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THE INTENSITY OF Si—H STRETCHING MODES AND CONJUGATION EFFECTS IN TRISUBSTITUTED SILANES $(R_i)_3SiH$

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Summary

The contributions of the effect of conjugation between the silicon atom and the R_i substituents, to the integrated intensity of ν(Si—H) modes ($\Delta A^{1/2}$) have been estimated for the IR spectra of 27 triorganosilanes. The nature of the relationship between the $\Delta A^{1/2}$ values and the sums of σ_p constants of the substituents has been determined for compounds where d_π—p_π interaction is the only type of conjugation present. In $(Alk)_nX_{3-n}SiH$ molecules with an Si—X bond of d_π—p_π character the n-alkyl groups possess abnormally high electron-donating properties which are probably caused by σ,d conjugation.

Introduction

Studies of the integrated intensity (A) of Si—H stretching modes in $(R_i)_3SiH$-type [1,2] and $(R_i)_2SiH_2$-type molecules [3] indicate that the intensity depends on the inductive effect of R_i substituents and on the effect of d_π—p_π interaction in Si—R_i fragments. Conclusions concerning the contribution of the d_π—p_π interaction derived from analysis of the Si—H mode intensities correspond, in general, to specific spectroscopic features of the d_π—p_π bonding effect established earlier during studies of frequencies of Si—H stretching modes of the same silane derivatives [4-12].

Analysis of frequencies and intensities of Si—H vibrations provides two essentially different sources of information concerning d_π—p_π interaction. According to the theory of vibration spectra [13,14], intensity is more sensitive than frequency to the influence of electronic effects of substituents. As established previously, the existence of σ,σ conjugation in the ground electronic state of organosilicon compounds can be derived from ν(Si—H) data [9,11]. Analysis of A(Si—H) intensities, in our opinion, should provide a closer insight into the above-mentioned effect. This was the first aim of our investigation. The second aim was to obtain additional data on the nature of the d_π—p_π interaction effect in organosilicon compounds.

Results and discussion

The $\Delta A^{1/2}$ values obtained in the present study and reported elsewhere [1, 2,15] are presented in Table 1. As described earlier in detail [2,3] $\Delta A^{1/2}$ represents the difference between the square roots of experimental values of ν(Si—H) mode intensities ($A^{1/2}_{\text{exp}}$) and of the values of intensities calculated with the assumption that intensity is only affected by the inductive effect of the substituents ($A^{1/2}_{\text{ind}}$).

As we have shown previously [1,2], the relationship between $A^{1/2}$ values of

TABLE 1

VALUES OF A, $\Delta A^{1/2}$, δ AND $\Sigma\sigma_p$ IN THE IR SPECTRA OF THE COMPOUNDS STUDIED

No.	Compound	A_{exp}	$\Sigma\sigma_p$	$\Delta A^{1/2}$	$\Delta A^{1/2}_{\text{calc}}$	δ
1	$(p\text{-}CH_3C_6H_4)_3SiH$	1.54[a]	0.03[b]	0.15		
2	$(C_6H_5)_3SiH$	1.40	0.03	0.18		
3	$(p\text{-}CH_3OC_6H_4)_3SiH$	1.61[a]	0.03	0.19		
4	$Cl(C_6H_5)_2SiH$	1.00	0.24	0.43		
5	$Cl_2(CH_2{=}CH)SiH$	0.80	0.42	0.76		
6	$Cl_2(p\text{-}BrC_6H_4)SiH$	0.77	0.45	0.80		
7	Cl_3SiH	0.48[a]	0.66	0.99		
8	$(C_6F_5)_3SiH$	0.47	1.02[c]	1.66		
9	$C_2H_5(p\text{-}CH_3C_6H_4)_2SiH$	1.53	−0.13	0.04	−0.07	0.11
10	$CH_3(p\text{-}CH_3C_6H_4)_2SiH$	1.59	−0.15	0.08	−0.10	0.18
11	$CH_3(C_6H_5)_2SiH$	1.59[d]	−0.15	0.14	−0.10	0.24
12	$C_2H_5(C_6H_5)_2SiH$	1.87	−0.13	0.23	−0.07	0.30
13	$CH_3Cl(CH_2{=}CH)SiH$	1.35	0.03	0.48	0.16	0.32
14	$CH_3Cl(p\text{-}ClC_6H_4)SiH$	1.12	0.06	0.43	0.21	0.22
15	$CH_3Cl(o\text{-}ClC_6H_4)SiH$	1.03	0.06	0.36	0.21	0.15
16	$CH_3Cl(\alpha\text{-}C_4H_3S)SiH$[e]	1.29	0.11	0.52	0.28	0.24
17	$CH_3Br(\alpha\text{-}C_4H_3S)SiH$[e]	1.38	0.12	0.53	0.29	0.24
18	CH_3Cl_2SiH	0.94	0.27	0.72	0.52	0.20
19	$(C_2H_5)Cl_2SiH$	0.96	0.29	0.71	0.54	0.17
20	$(CH_3)_2(p\text{-}CH_3C_6H_4)SiH$	1.65	−0.33	0.00	−0.36	0.36
21	$(CH_3)_2(C_6H_5)SiH$	1.69	−0.33	0.06	−0.36	0.42
22	$(CH_3)_2(p\text{-}ClC_6H_4)SiH$	1.64	−0.33	0.10	−0.36	0.46
23	$(n\text{-}C_4H_9)_2(p\text{-}CH_3C_6H_4)SiH$	1.60	−0.31	0.00	−0.34	0.34
24	$(n\text{-}C_3H_7)_2(p\text{-}CH_3C_6H_4)SiH$	1.86	−0.23	0.05	−0.22	0.27
25	$CH_3Cl[(CH_3)_3SiCH_2]SiH$	1.34	−0.16	0.31	−0.11	0.42
26	$(CH_3)_2ClSiH$	1.37	−0.12	0.37	−0.06	0.43
27	$(C_2H_5)_2ClSiH$	1.39	−0.08	0.34	0.00	0.34

