QUANTUM CHEMICAL CALCULATIONS ON ORGANOSILICON RADICALS, I. HÜCKEL LCAO-MO CALCULATIONS IMPROVED BY ω-TECHNIQUE*

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Publications on ESR spectra of organosilicon anion radicals date back to 1962. Calculations of spin densities are generally connected with the Hückel LCAO-MO method. We attempted to investigate the ESR spectral data of several trimethylsilyl substituted polyene, benzene and naphthalene derivatives.

The HMO method considers the coulomb and resonance integrals of a heteroatom as follows:

$$\alpha_H = \alpha_0 + h\beta$$

$$\beta_{HX} = k\beta$$

where α_0 is the coulomb integral of a carbon atom in benzene and β is the resonance integral of a carbon–carbon bond in benzene ring. The Hückel method improved by ω-technique modifies the coulomb integral of atom j proportionally to the charge density q_j:

$$\alpha_j = \alpha_0 + q_j\omega\beta$$

In this iterative process ω is an empirical factor, its value is generally chosen in the range 0.5 to 1.4.

In radical anions the unpaired electron is seated on the lowest unoccupied molecular orbital. According to the Hückel method the probability ϱ_{ij} of finding an electron on a given atom j in the molecular orbital i is called unpaired electron density or spin density. It has to be mentioned, however, that these terms are the same in the Hückel approximation although as a consequence of polarizing effect of the unpaired electron the spin density may differ from the unpaired electron density by magnitude and sign. At some atoms of a π system, negative spin density may be induced by means of spin polarization. This cannot be reflected by the HMO calculations. McLachlan's method [1] takes the mutual atom–atom polarization into consideration for the calculation of spin density and this way also negative spin density values are obtained.

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* Dedicated to Prof. G. Schay on the occasion of his 75th birthday.

Table I

Experimental hyperfine coupling constants, experimental and calculated spin density values

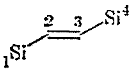
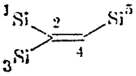
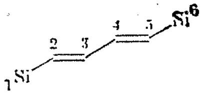
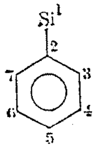
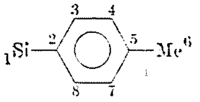
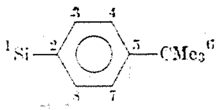
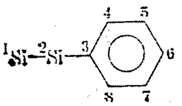
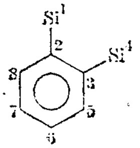
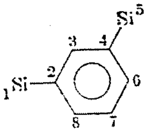
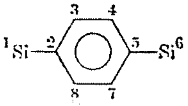
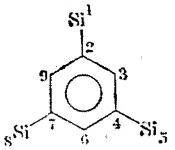
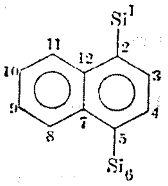
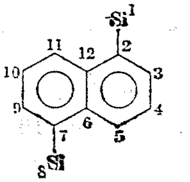
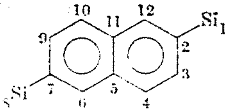
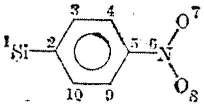
Number	Compound	Coupling constant (Gauss)	ϱ_i (exp)	ϱ_i (calc.)	
				A	B
I		$a_1 = 7.49$	0.353	0.376	0.399
II		$a_4 = 9.05$	0.431	0.411	0.434
III		$a_2 = 6.71$	0.320	0.316	0.326
		$a_3 = 3.22$	0.153	0.118	0.117
IV		$a_3 = 2.65$	0.098	0.102	0.104
		$a_4 = 1.06$	0.039	0.034	0.035
		$a_5 = 8.09$	0.300	0.289	0.309
V		$a_3 = 3.25$	0.121	0.098	0.098
		$a_4 = 1.47$	0.055	0.038	0.040
VI		$a_3 = 3.04$	0.113	0.110	0.113
		$a_4 = 1.22$	0.045	0.026	0.027
VII		$a_4 = 2.67$	0.099	0.102	0.0107
		$a_5 = 0.93$	0.034	0.034	0.028
		$a_6 = 8.15$	0.302	0.289	0.315
VIII		$a_5 = 0.46$	0.017	−0.013	−0.017
		$a_6 = 5.23$	0.194	0.169	0.182

Table I (continued)

Number	Compound	Coupling constant (Gauss)	ϱ_i (exp)	ϱ_i (calc.)	
				A	B
IX		$a_3 = 0.3$	0.011	−0.017	−0.025
		$a_6 = 6.94$	0.257	0.259	0.264
		$a_7 = 0.66$	0.024	−0.025	−0.035
X		$a_3 = 1.76$	0.065	0.068	0.071
XI		$a_3 = 4.62$	0.171	0.171	—
XII		$a_3 = 2.31$	0.086	0.075	0.076
		$a_8 = 3.19$	0.118	0.128	0.130
		$a_9 = 1.41$	0.052	0.048	0.048
XIII		$a_3 = 2.12$	0.079	0.076	0.078
		$a_4 = 1.66$	0.061	0.049	0.050
		$a_5 = 4.70$	0.164	0.177	0.183
XIV		$a_3 = 0.22$	0.008	0.115	0.009
		$a_4 = 4.49$	0.166	0.176	0.177
		$a_6 = 4.61$	0.171	0.197	0.202
XV		$a_3 = 1.08$	0.040	−0.009	—
		$a_4 = 3.35$	0.124	0.097	

Using the McConnell equation [2] the spin densities can be calculated from the measured proton hyperfine coupling constants and can be compared to the quantum chemically calculated spin densities.

