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Electron Spin Resonance and Electronic Structure of Triphenylmethyl[1,2]

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The anisotropic hyperfine splitting due to C^{13} in the methyl position of triphenylmethyl has been obtained from dilute solutions of triphenylmethyl in triphenylamine. Analysis of the measurements yields an estimate of density of unpaired electron at the methyl position. Estimates of densities at other positions are made from proton hyperfine splittings. The magnitudes of the densities require that some of them have negative sign. A simple valence bond approximation is in good agreement with the observations.

Several observations[3–6] of the electron spin resonance of triphenylmethyl have been described in the literature. In this paper we shall summarize the older observations, report some new ones and discuss the bearing which all of them have on the problem of the electronic structure of triphenylmethyl.

Experimental Observations

The proton hyperfine splitting in liquid solutions of triphenylmethyl was first reported by Jarrett and Sloan,[3] who observed a symmetrical spectrum of twenty-one groups of lines. It was found that the interval between adjacent groups was 1.5 oersteds and that each group consisted of at least four closely spaced lines. In addition there are two pairs of weak lines at each end of the spectrum.[7] The breadth of the entire spectrum is about 35 oersteds.

The hyperfine splitting in liquid solution produced by C^{13} in the methyl position is 26 oersteds.[4,5] The spectrum of triphenylmethyl containing about 50 atom % C^{13} in the methyl position contains a central group of twenty-one lines from the species containing C^{12} and two satellite groups of twenty-one lines each from the C^{13} species.

The new experimental observations which we report here are the spectra of solid solutions of triphenylmethyl in triphenylamine which yield information which is not contained in the spectra of the liquid solutions. Our aim had been to obtain well resolved hyperfine spectra from single crystals and to observe the anisotropies directly. Unfortunately we have been able to obtain only partial resolution of the spectra of the crystals. The spectrum of a single crystal is independent of its orientation and is indistinguishable from the spectrum of a polycrystalline sample. Apparently the number of orientations of the individual molecules in a single crystal is too large to permit resolution of the spectra of the individual orientations.[8] Absence of polarization and anisotropy in the optical spectra of the crystals leads to similar conclusions.

The electron spin resonance spectrum of $(C_6H_5)_3C^{12}$ in a dilute single crystal contains a single line about equal in breadth to the envelope of the spectrum in dilute liquid solution. The spectrum of $(C_6H_5)_3C^{13}$ consists of two broad lines separated by 45 oersteds with a separation and breadth which are independent of temperature over the range 4 to 300°K. The breadth of each line is greater than that of the line from $(C_6H_5)_3C^{12}$.

Experimental Details

The crystals were prepared as follows. A solution of triphenylmethyl in toluene containing a trace of triethylamine was prepared in a dumper on the vacuum line by the method of Lewis, Lipkin and Magel.[9] The solution was poured into a U tube into which excess triphenylamine had previously been distilled. The tube was sealed off, the contents shaken in order to saturate the solvent with triphenylamine and the saturated solution decanted to one side of the inverted U tube. The arm containing the solution was maintained at about 25° and the other at about 15° in order to distil the solvent slowly from the saturated solution. The substances were shielded from light during these operations. After satisfactory crystals were formed (this sometimes requires several repetitions of the process), the apparatus was broken open and the crystals removed and dried of solvent. They are stable in air for many months.

The magnetic resonance spectrum was observed in a spectrometer of high sensitivity. Because of the long spin lattice relaxation time,[10] it is necessary to maintain the microwave power incident on the sample at a low level for observation by slow passage methods. Even the normal output of a 2K25 Klystron is excessive when the sample is mounted in a cavity with $Q \sim 10^3$.

Discussion

Hyperfine splittings may be interpreted in terms of the spin density function. Spin density is a function of position which gives at each point the average value of spin (or spin magnetic moment). The operator whose matrix elements give spin density at a point $\vec{r}$ in the molecule is

$$\sum_k \sigma_{zk}\delta(\vec{r}_k - \vec{r})$$

where σ_{zk} is the Pauli spin operator for the component of spin of the kth electron along the Z-axis, $\vec{r}_k$ is the position of the kth electron, and $\delta(\vec{r}_k - \vec{r})$ is the delta function operator. The sum is carried out over all electrons. The spin density may be thought of as a spin weighted charge density. The contribution of each electron to the spin density at $\vec{r}$ is the product of the probability density for finding the electron at $\vec{r}$ and the average projection of that electron's spin along the Z-axis so that the spin density at each point is not proportional to charge density. In regions of high charge density spin density vanishes if the electrons are perfectly paired.