[a] Ref. 16. [b] The value of σ_p for X—C_6H_4-groups was assumed to be +0.01. [c] The value of σ_p for the C_6F_5-group was taken to be +0.34 (the mean value of data reported in ref. 18). [d] Ref. 17. [e] —C_4H_3S = 2-thienyl.

$(R_i)_3SiH$ silane derivatives ($A^{1/2}_{ind}$) and the sum of Taft inductive constants ($\Sigma\sigma^*$) of R_i substituents can be expressed by equation 1 if R_i do not form d_π—p_π bonds with the silicon atom.

$$A^{1/2}_{ind} = 1.35 - 0.19\ \Sigma\sigma^* \qquad (1)$$

Thus $\Delta A^{1/2}$ is not zero only for compounds whose substituents undergo conjugation with the silicon atom (for example by d_π—p_π interaction). The $\Delta A^{1/2}$ values of $(R_i)_3SiH$ compounds characterize the influence of conjugation effects in R_i—Si fragments on the intensity (and consequently on the polarity) of the Si—H bond. The difference ($\Delta\nu$) between the frequency of Si—H modes is calculated with the assumptions that the frequency position is influenced only by the inductive effect (ν_{ind}) and that the experimental value of the frequency (ν_{exp}) is an independent quantity that characterizes the conjugation effect in silane derivatives. The $\Delta\nu$ values for silane derivatives have been studied previously (see for example refs. 4-12). The values reflect the influence of the effect of conjugation with the silicon atom on the Si—H bond energy. The $\Delta\nu$ and $\Delta A^{1/2}$ values characterize two different properties of the Si—H bond, namely, its energy and polarity, respectively.

The experimental data obtained indicate that the influence of conjugation effects on the intensity is more pronounced in comparison with their influence on the frequency. Thus, the experimental value of ν(Si—H) increases by 160 cm^{-1} (8%) from $(C_2H_5)_3SiH$ to Cl_3SiH, and the value $\Delta\nu$ is 55 cm^{-1} (2.5%). For the same compounds $A^{1/2}$ increases by 0.72×10^2 $mol^{-1/2}\ l^{1/2}\ cm^{-1}$ (51%) and the value of $\Delta A^{1/2}$ is near 1.0×10^2 $mol^{-1/2}\ l^{1/2}\ cm^{-1}$ (71%). Owing to the high sensitivity of intensity to conjugation effects, the compounds under investigation were divided into two groups. In compounds 1-8 (group I) the only conjugation effect possible is d_π—p_π interaction. In compounds 9-27 (group II) σ,σ conjugation may also occur.

