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INVESTIGATION OF ORGANOSILICON RADICALS

II. METHYLSILYL RADICALS

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Summary

CNDO/2 calculations for a series of $Me_xH_{3-x}Si^{\cdot}$ (where $x = 0,1,2,3$) free radicals confirm the suggestion, based on electron spin resonance measurements and chemical evidence, that these radicals are not planar. The deviation from planarity decreases with increasing number of methyl groups, but the angle between the carbon—silicon bond and the plane of an assumed planar configuration is the same for methylsilyl, dimethylsilyl, and trimethylsilyl radicals.

Introduction

Study of silicon-centered free radicals is important since they play a role in several reactions. The radicals are usually obtained by abstraction of hydrogen from Si—H bonds by photochemically generated t-butoxyl radicals. All the evidence favours the pyramidal configuration for silyl radicals, see, for example, the ESR studies by Bennett et al. [1,2] and by Krusic and Kochi [3]. The results of the ESR investigation of $Me_xH_{3-x}Si^{\cdot}$ radicals ($x = 0,1,2,3$), by Bennett et al. are summarized in Table 1.

The most interesting feature of the coupling constants of the radicals is the trend in the α-proton splittings as methyl groups are progressively replaced by hydrogen; the splitting decreases from 17.29 gauss in $Me_2HSi^{\cdot}$ to 7.84 gauss in $H_3Si^{\cdot}$. In contrast, the methyl, ethyl and isopropyl radicals which are generally believed to be planar have α-proton coupling constants of 23.04, 22.38 and 22.11 gauss, respectively [4]. This strongly suggests that the geometry of the silyl radicals depends on the number of methyl groups present. The appearance of two bending modes in the infrared spectrum of $H_3Si^{\cdot}$ [5] also supports the pyramidal structure, and chemical evidence has been presented for the non-planarity of tri-substituted silyl radicals [6].

TABLE 1

HYPERFINE COUPLING CONSTANTS FOR THE $Me_xH_{3-x}Si^{\cdot}$ RADICALS (GAUSS)

Radical	α-H	β-H
Me_3Si	—	6.34
Me_2SiH	17.29	7.30
$MeSiH_2$	12.11	8.21
SiH_3	7.84	—

The values of the ESR isotopic ^{29}Si coupling is related to the *s* character of the unpaired electron and hence is dependent on hybridization and interbond angles [7,8]. The experimental conditions used for various methylsilyl radicals, however, varied to such an extent that the estimation of the bond angles could not be carried out unambigously. In this work CNDO/2 calculations with an *spd* basis have been carried out on silyl radicals.

Results and discussion

Calculations were carried out for various assumed arrangements of hydrogen atoms and methyl groups bonded to the central silicon atom, and the conformations with minimum total energy were taken to be the most probable arrangements. To calculate the molecular coordinates of the atoms the direction of the *p* orbital with unpaired electron on silicon atom was chosen to be the *z* axis and the perpendicular $x - y$ plane was the plane of the assumed planar configuration. The angles of deviation of the methyl groups and hydrogen atoms from the planarity were assumed to be 40°, 35°, 30°, 29°, 28°, 25°, 22°, 19°28′ (tetrahedral configuration), 18°, 15°, 14°, 10°, 5° and 0° (planar configuration), respectively. These angles correspond to C—Si—C and H—Si—H bond angles as indicated in Table 2. The calculated total energies are plotted against the deviation from planarity in Fig. 1 for silyl and methylsilyl radicals and in Fig. 2 for dimethylsilyl and trimethylsilyl radicals.

It can be seen that at the energy minimum the H—Si—H bond angle is about 98° for the silyl radical and 104° for the methylsilyl radical, while the C—Si—C bond angle is around 109.5° for the dimethylsilyl radical and 114° (between the tetrahedral and planar configurations) for the trimethylsilyl radical.

