attribution of small dipole moments to seemingly symmetrical molecules has been neglect of the unknown atomic polarization. The low atomic polarization values in the solid state and consequent appreciable dipole moments in solution calculated by Wright and his co-workers may be due, at least in part, to a considerable difference between the atomic polarization in the solid state and that in the liquid.[34]

Acknowledgment..—The writers wish to express their thanks to Prof. George F. Wright of the University of Toronto for a highly purified sample of *p*-benzoquinone.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES, CALIFORNIA]

The E.s.r. Spectra of Some Substituted Triarylmethyl Radicals[1a]

BY HENRY JUDEIKIS[1] AND DANIEL KIVELSON[1b]

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The e.s.r. spectra of several triarylmethyl radicals have been studied and proton coupling constants have been assigned. The coupling constants obtained for tri-*p*-chlorotriphenylmethyl are 2.64 ± 0.05 and 1.32 ± 0.05 gauss for the *ortho* and *meta* protons, respectively. For tri-*p*-methoxytriphenylmethyl the coupling constants are 2.89 ± 0.02, 0.34 ± 0.02 and 1.05 ± 0.10 (or 0.71 ± 0.10) gauss for *ortho*, methoxy and *meta* protons, respectively. Tentative assignments for *o*-toluyldiphenylmethyl are 2.8, 1.1, 2.5 and 2.2 gauss for the *para*, *meta*, *ortho* and methyl proton coupling constants, respectively.

The e.s.r. (electron spin resonance) spectrum of triphenylmethyl has been investigated by several workers[2-6] and considerable theoretical work has been done in an attempt to relate the spectral observations to molecular calculations.[5,7,8] The experimentally determined coupling constants a_i and the various calculated values for the spin density ρ_i are summarized in Table I. In many applications it has been found that good results can be obtained with McConnell's first order relation,[9] where Q is a factor that is approximately constant for all aro-

$$a_i = Q\rho_i$$

matic hydrocarbons and has an empirical value of −22.5 gauss.[10] In Table I it can be seen that the Q values obtained for triphenylmethyl are considerably smaller than 22.5 gauss.

TABLE I

E.S.R. PARAMETERS FOR TRIPHENYLMETHYL. ρ_p IS THE THEORETICAL SPIN DENSITY ON THE *para* CARBON AND a_p IS THE EXPERIMENTAL COUPLING CONSTANT OF THE *para* HYDROGEN. $|\rho_{exp}| = |a/22.5|$

	Valence bond[7] (planar)		Valence bond[5] (twisted)		Valence bond[6,8] (planar)		Experimental[6]		
Nucleus	ρ	$\|\rho/\rho_p\|$	ρ	$\|\rho/\rho_p\|$	ρ	$\|\rho/\rho_p\|$	$\|a\|$ gauss	$\|a/a_p\|$	$\|\rho_{exp}\|$
H (*ortho*)	0.200	1.099	0.188	1.074	0.159	0.783	2.53	0.913	0.112
H (*meta*)	− .104	0.571	− .099	0.566	− .105	0.517	1.11	0.401	.049
H (*para*)	.182	1.000	.175	1.000	.203	1.000	2.77	1.000	.123
C^{13} (methyl)	.564[5]		.616				22		

In order to extend the study of triarylmethyl radicals the e.s.r. spectra of several substituted triphenylmethyl radicals have been investigated. Toluene solutions of the radicals were prepared by reaction with silver in an inert atmosphere, and spectra were observed at −50° using an X-band spectrometer operating at a microwave frequency of 9.1 kmc. Further instrumental details and the methods of sample preparation are described elsewhere.[11]

