Normaldruck hydriert. Man filtrierte und dampfte ab. Nach Zusatz von alkoholischer Salzsäure und erneutem Abdampfen erhielt man aus Isopropanol-Ae 1,1 g (92%) farblose Prismen, Smp. 159–160°, die nach Misch-Smp., IR.- und NMR.-Spektrum identisch waren mit 2-Methyl-3-dimethylamino-indan-1-on-HCl [1].

$C_{12}H_{16}ClNO$	Ber.	C 63,8	H 7,1	Cl 15,7	N 6,2%
(225,7)	Gef.	,, 63,9	,, 7,2	,, 15,4	,, 6,2%

2-Methyl-indan-1,3-dion (VI, X=H) aus IVa: 1 g 2-Methyl-3-dimethylamino-inden-1-on (IVa) wurde mit 40 ml alkoholischer Salzsäure 24 Std. unter Rückfluss gekocht. Nach dem Abdampfen wurde mit Wasser versetzt und das ausgeschiedene Kristallisat abgenutscht. Aus Isopropanol 0,7 g (82%) farblose Nadeln, Smp. 84–85°, die nach Misch-Smp. und IR.-Spektrum identisch waren mit 2-Methyl-indan-1,3-dion.

$C_{10}H_8O_2$ (160,1) Ber. C 75,0 H 5,0 O 20,0% Gef. C 74,7 H 5,1 O 19,9%

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93. The electron spin resonance spectrum of the triphenylsilyl radical formed by the X-irradiation of monocrystalline triphenylsilane

by **M. Geoffroy** and **E. A. C. Lucken**

Institut de Chimie Physique, Ecole de Chimie de l'Université, 1211 Genève 4

(11. IV. 70)

Summary. The electron spin resonance spectrum of *X*-irradiated monocrystalline triphenylsilane has been studied at room temperature. The main radical species present is the triphenylsilyl radical, formed both as isolated radicals and pair-wise trapped radicals. For the radical pairs the analysis of the dipole coupling tensor indicates an inter-radical distance of 7.36 Å. The ^{29}Si hyperfine tensor has been determined, and the values discussed in terms of the electronic structure of the triphenylsilyl radical.

Introduction: The electron paramagnetic resonance (EPR) spectra of free radicals in which the unpaired electron is essentially located in a valence orbital of a carbon atom have been extensively studied and the values of the hyperfine coupling constants arising from the various magnetic nuclei associated with these species are on the whole well-understood [1]. Similar information concerned with radicals centered on silicon atoms in analogous compounds is much less abundant [2] [3] although the availability of such data covering a wide range of silicon compounds would undoubtedly cast much light on the problem of the electronic structure of compounds of such second row elements. We report here the EPR. spectrum of the oriented $Ph_3Si\cdot$ radical formed by X-irradiation of crystalline triphenyl silane and comment on the values of the hyperfine coupling constants which this yields.

Experimental. – Large single crystals of triphenylsilane (*Fluka AG*) were grown by slow evaporation of solutions in light petrol ether. The crystals are monoclinic and an idealised drawing is shown in Figure 1 together with the axes to which the hyperfine tensors are referred. These latter have been chosen so that one axis (z) is perpendicular to the symmetry plane of the crystal. These crystals were X-irradiated overnight at room temperature with the emission from a *Phillips* Type 1559 X-ray tube having a tungsten anticathode, the crystals being placed as close as possible to the window. They were mounted on axes suitable for rotation within the cavity of the EPR. spectrometer with the aid of a *Stoe* optical goniometer.

EPR. spectra were measured at room temperature in a J.E.O.L. MX1 spectrometer using 100 KHz modulation. The angle of rotation about an axis perpendicular to the magnetic field could be read to ± 1°. The magnetic field sweep was calibrated using the ^{55}Mn hyperfine components of Mn^{2+} ions in polycristalline MgO, and the g-factors were determined by reference to this material and to polycrystalline D.P.P.H. ($g = 2.0036$).

