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# A molecular model for an excess electron in silicon: electron addition to hexatrimethylsilyl disilane, a derivative with eight $\sigma$ -bonded silicon atoms

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**Abstract.** Exposure of the hexatrimethylsilyl disilane to ionizing radiation at 77 K gave ESR (EPR) spectra including <sup>29</sup>Si satellite features that are assigned to the radical anions I<sup>•-</sup>. Similar features were obtained from dilute solutions in certain solvents known to promote electron capture. The results are analysed in terms of extensive delocalization within the seven Si–Si  $\sigma$  bonds, with a small preference for the central Si–Si bond. There is no case for invoking extensive use of the 3d silicon orbitals, the data being fully accommodated using the normal 3s + 3p orbitals of the  $\sigma$  framework.

Similarly, using Freon (CFCl<sub>3</sub>) as a solvent that promotes specific electron loss, the parent radical cations have been prepared by radiolysis. The ESR spectra are discussed in terms of distortions involving stretching of one or two specific Si–Si bonds.

Thus, for this model compound, with seven Si–Si bonds, an excess electron is accommodated within the  $\sigma$  framework and is extensively delocalized. We suggest that these results lead to the conclusion that the conduction band for pure silicon is also based on the  $\sigma$  framework and that the more diffuse set of 3d orbitals do not make a major contribution.

## 1. Introduction

These studies arose from a range of related interests including:

(i) the fact that, for isolated nitrogen atoms in diamond, the residual unpaired electron is strongly confined to a single N–C  $\sigma^*$  orbital (Bower and Symons 1966, Every and Schonland 1965) whereas, for the isostructural centre of phosphorus atoms in silicon, it is extensively delocalized over many silicon atoms, whilst remaining centred on phosphorus (Feher 1959),

(ii) studies of paramagnetic centres generated on exposing carbon and silicon to high-energy positive muon beams (Brewer *et al* 1975, Cox 1995) (these studies led one of us to propose a ‘bond-centred’ model for one of these centres (Symons 1984b, Cox and Symons 1986), for which there is little or no chemical precedent) and

(iii) the development of techniques for using ionizing radiation to induce specific electron capture or electron loss in a range of materials, coupled with the use of low-temperature electron spin resonance (ESR) or electron paramagnetic resonance (EPR) spectroscopy to study the primary centres (Symons 1981, 1984a).

These three issues are discussed below following the description of the results. Our aim was to study electron gain and loss for a small molecule containing a silicon framework and we were able to obtain a supply of hexatrimethylsilyl disilane (I) with eight silicon atoms

linked together, for this purpose. (Note that, for all structures,  $R = \text{CH}_3$ ,  $(\text{Si}^{\bullet}\text{-Si})$  represents a  $(\sigma_1^2\sigma_2^1)$  three-electron bond and  $(\text{Si} \bullet \text{Si})$  represents a  $\sigma^1$  one-electron bond.)

We know of no comparable study involving silicon derivatives. ESR or EPR spectroscopy is a useful tool for studying the resulting paramagnetic centres. In our procedures, low temperatures (usually 77 K) are used such that primary reaction centres are trapped through immobility and can be studied at these temperatures. Possible formation of secondary paramagnetic centres can then be studied by controlled annealing.

## 2. Experimental details

Compound I was irradiated at 77 K either as the pure compound, or as dilute solutions in  $\text{CD}_3\text{OD}$ , methyltetrahydrofuran (MTHF) or  $\text{CFCl}_3$ , using a  $^{60}\text{Co}$   $\gamma$ -ray source or a 130 KV x-ray source. Doses were in the 10–100 Gy range and the results were independent of dose and sources.

ESR spectra were measured at 77 K using a Varian E 109 X-band spectrometer and an Archimedes computer with in-house programs for spectral manipulations.

