*-Fluorophenyl)diphenylmethyl. Figure 3 shows the high-frequency half of the ENDOR spectrum of this radical. The ENDOR spectrum is symmetrical about the free proton Larmor frequency of 14.966 MHz, so again no fluorine ENDOR is apparent. The two lines in the *meta*-proton coupling region have a relative intensity of 1:2, and we consequently assign the weaker line to the two *meta* protons of the substituted ring, and

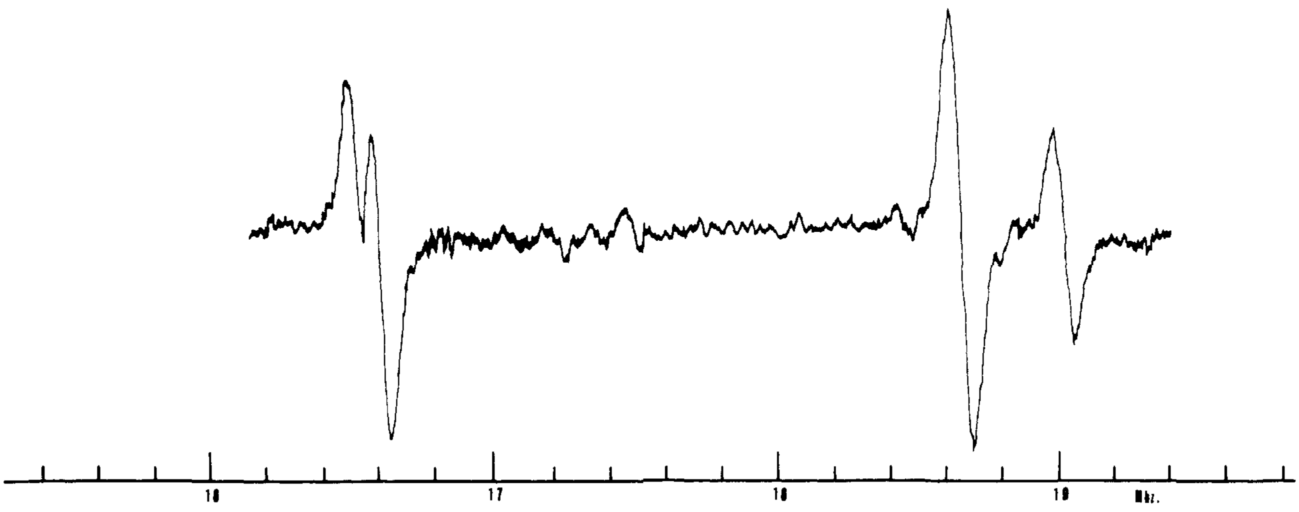

Figure 3. High-frequency half of the ENDOR spectrum of (p-fluorophenyl)diphenylmethyl.

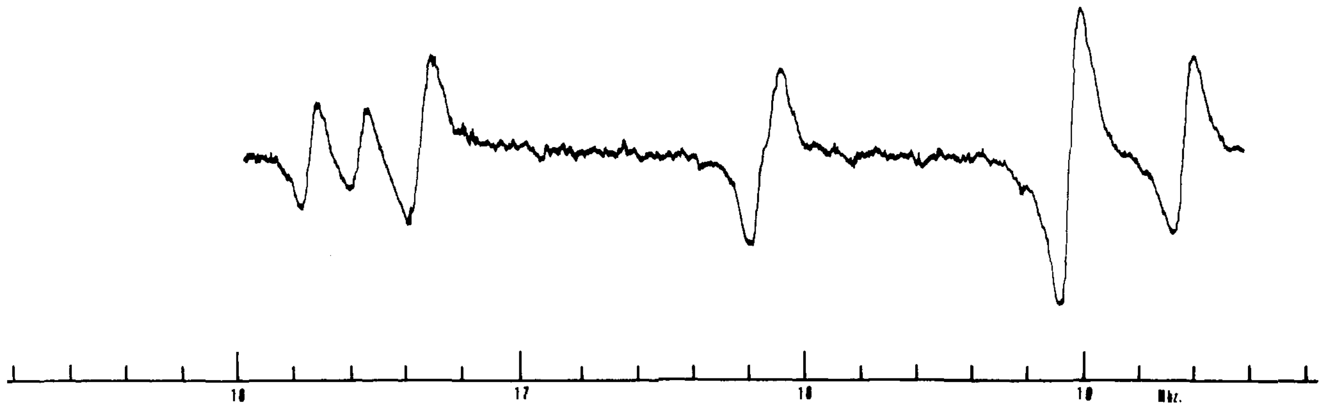

Figure 4. High-frequency half of the ENDOR spectrum of (o-fluorophenyl)diphenylmethyl.

the other to the four *meta* protons of the unsubstituted rings. Only two resolved lines appear in the 18–20-MHz region of the spectrum. The outer line is assigned to the *para* protons, while the inner line must correspond to the ENDOR of all six *ortho* protons of the molecule. The intensity ratio is 3.5:1. The *ortho* line is somewhat broader than the *para* line, and the ratio a_p/a_o is equal to 1.100.

