10. *Electron-spin Resonance Investigations of the Negative Ions of Four Organosilicon Compounds.*

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Electron-spin resonance spectra of the negative ions of 4-biphenylyltriphenylsilane, di-(4-biphenylyl)diphenylsilane, tetraphenylsilane, and tetra-4-biphenylylsilane have been recorded. The unpaired electron is located almost exclusively on the biphenyl substituent in the first radical, but is thought to exchange rapidly between all groups in the third. It has not been possible to determine the electron distribution in the second and fourth. An analogous all-carbon compound, tetraphenylmethane, is spontaneously reduced to the non-magnetic dinegative ion, which is stable only at low temperature and rearranges rapidly at room temperature to produce the biphenylyl mononegative ion.

The purpose of the present work was to investigate the electron exchange between the various substituent groups of the organosilicon radicals chosen, and in particular to find if there were appreciable spin density at the central silicon atom. Studies of the hyperfine structure of electron-spin resonance spectra often enable precise determination of isotropic hyperfine coupling constants of the unpaired electron with the various magnetic nuclei in the molecule.[1] In this way a concise picture of spin distribution in the molecule may be obtained. For an aromatic free radical the coupling constant of a given proton is proportional to the unpaired electron density in the π-orbital of the carbon atom to which it is attached. The most recent theoretical work on this topic demonstrates that this relation is valid to a high degree of approximation.[2]

In the present work we have been unable to determine precisely the hyperfine coupling constants at the sites of particular protons or at the central silicon atom, owing to the complex nature of the molecules concerned. On the other hand, certain information concerning spin distribution between the substituent groups of the radicals can be gained by analysing, as far as possible, the observed spectra.

The effect on spin-resonance spectra of the rate of spin-exchange has been studied by a number of workers, and several satisfactory theoretical treatments of the observed phenomena have been proposed.[3,4] We find that the rate of electron exchange between

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[1] Tuttle, Ward, and Weissman, *J. Chem. Phys.*, 1956, **25**, 189.

[2] McLachlan, Dearman, and Lefebvre, *J. Chem. Phys.*, 1960, **33**, 65.

[3] Anderson and Weiss, *Rev. Mod. Phys.*, 1953, **25**, 269.

[4] Anderson, *J. Phys. Soc. Japan*, 1954, **9**, 316.

substituent groups of the molecule together with the relative electron affinities of these groups are decisive factors in determining the molecular spin distribution.

A theoretical treatment of spin exchange has been proposed by Anderson and Weiss.[3] They investigate the effect on the absorption line width of strong exchange of the absorbing spin with neighbouring spins. Their results show that under these conditions $\Delta\omega' = \langle(\Delta\omega^2)\rangle/J/\hbar)$, where $\langle(\Delta\omega^2)\rangle$ is the mean square line width before exchange, $\hbar$ equals (Planck's constant)$/2\pi$, J is the exchange integral, and $\Delta\omega'$ the observed line width.

EXPERIMENTAL AND RESULTS.

Commercial samples of tetraphenylsilane, 4-biphenylyltriphenylsilane, di-(4-biphenylyl)diphenylsilane and tetra-4-biphenylylsilane were purified by recrystallisation and short-path distillation. Pure tetraphenylmethane was prepared by the method of Seibert and Bergstrom;[5] 4-methoxytetraphenylmethane labelled with approximately 40% of ^{13}C at the central carbon atom was prepared by Hardy's method[6] from triphenylmethanol 40% enriched with ^{13}C at the aliphatic carbon position.

Preparation of Negative Ions.—The compounds were treated with metallic sodium or potassium in dimethoxyethane or tetrahydrofuran in the usual manner to produce their negative ions.[7] No differences attributable to the particular solvent or metal were found. The tetraphenylmethane, tetraphenylsilane, and 4-methoxytetraphenylmethane negative ions were prepared at approximately $-70°$ and their spectra immediately observed at this temperature since these ions decomposed at higher temperatures to form other more stable products. Attempts to reduce tetraphenyltin and tetraphenylgermanium under the same conditions at room temperature or at $-70°$ were unsuccessful.

