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QUANTUM CHEMICAL CALCULATIONS OF SATURATED, UNSATURATED, AND AROMATIC COMPOUNDS OF SILICON

I. THE CALCULATION OF d_π–p_π INTERACTION AND σ BOND SYSTEMS

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SUMMARY

Compounds of carbon and silicon, with saturated radicals have much in common; with electron donor groups the *d*-orbitals of silicon can enter into a d_π–p_π interaction. Calculations have been carried out for the σ-bond system of saturated compounds using modified Del Re parameters. Calculated values are in good agreement with the experimental values found for dipole moments and proton signs.

INTRODUCTION

The majority of silicon compounds show significant deviations as compared to the analogous compounds of carbon. Alkanes and silanes differ but little from each other. However a silicon compound with an electron donor organic radical, *e.g.* phenyl or vinyl, differs in many respects from its carbon-counterpart because due to its unoccupied *d* orbitals, silicon is able to interact on a d_π–p_π level (similar to germanium and tin).

The kinetic studies have shown[1] that (trimethylsilyl)benzoic acids are stronger acids than benzoic acid. In case the trimethylsilyl group exhibited only an inductive (+*I*) effect, these acids ought to be significantly weaker. Further, in electrophilic aromatic substitutions, the inductive effect of the trimethylsilyl group ought to activate *ortho* and *para* positions, but due to the effect of the p_π–d_π bond, activation is significantly reduced[2,3]. The degree of p_π–d_π conjugation in aromatic silicon compounds depends upon the nature and the position of the other groups bonded to the phenyl ring[4].

On the basis of dipole moment measurements of *para*-substituted derivatives of tert-butylbenzene, trimethylphenylsilane, and trimethylphenyltin, Huang and Hui[5] postulated that d_π–p_π interactions are possible between carbon and silicon, and the carbon and tin atoms.

Mironov[6] observed that in the homologous series of $(CH_3)_3Si(CH_2)_nCH{=}CH_2$ type of compounds the chemical and physical properties, *e.g.* addition of di-rhodane group, Raman, IR frequencies, intensities, dipole moments, are not continuous uniform functions but exhibit maxima in the case of the alkyl group. These findings are explained by the fact that the π-electron pair of the vinyl group is delocalized and interacts with the 3*d* orbital of the silicon atom.

Cowell *et al.*[7] have proved by ESR studies on the di-anion of bis (2,2′-diphenylene)silane that the two single electrons are delocalized over the entire ring system. In a comparison of the ESR spectra of anions derived from $(CH_3)_3MC_6H_5$ type of compounds (where M=C, Si, Ge), Bedford[8] has demonstrated that, the trimethylsilyl, and trimethylgermyl groups are electron attracting in contrast to the tertiary butyl radical. Curtis and Allred[9] have published similar results of the ESR studies on anions derived from substituted biphenyl derivatives of silicon, germanium, and tin. The calculations based on the LCAO-MO method gave a π-bond order of 0.177 for Si–C, and 0.124 for Si–Ge bonding.

Schmidbaur[10] postulated similar p_π–d_π bonds between the silicon atom and the electronegative atoms or groups on the basis of the NMR spectra of methyl silanes. Ebsworth and Frankiss[11] refer to the anomalies of the chemical shifts also evident in analogous carbon compounds where p_π–d_π interactions are impossible. The d_π–p_π interactions have been pointed out in vinylmethylsilanes[12], and tetravinylsilane[13] according to NMR spectra, and the shielding of ^{19}F atoms in methyl- or ethylfluorosilanes[14].

On the basis of the ultraviolet spectra of vinyltrimethylsilane, divinyltetramethyldisilane, and divinyloctamethyltetrasilane, Armstrong and Perkins[15] propose the presence of d_π–p_π bonds in these compounds, and a weak d_π–p_π interaction even between silicon atoms which is supported by the hydrogen halide anti-Markownikow addition to the vinylsilane bond, and by quantum chemical calculations according to the F.E. method.

It was thought worthwhile to attempt a quantum-chemical evaluation, of the results just quoted and of the experimental data collected. In the case of saturated compounds and the σ-bonding system of unsaturated ones, we used the parameter-method of Del Re in our calculations; whereas with the π-systems our calculations were made according to the semi-empirical LCAO-MO method of Hückel. The results obtained are of value because they express tendencies although our calculations are not based on perfectly exact methods.

