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THE INTENSITY OF Si–H STRETCHING MODES AND THE EFFECT OF d_π–p_π INTERACTION IN ORGANOSILICON COMPOUNDS OF THE TYPE RR′R″SiH

A. N. EGOROCHKIN, N. S. VYAZANKIN and N. S. OSTASHEVA
Institute of Chemistry, U.S.S.R. Academy of Sciences, Gorky (U.S.S.R.)

O. V. KUZ'MIN and N. S. NAMETKIN
Topchiev Institute of Petrochemical Synthesis, U.S.S.R. Academy of Sciences, Moscow (U.S.S.R.)

I. F. KOVALEV and M. G. VORONKOV
Institute of Organic Chemistry, Siberian Department of the Academy of Sciences of the U.S.S.R., Irkutsk (U.S.S.R.)

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SUMMARY

The integrated intensity of the Si–H stretching mode in 20 triorganosilanes, R_3SiH, in which the R substituents exhibit no d_π–p_π bonding with the silicon atom has been measured. The intensity (A) is related to the sum of the Taft σ^* constants of the substituents R($\Sigma\sigma^*$) via the equation $A^{\frac{1}{2}} = -0.19\Sigma\sigma^* + 1.35$. When the substituents in R_3SiH undergo d_π–p_π bonding with the silicon atom the intensity is also influenced by the I effect of the substituents as well as by their d_π–p_π interaction. A comparison is made of two independent methods for estimating d_π–p_π interaction, *i.e.* analysis of the frequencies of the Si–H stretching modes and an analysis of their intensities.

INTRODUCTION

The frequency of the Si–H stretching mode, ν(Si–H), in the spectra of trisubstituted silanes, R_3SiH, is determined (*i*) by the inductive effect of the R substituents and (*ii*) by their conjugation with the silicon atom[1–6]. For R_3SiH compounds where type (*ii*) effects are absent, the dependence of ν(Si–H) on the sum of the inductive constants of the substituents ($\Sigma\sigma^*$) is linear[3]:

$$\nu = 2112 + 23.1\,\Sigma\sigma^* \tag{1}$$

This is a natural consequence of the high specificity of this mode of vibration. It has been accepted[2–6] that in trisubstituted silanes which possess effects of type (*ii*) the importance of the I effect in relation to the value of ν(Si–H) can also be described by eqn. (1). Equation (1) allows an estimation of the effect of conjugation upon the value of ν(Si–H). Thus using eqn. (1), calculated values of the frequencies, ν_{calc}, were found and the differences $\Delta\nu = \nu_{calc} - \nu_{exp}$ [where ν_{exp} is the experimental value of ν(Si–H)] were determined. The magnitude of the difference $\Delta\nu$ may be directly related to the conjugation effect. If d_π–p_π interaction is the main conjugation effect then the values of $\Delta\nu$ are positive. The effect of d_π–p_π interaction is opposite to the inductive substituent effect and for this reason it may be considered as equivalent to a decrease in the latter, leading to a decrease both in the value of the Si–H force constant and ν(Si–H). Analysis of the value of ν(Si–H) has therefore enabled an investigation of the effect of d_π–p_π interaction between a silicon atom and one[7], two and three[8,9] substituents, and has led to a discussion of the nature of the d_π–p_π interaction effect[7] and its dependence on the charge on the silicon atom[8,10]. It has also provided an estimation of other conjugation effects (σ, σ; σ, π; σ, p) in organosilicon compounds[10–12].

It has been suggested (see for example ref. 13) that a study of the intensities of the infrared absorption bands could lead to a much greater amount of information on the electronic substituents effects than an investigation of the frequencies of individual modes. For this reason, the present work has been undertaken with the aim of using the integrated intensities of Si–H stretching modes for estimating the extent of d_π–p_π interaction in organosilicon compounds.

RESULTS AND DISCUSSION

It is well-known[14–16] that the integrated intensity of the Si–H bands depends on the nature of the three substituents bound to the silicon atom. In general it is expected that the intensity will decrease as the electron-attractive substituent effect increases.

