QUANTUMCHEMICAL CALCULATIONS ON $(C_6H_5)Si(CH_3)_3$ BY VARIOUS METHODS

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Introduction

Quantumchemical calculations on organosilicon compounds involve many problems. Appropriate parameters for silicon atom and various Si—X bonds are inexistent in most quantumchemical methods. A great many of the methods cannot take the participation of Si 3d orbitals in chemical bonds into consideration. Similarly, in applying all valence electron methods, problems are caused by the high number of centres and orbitals. For this reason a computer with proper capacity and considerable running time is necessary for the calculations. In our work various methods were applied for trimethylphenylsilane ($C_6H_5Si(CH_3)_3$) and the results were interpreted in terms of experimental data.

The applied quantumchemical methods; input parameters

Del Re method

For the calculation of σ bond system Del Re method was used, modified and extended for organosilicon compounds [1].

Hückel method and Hückel method improved by ω-technique

The Hückel method [2] is a simple, approximate, one-electron LCAO—MO method for calculations on π systems. Rather than assuming arbitrarily the coulomb and resonance integrals required for our calculations they were taken from integral tables [3] in the knowledge of bond lengths and ionization energies. For the calculation of these integrals Slater atomic orbital eigenfunctions were chosen, then the coulomb α_i and resonance β_{ij} integrals were expressed in parametric form:

$$\alpha_i = \alpha + h_i\beta$$

$$\beta_{ij} = k_{ij}\beta .$$

An iterative version of the Hückel method is the ω-technique [4, 5] accounting for the change of the atomic coulomb integral as a function of electron density q_i on the atom as follows:

$$\alpha_i = \alpha_i^0 + (n_i - q_i)\omega\beta \,.$$

PPP method

The PPP method is one of the most wide-spread and most efficient π electron methods [6, 7]. In this method, the valence state ionization energies I_i and the one-centre electronic repulsion integrals γ_{ii} required for calculating the diagonal elements of the Fock matrix were taken from the work by Hinze and Jaffe [8], and by Levison and Perkins [9], respectively. For the estimation of the two-centre electronic repulsion integrals the following empirical equations were used:

Mataga and Nishimoto [10]: $\gamma_{ij}^{MN} = (a_{ij} + R_{ij})^{-1}, \; a_{ij} = 2(\gamma_{ii} + \gamma_{jj})^{-1}$

Ohno [11]: $\gamma_{ij}^{OH} = (a_{ij}^2 + R_{ij}^2)^{-1/2}$

Chojnacki [12]: $\gamma_{ij}^{CH} = 0.4 \, \gamma_{ij}^{MN} + 0.6 \, \gamma_{ij}^{OH}$

Dörr and al. [13]: $\gamma_{ij}^{D} = 0.7 \cdot R_{ij}^{-1}$,

where R_{ij} is the bond distance.

The resonance integral of the carbon—carbon bond was chosen to be —2.39 eV [6], that of the silicon—carbon bond was determined by the Wolfsberg—Helmholz formula [14]:

$$\beta_{SiC}^{\circ} = 1/2 \; k \, (I_{Si} + I_C) \, S_{SiC} \cdot \cos \alpha \,,$$

where k is a proportionality coefficient (0.6426),

S_{SiC} is an overlap integral, its value being calculated [3] on the basis of the bond distance and the Burns' effective nuclear charges [15],

$\cos \alpha$ resulted from the consideration of the partial overlapping between p and d orbitals due to the tetrahedral orientation of silicon atom ($\alpha = 19°28'$) [16].

The parameters of the calculations taking into account the hyperconjugative effect of methyl groups ($I_{C'}$, I_{H_3}, $\gamma_{C'C'}$, $\gamma_{H_3H_3}$, $\beta_{SiC'}$, $\beta_{C'H_3}$) were assumed according to Nagy [16].

IPPP method

In the IPPP method [17, 18] the parameters are not constants, but vary in the process of calculation depending on the charges. In our calculations the ionization energies I_i were altered as a function of the effective nuclear charges Z_i^*, using the following equation:

$$I_i = -a_i \exp (b_i Z_i^*)$$

The constants a_i and b_i were determined by means of isoelectronic series [16].

