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INVESTIGATION OF THE Si–H BOND USING AN ULTRAVIOLET SPECTROPHOTOMETRIC METHOD

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SUMMARY

The results of our investigations show that the Si–H bond connected to an aromatic system does not display any hyperconjugative effect towards the ring. When hydrogen atoms are replaced by methyl or phenyl groups at the silicon atom the $+I$ effect of silicon increases and the polarity of the Si–H bond is reduced.

The aim of the present paper is to investigate whether there is hyperconjugative effect in the $-SiH_x$ system (where $x=1, 2, 3$) similar to that of the analogous carbon groups. This effect was studied in two series of compounds, *i.e.*, $Ph_xEH_{(4-x)}$ (where $x=1, 2, 3, 4$; $E=C$ or Si) and $Ph(CH_3)_xEH_{(3-x)}$ (where $x=0, 1, 2, 3$; $E=C$ or Si). The effect of hyperconjugation of the C–H bond in these types of compounds can be demonstrated by recording the ultraviolet spectra produced as a consequence of phenyl substitution. The hyperconjugative effect of the $-Si\equiv H_3$ group was earlier investigated by Goodman, Konstam and Sommer[1]. On the basis of the ultraviolet intensity they stated that the d_π–p_π effect between the d-orbitals of silicon and the aromatic ring can exceed any possible hyperconjugative effect. It is known from the quantum-chemical calculations of Santry and Segal[2] that silicon sets up a bond with hydrogen of the 1s state in the spd hybrid state. Thus the eigen-function 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 eigen-function of the bonding orbital can be given by the SCF-LCAO method by the following linear combination:

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

where φ_H is the eigen-function of the 1s-orbital of the H atom. The value of the partial charge share is 0.147 and the dipole moment of the Si–H bond is 1.04 D, identical with the experimental data (approx. 1 D) of Altshuller and Rosenblum[3]. Thus, atoms have a relatively large partial charge in the Si–H bond and the hydrogen atom produces an intensive electron-withdrawing (inductive) effect on the neighbouring groups through the silicon atom. The magnitude of the inductive effect of hydrogen is between that of methyl and chloromethyl groups as shown by Engelhardt's investigations[4]:

$Cl > CH_2Cl > H > CH_3$

We have already demonstrated that the bond between the phenyl group and the silicon atom is of d_π–p_π character, in agreement with other workers[5,1]. The silicon atom displays a $+I$ and a $-M$ effect towards the phenyl group. The more electronegative hydrogen atoms attached to silicon primarily influence the $+I$ effect of silicon but also, to a slight extent, 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.

EXPERIMENTAL

Two series of compounds were prepared: phenylmethane and substituted phenylmethanes, and phenylsilane and substituted phenylsilanes, respectively.

The phenylmethane derivatives (triphenylmethane, diphenylmethane, isopropylbenzene and tert-butylbenzene) were prepared by Friedel–Crafts reactions[6]. Ethylbenzene was synthesised from acetophenone by Clemmensen's reduction[7]. Tetraphenylsilane was obtained from tetraethoxysilane and chlorobenzene as already described[8]. Triphenylsilane was obtained by Grignard's reaction from silicochloroform and bromobenzene. Phenyltrisilane, methylphenyldisilane and dimethylphenylsilane were prepared by a reductive method from the appropriate chlorsilane and lithium aluminium hydride. The compounds were purified partly by distillation and partly by recrystallization. The purification was controlled using gas chromatography.

The ultraviolet spectra were recorded by means of a Spectromom Type 201 ultraviolet spectrophotometer, using cyclohexane solutions. The structure of the spectra is analogous to that of benzene. Our investigations were first concerned with the position and variation in intensity of the α-band. The characteristic spectral data are given in Table 1.