The electron spin resonance spectra of compounds investigated by Hückel method were recorded at temperatures between −60 °C and −80 °C using 1,2-dimethoxyethane as solvent [3, 4]. In the calculation of spin density −21 G and −27 G were taken as proportionality factors in the McConnell equation for the polyene and aromatic derivatives, respectively.

In the course of Hückel calculations, two kinds of parameter set were adopted, to be marked A and B in the following (A: $h_{Si} = -1,5$, $k_{CSi} = 0.574$, $k_{SiSi} = 0.051$, $\lambda = 0.35$; B: $h_{Si} = -1.8$, $k_{CSi} = 0.665$, $k_{SiSi} = 0.051$, $\lambda = 0.40$). The value of ω was chosen as 0.9.

Table I summarizes the investigated compounds, the numbering of atoms in the compounds, the experimental coupling constants, the values of spin densities calculated from the experimental data by means of McConnell equation and the results of quantum chemical calculations with A and B parameters (applying the McLachlan procedure). In the case of p-methyl- and p-t-butyltrimethylsilylbenzene (compounds V and VI) the hyperconjugative effect was taken by three different means into consideration: heteroatom model, pseudo double bond model and inductive model. In every case the parameters suggested by Streitwieser [5] were adopted. Since according to the results all the hyperconjugative approximations equally can be used, the average of the spin densities calculated by different methods are represented in Table I.

A good agreement was found between calculated and experimental spin densities, and this fact was confirmed by correlation calculation. The correlation coefficients are 0.975 and 0.987 in calculations with A and B parameters, respectively.

West and Sipe also published the results of quantum chemical calculations on organosilicon radical anions [6, 7]. They used the simple Hückel method without iteration process and found a slightly worse correlation between experimental and calculated results.

We have also made calculations relating to the ^{29}Si hyperfine coupling constants. Gerson et al. [8] expressed this coupling constant (a_{Si}) by the following equation:

$$a_{Si} = Q_{Si}\varrho_{Si} + Q_{CSi}\varrho_{\mu}$$

where the first term indicates the participation of the 1s and 2s atomic orbitals of silicon and the second term stands for that of the 3s orbital in the sp^3 silicon hybrids to the ^{29}Si hyperfine coupling constant, Q_{Si} and Q_{CSi} are proportionality factors, ϱ_{Si} is the unpaired electron density on silicon atom and ϱ_{μ} is the spin population at the substituted carbon centre μ.

Table II represents our results with the ^{29}Si coupling constants. As Q_{Si} is much less than Q_{CSi} and also ϱ_{Si} is smaller than ϱ_μ according to the calculations, the ^{29}Si coupling constant appears to much more depend on the spin density of the substituted carbon atom than on the spin density at silicon atom.

Table II

^{29}Si coupling constants and calculated spin density values on carbon atom μ. (Numbers in the first column refer to the same compounds as in Table I)

Compound No.	Coupling constant (Gauss)	ϱ (calc.)	
		A	B
I.	$a_1 = 6.72$	0.376	0.399
III.	$a_1 = 5.73$	0.316	0.326
IV.	$a_1 = 5.18$	0.275	0.295
V.	$a_1 = 4.26$	0.271	0.287
VI.	$a_1 = 4.67$	0.263	0.286
VII.	$a_1 = 0$	—	—
	$a_2 = 5.42$	0.274	0.290
VIII.	$a_1 = 4.48$	0.233	0.250
IX.	$a_1 = 4.06$	0.173	0.190
X.	$a_1 = 6.17$	0.247	0.268
XI.	$a_1 = 3.0-4.5$	0.065	—
XIII.	$a_1 = 4.63$	0.204	0.211
XIII.	$a_1 = 3.53$	0.164	0.164
XIV.	$a_1 = 2.67$	0.092	0.096
XV.	$a_1 = 2.76$	0.017	—

Plotting the coupling constant against the spin population of carbon atom C_μ a linear correlation was actually found. The least squares method gives the slope and the axial section of the straight lines calculated with A and B parameters:

$$a_{Si} = -0{,}26 + 20{,}3\,\varrho_\mu \qquad \text{(A)}$$

$$a_{Si} = 1{,}6 + 12{,}5\,\varrho_\mu \qquad \text{(B)}$$

Neglecting the value of axial section leads to a McConnell type relationship for the ^{29}Si hyperfine coupling constant.