The hyperfine interaction arises from coupling between the magnetic dipole moments associated with the electron and nuclear spins.[11] The Hamiltonian describing the coupling of electron magnetic

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[2] (2) Presented in part at the meeting of the American Chemical Society in New York, N. Y., September, 1957.

[3] (3) H. S. Jarrett and G. J. Sloan, *J. Chem. Phys.*, **22**, 1783 (1954).

[4] (4) S. I. Weissman and J. C. Sowden, THIS JOURNAL, **75**, 520 (1953).

[5] (5) S. I. Weissman, T. R. Tuttle, Jr., and E. de Boer, *J. Phys. Chem.*, **61**, 28 (1957).

[6] (6) J. H. Lupinski, *J. Chem. Phys.*, **26**, 1766 (1957).

[7] (7) H. S. Jarrett, private communication.

[8] (8) A preliminary investigation of the crystal structure by Professor Lindsay Helmholz reveals that the unit cell contains sixteen molecules.

[9] (9) G. N. Lewis, D. Lipkin and T. Magel, THIS JOURNAL, **66**, 1579 (1944).

[10] (10) S. Weissman, G. Feher and E. Gere, *ibid.*, **79**, 5584 (1957).

[11] (11) The coupling of the orbital motion of the electron with the nuclear magnetic moment is not important in the hyperfine structure of aromatic free radicals.

moment μ_0 with nuclear magnetic moment μ_{Nz} situated at $\vec{r}$ is[12,13]

$$H = \mu_0\mu_{NZ} \sum_k \left[\frac{8\pi}{3} \sigma_{zk}\delta(\vec{r_k} - \vec{r}) + \sigma_{zk} \frac{3\cos^2\theta_k - 1}{|\vec{r_k} - \vec{r}|^3} \right] \quad (1)$$

$\vec{r_k}$ is the position of the kth electron, and θ_k is the angle between $\vec{r_k}$ and the Z-axis. The sum is carried out over all electrons.

The matrix elements of H may be written

$$Hmn = \mu_0\mu_{NZ} \left[\frac{8\pi}{3} \rho_{mn}(\vec{r}) + \int \frac{3\cos^2\theta - 1}{r^3} \rho_{mn}(\vec{r})\mathrm{d}v \right] \quad (2)$$

where

$$\rho_{mn}(\vec{r}) = (m| \sum_k \sigma_{zk}\delta(\vec{r_k} - \vec{r})\, |n)$$

$\rho_{mn}(\vec{r})$ must be evaluated with wave functions which include the motion of the molecule with respect to the laboratory axes. In liquid solutions where tumbling is rapid the spin density has spherical symmetry and only the first term in the bracket (equation 2) contributes.[14] In stationary molecules both terms contribute, the first term leading to isotropic splittings, the second to anisotropic splitting.[15]

We now apply the considerations of the preceding paragraphs to triphenylmethyl. Let us adopt as the unit of spin density the value at the nucleus in the hydrogen atom in its normal state with eigenvalue of $\sigma_z = 1$. (Our choice implies use of πa_0^3 as the unit of volume.) In these units, the sum of the absolute values of the spin densities at the position of all the protons in triphenylmethyl is 0.069. This number is obtained from the total proton splitting in liquid solution. The appearance of spin density at the positions of the protons requires unpairing in the σ bonds since spin density associated with π orbitals vanishes at the protons. A number of studies have shown that electrostatic interaction between π and σ electrons yields spin densities which are of the correct order of magnitude at the ring protons.[16–20] Further, the spin density at each proton in an aromatic free radical is approximately proportional to the integrated spin density on the adjoining carbon.[20–22] The constant of proportionality may be estimated from observations of other free radicals. In benzene negative ion the total proton splitting is 22.5 oersteds.[5] Under the assumption that the same constant of proportionality may be used in triphenylmethyl as in benzene negative ion, we find that the integrated spin density over all carbon atoms 2, 3, 4, 5, 6 is 1.57.[23]

We next consider the spin density at the methyl carbon. Since there are no hydrogen atoms attached to this carbon, we have only the C^{13} splittings for estimation of the integrated spin density. Use of the isotropic C^{13} splitting is not as clear cut as the use of the isotropic proton splitting because both the integrated density on the methyl carbon itself and the π densities on the three adjacent carbon atoms contribute to the spin density at the nucleus. At the present there are available neither sufficient experimental data nor theoretical calculations to permit reliable estimates of the various contributions. If we assume, nevertheless, that the spin density at a carbon nucleus is proportional to the integrated density in the 2p orbital on the same atom, then we can obtain a constant of proportionality from the isotropic splitting of C^{13} in naphthalene negative ion.[24] Using this constant of proportionality to calculate the integrated spin density on the methyl carbon on triphenylmethyl, we obtain the value of 0.68. We shall see in the next paragraphs that analysis of the anisotropic splitting leads to the same value, but the agreement can only be considered as fortuitous at the present time.

