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# THE INFLUENCE OF INTERMOLECULAR INTERACTIONS ON THE Si—H BOND VIBRATION IN SILATRANE AND ITS C-SUBSTITUENTS

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## Summary

Spectra of the silatrane $HSi(OCHRCH_2)_3N$ and its 3,7,10-trimethyl- and -trifluoromethyl derivatives have been studied. The dependences of frequency and integral intensity of the Si—H vibration on solvent polarity and temperature have been established. It has been shown that interaction of silatrane molecules with the solvent is universal in character. The phenomenon of the changing Si—H vibration is explained by the possible formation of a three-centred orbital bending the atoms of hydrogen, silicon and nitrogen. In contrast to triethoxysilane, a dependence between $\nu$(Si—H) and $\Sigma\sigma^*$ values of substituents in the cycle has been observed for silatranes.

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## Introduction

The $\nu$(Si—H) vibration in the IR spectra of acyclic molecules of the type HSiX′X″X‴ has a characteristic form; its frequency and intensity are defined mainly by the electronic effects of substituents at the silicon atom [1—5]. It has already been shown that the change in the stretching vibration, $\nu$(Si—H) may be used, to determine the interaction between the silicon and nitrogen atoms in the silatrane $HSi(OCH_2CH_2)_3N$ [6]. The considerable reduction in the frequency of this vibration (by 77 and 57 $cm^{-1}$ in methanol and chloroform, respectively) compares with that of triethoxysilane, $HSi(OCH_2CH_3)_3$, in carbon tetrachloride and demonstrates the existence of trans-annular Si ← N bonding [6] (Table 1).

## Results and discussion

In order to define the nature of the Si—H bond in silatrane and its C-substituents we have studied the influence of the nature of substituent R, solvent and

TABLE 1

$\nu$(Si—H) FREQUENCIES AND INTEGRAL INTENSITIES $A$(Si—H) OF THE Si—H BOND STRETCHING VIBRATION IN COMPOUNDS OF THE TYPE $HSi(OCHRCH_2)_3N$ WHERE R = H (I), $CH_3$ (II), $CF_3$ (III) AND $HSi(OCH_2CH_3)_3$ (VI)

| | Solvent | I | | | II | | | III | | | VI | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $\nu$ (cm$^{-1}$) | $A$ | $\Delta\nu_{1/2}$ | $\nu$ (cm$^{-1}$) | $A$ | $\Delta\nu_{1/2}$ | $\nu$ (cm$^{-1}$) | $A$ | $\Delta\nu_{1/2}$ | $\nu$ (cm$^{-1}$) | $A$ | $\Delta\nu_{1/2}$ |
| 1 | $CCl_4$ | 2175 | | | 2166 | 990 | 41.5 | | | | 2192 | 710 [13] | 46.5 |
| 2 | $CHCl_3$ | 2137 | 1210 | 56 | 2132 | 900 | 59 | 2210 | 1190 | 54 | 2197 | 670 | 51 |
| 3 | $CH_2Cl_2$ | 2127 | 1070 | 52 | 2118 | 930 | 54 | 2196 | 1500 | 46 | | | |
| 4 | $ClC_6H_5$ | 2143 | 1190 | 45 | 2136 | 1230 | 47 | 2206 | 1680 | 57 | 2192 | 720 | 53 |
| 5 | $ClCH_2CH_2Cl$ | 2126 | 1400 | 52 | 2118 | 1070 | 54 | 2194 | 1810 | 50 | 2194 | 730 | 56 |
| 6 | $CH_3CN$ | 2116 | 1420 | 48 | 2106 | 1100 | 48 | 2171 | 1820 | 43 | 2195 | 770 | 60 |
| 7 | $CH_3OH$ | 2133<br>2117 [1] | | | 2127 | | | | | | | | |
| 8 | Solid or liquid | 2092<br>2090(vw) $^a$ | 1130 | 52 | 2115<br>2114(vw) | 900 | 42 | 2172 | | | 2194 [12]<br>2195(s) [12] | | |

$^a$ $\nu$(Si—H) frequencies in Raman spectra.

temperature upon $\nu$(Si—H) and integral intensity, $A$(Si—H), in the IR spectra of compounds of the type $HSi(OCHRCH_2)_3N$, where R = H (I), $CH_3$ (II), $CF_3$ (III), $HSi(OCH_2CH_2)_2(OCH(CF_3)CH_2)N$ (IV), $HSi(OCH_2CH_2)(OCH(CF_3)CH_2)_2N$ (V) and $HSi(OCH_2CH_3)_3$ (VI). We have also determined the influence of temperature on $\nu$(Si—H) in the Raman spectra of compounds I and II.