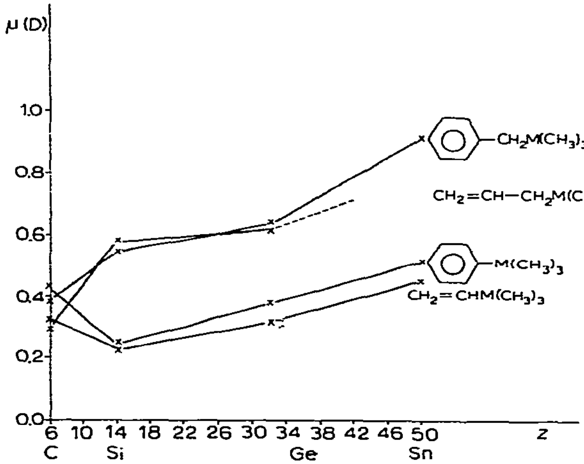
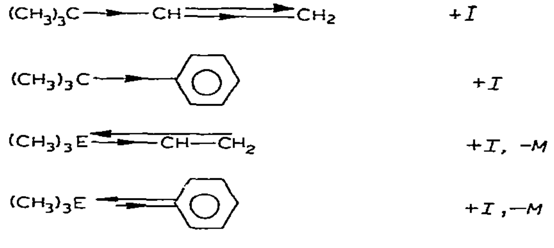


Fig. 1. The change of dipole moment in the vinyl, phenyl, allyl and benzyl derivatives of Group IV elements.

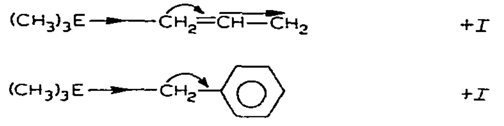
RESULTS AND DISCUSSION

It is evident from Fig. 1 that the lowest dipole moments among phenyl and vinyl type compounds occur in silicon derivatives[16]. In the case of benzyl and allyl compounds, dipole moment rises from carbon to tin. Values for germanium and silicon compounds are nearly the same, in accordance with the electronegativity values, and the relationship, between these two elements.

An interesting graphical pattern was observed on plotting the wave numbers of UV absorption maxima of the homologous series as a function of the atomic number Z of the heteroatom C, Si, Ge, or Sn(Fig. 2). In the phenyl series there is a minimum with the Si homolog, whereas in the other series there is a continuous bathochromic shift from carbon to tin[18-20]. An explanation of these results is possible only if the following bond structures are postulated for the types of compounds mentioned:



E = Si, Ge, or Sn



E = C, Si, Ge, Sn

Only a $+I$ effect is manifested in tert-butylethylene and tert-butylbenzene. These compounds have high dipole moments. In other vinyl and phenyl compounds also a $-M$ effect (d_π–p_π interaction) is evident whereas the $+I$ effect increases from silicon to tin[21] the $-M$ effect decreases and thus, starting with Si, dipole moments increase again.

In allyl and benzyl derivatives, the methylene group greatly hinders the conjugation. Thus to the atom (E) having only a $+I$ effect the two-directional hyperconjugative effect of the methylene group is added towards the vinyl or phenyl group on one hand, and towards the silicon atom, on the other. The quantum chemical calculations did show that the hyperconjugative effect is greater in the direction towards the organic radical than towards the silicon atom. It should be noted however that in these compounds there is a further interaction of the d-orbital of the silicon and the p_π-orbital of the carbon in β-position to it and thus a d–π effect is manifested. The phenomenon is similar to that in benzene derivatives substituted with a fluoroalkyl group, as there the unshared pair of electrons of the fluorine atoms engenders p–π interaction with the π-system of the aromatic ring[22]. Due to the unidirectional enhancing tendency of the $+I$ and hyperconjugation effects, the dipole moments, and bathochromic shift of UV maxima, increase from carbon to tin, in allyl and benzyl derivatives.