The anisotropic part of the splitting yields an independent and more reliable estimate of the integrated spin density at the methyl carbon. We assume that the spin density about each carbon is a constant multiple of the spin density associated with a carbon 2p orbit. The assumption is certainly not completely correct since, although the 2p function vanishes at the nucleus, the spin density does not. However, the deviations become important only where the p part of the distribution is small. It has been shown that

$$(p|3\cos^2\theta - 1|p) = \frac{2}{5}(3\cos^2\alpha - 1)$$

where θ is the angle between position vector and Z-axis and α is the angle between axis of the p function and the Z-axis.[5,25] Similarly if $\rho(\vec{r})$ is the spin density associated with a p function whose axis makes angle α with the Z-axis

$$\int \rho(\vec{r}) \frac{3\cos^2\theta - 1}{r^3} \mathrm{d}v = \frac{2}{5}(3\cos^2\alpha - 1)\left\langle \frac{1}{r^3} \right\rangle \int \rho(\vec{r})\mathrm{d}v$$

$<1/r^3>$ is evaluated for a carbon $2p$ function, and $\int \rho(\vec{r})\,\mathrm{d}v$ is confined to contributions from the atom in question. The shape of a magnetic resonance absorption for angles randomly distributed has been worked out by Pake[26] in his study of nuclear resonance of hydrated crystals. Adaptation of his result to our case leads to

$$\Delta H_A = \frac{4}{5}\mu_{C^{13}} \left\langle \frac{1}{r_3} \right\rangle \int \rho(\vec{r})\mathrm{d}v$$

where ΔH_A is the contribution of the anisotropic splitting to the interval (in oersteds) between maxima of the C^{13} doublet, and $\mu_{C^{13}}$ is the moment of C^{13}.

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(12) E. Fermi, *Z. Physik*, **60**, 320 (1930).

(13) A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc.* (*London*), **205**, 135 (1951).

(14) S. I. Weissman, *J. Chem. Phys.*, **22**, 1378 (1954).

(15) Certain combinations of spin orbit interaction, orbital degeneracy and anisotropic splitting factors yield additional contributions both to isotropic and anisotropic splittings. These appear to be negligibly small for aromatic free radicals. These matters are discussed by H. M. McConnell, *ibid.*, in press.

(16) R. Bersohn, *ibid.*, **24**, 1066 (1956).

(17) H. M. McConnell, *ibid.*, **24**, 764 (1956).

(18) S. I. Weissman, *ibid.*, **25**, 890 (1956).

(19) H. S. Jarrett, *ibid.*, **25**, 1289 (1956).

(20) H. M. McConnell and D. Chestnut, *ibid.*, **28**, 107 (1958).

(21) E. de Boer, *ibid.*, **25**, 190 (1956).

(22) T. R. Tuttle, Jr., Ph.D. Thesis, Washington University, 1957.

(23) It should be noted that integrated spin density is dimensionless, while spin density itself has dimensions of reciprocal volume.

(24) T. Tuttle and S. Weissman, *J. Chem. Phys.*, **25**, 189 (1956).

(25) F. Reif and E. Purcell, *Phys. Rev.*, **91**, 631 (1953).

(26) G. E. Pake, *J. Chem. Phys.*, **16**, 327 (1948).

In order to find ΔH_A from the measured splitting of 45 oersteds, we must decide about the sign of the isotropic splitting relative to the anisotropic part. The choice of "normal" signs, *i.e.*, those which would accompany a single electron in a hybrid s-p orbit, would require that $\Delta H_A = 71$ oersteds. Choice of abnormal signs leads to $\Delta H_A = 19$ oersteds. We require $\langle 1/r^3 \rangle$ for a 2p orbit in order to complete the analysis of the experiment. We have computed $\langle 1/r^3 \rangle$ for Torrance's[27] self consistent field atomic 2p function for a carbon atom in the configuration (2s)(2p).[3] The result is $\langle 1/r^3 \rangle = 0.980 \times 10^{25}$ cm.$^{-3}$. The two possible values of ΔH_A, 71 and 19 oersteds yield $\int \rho(\vec{r})dv = 2.54$ and 0.68, respectively. The former result seems impossibly high, while the latter appears reasonable.