Optical Measurements.—Optical spectra were measured with a Cary recording spectrophotometer. A solution of the reduction product of tetraphenylmethane in dimethoxyethane shows at $-70°$ a symmetrical absorption band centred at approximately 640 mμ. The biphenylyl negative ion prepared in an identical manner shows an absorption band centred at 650 mμ with a marked shoulder on the violet side.

Magnetic Measurements.—The electron-spin resonance spectrometer used for all the measurements has previously been briefly described.[7] Negative ions were prepared in as dilute a solution as the sensitivity of the instrument allowed, modulation amplitudes were maintained at a minimum ($\sim$0·02 gauss), and power input to the cavity was lowered until no saturation effects could be detected. Initial measurements were made at $-70°$. Under these conditions high resolution of spectra is usually possible. This is demonstrated by the spectrum of the biphenylyl negative ion shown in Fig. 1. The spectra of the other negative ions are shown in Figs. 2—4.

The green solutions formed on reduction of tetraphenylmethane and 4-methoxytetraphenylmethane in dimethoxyethane at $-70°$ showed no resonance absorption.

Stability of Ions.—Solutions of the 4-biphenylyldiphenylsilane, di-(4-biphenylyl)diphenylsilane, and tetrabiphenylylsilane negative ions are stable at room temperature, in the absence of oxygen, in contrast to those of the negative ions of tetraphenylmethane, 4-methoxytetraphenylmethane, and tetraphenylsilane, which decompose rapidly on warming from $-70°$ to room temperature. The green solutions of the non-magnetic reduction products of tetraphenylmethane and 4-methoxytetraphenylmethane become muddy brown when warmed in the presence of metal ion to room temperature. A resonance absorption identical with that of the biphenylyl negative ion may be detected immediately in both cases.

No attempt has been made to exclude metal completely from the solution during warming. On the other hand, appreciable concentrations of biphenylyl negative ion are produced rapidly only when the solution is shaken over the metal film.

Complex changes in spectra are seen when the tetraphenylsilane negative ion is warmed to room temperature. We think that the green solution initially formed in this case is the mononegative ion, since the reaction is carried out quickly at low temperature, and no spectra other than the one reported are seen unless the temperature is raised. A complicated decomposition

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[5] Seibert and Bergstrom, *J. Org. Chem.*, 1945, **10**, 544.
[6] Hardy, *J.*, 1929, 1000.
[7] Tuttle and Weissman, *J. Amer. Chem. Soc.*, 1958, **80**, 5342.

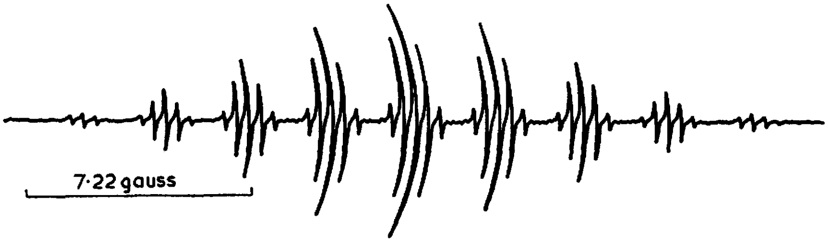

FIG. 1.

FIG. 2.

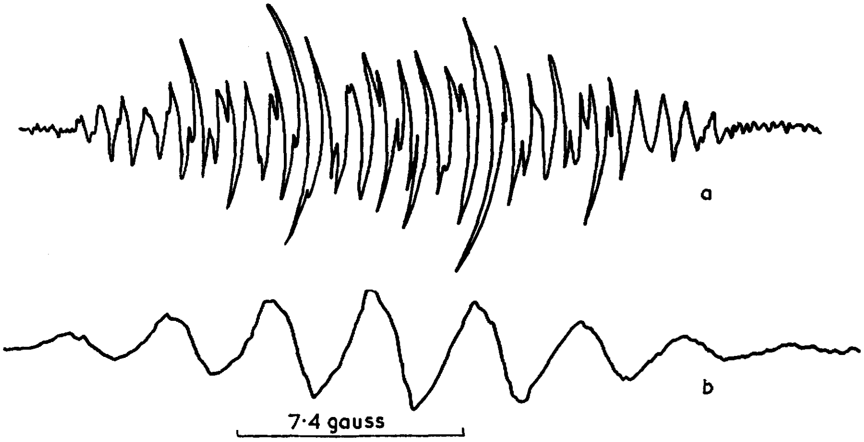

FIG. 3.