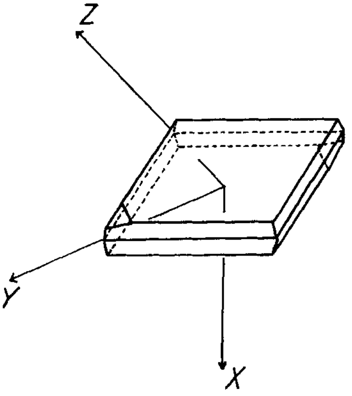


Fig. 1. *Idealised crystal of triphenylsilane and the reference axes*

Results. – A typical spectrum of irradiated triphenylsilane is shown in Figure 2, and the manner in which peaks A, B und C evolve on rotation about the x, y and z axes is shown in Figure 3. It is clear that the most intense peaks in the spectrum may be interpreted as being due to a radical (A) showing no hyperfine structure and having an essentially isotropic g-tensor and two pair-wise trapped radicals (B and C) with a similarly isotropic g-tensor. The dipole splitting of the triplet radical pairs ($S = 1$)

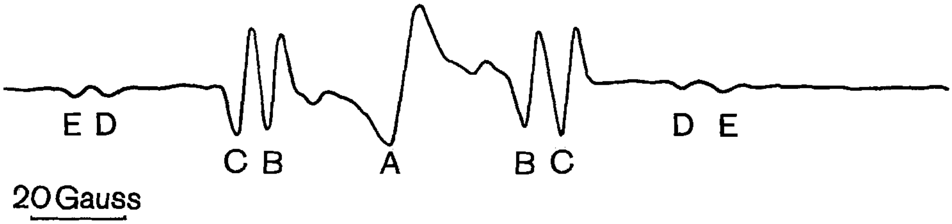


Fig. 2. *Typical EPR. spectrum of* X-*irradiated triphenylsilane*

$$\mathcal{H} = g\beta S\cdot H + D\left(S_z^2 + \frac{S^2}{3}\right) + E\left(Sx^2 - Sy^2\right) \tag{1}$$

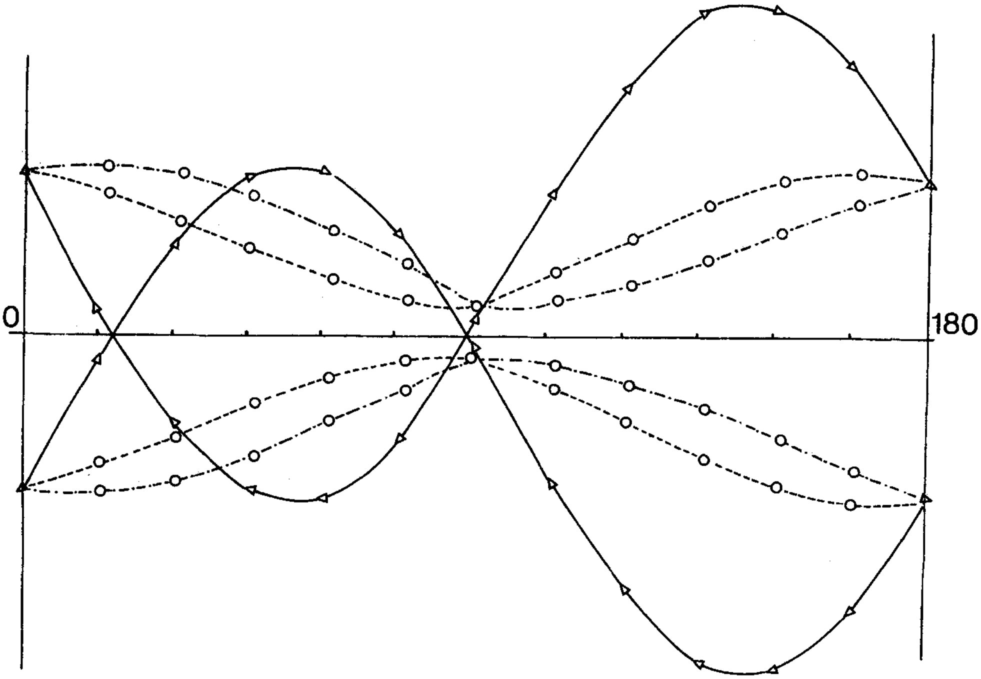


Fig. 3. *Variation of dipole splitting with orientation*
Solid lines: rotation about *z*, Broken lines: rotation about *y*

was analysed to first order according to the usual spin hamiltonian [1] to yield the values of D, E and the direction cosines of the principal axes shown in Table 1. The small value of E shows that the interaction is well represented by that between point dipoles; on this assumption the value of D implies an inter-dipole distance of 7.36 Å.