Dependence of the effective nuclear charges on the partial charges can be expressed as follows:

$$Z_C^* = Z_C^{*\circ} + 0.35\,(\delta_C^\sigma + \delta_C^\pi)$$

$$Z_{Si}^* = Z_{Si}^{*\circ} + 0.5\ \delta_{Si}^\sigma + 0.35\ \delta_{Si}^\pi\,,$$

where $Z_C^{*\circ}$, $Z_{Si}^{*\circ}$ are effective nuclear charges calculated according to the Burns rules,

δ_C^σ, δ_{Si}^σ are σ partial charges obtained by Del Re calculations,

δ_C^π, δ_{Si}^π are π partial charges.

The ionization energies were varied in an iterative process on the basis of π partial charges until self-consistency.

EHT method

The Extended Hückel method [19, 20] is an all valence electron method. The ionization energies necessary for the calculations were chosen on the basis of data published by Hinze [21] (for *s* and *p* orbitals) and by Levison and Perkins [9] (for silicon 3*d* orbitals).

CNDO/2 method

The CNDO/2 method [22, 23, 24] is the most correct all valence electron method as compared to those developed earlier. The calculations were carried out with original parametrization (on spd basis).

The input parameters of the various calculations on $C_6H_5Si(CH_3)_3$ molecule are summarized in Table 1. The geometrical data used were as follows: $R_{CC} = 1.397$ Å, $R_{SiC} = 1.853$ Å, $R_{SiC'} = 1.888$ Å, $R_{CH} = 1.0864$ Å, $R_{C'H} = 1.093$ Å [25]. (The atom marked C′ is the carbon atom of methyl groups attached to silicon atom.)

Table 1

Input parameters of quantumchemical calculations for $C_6H_5Si(CH_3)_3$

Method	Parameters		
Del Re	$\delta_C^\circ = 0.07$ (sp^3) $= 0.12$ (sp^2) $\delta_H^\circ = 0$ $\delta_{Si}^\circ = -0.10$	$\gamma_{CC} = 0.1$ $\gamma_{CH} = -0.2$ $\gamma_{HC} = 0.4$ $\gamma_{SiC} = 0.2$ $\gamma_{CSi} = 0.4$	$\varepsilon_{CC} = 1.00$ $\varepsilon_{CH} = 1.00$ $\varepsilon_{SiC} = 0.90$
Hückel Hückel ω-techn.	$h_{Si} = -1.8152$ $k_{SiC} = 0.3374$	$\omega = 1.0$	
PPP	$I_C = -11.16$ eV $I_{Si} = -1.10$ eV $I_{C'} = -11.19$ eV $I(_{H_3}) = -10.26$ eV	$\gamma_{CC} = 11.13$ eV $\gamma_{SiSi} = 3.762$ eV $\gamma_{C'C'} = 9.71$ eV $\gamma_{H_3H_3} = 9.33$ eV	$\beta_{CC}^\circ = -2.39$ eV $\beta_{SiC}^\circ = -1.3151$ eV $\beta_{SiC'}^\circ = -1.5521$ eV $\beta_{C'H_3}^\circ = -7.4013$ eV
IPPP	$I_C = -0.6133 \exp(1.0362\, Z_C^*)$ $I_{Si} = -0.2066 \exp(0.9555\, Z_{Si}^*)$		
EHT	$I_s(C) = 21.01$ eV $I_p(C) = 11.27$ eV $I_s(H) = 13.60$ eV $I_s(Si) = 17.31$ eV $I_p(Si) = 9.19$ eV $I_d(Si) = 1.10$ eV	$\xi_s(C) = 1.575$ $\xi_p(C) = 1.400$ $\xi_s(H) = 1.000$ $\xi_s(Si) = 1.616$ $\xi_p(Si) = 1.133$ $\xi_d(Si) = 0.583$	

Results, discussion

The experimental data for trimethylphenylsilane are presented in Table 2. The results of the calculations by various methods are described in the following part.

Fig. 1 illustrates the partial charges obtained by Del Re method, Hückel method and Hückel method with ω-technique, respectively.

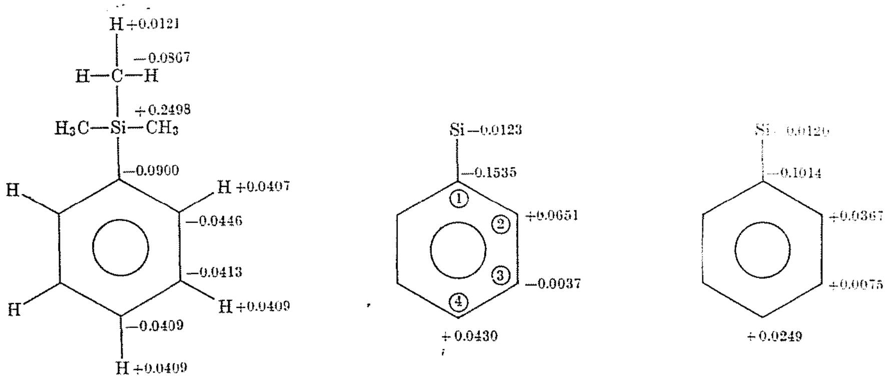
The effect of the variation of parameter ω was investigated for several compounds, and it was concluded that the best agreement with the experimental data was achieved for organosilicon compounds with ω values ranging from 0.8 to 1.0 [30]. The charges presented in Fig. 1/b and Fig. 1/c indicate