TABLE 2

C—Si—C AND H—Si—H BOND ANGLES CORRESPONDING TO VARIOUS ASSUMED DEVIATIONS FROM THE PLANAR CONFIGURATION

Deviation from planarity	Bond angle	Deviation from planarity	Bond angle
40°	83°08′	19°28′	109°28′
35°	90°22′	18°	110°54′
30°	97°10′	15°	113°34′
29°	98°28′	14°	114°20′
28°	99°46′	10°	117°04′
25°	103°26′	5°	119°14′
22°	106°50′	0°	120°

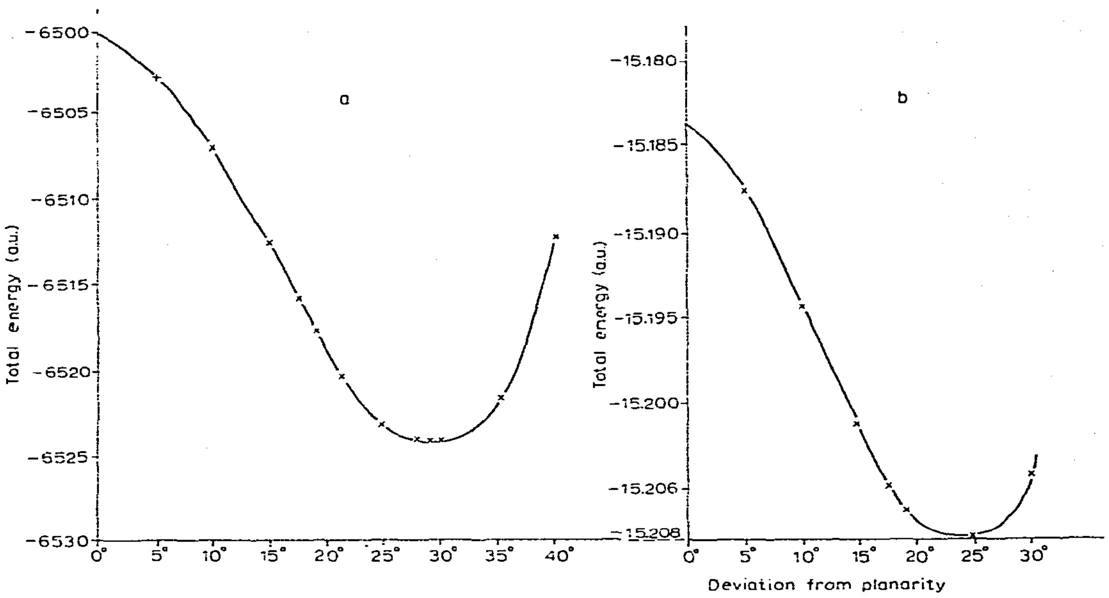

Fig. 1. Calculated total energies as a function of deviation from planarity, (a) silyl radical, (b) methylsilyl radical.

With increasing methyl substitution the radical becomes more planar, but even the trimethylsilyl radical is non-planar.

In the above calculations it was assumed that in the methylsilyl and dimethylsilyl radicals the deviations of the methyl groups and the hydrogen atoms from the planar configuration were the same. There is another possibility, namely that the positions of the methyl groups, related to the $x-y$ plane correspond of that in the trimethylsilyl radical and the hydrogen atoms maintain the deviation from the planar configuration observed in the silyl radical. To study

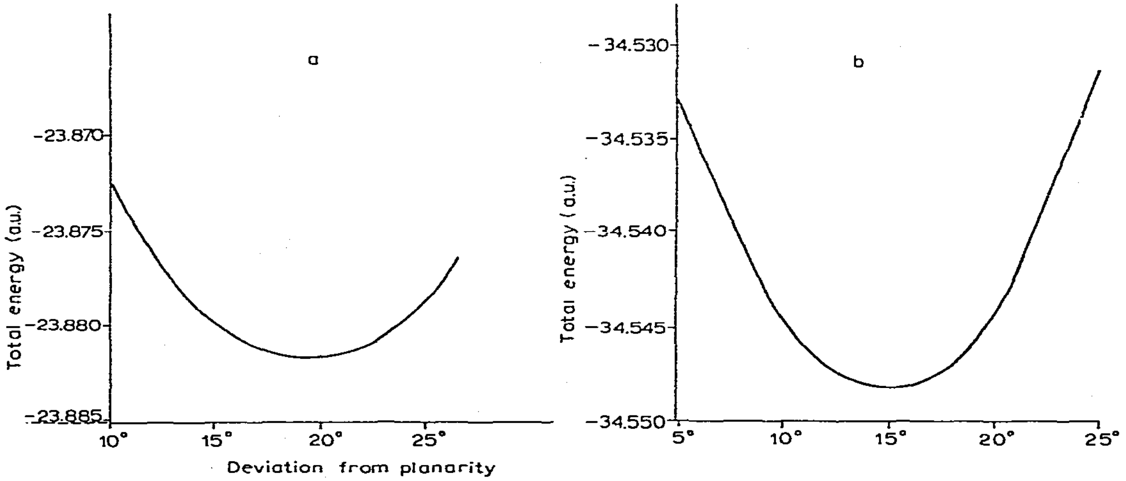

Fig. 2. Calculated total energies as a function of deviation from planarity, (a) dimethylsilyl radical, (b) trimethylsilylradical.

