INVESTIGATION OF THE STRUCTURE OF PHENYL-SILANES

By

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The scope of the present paper has been to decide whether there is a hyperconjugative effect in the $SiH_{(4-x)}$ system (where $x = 1, 2, 3$), as in analogous carbon groups. This effect was studied in two compound series, namely $Ph_xEH_{(4-x)}$ (where $x = 1, 2, 3, 4$; E = C or Si atom) and Ph $(CH_3)_xEH_{(3-x)}$ (where $x = 0, 1, 2, 3$; E = C or Si atom). The effect of hyperconjugation of the C—H bond in these types of compounds can be proved by recording ultraviolet spectra subsequent to phenyl substitution. Earlier, the hyperconjugative effect of the $-Si{\equiv}H_3$ group had been investigated by GOODMAN et al. [1]. They stated on the basis of discussion of ultraviolet intensity that the $d\pi-p\pi$ effect between d orbitals of silicon and the aromatic ring might exceed the possible hyperconjugative effect. It is known by quantum-chemical calculations of SANTRY and SEGAL [2] that silicon sets up a connection with hydrogen of $1s$ state in spd hybrid state. Thus the eigenfunction of the hybrid orbital of silicon in SiH_4 is

$$\varphi_t = 0.560\chi_{3s} + 0.731\chi_{3p} + 0.383\chi_{3d}$$

The eigenfunction of the bonding orbital by the SCF-LCAO method can be given in the following linear combination:

$$\Phi = 0.653\,\varphi_t + 0.757\,\varphi_H$$

where φ_H is the eigenfunction of $1s$ orbital of atom H. Regarding the former statements the value of the partial charge share is 0.147, dipole moment of Si—H bond is 1.04 D, identical with the experimental value which is roughly 1 D [3]. Thus atoms have a relatively large partial charge in Si—H bond and the hydrogen atom produces intensive electron withdrawing (inductive) effect on the adjacent groups through silicon atom.

The bond between phenyl group and silicon atom is of $d\pi-p\pi$ character proved by us earlier, in agreement with other authors [1, 4]. Silicon atom displays $+I$ and $-M$ effects towards the phenyl group. The more electronegative hydrogen atoms belonging to silicon primarily influence the $+I$ effect of silicon, and partly even its mesomeric effect. The ratio of these two opposite effects produces a hypsochromic or a bathochromic shift in the ultraviolet spectra of the phenyl substituted silanes.

Two series of compounds were prepared for the measurements: the series of phenyl-methane, substituted phenyl-methane and the series of phenyl-silane and substituted phenyl-silane, respectively.

The ultraviolet spectra of the compounds were recorded by means of a Spectromom 201 type ultraviolet spectrophotometer, using cyclohexane solutions. The structure of the spectra is analogous to that of benzene. First of all we followed with attention the position and variations of intensity of the α-band in our investigations. The characteristic data of the spectra are compiled in Table I.

We tried to represent the wave numbers belonging to the absorption maxima of the silicon compound series plotted against wave numbers of absorption maxima of the carbon compound series applying KARAPETIANS' comparative theorem [5]. This representation does not reflect a linear correlation (Fig. 1), verifying the various effects causing the difference between the silicon and carbon homologous series. One finds the same non-linear correlation between the number of hydrogen atoms and the absorption maxima of the different compound series (Fig. 2). The characteristic curves of compound series containing silicon or carbon are of different running down. Increasing number of hydrogen atoms causes a bathochromic shift in the spectrum of the

Table I

UV absorption maxima and extinction coefficients of the compound series $Ph_xEH_{(4-x)}$ and $Ph(CH_3)_xEH_{(3-x)}$

Compound	λ_{max} (nm)	ν_{max} (cm^{-1})	ε_{max}
$PhSiH_3$	264.6	37 795	323.2
Ph_2SiH_2	264.8	37 765	964.0
Ph_3SiH	265.2	37 710	1291.0
Ph_4Si	265.4	37 680	1518.0
$PhCH_3SiH_2$	264.4	37 820	279.9
$Ph(CH_3)_2SiH$	264.4	37 820	232.8
$Ph(CH_3)_3Si$	265.6	37 650	223.0
$PhCH_3$	262.4	38 110	243.9
Ph_2CH_2	262.2	38 150	422.3
Ph_3CH	262.0	38 170	775.0
$PhCH_3CH_2$	261.8	38 195	209.0
$Ph(CH_3)_2CH$	261.0	38 300	182.9
$Ph(CH_3)_3C$	258.0	38 760	198.0

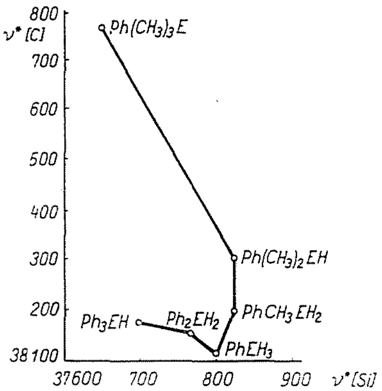

Fig. 1. Correlations between the absorption wave numbers of the compounds belonging to the series Ph$_x$SiH$_{(4-x)}$ and Ph(CH$_3$)$_x$SiH$_{(3-x)}$ and of the analogous carbon compounds