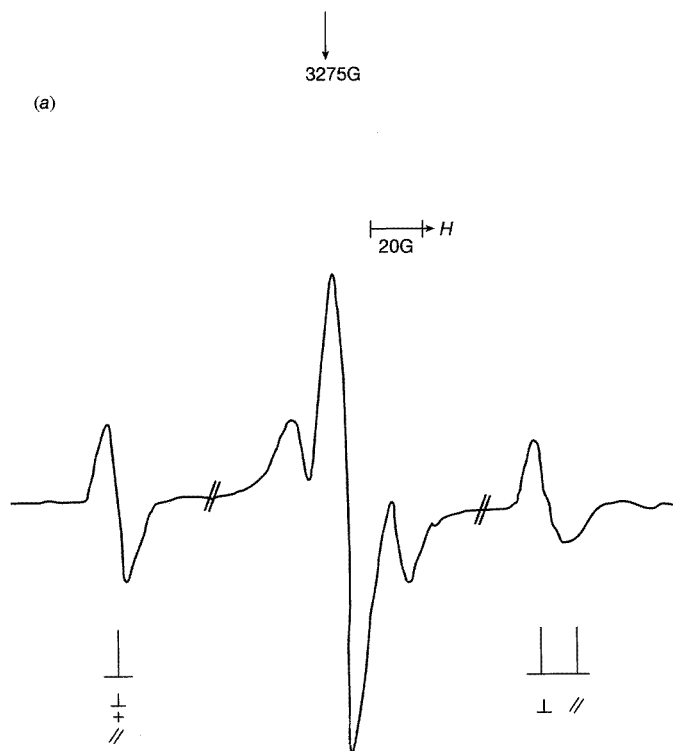
## 3. Results

These are collated in table 1 together with data for related radicals. Two typical ESR spectra are shown in figure 1. (The centre features comprise a singlet assigned to the radical anions, and a 1 : 2 : 1 triplet assigned to  $\text{H}_2\text{C}^{\bullet}\text{Si-}$  centres formed from the parent radical cations by proton loss.)

### 3.1. Electron-capture centres

Since it was not initially possible to identify the centres formed in the pure material unambiguously, we used various solvents which are known to promote either specific electron gain or electron loss from the solute molecules. (Symons 1981, 1984a). For electron capture, we favour using either  $\text{CD}_3\text{OD}$  or  $(\text{CD}_3\text{OD} + \text{D}_2\text{O})$  glasses, or MTHF glasses. In this case we were able to use both matrices. We stress that these solvents freeze to give good glasses, thereby preserving the random distribution of the fluid solutions and avoiding phase separation.

For the  $\text{CD}_3\text{OD}$  systems, features for trapped solvent radicals ( $\bullet\text{CD}_3 + \text{CD}_2\text{OD}$  mainly) prevent good analysis of the central components, but satellite lines from radicals containing  $^{29}\text{Si}$ ; ( $I = 1/2$ ; 4.7% abundance) form doublet features well separated from the central components (figure 1). For the MTHF glasses, signals from solvent radicals block a far larger portion of the central range, but again the  $^{29}\text{Si}$  features were readily detected. These were identical with those for the  $\text{CD}_3\text{OD}$  solvent systems. Also, an identical doublet was obtained after irradiation of the pure compound (figure 1). On annealing the MTHF glasses above 77 K it was possible to induce loss of the solvent radical signals selectively, leaving a relatively narrow central singlet with slight  $g$ -asymmetry. This is identified as belonging to the parent solute radical anion, as are the  $^{29}\text{Si}$  satellites. It is noteworthy that, if these glasses are irradiated in the absence of any solute, very intense colours grow rapidly (violet for  $\text{CD}_3\text{OD}$  and blue for MTHF). These are assigned to shallowly trapped electrons ( $e_t^-$ ). If the solute molecules capture electrons efficiently, few (if any)  $e_t^-$  centres survive. In the present case, only pale colours were detected, showing that the solute centres are indeed formed by electron capture. Data for this centre are given in table 1.



**Figure 1.** (a) First derivative X-band ESR spectrum for compound I after exposure to ionizing radiation at 77 K, showing central features assigned to the radical anions (singlet) plus a triplet from  $\text{H}_2\text{C}^\bullet\text{-Si}$  radicals, and outer features to radical anions containing  $^{29}\text{Si}$ . (b) As in (a), but using a dilute solution in  $\text{CD}_3\text{OD}$ . The central features are assigned to solvent radicals, and the outer doublet to the radical anions of I containing  $^{29}\text{Si}$ .