Tri-*p*-chlorotriphenylmethyl (See Fig. 1).—The observed spectrum of tri-*p*-chlorotriphenylmethyl appears in Fig. 2. The spectrum has been interpreted in terms of splitting constants of 2.64 ± 0.05 and 1.32 ± 0.05 gauss for the *ortho* and *meta* protons, respectively. The calculated spectrum is indicated in Fig. 2. The assignment of the larger splitting constant to the *ortho* protons was made in view of the calculations on triphenylmethyl, where the unpaired spin density is considerably larger in the *ortho* positions than in the *meta* positions. (See Table I.) Note the rather large increase in the *meta* splitting over that observed in triphenylmethyl. The lines are quite broad in the tri-*p*-chlorotriphenylmethyl radical, presumably because of unresolved hyperfine splittings and quadrupole moment effects arising from the two chlorine isotopes, both of which have a spin of 3/2 but slightly different magnetic dipole and electric quadrupole moments. If the ratio of the two proton splitting constants is not exactly 2:1, the hyperfine components arising from these two nonequivalent groups of protons would not exhibit

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[1] (a) Supported in part by grants from the National Science Foundation and the Research Corporation. (b) Alfred P. Sloan, Foundation Fellow.

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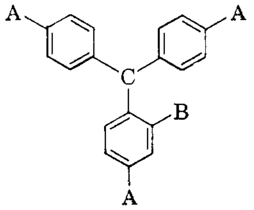

Fig. 1.—A → H and B → H, triphenylmethyl; A → Cl and B → H, tri-*p*-chlorotriphenylmethyl; A → OCH$_3$ and B → H, tri-*p*-methoxytriphenylmethyl; A → H and B → CH$_3$, *o*-toluyldiphenylmethyl.

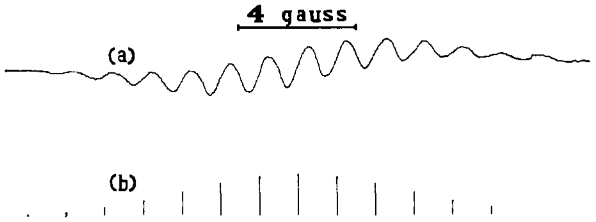

Fig. 2.—Experimental and calculated spectra of tri-*p*-chlorotriphenylmethyl: (a) experimental spectrum of a $10^{-3}F$ solution of tri-*p*-chlorotriphenylmethyl in toluene at 298°K.; (b) calculated spectrum with *ortho* proton coupling constant = 2.64 gauss and *meta* proton coupling constant = 1.32 gauss. The four outermost lines in the calculated spectra, which have relative intensities of less than 2% of that of the center line, are not shown.

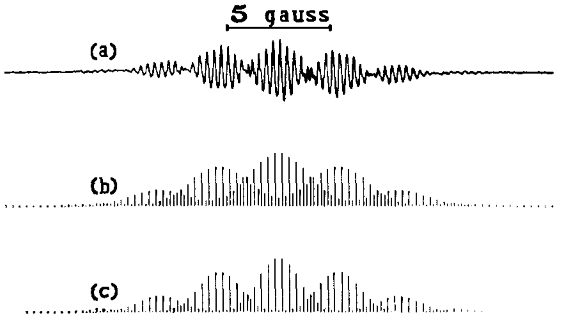

Fig. 3.—Experimental and calculated spectra of tri-*p*-methoxytriphenylmethyl; (a) experimental spectrum of a $10^{-3}F$ solution of tri-*p*-methoxytriphenylmethyl in toluene at 220°K.; (b) calculated spectrum of tri-*p*-methoxytriphenylmethyl with *ortho* proton coupling constant = 2.89 gauss, *meta* proton coupling constant = 1.02 gauss and methoxy proton coupling constant = 0.34 gauss, (c) calculated spectrum of tri-*p*-methoxytriphenylmethyl with: *ortho* proton coupling constant = 2.89 gauss, *meta* proton coupling constant = 0.68 gauss and methoxy proton coupling constant = 0.34 gauss.

