INVESTIGATION OF THE BOND STRUCTURE OF BENZYL-SUBSTITUTED SILICON DERIVATIVES

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(Received March 12, 1970)

The investigation of the bond structure of phenyl-substituted silicon-organic compounds [1] has revealed the existence of a $d\pi - p\pi$ bond between the silicon atom and the phenyl group. The purpose of the present work has been to throw light on the influence of the silicon atom through the methylene group on the σ and π electron system of the ring. Calculations have been made in connection with the bond structure of trimethyl-benzyl-silane (I), p-(bis-trimethyl-silyl)-xylene (II), neopentyl-benzene (III) and p-bis-neopentyl-benzene (IV).

In calculating the σ bond system, the parameter method of Del Re [2] was used. However, Del Re has given the coulomb, resonance and inductive parameters for the C—H, C—N, C—O, C—C, N—H and C-halogen bonds only. The extension of the method for Si—H, Si—C, Si—N and C—H bonds will be given in another paper [3]. The numbering of the atoms in the σ bond system of the compounds studied is shown in Fig. 1. Calculated degrees of bond polarity are given in Table 1, partial charges in Table 2 and bond moments

Table 1

Calculated σ-bond polarities

Bond polarity (Q_{A-B})	Compound			
	I	II	III	IV
C_1-H_1	+0.0102	+0.0102	+0.0193	+0.0193
C_1-Si	+0.0576	+0.0576	—	—
C_2-Si	+0.0662	+0.0662	—	—
C_1-C_2	—	—	−0.0166	−0.0166
C_2-H_2	+0.0148	+0.0148	—	—
C_3-C_2	+0.0515	+0.0516	−0.0077	−0.0077
C_3-H_3	—	—	+0.0247	+0.0247
C_4-C_3	−0.0073	−0.0073	+0.0368	+0.0369
C_4-H_4	+0.0414	+0.0414	—	—
C_5-C_4	−0.0007	—	−0.0088	−0.0088
C_5-H_5	+0.0410	—	+0.0415	+0.0415
C_6-C_5	−0.0001	—	−0.0008	—
C_6-H_6	+0.0409	—	+0.0410	—
C_7-C_6	—	—	−0.0001	—
C_7-H_7	—	—	+0.0409	—