At −70° the esr spectrum consists of broad unsymmetrical lines which may be due to the lack of averaging of the large ^{19}F hyperfine anisotropy. Thus, the ^{19}F coupling constant cannot be determined from the esr spectrum at the temperature of the ENDOR experiment. At room temperature the esr is sharp and symmetrical, and the large fluorine coupling constant is readily determined. The coupling constants given in Table I are from the −70° ENDOR spectrum except for ^{19}F which constant was obtained from the esr spectrum at room temperature. Our values agree with those reported by Sinclair and Kivelson,[27] except that they could not resolve the inequivalent *meta* protons. An ENDOR enhancement due to ^{19}F would be expected to occur at about 23 MHz. This region was carefully searched, but no signal was found at −70°. Higher temperatures were not tried since even the proton ENDOR enhancements rapidly disappeared as the temperature was raised.

Tris(p-fluorophenyl)methyl. The ENDOR spectrum of this radical is symmetrical about the proton Larmor frequency, and the high-frequency region consists of one line in the *meta* region and one in the *ortho–para* region of triphenylmethyl. As in the case of the monofluoro compound described above, the esr spectrum is broad and unsymmetrical at −70°, but becomes well resolved at room temperature. The ^{19}F coupling constant was obtained from the esr spectrum at room temperature and is reported in Table I along with the proton coupling constants obtained from ENDOR at −70°. No ^{19}F ENDOR was observed at its expected frequency.

(o-Fluorophenyl)diphenylmethyl. The high-frequency half of the ENDOR spectrum of this radical is shown in Figure 4. The spectrum is symmetrical about the proton Larmor frequency of 14.943 MHz, and thus, no ^{19}F ENDOR is apparent. The spectrum is seen to consist of six lines, of which the fourth is a barely resolved doublet. The third, fifth, and sixth lines can be assigned to the *meta*, *ortho*, and *para* protons of the unsubstituted phenyl rings by analogy with the triphenylmethyl radical. The resulting coupling constants are each larger than those in triphenylmethyl, but a_p/a_o is 1.102 and the intensity ratio of the ENDOR signals is approximately 2:1 for the *ortho–para* pair. This leaves the first, second, and fourth (doublet) signals to be assigned to the four protons of the fluori-

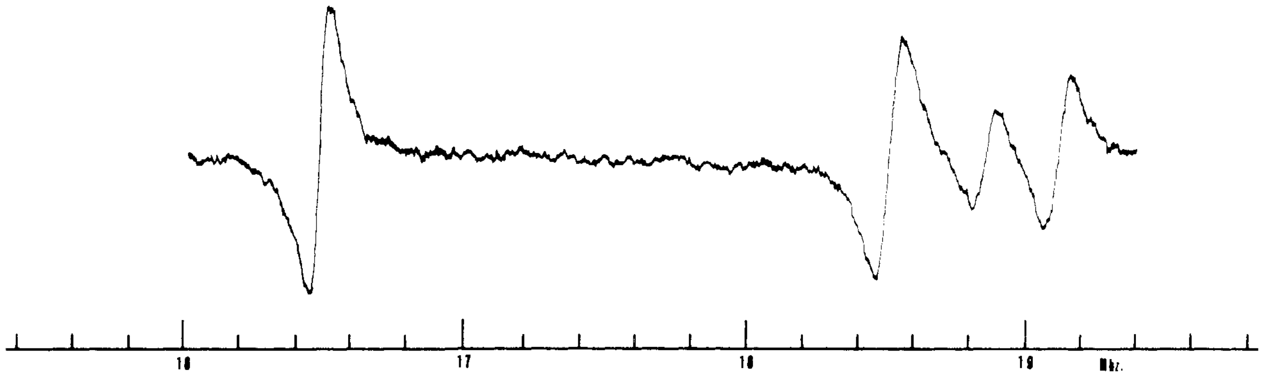

Figure 5. High-frequency half of the ENDOR spectrum of (*p*-tolyl)diphenylmethyl. Proton Larmor frequency is 14.876 MHz.