Table 2

Experimental data for $C_6H_5Si(CH_3)_3$

Ultraviolet spectrum	$\lambda_{max} = 188, 211, 264$ nm ($\Delta E = 6.59, 5.88, 4.70$ eV)	ethanol solution	[26]
Dipole moment	$\mu = 0.248$ D	by Onsager's method	[27]
Ionization potential	I = 8.79 eV		[28]
^{13}C chemical shifts	C_1: +11.3 ppm C_2: + 4.7 ppm C_3: — 0.8 ppm C_4: + 0.2 ppm	reference material: benzene	[29]

that the $(CH_3)_3Si$ group cannot be strongly ortho and para orienting (as it would result from the +I effect of the silicon, neglecting the —M effect of the silicon atom), since in these positions there are small positive charges unfavourable to electrophylic attack. At the same time the free valences of carbon atoms ($F(C_i)$) are larger in ortho and para position than in meta positions (Table 3), this result is in accordance with the weak ortho and para orienting behaviour of the $(CH_3)_3Si$ group [31]. The orienting effect of a trimethylsilyl group is correctly reflected by the trend in partial charges by both kinds of Hückel calculations. The resulting $\sigma\pi$ dipole moment calculated by ω-technique shows better agreement with the experimental value. The bond between the silicon and aromatic carbon atom has a $(p-d)\pi$ character of 11%. The electronic transition energy (Δm) is lower than in benzene, the calculations are in accordance with the bathochromic shift



a b c

Fig. 1. Charge distribution of $C_6H_5Si(CH_3)_3$: (a) σ distribution, (b) π charge distribution by Hückel method, (c) π charge distribution by ω-technique ($\omega = 1,0$)

Table 3

Results of Hückel calculations

	Hückel $\omega = 0$	Hückel ω-techn. $\omega = 1.0$
Δm	1.8438 β	1.8767 β
$\mu_{\sigma\pi}$	0.74 D	0.53 D
p(SiC)	0.1167	0.1137
$p(C_1C_2)$	0.6560	0.6588
$p(C_2C_3)$	0.6690	0.6683
$p(C_3C_4)$	0.6652	0.6656
$F(C_1)$		0.3007
$F(C_2)$		0.4049
$F(C_3)$		0.3981
$F(C_4)$		0.4008

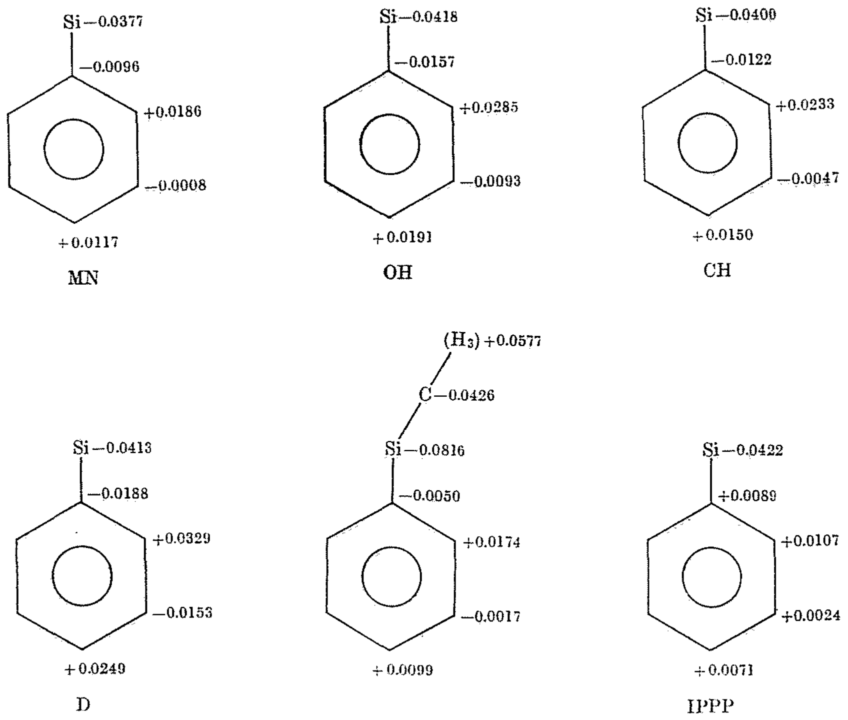
indicated by the ultraviolet spectra. The most important results of the Hückel calculations are recapitulated in Table 3.

