QUANTUMCHEMICAL CALCULATIONS ON ORGANOSILICON RADICALS II

CNDO/2 CALCULATIONS FOR METHYLPHENYLSILANE RADICAL ANIONS

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Earlier spin density calculations were carried out on phenylsilane derivatives by Hückel LCAO—MO method using the McLachlan procedure, and the results were compared with the experimental spin densities applying the McCONNELL equation [1]. SIPE and WEST found a good correlation between the calculated and experimental spin densities of phenylsilane anion radicals [2]. The same conclusion was drawn from Hückel calculations improved by ω-technique [3]. The spin densities related to phenylsilane anion radicals can be calculated by CNDO/2 method applying this procedure for molecules of open shell configuration.

Calculations were carried out with spd basis set for trimethylphenylsilane, dimethylphenylsilane, methylphenylsilane and phenylsilane anions. The numbering of atoms in the arylsilane molecules is indicated in Fig. 1.

The aromatic π systems consist of the π electrons of the p(z)orbitals belonging to the ring carbon atoms and the d orbitals of the silicon atom. The calculated electron densities on the p(z) orbital of carbon atoms are compiled in Table 1. These values are the most interesting for investigating the

Table 1

Calculated electron densities on the p(z) orbital of carbon atoms

	PhSiMe$_3$	PhSiMe$_2$	PhSiH$_2$Me	PhSiH$_3$
C$_1$	1.1101	0.9830	0.9090	0.9053
C$_2$	1.0764	1.0542	1.0165	0.9351
C$_3$	1.0241	1.0162	1.0185	1.0358
C$_4$	1.2120	1.1537	1.0805	1.0082

validity of McCONNELL relation in connection with the CNDO results. It has to be mentioned that the role of d orbitals is overestimated by the CNDO/2 method, thereby excessive electron densities appear on the silicon d orbitals. Table 2 shows the spin densities on the p(z) orbital of carbon atoms and the d orbitals of silicon atom.
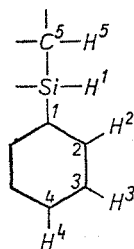
Fig. 1. Numbering of the atoms in the arylsilane anions

Table 2

Calculated spin densities on the p(z) orbital of carbon atoms and the d orbitals of silicon atom

	PhSiMe$_3$	PhSiHMe$_2$	PhSiH$_2$Me	PhSiH$_3$
C$_1$	0.1316	0.0136	−0.0210	−0.0026
C$_2$	0.1691	0.1617	0.0857	0.0057
C$_3$	−0.0638	−0.0746	−0.0430	0.0029
C$_4$	0.3280	0.2399	0.1089	0.0066
Si d(z^2)	0.0089	0.0032	0.0631	0.0698
d(xz)	−0.0005	−0.0002	−0.0095	−0.0096
d(yz)	0.1682	0.1790	0.0612	−0.0031
d(x^2−y^2)	0.0027	0.0106	0.0577	0.1149
d(xy)	0.0000	−0.0003	−0.0053	−0.0055

The ESR spectra of trimethylphenylsilane and dimethylphenylsilane anion radicals were recorded by GERSON et al. [4]. MAKAROV et al. reported proton hyperfine coupling constants for trimethylphenylsilane and phenylsilane [5]. The experimental splitting constants are represented in Table 3. The ESR

Table 3

Experimental hyperfine coupling constants

	a(H$_1$)	a(H$_2$)	a(H$_3$)	a(H$_4$)	a(H$_5$)
PhSiMe$_3$[a]	—	2.65	1.06	8.09	0.26
PhSiHMe$_2$[a]	0.81	2.70	0.97	8.12	0.13
PhSiH$_3$[b]	—	1.90	0.90	6.00	—

[a]Values taken from Ref. [4][b]; values taken from Ref. [5]

spectrum of methylphenylsilane radical anion has not been measured. According to the experimental results, hyperfine splittings attributed to methyl protons and protons attached to silicon atom are fairly small. There is a linear correlation between the coupling constants and the carbon π electron densities for both the trimethylphenylsilane and the dimethylphenysilane (Fig. 2). The results are worse for phenylsilane. A good agreement can be observed between the hyperfine coupling constants and the corresponding π spin densities. The spin density is the highest on the carbon atom in para position and the
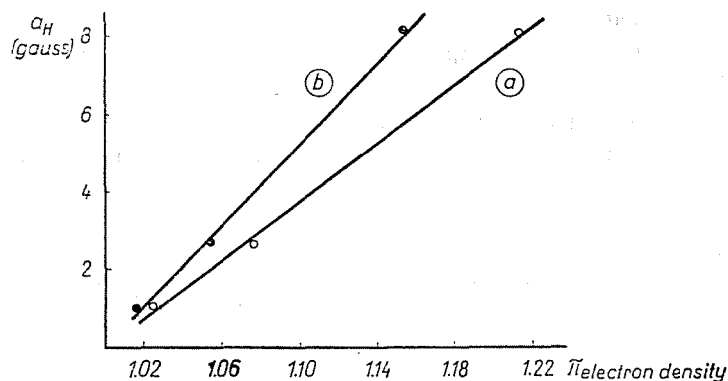
Fig. 2. Correlation between proton hyperfine coupling constants and carbon π electron densities in trimethylphenylsilane (a) and dimethylphenylsilane (b)

