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INVESTIGATION OF ORGANOSILICON RADICALS

I. METHYLPHENYLSILANE ANION RADICALS

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Summary

CNDO/2 calculations with an *spd* basis set have been carried out on methylphenylsilane 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 molecules are discussed. The equilibrium carbon—silicon bond distance in the trimethylphenylsilane molecule and corresponding anion radical have also been investigated.

Introduction

Accounts of the ESR spectra of organosilicon anion radicals have appeared in the literature since 1962. Spin density calculations have been carried out by Hückel LCAO-MO method using the McLachlan procedure, and the results compared with the experimental spin densities derived from the McConnel equation [1]. Sipe and West found a good correlation between the calculated and experimental spin densities of phenylsilane anion radicals [2], and similar agreement was found for Hückel calculations improved by the ω-technique [3]. The values of the ^{29}Si hyperfine coupling constants were found to depend much more on the spin density at the carbon atom bearing the silicon substituent than on the spin density at the silicon atom. The spin densitites in phenylsilane anion radicals have now been calculated by the CNDO/2 method using this procedure applicable to molecules of open shell configuration, and the results are described below.

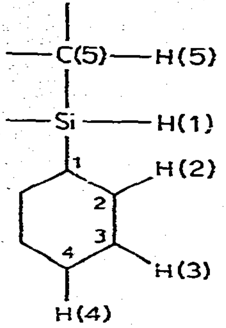

Fig. 1. Numbering of atoms in the arylsilane anions.

Results and discussion

Calculations were carried out with an *spd* set for trimethylphenylsilane, dimethylphenylsilane, methylphenylsilane and phenylsilane anions. The numbering of atoms in the arylsilane molecules is indicated in Fig. 1. The aromatic π system consists 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 the carbon atoms are summarized in Table 1. These values are relevant in assessing the validity of the McConnel relation in connection with the CNDO results. It must be mentioned that the role of *d* orbitals is overestimated by the CNDO/2 method, and thus exaggerates the electron densities in the silicon *d* orbitals. Table 2 shows the spin densities in the $p(z)$ orbital of carbon atoms and the *d* orbitals of silicon atom.

The ESR spectra of trimethylphenylsilane and dimethylphenylsilane anion radicals were reported by Gerson et al. [4]. Makarov et al. reported proton hyperfine coupling constants for trimethylphenylsilane and phenylsilane [5]. The experimental splitting constants are listed in Table 3. The ESR spectrum of methylphenylsilane radical anion has not been measured. The experimental results show that hyperfine splittings attributed to methyl protons and protons attached to a 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 dimethylphenylsilane (Fig. 2), but the correlation is not as good for phenylsilane. Good agreement can be observed between the hyperfine coupling constants and the corresponding π spin densities. The spin density is largest at the carbon atom in the *para* position and smallest at that

TABLE 1

CALCULATED ELECTRON DENSITIES ON THE $p(z)$ ORBITAL OF CARBON ATOMS

	$\mathrm{PhSiMe_3}$	$\mathrm{PhSiMe_2}$	$\mathrm{PhSiH_2Me}$	$\mathrm{PhSiH_3}$
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

TABLE 2

CALCULATED SPIN DENSITIES ON THE $p(z)$ ORBITAL OF CARBON ATOMS AND THE d ORBITALS OF SILICON ATOM

	$PhSiMe_3$	$PhSiHMe_2$	$PhSiH_2Me$	$PhSiH_3$
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

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.

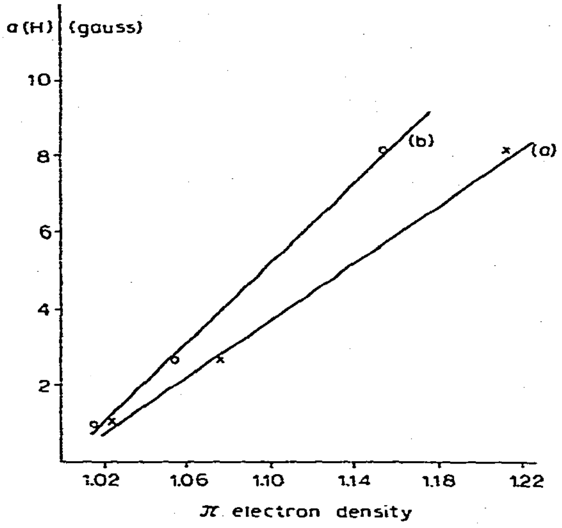

Fig. 2. Correlation between proton hyperfine coupling constants and carbon π electron densities, in (a) trimethylphenylsilane and (b) dimethylphenylsilane.

in the *meta* position. The hyperfine splitting constants follow the same order. Simple linearity in the spin density vs. hyperfine splitting constant function cannot be expected, because the McConnel relation holds only for neutral radicals. To take account of the excess charge, the McConnel equation should include another parameter which expresses the dependence of the hyperfine coupling constant on the spin densities of the neighbouring atoms.

It is noteworthy that Makarov et al. reported almost the same hyperfine coupling constants for ring protons in trimethylphenylsilane but the assignation to the experimental values differs from that suggested by Gerson et al. Makarov assumed a smaller hyperfine splitting for *ortho* protons and a larger splitting for *meta* protons. The CNDO calculations, which are consistent with those made by the Hückel approximation, confirm the assignments made in Table 3.

The calculations for the methylphenylsilane radical anions give an increasingly poorer correlation with the experimental results as the methyl groups on the silicon atom are progressively substituted by hydrogen atoms. But even for the phenylsilane anion the calculated spin density value is largest at the *para* carbon atom and smallest at the *meta* carbon atoms, as is the case for the hyperfine coupling constants. From the calculated spin densities of methylphenylsilane the hyperfine splitting pattern can be predicted to be similar to those of trimethylphenylsilane and dimethylphenylsilane.