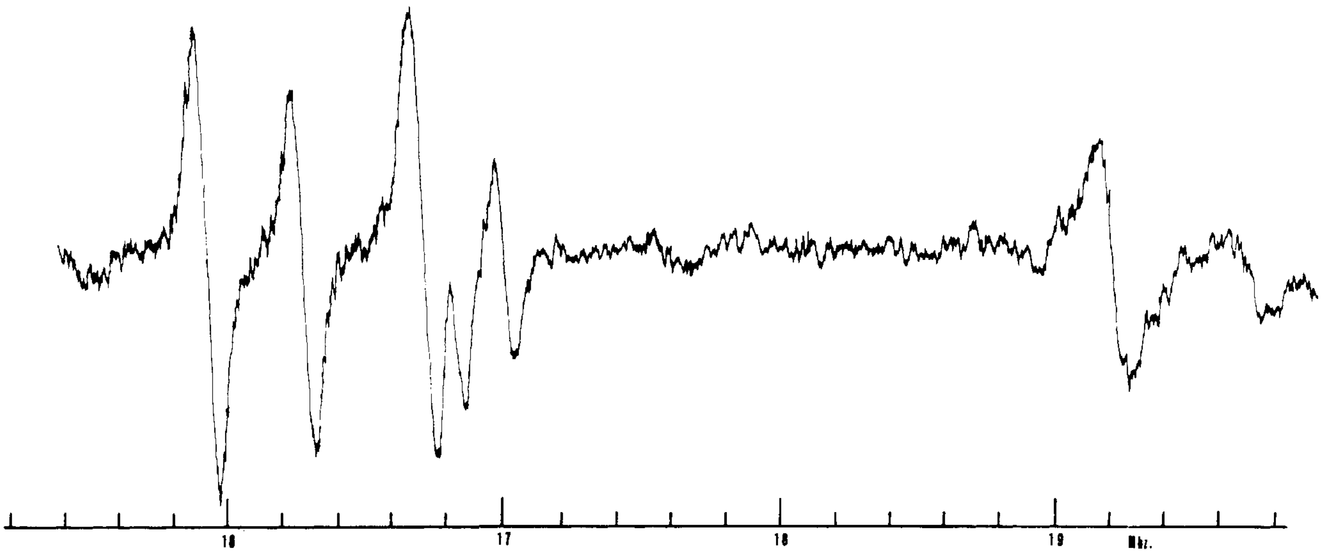

Figure 6. High-frequency half of the ENDOR spectrum of (*o*-tolyl)diphenylmethyl. Proton Larmor frequency is 14.966 MHz.

nated ring. Magnetic resonance cannot distinguish between these positions, but molecular orbital theory always gives $a_o \sim a_p > a_m$ for this type of radical. We therefore assign the weakly coupled pair of lines to the *meta* protons and the poorly resolved 1:1 doublet to the *ortho–para* pair. The assignment of the proton coupling constants is given in Table I. Assignments of coupling constants to the 3 and 5 positions and the 4 and 6 positions are arbitrary. In principle, to find the fluorine splitting constant, knowing all the proton splitting constants, it is only necessary to determine the total width of the esr spectrum. In this case, because of the many equivalent protons and the relatively small fluorine coupling constant, the end lines are very weak and easily confused with ^{13}C satellites or lost in the noise. The fluorine splitting was found by first calculating an esr spectrum based on only the *proton* coupling constants, cutting the calculated spectrum in half, and matching the two halves to the wings of the observed spectrum. The gap in the center was then assigned as the missing fluorine coupling. A new spectrum was then calculated which included this constant which was compared again with the experimental spectrum. The lines in the wings of the spectrum occur in groups, so that it is possible that this method might give a splitting which is incorrect by some multiple of the group splitting. Various possibilities were tried and compared with the observed spectrum. The 1.35-G splitting constant given in Table I was found to be clearly the most satisfactory in reproducing the observed spectrum.

(*p*-Tolyl)diphenylmethyl. Figure 5 shows the high-frequency half of the ENDOR spectrum of this radical. It is virtually identical with the ENDOR spectrum of triphenylmethyl[12] except for the addition of a fourth line at a higher frequency which we attribute to the methyl proton ENDOR. As discussed previously,[12] for similar types of protons with ENDOR signals which are relatively close in frequency, the intensities serve as a rough guide to the relative number of protons contributing to each signal. It is somewhat surprising to note in this case that the intensity ratios of the three lines are 6:2.6:3.8 in the order of increasing frequency. According to our assignment of these signals to *ortho*, *para*, and methyl protons, respectively, the ratios of numbers of protons involved is 6:2:3. The interesting feature is that the methyl proton ENDOR signals appear to behave very much like those of the ring protons as far as intensity and line width are concerned, although their coupling mechanism with the electron spin is very different. We find coupling constants (given in Table I) essentially identical with those reported earlier by Sinclair and Kivelson.[27]