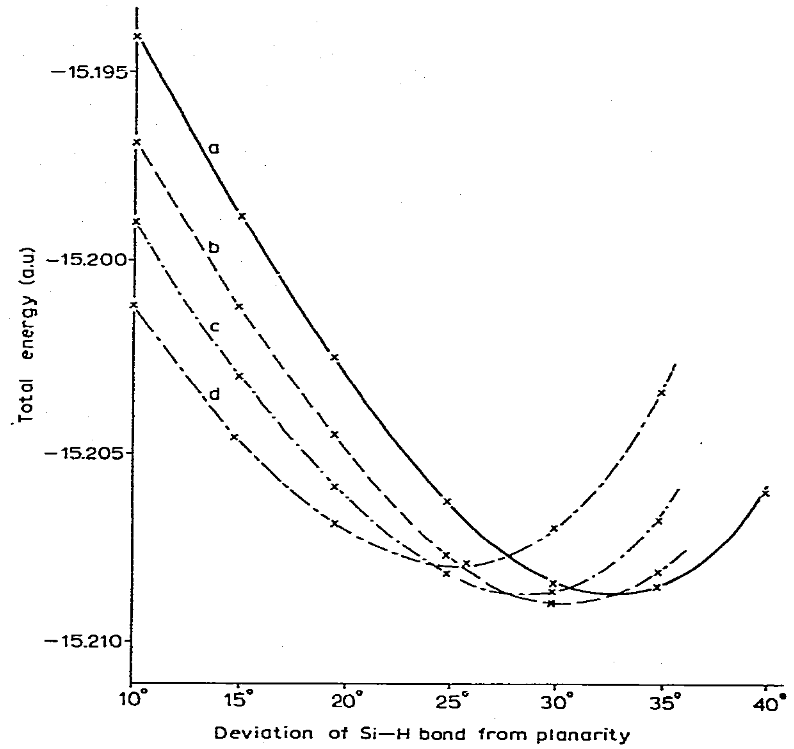

Fig. 3. Plot of total energy against the angle between the Si—H bond and the $x - y$ plane. The angle between the C—Si bond and the $x - y$ plane is for curve a, 10°; b, 15°; c, 19°28′; d, 25°.

this possibility a series of calculations for both radicals was carried out in which various angles were assumed between the methyl groups and the $x - y$ plane as well as between the hydrogen atoms and the $x - y$ plane. The results are presented in Fig. 3 for the methylsilyl radical and in Fig. 4 for the dimethylsilyl radical. It can be seen that minimum total energy is obtained for both radicals when the angle of the C—Si bond with the $x - y$ plane is the same (about 14-15°) as in the trimethylsilyl radical, and that of Si-H bond (about 29-30°) in the silyl radical. This means that the C—Si—C bond angle is 114° and the H—Si—H bond angle 99°.

To check the validity of the indicated trends, CNDO calculations were

TABLE 3

TOTAL ENERGIES FOR METHYL AND ETHYL RADICALS

Deviation from the planar configuration	Total energy (a.u.)	
	CH_3	C_2H_5
19°28′	−9.097319	—
15°	−9.106848	−17.822947
10°	−9.113030	−17.829901
5°	−9.115908	−17.833076
0°	−9.116704	−17.833750