The mode of the Si–H vibration is highly characteristic. If only the Si–H coordinate is considered the contribution of all other coordinates to this mode may be ignored[17]. Under these circumstances only the Si–H bond takes part in the vibration discussed, while the bulk and mass of the R substituent has no effect on either the frequency or the mode of this vibration. For this reason the integrated intensity of the Si–H stretching mode should be determined by the square of the first derivative of the dipole moment of the Si–H bond in the Si–H normal coordinate:

$$\left(\frac{\partial\mu(\text{Si–H})}{\partial q(\text{Si–H})}\right)^2$$

On the basis of this argument it follows that changing the R substituents should change the intensities of the Si–H band. This may be explained in terms of the electronic effect of these substituents on the dipole moment of the Si–H bond. To a first approximation, the electronic effects of the substituents may be separated into the sum of the components of the inductive and conjugation effects[18]. Thus for a study of the conjugation effects arising from the interaction of the silicon atom with various substituents on the basis of the Si–H band intensities it is necessary (*a*) to establish the pattern of dependency between the Si–H band intensities and the inductive effect of the three substituents at the silicon atom and (*b*) to possess a method for separating the influence of the inductive and conjugation effects (including d_π–p_π interaction) on the intensity.

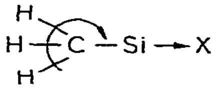
In order to investigate the dependence of the integrated intensity of the Si–H mode on the *I* substituent effect where that substituent is R in R_3SiH molecules, it is necessary that a sufficient number of compounds should be available in which the substituents influence the Si–H band intensities via the inductive mechanism alone. Hence we have employed the intensities of the Si–H bands in the spectra of those

TABLE 1

No.	*Compound*	$A^{\frac{1}{2}}_{exp}$	$\Sigma\sigma^{\star}$	$A^{\frac{1}{2}}_{calc}$	$\Delta A^{\frac{1}{2}}$	$\Delta\nu^{a}$ (cm^{-1})
1	$(n\text{-}C_5H_{11})_3SiH$	1.40[b]	−0.49	1.44	−0.04	
2	$C_2H_5(n\text{-}C_5H_{11})_2SiH$	1.44	−0.42	1.43	+0.01	
3	$(n\text{-}C_4H_9)_3SiH$	1.45[b]	−0.39	1.42	+0.03	
4	$C_2H_5(n\text{-}C_4H_9)_2SiH$	1.42	−0.35	1.42	0.00	
5	$(n\text{-}C_3H_7)_3SiH$	1.46[b]	−0.345	1.42	+0.04	
6	$C_2H_5(n\text{-}C_3H_7)_2SiH$	1.43	−0.33	1.41	+0.02	
7	$(C_2H_5)_3SiH$	1.41[c]	−0.30	1.41	0.00	
8	$ClCH_2CH_2CH_2(n\text{-}C_3H_7)_2SiH$	1.30	−0.09	1.36	−0.06	
9	$ClCH_2CH_2CH_2(C_2H_5)_2SiH$	1.31	−0.06	1.36	−0.05	
10	$(ClCH_2CH_2CH_2)_2(C_2H_5)SiH$	1.29	+0.18	1.32	−0.03	
11	$ClCH_2(n\text{-}C_3H_7)_2SiH$	1.22	+0.82	1.19	+0.03	
12	$ClCH_2(C_2H_5)_2SiH$	1.19	+0.85	1.19	0.00	
13	$CH_3(n\text{-}C_5H_{11})_2SiH$	1.37[d]	−0.32	1.41	−0.04	
14	$CH_3(n\text{-}C_4H_9)_2SiH$	1.36[d]	−0.26	1.40	−0.04	
15	$CH_3(n\text{-}C_3H_7)_2SiH$	1.40	−0.23	1.39	+0.01	
16	$CH_3(C_2H_5)_2SiH$	1.34	−0.20	1.39	−0.05	
17	$(CH_3)_3SiH$	1.40[b]	0.00	1.35	+0.05	
18	$ClCH_2CH_2CH_2(CH_3)(C_2H_5)SiH$	1.36	+0.04	1.35	+0.01	
19	$ClCH_2CH_2CH_2(CH_3)_2SiH$	1.33	+0.14	1.32	+0.01	
20	$(ClCH_2CH_2CH_2)_2(CH_3)SiH$	1.27	+0.28	1.30	−0.03	
21	$(i\text{-}C_5H_{11})_3SiH$	1.36	−0.49	1.44	−0.08	
22	$C_2H_5(i\text{-}C_5H_{11})_2SiH$	1.39	−0.42	1.43	−0.04	
23	$(i\text{-}C_4H_9)_3SiH$	1.35	−0.375	1.42	−0.07	
24	$CH_3(i\text{-}C_4H_9)_2SiH$	1.32	−0.25	1.40	−0.08	
25	$(i\text{-}C_3H_7)_3SiH$	1.37	−0.57	1.46	−0.09	
26	$C_2H_5(i\text{-}C_3H_7)_2SiH$	1.39	−0.48	1.44	−0.05	
27	$C_6H_5(CH_3)_2SiH$	1.30[e]	+0.60	1.24	+0.06	6
28	$(C_6H_5)_2(CH_3)SiH$	1.26[f]	+1.20	1.12	+0.14	16
29	$(C_6H_5)_3SiH$	1.12[g]	+1.80	1.01	+0.11	28
30	$(n\text{-}CH_3C_6H_4)_3SiH$	1.24[b]	+1.35	1.09	+0.15	16
31	$(n\text{-}CH_3OC_6H_4)_3SiH$	1.27[b]	+1.41	1.08	+0.19	26
32	$(n\text{-}ClC_6H_4)_3SiH$	1.12[b]	+2.61	0.85	+0.27	36
33	$Cl(CH_3)_2SiH$	0.97[b]	+2.90	0.80	+0.17	11
34	$Cl_2(CH_3)SiH$	0.96[b]	+5.80	0.25	+0.71	33
35	Cl_3SiH	0.69[b]	+8.70	−0.30	+0.99	55
36	$Cl(C_6H_5)_2SiH$	1.00[b]	+4.10	0.57	+0.43	39
37	$(AlkO)_3SiH$	1.25[f]	+4.50	0.50	+0.75	10
38	$(C_6H_5O)_3SiH$	0.73[f]	+7.14	0.00	+0.73	44

