

QUANTUMCHEMICAL CALCULATIONS ON ORGANOSILICON RADICALS IV.

PENTAMETHYLDISILANE AND TETRAMETHYLDISILANE RADICALS

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ESR spectra of methylsilyl neutral radicals and CNDO/2 calculations showed these radicals to have pyramidal structure [1]. With increasing methyl substitution the radical becomes nearer to planar, but even the trimethylsilyl radical is non-planar. The C—Si—C bond angle in the radicals is approximately 114° , the H—Si—H bond angle is about 99° . The CNDO/2 calculations exaggerate the negative charges at the hydrogen atoms attached directly to silicon, so the values obtained for the SiH_3 radical are less reliable than the values calculated for the $(\text{CH}_3)_3\text{Si}$ radical. However, the calculations are likely to follow correctly the trends of changes in the configuration of radicals and are in accordance with the experimental ESR results.

As a continuation of our investigations related to methylsilyl radicals, CNDO/2 calculations with spd basis were carried out for pentamethyldisilane $[(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_2]$ and tetramethyldisilane $[(\text{CH}_3)_3\text{SiSiHCH}_3]$ radicals in which the change of the tetrahedral Si(1)-Si(2)-C bond angle in hexamethyldisilane molecule was expected to occur (in the radicals the carbon atom is bound to the silicon atom with unpaired electron). On the basis of the calculations we intended to decide whether the three atoms attached to the silicon atom designated by number 2 were in a plane (with 120° bond angles).

The total energy of the two investigated radicals were calculated for two different arrangements of the $\text{Si}(\text{CH}_3)_3$ group: a) the silicon atom designated by number 1 was symmetrically surrounded by the three methyl groups (6 hydrogens were nearer, 2 hydrogens farther from the silicon atom); b) one of the methyl groups was rotated by 180° along the Si—C axis. It is seen from Figs 1 and 2 that for both radicals the total energy is smaller in case a). In the Figures the energy of the radicals is plotted against the Si—Si—C and Si—Si—H bond angle (in tetramethyldisilane the two angles were taken to be identical). For pentamethyldisilane the minimum of the curve indicates a Si—Si—C bond angle at about 113.5° , which corresponds to a state between the tetrahedral and the planar arrangements. The position of the methyl groups bonded to Si(1) according to case b) would result in a greater deviation from the planar configuration. For tetramethyldisilane the minimum of

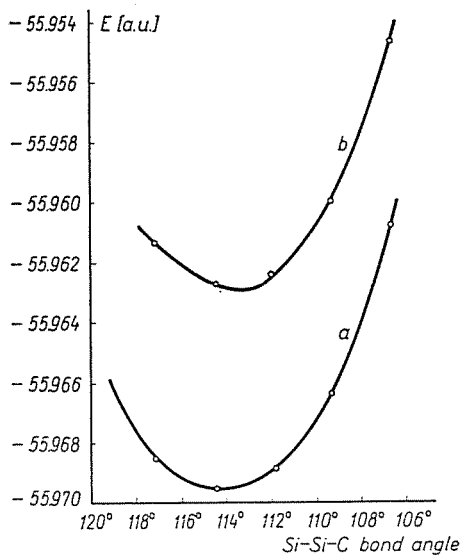


Fig. 1. The total energy of pentamethyldisilane radical as a function of Si-Si-C bond angle in the case of (a) symmetric, (b) asymmetric arrangement of the $(\text{CH}_3)_3\text{Si}$ group

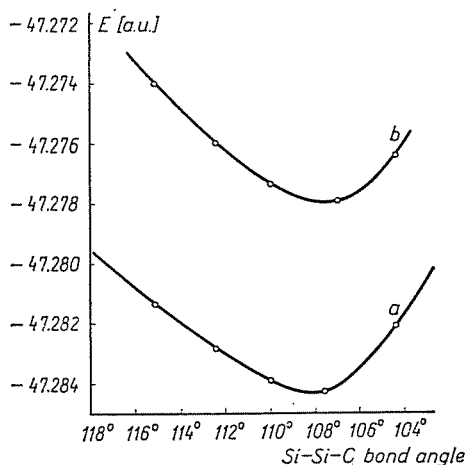


Fig. 2. The total energy of tetramethyldisilane radical as a function of Si-Si-C bond angle in the case of (a) symmetric, (b) asymmetric arrangement of the $(\text{CH}_3)_3\text{Si}$ group

curve a) is at 107.5° . Varying, however, both the Si-Si-C and Si-Si-H bond angles in this radical, it was found that the optimal Si-Si-C bond angle also was about 114° , the Si-Si-H bond angle corresponding to energy minimum was between 99° and 100° (Table 1).