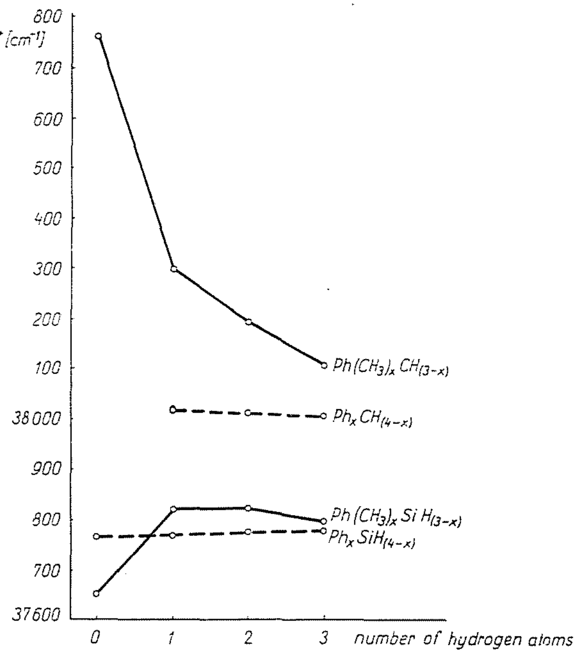

Fig. 2. Absorption wave numbers of the compounds belonging to the series Ph$_x$EH$_{(4-x)}$ and Ph(CH$_3$)$_x$SiH$_{(3-x)}$ in the function of number of hydrogen atoms

Ph(CH$_3$)$_x$CH$_{(3-x)}$ series because hyperconjugation of identical direction of increasing number of hydrogens strengthens the $+I$ effect of the carbon atom attached to the phenyl ring. This consideration means an upward shift of one of each degenerated $\pi-\pi^*$ levels of benzene and this effect increases with the number of hydrogen atoms.

The hydrogen atoms in the silicon compounds have only $-I$ effect, though the silicon influences $+I$ and $-M$ effects. $+I$ effect changes energy levels in the same way as described in the case of carbon analogues. $-M$ effect influences these two levels above all, shifting down both, but the upper one to a greater extent. The substituents connected to silicon alter the extent and ratio of $+I$ and $-M$ effects. The inductive effect of the hydrogen atom is greatest in the homologous series studied and the order of inductive effect is the following:

$$\mathrm{H} > \mathrm{Ph} > \mathrm{CH_3}$$

Entering hydrogen atoms decrease the $+I$ effect of silicon, thus the $-M$ effect ($d\pi - p\pi$ bond character) decreases too. This latter means diminution of the coulomb integral of silicon which leads to a hypsochromic shift proved by quantum chemical calculations [5]. This phenomenon is represented by the hypsochromic shift presented by the increasing number of hydrogen atoms in compounds of $\mathrm{Ph}_x\mathrm{SiH}_{(4-x)}$ series, at the same time an opposite shift is found in the case of carbon analogues. The $\mathrm{Ph(CH_3)}_x\mathrm{SiH}_{(3-x)}$ series (where $x = 0, 1, 2$) shows a hypsochromic shift of low extent compared to trimethyl phenylsilane. Hydrogen atoms connected to silicon have only inductive and no hyperconjugative effect verified by the small hypsochromic shifts.

Therefore the $+I$ effect of silicon is reduced with increasing number of hydrogen atoms which is verified experimentally by the rise of the UV maxima intensities in the $\mathrm{Ph(CH_3)}_x\mathrm{SiH}_{(3-x)}$ series.

Earlier ROBERTSON and MATSEN [6] established by means of quantum-chemical calculations that the inductive effect of the substituent of phenyl ring changes mostly the coulomb integral of the carbon atom substituted and the inductive effect is responsible for alterations of intensity for the most part. Oscillator strength is expressed as follows:

$$f = 1.085 \cdot 10^{-5} \nu^* DG$$

where ν is the wavenumber of UV maximum (which changes but slightly in the compound series investigated), D is dipole strength, G is degree of degeneration (in this case G 1). Therefore alteration of intensity is in connection with transition dipole strength. In order to state the relation between inductive-, mesomeric effect and absorption intensity we performed quantum-chemical calculations of the phenyl-silicon group by HÜCKEL's LCAO—MO one-electron molecular orbital calculation method. The coulomb integral was chosen for carbon atoms of the ring as α, the resonance integral for the carbon—carbon bond as β, coulomb integral for carbon atom connecting to silicon as $(\alpha - \delta_1\beta)$, coulomb integral for silicon as $(\alpha - \delta_0\beta)$ and resonance integral for the silicon—carbon bond as $0.3\ \beta$. δ_0 and δ_1 are variation parameters. Results of the calculations are plotted in Fig. 3, demonstrating that change of the mesomeric effect (δ_1) hardly influences absorption intensity. Transition dipole-moment passes through minimum with alteration of the inductive effect (δ_1). Inductive effect decreases absorption maximum intensities with increasing number of hydrogen atoms in $Ph(CH_3)_xSiH_{(3-x)}$ series, i.e. the conditions are proper to the left part of the curves.