(*o*-Tolyl)diphenylmethyl. The high-frequency half of the ENDOR spectrum of the *ortho*-methyl substituted radical is shown in Figure 6. The third, sixth, and seventh lines from the left are assigned as the *meta*, *ortho*-, and *para*-proton ENDOR signals of the unsubstituted rings by analogy with triphenylmethyl. The four remaining weakly coupled lines are then assumed to arise from the protons of the methyl-substituted ring. Since these lines represent coupling constants less than half of the *ortho–para* values found in triphenylmethyl, this ring must be severely distorted. The most probable distortion is a twisting of the ring away from coplanarity with the plane of the three central C–C bonds, which would be expected to decrease the spin density in the ring. The proton coupling constants of the other rings would be expected to increase from their values in triphenylmethyl, as is observed. On this basis we assign the fourth and fifth lines to the *ortho* and *para* ring protons of the substituted ring. The remaining two lines must then account for the *meta* and the methyl protons. Kispert, *et al.*,[25] have studied the ENDOR of a triphenylmethyl radical substituted in the *ortho* position of one ring with the group $-CH_2SCH_3$. Its ENDOR spectrum is similar to that of our radical shown in Figure 6. By deuteration of the pendant group in the methylene position, they show that the 0.9-G coupling constant may be attributed to the *meta* protons, while their methylene protons have a much smaller coupling constant. On the basis of their observations we assign the first, most weakly coupled line to the methyl protons, and the second line to the *meta* protons. Our assignment of coupling constants for this radical is given in Table I. Kispert, *et al.*, also observed a doubling of the *ortho*- and *para*-proton ENDOR lines of the unsubstituted rings at low temperatures in their radical with the *o*-CH_2SCH_3 substituent. They attribute this to an inequivalent twisting of the two unsubstituted rings which is caused by the large *ortho* substituent on the third ring. The angles of twist are interchanged as the molecule makes conformational changes between right- and left-handed forms, and the doublet signals are observed to collapse at elevated temperature. Although our spectrometer gives line widths which are two to three times narrower than that used by Kispert, *et al.*, we see no doubling of the ENDOR signals of the unsubstituted rings of (*o*-tolyl)diphenylmethyl at −70° in toluene. The *ortho* and *para* signals are, however, about 50 kHz broader than the 70-kHz, peak-peak line widths of the other lines in the spectrum. This may represent an unresolved small splitting of the lines or a larger splitting which is only incompletely averaged at −70°.

Esr spectra computed from the coupling constants assigned in Table I are in substantial agreement with the observed one although peculiar line-width effects which might be associated with the interconversion of right- and left-handed isomers make the comparison difficult. This system deserves further study and will be reported on in detail in a later communication.

Discussion

Fluorine ENDOR. One of the purposes of this investigation was to compare the intensity and line width of fluorine ENDOR in solution with that of protons. We have, however, not observed any ENDOR enhancements due to ^{19}F even after the fluorine coupling constant had been determined from esr so that the frequency of its ENDOR could be calculated. ENDOR of ^{19}F is known to be possible in solution since we have observed strong signals due to this nucleus from hexakis(trifluoromethyl)benzene anion[30,31] in dimethoxyethane solution. The explanation for the different behavior probably lies in the difference in the electron–nuclear interactions in these different type systems. The esr line widths of the hexakis(trifluoromethyl)benzene anion remain narrow down to the freezing point of the solvent,[30] whereas those of the fluorinated triphenylmethyl radicals broaden rapidly as the temperature is lowered. This broadening is not observed ordinarily in triarylmethyl radicals and is thus probably due to the lack of averaging of the very large traceless part of the ring-substituted fluorine hyperfine tensor as the random tumbling motions of the molecule slow down. The traceless part of the perfluoromethyl tensor is considerably smaller, and it can be better averaged by internal rotation. At low temperatures in the fluorine ring substituted radicals, the ^{19}F ENDOR signal must be very broad due to the contribution from the unaveraged dipole–dipole part of the coupling. The lack of averaging of the fluorine tensor does not contribute to the line width of proton ENDOR, however. At higher temperature, the anisotropic part of the hyperfine interaction contributes to the spin-lattice relaxation of the fluorine, as well as the electron. The radical becomes more difficult to saturate, and also the nuclear transitions induced by the radiofrequency field may not be competitive with the natural nuclear relaxation rate. This latter condition is certainly a requirement for observing an ENDOR enhancement. The observation of proton ENDOR in tris(*p*-fluorophenyl)methyl requires ten times as much microwave power incident upon the cavity as does triphenylmethyl at comparable nuclear radiofrequency fields. A likely ENDOR mechanism for these systems involves the enhancement of a nuclear transition rate by the radiofrequency field, the process being one of two steps—a nuclear spin flip plus a simultaneous electron–nuclear spin flip—which must be rate limited at the nuclear spin-flip step.[32] If the cross relaxation step is rate limiting, driving the nuclear transition will not affect the electron spin relaxation rate and no ENDOR will be observed. The fluorine ring substituted triphenylmethyl radicals may be examples of systems in which the nuclear spin relaxation is rate limiting for the protons over a certain temperature range while for the fluorine nuclei the cross relaxation process is rate limiting over this same range. Thus the proton ENDOR can be observed while that of the fluorines cannot.