Concerning the results of the PPP calculations, the π charge distribution is shown in Fig. 2, the electronic transition energies $^1E_{CI}$, the ionization energies I, the $\sigma\pi$ resulting dipole moments $\mu_{\sigma\pi}$ and the π bond orders p_{ij} are presented in Table 4.

According to the results obtained by using various methods for the calculation of γ_{ij}, the MN calculations approximated most closely the experimental values of electronic transition energies. The calculated dipole moments hardly show a change (the greatest difference being 0.031 D), the closest agreement is again achieved by MN calculation. Also the change of π bond orders is very slight. As concerns the π charge distribution, the D calculation provides the most polarized charges, and the charges obtained by MN calculation are polarized in the slightest degree. The MN method gives the best result for the ionization energy of the molecule, though the calculated value is by 1.6 eV higher as the experimental one.

All the results mentioned match well the results of similar calculations for vinyl and phenoxysilanes [32].

The consideration of the hyperconjugative effect of the methyl groups resulted in a slight change of the electronic transition energies and ionization energy and impaired the calculated dipole moment values. From this experience it was concluded that for the π system of larger molecules (e.g. containing a phenyl group) the hyperconjugation of CH_3 groups is not reasonable to



MN OH CH

D IPPP

Fig. 2. π charge distribution of $C_6H_5Si(CH_3)_3$ calculated by PPP method

be taken into account. The iterative PPP method gave somewhat worse results for electronic transition energies and better results for ionization energy and dipole moment. The calculation indicated positive π partial

Table 4

Results of PPP calculations

	PPP MN	PPP OH	PPP CH	PPP D	PPP hyperconj.	IPPP
$^1E_{CI}$ (eV)	4.781	4.828	4.809	4.812	4.775	4.764
	5.748	5.010	5.343	4.968	5.684	5.626
	6.529	6.411	6.469	6.577	6.416	6.393
I (eV)	10.446	11.403	11.020	11.106	10.401	10.303
$\mu_{\sigma\pi}$ (D)	0.298	0.329	0.316	0.312	0.075	0.288
SiC	0.193	0.204	0.199	0.203	0.188	0.202
C_1C_2	0.654	0.653	0.653	0.653	0.654	0.653
p_{ij} C_2C_3	0.669	0.670	0.669	0.670	0.669	0.669
C_3C_4	0.665	0.665	0.665	0.665	0.665	0.665

charges for the carbon atoms of the phenyl group and considerable negative charge on the silicon atom. The $\sigma\pi$ partial charges obtained by Del Re and PPP calculations showed the best correlation with the ^{13}C chemical shifts if hyperconjugation was considered, but even in this case the correlation was worse than for the CNDO/2 calculation. Compared with the result of Hückel method, the PPP calculation provided a higher value for the π bond order (0.19 to 0.20) of the silicon — aromatic carbon bond.

The EHT method gave the worst results. This method indicates baseless charges in compounds containing heteroatom and is not suitable for calculating the dipole moment. The partial charge of aromatic carbon atoms does not show correlation with the ^{13}C chemical shifts. For the electronic transition energy (Δm) 4.033 eV, for the ionization energy (I) 10.427 eV was obtained.

Considering the results of calculations by the CNDO/2 method it was found that the calculated dipole moment 0.33 D was in a good agreement with the experimental value. The bond order between the silicon and aromatic carbon atom is 1.087, which is very near to the value calculated by the Hückel method improved by ω-technique. On the basis of the CNDO/2 method, the bond orders were calculated by two different ways: either as the sum of squares of the corresponding density matrix elements (A) [33], or as the sum of the products of the corresponding density matrix and overlap integral matrix elements (B). The values of bond orders are presented in Table 5.

The bond orders by both methods are seen to show the same trend, but method B results in unfoundedly low bond orders. Even the data obtained by method A can only be applied to establish tendencies, since these values appear to be somewhat low. On the basis of the Hückel method, the aromatic carbon—carbon bond orders are expected in the range 1.6 to 1.7, and the carbon—hydrogen bond orders are likely to approach unity.