[a] $\Delta\nu$ values are taken from refs. 3–7. [b] Ref. 14. [c] Lit. value[14]: $A^{\frac{1}{2}} = 1.40$. [d] Ref. 16. [e] Lit. value[15]: $A^{\frac{1}{2}} = 1.29$. [f] Ref. 15. [g] Lit. value[15]: $A^{\frac{1}{2}} = 1.14$.

R_3SiH compounds[14–16] in which R is an alkyl group starting from $R{=}C_2H_5$ (compounds 1,3,5 and 7 in Table 1). In particular we have used no data on molecules with the methyl group attached to the silicon atom (or with a branched alkyl radical) since in the former case conjugation may take place *i.e.*

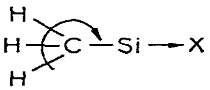


while in the second case the tetrahedral bond angles of the silicon atom may be distorted through steric hindrance. We have also investigated the integrated intensity of the Si–H modes in the spectra of R_3SiH compounds where $R = ClCH_2CH_2CH_2$ or $ClCH_2$ (Table 1, compounds 8–12). Since the chlorine and silicon atoms in these compounds are separated by methylene groups the normal d_π–p_π interaction between the 3*d* orbitals of the silicon and the electron pairs of the chlorine is not observed. Thus the above substituents exhibit only the inductive effect.

Brown[19] has given a theoretical explanation for the correlation between the σ constants of Hammett and Taft and the $A^{\frac{1}{2}}$ value where A is the integrated intensity of a particular band. According to Brown, these two quantities are connected by the linear equation,

$$A^{\frac{1}{2}} = 1.35 - 0.19\,\Sigma\sigma^* \quad (\text{for } r = 0.93) \tag{2}$$

where $A =$ the integrated intensity of a Si–H band in the IR spectra of compounds 1–12, and $\Sigma\sigma^*$ the sum of the Taft inductive constants for the three substituents bound to the silicon atom. From eqn. (2) the $A^{\frac{1}{2}}_{\text{calc}}$ values may be determined for compounds 13–20 where methyl groups are bound to the silicon atom. These values are virtually identical with the $A^{\frac{1}{2}}_{\text{exp}}$ value. Thus σ,σ conjugation in



does not essentially affect the integrated intensity of the Si–H modes, provided that the substituents attached to the silicon (*i*) do not undergo $d_\pi - p_\pi$ interaction and (*ii*) produce an overall inductive effect less than unity on the σ^* scale. This conclusion is in agreement with results obtained for the dependence of the inductive effect of the substituents on the ν(Si–H) values. Equation (2) is valid for all substituents which do not undergo d_π–p_π interactions with the silicon atom and including methyl groups[3].

The $A^{\frac{1}{2}}_{\text{calc}}$ values for compounds 21–26 containing branched alkyl groups bound to the silicon atom were also found from eqn. (2). In all cases the $A^{\frac{1}{2}}_{\text{exp}}$ values were considerably less than the $A^{\frac{1}{2}}_{\text{calc}}$ values. This may be due to the fact that the branched groups distort the tetrahedral bond angles of the silicon atom.

