INTENSITY OF BANDS OF STRETCHING VIBRATIONS OF Si–H BOND IN IR SPECTRA OF SILAFLUORENES AND dπ–pπ INTERACTION


Organosilicon derivatives of fluorene (silafluorenes), in which the silicon atom enters into the cyclic system, have a number of properties that differentiate them from the corresponding noncyclic phenyl derivatives. This is indicated both by the chemical data and by the results of studying the silafluorenes via UV and ESR spectroscopy [1, 2].

It is known [3] that when going from compounds of type \( \overset{\text{X}}{\text{C}}=\text{C}X \) or \( \overset{\text{X}}{\text{C}}=\text{C}X \) to compounds of type \( \overset{\text{X}}{\text{C}}=\text{C}X \) (where \( X \) is an organic substituent that is capable of conjugation with a \( \pi \)-electron system) the degree of coplanarity of the two aromatic rings increases, and in view of this the ability of the rings to conjugate with the \( X \) substituent increases. In the case where \( X \) is an organosilicon substituent, in which the silicon atom is \( \alpha \) to the aromatic ring, the main effect of the conjugation is \( d^\pi-p^\pi \) interaction. The effect of \( d^\pi-p^\pi \) interaction consists in a partial delocalization of the \( \pi \)-electrons of the aromatic rings on the vacant 3d-orbitals of the silicon atom. Here the organosilicon substituent, due to \( d^\pi-p^\pi \) interaction, exhibits a negative mesomeric \(-M\)-effect. These considerations make it possible to assume that the degree of \( d^\pi-p^\pi \) interaction between the silicon atoms and the \( \pi \)-electrons of the aromatic rings should increase when going from phenyl derivatives of type \( \text{C}_6\text{H}_5\text{R} \) to silafluorenes \( \overset{\text{H}}{\text{C}}=\text{C}X \). The purpose of the present paper was to experimentally verify this assumption via IR spectroscopy.

In theoretical papers [4] it was shown that the electronic effects of substituents (also including conjugation effects) are manifested with special clarity when the intensities of the absorption bands in the IR spectra are measured. Consequently, to study the \( d^\pi-p^\pi \) interaction in the bonds of the silicon atom with aromatic rings we analyzed the effect of substituents on the intensity of the absorption bands of the stretching vibrations of the Si–H bond in two series of compounds (fluorene derivatives and phenyl derivatives) (Table 1). The stretching vibration of the Si–H bond in silane derivatives is highly characteristic in shape [5]. Consequently, the frequency and intensity (\( \Delta \)) of the bands of this stretching vibration are determined by the electronic effects of the substituents attached to the silicon atom. The principal electronic effects are the inductive effect and \( d^\pi-p^\pi \) interaction. Previously it was shown [6–8] that in compounds, devoid of substituents that are capable of \( d^\pi-p^\pi \) interaction with the silicon atom, the \( A^{1/2} \) values are related to the sum of the Taft inductive constants of the substituents \( \Sigma^* \) by linear equations.

\[
A^{1/2}_{\text{ind}} = 1.35 - 0.19\Sigma^* \quad \text{(for RSH compounds)} \\
A^{1/2}_{\text{ind}} = 1.72 - 0.12\Sigma^* \quad \text{(for RSIIH compounds)}
\]

For those compounds in which the \( R \) substituents are capable of \( d^\pi-p^\pi \) interaction with the silicon atom, the experimental values of the intensity \( A^{1/2}_{\text{expt}} \) differ from the \( A^{1/2}_{\text{ind}} \) values, calculated from Eqs. (1) and (2). The differences \( \Delta A^{1/2} = A^{1/2}_{\text{expt}} - A^{1/2}_{\text{ind}} \) arise as the result of \( d^\pi-p^\pi \) interaction. The effect of \( d^\pi-p^\pi \)
interaction consists in the donation of electron density on the silicon atom, i.e., it acts in the opposite direction to the inductive $-I$-effect. Consequently, $d_π−p_π$ interaction leads to a reduction in the electron-acceptor properties of the substituents that enter into this interaction. In view of this an increase in the values of $A_{\text{expt}}^{1/2}$ over $A_{\text{ind}}^{1/2}$ is observed and the creation of $\Delta A^{1/2}$.

From Table 1 it can be seen that the $\Delta A^{1/2}$ values in the silafluorenes exhibit a tendency to exceed the $\Delta A^{1/2}$ values in the corresponding phenyl derivatives. However, it should be mentioned that the error in measuring $A$ is $\pm 10\%$. Consequently, only for the fourth pair of compounds can it be definitely concluded that $\Delta A^{1/2}$ has a greater value in the silafluorenes. This indicates that in chlorosilafluorene the degree of $d_π−p_π$ interaction between the silicon atom and the $\pi$-electrons of the aromatic rings is greater than in diphenylchlorosilane, which does not have a direct chemical bond between the aromatic rings.

**EXPERIMENTAL METHOD**

The IR spectra were obtained on a UR-20 spectrophotometer for CCl$_4$ solutions (concentration 0.04–0.1 mole/liter). The frequency values of the stretching vibrations of Si–H bonds (10$^4$ mole$^{-1}$·liter$^{-1}$·cm$^{-1}$) was measured by the logansen method [9]. The purity of the compounds was checked by GLC. The $σ^*$ constants of the fluorene group $\begin{array}{c} \text{C} \\ \text{H} \end{array}$ were calculated from the data given in [10], where the value $σ^* = 0.5$ is given for the radical $\begin{array}{c} \text{C} \\ \text{H} \end{array}$.

**CONCLUSIONS**

We measured the intensity of the bands of the stretching vibrations of the Si–H bond in the IR spectra of the organosilicon derivatives of fluorene and the corresponding phenyl derivatives. A greater degree of $d_π−p_π$ interaction of the silicon atom with the aromatic rings was established in chlorosilafluorene than in diphenylchlorosilane. This is caused by the coplanarity of the rings of the fluorene fragment.

**LITERATURE CITED**