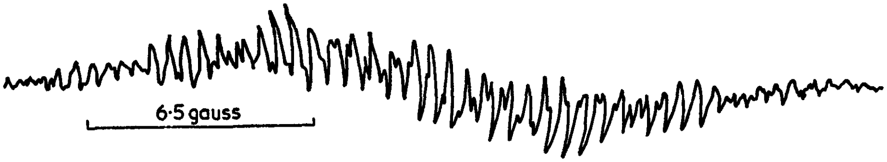

FIG. 4.

Electron-spin resonance spectra of negative ions from: FIG. 1, biphenyl; FIG. 2, tetraphenylsilane; FIG. 3, 4-biphenylyltriphenylsilane (a, high resolution; b, low resolution); FIG. 4, di-(4-biphenylyl)diphenylsilane.

of the molecule evidently sets in at higher temperatures. We have not attempted a chemical analysis of any of the warmed solutions. Admission of oxygen spontaneously destroys the colour and resonance absorption, if any, of all the negative ions prepared.

DISCUSSION

4-*Biphenylyltriphenylsilane Negative Ion.*—The magnetic resonance spectrum (Fig. 3) of this compound shows clearly seven major groups. The intensity ratios of these groups, obtained by graphical integration, are 1·6 : 4·6 : 7·2 : 8 : 7·2 : 4·6 : 1·6. The intensities of the outermost weak lines are unreliable because of the unfavourable signal-to-noise ratio. The intensities compare favourably with those calculated for 4-deuterobiphenyl which are 1 : 4 : 7 : 8 : 7 : 4 : 1.

Similarly the total splitting between extreme lines of the spectrum for the 4-biphenylyldiphenylsilane radical (20·6 gauss) is close to that of 4-deuterobiphenylyl negative ion at 20·4 gauss, and markedly different from that of biphenylyl at 24·2 gauss.[8]

Because of the striking similarities of the 4-deuterobiphenylyl and the 4-phenyltetraphenylsilane negative ion spectra we think that the odd electron in the latter case is probably localised almost exclusively on the biphenyl substituent of the molecule. We can estimate an upper limit for the interaction of the benzene rings with the unpaired electron in the following manner. Strong interaction of a benzene ring with an electron largely localised on the biphenylyl substituent should produce a spectrum with many more lines than are actually observed. We assume therefore that the resolved hyperfine splitting shown is the result of interaction with the biphenylyl substituent alone, and that the line breadth is a measure of the upper limit of interaction of a benzene ring with the biphenylyl substituent. We may construct a molecular orbital between the wave functions of a benzene and a biphenyl ring by using the minimum and the total hyperfine splittings, respectively, as squares of the wave-function coefficients. These are 0·2 gauss and 20·6 gauss, respectively. Normalisation and use of first-order perturbation theory leads to the following upper limit for the ratio, H_{12} (energy of interaction between the biphenyl and benzene rings)to $(E_2 - E_1)$ (energy difference between these rings): $H_{12}/(E_2 - E_1) < 0{\cdot}1$.

Clearly the weak interaction energy between the benzene and the biphenyl ring systems, plus the fact that the biphenylyl substituent is the most electronegative group, determine the location of the spin density in the molecule.

We note that the hyperfine splittings of each of the seven major groups of the spectrum are not quite those expected from a pure 4-deuterobiphenyl spectrum. This is not surprising since the presence of the silicon atom should perturb the spin distribution in the biphenyl substituent to a certain degree and thus produce the small differences noted.

Tetraphenylsilane Negative Ion.—The spectrum of the tetraphenylsilane negative ion (Fig. 2) shows an odd number of hyperfine lines, and on increasing the signal-to-noise ratio until the central peaks were well off scale and examining the spectrum in the wings it appeared that there were 17 in all. Since one electron located on one ring should give an even number of lines, and taking into account the symmetry of the molecule, it must be assumed that the odd electron is rapidly exchanging between the four rings of the molecule. We introduce below the question of its possible partial location on the silicon central atom.