Turning to the intensities of the Si–H bands for those compounds in which the substituents undergo d_π–p_π bonding with the silicon atom (compounds 27–28). In these cases it was found that the experimental intensities of the band in the spectra of these compounds were always greater than computed values*. This means that in compounds 27–38 the mesomeric effect influences the intensity in addition to the *I* effect. This means that the mesomeric effect is also opposite to the inductive effect. On a formal basis this may be explained by a decrease in the attractive properties of the substituents and for this reason the experimental intensities will exceed the calculated ones only if the *I* effect is taken into account. The main mesomeric effect acting in such compounds is d_π–p_π interaction and hence it is pertinent at this point

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* In computing the $A^{\frac{1}{2}}_{\text{calc}}$ values it was assumed that for all compounds involving d_π–p_π interaction the influence of the *I* effect of the substituents on the overall intensity may be described by eqn. (2). It should be noted that a similar hypothesis serves as the basis for separating the inductive and mesomeric effects in carbon chemistry[18].

to discuss d_π–p_π interaction in relation to the integrated Si–H band intensity in greater detail. The intensity of a Si–H absorption band is proportional to the square of the first derivative of the dipole moment of the bond in the normal coordinate, *i.e.*

$$A \sim \left(\frac{\partial \mu}{\partial q}\right)^2$$

Since the mode of this vibration is highly characteristic, the Si–H bond may to a good approximation be regarded as a diatomic molecule for which

$$\frac{\partial \mu}{\partial q} \approx \frac{\mu}{r_0}$$

where r_0 is an interatomic distance[13]. The difference between the electronegativities of the silicon and hydrogen atoms leads to the following polarity for the Si–H bond in trialkylsilanes *viz.* $\mathrm{Alk_3Si^{\delta+}}$–$\mathrm{H^{\delta-}}$. An increase in the electron-attractive properties of the substituents bound to the silicon atom (transition from trialkylsilanes to compounds with $ClCH_2CH_2CH_2$ and $ClCH_2$ groups) decreases the dipole moment of the Si–H bond and the band intensity of this bond*. Considering those compounds in which the substituents undergo d_π–p_π bonding with the silicon atom (compounds 27–38 of Table 1) in addition to the electron-attractive *I* effect these substituents also exhibit an electron-releasing effect due to conjugation (which arises from a shift in the electron density at the silicon atom due to d_π–p_π intreaction). As a result such substituents are less electron attractive than might be expected on the basis of their *I* effect. Thus the polarity and dipole moment of the Si–H bond and the experimental intensities of the Si–H band in compounds with such substituents are considerably greater than the values to be expected in the absence of d_π–p_π interaction.

For this reason, the difference $\Delta A^{\frac{1}{2}} = A^{\frac{1}{2}}_{\mathrm{exp}} - A^{\frac{1}{2}}_{\mathrm{calc}}$ may be used as a measure of these conjugation effects (where d_π–p_π interaction is the main constituent) in compounds 27–38. The observed values of $\Delta A^{\frac{1}{2}}$ in fact indicate a measurable increase in the Si–H bond polarity as a result of conjugation between the substituents and the silicon atom.

Analysis of the $\Delta A^{\frac{1}{2}}$ values given in Table 1 leads to the following conclusions:

(*a*). For molecules of the type R_3SiH in which at least one substituent R undergoes d_π–p_π interaction with the silicon atom, the $\Delta A^{\frac{1}{2}}$ values change over a wide range, *i.e.* from values close to zero (in dimethylphenylsilane) to 1.0 (in trichlorosilane). This indicates that the magnitude of d_π–p_π interaction is essentially determined by the nature of the neighbouring groups to the silicon atom.

(*b*). The Si–Cl bond has a greater tendency to undergo d_π–p_π interaction in relation to the Si–Aryl bond. The overall d_π–p_π effect in triorganyloxysilanes, $(RO)_3SiH$, is smaller than that in trichlorosilane, Cl_3SiH.

(*c*). Increasing the number of chlorine atoms at the silicon atom in methylchlorosilanes leads to a considerable increase in the total d_π–p_π interaction.

(*d*). Overall d_π–p_π interaction increases in going from dimethylphenylsilane to methyldiphenylsilane. In arylsilanes, the d_π–p_π nature of the Si–Aryl bond

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* Independent confirmation of the decrease in electron density at the hydrogen atom of the Si–H bond is provided by a downfield shift of the ^{1}H NMR signal when the attractive properties of the substituents at the silicon atom are increased (see, for example, refs. 20 and 21).

depends on the various substituents present in the aromatic ring. As the *I* effect of the aryl substituents increases (moving from compounds 30 and 31 to 32) the magnitude of the positive charge at the silicon atom increases with the result that d_π–p_π bonding involving the Si–Aryl group increases.