TABLE 1

UV ABSORPTION MAXIMA AND EXTINCTION COEFFICIENTS OF THE 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	37795	323.2
Ph_2SiH_2	264.8	37765	964.0
Ph_3SiH	265.2	37710	1291.0
Ph_4Si	265.4	37680	1518.0
$PhCH_3SiH_2$	264.4	37820	279.9
$Ph(CH_3)_2SiH$	264.4	37820	232.8
$Ph(CH_3)_3Si$	265.6	37650	223.0
$PhCH_3$	262.4	38110	243.9
Ph_2CH_2	262.2	38150	422.3
Ph_3CH	262.0	38170	775.0
$PhCH_3CH_2$	261.8	38195	209.0
$Ph(CH_3)_2CH$	261.0	38300	182.9
$Ph(CH_3)_3C$	258.0	38760	198.0

RESULTS AND DISCUSSION

The wave-numbers of the absorption maxima of the silicon series were first plotted against the wave-numbers of the absorption maxima of the carbon series applying Karapetians' comparative theorem[9]. This representation does not result in a linear correlation (see Fig. 1) thus verifying the various effects that contribute to the difference (Fig. 1) between the silicon and carbon homologous series. Similarly, there is a non-linear correlation between the number of hydrogen atoms and the absorption maxima of the different series (Fig. 2). The characteristic curves of the silicon and carbon series are of different slope. An increase in the number of hydrogen atoms causes a bathochromic shift in the spectrum of the $Ph(CH_3)_xCH_{(3-x)}$ series because the hyperconjugation, of identical direction, of the increasing number of hydrogens strengthens the $+I$ effect of the carbon atom attached to the phenyl ring. This leads to an upward shift of one of each degenerated π–π^* levels of benzene which increases with the number of hydrogen atoms.

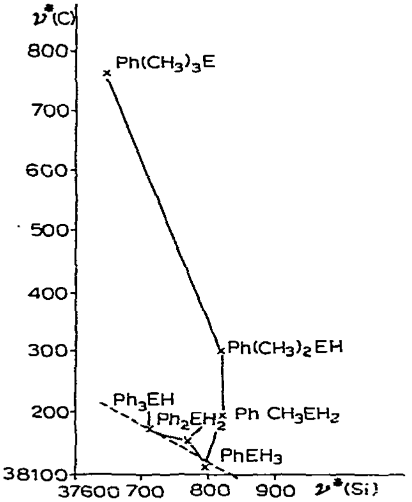

Fig. 1. Correlation between the absorption wave-numbers of $Ph_xSiH_{(4-x)}$ and $Ph(CH_3)_xSiH_{(3-x)}$ series and of the analogous carbon compounds.

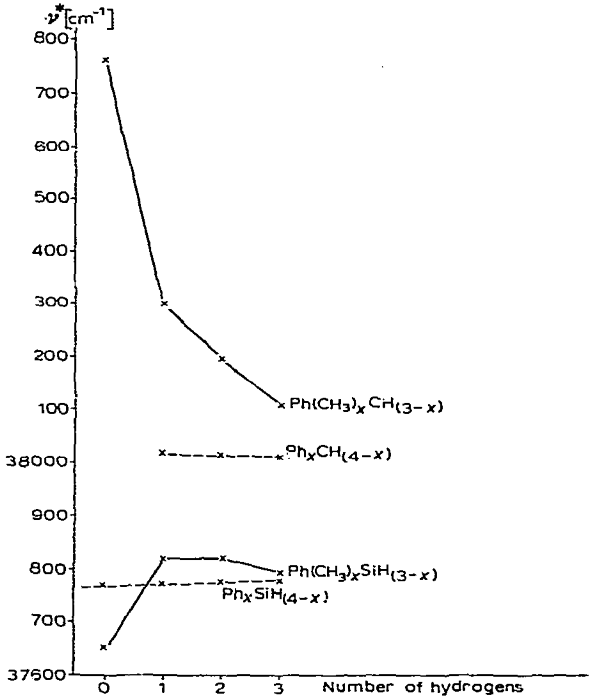

Fig. 2. Absorption wave-numbers of $Ph_xSiH_{(4-x)}$ and $Ph(CH_3)_xSiH_{(3-x)}$ series as a function of number of hydrogen atoms.