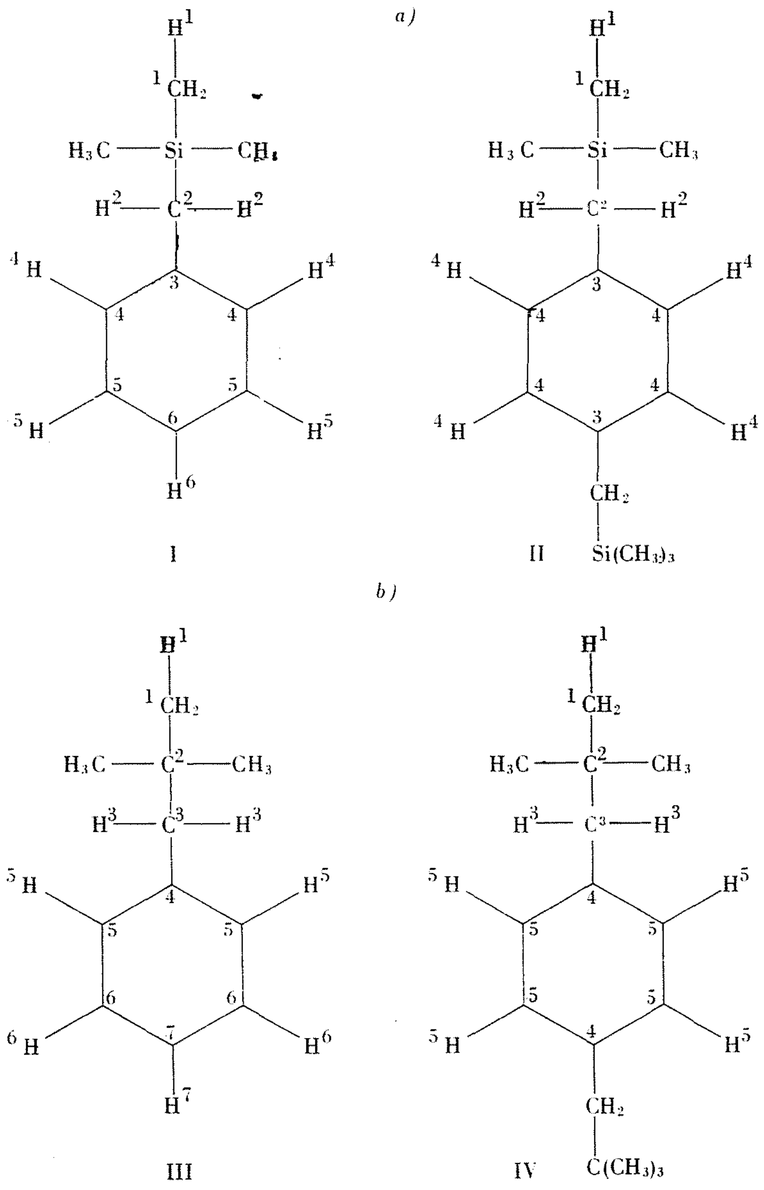

Fig. 1. Numbering of the atoms in compounds I—IV (to the calculation of the σ-bond system)

in Table 3. The presence of the silicon atom makes the carbon atoms in its vicinity more negative in comparison with the atoms in analogous position in the corresponding carbon compounds. Although the effect decreases with the distance of atoms, it is still remarkable in the case of carbon atoms in the γ position.

Table 2

σ partial charges

Partial charge q	Compound			
	I	II	III	IV
qC_1	−0.0882	−0.0882	−0.0413	−0.0413
qH_1	+0.0102	+0.0102	+0.0193	+0.0193
qSi	+0.2390	+0.2390	—	—
qC_2	−0.0443	−0.0443	−0.0575	−0.0575
qH_2	+0.0148	+0.0148	—	—
qC_3	−0.0662	−0.0661	−0.0048	−0.0048
qH_3	—	—	+0.0247	+0.0247
qC_4	−0.0347	−0.0341	−0.0545	−0.0544
qH_4	+0.0414	+0.0414	—	—
qC_5	−0.0403	—	−0.0334	−0.0327
qH_5	+0.0410	—	+0.0415	+0.0415
qC_6	−0.0408	—	−0.0402	—
qH_6	+0.0409	—	+0.0410	—
qC_7	—	—	−0.0408	—
qH_7	—	—	+0.0409	—

Table 3

σ bond dipole moments

Bond dipole moment (Debye)	Compound			
	I	II	III	IV
mC_1-H_1	0.0533	0.0533	0.1010	0.1010
mC_1-Si	0.5173	0.5173	—	—
mC_2-Si	0.5946	0.5946	—	—
mC_2-C_1	—	—	0.1228	0.1228
mC_2-H_2	0.0776	0.0776	—	—
mC_3-C_2	0.3811	0.3812	0.0567	0.0567
mC_3-H_3	—	—	0.1291	0.1291
mC_4-C_3	0.0492	0.0489	0.2724	0.2725
mC_4-H_4	0.2165	0.2167	—	—
mC_5-C_4	0.0046	—	0.0594	0.0589
mC_5-H_5	0.2144	—	0.2170	0.2173
mC_6-C_5	0.0004	—	0.0055	—
mC_6-H_6	0.2142	—	0.2144	—
mC_7-C_6	—	—	0.0005	—
mC_7-H_7	—	—	0.2142	—

In calculating the dipole moments of the bonds the following bond lengths were used:

C—H	1,09 Å
C—C (alkyl)	1,54 Å
C—C (aromatic)	1,40 Å
Si—C (alkyl)	1,87 Å

The σ dipole moments (μ_σ) of molecules could be determined from the bond dipole moments by vectorial addition.

Bis-derivatives are symmetrical. If the two trimethyl-silyl groups (or the corresponding carbon-containing group) are in the trans position, no resultant dipole moment exists. Taking rotation into consideration, a certain dipole moment appears:

$$\mu_\varphi^2 = 2\,(M \sin \Theta)^2\,(1 + \cos \varphi)$$

where

M stands for the precessing group moments,
Θ for the angle between these moments and rotation axis, and
φ for the angle between the two group moments (angle of rotation).

