in the octafluorocyclobutane experiments. The first step in the formation of CF_2: from this parent must involve scission of a carbon–carbon bond. The butane diradical thus formed and all intermediate diradicals must be extremely unstable. Apparently, the butane diradical either reverts quickly back to the parent compound or it completely unzips to CF_2:

Finally, an interesting consideration in this work is the possible presence of species other than CF_2: and $CF_3\cdot$ which could lead to the same chlorination and warm-up products observed. For example, can CF_2: exist in singlet and/or triplet states? We have recently acquired some preliminary gas phase data which favors the existence of both states and assigns the ground state to the singlet. This same evidence indicates that the captive CF_2: radicals studied in this work are not in the ground singlet state as might be expected but are rather in some excited triplet state. This should be regarded as preliminary information which we plan to investigate more thoroughly in the near future. Another possibility is the presence of ions and radical-ions such as CF_3^+ and $CF_2\cdot^+$. These could certainly explain the halogenation and warm-up products as easily as the pure radicals. However, it is felt that their presence in high concentration is unlikely because: (1) The plasma in which they are created probably contains these ions initially, but on the average, the plasma contains just as many electrons which would neutralize the ionic charge in the matrix (it is highly unlikely that electrons would be trapped along with the ions). (2) Build-up of a space charge about the cold finger due to accumulation of ions would cut down the efficiency in time. No such effect was noticed. (3) A metal spatula cooled to liquid nitrogen temperatures and placed in contact with the deposit does not seem to discharge it or affect it in any way.

Acknowledgments.—The author is especially indebted to Drs. H. L. Smith and J. J. Drysdale for their interest and helpful suggestions in this work. Also, to Dr. D. G. Hummel for his extremely pure samples of hexafluoroethane and octafluorocyclobutane.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY]

Microwave Absorption and Molecular Structure in Liquids. XLVI. The Apparent Dipole Moments of Several Symmetrical Molecules[1,2]

BY ERNEST N. DICARLO[3] AND CHARLES P. SMYTH

RECEIVED NOVEMBER 13, 1961

The dielectric constants and losses at wave lengths of 1.25 and 3.22 cm. and 575 m. have been measured for hexachlorobenzene, hexamethylbenzene and 4,4′-dinitrobiphenyl in benzene solution at 20°, *p*-dinitrobenzene in benzene solution at 25° and iron pentacarbonyl as the pure liquid at 20°. Dielectric constant and loss measurements have also been made at wave lengths of 3.22 cm. and 575 m. on benzene solutions of phenanthrene and chloranil at 40°, anthraquinone and *p*-benzoquinone at 50° and tetramethyl-1,3-cyclobutanedione at 20°. The dielectric constant and loss were also measured at 3.22 cm. wave length for *p*-benzoquinone in benzene solution at 20°. The results were used to calculate upper limits to the permanent dipole moments of the above molecules. The absence of frequency dependence of the dielectric constant data excludes any dipole moment values greater than approximately 0.5 *D*, while the absorption data exclude any values greater than 0.10 or 0.20 *D*, depending upon the concentration of the solution measured.

This study was undertaken because many careful dielectric constant measurements at radio frequencies have indicated the possession of small but appreciable dipole moments for supposedly symmetrical molecules.[4,5] Whether a molecule has a permanent dipole moment or not can be determined by measuring the frequency dependence of the dielectric constant and loss in the region where anomalous dielectric dispersion should occur if the molecule were polar.[6] In this frequency region, the dielectric constant of a polar liquid decreases with increasing frequency with most of the decrease occurring within a 100-fold frequency range. In this same range, the dielectric loss changes from a small value through a maximum to a small value again. The loss factor due

TABLE I

SOURCES, METHODS OF PURIFICATION, MELTING POINTS AND REFRACTIVE INDEX

Compound	Source	M.p., °C.
p-Dinitrobenzene[a]	A	175.0–175.8
Hexachlorobenzene[a]	A	230.2–231.0
Chloranil[a]	A	294.2–294.6 (sealed tube)
Hexamethylbenzene[a]	B	166.3–167.0
4,4′-Dinitrobiphenyl[a]	B	239.8–240.6
Anthraquinone[a]	B	284.8–285.6 (sublimes)
Tetramethylcyclobutanedione[a]	B	114.5–114.9
Phenanthrene[b]	B	102.6–103.9
p-Benzoquinone[d]	C	113.4–113.5 n_D 19.7°
Iron pentacarbonyl[c]	D	1.51705

[a] Repeated crystallization from benzene and drying under vacuum over phosphorus pentoxide in an Abderhalden pistol. [b] Repeated crystallization from benzin (60–70°) and drying under vacuum over phosphorus pentoxide in an Abderhalden pistol. [c] Fractionally distilled. [d] Repeated crystallization from 95% ethanol. Purified by G. F. Wright.

