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QUANTUM CHEMICAL CALCULATIONS OF SATURATED, UNSATURATED, AND AROMATIC COMPOUNDS OF SILICON
III*. PHENYL DERIVATIVES

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SUMMARY

Quantum chemical calculations have been carried out in the study of σ and π electron systems of phenylsilanes d_π–p_π bonding between the unoccupied d orbital of the silicon atom and the phenyl ring is about 11%; the silicon atom has a partial charge of about −0.01. The directions of the σ and π dipole moments of the Si–C bond are opposed to each other. When two or more phenyl groups are bonded to a silicon atom no conjugative bonding occurs across the silicon atom.

INTRODUCTION

Quantum chemical calculations for the phenyl derivatives of silicon and for analogous carbon compounds have been carried out according to the method discussed in former communications[1,2]. The σ systems of trimethylphenylsilane and the corresponding tert-butylbenzene can be studied with the method of Del Re.

RESULTS AND DISCUSSION

The partial σ-charges of the two compounds are shown in Fig. 1. The largest difference is observed between the partial charge of the silicon bound to the phenyl group and that of the carbon atom bound to the phenyl group. There is a smaller difference between charges of the carbon atoms at the site of junction, but also in the case of the further atoms the electrorepulsing character is greater in silicon than in carbon. Thus the dipole moments of bonds formed by silicon are significantly higher than the corresponding values for the bonds formed by the central carbon atom in tert-butylbenzene. At the same time it can be seen that in trimethylphenylsilane the calculated dipole moment (0.8766 D) of the σ bond between the silicon atom and the aromatic carbon atom is higher than the bond moment vectors (0.4522 D) directed towards the methyl groups.

The σ-dipole moment calculated for tert-butylbenzene is 0.156 D (experimental

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* For Part I see ref. 1; for Part II see ref. 2.

value being 0.55 D) indicating that the effects of the σ-system on the electrons of the π-system is not negligible. The $+I$ effect of the tert-butyl group changes the coulomb integral of the aromatic carbon at the site of junction. The coulomb integral of this carbon atom may be said to be $\alpha + k \cdot \beta$, and that of the others, in a zeroth approximation, to be α. In the course of calculations according to the ω-technique the latter integral is slightly altered, and at the end of the iteration process π dipole moment can be calculated from the partial π charges. If the value of k is varied we can reach a π dipole moment (0.394 D) that, when added to the calculated σ dipole moment, gives the experimental dipole moment. Thus the measure of the σ–π interaction, the shift of the π electrons, and the partial π charges can be estimated.

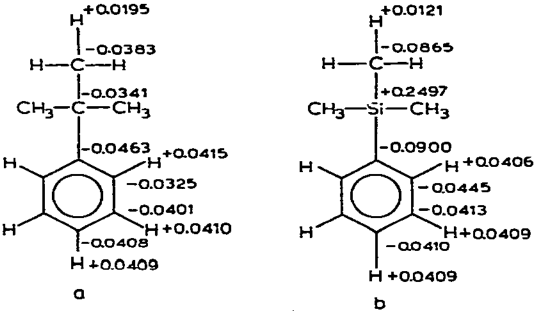

Fig. 1. σ-charge distribution; a. tert-butylbenzene; b. trimethylphenylsilane.

According to the calculations, the π dipole moment coincides with the direction of the σ dipole moment when a negative value for k is conjectured. In Fig. 2, π dipole

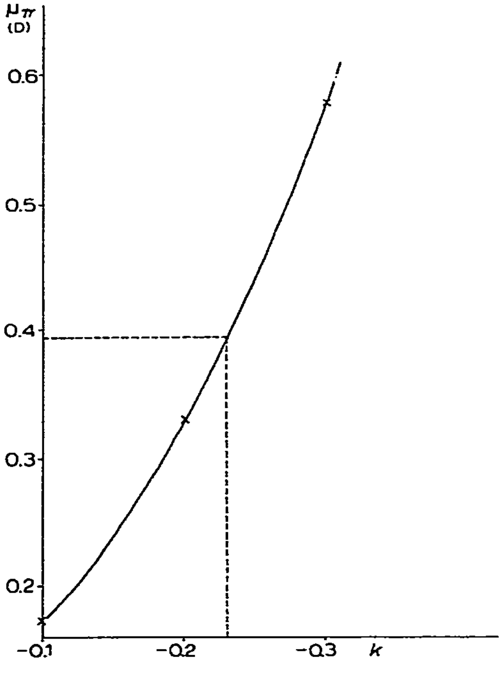

Fig. 2. Change of the π dipole moment of tert-butylbenzene as the function of variation parameter k.

moment is shown as a function of k. The required dipole moment can be ascertained using this curve and beginning with $k = -0.288$. The approximate partial π charges, and the resultant partial (σ,π) charges are shown in Fig. 3.