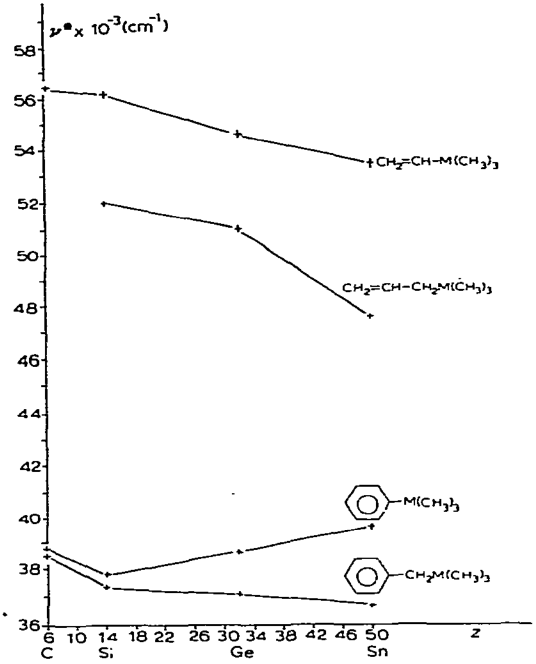


Fig. 2. UV absorption maxima of vinyl, phenyl as well as of allyl and benzyl derivatives of Group IV elements.

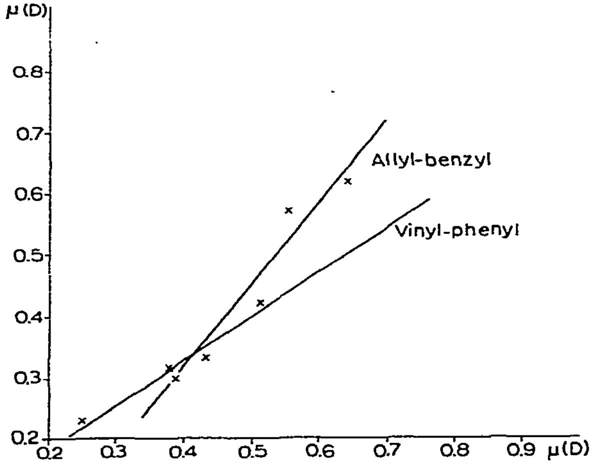


Fig. 3. Correlation between dipole moments of the vinyl and phenyl derivatives of Group IV elements.

According to Karapetjans, there exists a linear correlation between the dipole moments of the vinyl and phenyl derivatives of elements in the same group (*Cf.* Fig. 3). Silicon, germanium, and tin derivatives are found in their natural order of sequence along the straight line, carbon anomalously follows germanium which further indicates the specific bond structure of carbon compounds.

Owing to its behaviour towards electron donor groups, silicon resembles boron in many respects *e.g.* the quantum-chemical calculations of Armstrong and Perkins for vinyl esters of boric acid[23], and those of Mattheson for phenylborates[24]. In these compounds there is a p_π–p_π interaction between the unoccupied p orbital of boron and the π-system of the vinyl, and phenyl radical, respectively.

Quantum-chemical calculations

Saturated silicon compounds. In our calculations of the σ bond system of saturated compounds we utilized the parameter-method of Del Re[25]. According to this, the coulomb parameter of the atoms involved in the bond is approximated from a less involved state of the atom, by correcting the data of this state, taking into account the effects of the adjacent atoms.

$$\delta_A = \delta_A^\circ + \sum_B \gamma_{A(B)} \cdot \delta_B$$

where δ_A = coulomb parameter of atom A within the molecule;
δ_A° = coulomb parameter of the same A atom before the formation of the bond; (δ_A° is dependent also on the hybridization state of the atom)
δ_B = coulomb parameter of atom B next to atom A;
$\gamma_{A(B)}$ = induction parameter, represents the effect of atom B upon atom A.

The degree of bond polarity can thus be calculated according to the eqn.:

$$Q_{A-B} = \frac{\delta_A - \delta_B}{2\varepsilon_{A-B}}$$

where Q_{A-B} = polarity of the bond between atoms A and B;
ε_{A-B} = parameter of the integral of the exchange between the same atoms A and B

and thereby the partial charge proportion q_A of an atom.

In the course of our calculations we determined δ° for the silicon atom on the basis of group electronegativity; for the determination of induction parameters and exchange integrals, variance analyses on compounds of known dipole moments were carried out, taking into account the proton signs known from the literature, and approximately proportional to partial charges of the hydrogen atoms. The parameters used in the calculations are listed in Table 1. Data in Table 2 show that, in the case of simple hydrocarbons, the degrees of bond polarities calculated with the modified Del Re constants in better agreement with figures found in the literature[26].