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[1] This research was supported by the U. S. Army Research Office (Durham). Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

[2] This paper represents part of the work submitted by E. N. DiCarlo to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Esso Foundation Fellow, 1960–1961. National Science Foundation Summer Fellow, 1961.

[4] C. C. Meredith, L. Westland and G. F. Wright, *J. Am. Chem. Soc.*, **79**, 2385 (1957).

[5] P. Podleschka, L. Westland and G. F. Wright, *Can. J. Chem.*, **36**, 574 (1958).

[6] C. P. Smyth, "Dielectric Behavior and Structure," McGraw–Hill Book Company, New York, N. Y., 1955, Chap. II.

to dipole orientation polarization is a maximum at a wave length known as the critical wave length. On the other hand, if the molecule is non-polar, the dielectric constant is essentially independent of frequency and the dielectric absorption is very nearly zero.

Purification of Materials.—The substances investigated were obtained from (A) Matheson, Coleman and Bell, (B) The Eastman Kodak Company, (C) Prof. George F. Wright, University of Toronto, and (D) A.D. Mackay, Inc. The source of each compound, method of purification and melting point or refractive index are listed in Table I.

The benzene used was obtained from the Allied Chemical Corporation and was of the reagent grade, thiophene-free quality. It had been stored over Drierite for three months. The solutions were also stored over Drierite until immediately prior to measurement.

Experimental Results

The dielectric constants and losses measured by methods described elsewhere,[7-9] together with refractive index data, are listed in Table II. The concentration in terms of weight per cent of solute is listed after each solution. The measurements at 1.25 and 3.22 cm. were made employing waveguide techniques, while at 575 m. a heterodyne-beat apparatus was used. Refractive index measurements were carried out using a Bausch and Lomb precision refractometer equipped with a sodium vapor lamp.

TABLE II

DIELECTRIC CONSTANTS, LOSSES AND SQUARES OF REFRACTIVE INDEX

Wave length	Dielectric constant Benzene	Dielectric constant Solution	Loss factor Benzene	Loss factor Solution
		Hexachlorobenzene (20°)		
	Benzene	Solution (3.77%)	Benzene	Solution
575 m.	2.285	2.291		
3.22 cm.	2.285	2.292	0.00049	0.00052
1.25 cm.	2.284	2.291	0.0034	0.0038
n^2D	2.2515	2.2587		
		Hexamethylbenzene (20°)		
	Benzene	Solution (6.13%)	Benzene	Solution
575 m.	2.283	2.287		
3.22 cm.	2.282	2.286	0.00046	0.00047
1.25 cm.	2.286	2.291	0.0025	0.0023
n^2D	2.2515	2.2567		
		Phenanthrene (40°)		
	Benzene	Solution (15.53%)	Benzene	Solution
575 m.	2.243	2.320		
3.22 cm.	2.242	2.319	0.00051	0.00046
n^2D	2.2149	2.2970		
		Iron pentacarbonyl (20°)		
	Pure liquid		Pure liquid	
575 m.	2.626			
3.22 cm.	2.618		0.0046	
1.25 cm.	2.621		0.0098	
n^2D	2.3014			
		p-Dinitrobenzene (25°)		
	Benzene	Solution (2.67%)	Benzene	Solution
575 m.	2.274	2.286		
3.22 cm.	2.275	2.284	0.00036	0.00055
1.25 cm.	2.275	2.285	0.0027	0.0036
n^2D	2.2540 (19.1°)	2.2584 (19.1°)		
		4,4′-Dinitrobiphenyl (20°)		
	Benzene	Solution (satd.)	Benzene	Solution
575 m.	2.283	2.287		
3.22 cm.	2.280	2.283	0.00048	0.00047
1.25 cm.	2.286	2.287	0.0012	0.0014
n^2D	2.2515	2.2526		
		p-Benzoquinone (50°)		
	Benzene	Solution (*ca.* 7%)	Benzene	Solution
575 m.	2.224	2.258		
3.22 cm.		2.318 (20°)		0.00063 (20°)
	2.223	2.257	0.00052	0.00055
n^2D	2.1978	2.2051		
		Chloranil (40°)		
	Benzene	Solution (2.62%)	Benzene	Solution
575 m.	2.246	2.253		
3.22 cm.	2.244	2.250	0.00046	0.00059
n^2D	2.2149	2.2205		
		Anthraquinone (50°)		
	Benzene	Solution (sat'd.)	Benzene	Solution
575 m.	2.224	2.229		
3.22 cm.	2.223	2.228	0.00042	0.00041
n^2D	2.1972	2.2006		
		Tetramethyl-1,3-cyclobutanedione (20°)		
	Benzene	Solution (14.4%)	Benzene	Solution
575 m.	2.284	2.300		
3.22 cm.	2.283	2.301	0.00053	0.00066
n^2D	2.2523	2.2195		