Figure 1 shows the dependence of $\nu$(Si—H) upon the function of solvent polarity, $(\epsilon - 1)/(2\epsilon + 1)$. $\nu$(Si—H) for triethoxysilane does not actually depend on this value. On the contrary, $\nu$(Si—H) for silatranes I—III decrease linearly with an increase in solvent polarity. This dependence corresponds to the following regression equations:

$\nu(\text{Si—H}) = 2225 - 228(\epsilon - 1)/(2\epsilon + 1)$ (I, $r = 0.984$, $s = 3.7$)

$\nu(\text{Si—H}) = 2219 - 236(\epsilon - 1)/(2\epsilon + 1)$ (II, $r = 0.989$, $s = 3.5$)

$\nu(\text{Si—H}) = 2322 - 306(\epsilon - 1)/(2\epsilon + 1)$ (III, $r = 0.978$, $s = 3.7$)

(The $\nu$(Si—H) values in methanol do not correlate well probably because of specific intermolecular interactions.) Similar values obtained with independent variables testify to the same nature of interaction of silatrane molecules with solvent. Coefficient R is not improved by including a dispersion value characterized by the function $(n^2 - 1)/(n^2 + 2)$ into the correlation. The corresponding values of pair ($r_{xy} = 0.976$, $r_{xz} = 0.626$, $r_{yz} = 0.640$) and quotient ($r_1 = 0.976$, $r_2 = 0.124$, $r_3 = 0.016$) coefficients of three-parameter correlations show the independence of $(\epsilon - 1)/(2\epsilon + 1)$ and $(n^2 - 1)/(n^2 + 2)$ variables and a very weak dependence of $\nu$(Si—H) on the dispersion value. The results obtained indicate that intermolecular interaction of silatrane molecules with solvents is

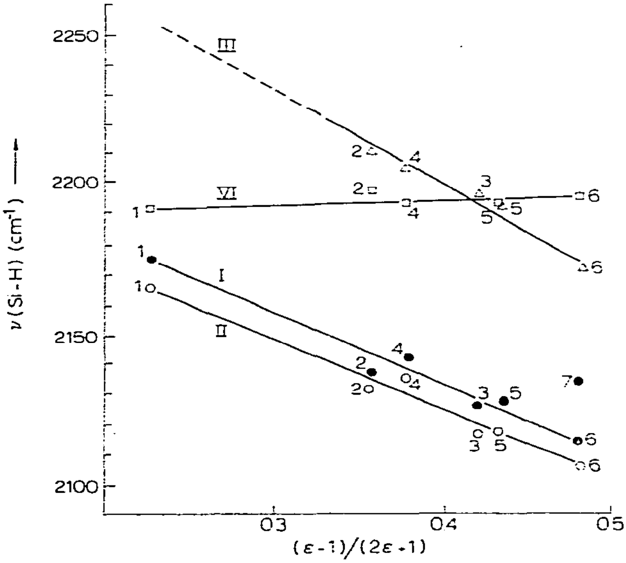

Fig. 1. The dependence of $\nu$(Si—H) solvent polarity for compounds of the type $HSi(OCHRCH_2)_3N$ (R = H (I), $CH_3$ (II), $CF_3$ (III) and $HSi(OCH_2CH_3)_3$ (VI)).

universal and shows a predominant contribution from induction-orientation forces.