Table 1

The total energy of tetramethyldisilane as a function of Si—Si—C and Si—Si—H bond angles

Si—Si—C angle	Si—Si—H angle	Total energy (a.u.)
109.5°	112°	-47.283400
	109.5°	-47.283865
	107.5°	-47.284225
	104°	-47.284280
	101.5°	-47.283898
	99°	-47.283046
	112°	112°
109.5°		-47.283420
107°		-47.284013
104°		-47.284323
101.5°		-47.284410
99°		-47.284090
114.5°		114.5°
	112°	-47.282048
	109.5°	-47.282689
	107°	-47.283444
	104°	-47.283994
	101.5°	-47.284421
	99°	-47.284559
	96°	-47.284352

It is interesting to note that the dipole moment of the tetramethyldisilane radical, calculated by CNDO/2 method has a minimum in the configuration which appears to be the most stable on the basis of energy minimum (Table 2). In hexamethyldisilane (from which the pentamethyldisilane radical can be derived by the abstraction of a methyl group), the Si—Si bond order is 1.07, calculated by CNDO/2 method, this means a weak connection between the *d* orbitals of the neighbouring silicon atoms. The (*d*—*d*) π contribution to the bond order is altogether 0.0185. This result is supported by LCVO—MO calculations, carried out by NAGY [2], according to which the (*d*—*d*) π interaction between silicon atoms in disilanes can be neglected even in the case where groups with electron donating ability (OCH₃,F) are attached to the silicon atoms. The Si—Si bond order increases in the radicals (1.20 for pentamethyldisilane and 1.17 for tetramethyldisilane).

In Table 3 the calculated electron densities of atoms for hexamethyldisilane molecule, pentamethyldisilane and tetramethyldisilane radicals have

been summarized. The atoms and groups attached to a particular atom are indicated by subscripts in the Table. (Since the tetramethyldisilane radical is asymmetric, the electron densities of hydrogen atoms in a methyl group are not the same, in the Table the mean values of the electron densities for the hydrogen atoms have been recorded. The situation is the same for the hydrogens of the $\text{CH}_3\dot{\text{S}}\text{i}$ group.) The electron densities of the atoms for $(\text{CH}_3)_3\text{Si}$ groups do not show significant changes. The CNDO/2 method

Table 2

The calculated dipole moment of tetramethyldisilane as a function of Si— $\dot{\text{S}}\text{i}$ —C and Si— $\dot{\text{S}}\text{i}$ —H bond angles

Si— $\dot{\text{S}}\text{i}$ —C angle	Si— $\dot{\text{S}}\text{i}$ —H angle	Dipole moment $\times 10^{22}$ (Cm)
117°	117°	0.908
114.5°	114.5°	0.899
112°	112°	0.891
109.5°	109.5°	0.892
107°	107°	0.906
104°	104°	0.979
114.5°	112°	0.889
114.5°	109.5°	0.881
114.5°	107°	0.874
114.5°	104°	0.869
114.5°	101.5°	0.767
114.5°	99°	0.930

Table 3

Electron densities of atoms in hexamethyldisilane molecule, pentamethyldisilane and tetramethyldisilane radicals

	$\text{Me}_3\text{SiSiMe}_2$	$\text{Me}_3\text{Si}\dot{\text{S}}\text{iMe}_2$	$\text{Me}_3\text{Si}\dot{\text{S}}\text{iHMe}$
H_{SiMe}	0.9492	0.9496	0.9444
$\text{H}_{\dot{\text{S}}\text{iMe}}$	—	0.9376	0.9321
H_{Si}	—	—	1.1508
C_{Si}	4.1491	4.1445	4.1410
$\text{C}_{\dot{\text{S}}\text{i}}$	—	4.1460	4.1590
Si	4.0307	4.0661	4.0664
$\dot{\text{S}}\text{i}$	—	4.0374	3.9052

attributes excessively large negative partial charges to the hydrogen atom bound to silicon, in accordance with our previous experiences [1, 3]. The unpaired electron of the Si(2) atom in the radicals is localized on this atom in a great degree. The calculated spin density values also indicate that there is no strong conjugative connection between the two silicon atoms, the unpaired electron is not delocalized in the radicals. The spin density is much greater on the Si(2) atom (0.7090 for pentamethyldisilane and 0.7561 for tetramethyldisilane), than on Si(1) atom (0.1541 for pentamethyldisilane radical and 0.1316 for tetramethyldisilane radical).

This result is supported by ESR investigations carried out for the two radicals by BENNETT et al. [4]. The proton hyperfine coupling constants for the methyl groups bonded to Si(1) are much smaller than those attributed to methyl groups on Si(2). In the case of pentamethyldisilane radical the corresponding coupling constants are 0.47 Gauss and 8.21 Gauss, for tetramethyldisilane radical these values are 0.30 Gauss and 8.15 Gauss.

Summary

CNDO/2 calculations were carried out for hexamethyldisilane molecule, pentamethyldisilane and tetramethyldisilane free radicals. The change in the total energy of the radicals was investigated as a function of Si-Si-C and Si-Si-H bond angles. According to the calculations the Si-Si-C bond angle is about 114° for both radicals, the Si-Si-H bond angle has a value of about 99° in tetramethyldisilane radical. The delocalization of the unpaired electron is not significant in the radicals, the spin density is small in the $(\text{CH}_3)_3\text{Si}$ group.

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