Let us consider the $\Delta A^{1/2}$ values for compounds of the first group. As can be seen from Table 1, the values vary over a wide range depending on the nature of the three substituents at the silicon atom. This indicates a considerable variation in the degree of d_π—p_π interaction in the given compounds for different substituents. The data reported on the nature of d_π—p_π interaction effects enable us to relate the value of $\Delta A^{1/2}$ to the electronic effects of substituents. According to theoretical studies, d_π —p_π bonding increases with an increase in the effective positive charge on an atom possessing a vacant *d*-orbital [10-12,19,20]. Determination of the absolute value of the charge on a silicon atom is a difficult task and has been solved only for a limited number of compounds. For $(C_6H_5)_3SiH$ and Cl_3SiH the charge values on the silicon atom, expressed in units of electron charge are +0.18 and +0.29, respectively [21]. The task can be simplified by determining values proportional to the effective charges on the silicon atom. For $(R_i)_3SiH$ compounds (where R_i are substituents that do not form d_π—p_π bonds with the silicon atom) the positive effective charge increases with the electron-attracting properties of the R_i substituents, i.e. with an increase in the —*I* effect of these substituents. In correlation analysis the inductive effect is quantitatively expressed by σ_i values. Introduction of typical electron-attracting substituents (for example, halogens) to a silane molecule changes the effective charge in a more complex way. Typical electron-attracting substituents form d_π—p_π bonds with the silicon atom. The —*I* effect and the effect of d_π—p_π interaction have opposing results. A —*I* effect creates a positive charge on the silicon atom, while d_π—p_π interaction, which is accompanied by electron density transfer to the silicon atom, produces a negative charge. So, the resultant value of the effective charge on the silicon atom is determined by the relation between donor (d_π—p_π interaction) and acceptor (—*I* effect) properties of the substituents. The change of the effective charge on the silicon atom under the influence of d_π—p_π interaction effect (or of —*I* effect) can be expressed quantitatively. The mechanism of d_π—p_π interaction between the silicon atom and substituent X is formally similar to the effect of conjugation between substituent X and an aromatic ring or a vinyl group [5]. Therefore, the relative capabilities of substituents to form d_π—p_π bonds with silicon atoms may be correlated with their resonance constants σ_R.

Thus, the sum $\sigma_I + \sigma_R$ is a quantity proportional to the values of the effective charges on the silicon atom under the influence of the substituents. This sum represents the Hammet constant σ_p. If we assume in the first approximation that the substituents affect the charge on the silicon atom independently, then a quantity proportional to the effective charge is obtained by summing the σ_p constants of the substituents (the values of $\Sigma\sigma_p$ are presented in Table 1). Bearing in mind this assumption, a correlation between the values of $\Delta A^{1/2}$ and $\Sigma\sigma_p$ of the substituents for compounds 1-8, where d_π—p_π interaction is the only type of conjugation possible, is valid (Fig. 1). The relationship between these two values is expressed by a linear equation (eqn. 2).

$$A^{1/2} = 1.47\ \Sigma\sigma_p + 0.12 \quad (r = 0.996) \tag{2}$$

The linear relationship between the degree of d_π—p_π interaction and the

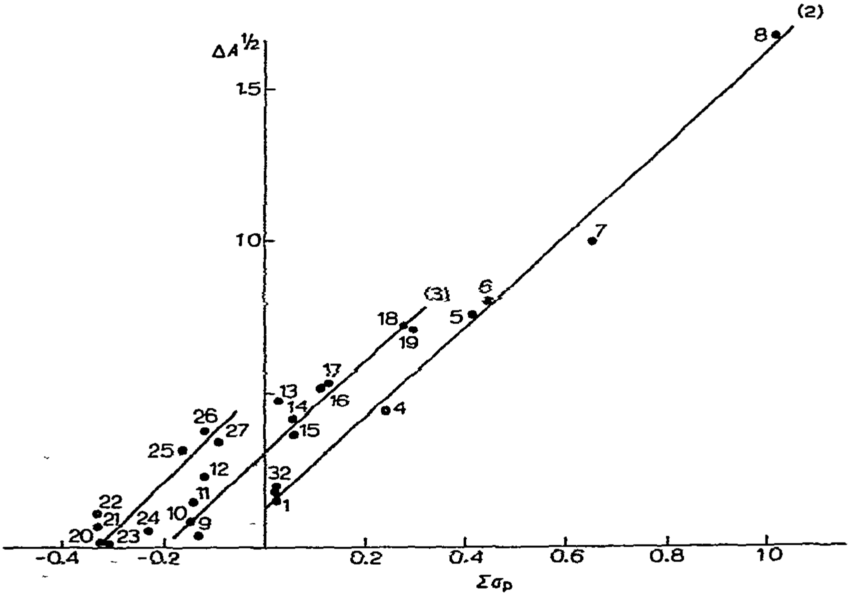


Fig. 1. The interdependence of $\Delta A^{1/2}$ and $\Sigma\sigma_p$. The numbering of the points refer to the numbering of compounds in Table I.