### 3.2. Electron-loss centres

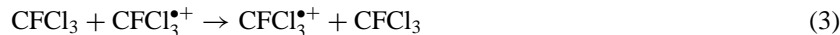
In order to generate only  $e^-$ -loss centres, we have used Freon ( $\text{CFCl}_3$ ) as solvent:



In this case, the electrons are efficiently trapped by reaction with the solvent according to



but the 'hole' centres ( $\text{CFCl}_3^{\bullet+}$ ) migrate by electron transfer according to



until they react with the solute to give the radical cation ( $\text{S}^{\bullet+}$ ):



In this case, the signal from the solvent radicals ( $\text{CFCl}_2^\bullet$ ) is very broad and does not seriously interfere.

Two centres were obtained, with overlapping features in the central region. One shows a range of small proton splittings of about 3.5 G, with at least eight features, whilst the other consists of a narrow singlet species. Resolution was not greatly improved on warming,

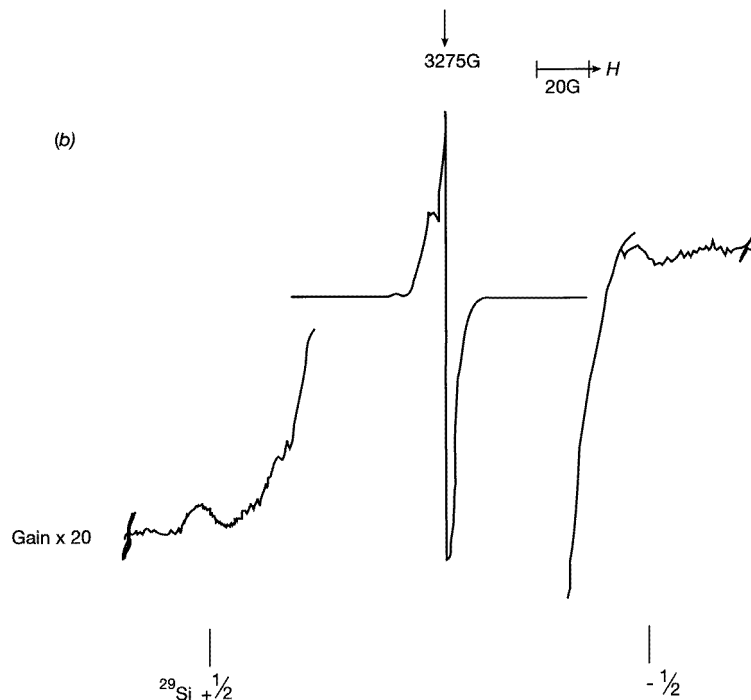


Figure 1. (Continued)

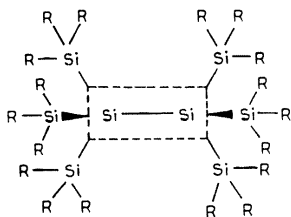
nor did the splitting vary significantly. Unfortunately, no well defined  $^{29}\text{Si}$  satellites were resolved for this system.

## 4. Discussion

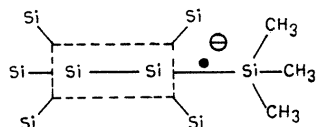
### 4.1. Identification and structure

We assume that, in the solvent studies, only the primary  $e^-$ -loss and  $e^-$ -gain centres were formed. The results show that these were also formed in the irradiated pure compound as the major centres.

I (Hexatrimethylsilyl disilane) ( $R = \text{CH}_3$ )

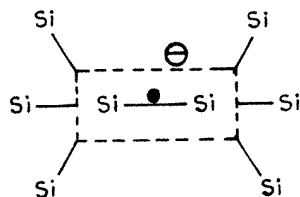


For the  $e^-$ -gain centre, we deduce that the electron is not delocalized extensively into C-H or Si-C orbitals because of the absence of  $^1\text{H}$  hyperfine splitting. This rules out the localized centre (structure II),