Table 5

CNDO/2 bond orders

Bond	Bond orders	
	A	B
Si—C_1	1.0866	0.9770
C_1—C_2	1.3487	0.9256
C_2—C_3	1.4494	0.9522
C_3—C_4	1.4420	0.9513
C_2—H_2	0.9467	0.6772
C_3—H_3	0.9579	0.6809
C_4—H_4	0.9582	0.6813

Table 6

Variation of Si—C bond order vs. bond distance

Bond distance (Å)	Bond order	
	A	B
1.75	1.1238	1.0649
1.80	1.1076	1.0214
1.853	1.0866	0.9770
1.90	1.0686	0.9374

Investigating the same bond, the correlation between the bond orders calculated by both methods A and B is extremely good. We studied the change in the Si—C (aromatic) bond order of the molecule in dependence of bond distances ranging from 1.75 to 1.90 Å. The results have been compiled in Table 6. The correlation coefficient between the A and B bond orders is 0.992. The bond order is considerably affected by the Si—C bond distance; the bond order is expected to increase if the bond distance decreases. The calculated dipole moment is next to the experimental result when the bond distance is about 1.85 Å. The calculated dipole moments are in this order: 1.75 Å — 0.097 D; 1.853 Å — 0.32 D; 1.90 Å—0.586 D.

The equilibrium silicon—carbon (aromatic) bond distance appears to be 1.886 Å, the total energy of the molecule indicates a minimum at this value [34]. The calculations are consistent with the experimental silicon—carbon (aromatic) bond length of 1.87 Å determined by X-ray diffraction method for phenylsilanes [35].

The partial charges obtained by CNDO/2 method are presented in Fig. 3. In many respects the same trends can be observed as for the partial charges

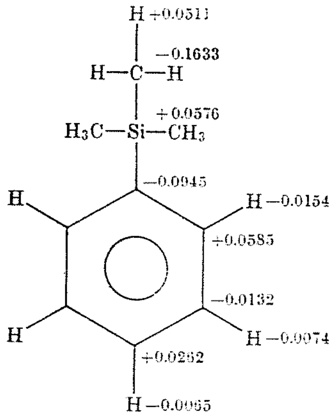


Fig. 3. Charge distribution for $C_6H_5Si(CH_3)_3$ calculated by CNDO/2 method

Table 7

^{13}C NMR chemical shifts (reference material: benzene) and electron densities calculated by CNDO/2 method

	Chemical shift	Electron density	Partial charge
C_1	+11.3	4.0945	−0.0945
C_2 (orto)	+4.7	3.9415	+0,0585
C_3 (meta)	−0.8	4.0132	−0.0132
C_4 (para)	+0.2	3.9738	+0.0262

calculated by the Del Re and the Hückel method with ω-technique, for instance, in both cases the greatest negative charges can be located on the carbon atoms, in meta positions from among the ring carbon atoms, and the partial charge becomes increasingly positive in meta-para-ortho order.

The ^{13}C NMR chemical shifts of the molecule are comparable to the calculated electron densities as well as the partial charges of carbon atoms. From data in Table 7, a good correlation is seen between the experimental and calculated electron densities for carbon atoms in ortho, meta and para positions; in the case of the carbon atom linked to the silicon the data cannot be compared to characteristics of other carbon atoms because of the different chemical setting.

According to the CNDO/2 calculation, the ionization energy of the molecule is 11.52 eV, a value by 2.7 eV higher than the experimental one. MAIRE and LIMOUZIN found in photoelectron spectroscopic investigations the π_2 and π_3 molecular orbital levels of trimethylphenylsilane to be degenerate [36]. The lack of level splitting does not mean, however, that the role of *d* orbitals is negligible. It was proven by MAIRE based on the photoelectron spectra of compounds p-$ClC_6H_4M(CH_3)_3$ (where M=C, Si, Ge, Sn) that the splitting of π_2 and π_3 levels showed a minimum in the case of the silicon derivative, this experimental fact could be explained by the existence of $(p-d)\pi$ interaction [37]. In the trimethylphenylsilane the mentioned degeneration of the levels is a result of the +I and −M effects of silicon acting oppositely.

Summary

In this work the structure of trimethylphenylsilane ($C_6H_5Si(CH_3)_3$) was investigated by various quantumchemical methods. Proper conclusions on the bond structure could be drawn on the basis of Hückel method with ω-technique, PPP and CNDO/2 methods.

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