lowest in meta position. The hyperfine splitting constants follow the same order. No simple linearity in the spin density vs. hyperfine splitting constant function can be expected because the McConnell relation holds only in the case of neutral radicals. For excess charge effects the McConnell equation should include another additive part which expresses the dependence of the hyperfine coupling constant on the spin densities of the neighbouring atoms.

It is worth of mentioning that Makarov et al. reported nearly the same hyperfine coupling constants for ring protons in trimethylphenylsilane but the assignation of the experimental values differs from that suggested by Gerson et al. Makarov assumed a smaller hyperfine splitting for orto protons and a larger splitting for meta protons. The CNDO calculations in accordance with the results of the Hückel approximation confirmed the assignation illustrated in Table 3.

The calculated results for methylphenylsilane radical anions appear to give an increasingly poor correlation with the experimental data, if the methyl groups on the silicon atom are gradually substituted by hydrogen atoms. But even in the case of phenylsilane anion the calculated spin density value is the highest on the carbon atom in para position and the lowest on the carbon atoms in meta position which is also the case for the hyperfine coupling constants. From the calculated spin densities of methylphenysilane a similar hyperfine splitting pattern can be predicted for the spectrum of this molecule as in the case of trimethylphenylsilane and dimethylphenylsilane.

Data in Table 2 show a considerable spin location on the d orbitals of silicon atoms, responsible for the observed lower total splitting parameter in phenylsilanes than in simple aromatic anion radicals. (It should be noticed that negative spin densities on p(z) and d orbitals have an opposite effect.) At the same time thet electron density values of silicion d orbitals indicate a $d\pi$—$p\pi$ interaction which was proved earlier to exist for the neutral molecules [6, 7].

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The calculated bond order values for the bond between silicon and ring carbon atom tend to decrease upon changing the methyl groups on the silicon gradually by hydrogen atoms. It is interesting to compare these bond orders with the corresponding bond orders in the neutral molecules, calculated also by the CNDO/2 method (Table 4). The data tend to decrease in the opposite

Table 4

Bond order between silicon atom and aromatic carbon atom for anion radicals and neutral molecules

	$PhSiMe_3$	$PhSiHMe_2$	$PhSiH_2Me$	$PhSiH_3$
Radicals	1.35	1.26	1.08	0.98
Neutral molecules	1.09	1.11	1.12	1.15

direction. Considering the charge distribution for the anion radicals and neutral molecules (Table 5) it can be observed that the unpaired electron residence

Table 5

Partial charge distribution in methylphenylsilane anion radicals and neutral molecules

	$PhSiMe_3$		$PhSiHMe_2$	
	Anion	Neutral	Anion	Neutral
H_1	—	—	−0.2180	−0.1523
H_2	−0.0575	−0.0154	−0.0470	−0.0130
H_3	−0.0635	−0.0074	−0.0556	−0.0046
H_4	−0.0624	−0.0065	−0.0539	−0.0040
H_5	+0.0154	+0.0518	+0.0181	+0.0596
C_1	−0.1423	−0.0945	−0.0883	−0.1062
C_2	−0.0132	+0.0585	+0.0005	+0.0700
C_3	−0.0080	−0.0132	−0.0110	−0.0167
C_4	−0.1111	+0.0262	−0.0821	+0.0360
C_5	−0.1511	−0.1633	−0.1508	−0.1747
Si	−0.1075	+0.0576	−0.1380	+0.1465

	$PhSiH_2Me$		$PhSiH_3$	
	Anion	Neutral	Anion	Neutral
H_1	−0.2356	−0.1516	−0.2570	−0.1546
H_2	−0.0328	−0.0080	−0.0227	−0.0049
H_3	−0.0465	−0.0019	−0.0385	+0.0021
H_4	−0.0395	−0.0018	−0.0386	+0.0016
H_5	+0.0174	+0.0704	—	—
C_1	−0.0816	−0.1103	−0.0993	+0.0843
C_2	+0.0236	+0.0716	+0.0518	−0.0162
C_3	−0.0154	−0.0133	−0.0286	−0.1294
C_4	−0.0395	+0.0339	+0.0047	+0.0450
C_5	−0.1581	−0.1889	—	—
Si	−0.1142	+0.2622	−0.0338	+0.4153

on the silicon atom intensifies going from trimethylphenylsilane anion to phenylsilane anion, which is confirmed by the difference between the partial charge of silicon atom in neutral molecules and in anion radicals and by the total spin density values on silicon atoms. At the same time the polarity of the bond between silicon and aromatic carbon increases. These tendencies partly results in bond orders below 1 in phenylsilane. The other factor is that the CNDO calculations results in excessive negative charges at hydrogen atoms attached directly to silicon, thus the role of these hydrogens is overestimated.