Discussion of Results

Each dielectric constant at 3.22 cm. and 1.25 cm. in Table II is the average of five independent determinations, all of which were in agreement to within 0.03%. Four independent measurements of the dielectric absorption at 3.22 cm. agreed to within 10% in all cases, except for the *p*-dinitrobenzene determination, where the agreement was to within 20%. However, the error in the loss data at 1.25 cm. was very large ,except in the case of iron pentacarbonyl. Therefore, these losses were not used in any of the calculations excepting those involving iron pentacarbonyl. As can be seen from the data on benzene, the uncertainty in the dielectric constant at the frequencies used in the measurements is of the order of 0.1%. With an uncertainty of this magnitude, the criterion of variation of dielectric constant with frequency could not be used to detect the presence of extremely small dipole moments, since some of the solutions studied were so dilute that the variation for compounds having moments less than 0.5 *D* could possibly be smaller than the experimental error. However, the reliability in the dielectric absorption measurements at 3.22 cm. was sufficient so that, in some cases, moments of 0.10 *D* would have been detected if present.

The temperatures at which the measurements were carried out were chosen so that all the substances listed, if polar, would exhibit maximum

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(7) J. G. Powles and C. P. Smyth, "Physical Methods of Organic Chemistry," A. Weissberger, editor, Vol. I, 3rd Ed., Interscience Publishing Co., New York, N. Y., 1960, Part III, Chap. XXXVIII, XXXIX.

(8) H. L. Laquer and C. P. Smyth, *J. Am. Chem. Soc.*, **70**, 4097 (1948).

(9) W. M. Heston, Jr., A. D. Franklin, E. J. Hennelly and C. P. Smyth, *ibid.*, **72**, 3443 (1950).

dielectric absorption somewhere between 2 and 10 cm., making the 3 cm. wave length ideal for such a study. The Debye equation as used by Jackson and Powles[10] and Heston and Smyth[11] and given in equation 1 was employed in the interpretation of the loss measurements

$$\mu = \left[\frac{27\epsilon''kT[1 + [2\pi f\tau]^2]}{8[\epsilon' + 2]^2 Nc\pi^2 f\tau}\right]^{1/2} \qquad (1)$$

where μ is the permanent dipole moment, ϵ' is the dielectric constant, T is the absolute temperature, k is the Boltzmann constant, f is the frequency in cycles per second, τ is the relaxation time in seconds, N is Avogadro's number, c is the number of moles of polar solute per cc. of solution and ϵ'' is the dielectric loss. For the solution measurements, ϵ'' is equal to the loss of the solution minus the loss of the solvent. Using this method, the value of the relaxation time has to be estimated from existing data in the literature. However, it was found that the calculated dipole moments were fairly insensitive to the choices of τ made for the particular molecules considered in this study. Designations of upper limits to the dipole moments were made by considering the reliability of the absorption data and the concentration of the solution measured. Only when fairly concentrated solutions were investigated could moments of 0.10 D be excluded.

Hexachlorobenzene, Hexamethylbenzene and Phenanthrene.—For hexachlorobenzene and phenanthrene, the observed dielectric constants of the solutions studied are invariant with frequency well within the experimental error. For hexamethylbenzene, the dielectric constant at 1.25 cm. is in disagreement with the other two values to about 0.2%. However, approximately the same variation was found with the solvent, benzene. The losses at 3.22 cm. of the respective solutions are identical with those of the solvent within the experimental error. Considering the magnitude of the concentration of the solution measured, it is concluded that hexamethylbenzene and phenanthrene, if polar, cannot have permanent dipole moments greater than 0.10 D, while hexachlorobenzene cannot have a moment greater than 0.20 D. As can be seen from the refractive index data, these molecules exhibit little atomic polarization, P_A. The variation of the dielectric constant and the square of the refractive index with concentration are practically identical. In this sense, these substances do not fall logically in line with the rest of the compounds investigated, all of which show an appreciable P_A. Phenanthrene was investigated due to the suggestion of Professor Kauzmann of this Laboratory. O. Sovers and W. Kauzmann[12] found that a non-uniform distribution of charge densities is brought about by *d*-hybridization, which is in marked contrast to the uniform distribution resulting from the use of pure *p*-orbitals. This effect gives a dipole moment along the two-fold axis of *ca.* 0.17 D.