The silatrane molecules are characterised by a large amplitude of the change in the Si—H frequency variation depending on the solvent polarity. This is not the case for the $\nu$(Si—H) value of triethoxysilane and other vibrations of silatrane molecules. The displacement of vibration levels under the influence of intermolecular interactions in the valent—optic approximation may be compared with spectroscopic parameters, $(\partial\mu/\partial q)_0$ and $(\partial\alpha/\partial q)_0$ as well as with the change in generalized vibration coordinates $\Delta q$ [7]. The $A$(Si—H) value defined by $(\partial\mu/\partial q)_0$ does not actually depend on the solvent polarity function (Table 1). The intensity $I$(Si—H) defined by $(\partial\alpha/\partial q)_0$ is close to 0 for silatranes (in the Raman spectra the Si—H vibration is very weak). The considerable dependence of $\nu$(Si—H) of silatranes on the solvent polarity is explained by the fact that the solvent alters the electronic structure of the silatrane molecules. The transannular Si←N bonded moiety is probably the most labile fragment. In fact one can note a strong dependence of electron transition energy on the solvent polarity, even for acyclic molecules with intermolecular interaction Sn ← N, which is not observed in similar compounds having no coordinational interaction [8].

The nature of H—Si ← N interactions, in silatranes is explained by the existence of three-centred bonding in this fragment [9,10]. The bonding energy of silicon and hydrogen atoms in the range of the hypervalent scheme in Hückel's approximation is expressed by the following ratio:

$$|E_{\mathrm{Si-H}}| = \frac{\beta^2_{\mathrm{Si-H}}}{\alpha_{\mathrm{Si}} - \alpha_{\mathrm{H}} + \dfrac{\beta^2_{\mathrm{N-Si}}}{\alpha_{\mathrm{Si}} - \alpha_{\mathrm{N}}}}$$

It is evident that the $E_{\mathrm{Si-H}}$ value decreases with an increase in $\beta_{\mathrm{N\to Si}}(r_{\mathrm{N\to Si}})$. Experimentally it is demonstrated by reducing the Si—H bond force constant and hence $\nu$(Si—H). Thus the reduction in $\nu$(Si—H) value with increasing solvent polarity is explained by increasing the degree of Si ← N interaction that is due to shortening the silicon—nitrogen distance. The formation of the Si—H bond due to a combination of the hydrogen $s$-orbital and the silicon $p_z$-orbital rather than that of the hydrogen $s$-orbital and the silicon $sp^3$-hybrid orbital as in triethoxysilane may be the second factor reducing $\nu$(Si—H) in pentacoordinated compounds of silicon.

The change of $\nu$(Si—H) is very small for model acyclic molecules of the type $H(CH_3)_nSi(OCHRCH_3)_{3-n}$ with variation of the substituents R. For $HSi(OCHRCH_3$ with R = H: $\nu$(Si—H) = 2194 cm$^{-1}$ [12]; with R = $CH_3$: $\nu$(Si—H) = 2192 cm$^{-1}$ [12]. For $H(CH_3)Si(OCHRCH_3)_2$ with R = H: $\nu$(Si—H) = 2165 cm$^{-1}$ [4]; R = $CF_3$: $\nu$(Si—H) = 2178 cm$^{-1}$.

In the IR spectra of silatranes I and II the transition from R = H to R = $CH_3$ in any solvent produces a change in $\nu$(Si—H) of approximately 10 cm$^{-1}$; for silatranes II and III the variation from R = $CH_3$ to R = $CF_3$ changes $\nu$(Si—H) by about 70 cm$^{-1}$.

The value of the quotient ($r_2$ 0.990) coefficient of three-parameter correlation (17 points) show the strong dependence of $\nu$(Si—H) on the inductive effect