If other line-broadening mechanisms are ignored and the line width before exchange taken to be of the order of the hyperfine frequency a, use of the Anderson–Weiss [3] formula allows us to calculate a fairly conservative upper limit for the exchange integral $H_{\mathrm{Ph-Ph}}$: $aa/H_{\mathrm{Ph-Ph}} \geqslant b$, where b is the observed line width. The line width measured is of the order 1·7 Mc./sec. and the line splitting 3·4 Mc./sec. Therefore, $H_{\mathrm{Ph-Ph}} \leqslant$ 6·8 Mc./sec.

A lower limit for the exchange energy is set by the observed hyperfine frequency a, ~3·4 Mc./sec.: $H \geqslant 3{\cdot}4$ Mc./sec.

We note that the total splitting of the spectrum is no greater than 17·4 gauss. This is less than the average width of the spectra of most of the aromatic negative ions recorded previously, which are usually of the order of 20 gauss.[8] If we assume that the electron distribution in the molecule is not greatly affected by the silicon substituent, and in the light of the results from 4-biphenylyltriphenylsilane this is not too bad an approximation, we may attribute the decrease in breadth of the spectrum relative to that of deuterobenzene to the presence of the central silicon atom. The total splitting expected from the deuterobenzene negative ion is approximately 18·3 gauss. Therefore we estimate that 0·9 gauss is accounted for by the central silicon atom. If we construct a molecular orbital between the benzene ring system and the silicon atom, taking the coefficients of

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[8] De Boer, Ph.D. Thesis, Free University, Amsterdam, 1957.

the linear combination of atomic orbitals as the square roots of the coupling constants, normalisation and application of simple first-order perturbation theory yields $H_{\text{Si-Ph}}/E_{\text{Ph}}-E_{\text{Si}} = 0{\cdot}8$, where $H_{\text{Si-Ph}}$ represents the interaction energy between the silicon and the phenyl ring systems, and $E_{\text{Ph}}-E_{\text{Si}}$ the energy difference between the two systems. Since we suspected that the electron does spend some time on the silicon central atom, perhaps in a vacant 3*d* orbital, we searched for signs of a splitting from the naturally occurring ^{29}Si isotope present in 4·67% abundance. No such splitting was observed.

Tetra-4-biphenylylsilane.—We were unable to resolve the spectrum of this negative ion to any greater extent than that of a single broad line. It seems reasonable to assume that the unpaired electron is evenly distributed between the four biphenyl rings of this molecule. In this event it is possible that the many chemically unequivalent protons present give rise to an exceedingly large number of lines which are unresolved under the existing experimental conditions.

Di-(4-biphenylyl)diphenylsilane.—It was not possible to analyse the complicated spectrum of this negative ion shown in Fig. 4. No conclusions concerning the electron distribution in this molecule can be made.

Tetraphenylmethane.—We think that the green solution with an optical absorption band at 640 mμ, immediately formed on reduction of tetraphenylmethane at low temperature, is the dinegative ion. Warming in the presence of metal ion causes rearrangement of this radical to the biphenyl negative ion. At first we reduced the tetraphenylmethane at room temperature and a signal characteristic of biphenyl was almost immediately observed. The possibility existed that, in fact, we had made the tetraphenylmethane mononegative ion and that a spectrum similar to that of biphenyl could arise from rapid electron exchange between pairs of phenyl rings of the tetraphenylmethane negative ion. This was suggested by *X*-ray evidence on tetraphenylmethane which shows that the phenyl rings are ranged in two pairs mutually at right angles.[9]

To test this theory we synthesised 4-methoxytetraphenylmethane labelled with 40% of ^{13}C at the central carbon atom. This compound was chosen because of the ease of its preparation from commercially available triphenylmethanol enriched with ^{13}C at the aliphatic carbon position. Only the biphenyl resonance spectrum was observed on reduction at room temperature and no splitting from the ^{13}C could be detected. Subsequent reduction at low temperature produced a green solution which showed no resonance absorption, but on warming in the presence of metal ion this solution discoloured and spontaneously produced a radical showing the characteristic biphenyl resonance spectrum. We conclude from these experiments that tetraphenylmethane and 4-methoxytetraphenylmethane are initially reduced to dinegative ions, both of which rapidly decompose on warming in the presence of metal ion to produce, among other products, the biphenyl negative ion.

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[9] Sumsion and Maclachlan, *Acta Cryst.*, 1950, **3**, 217.