For some compounds, the results of our Hückel calculations were compared with the data from ultraviolet spectra to test the efficiency of the calculations. In the ultraviolet spectra of aromatic compounds the p-band is more sensitive to the changes in the structure of the compounds than is the α-band.

Streitwieser found a linear correlation between the position of the p-band (in cm $^{-1}$) and the difference of the highest occupied (ε_m) and the lowest unoccupied (ε_{m+1}) HMO energy levels in β units [5]:

$$\tilde{\nu} = (19020 \pm 330)\ (\varepsilon_{m+1} - \varepsilon_m) \pm (10520 \pm 340)$$

The experimental $\varepsilon_{m+1} - \varepsilon_m$ values (calculated on the basis of the equation suggested by *Streitwieser*) and the difference of the corresponding energy levels in the HMO approximation are compiled in Table III for some organosilicon compounds and the corresponding carbon derivatives. The same tendency can be observed in the experimental and calculated values for all the compounds including the organie derivatives.

Table III

Experimental and calculated ultraviolet transition energies in β units (with A and B parameters for organosilicon compounds)

Compound	$-(\varepsilon_{m+1} - \varepsilon_m)$	
	experimental	calculated
$PhCMe_3$	1,969[a]	1,981
p-Me_3CPhMe	1,965[a]	1,973
p-$Me_3CPhCMe_3$	1,915[a]	1,962
$PhSiMe_3$ (IV)	1,929[a]	A: 1,854 B : 1,864
p-$Me_3SiPhMe$ (V)	1,779[a]	A : 1,809 B : 1,817
p-$Me_3SiPhSiMe_3$ (X)	1,782[a]	A : 1,752 B : 1,760
1,6$(SiMe_3)_2C_{10}H_6$ (XII)	1,21[b]	A : 1,165 B : 1,167

a: Values taken from ref. [9]; b: Values taken from Ref. [10]

Radical anions are obtained during electrochemical reduction. This fact results in a connection between the polarographic half-wave reduction potential and the energy level of the lowest antibonding HMO level (ε_{m+1}) in β units [11]:

$$E_{1/2}(\mathrm{TNBAI}) = (2{,}407 \pm 0{,}182)\,\varepsilon_{m+1} - (0{,}386 \pm 0{,}093),$$

where$E_{1/2}$ (TNB AI) is the half-wave potential in dimethylformamide solution using tetra-n-butylammoniumiodide (TNBAI) as supporting electrolyte. We attempted to measure the half-wave potential of some available organosilicon compounds. In these experiments tetra-n-butylammoniumchloride (TNBACl) was used as supporting electrolyte. The value of $E_{1/2}$ is different for TNBAI and TNBACl. The data in the literature generally refer to TNBAI. In polarographic measurements with TNBACl on organic compounds for which the half-wave potential with TNBAI was determined by other authors, a relationship was found between $E_{1/2}$ (TNBAI) and $E_{1/2}$ (TNBACl):

$$E_{1/2}(\mathrm{TNBAI}) - E_{1/2}(\mathrm{TNBACl}) + 0{,}17\ V$$

Comparing the experimental ε_{m+1} values (calculated by the equation suggested by Streitwieser) and the corresponding HMO levels shows the calculated ε_{m+1} levels to follow nearly the same order as the experimental values. The only exception is the p-nitrotrimethylsilylbenzene for which the Hückel parameters of nitro group were not varied but taken from Ref. [4]

Table IV

Half-wave reduction potentials and the experimental and calculated energy level of the lowest unoccupied molecular orbital (ε_{m+1}) in β units

Compound	$E_{1/2}$ (V)	$-\varepsilon_{m+1}$ (exp.)	$-\varepsilon_{m+1}$ (calc.)	
			A	B
II	2,0[a]	0,660	0,484	0,466
III	1,8[b]	0,583	0,401	0,391
X	2,34	0,808	0,733	0,739
XII	1,8[c]	0,583	0,489	0,485
XV	0,57	0,072	0,176	—
Dimethylphenylvinylsilane	2,25	0,770	0,710	0,707

a: Values taken from Ref. [12]; b: from Ref. [13]; c: from Ref. [10]

$$(\alpha_N = \alpha + 2{,}2\beta, \quad \alpha_O = \alpha + 1{,}88\beta, \quad \beta_{CO} = 1{,}2\beta, \quad \beta_{NO} = 1{,}67\beta).$$

The calculation in connection with ESR, UV and polarographic experimental results prove that the Hückel method improved by ω-technique reflects fairly well the changes in the structure of molecules if the parameters of coulomb and resonance integrals are carefully chosen.

Summary

Spin density values on trimethylsilyl substituted polyene, benzene and naphthalene derivatives were calculated using the Hückel method improved by ω-technique. In order to obtain negative spin densities the McLachlan procedure was applied. The experimental spin density values calculated from the ESR proton coupling constants by the McConnell equation were compared with the results of HMO calculations. Investigations on ^{29}Si coupling constants showed these constants to depend much more on the spin density of the substituted carbon atom than on the spin density at silicon atom. Polarographic half-wave reduction potentials were also compared with the results of HMO calculations.

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