Effects of *para* or *meta* Substitution. The spin density distribution in the triphenylmethyl radical appears to be relatively little affected by fluorine or methyl substitution in the *meta* or *para* position. The

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ratio of fluorine to proton coupling constant at the *para* position is 2.22 for (*p*-fluoromethyl)diphenylmethyl and 2.25 for tris(*p*-fluorophenyl)methyl in reasonable agreement with other radicals. The anion of *p*-fluoronitrobenzene has the ratio 2.12.[18] The fluorine–proton coupling ratio at the *meta* position of triphenylmethyl is 1.38 while for *m*-fluoronitrobenzene anion it is 2.66,[23] a striking difference considering the similarity in the spin distribution in the phenyl rings as gauged by the proton coupling constants. The variation of this ratio from molecule to molecule and position to position does not support a linear McConnell-type relation between carbon atomic orbital spin density and fluorine coupling constant. These variations, however, appear to be adequately accounted for by Hinchliffe and Murrell's calculations.[23] Methyl group substitution in the *para* position has only a barely measurable effect on the proton coupling constants of triphenylmethyl. The ratio of the coupling constants of *para* methyl to *para* proton is found to be 1.067, in good agreement with the rough constancy of this ratio suggested by many authors in the past.[14–16]

Effects of *ortho* Substitution. Addition of a bulky substituent to the *ortho* position of triphenylmethyl has a large effect on the spin density distribution in the radical. The proton coupling constants of the unsubstituted rings increase, becoming similar to those of diphenylmethyl[33] (Table I), and those on the substituted ring are greatly reduced. The most reasonable explanation of this effect based on Hückel molecular orbital theory and molecular models is that steric forces cause a twisting of the substituted ring away from the central plane of the radical. The twisted ring becomes less conjugated with the rest of the molecule and gives up spin density to the larger π system. This argument is supported by our observation that the bulkier methyl substituent leads to a larger redistribution of spin density than does the fluorine. Kispert, *et al.*,[25] have suggested that a direct interaction between the sulfur in their *o*-CH_2SCH_3 substituent and the central carbon atom of the radical contributes to the stability of a twisted conformation. However, the similarity between their coupling constants and those of (*o*-tolyl)diphenylmethyl reported here suggest that only steric forces are required. The steric molecular orbital model described above is adequate to account for all the observed coupling constants of the radical except those of the substituents themselves. Both the methyl proton and fluorine coupling constants are considerably smaller than would have been predicted from a comparison with the *ortho*-proton coupling constant of the substituted ring. The methyl proton to ring proton coupling constant ratio is 0.51 compared with 1.067 observed on substitution in the *para* position. Likewise, the *o*-fluorine:proton coupling constant ratio is reduced to 0.66 from a *para* position ratio of 2.25. We suggest that this large change in "effective Q value" for *ortho* substituents must be due to a direct interaction of methyl-proton and fluorine orbitals with the π orbital of the central carbon atom which carries a large positive spin density. The reduced fluorine splitting observed here is consistent with the low value of a_F/a_H found by Trapp, *et al.*,[24] for the *ortho* position of perfluorotriphenylmethyl and which would not have been accounted for by the theory of Hinchliffe and Murrell.[23] The reduced Q^{CH_3} for methyl groups *ortho* to a substituent with a large positive spin density has been observed previously by Allendoerfer and Rieger[34] in variously substituted 2,6-dimethylnitrobenzene anions. They observed a decrease in this quantity as the ring twist increased with respect to the plane of the nitro group. Since a methyl group at the *ortho* position is expected to obtain positive spin density from the ring at the proton positions, the direct interaction with the central carbon π orbital of triphenylmethyl must contribute a negative spin polarization at the protons.

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