Accordingly, μ_φ is a σ dipole moment belonging to a rotation state characterized by a given angle φ. Assuming free rotation, the resultant dipole moment will be the integral mean of μ_φ^2 for an entire rotation:

$$\mu_\sigma^2 = \overline{\mu_\varphi^2} = \frac{1}{2\pi} \int_0^{2\pi} 2(M \sin \Theta)^2\,(1 + \cos \varphi)\,d\varphi$$

$$\mu_\sigma = \sqrt{2}\; M \sin \Theta$$

As reflected by the data in Table 4, the presence of silicon atom increases the dipole moment.

Calculations concerning the π bond system were carried out for trimethyl-benzyl-silane. The numbering of the atoms belonging to the electron system of the compound is shown in Fig. 2.

The hyperconjugation of the hydrogen atoms attached to carbon atom 2 can be interpreted by assuming that the two hydrogen atoms produce a pseudo p-orbital which overlaps the p-orbital of carbon atom 2 (hence indirectly also the π electron system of the ring and one vacant d orbital of the silicon atom). Thus a nine-central π electron system is formed.

In the case of allyl-substituted silicon derivatives a further effect exists besides hyperconjugation: a $d - \pi$, or long bond between the d-orbital of

Table 4

Calculated σ-dipole moments

	Compound			
	I	II	III	IV
μ_σ (D)	0.212	0.072	0.136	0.051

the silicon atom and $p\pi$-orbital of a carbon atom in β position [4]. The situation is similar to that in fluoro-alkyl-substituted benzene derivatives in which, according to SHEPPARD [5] the lone pair p electrons of fluor atoms produce a $p-\pi$ interaction with the π-system of the ring. As benzyl compounds are pseudo-allyl compounds or more precisely analogous to allyl compounds it is reasonable to assume long bonds in the case of trimethyl-benzyl-silane. Calculations were made both taking and not taking the existence of long bonds into consideration.

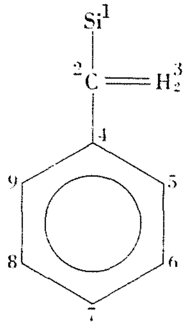

Fig. 2. Numbering of the atoms belonging to the π electron system of trimethyl-benzyl-silane

In calculating with the one-electron LCAO-MO method the elements of the energy matrix (coulomb and resonance integrals) were expressed in parametric form: α denoted the coulomb integral of the $p\pi$-orbital of the carbon in the benzene ring, and β the resonance integral of the carbon-carbon $(p\pi - p\pi)$ bond in benzene. Some of the parameters were calculated by means of integral tables [6], while the parameters concerning hyperconjugation were taken from the literature [7]. The coulomb and resonance integrals in parametric form are as follows:

$$\alpha_1 = \alpha - 1{,}8152\,\beta$$
$$\alpha_2 = \alpha_4 = \alpha_5 = \alpha_6 = \alpha_7 = \alpha_8 = \alpha_9 = \alpha$$
$$\alpha_3 = \alpha - 0{,}5\,\beta$$
$$\beta_{12} = 0{,}3374\,\beta$$
$$\beta_{14} = 0{,}1283\,\beta \text{ (with long bond); } \beta_{14} = 0 \text{ (without long bond)}$$
$$\beta_{23} = 3{,}06\,\beta$$
$$\beta_{24} = 0{,}8\,\beta$$
$$\beta_{45} = \beta_{56} = \beta_{67} = \beta_{78} = \beta_{89} = \beta$$