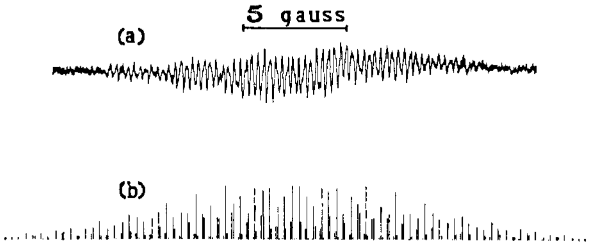

Fig. 4.—Experimental and calculated spectra of *o*-toluyldiphenylmethyl: (a) experimental spectrum of a $3 \times 10^{-4}F$ solution of *o*-toluyldiphenylmethyl in toluene at 220°K.; (b) calculated spectrum of *o*-toluyldiphenylmethyl with *ortho* proton coupling constant = 2.5 gauss, *meta* proton coupling constant = 1.1 gauss, *para* proton coupling constant = 2.8 gauss and methyl proton coupling constant = 2.2 gauss. The sixteen outermost lines at each end of the calculated spectra which have relative intensities of less than 7% that of the most intense lines, are not shown.

exact coincidences, and, consequently, the lines might be broader. If this were the case, the outermost hyperfine components would be broader than the central ones. An uncertainty of ±0.05 gauss has been estimated in the splitting constants, leading to an uncertainty of about 6% in the 2:1 ratio of the splitting constants.

Tri-*p*-methoxytriphenylmethyl (See Fig. 1).—The observed spectrum of tri-*p*-methoxytriphenylmethyl appears in Fig. 3. A careful examination of the central group of hyperfine components shows that the group consists of an even number of lines (*i.e.*, the center of the spectrum lies between two lines of equal intensity). This pattern must arise from an odd number of equivalent protons and the small hyperfine splitting constant of 0.34 ± 0.02 gauss can, therefore, be assigned to the methoxy protons. The splitting of 2.89 ± 0.02 gauss is not very different from the value assigned to the *ortho* protons in triphenylmethyl; consequently, it has been attributed it to the *ortho* protons in tri-*p*-methoxytriphenylmethyl. If the *meta* protons are now considered, the spectrum should consist of 490 hyperfine components; many fewer are observed which indicates that a high incidence of superposition of lines occurs. Calculations indicate that the ratio of *meta* to methoxy proton coupling constants must be very nearly integral. The hyperfine components broaden with displacement from the center of each group, the broadening occurring on the side of the line away from the center. This suggests that the ratio of *meta* to methoxy proton coupling constants may be slightly larger than integral. In Fig. 3 the calculated spectra are indicated for *meta*:methoxy ratios of 3:1 and 2:1. Because of uncertainties in the measurement of intensities, it was not possible to distinguish unambiguously between these two although the former was preferred. Taking the slight deviation from integral values of the ratio into consideration the value 1:05 ± 0.10 gauss was assigned to the *meta* splitting although 0.71 ± 0.10 gauss remains a possibility.

The *meta* splitting is about the same as in triphenylmethyl but the *ortho* splitting has increased by about 15%. The methoxy splittings are very small, in marked contrast to what is observed in alkoxy substituted semiquinones[12] where a large spin density is apparently localized on the oxygen.

***o*-Toluyldiphenylmethyl** (See Fig. 1).—This compound was studied in order to determine the effect on the spin densities of additional inter-ring strains. More symmetrical molecules such as tri-*o*-toluylmethyl would be more ideally suited for these studies, but they probably are not stable. The observed spectrum of *o*-toluyldiphenylmethyl

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is shown in Fig. 4. The spectrum consists of over 60 hyperfine components with an average spacing of 0.1 to 0.2 gauss. The fact that there are not many more component lines giving rise to an unresolvable single broad line indicates that protons in similar positions on different rings may well have very similar splitting constants. The spectrum appears to be symmetrical about its center. The two most intense components are 2.83 ± 0.03 gauss apart and because of the similarity of their splitting to that of the corresponding lines in triphenylmethyl (2.77 ± 0.02 gauss),[6] this value was chosen as the splitting constant for all three para hydrogens. Calculations[5,13,14] indicate that spin densities decrease in approximately the same proportion at various ring positions in going from planar to propeller configurations of the radicals. If one assumes that the methyl group does not affect the spin densities at the other positions on the toluyl ring, one can, in the light of the discussion above and the similarity between the *para* coupling constant in triphenylmethyl and *o*-toluyldiphenylmethyl, take the *meta* and *ortho* splitting constants equal to those in triphenylmethyl, *i.e.* 1.1 ± 0.1 and 2.5 ± 0.1 gauss, respectively. Even with all these approximations of equivalence of protons on different rings one must assume, if one is to account for the relatively few lines observed, that the splitting due to the methyl protons is an integral multiple (or dividend) of one of the ring proton coupling constants.