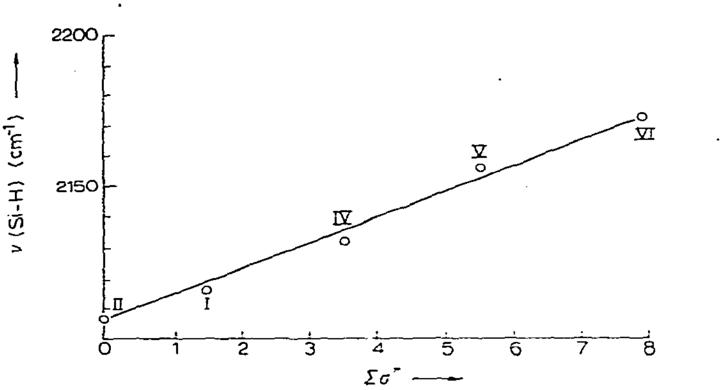

Fig. 2. The $\nu$(Si—H)/$\Sigma\sigma^*$ dependence for silatranes of the type $HSi(OCHRCH_2)_3N$ with R = H (I), $CH_3$ (II) and $HSi(OCH_2CH_2)_n(OCH(CF_3)CH_2)_{3-n}$ where $n$ = 2 (IV), 1 (V), 3 (VI) (the solvent is acetonitrile).

of the substituents R (eq. 1). The high conductivity of the alicyclic fragment

$$\nu(\text{Si—H}) = 2201\ (\pm 12) - 199\ (\pm 41)\,\frac{\epsilon - 1}{2\epsilon + 1} + 10\ (\pm 1)\ \Sigma\sigma_R^* \qquad (1)$$

$(r = 0.991;\ r_1 = 0.969,\ r_2 = 0.990,\ r_3 = 0.967)$

inductive effect is a characteristic feature of cyclic molecules [11].

The steric constants, $E_s^0$ (—0.25(H), 0($CH_3$), 215($CF_3$)), are not parallel to the inductive effects over the interval studied.

The crystal field effect considerably reduces $\nu$(Si—H) (Table 1). In the above range is shown that the Si—N distance of silatrane molecules in solution is greater than in the crystalline state. $\nu$(Si—H) in the vibration spectra of silatrane (I) at 80—100 K splits into three components (2073, 2088 and 2100 cm$^{-1}$)

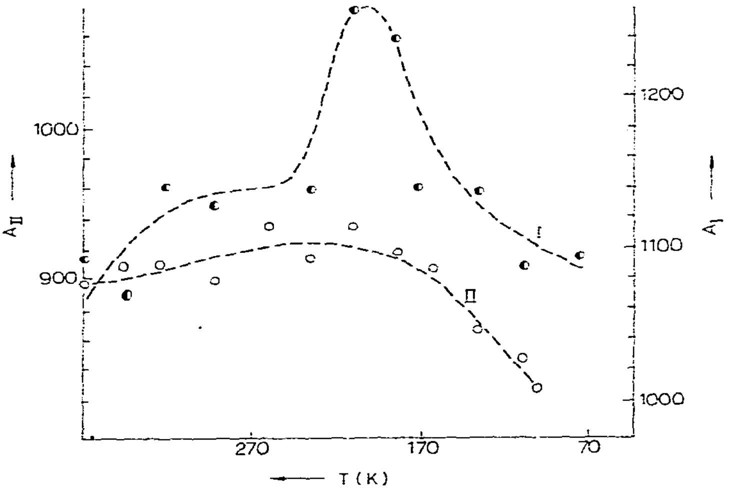

Fig. 3. The change of intensity $A$(Si—H) for compounds $HSi(OCH_2CH_2)_3N$ (I) and $HSi(OCH(CH_3)CH_2)_3N$ (II) with temperature.

whose appearance is caused by non-equivalence of the molecular environment within the crystal lattice. In compound II under the same conditions there is only one maximum.

Usually a decrease in temperature lowers the intensity of vibrations for molecules in the condensed state. But for the silatranes studied $A$(Si—H) is only dependent upon temperature below 200 K: at high temperatures the intensity is practically constants (Fig. 3). This effect is more pronounced in silatrane I.

## Experimental

IR spectra of the silatranes as (KBr tablet or suspensions in vaseline oil) were recorded on a FTS-20 PA spectrophotometer in the 450—3000 $cm^{-1}$ range. The $A$(Si—H) values of silatranes and triethoxysilane were defined using published techniques (using IUPAC scales) [14]. The concentration was about 0.02—0.06 mol $l^{-1}$. The Raman spectra of crystal patterns were obtained on a RGS-2 spectrophotometer. The excitation line was 4880 Å of an $Ar^+$ laser.

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