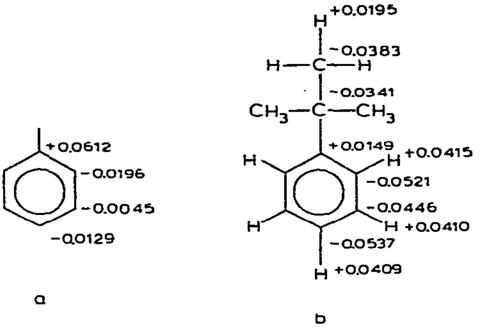

Fig. 3. Charge distribution of tert-butylbenzene; a. π charges; b. total charge.

In the case of trimethylphenylsilane $\alpha_{Si} = \alpha - 1.8152\ \beta$, $\beta_{SiC} = 0.3374\ \beta$, where α_{Si} is the coulomb integral of silicon and β_{SiC} is the exchange integral of the silicon–carbon bond on the basis of integral equations[2]. The results of the zeroth approximation were improved with the help of the ω-technique. The variation in the value of ω caused the results of the iteration process to differ to certain extent and hence the calculations were carried out for various values of ω. It is evident from Table 1

TABLE 1

CALCULATED FIGURES FOR TRIMETHYLPHENYLSILANE

	ω					
	0.0	0.5	0.7	0.9	1.0	1.2
E_1	$+2.0822\beta$	$+2.0785\beta$	$+2.0776\beta$	$+2.0770\beta$	$+2.0767\beta$	$+2.0763\beta$
E_2	$+1.1381\beta$	$+1.1261\beta$	$+1.1227\beta$	$+1.1120\beta$	$+1.1185\beta$	$+1.1163\beta$
E_3	$+1.0000\beta$	$+1.0129\beta$	$+1.0170\beta$	$+1.0206\beta$	$+1.0222\beta$	$+1.0253\beta$
E_4	-0.8438β	-0.8510β	-0.8534β	-0.8557β	-0.8567β	-0.8587β
E_5	-1.0000β	-0.9872β	-0.9832β	-0.9796β	-0.9770β	-0.9751β
E_6	-1.7897β	-1.7896β	-1.7898β	-1.7900β	-1.7901β	-1.7905β
E_7	-2.0288β	-2.0137β	-2.0329β	-2.0341β	-2.0347β	-2.0558β
Δm	-1.8438β	-1.8639β	-1.8704β	-1.8762β	-1.8789β	-1.8840β
q_1	-0.0123	-0.0121	-0.0120	-0.0120	-0.0120	-0.0119
q_2	-0.1535	-0.1218	-0.1127	-0.1049	-0.1014	-0.0900
q_3	$+0.0651$	$+0.0469$	$+0.0422$	$+0.0384$	$+0.0367$	$+0.0338$
q_4	-0.0037	$+0.0044$	$+0.0060$	$+0.0071$	$+0.0075$	$+0.0108$
q_5	$+0.0430$	$+0.0312$	$+0.0283$	$+0.0259$	$+0.0249$	$+0.0231$
q_6	-0.0037	$+0.0044$	$+0.0060$	$+0.0071$	$+0.0075$	$+0.0108$
q_7	$+0.0651$	$+0.0469$	$+0.0422$	$+0.0384$	$+0.0367$	$+0.0338$

that with various ω values, the eigen-values (E_i) of the system are slightly, but the partial charges (q_i) are significantly altered. On the basis of calculations carried out for a number of organosilicon compounds it can be said that results are in best agreement with experimental findings for values of ω between 0.6 and 1.0[4]. The rate of convergence is changed with the change in the value of ω, thus with $\omega=0.5$ it needed 9, with $\omega=1.0$ it needed 37 iteration steps to obtain self-consistent partial charges with errors less than 10^{-4}.