Table 6

Bond polarity values for silicon — aromatic carbon bonds in methylphenylsilane neutral molecules and anion radicals

	PhSiMe$_3$	PhSiHMe$_2$	PhSiH$_2$Me	PhSiH$_3$
Neutral molecules	0.0296↓	0.0026↓	0.0187↑	0.0494↑
Radicals	0.4000↑	0.5492↑	0.5772↓	0.8049↑

The bond polarity values are compiled in Table 6 for silicon-aromatic carbon bond. An arrow pointing upwards indicates a negative polarity on silicon, an arrow in the opposite direction represents a bond polarity with negative charge on carbon atom. The values show a slight change for the neutral molecules and significant changes for anion radicals. Obviously the results for phenylsilane are not realistic because of the exaggerated partial charges on hydrogen atoms attached to silicon.

The calculated spin densities cannot be compared with Si[29] hyperfine coupling constants since there is an experimental value available only in the case of trimethylphenylsilane.

As it was mentioned earlier the calculated Si—C bond order is higher for trimethylphenylsilane anion radical than for the corresponding neutral molecule. In order to investigate the efficiency of the CNDO method in determining equilibrium bond distances and to study the change of silicon—carbon bond length as a function of bond order, CNDO calculations were carried out for trimethylphenylsilane neutral molecule and anion radical in which the silicon—carbon bond distance ranged from 1.75 Å to 1.95 Å and the calculated total energy was plotted against the bond distance (Fig. 3.). According to the calculations, (Table 7) the equilibrium bond distances appear to be 1.886 Å and 1.848 Å for the neutral molecule and for anion radical, respectively. The value for the neutral molecule seems fairly reasonable and can be compared to the experimental Si—C bond length of 1.87 Å in tetraphenylsilane [8]. If the bond order increases the equilibrium bond distance decreases as it is the case for the anion radical.
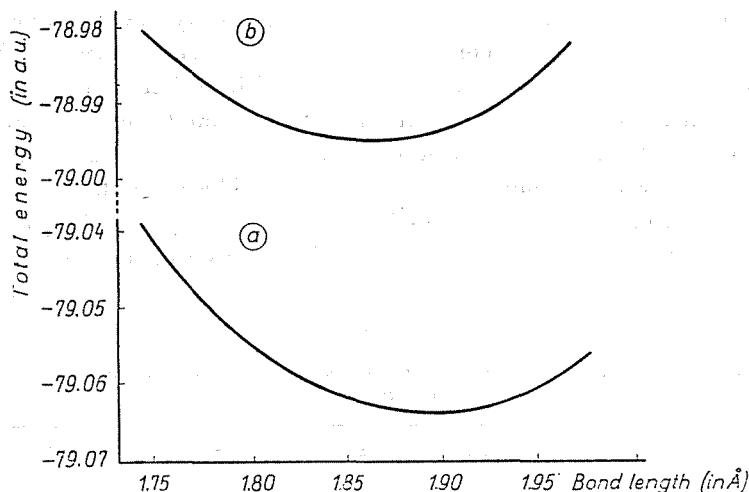
Fig. 3. Plot of total energy in trimethylphenylsilane neutral molecule (a) and anion radical
(b) against Si—C bond length

Table 7

*Calculated total energy of trimethylphenylsilane neutral molecule and anion radical vs. Si-C bond
length*

Bond length (Å)	Total energy (a. u.)	
	Neutral molecule	Anion radical
1.75	−79.0424	−78.9853
1.80	−79.0548	−78.9936
1.85	−79.0616	−78.9960
1.90	−79.0628	−78.9935
1.95	−79.0602	−78.9869

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Summary

CNDO/2 calculations with an spd basis set have been carried out on methylphenylsi-
lane anion radicals, and the calculated spin density values compared with the experimental
hyperfine coupling constants. The CNDO method overestimates the role of *d* orbitals and the
partial charges on hydrogen atoms attached to silicon atom. The partial charge distribution
and the carbon–silicon bond order in the anion radicals and the corresponding neutral mole-
cules are discussed. The equilibrium carbon–silicon bond distance in the trimethylphenylsilane
molecule and corresponding anion radical has also been investigated.

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