Measurement of the Central Atom (^{29}Si) Couplings in Triphenylsilyl and Related Radicals

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By γ-irradiation of the completely deuteriated compounds, $(C_6D_5)_nSiD_{3-n}$ (where n = 1–3), at 77 K, the anisotropic ^{29}Si couplings in the corresponding radicals, $(C_6D_5)_nSiD_{3-n}$, have been measured for the first time.

The triphenylmethyl (trityl) radical provides the archetypal example of a stable radical, and exists in solution in equilibrium with its *para*-quinoid dimer.[1] The very weak C–X bonds in a variety of triphenylmethyl compounds $(Ph_3C-X)^2$ are also in accord with particular stability of the trityl radical, which arises largely from its highly delocalised nature, as has been confirmed by ESR studies.[3] The corresponding silicon centred radical is far more elusive, however; for instance, hexaphenyldisilane shows no sign of decomposition even at its melting point (268–370 °C).[4] Bond dissociation energy measurements[2] indicate that Ph_3Si is *ca.* 8 kcal mol^{-1} (1 cal =

4.184 J) more stable than Me_3Si and thus imply that there is a relatively weak stabilising interaction between the phenyl groups and the silicon radical centre.

There is no direct evidence available on this matter from ESR studies, since it has proved impossible, so far, to generate unsubstituted Ph_3Si radicals in fluid solution, although the sterically hindered analogues tris(3,5-di-*tert*-butylphenyl)silyl[5] and trimesitylsilyl[6] radicals have been observed, and appear to be partially (*ca.* 20%) delocalised species according to the ring proton hyperfine data.

The most direct measure of the configuration of a silicon

Table 1 Hyperfine coupling data for phenylsilyl and related radicals

Radical	A (^{29}Si)/G[a]			
	$\parallel$	$\perp$	iso	$2B$
$(C_6D_5)\dot{S}iD_2$	218	144	169	49
$(C_6D_5)\dot{S}iD$	206	137	160	46
$(C_6D_5)_3\dot{S}i$	190	130	150	40
$Me_3\dot{S}i$	233[b]	155[b]	181[c]	52
$Et_3\dot{S}i$	221	—	170[d]	51
$Bu^t_3\dot{S}i$	215	—	163[e]	52

[a] 1G = 10^{-4} T. [b] J. H. Sharp and M. C. R. Symons, *J. Chem. Soc. A*, 1970, 3084. [c] Ref. 8. [d] Ref. 9. [e] Ref. 10. All other data are from the present work.

radical centre is provided by the measurement of the ^{29}Si hyperfine coupling. In trimesitylsilyl,[6] the isotropic splitting was measured at 135 G, and can be interpreted in terms of some delocalisation of the unpaired electron since it is reduced from the values typically found for trialkylsilyl radicals (Table 1). The complicating factor is that silyl radicals possess pyramidal configurations of the silicon centres:[7] therefore, a reduction in the isotropic ^{29}Si splitting might reflect not only delocalisation of the unpaired electron but the adoption of a more planar configuration, leading in any case to a SOMO of lower silicon 3s character.

An alternative approach is to measure the ESR spectrum of the radical in a solid matrix so that the principal values of the ^{29}Si tensor are determined and from which may be extracted both the 3s and 3p orbital populations: thus details of the configuration of the radical centre and the degree of spin-delocalisation are both obtained.

In our initial experiments, we studied γ-irradiated polycrystalline Ph$_3$SiH, but were unable to resolve ^{29}Si features since the spectral region in which they are present is obscured by the wings of the intense central signal from Ph$_3\dot{S}$i radicals containing non-magnetic silicon nuclei. In order to reduce the linewidth of this central peak (approximately by a factor of 3.257, which is the ratio of H/D magnetic moments), we synthesised the fully deuteriated compound $(C_6D_5)_3$SiD and recorded the ESR spectrum shown in the Fig. 1, following γ-irradiation, in which the parallel and perpendicular ^{29}Si features are clearly disclosed. Similarly, we have obtained the corresponding ^{29}Si hyperfine components in the radicals $(C_6D_5)_2\dot{S}iD$ and $C_6D_5\dot{S}iD_2$ (Table 1) since we were also unable to detect clear ^{29}Si features in the ESR spectra obtained from the corresponding protic analogues Ph$_2$SiH$_2$ and PhSiH$_3$.

It is noteworthy that, at 150 G, the derived isotropic ^{29}Si coupling in $(C_6D_5)_3\dot{S}i$ is greater than that in the trimesitylsilyl radical as measured in fluid solution.[6] We consider that this is due to a steric effect where the more bulky mesityl groups force a more planar geometry at the radical centre. [The trend in isotropic ^{29}Si couplings in the series Me$_3\dot{S}i$,[8] Et$_3\dot{S}i$,[9] Bu$^t_3\dot{S}i$[10] (Table 1) probably reflects a similar effect.] Therefore, we believe that the present data provide a reliable representation of the electronic influence of phenyl substituents on a silicon centred radical. The anisotropic couplings ($2B$) reflect a reduction in the 3p spin population of *ca.* 0.23 by the three phenyl groups so that spin delocalisation is appreciable.