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

$$H > Ph > CH_3$$

The hydrogen atoms entering decrease the $+I$ effect of silicon and thus the $-M$ effect, the d_π–p_π bond character also decreases. The latter leads to a diminution of the coulomb integral of silicon which produces the hypsochromic shift predicted by quantum chemical calculations[5]. This phenomenon is illustrated by the hypsochromic shift produced by increasing the number of hydrogen atoms in compounds of the $Ph_xSiH_{(4-x)}$ series; an opposite shift is found in the case of the carbon analogues. The $Ph(CH_3)_xSiH_{(3-x)}$ series (where $x=0$, 1, 2) shows a lower hypsochromic shift compared to trimethylphenylsilane. Hydrogen atoms bonded to silicon have only inductive (and no hyperconjugative) effect, verified by the small hypsochromic shifts. This supposition is also supported by other experimental data; for example, a very small hypsochromic shift, compared to trimethylphenylsilane, is found in the spectra of phenyltriethoxysilane (λ_{max}, 263.8 nm; ε_{max}, 440) and methylphenyldiethoxysilane

TABLE 2

GROUP ELECTRONEGATIVITY IN THE $Ph_xSiH_{(4-x)}$ SERIES

Compound	Group electronegativity
$PhSiH_3$	2.151
Ph_2SiH_2	2.135
Ph_3SiH	2.119
Ph_4Si	2.103

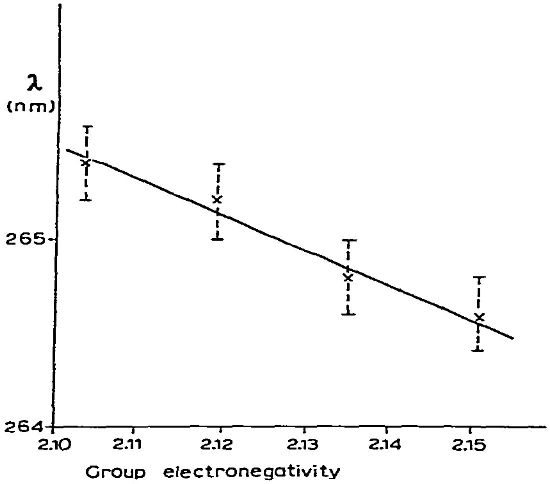

Fig. 3. Group electronegativity of $-SiH_{(4-x)}$ as a function of absorption maxima wavelength of series, $Ph_xSiH_{(4-x)}$.

(λ_{max}, 263.6 nm; ε_{max},350). The Si–H and Si–O bonds have roughly equal dipole moments while there is a large d_π–p_π interaction of opposite direction besides a large inductive effect (+I) producing the same partial charge (~0.15) as in the Si–H bond.

In order to substantiate the above hypothesis we calculated the electronegativity of the $SiH_{(4-x)}$ silyl group (Table 2) on the basis of Ponomarenko and Yegorov's[10] investigations and plotted these electronegativities against wavelengths of UV maxima. The correlation is linear as shown in Fig. 3 and proves the exclusive presence of inductive effects, because group electronegativity mainly influences inductive effect. The other series of compounds observed does not show such good linearity.

Therefore, the +I effect of silicon is reduced with increasing number of hydrogen atoms as verified experimentally by the increase in UV maxima intensities in the $Ph(CH_3)_xSiH_{(3-x)}$ series.

Earlier, Robertson and Matsen[11] established by means of quantum-chemical calculations that the inductive effect of substitution of the phenyl ring mostly changes the coulomb integral of the carbon atom substituted and the inductive effect for the most part is responsible for the alteration of intensity. Oscillator strength is expressed as follows:

$$f = 1.085 \cdot 10^{-5}\, v^* D G$$

where v^* is the wavenumber of the UV maximum (which changes only to a very small extent in the series of compounds investigated), D is dipole strength and G is degree of degeneration (1 in the present case). Therefore, alteration of intensity is related to transition dipole strength. In order to determine the relation between inductive effect, mesomeric effect and absorption intensity we carried out quantum-chemical calculations of the phenylsilicon group by Hückel's LCAO-MO one-electron molecular orbital calculation method. The coulomb integral for carbon atoms of the ring was taken as α, the resonance integral for the carbon–carbon bond as β, the coulomb integral for the carbon atom bonded to silicon as $(\alpha - \delta_1\beta)$, the coulomb integral for silicon as $(\alpha - \delta_0\beta)$ and the resonance integral for the silicon–carbon bond as 0.3β, δ_0 and δ_1 are variation parameters. The results of the calculations are presented in Fig. 4 and demonstrate that change of mesomeric effect (δ_0) has little influence on