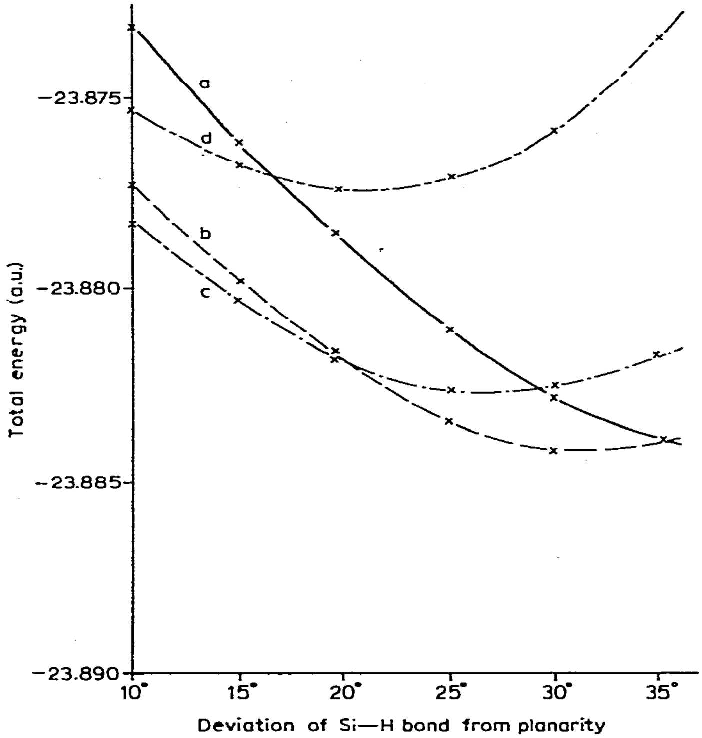

Fig. 4. Plot of total energy against the angle between the Si—H bond and the $x - y$ plane. The angle between the C—Si bond and $x - y$ plane is for curve a, 10°; v, 15°; c, 19°28′; d, 25°.

carried out for methyl and ethyl free radicals, which should be planar. The calculated total energies (Table 3) show, in agreement with the experimental results, that both molecules are planar.

The calculated electron densities for $Me_xH_{3-x}Si^{\bullet}$ radicals in the most stable configurations are presented in Table 4. The electron densities on the silicon atoms and the measured α-hydrogen coupling constants show a good correlation (Fig. 5). The magnitude of the change of the electron density at the α-hydrogens decreases as the number of hydrogen atoms attached to the central silicon atom decreases. This trend is not observed if an identical deviation of methyl groups and hydrogen atoms from the $x - y$ plane is assumed, or, for example, if the tetrahedral configuration is assumed for all the radicals concerned.

The relationship between the experimental hyperfine coupling constants and

TABLE 4

ELECTRON DENSITIES IN THE $Me_xH_{3-x}Si^{\bullet}$ RADICALS

x	Si	C	H(Si)	H(Me)
0	3.5414	—	1.1529	—
1	3.7264	4.1895	1.1570	0.9258
2	3.8848	4.1733	1.1615	0.9364
3	4.0229	4.1595	—	0.9461

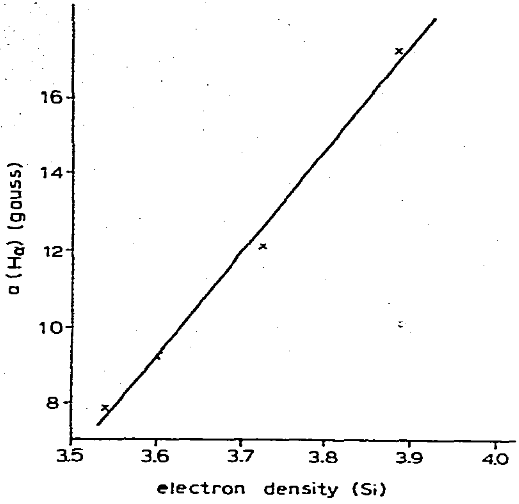

Fig. 5. Correlation between the calculated electron densities on the silicon atoms and the measured hyperfine coupling constants for the α-hydrogens in $Me_xH_{3-x}Si^{\cdot}$ radicals.

the calculated spin densities at various atoms of the radicals can be evaluated only with difficulty since the CNDO approximations preclude an accurate assesment of the spin polarization contribution to the unpaired electron density. Unfortunately the INDO method has not been extended to compounds containing silicon. In terms of the CNDO calculations, however, the change of the coupling constants of the β-protons (on methyl carbon atoms) shows the same tendency as the calculated spin density values at the *s* orbital of the corresponding carbon atoms (0.0108 for $MeSiH_2$, 0.0656 for Me_2SiH and 0.0078 for Me_3Si radical). The hyperfine coupling constant of α-protons (on silicon atom) increases on progressive replacement of the hydrogen atoms by methyl groups, and the calculated total spin density at silicon atom increases in the same direction (0.7850 for SiH_3, 0.7966 for $MeSiH_2$ and 0.8052 for Me_2SiH radical.)

The force constant of Si—H bond in SiH_4 is 2.77 mdyn/Å [5] and that in the $H_3Si^{\cdot}$ radical is 2.212 mdyn/Å [9]. On the basis of CNDO/2 calculations the calculated bond order for SiH_4 is 0.96 and that for the $H_3Si^{\cdot}$ is 0.92, the trend being the same as that for the corresponding force constants.

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