

QUANTUMCHEMICAL CALCULATIONS ON ORGANOSILICON RADICALS III

CNDO/2 CALCULATIONS FOR METHYLSILYL RADICALS

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Investigation of silicon-centered free radicals are of particular interest for chemists since they play an important role in a number of reactions. These radicals are generally obtained by abstracting hydrogen atoms from photochemically generated t-butoxyl radicals. All structural information discussed to now favours pyramidal silyl radical. Reports were presented on electron spin resonance study of a series of transient silicon-centered free radicals by BENNETT et al. [1, 2] and KRUSIC and KOCHI [3]. Results of the ESR investigation on $\text{Me}_x\text{SiH}_{(3-x)}$ radicals (where $x = 0, 1, 2, 3$), carried out by BENNETT et al. are summarized in Table 1.

Table 1

Hyperfine coupling constant of the $\text{Me}_x\text{SiH}_{(3-x)}$ radicals (in 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 most interesting feature in coupling constants of these 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 dimethylsilyl radical to 7.84 gauss in silyl radical. The methyl, ethyl and isopropyl radicals however, 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 SiH_3 [5] gives support to the pyramidal structure, too. Chemical evidence has also been presented for the non-planarity of trisubstituted silyl radicals [6]. When free radicals are generated from compounds containing an asymmetric

carbon atom which bears the unpaired electron, the optical activity of the parent compounds is lost. The loss of optical activity can be ascribed to the planar configuration. The same way the silyl radical derived from an optically active hydrosilane has been presumed to lose its optical activity. However, the silyl radical produced from an optically active hydrosilane undergoes chlorine abstraction mostly with retention of configuration.

The value of the ESR isotopic ^{29}Si coupling is diagnostic for the s character of the unpaired electron and hence dependent on hybridization and interbond angles [7.8]. The experimental conditions for different methylsilyl radicals, however, varied too much to permit unambiguous evaluation of the results and the estimation of the bond angles. In this work CNDO/2 calculations with spd basis were applied to study the non-planarity of silyl radicals.

Calculations were carried out with different assumed arrangements of hydrogen atoms and methyl groups bonded to the central silicon atom, and the conformations with minimum total energy were accepted as the most likely arrangements. To calculate the molecular co-ordinates 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° , $19^\circ 28'$ 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

Table 2

C—Si—C and H—Si—H bond angles corresponding to the different assumed deviations from the planar configurations

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

total energies have been plotted against the deviation from planarity in Fig. 1 for silyl and methylsilyl radicals and in Fig. 2 for dimethylsilyl and trimethylsilyl radicals.

At energy minimum the H—Si—H bond angle is seen to be about 98° in the case of silyl radical, 104° for methylsilyl radical, the C—Si—C bond angle is around $109,5^\circ$ for dimethylsilyl radical and 114° (between tetrahedral

and planar configurations) for trimethylsilyl radical. With increasing methyl substitution the radical becomes nearer to planar, but even the trimethylsilyl radical is non-planar.

In previous calculations the discrepancy of the methyl groups and the hydrogen atoms from the planar configuration was assumed to be the same in the methylsilyl and dimethylsilyl radicals. There is another possibility, namely that in these two radicals the positions of the methyl groups, related to the

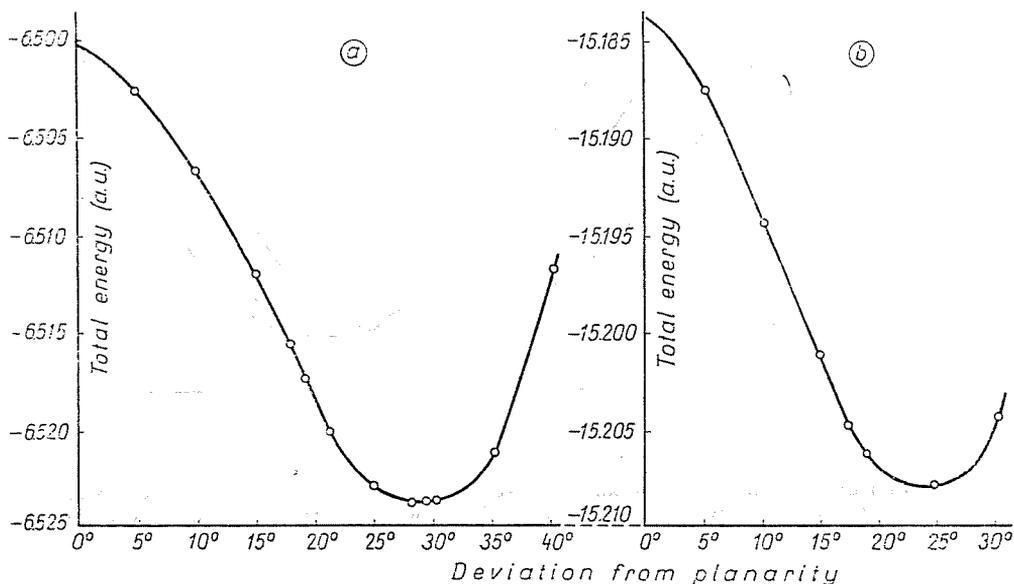


Fig. 1. Calculated total energies vs. deviation from planarity: a. silyl radical, b. methylsilyl radical