At this point we note that an earlier interpretation[5] of the isotropic splitting for which one of us (S.I.W.) bears principal responsibility now appears to be unjustified. When only the isotropic splitting had been measured, it seemed to be too large for any reasonable assignment of spin density. Hence the suggestion was made that the three central bonds in triphenylmethyl are not coplanar and that s-p hybridization of a singly occupied molecular orbital accounted for the isotropic splitting. The newer results do not rule out deviations from coplanarity, but they do not require them.

Some of the proposed electronic structures for triphenylmethyl may be tested against the above experimental results. We note that all one configuration molecular orbital descriptions lead to difficulties. In all such descriptions the integrated spin density on each atom has the same sign. The sum of the integrated spin densities must be plus one for the state of positive spin.[20,22] However, the experiments indicate that the sum of the *absolute* values of the integrated spin densities on all 2, 3, 4, 5 and 6 carbon atoms and on the methyl carbon is approximately 2.2. Hence negative spin densities must appear at some atoms. Single configuration molecular orbital descriptions cannot yield such a result. The Hückel[28] approximation, in particular, yields zero spin density on carbon atoms 1, 3, 5, 0.077 on each of the other ring carbons and 0.30 on the methyl carbon. The simple Hückel function fails to yield both the observed pattern of proton splittings and the magnitude of the methyl carbon splittings.

The Pauling–Wheland valence bond theory, on the other hand, yields results in far better agreement with experiment. Brovetto and Ferroni[29] have calculated spin densities at the *ortho*, *meta* and *para* carbons from a Pauling–Wheland valence bond function. They find that the integrated spin densities alternate in sign from one carbon atom to the next and that the relative values yield a proton hyperfine pattern in excellent agreement with experiment. Their work demonstrates, in fact, that a valence bond model yields alternating signs of spin density for starred and unstarred atoms in all odd-alternant free radicals. We have extended Brovetto and Ferroni's calculations to include all the carbon atoms in triphenylmethyl. The results are shown in Fig. 1a.

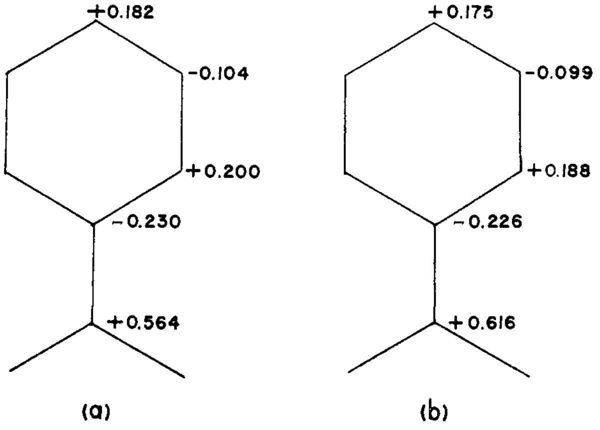

Fig. 1.—Spin densities in triphenylmethyl according to valence bond theory: (a) for planar triphenylmethyl; (b) for propeller shaped triphenylmethyl.

The calculations of Brovetto and Ferroni may be improved by a simple approximation which takes into account the propeller twisting of the three rings. Such twisting appears to be required on steric grounds. If allowance for the twist is made by decrease of the resonance integrals between the methyl carbon and its three neighbors to 0.85 of the value for other neighbors, the spin densities shown in Fig. 1b are obtained. Our choice of 0.85 corresponds to a rotation of 30 degrees for each ring.

A wave function obtained by Murrell[30] in which the ground state of triphenylmethyl is a mixture of four configurations yields integrated spin density 0.68 on the methyl carbon. However it does not yield the observed pattern of proton hyperfine splittings.

Conclusion

While the *total* spin and magnetic moment of triphenylmethyl are very closely equal to the values for a single electron, the distribution of spin in the molecules is adequately treated only through consideration of the spins of all the electrons, excluding perhaps the 1s electron in carbon. The fact that spin on the methyl carbon corresponds to about two-thirds of an electron does not limit the absolute magnitude of spin densities at other positions, nor does it imply localization of "the unpaired electron." It merely limits their algebraic sum to one-third. The valence bond theory predicts the appearance of negative spin on the unstarred carbons, if the methyl carbon is taken as starred. There is indirect evidence that this prediction is correct.[31]

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(27) C. C. Torrance, *Phys. Rev.*, **46**, 388 (1934).

(28) E. Hückel, *Z. Elektrochem.*, **43**, 827 (1937).

(29) P. Brovetto and S. Ferroni, *Il Nuovo Cimento*, **5**, 142 (1957).

(30) J. N. Murrell, *J. Chem. Phys.*, **26**, 1738 (1957).

(31) We are attempting direct measurements of the signs of the spin densities.