In Fig. 4 the (σ,π) partial charges are plotted according to calculations with $\omega=0.5$, and $\omega=1.0$. The π dipole moment of the Si–C bond is 0.107 D in both the cases (its direction points towards the silicon) the (overall) σ,π dipole moment is directed towards the carbon atom. Also the π dipole moment of the molecule is directed opposite to the σ dipole. The dipole moments calculated on the basis of the partial charges of trimethylphenylsilane are given in Table 2. (Bond lengths used in these calculations are 1.87 Å for $Si-C_{alk}$, 1.853 Å for $Si-C_{ar}$, 1.393 Å for C–C, and 1.09 Å for C–H.) The experimental values of 0.25 D[3], or 0.44 D are reported[5]. Thus the calculated results lead to good approximations, especially when $\omega=1.0$. Zeroth approximation generally show, significantly larger values of dipole moments than found experimentally (*e.g.* in a zeroth approximation $\mu_\pi=1.050$ D).

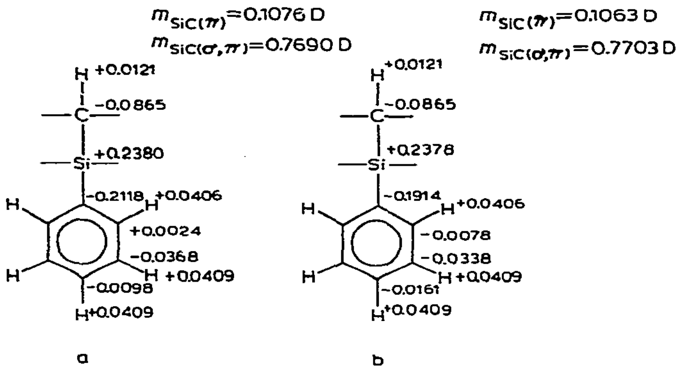

Fig. 4. Resultant charges of trimethylphenylsilane; a. $\omega=0.5$; b. $\omega=1.0$.

TABLE 2

CALCULATED DIPOLE MOMENTS OF TRIMETHYLPHENYLSILANE

μ_σ (D)	μ_π (D)		$\mu_{\sigma,\pi}$ (D)	
	$\omega=0.5$	$\omega=1.0$	$\omega=0.5$	$\omega=1.0$
0.309	0.931	0.838	0.622	0.529

The partial π charge distribution shows that the $(CH_3)_3Si$ group cannot be *ortho-* or *para*-directing (as it would follow from the $+I$ effect of Si disregarding its $-M$ effect) because on the carbon atoms at *para* or *ortho* positions there is a small positive partial charge which does not favour electrophilic attack. However, attack on *ortho* or *para* sites is facilitated because the free valency of the carbon atoms is greater in those than in *meta* positions (*cf.* Fig. 5). Accordingly, experimental findings showed that the trimethylsilyl group is slightly *ortho-para*-directing. According to studies of Speier[6], nitration of trimethylphenylsilane between 25 and 75° with HNO_3

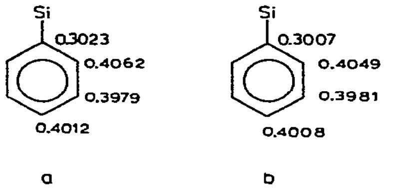

Fig. 5. Free valency of the carbon atoms of trimethyl-phenylsilane when a. $\omega=0.5$; b. $\omega=1.0$.

in glacial acetic acid, yields 27.7 per cent *ortho*, 29.6 per cent *meta*, and 27.9 per cent *para* derivative (also some nitrobenzene being formed in both cases because of the cleavage of Si–C bond).

The values of Δm (the smallest electron transitions) always represent a bathochromic shift, referred to benzene irrespective of the value of ω. In contrast, the UV spectra of trimethylphenylgermanium, and of trimethylphenyltin exhibit maxima at shorter wavelengths than those for trimethylphenylsilane (hypsochromic shift) (see also ref. 7).

The π bond orders can be calculated (*cf.* Fig. 6) knowing the linear coefficients

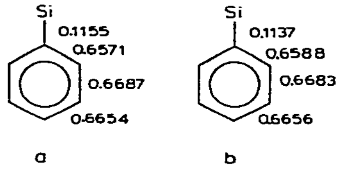

Fig. 6. π-Bond orders of trimethylphenylsilane; a. $\omega=0.5$; b. $\omega=1.0$.