On the basis of parameters (Table 1) the σ-charge distribution of some saturat-

TABLE 1

MODIFIED DEL RE PARAMETERS

Bond	ε_{A-B}	δ_A°		δ_B°		$\gamma_{A(B)}$	$\gamma_{B(A)}$
		sp^3	sp^2	sp^3	sp^2		
C–C	1.00	0.07	0.12	0.07	0.12	0.1	0.1
C–H	1.00	0.07	0.12		0.00	−0.2	0.4
C–Si	0.90	0.07	0.12		−0.10	0.4	0.2
H–Si	0.125	0.00			−0.10	−0.4	0.4

TABLE 2

DEGREES OF BOND POLARITIES CALCULATED ACCORDING TO THE METHOD OF DEL RE

A = calculated with the original parameters; B = calculated with modified parameters; C = figure found in the literature; D = proton sign τ.

Compound		$\varrho_{C(1)-H}$	$\varrho_{C(2)-H}$	ϱ_{C-C}
CH_4	A	0.0405		
	B	0.0159		
	C	0.015		
	D	9.77		
CH_3CH_3	A	0.0389		0.000
	B	0.0184		0.000
	C	0.018		0.000
	D	9.14		
$C(1)H_3C(2)H_2CH_3$	A	0.0388	0.0380	0.0015
	B	0.0178	0.0213	0.0044
	C	0.019	0.020	0.004
	D	9.10	8.55	
$[C(1)H_3]_3C(2)H$	A	0.0370	0.0386	0.0027
	B	0.0189	0.0247	0.0096
	C			
	D	9.113	8.439	
$[C(1)H_3]_4C(2)$	A	0.0444		0.0027
	B	0.0193		0.0158
	C	0.020		0.010
	D	9.08		

TABLE 3

PARTIAL CHARGES FOR MEMBERS OF THE SERIES $(CH_3)_xSiH_{(4-x)}$, WHERE $x=0$, 1, 2, 3 OR 4

Compound	$q_{H(Si)}$ (τ)	$q_{H(C)}$ (τ)	q_C	q_{Si}	ϱ_{Si-C}
SiH_4	−0.1464(6.78)			0.5856	
CH_3SiH_3	−0.1504(6.45)	0.0109(9.88)	−0.0876	0.5061	0.0549
$(CH_3)_2SiH_2$	−0.1560	0.0106	−0.0876	0.4236	0.0558
$(CH_3)_3SiH$	−0.1640(6.145)	0.0103(9.925)	−0.0880	0.3353	0.0571
$(CH_3)_4Si$		0.0098(10.00)	−0.0886	0.2368	0.0592

ed silicon compounds has been calculated. Fig. 4 shows the molecule diagram of tetramethyl- and tetraethyl-silane. Table 3 lists results of calculations for the $(CH_3)_x$-$SiH_{(4-x)}$ homologous series. The correctness of the choice of parameters is obvious from the good agreement between the experimental values of dipole moments and those calculated from partial charges (respectively, degrees of bond polarities) (*cf.* Table 4). A further proof for the usefulness of our parameters consists in the linear correlation (*cf.* Fig. 5) between partial charges of hydrogen atoms in various organic and organosilicon compounds and the experimental τ proton sign of the same hydrogen atoms. It is to be seen that only methane is farther off the straight line.

A comparison of silicon derivatives with the analogous carbon compounds thus reveals that hydrogen of the methyl group of trimethylmethane carries a greater

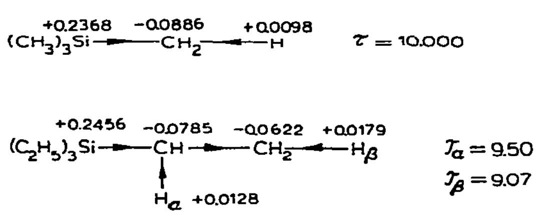


Fig. 4. Molecular diagram of tetramethylsilane, and tetraethylsilane.