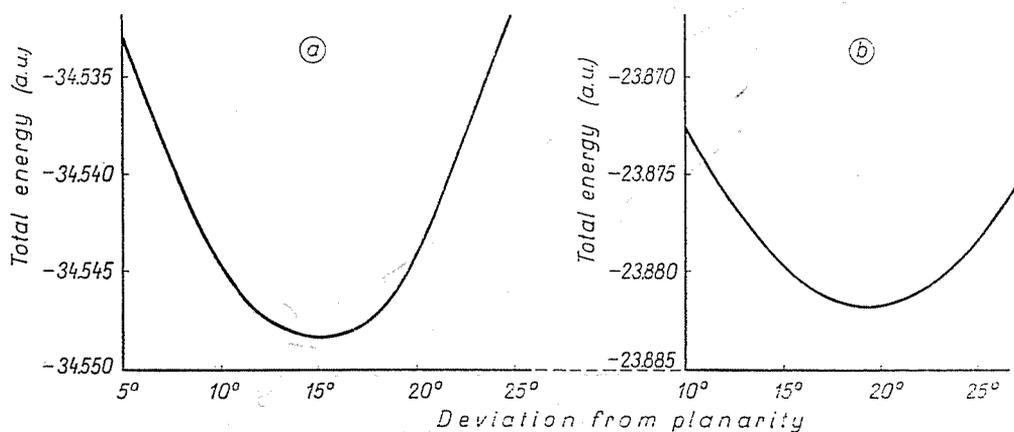


Fig. 2. Calculated total energies vs. deviation from planarity: a. dimethylsilyl radical, b. trimethylsilyl radical

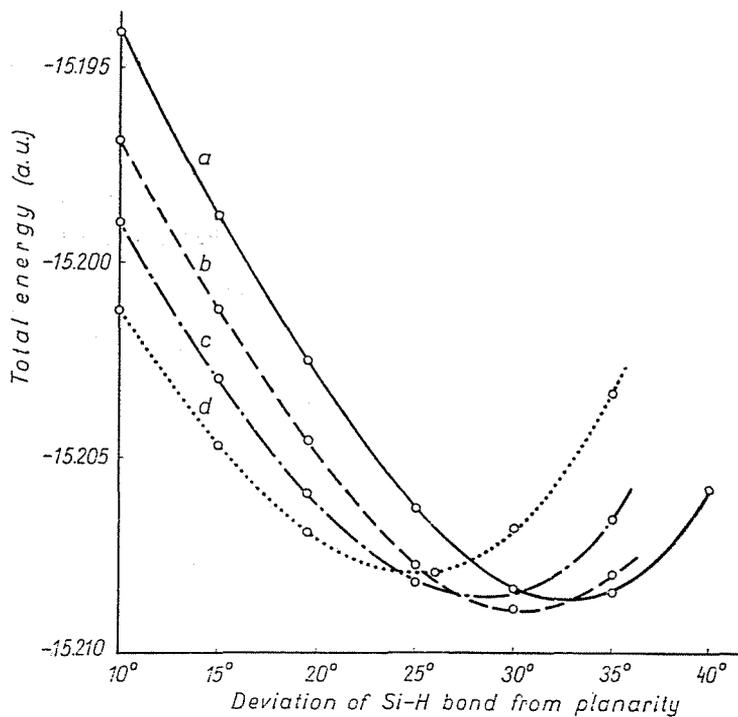


Fig. 3. Plot of total energy vs. the angle between Si-H bond and x-y plane. Curves a, b, c, d refer to angles of 10°, 15°, 19°28' and 25° between C-Si bond and x-y plane

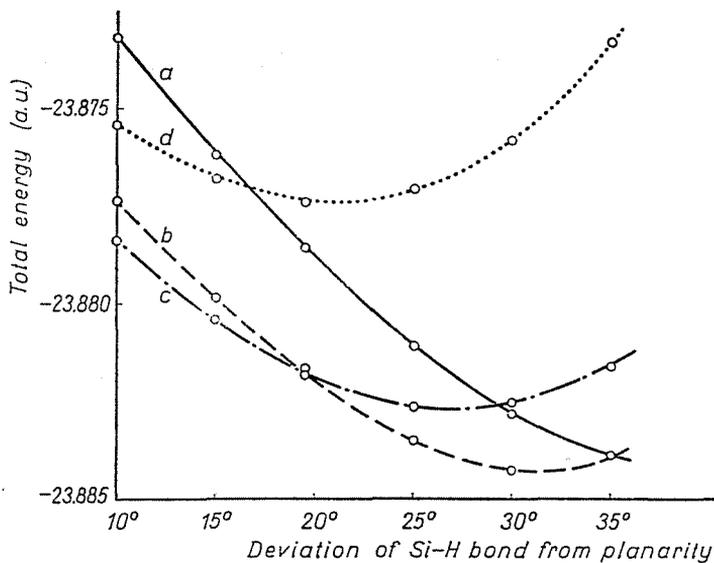


Fig. 4. Plot of total energy vs. the angle between Si-H bond and x-y plane. Curves a, b, c, d refer to angles of 10°, 15°, 19°28' and 25° between C-Si bond and x-y plane