TABLE 3

LINEAR COEFFICIENTS OF TRIMETHYLPHENYLSILANE (when $\omega=1.0$)

	c_1	c_2	c_3	c_4	c_5	c_6	c_7
E_1	0.0406	0.4701	0.4174	0.3813	0.3717	0.3813	0.4174
E_2	0.0658	0.5742	0.2320	−0.3232	−0.5911	−0.3232	0.2320
E_3	0.0000	0.0000	0.5036	0.4963	0.0000	−0.4963	−0.5036
E_4	0.1913	0.5503	−0.3427	−0.2441	0.5536	−0.2411	−0.3427
E_5	0.0000	0.0000	0.4963	−0.5036	0.0000	0.5036	−0.4963
E_6	0.7673	0.0843	−0.2163	0.3109	−0.3426	0.3109	−0.2163
E_7	0.6073	−0.3734	0.3282	−0.3064	0.2976	−0.3064	0.3282

characteristic of the molecular orbitals of trimethylphenylsilane (Table 3). The silicon–carbon bond has a double character, but the participation of d_π–p_π bonding is comparatively small (11.5%). According to calculations based on ESR data, Curtis and Allred[8] found the silicon–carbon bond order to be 0.18, in the case of one negatively charged (trimethylsilyl)biphenyl radical ion.

The total energy of the electrons is $6\alpha+8.435\beta$; the molecule possesses 0.435β delocalisation energy.

The σ and π electron systems of *p*-bis(trimethylsilyl)benzene can be calculated in a way similar to that used for trimethylphenylsilane. σ Charge distribution shown in Fig. 7 does not differ very much from that of mono-substituted derivatives. For

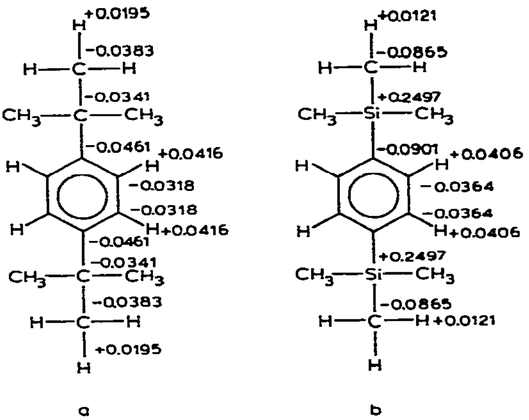

Fig. 7. σ Charge distributions; a. di-tert-butylbenzene; b. *p*-bis(trimethylsilyl)benzene.

comparison also the σ charges of the analogous compound *p*-di-tert-butylbenzene are shown. The eigen-values of the octa-centric π-system are slightly dependent on the value of ω (*cf.* Table 4). When ω is 1.0 the energy attributable to a π–π* transition is 1.7277 β. An approximately linear correlation results (Fig. 8) when calculated Δ*m* values of benzene, trimethylphenylsilane, and *p*-bis(trimethylsilyl)benzene are plotted

TABLE 4

ENERGIES OF THE MOLECULAR ORBITALS OF *p*-BIS(TRIMETHYLSILYL)BENZENE

	$\omega=0.5$	$\omega=1.0$
E_1	$\alpha+2.1442\beta$	$\alpha+2.1437\beta$
E_2	$\alpha+1.2596\beta$	$\alpha+1.2428\beta$
E_3	$\alpha+1.0257\beta$	$\alpha+1.0442\beta$
E_4	$\alpha-0.7171\beta$	$\alpha-0.7285\beta$
E_5	$\alpha-0.9743\beta$	$\alpha-0.9558\beta$
E_6	$\alpha-1.6817\beta$	$\alpha-1.6808\beta$
E_7	$\alpha-1.8949\beta$	$\alpha-1.9014\beta$
E_8	$\alpha-2.0457\beta$	$\alpha-2.0482\beta$