Using equation 1, and assuming a dipole moment of 0.17 D and a critical wave length, λ_m, somewhere between 3 and 10 cm., one calculates absorptions approximately three times greater than that observed at 3.22 cm.: $\epsilon'' = 0.0017$ ($\lambda_m = 3$ cm.), $\epsilon'' = 0.0014$ ($\lambda_m = 7$ cm.), $\epsilon'' = 0.0012$ ($\lambda_m = 10$ cm.). Such losses would have been easily detectable. The critical wave length range (3–10 cm.) is very conservative when compared with the values of λ_m found at 40° in benzene solution for 9-bromophenanthrene[13] (5.86 cm.) and phenanthrenequinone[14] (3.86 cm.). It is used here merely to point out that the argument [$\mu < 0.10$ D) does not depend on a particular choice of λ_m.

Iron Pentacarbonyl.—Previous dipole moment measurements of iron pentacarbonyl in benzene solution[15–17] have yielded moments of the order of 0.6–0.8 D. In the above work the atom polarization was taken as zero. Assuming P_A equal to 20% of the electronic polarization, P_E, the static dipole moment vanishes.[17] Electron diffraction data[18] favor a trigonal bipyramidal (D_{3h}) structure which would have no dipole moment. Assuming a Debye line shape, two independent estimates of the relaxation time were made from a linear plot of ϵ' *vs.* $\epsilon''\omega$,[19] where ω is the angular frequency. Because of the exceedingly small variation of ϵ' with frequency, the two estimates differed so widely as to be meaningless. Dipole moments of 0.15 and 0.10 D were calculated from the 1.25 and 3.22 cm. data, respectively,[20] assuming a critical wave length somewhere between 0.6 and 2 cm. Also, the variation of dielectric constant with frequency, about 0.4% from 575 m. to 3.22 cm., is too small to account for a moment of 0.8 D for iron pentacarbonyl. These results show that, at least, a large part of the difference between the total polarization and P_E is due to a large atomic polarization.

***p*-Dinitrobenzene and 4,4′-Dinitrobiphenyl.**—*p*-Dinitrobenzene has been studied in the vapor phase,[21] in benzene solution[5,22] and in the solid state.[3] Coop and Sutton[21] found that the total polarization P was constant from 199.6 to 255.2° and differed by not more than 1 cc. from the value in benzene solution[22] at 25°. Therefore, an assignment of 8.2 cc., $P - P_E$, was made to the atomic polarization, P_A.[21] Wright, *et al.*,[5] however, from dielectric constant determinations of pellets of this substance, concluded that the distortion polarization, $P_E + P_A$, was only about 2 cc. higher than P_E. Since their measured polarization values in benzene solution varied appreciably with temperature, they concluded that *p*-dinitrobenzene

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[21] I. E. Coop and L. E. Sutton, *J. Chem. Soc.*, 1269 (1938).

[22] C. G. Le Fèvre and R. J. W. Le Fèvre, *ibid.*, 957 (1935).

had a permanent moment which varied from about 0.8 to 0.7 D over a range of 20°.

The findings of the present work agree with the assignment of an abnormal P_A, to this substance. The observed dielectric constants of the solution studied are invariant with frequency well within experimental error, excluding permanent moments greater than *ca.* 0.5 D. Also, assuming a dipole moment of 0.8 D, one calculates a 3.22 cm. absorption ten times greater than that observed. Considering that the loss measurements in this case were no more reliable than 20%, it is concluded that *p*-dinitrobenzene cannot have a permanent moment greater than 0.20 D. The estimate of τ, 19×10^{-12} sec., was made from a consideration of the relaxation time measured for *p*-nitrotoluene.[23] However, as was mentioned earlier, the choice of τ is not critical. For example, moment values of 0.19, 0.17, 0.17, 0.18 and 0.20 D are obtained for *p*-dinitrobenzene using relaxation times of 9, 14, 19, 28 and 38×10^{-12} sec., respectively.