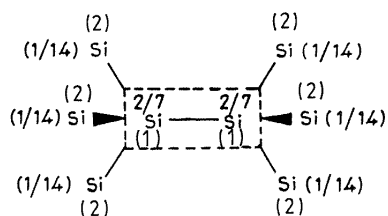


which could have been trapped by specific stretching of one Si-C bond. From the  $^{29}\text{Si}$  hyperfine splitting we have estimated approximate values for the silicon 3p and 3s contributions to the semi-occupied molecular orbital (SOMO). This is achieved using calculated atomic parameters (Morton and Preston 1978), linking the isotropic coupling to 3s and the anisotropic coupling to 3p character. We stress that this is a crude approximation, but wide experience has shown that it gives a very useful measure of the SOMO for such systems. In the present case the silicon nuclei responsible for the doublet contribute about 14.4% 3s and about 13% 3p, giving a total spin density of about 27.4% and a p-to-s ratio of about one. It is difficult to estimate the number of equivalent nuclei contributing to these features, but our attempts at simulation using a variety of subtraction methods to isolate the central features gave intensities corresponding to about two. The results certainly rule out just one and also rule out four. We tentatively conclude that there are two equivalent strongly coupled silicon nuclei in the radical anions.

This might be taken as evidence for structure III,



with the central Si-Si bond stretched so as to confine the electron to this unique Si-Si bond. However, even with little bond-angle relaxation resulting from bond stretching, the p-to-s ratio should be 3 or more and a value of one would be most unexpected. Also, the total spin density on the two central Si atoms is only about 55%. So we reject this simple model III and consider the results expected for the other extreme in which there is equal spin-density within each of the seven bonds as shown in structure IV.



If, in addition, we postulate an equal distribution of the electron between each silicon atom in each bond, this gives spin densities of 1/14 on the six outer atoms and 2/7 on each of the central atoms.

In summary, the results show that there is a large, almost isotropic hyperfine coupling to the two central  $^{29}\text{Si}$  nuclei (Si(1)). No other  $^{29}\text{Si}$  satellites could be detected; so the coupling to  $^{29}\text{Si}$  for Si(2), the six outer atoms, must be relatively small (less than about 65 G). Also, the  $^1\text{H}$  coupling is very small so that very little spin density reaches the methyl groups. Although there are no well defined parallel ( $z$ ) and perpendicular ( $x, y$ ) features, the  $^{29}\text{Si}$ (1) coupling is slightly anisotropic, and approximate values for  $A_{\parallel}$  and  $A_{\perp}$  were estimated in the normal way (see figure 1(a) and table 1) (see, e.g., Symons (1978)). These are then used

to estimate the isotropic coupling constant ( $A_{iso}$ ) and anisotropic coupling constant ( $2B$ ). These in turn are used to estimate highly approximate but nevertheless very useful orbital spin densities, using the calculated atomic parameters  $A^0$  and  $2B^0$  for unit spin densities (Morton and Preston 1978, Symons 1978). These calculations yield the approximate 3s and 3p<sub>z</sub> orbital populations listed in table 1. We stress that, since the natural abundance of  $^{29}\text{Si}$  nuclei is very low (4.7%), we can only detect radicals containing a single  $^{29}\text{Si}$  unit.

**Table 1.** ESR data for the radical centres of compound I together with other relevant data.

Radical centre		Hyperfine coupling (G <sup>a</sup> )			Orbital populations <sup>b</sup> (Si)		Reference
		$A_{\parallel}$	$A_{\perp}$	$A_{iso}$	3s	3p	
$\text{I}^{\bullet-}$	$^{29}\text{Si}$	-184	-172	-176	0.105	0.110	This work
	$^1\text{H}$	—	—	< 2	—	—	This work
$\text{H}_2\text{C}^{\bullet}-\text{Si}$	$^1\text{H}$	—	—	22	—	—	This work
	$\text{I}^{\bullet+}$	$^1\text{H}$	—	—	3.5	—	This work
$(\text{CH}_3)_3\text{Si}^{\bullet}$	$^{29}\text{Si}$	-233	-155	-181	0.12	0.65	Sharp and Symons (1976)
	$^1\text{H}$	—	—	6.3	—	—	
$(\text{CH}_3)_3\text{Si}^{\bullet} \bullet \text{Si}(\text{CH}_3)_3$	$^1\text{H}$	—	—	5.6	—	—	Wang (1981)

<sup>a</sup> 1 G  $\equiv$  10<sup>-4</sup> T.