x - y plane would correspond to that in the trimethylsilyl radical and the hydrogen atoms would maintain the deviation from the planar configuration as it was observed in the silyl radical. To study this possibility a series of calculations for both radicals was carried out, with different angles 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 represented in Fig. 3 for the methylsilyl radical and in Fig. 4 for the dimethylsilyl radical. Minimum total energy is seen to be obtained for both radicals when the angle of the C—Si bond with the x - y plane is the same (about 14 to 15°) as in the trimethylsilyl radical, and that of Si—H bond is identical (about 29 to 30°) to that in the silyl radical. It means that the C—Si—C bond angle is 114° and the H—Si—H bond angle is 99°.

To control the validity of the tendencies concluded on the basis of the calculated results, CNDO calculations were carried out for methyl and ethyl free radicals assumed to be planar. In agreement with the experimental results the calculated total energies (Table 3) show both molecules to be planar.

Table 3
Total energies for methyl and ethyl radicals

Deviation from the planar configuration	Total energy (a. u.)	
	CH ₃	C ₂ H 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

The calculated electron densities for Me_xSiH_(3-x) radicals in the most stable configurations are presented in Table 4. The electron densities on silicon

Table 4
Electron densities in the Me_xSiH_(3-x) radicals

x	Si	C	H(Si)	H(Me)
0	3.5414	—	1.1529	—
1	3.7264	4.1895	1.1570	0.9258
2	3.8842	4.1733	1.1615	0.9364
3	4.0229	4.1595	—	0.9461

atoms and the measured α -hydrogen coupling constants are in good correlation (Fig. 5). The change of electron density of α -hydrogens shows a definite decreasing tendency with increasing number of hydrogen atoms bonded to the central

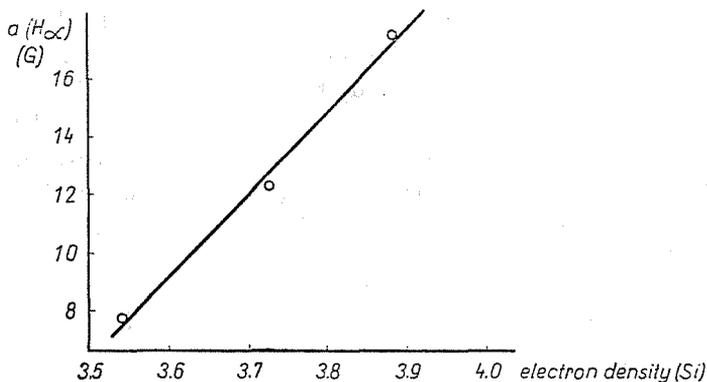


Fig. 5. Correlation between calculated electron densities on silicon atoms and measured hyperfine coupling constants of α -hydrogens for $\text{Me}_x\text{SiH}_{(3-x)}$ radicals

silicon atoms. This tendency is not manifested if an identical deviation of methyl groups and hydrogen atoms from the x - y plane is accepted or, for example, tetrahedral configuration is assumed for all the radicals concerned.

The relationship between the experimental hyperfine coupling constants and the calculated spin density values at different atoms of the radicals are difficult to evaluate since the CNDO approximations are too extreme to give a proper account of the spin polarization contribution to the unpaired electron density. Unfortunately the INDO method has not been developed for compounds containing silicon. According to the CNDO calculations it may be mentioned, however, that the change of the coupling constants of 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 if gradually substituting the hydrogen atoms by methyl groups and does the calculated total spin density at silicon atom (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 equals 2.77 mdyne/Å [5] and that in SiH_3 radical is 2.212 mdyne/Å [9]. On the basis of CNDO/2 calculations the calculated bond order for SiH_4 is 0.96 and for SiH_3 radical is 0.92 which indicates the same tendency as the corresponding force constants.

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Summary

CNDO/2 calculations for a series of $\text{Me}_x\text{SiH}_{(3-x)}$ (where $x = 0, 1, 2, 3$) free radicals support the suggestion based on electron spin resonance measurements and chemical evidences that these radicals, contrary to the analogous carbon-centered radicals, are not planar. The extent of deviation from planarity is decreasing with increasing number of methyl groups. According to the calculations the angle between the carbon-silicon bond and the plane of the assumed planar configuration is the same for methylsilyl, dimethyl and trimethylsilyl radicals.

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