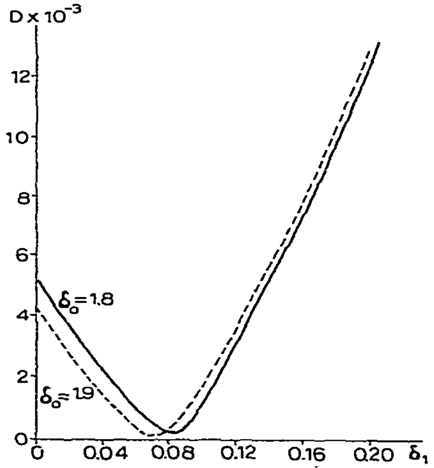

Fig. 4. Change of dipole strength as a function of variation parameters, δ_0 and δ_1.

absorption intensity. The transition dipole-moment passes through a minimum with alteration of inductive effect (δ_I). The inductive effect decreases and absorption maximum intensities increase with increase in the number of hydrogen atoms in the $Ph(CH_3)_xSiH_{(3-x)}$ series, *i.e.*, the conditions are proper to the left-hand part of the curves.

TABLE 3

VALUES OF DEL RE'S PARAMETERS

	C–C	C–H	C–Si	Si–H
ε_{A-B}	1.00	1.00	0.90	0.125
δ_A^0	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
$\gamma_{B(H)}$	0.1	0.4	0.2	0.4

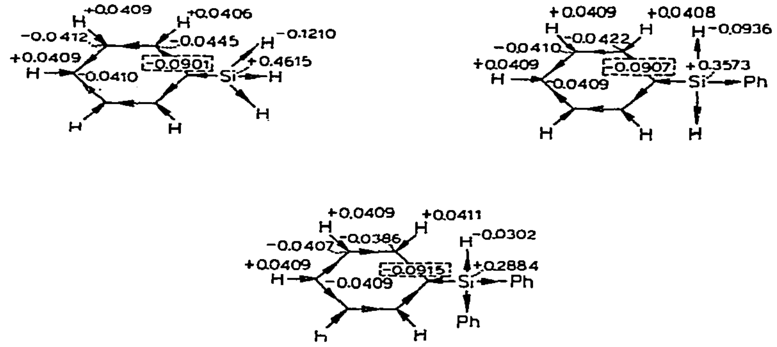

Fig. 5. σ-Charge distribution of compounds of series, $Ph_xSiH_{(4-x)}$.

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

The calculations were performed by Del Re's modified method[12]. Actual values of coulomb, inductive and resonance parameters are given in Table 3, where resonance integrals are indicated as ε, coulomb parameters as δ_0 and inductive parameters as γ.

Approximate 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 are presented in Fig. 5. The scheme demonstrates the growing partial negative charge of the aromatic carbon bonded to silicon with decrease in the number of hydrogen atoms, indicating the increasing $+I$ effect of silicon. The polarity of the silicon–hydrogen bond (negative charge of the hydrogen atom) diminishes at the same time in accordance with the change of NMR signal. The values of chemical shifts (τ-signals) are as follows: 5.81 for phenyltrisilane; 5.14 for diphenylsilane; 4.57 for triphenylsilane. The charge of the hydrogen of the ring varies only to a small extent.

For the $Ph(CH_3)_xSiH_{(3-x)}$ series, Del Re's approximate calculation shows that the members of the series show roughly identical σ-charge distribution. The effects are more striking when the calculations are made for analogous systems where the phenyl group is exchanged for the vinyl group. σ-Charge distributions of the first and last members of the series are presented in Fig. 6. The tendency of the $+I$ effect of the silicon atom towards the connecting carbon to increase and the partial negative charge of this atom, together with the decrease of the number of hydrogen atoms, is also to be seen here.

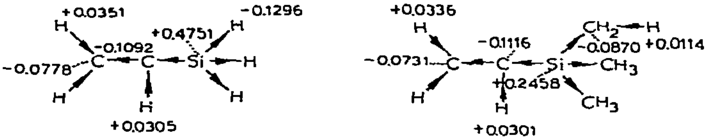

Fig. 6. σ-Charge distribution of compounds, $(CH_3)_3SiCH{=}CH_2$ and $H_3SiCH{=}CH_2$.

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