Since the Q value for methyl protons has been found to be about equal to that for ring protons,[15] one would expect the methyl proton coupling constant to have approximately the same value as the coupling constant of the *ortho* proton of the substituted ring. The methyl proton coupling constant, therefore, should be about 2.5 gauss. Values of this constant below 1 gauss yielded calculated spectra in very poor agreement with the observed one. A series of calculations were carried out with the constant between 1 and 2.8 gauss. The best correspondence between theory and observation was at 2.2 ± 0.2 gauss; this calculated spectrum is exhibited in Fig. 4. Several discrepancies exist between the two spectra in Fig. 4, but the overall patterns are in reasonably good agreement.

These rather tentative assignments tend to indicate that the substituted methyl group does not alter the relative orientations of the rings very much, probably due to the fact that the rings are already twisted out of planarity in the unsubstituted triphenylmethyl. The results indicate that the spin density on the *ortho* carbon to which the methyl is attached is about 90% of the spin density on the other *ortho* carbons. Since both the electronic theory and the spectral analysis are subject to considerable uncertainty, this figure should not be taken too seriously.

Summary.—Chloride substitution in the *para* position increases slightly the spin density at the *ortho* carbon and rather more the spin density at the *meta* position. Methoxy substitution in the *para* position does not seem to affect the *meta* carbon spin density but increases considerably the spin density on the *ortho* carbon; the spin density on the oxygen appears to be small. C^{13} studies on these compounds are contemplated; these may throw light on the effect of substituents upon spin densities, a phenomenon that has not yet been well studied, and upon the question of the planarity of the methyl structure.[16]

NOTE ADDED IN PROOF.—It is interesting to compare the recent measurements[17] on tris-*p*-nitrophenylmethyl with those in the present study. In tris-*p*-nitrophenylmethyl the proton coupling constants are 1.14 ± 0.02 and 2.50 ± 0.02 gauss for the *meta* and *ortho* protons, respectively.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA]

The Energy Dependence of Cross Sections of Some Ion–Molecule Reactions[1]

BY LOWELL P. THEARD AND WILLIAM H. HAMILL

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The energy dependence of reaction cross sections has been observed for various ion–molecule reactions. The secondary ions $C_4H_{10}Br_2^+$, $C_4H_9Br^+$, $C_4H_{10}Br^+$, $C_2H_6Br_2^+$ and $CHBr_2^+$ from C_2H_5Br; $C_6H_{14}I_2^+$ from *n*-C_3H_7I and $C_6H_{14}Cl^+$ from *s*-C_3H_7Cl indicate low energy limits of stability. Tropylium and substituted tropylium ions appear to result from reactions of CH_3^+, CD_3^+, $CHCl_2^+$ and CCl_3^+ with C_6H_6; they give evidence of transitions in reaction cross sections at *ca.* 1.3–2.0 ev. ion energy which are identified with instability resulting from head-on collisions.

Introduction

The recent literature on ion–molecule reactions reports comparatively few examples which are consistent with the point particle ion-induced dipole description.[2,3] It has been pointed out in recent publications[4,5] that for every ion–molecule interaction one must expect a transitional relative translational energy E_t above which only head-on encounters can occur. The functional dependence changes from $Q=f(E_e^{-1/2})$ for $E_e < E_t$ to $Q=f(E_e^{-1})$ for $E_e > E_t$, where E_e is the terminal ion energy, due to the repeller field, at the exit slit of the ionization chamber. At sufficiently high ion-molecule relative velocity the secondary ion

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[1] This article is based on a thesis submitted by L. P. Theard in partial fulfillment of the requirements for the Ph.D. Degree in the University of Notre Dame, June 1960. This work was performed under the auspices of the Radiation Laboratory, University of Notre Dame, supported in part by the U.S.A.E.C. under contract AT(11-1)-38.

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