Table 1. *Components of the dipole interaction tensors and their direction cosines*
(radical pairs B and C)

	D = 71.6 gauss; E = −1.0 gauss		
Direction cosines:	x	0.53	0.41 ± 0.73
	y	0.65	0.35 ± 0.66
	z	0.53	0.83 ± 0.08

The radical species which would most probably be formed on irradiation of triphenylsilane is triphenylsilyl; $\cdot SiPh_3$. Such a radical should exhibit weak hyperfine satellites owing to the presence of ^{29}Si (relative abundance 4.70%; $I = {}^1/_2$). These satellites on the radical pairs B and C are clearly the weak lines D and E of Figure 1. For the central radical A the distance of the satellites is such that they are hidden by the main lines of B and C in most orientations. We therefore identify all three radical species, A, B and C with $\cdot SiPh_3$. This identification of A with the separate components of B and C is substantiated by the observation that at room temperature over a period of days radical A increases at the expense of the pair-wise trapped species B and C, presumably by a process of hydrogen-atom transfer.

A detailed discussion of the hyperfine structure to be expected in radical pairs has been recently given by *Itoh, Hayashi* & *Nagakura* [4]. For a radical pair in which only one nucleus of spin $I = {}^1/_2$ on each component shows an appreciable hyperfine coupling constant, if A_1 and A_2 are the values of the hyperfine coupling constants for the isolated components at that particular orientation in the magnetic field, then each of the two components of the dipole-split spectrum consists of two symmetrically disposed doublets, the separation of the outer pair being given by ${}^1/_2 \mid A_1 + A_2 \mid$ and of the inner pair by ${}^1/_2 \mid A_1 - A_2 \mid$. Second order effects disturb this arrangement if the singlet-triplet separation is small compared with the *Zeeman* energy.

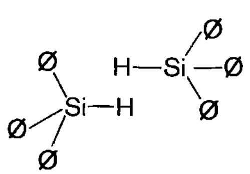
In the present case the inner components of the hyperfine structure arising from the ^{29}Si nucleus are hidden under the large peak arising from the ^{28}Si isotope. Furthermore for most orientations only the components at the extremities of the spectrum could be clearly located. The separation between the outer components of the quadruplet was therefore taken to be twice the separation between the satellite and the main line, and the variation of this separation with orientation is shown in Figure 4. Analysis of these values in the usual way gives the values of the average hyperfine splitting tensor shown in Table 2.

Table 2. *Average ^{29}Si hyperfine coupling tensor and direction cosines*
(±)120; (±)52; (±)66 gauss

Value	Direction cosines		
	x	y	z
(±)120	0.61	0.78	0.08
(±)52	– 0.66	0.48	0.56
(±)66	– 0.40	0.38	– 0.83

Average g-value 2.0029.

Discussion. – A structure determination of crystalline triphenylsilane does not appear to be available and thus little comment about the radical-pair formation can be made. Previous observations of radical pairs have always been made in crystals containing pairs of labile hydrogen atoms, for example in the hydrogen-bonded dimers of the oximes. Such association is unlikely in the present case but possibly the triphenylsilane molecules are packed together in a head to head configuration such as I



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although the inter dipole distance of 7.3 Å is perhaps rather small for this to be correct.

The isotropic coupling constant of an electron in a 3*s* orbital of ^{29}Si has been calculated from *Hartree-Fock* wave-functions for atomic silicon to be 1220 gauss while the three components of the anisotropic coupling constant for an electron in the corresponding 3*p* orbital are 62, –31, and –31 gauss [5]. In the present case the unpaired electron is presumably in a $3s$-$3p$ hybrid, and the coupling constants in principle yield the s-p ratios. The first problem is that as usual only the absolute magnitudes of the components of the average coupling tensor are available; however if any appreciable s-character to the orbital is present it will dominate the sign of the coupling tensor and we may reasonably suppose that all three components given in Table 1 are positive since the ^{29}Si magnetic moment is negative. In these circumstances the hyperfine coupling tensor may be decomposed into its isotropic and anisotropic components to yield:

$$a_{\text{iso}} = 79.6 \text{ gauss}; \; a_{\text{aniso}} = 40.5; \; -27.2; \; -13.3 \text{ gauss}.$$

As stated above the present measurements yield only average values of the hyperfine coupling tensor. The isotropic part of the coupling should be essentially unaffected by this whereas the anisotropic components will be lower than those of the isolated radical. In these circumstances the value obtained for the isotropic constant shows that the s-character of the orbital bearing the unpaired electron is rather small, approximately 6%. This value of the isotropic coupling constant should be compared with those obtained for various silyl radicals, observed in the fluid state, shown in Table 3. In all these cases the isotropic coupling is much higher implying as much as