<sup>b</sup> Using calculated atomic  $^{29}\text{Si}$  coupling constants for unit standard deviation of  $A_{iso}^0 = -1641$  G and  $2B^0 = -81.6$  G (Morton and Preston 1978).

We consider two limiting models. In model (i) the central Si(1)–Si(1) bond stretches and the electron becomes localized primarily in the  $\sigma^*$  central antibond. In the other, model (ii), the excess electron is shared equally between all seven Si–Si bonds.

For model (i) if no flattening occurs at the Si(1) units there should be approximately  $0.5 \times 0.25 = 0.125$  3s character and  $0.5 \times 0.75 = 0.375$  3p<sub>z</sub> character on each Si(1) atom. Thus, although the estimated 3s population of about 0.11 is quite reasonable for this model, the 3p character (0.10) is far too low. Indeed, had this model been correct, we would have required  $A_{\parallel}$ - and  $A_{\perp}$ -values of about 206 G and 161 G, respectively. These can be totally rejected.

Had model (i) been correct, we would have predicted slight flattening of the (Si)(1)–Si(1) units, which would result in a loss of 3s and gain of 3p<sub>z</sub> characters. In fact, the latter is already far too small; so this simply makes the model worse. We therefore turn to model (ii).

For model (ii), we again assume sp<sup>3</sup> hybridization, with equal sharing between all seven Si–Si bonds and equal sharing between each silicon atom within each bond. Hence, for the two Si(1) atoms, the total spin density on each is  $4 \times 1/14 = 2/7$ . However, for each Si(2) it is only about 1/14. The latter result shows that the hyperfine splitting from the outer Si(2) atoms would be far too small to be detected in the spectra obtained. For the centre Si(1) atoms with spin densities of 2/7 each, the 3s character should be about 0.07 on each, which requires  $A_{iso}$ -values of about 115 G. This is too low but would have been detectable. However, the total anisotropic coupling has to be zero on each Si(1) in this model. This is because the three 3p orbitals are now equally populated, and hence the total dipolar coupling is zero. The results clearly fall between these two limits. The isotropic coupling falls between the two limiting values and is reproduced using 65% of the localized model (i). On the other hand, the anisotropic coupling corresponds to about 30% of this model and 70% of the delocalized model. In view of the many uncertainties involved, these

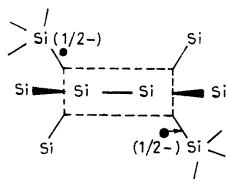
results are, in our view, quite reasonable, and we argue that the two models make about equal contributions to the real structure. This result accords nicely with expectation. It also requires that there is very little distortion of the structure, despite the fact that it is free to distort. Had distortion been important, we would expect the electron to be trapped in the stretched bond, which would lead catastrophically to further stretching and deep trapping at one site, which is not observed.

Hyperfine coupling to the six outer silicon nuclei should occur but, since the spin densities thereon are predicted to be less than about 1/14, we would not have been able to detect these features because of the intense central components. This also fits in with the absence of any resolved  $^1\text{H}$  hyperfine splitting from the methyl protons.

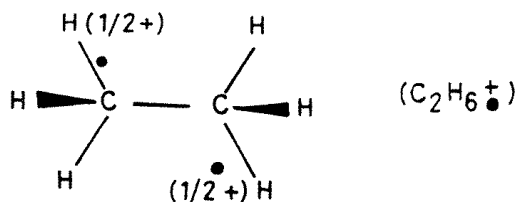
#### 4.2. Electron-loss centres

Absence of any well defined  $^{29}\text{Si}$  hyperfine features for the centres suggests that models of this sort are not suitable for the  $e^-$ -loss centres formed from I, using  $\text{CFCl}_3$  as solvent. It is possible that the minor narrow-line component is due to the delocalized species, but the intensity of the central line is strong enough to lead to detectable  $^{29}\text{Si}$  satellites, by comparison with the anion features.