For the 0-th approximation the eigenvalues, linear coefficients, π partial charges, bond moments and the dipole moments μ_π of the molecule due to the π electron system were calculated. When the existence of a $d-\pi$ bond was assumed, the π dipole moment was found to decrease remarkably (see Table 5). Using the σ dipole moments calculated by the method of Del Re the resultant dipole moment $\mu_{\sigma,\pi}$ of the molecule has been calculated. The comparison of the data in Table 5 with the experimental dipole moment which is equal to 0,55 D [1] reveals that the assumption concerning the existence of the $d - \pi$ bond was reasonable. In the case of the nine-central system containing the long bond the ω-technique was used in order to take the electron-electron interactions into consideration, starting with the data of the 0-th approximation. It has been stated in an earlier paper [8] that the results calculated by the ω technique best agree with experimental data for $\omega \cong 1.0$. The energies of the molecular orbitals (in α and β units) calculated for $\omega = 0$ (0-th approximation) and $\omega = 1.0$ are given in Table 6. The eight electrons of the π system (two from the CH_2 group exerting the hyperconjugation effect, and six from the phenyl group) are situated on the first four orbitals. In the last row of the table the calculated energies of the smallest $\pi - \pi^*$ transition are given, the value of which does not change remarkably during the calculation by the ω technique. The α band in the ultraviolet spectrum of trimethyl-benzyl-silane is at greater wave-length (267 nm) [1] than the corresponding band of benzene (255 nm). The calculated $\pi - \pi^*$ transition is 2β for benzene, whereas it is smaller in the case of trimethyl-benzyl-silane, in agreement with experimental

Table 5

Calculated dipole moments of trimethyl-benzyl-silane

	μ_π (D)	$\mu_{\sigma,\pi}$ (D)
Without long bond	1.137	1.325
With long bond	0.365	0.490

Table 6

Energies of the molecular orbitals of trimethyl-benzyl-silane

	$\omega = 0$	$\omega = 1.0$
E_1	$\alpha+2.9969\beta$	$\alpha+2.9949\beta$
E_2	$\alpha+1.9513\beta$	$\alpha+1.9517\beta$
E_3	$\alpha+1.0000\beta$	$\alpha+0.9988\beta$
E_4	$\alpha+0.9618\beta$	$\alpha+0.9633\beta$
E_5	$\alpha-0.9803\beta$	$\alpha-0.9787\beta$
E_6	$\alpha-1.0000\beta$	$\alpha-1.0012\beta$
E_7	$\alpha-1.7880\beta$	$\alpha-1.7927\beta$
E_8	$\alpha-2.0034\beta$	$\alpha-2.0044\beta$
E_9	$\alpha-3.4535\beta$	$\alpha-3.4469\beta$
Δm	-1.9422β	-1.9421β

data. Omitting the long bond, $\Delta m = -1.9464\,\beta$ is obtained in the 0-th approximation which is in poor agreement with the data of the ultraviolet spectrum.

The π partial charges and the resultant σ, π charge distribution of the molecule calculated with $\omega = 1.0$ are presented in Fig. 3. The correctness of calculation is proved by the good agreement of the σ, π partial charge calculated for silicon atom and the Si^{29} chemical shift of the compound ($\delta_{Si}{}^{29} = -23.4$) with the corresponding quantities of other substituted silicon compounds [9, 10], as shown in Fig. 4. The π-bond orders of the molecule are given in Fig. 5. Comparing these bond orders with the π-bond orders of trimethyl-allyl-silane [4] plotted in Fig. 6, the π-bond orders of the silicon-α-carbon bond and silicon-β-carbon bond appear to be about equal in the two compounds. This proves that benzyl group can be considered analogous to allyl group.

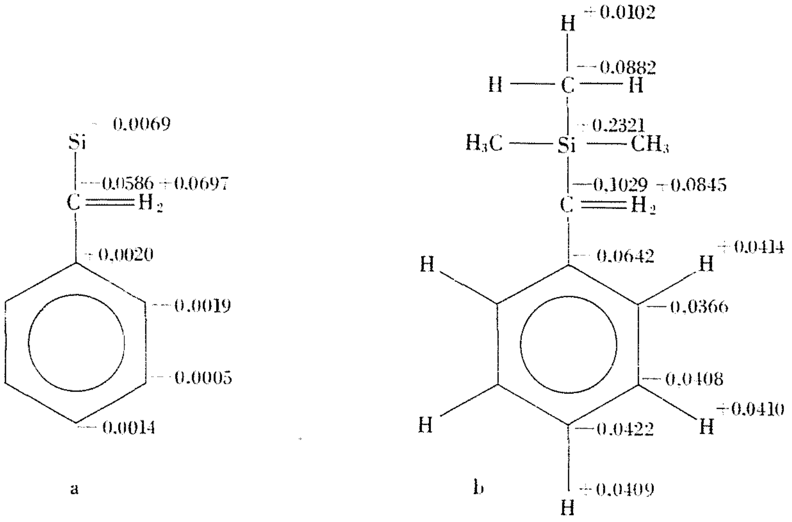

Fig. 3. π partial charges (a) and resultant charge distribution (b) in trimethyl-benzyl-silane