It is interesting to compare the p : s ratios that are obtained for the series $(C_6D_5)_3\dot{S}i$, $(C_6D_5)_2\dot{S}iD$, $(C_6D_5)_2\dot{S}iD_2$: 5.07 : 1, 5.03 : 1, 4.66 : 1. Since the values relate only to a range of bond angles of 112.7–112.2° and are not therefore significantly different, the point is made that the increased delocalisation of the unpaired electron does not render the radical centre more planar, despite the implication of partial π-bonding between the phenyl groups and the silicon atom. If anything, the silicon centre is slightly more pyramidal when three phenyl groups

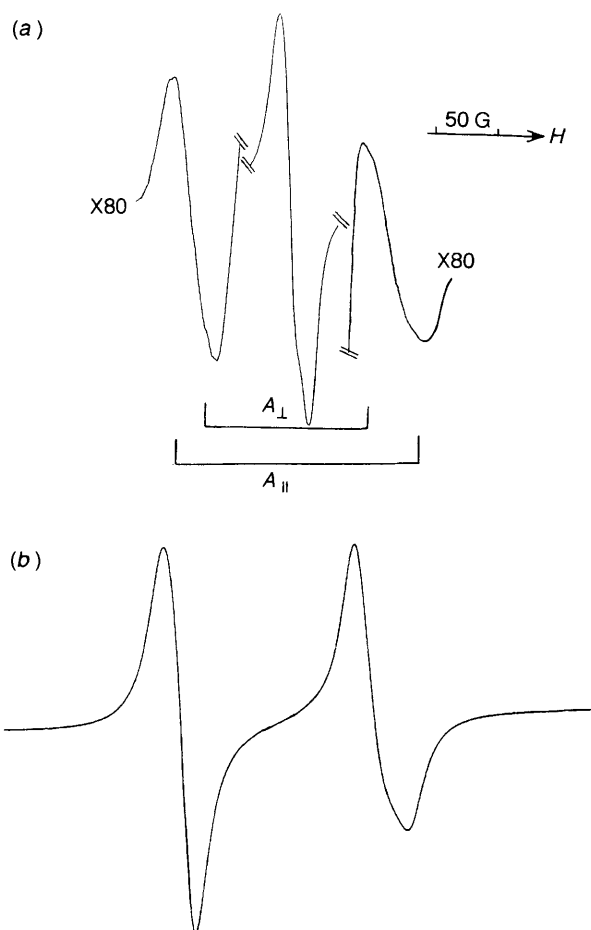**Fig. 1** (*a*) X-Band ESR spectrum recorded following γ-irradiation of $(C_6D_5)_3$SiD showing ^{29}Si features from $(C_6D_5)_3\dot{S}i$ radicals; (*b*) simulation using $A_\parallel$ and $A_\perp$ values given in the text along with $g_\parallel$ = 2.002; $g_\perp$ = 2.006; ΔH_{pp} = 18 G

are present. This must relate to the substituent electronegativity effect which operates in the direction of increased bending, because carbon is more electronegative than silicon (the ratio of 5.03 : 1 in the Me$_3\dot{S}i$ radical implies that this is a more planar radical than is Ph$_3\dot{S}i$, probably because of the greater electronegativity of an sp^2 than an sp^3 carbon atom). The intrinsic energy barrier against making a silyl radical planar (13 kcal mol^{-1})[11] is not overcome by the gain in delocalisation energy (*ca.* 2 kcal mol^{-1} per phenyl group)[2]. The former will be increased as the number of electronegative substituents increases and, according to the present results, dominates over the geometry that is chosen.

The case is similar to but less extreme than that for Cl substituents where it is clear that their increasing number profoundly decreases the Cl–Si–R bond angles at the radical centre, but delocalisation nonetheless increases along the series Me$_2\dot{S}iCl$, Me$\dot{S}iCl_2$, $\dot{S}iCl_3$.[12]

There is one previous report that claims a determination of the ^{29}Si hyperfine tensor from an ESR study of an X-irradiated single crystal of Ph$_3$SiH.[13] The paramagnetic species was assigned to a radical pair, and on the basis of the crystal orientation dependence of features assigned to ^{29}Si satellites, an isotropic coupling of *ca.* 80 G was derived, which is considerably lower than we measure in the present work. However, we believe that this reported value is incorrect, for the following reasons. Firstly, the features assigned to ^{29}Si lines appear to be at least five times too intense given the natural abundance of ^{29}Si (4.7%). Secondly, it does not seem reasonable that the isotropic coupling in Ph$_3\dot{S}i$ should be so

dramatically lower than that in trimesitylsilyl (135 G; as explained earlier, the converse is more reasonable), particularly by comparison of the series $Me_3\dot{S}i$, $Ph_3\dot{S}i$, $Mes_3\dot{S}i$ [a(^{29}Si) 181 G,[8] 79.6 G,[13] 135 G[6]] with the corresponding germanium centred radicals, $Me_3\dot{G}e$, $Ph_3\dot{G}e$, Mes_3Ge [a(Ge) 84.7 G,[14] 84 G,[15] 68.4 G[6]]. In contrast, our value of a(^{29}Si) for $Ph_3\dot{S}i$, at 150 G, is in good accord with these data.

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