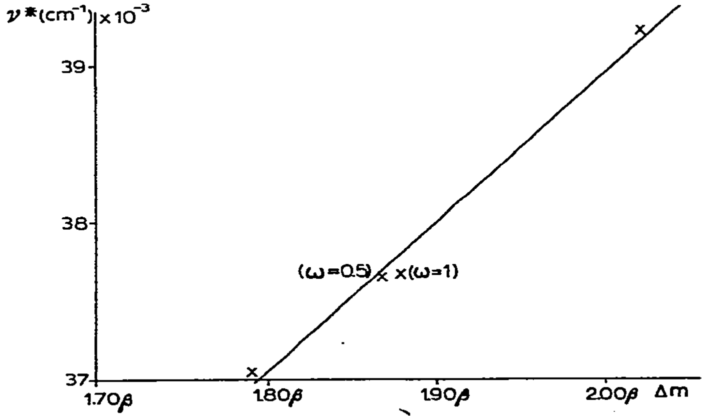

Fig. 8. Correlation between calculated Δ*m* energy and the wave numbers of absorption maxima.

in function of wave numbers of the ultraviolet absorption maximum (α-band). The total energy of the π-electrons of *p*-bis(trimethylsilyl)benzene is $6\,\alpha+8.8613\,\beta$ and the delocalisation energy, referred to that of benzene, is $0.8613\,\beta$.

As compared with trimethylphenylsilane, the π-charge distribution of the molecule (Fig. 9a) shows greater alterations than does the σ-charge distribution. The shift of the charge towards silicon is smaller and both the silicon atoms participate uniformly with the π-sextet. Also the dipole moment (0.0978 D) of the π bond between Si and C is less than that in trimethylphenylsilane (0.1070 D). Perkins[9] performed P–P–P calculations for this molecule, and compared experimental spectral data[10] with calculated electron transitions, and has attributed -0.02 partial charge to the *d*-orbitals of silicon, *i.e.* nearly twice the value we have calculated. In the case of trimethylphenylsilane the d_π–p_π bond character is more prominent because the π-sextet pertains to one silicon atom. In di-substituted compounds the two silicon atoms attract the π-sextet symmetrically. At the same time, in these two compounds the π-bond order of the Si–C bond is greater than that in the vinyl derivative[2] since the π electrons of the aromatic ring are much more mobile than those of only one double bond.

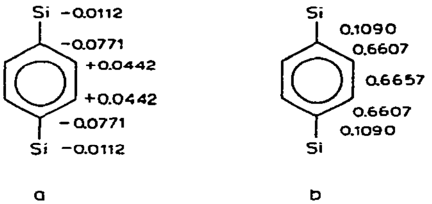

Fig. 9. a. π Charge distribution of *p*-bis(trimethylsilyl)benzene; b. π bond orders of *p*-bis(trimethylsilyl)-benzene.

According to the calculations of Perkins, the π-bond order of four bonds in the ring is reduced by 2.5%, and the π-bond order of remaining two bonds is increased by 1%, compared to the π bonds between the carbon atoms of the benzene ring (where the bond order is 0.667). Our calculations show, however, that π bond order is reduced in all C–C bonds, by 1% in four, and by 0.2% in two (*cf.* Fig. 8b).

For trimethylphenylsilane and *p*-bis(trimethylsilyl)benzene we have calculated the experimental and theoretical oscillator-strength proportional to the intensity of the UV absorption maximum. The calculations relevant to the *p*-band of the spectra are summarized in Table 5. The ratio of the experimental oscillator strengths of the two compounds practically agrees with the ratio of theoretical oscillator strengths (last line in Table 5).

TABLE 5

EXPERIMENTAL AND THEORETICAL OSCILLATOR STRENGTHS

Compound	*J*(exptl.)	*J*(theor.)
Trimethylphenylsilane	0.170	0.516
p-Bis(trimethylsilyl)benzene	0.165	0.513
ratio	1.029	1.006

If more than one phenyl groups are bound to one silicon atom, neither the UV spectra nor the vibrational fine structure are changed indicating that in tetraphenylsilane the phenyl rings do not enter in conjugative bonding with each other across the silicon atom. Most probably, each phenyl group forms a d_π–p_π bond with a separate unoccupied *d* orbital. Similar conclusion has been depicted for phenyl groups bonded to central phosphorus, arsenic and sulphur atoms[11].

Si–H groups (in contrast to C–H groups) bonded to a phenyl ring do not exert hyperconjugative effects in the direction of the ring, as stated in a former communication[12].

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