The above conclusion regarding the extent of d_π–p_π interaction deduced from an analysis of Si–H band intensities agree qualitatively with the ν(Si–H) values [3–11]. It has already been noted above that the $\Delta\nu$ values (those for compounds 27–38 are listed in the last column of Table 1) may be used as a measure of d_π–p_π interaction in the analysis of ν(Si–H) modes. Thus at first glance it might be expected that both $\Delta A^{\frac{1}{2}}$ and $\Delta\nu$ values which are quantifying the d_π–p_π effect should be proportional to each other. However, the interdependence of these quantities is non-linear:

$$\Delta\nu = 55\,(\Delta A^{\frac{1}{2}})^{\frac{2}{3}} \qquad (3)$$

The absence of a linear dependence between $\Delta\nu$ and $\Delta A^{\frac{1}{2}}$ is not surprising since the frequency and the force constant of the Si–H stretching mode is proportional to the energy, while the integrated intensity depends on the polarity (dipole moment) of the Si–H bond. Only trialkoxysilanes $(\mathrm{AlkO})_3\mathrm{SiH}$ deviate from this dependence. For these compounds the $\Delta\nu$ values are rather small while the corresponding $\Delta A^{\frac{1}{2}}$ values are large. Analysis of ν(Si–H) values shows that as the number of alkoxy groups in alkoxysilanes increases the extent of d_π–p_π interaction in the molecule decreases. The alkoxy group bound to the silicon atom acts as an electron donor[5,8,9] and thus an increase in the number of alkoxy groups leads to an increase in the negative charge at the silicon atom. For this reason the accepted values of σ^* quoted in the literature for these groups are somewhat meaningless in those cases where the $A^{\frac{1}{2}}$ values and $\Delta A^{\frac{1}{2}}$ values are high for alkoxysilanes.

Thus in the present work a comparison has been made of the value of the two methods for estimating conjugation effects in those cases where silicon atom participation occurs. Both of these methods are based on an analysis of the spectroscopic parameters associated with the Si–H bond. The first method involves an analysis of Si–H stretching frequencies which in a similar manner to the force constants are related to the bond energy of the Si–H bond. The second method involves an analysis of the integrated intensities of the Si–H stretching bands which are related to the polarity of the Si–H bond. The effect of d_π–p_π interaction involving Si–R bonds on the energy and polarity of the Si–H bond is different, and this leads to a non-linear correlation between $\Delta\nu$ and $\Delta A^{\frac{1}{2}}$.

EXPERIMENTAL

The IR spectra were measured on a UR-20 "Zeiss" spectrometer. Carbon tetrachloride solutions (0.04–0.09 mole/l) were used for the spectral investigations, the instrument being calibrated by using the simplest compounds studied containing a Si–H bond, *i.e.* $(\mathrm{C_2H_5})_3\mathrm{SiH}$, $(\mathrm{C_6H_5})_3\mathrm{SiH}$. The integrated intensity of the Si–H bands A ($\mathrm{mole^{-1}\cdot l\cdot cm^{-2}} \times 10^4$) was measured by Iogansen's method[24].

The purities of the investigated compounds were controlled by means of GLC analysis. Preparative chromatography was employed when the impurity content was greater than 2%.

Compounds 2, 4, 6, 7, 15, 21–26 were prepared using methods previously described[25]. The syntheses of the previously unreported compounds 8–12, 18–20 will be described in a separate paper. The present paper gives only their main physicochemical properties (Table 2).

TABLE 2

PROPERTIES OF PREVIOUSLY UNREPORTED COMPOUNDS

Compound	*B.p.* [°*C/mmHg*]	n_D^{20}	d_4^{20}
$(ClCH_2CH_2CH_2)_2(CH_3)SiH$	83/3	1.4730	1.0345
$(ClCH_2CH_2CH_2)_2(C_2H_5)SiH$	134/17	1.4761	1.0245
$ClCH_2CH_2CH_2(CH_3)_2SiH$	61/5	1.4348	0.8919
$ClCH_2CH_2CH_2(C_2H_5)_2SiH$	99/30	1.4495	0.9005
$ClCH_2CH_2CH_2(n\text{-}C_3H_7)_2SiH$	122/30	1.4520	0.8880
$ClCH_2CH_2CH_2(CH_3)(C_2H_5)SiH$	71/30	1.4430	0.9020
$ClCH_2(C_2H_5)_2SiH$	135–140/749	1.4394	0.9080
$ClCH_2(n\text{-}C_3H_7)_2SiH$	96/30	1.4450	0.8940

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