Calculations regarding the σ bonding system of the compounds also prove the decreasing inductive effect of silicon influencing the ring (especially the carbon atom to which silicon is connected) with increasing number of hydrogen atoms.

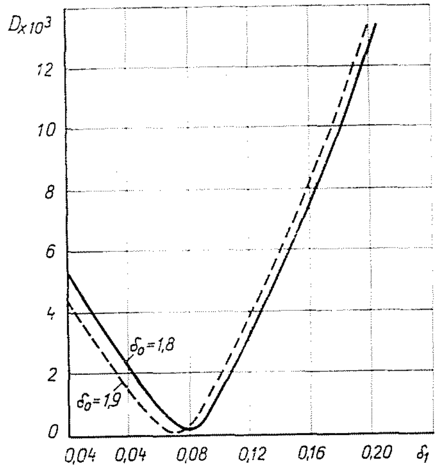

Fig. 3. The change of the dipole strength in the function of variation parameters δ_0 and δ

The calculations were performed by DEL-RE's modified method [7]. Actual values of coulomb, inductive and resonance parameters are compiled in Table II where resonance integrals are denoted by ε, coulomb parameters by δ_0 and inductive parameters by γ.

Table II

Values of the Del-Re parameters

	C—C	C—H	C—Si	Si—H
ε_{AB}	1.00	1.00	0.90	0.125
δ_A	sp^3: 0.07; sp^2: 0.12	sp^3: 0.07; sp^2: 0.12	sp^3: 0.07; sp^2: 0.12	—0.10
δ_B^0	sp^3: 0.07; sp^2: 0.12	0.00	—0.10	0.00
$\gamma_{A(B)}$	0.1	—0.2	0.4	—0.4
$\gamma_{B(A)}$	0.1	0.4	0.2	0.4

Approximative calculations were performed for the σ bonding system of the first three members of the $Ph_xSiH_{(4-x)}$ series (where $x = 1, 2, 3$). Charge distribution of σ electrons is represented in Fig. 4. This scheme demonstrates the growing partial negative charge of the aromatic carbon connected to silicon with decrease of the number of hydrogen atoms which indicates the ncreasing $+I$ effect of the silicon. Polarity of the silicon—hydrogen bond (negative charge of hydrogen atom) diminishes at the same time. It is in conformity with the change of NMR signs. Values of chemical shifts (τ-signs) are as follows: 5.81 for phenyl-trisilane; 5.14 for diphenyl-silane; 4.57 for triphenylsilane. Charge of the hydrogen of the ring varies but slightly.

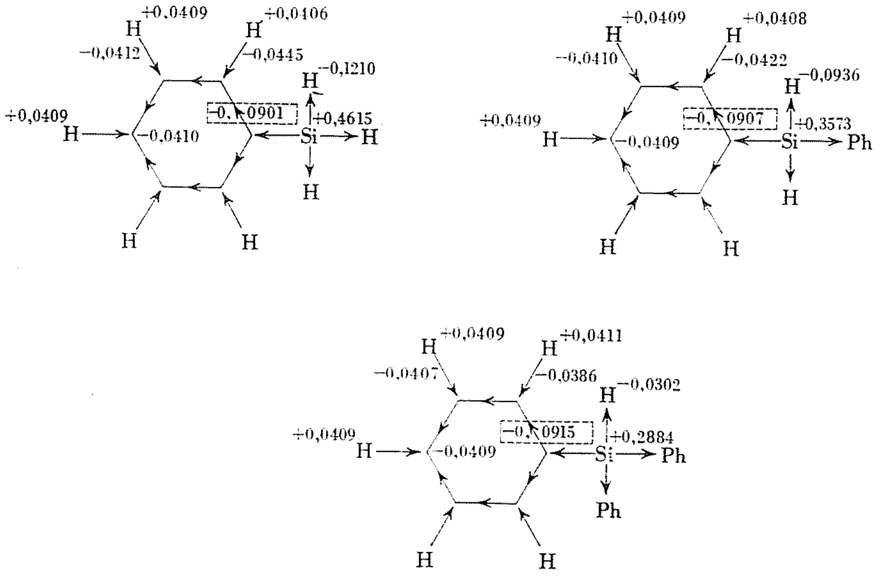

Fig. 4. σ-charge distribution of compounds belonging to the series $Ph_xSiH_{(4-x)}$

Summary

It has been stated that the Si—H bond connected to an aromatic system does not display hyperconjugative effect towards the ring, while replacing the hydrogen atoms of the silicon by methyl or phenyl groups, its $+I$ effect grows simultaneously reducing the polarity of the Si—H bond.

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