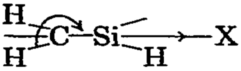
charge on the silicon atom was established previously while studying the frequency of ν(Si—H) stretching modes in arylsilanes [11].

Let us now consider the values of $\Delta A^{1/2}$ for compounds 9-27 of the second group. These compounds contain n-alkyl groups bonded to the silicon atom, along with substituents that undergo $d_\pi—p_\pi$ interaction with this atom. Therefore, both conjugation effects ($d_\pi—p_\pi$ interaction and σ,σ conjugation) may be expected here. As shown in Fig. 1, the points corresponding to compounds 9-27 deviate from the linear graph (2) representing the relationship between $\Delta A^{1/2}$ and $\Sigma\sigma_p$ for the compounds of the first group. The degree of deviation for compounds with two n-alkyl groups at the silicon atom (20-27) is twice as great as for compounds with only one n-alkyl group (see also in Table 1 the values of δ that represent the difference between experimental values of $\Delta A^{1/2}$ and values of $\Delta A^{1/2}_{\text{calc}}$ calculated from equation 2). The mean value of δ for compounds 9-19 is 0.22 ± 0.05 and for compounds 20-27 it is 0.38 ± 0.05; i.e. the relationship between $\Delta A^{1/2}$ and $\Sigma\sigma_p$ for these two groups of compounds may be expressed by equations 3 and 4.

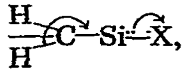
$$\Delta A^{1/2} = 1.47\ \Sigma\sigma_p + 0.34 \qquad (3)$$

$$\Delta A^{1/2} = 1.47\ \Sigma\sigma_p + 0.50 \qquad (4)$$

The values $\delta_1 = 0.22$ and $\delta_2 = 0.38$ represent a contribution of the effect of σ,σ conjugation between one or two n-alkyl groups and the silicon atom. The considerable effect of electron-donating properties of alkyl groups on the polarity of the Si—H bond should be taken into account when studying



σ,σ conjugation. Abnormally high electron-donating properties of alkyl groups lead to high values of $A^{1/2}_{\text{exp}}$. Since, when calculating $A^{1/2}_{\text{ind}}$, n-alkyl groups are assumed to produce only an inductive effect, the difference $\Delta A^{1/2} = A^{1/2}_{\text{exp}} - A^{1/2}_{\text{ind}}$ is abnormally high for compounds with σ,σ conjugation. Analysis of δ values and of the relative positions of the linear graphs in Fig. 1, indicates that σ,σ conjugation effects are higher when the molecule contains two n-alkyl groups.

In conclusion, let us study more closely the mechanism of the phenomenon that we considered to be σ,σ conjugation, in accordance with classical conceptions. Analysis of frequency and intensity of Si—H stretching modes as well as consideration of chemical shifts in NMR spectra [1-4,22,23] established that alkyl groups of organosilicon compounds that do not exhibit the effect of $d_\pi—p_\pi$ interaction evidently possess only an inductive effect and do not undergo conjugation. The total inductive effect of substituents bonded to the silicon atom may reach 1.5 in units of σ^* (for example, in $ClCH_2(CH_3)SiH_2$). It has been shown for the methyl group, that if there are other substituents bonded to the silicon atom, as well as a methyl group, which are capable of $d_\pi—p_\pi$ interaction, then the anomalous properties of the CH_3 group are distinctly revealed by a lower total inductive effect of substituents [11,12]. Thus, anomalous properties of n-alkyl groups are observed when the $3d$-orbitals of the silicon atom are involved in conjugation. Therefore, in our opinion, it is more correct to interpret conjugation involving n-alkyl groups as σ,d conjugation rather than as σ,σ conjugation. This can be described by the structure  $\mathrm{H_2C{-}Si{-}X}$, where the Si—X bond has partial multiple character due to d_π—p_π interaction.

Experimental

IR spectra of carbon tetrachloride solutions (0.04-0.09 mol l^{-1}) were measured on a UR-20 "zeiss" spectrometer. The instrument was calibrated using compounds containing a Si—H bond that had been studied previously (for example $(C_2H_5)_3SiH$ and $(C_6H_5)_3SiH$). The integrated intensity A(mol^{-1} l cm^{-2} × 10^4) of the Si—H bonds was measured by Iogansen's method [24].

The purity of the investigated compounds was controlled by means of GLC analysis. Preparative chromatography was employed when the impurity content exceeded 2%.

The investigated compounds were prepared by previously described methods [25].

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