4,4′-Dinitrobiphenyl has been studied in benzene[4,24] and in dioxane[4] solution and in the solid state.[4] Le Fèvre and Vine made an assignment of 21.5 cc. to P_A on the assumption that this substance would have axial symmetry and, therefore, no dipole moment. Wright, *et al.*, from solid state measurements obtained a distortion polarization only 0.8 cc. higher than that ascribed to electronic polarization. Their determination of the total polarization in benzene solution at 40° was about 10 cc. lower than that observed by Le Fèvre and Vine at 25° in the same solvent. They assign a value of 0.7 to 1.0 D to the dipole moment and conclude that this molecule must have a non-linear structure. The dielectric loss measurements in Table II indicate that this compound, if polar, cannot have a permanent moment greater than 0.20 D and, therefore, confirm the existence of a large P_A. The dielectric constants measured for the saturated solution are identical at 575 m. and 1.25 cm. The dielectric constant at 3.22 cm. is in disagreement with the other two values to about 0.2% but about the same variation was observed with benzene.

Quinones.—The difference, $P - P_E$, for *p*-benzoquinone has been shown to be about 8 cc.[4,21,25–28] or about 20% of the total polarization, which amounts to an abnormal P_A if this molecule is nonpolar. This discrepancy coupled with some question about the temperature dependence of P has led to the assignment of a dipole moment of *ca.* 0.7 D.[25–27] Wright's directly determined P_A (1.7 cc.) agrees with this assignment. However, Coop and Sutton's temperature study[21] of P indicated the compound to be non-polar. Electro-optic birefringence measurements[29] agree with a centro-symmetric structure and exclude dipole moments greater than 0.15 D. The birefringence study also showed that the large value of $P - P_E$ is not caused by contributions from the orbital moments of the lone pair electrons of the oxygen atoms under the action of the external field as had been proposed.[30] From refractive index measurements in the infrared region, Cartwright and Errera[31] made an assignment of 9.5–16.2 cc. to P_A. Intensity measurements in the infrared region on *p*-benzoquinone solutions[32] also favor a large P_A.

Our results indicate that this molecule cannot have a permanent moment greater than 0.10 D. Based on shape and size considerations, *p*-benzoquinone, if polar, would be expected to have maximum dielectric loss somewhere between 1 and 3 cm. at the temperatures used in the measurements. A dipole moment of 0.7 D would have led to a much more intense absorption at 20°, approximately ten times greater than that observed. There also would have been a detectable variation of absorption with temperaure, but as can be seen from Table II, the losses observed for the solution are practically identical at 20° and 50°.

A dipole moment 0.71 D has been reported for anthraquinone[4] and one of 0.6 S for chloranil.[33] The results in Table II indicate an upper limit of 0.20 D for chloranil. No attempt was made to interpret the loss measurements on anthraquinone due to its extremely low solubility in benzene. However, a moment of 0.7 D would have led to a much greater absorption than that observed even for the extremely dilute solution measured.

Tetramethyl-1,3-cyclobutanedione has been studied by several investigators.[5,21,28] Coop and Sutton[21] found that in the vapor phase the polarization is constant over a 60° range of temperature. The polarization value at 25° in benzene solution[28] differs by only 1.6 cc. from that of the vapor at 225°, hardly indicative of orientation polarization. It was concluded from the vapor measurements that this molecule was non-polar, possessing an atomic polarization of *ca.* 10 cc.. However, the solid measurements[5] gave an atomic polarization of only 0.9 cc., which would indicate a permanent moment of *ca.* 0.8 D. Considering the concentration of the solution investigated and assuming λ_m to lie somewhere between 2 and 4 cm., an upper limit of 0.10 D is calculated from the loss data in Table II agreeing with an exceptionally large atomic polarization.

The determination of these small upper limits for the dipole moments of the probably symmetrical molecules which have been considered is not to be regarded as establishing the existence of such small moments. Actually, with the exception of iron pentacarbonyl, the moments are experimentally indistinguishable from zero, and the upper limits given are the maximum possible experimental errors. The principal reason for the frequent

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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]

RECEIVED AUGUST 28, 1961

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	$\lvert\rho/\rho_p\rvert$	ρ	$\lvert\rho/\rho_p\rvert$	ρ	$\lvert\rho/\rho_p\rvert$	$\lvert a\rvert$ gauss	$\lvert a/a_p\rvert$	$\lvert\rho_{exp}\rvert$
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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