Detection of resolved  $^1\text{H}$  hyperfine coupling for the major centre rules out this model, and also the analogue of structure III with one stretched bond between the two central atoms. We suggest that the structure resembles structure II, with one electron in the stretched bond rather than three, or possibly the symmetrical analogue V



in which two bonds are elongated. We suggest this by analogy with the radical cation of ethane, which has structure VI



as established by ESR spectroscopy (Iwasaki *et al* 1981). In either case, appreciable  $^1\text{H}$  coupling should result, but it is difficult to make clear predictions. For the radicals  $\bullet\text{Si}(\text{CH}_3)_3$  (6.3 G) (Sharp and Symons 1976) and  $(\text{CH}_3)_3\text{Si} \bullet \text{Si}(\text{CH}_3)_3^+$  (structure VII)



(5.6 G) (Wang and Williams 1981) it seems that there is free rotation of the methyl groups, so that the isotropic coupling constants are all equal. If the model in which the hole is confined to one stretched Si-Si bond (structure II) is correct, then the coupling should be close to that for structure VII, i.e. about 5.6 G. The ethane cation structure V should give about half this value, i.e. about 2.8 G. In our work, the components that are resolved give

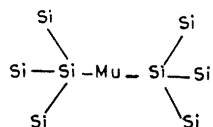


splittings of about 3.6 G; so both models are possible. (We stress that the number of lines involved was not sufficiently well defined to permit a distinction.)

We tentatively conclude that, for the hole centres, the unit is not fully delocalized, and is either trapped in one stretched bond or in two. To our surprise, this involves the outer silicon bonds rather than the central bond. It is reasonable to suggest that the minor species showing no  $^1\text{H}$  splitting is in fact the localized species analogous with structure III and that there is a statistical distribution of singly stretched bond species (about 6:1). This is in good qualitative agreement with the spectra. These must be deep traps since they do not interconvert, on the ESR time scale, even on annealing.

#### 4.3. Relevance of muonium centres in silicon

Some time ago, one of us proposed that a centre detected by muon spin rotation spectroscopy ( $\mu^+\text{SR}$ ), formed on exposure of pure silicon to a muon beam at very low temperatures, known as 'anomalous muonium' was best understood in terms of the 'bond-centre' model shown in structure VIII



(Symons 1984b). This model, now called the 'bond-centre' model, is widely accepted. The envisaged structure placed a node through the centre of the stretched Si-Si bond with the muon held close to this node. This nicely explains the very small isotropic muon hyperfine splitting and also the anisotropy. The tendency for the excess electron to occupy the  $\sigma^*$  Si-Si orbitals, found in the present study, fits in with this model. Clearly 'protonation' must tend to localize the orbital into just one of the bonds.

## 5. Conclusions

The results for the electron adduct show that the Si-Si framework is the best region for the excess electron, and that the tendency to spread between many Si-Si bonds, without significant distortion, is already apparent even when only eight silicon atoms are involved. This leads nicely to the 'conduction band' model of silicon itself. There is no need to invoke major 3d orbital participation to accommodate our results.

The model seems to fail for the corresponding hole centre, probably because of the freedom of our system to relax in a variety of ways without restriction. These distortions are not available for elemental silicon. Even so, the results require that the hole be confined to the  $\text{sp}^3$   $\sigma$ -bonded framework of the radical cation.

The results strongly support the view that the electron-acceptor orbitals in silicon consist of a summation of  $\sigma^*$  orbitals. These are well represented using the normal  $3s + 3p$  orbitals of the  $\sigma$  framework. There is no case for invoking major contributions from silicon 3d orbitals. Thus the contrast with carbon is not solved by invoking the 3d levels (as is often done by chemists!). The differences, nicely demonstrated by the N centres in carbon and P centres in silicon discussed above, lie in part in the weaker  $\sigma$  bonds in silicon, making the  $\sigma^*$  orbitals more available, and in the most satisfactory mode of distortion, if any. For the N-C system, just one N-C bond stretches, lowering the  $\sigma^*$  level and trapping the excess electron. For the silicon system a similar stretching of one P-Si bond would have the same effect but, in this case, local distortion is rejected in favour of extensive delocalization.

## Acknowledgments

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