Data in Table 2 show a considerable location of spin on the *d* orbitals of silicon atoms which is responsible for the smaller total splitting parameter in phenylsilanes compared with simple aromatic anion radicals. (It should be noticed that negative spin densities on $p(z)$ and d orbitals have opposite effects.) The electron density values for the silicon d orbitals indicate a $d\pi$—$p\pi$ interaction, as was proved earlier for the neutral molecules [6,7].

The calculated bond order values for the bond between silicon and ring carbon atom decrease as the methyl groups on the silicon are progressively replaced by hydrogen atoms. It is interesting to compare these bond orders with those in the neutral molecules as calculated by the CNDO/2 method (Table 4); for the latter the change in the bond order is in the opposite direction. The charge distribution for the anion radicals and neutral molecules (Table 5) indicate that the residence of the unpaired electron at the silicon atom increases progressively on going from the trimethylphenylsilane to the phenylsilane anion, and this is confirmed by (*i*) the difference between the partial charge of silicon atom in neutral molecules and in anion radicals, and (*ii*) the total spin density values on silicon atoms. At the same time the polarity of the bond between silicon and aromatic carbon increases. These trends may be partly responsible for the fact

TABLE 4

BOND ORDER BETWEEN THE SILICON ATOM AND THE 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

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

that the bond order is < 1 in phenylsilane. The other factor is that the CNDO calculations exaggerate the negative charges at the hydrogen atoms attached directly to silicon, so that the role of these hydrogens is overestimated.

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

TABLE 6

BOND POLARITY VALUES FOR SILICON—AROMATIC CARBON BONDS IN METHYLPHENYLSILANE NEUTRAL MOLECULES AND ANION RADICALS

	$PhSiMe_3$	$PhSiHMe_2$	$PhSiH_2Me$	$PhSiH_3$
Neutral molecules	0.0296↓	0.0026↓	0.0187↑	0.0494↑
Radicals	0.4000↑	0.5492↑	0.5772↑	0.8049↑

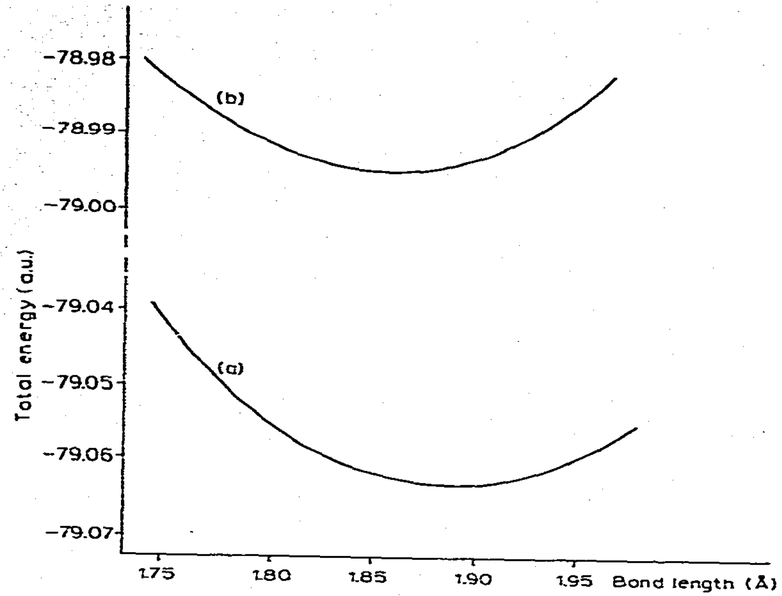

Fig. 3. Plot of total energy in trimethylphenylsilane, (a) neutral molecule and (b) anion radical; against Si—C bond length.

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

As mentioned earlier, the calculated Si—C bond order is larger for the 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 the trimethylphenylsilane neutral molecule and the anion radical in which the silicon—carbon bond distance was varied in the range 1.75-1.95 Å and the calculated total energy was plotted against the bond ditance (Fig. 3). The calculations (Table 7) indicate that the equilibrium bond distance is 1.886 Å for the neutral molecule and 1.848 Å for the anion radical. The value for the neutral molecule

TABLE 7

CALCULATED TOTAL ENERGY OF TRIMETHYLPHENYLSILANE NEUTRAL MOLECULE AND ANION RADICAL IN THE FUNCTION OF 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

is reasonable, and is consistent with the experimental Si—C bond length of 1.87 Å in tetraphenylsilane [8]. As the bond order increases the equilibrium bond distance decreases, as for the anion radical.

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References

1 H.M. McConnel, J. Chem. Phys., 17 (1949) 264.
2 H.J. Sipe and R. West, J. Organometal. Chem., 70 (1974) 353, 367.
3 J. Réffy, J. Karger-Kocsis and J. Nagy, Kém. Közl., in press.
4 F. Gerson, J. Heinzer, H. Bock, H. Alt and H. Seidl, Helv. Chim. Acta, 51 (1968) 707.
5 J.G. Makarov, V.M. Kazakova and Y.K. Syrkin, Zh. Strukt. Khim. (Eng. Trans.), 8 (1967) 137.
6 J. Nagy and J. Réffy, J. Organometal. Chem., 23 (1970) 71.
7 J. Nagy and J. Réffy, J. Organometal. Chem., 23 (1970) 79.
8 M. Yokoi, J. Chem. Soc. Japan, 73 (1952) 822.