TABLE 4

CALCULATED AND EXPERIMENTAL VALUES OF DIPOLE MOMENTS FOR MEMBERS OF THE SERIES $(CH_3)_xSiH_{(4-x)}$, WHERE $x=0$, 1, 2, 3 OR 4

Compound	μ(D)		$\mu_O-\mu_c$ (D)
	Calcd.	Exptl.	
SiH_4	0.000	0.00	0.00
CH_3SiH_3	0.632	0.73	0.10
$(CH_3)_2SiH_2$	0.729	0.76	0.03
$(CH_3)_3SiH$	0.704	0.60	−0.10
$(CH_3)_4Si$	0.000	0.00	0.00

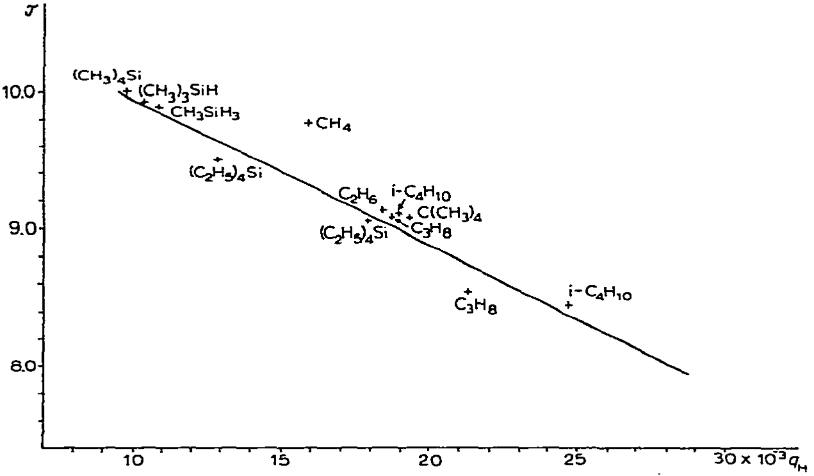


Fig. 5. Correlation between the partial charge q_H and the proton sign τ of hydrogen atoms of organic, and organosilicon compounds.

partial charge (0.0189) than the hydrogen of trimethylsilane (0.0103) since, due to its $+I$ effect, silicon reduces the partial positive charge of the methyl-hydrogen and is responsible for the increase of the proton sign occurring at the same time.

A similar statement is valid when a comparison between the partial charge (0.0184) of hydrogen in ethane and that (0.0109) in the methyl radical of methyltrisilane is made, or for a comparison of hydrogen in tetramethylmethane (0.0193) and that in tetramethylsilane (0.0098). It can be stated that in the case of silanes an approximately linear correlation exists also between the τ proton sign of the hydrogen bound to silicon, and its calculated partial charge. In contrast to carbon, silicon is more electronegative than hydrogen, thus Si in a Si–H bond has negative polarity. The Si–H

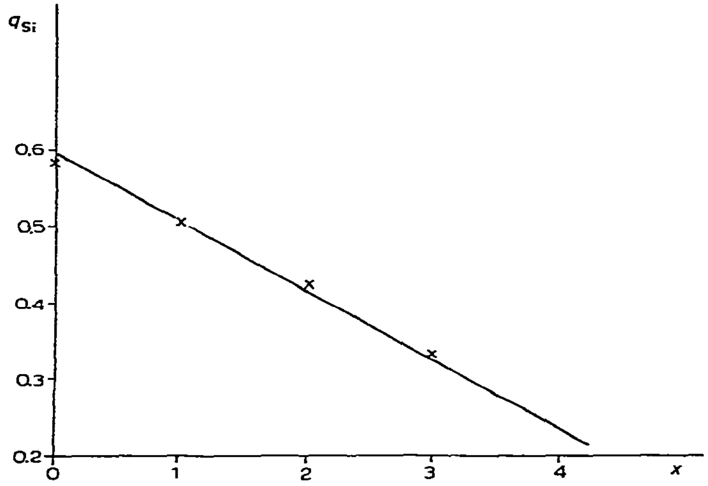


Fig. 6. Changes of the partial charge of silicon in the series $(CH_3)_xSiH_{(4-x)}$.

bond is significantly more polar (degree of bond polarity is 0.14 to 0.16) than a C–H bond (degree of bond polarity 0.01 to 0.02). Thus in the homologs series $(CH_3)_xSiH_{(4-x)}$ the total charge of silicon decreases directly with the increase of the number of methyl groups (*cf.* Fig. 6).

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