In Fig. 5 also the free π valences for the ortho, meta and para position relative to the side-chain are marked. Free valences influence the course of electrophile substitution reactions of the ring. Free valence is greatest in the ortho and smallest in the meta position. On the other hand, the π partial charge is greatest in the ortho and smallest in the meta position. These calculated results are in good agreement with the experimental results of BENKESER and BRUMFIELD [11], namely that 80% ortho-nitro and 20% para-nitro derivative is obtained when trimethyl-benzyl-silane is allowed to react with $Cu(NO_3)_2$ in acetic anhydride. Partial charges calculated with neglection of the long bond are inconsistent with the above results. In the latter case $+0.0234$, -0.0115 and -0.0378 could be calculated as π partial charges on the carbon

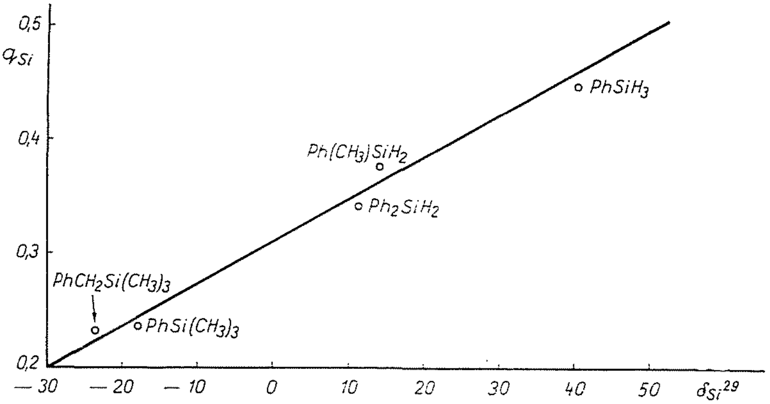

Fig. 4. Correlation between the Si^{29} chemical shift and partial charge on the silicon atom in the case of some silicon-organic compounds. (Chemical shifts are related to polydimethylsiloxane of a viscosity of 10cSt.)

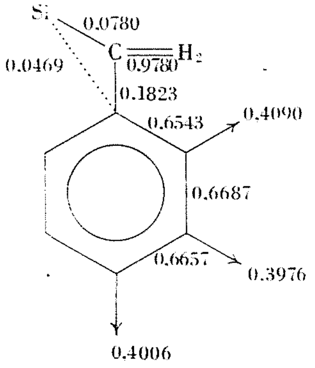

Fig. 5. π-bond orders and free valences in trimethyl-benzyl-silane

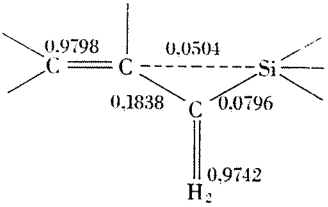

Fig. 6. π-bond orders in trimethyl-allyl-silane

atoms in the ortho, meta and para position, respectively. In this case the charge distribution would hinder electrophile substitution in the ortho position.

The π dipole moment of the molecule calculated from the partial charges obtained by the ω-technique is 0.288 D, whereas the resultant dipole moment is 0.420 D. The agreement of $\mu_{\sigma,\pi}$ dipole moments with experimental values was not as good as in the case where $d-\pi$ bond was assumed without using the ω-technique. This is probably due to the fact that σ dipole moments can be poorly approximated even by calculations according to Del Re.

Summary

Calculations were made in connection with benzyl-substituted silicon derivatives and their carbon analogues. In the case of σ-bond systems, the method of Del Re, in the case of π-bond systems the one-electron Hückel-LCAO-MO method was used. With trimethyl-benzylsilane a long bond was assumed between a silicon atom and a carbon in β position besides hyperconjugation. Partial charges, σ- and π-dipole moments, the energies of the molecular orbitals of the π system, the π bond orders and the energy of the smallest electron transfer were calculated, and compared with experimental data.

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