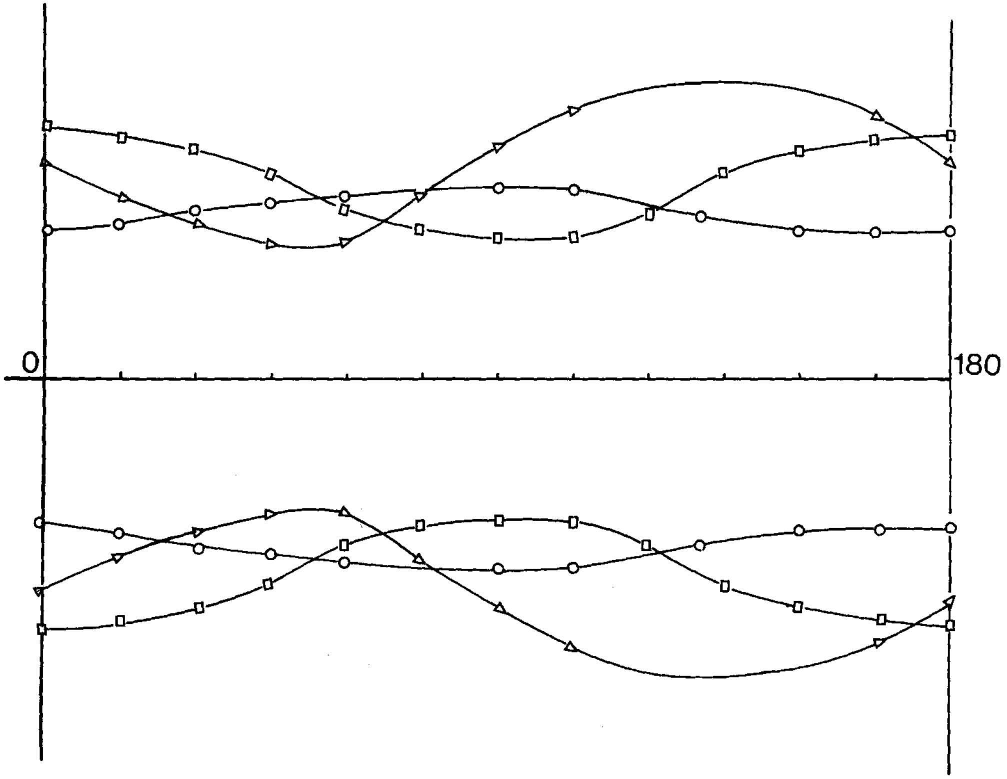

Fig. 4. *Variation of ^{29}Si hyperfine spl$_8$tting w$_8$th orientation*
— rotation about y, — rotation about x, — rotation about z

21% *s*-character in $\cdot SiH_3$. In the corresponding carbon compound, $\cdot CH_3$, the ^{13}C coupling constant is 38.34 gauss implying an *s*-character of 3% in accord with the generally accepted planarity of the methyl radical. As already stated the crystal structure of triphenylsilane, is not known; one may reasonably assume however that the three C-Si bonds are not coplanar and that the size of the phenyl groups would prevent any appreciable flattening of the molecule in the trapped triphenylsilyl radical. In these circumstances the low value of the isotropic coupling constant is, to say the least of it, strange.

Table 3. *^{29}Si Coupling Constants of Silyl Radicals*

Silyl radical	$a_{^{29}Si}$ (Gauss$_9$)	Reference
$\cdot SiH_3$	266	[2]
$\cdot SiH(CH_3)_2$	183.05	[3]
$\cdot Si(CH_3)_3$	181.14	[3]

The anisotropic parts of the apparent coupling tensor give only a lower limit to the *p*-character of the silicon valence orbital. The principal value 40.5 implies 65% *p*-character whereas the other components imply 87% and 42% respectively. The anisotropic coupling tensor is thus in accord with the isotropic coupling in as much as a small *s*-character implies a high *p*-character and vice-versa.

This discussion has been based on the hypothesis that the three components of the coupling tensor are all of the same (positive) sign. If the signs of the three components are not identical then the isotropic coupling constant is necessarily less than 79 gauss while a negative isotropic coupling constant cannot be intrepreted in terms of the *s*-character of the ^{29}Si orbital. Furthermore if the signs are not all the same the resultant anisotropic components will be even larger and imply an even higher *p*-character than that already quoted.

Despite the uncertainties consequent upon the lack of knowledge of the crystal structure of triphenylsilane and the difficulty in both obtaining the ^{29}Si coupling tensor and decomposing it into its isotropic and anisotropic components it seems clear that the ^{29}Si coupling constants of $\cdot SiPh_3$ are not in accord with the predictions of simple valence theory.

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