# SPECTROSCOPIC STUDY OF ORGANOSILICON DERIVATIVES OF THIOPHENE

## II.* PMR SPECTRA OF 2-(ORGANOSILYL)THIOPHENES AND $d_\pi-p_\pi$ CONJUGATION

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It is shown that the chemical shifts of hydrogen atoms in the 3 position of the thiophene ring in the PMR spectra of 2-substituted thiophenes are linearly associated with the Hammett $\sigma_n$ substituent constants. On the basis of this, it was concluded that silyl substituents in 2-silylthiophenes have electron-acceptor character. It was established that the degree of $d_\pi-p_\pi$ conjugation between the d orbitals of the silicon atom and the p electrons of the thiophene ring depends on the nature of the other three substituents attached to the silicon atom. The data from the IR spectra of organosilylthiophenes that contain a Si−H bond also attest to the presence of $d_\pi-p_\pi$ conjugation in these compounds.

Our investigations of heteroorganic compounds of the silicon subgroups by IR and PMR spectroscopy [2,3] attest to increased multiplicity of the M−X bonds, where M = Si and Ge and X is a group V-VII element or an $\alpha$-unsaturated hydrocarbon radical. It is presently assumed that the increased multiplicity of these bonds is a consequence of $d_\pi-p_\pi$ conjugation between the d orbitals of M and the unshared pair of p electrons of X. The goal of the present research is a more detailed study by PMR spectroscopy of the electronic effects in substituted thiophenes having silyl groups in the 2 position.

It follows from the data in Table 1 that the chemical shifts of the protons in the 3 position of the thiophene ring ($\tau_3$) decrease systematically as the −I effect of the other three substituents attached to the silicon atom increases. We have previously observed a similar phenomenon for the $\beta$ protons in $CH_2=CHSi(R_i)_3$ [5].

By treatment of literature data on the $\tau_3$ chemical shifts in a series of thiophenes containing various substituents (from $NO_2$ to $NH_2$) in the 2 position, we obtained the equation $\tau_3 = -1.44\sigma_n + 3.27$ ($n = 16$, $r = 0.95$). Hence, the extremely approximate character of the above-noted dependence of $\tau_3$ in 2-silyl derivatives of thiophene on the −I effect of the three substituents attached to the silicon atom becomes understandable. In fact, $\tau_3$ correlates satisfactorily with $\sigma_n$ of the $SiX_3$ groupings, which takes into account both the inductive and mesomeric effects in this bond. It is noteworthy that, in the IR spectra of vinyl derivatives ($CH_2=CHX$), the frequency of the deformation vibration of $=CH_2$, in addition to the I effect of X, depends markedly on the effect of conjugation of X with the $\pi$ electrons of the vinyl group [6]. The $\sigma_n$ constants calculated from the equation $\tau_3 = -1.44\sigma_n + 3.27$ for $Si(C_2H_5)_5$, $Si(CH_3)_3$, and $SiCl_3$ groupings are 0.35, 0.38, and 0.64, respectively. This attests to the overall electron-acceptor character of the indicated groupings. For comparison, the chemical shifts of various hydrogen atoms for 2-methyl- and 2-bromothiophene are presented in Table 1. A comparison of them with the shifts in organosilicon derivatives is also evidence for the electron-acceptor character of trialkylsilyl groups.

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*See [1] for communication I.

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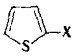
TABLE 1. Chemical Shifts in the PMR Spectra of 2-Substituted Thiophenes



| Comp. | X | Chemical shifts, , ppm | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $\tau_3$ | $\tau_4$ | $\tau_5$ | $\tau_{CH_3}$ | $\tau_{CH_2}$ | $\tau_{Si-H}$ | $\Sigma\sigma^*$ |
| I | $CH_3$ | 3,40 | 3,27 | 3,11 | 7,72 | — | — | — |
| II | Br | 3,08 | 3,31 | 2,95 | — | — | — | — |
| III | $Si(C_2H_5)_3$ | 2,76 | 2,93 | 2,57 | 9,00[a] | 9,21[a] | — | -0,3[b] |
| IV | $Si(CH_3)_3$ | 2,73 | 2,89 | 2,54 | 9,75 | — | — | 0,0 |
| V | $Si(CH_3)_2H$ | 2,65 | 2,85 | 2,53 | 9,70 | — | 5,31 | 0,49 |
| VI | $Si(CH_3)H_2$ | 2,63 | 3,02 | 2,75 | 9,65 | — | 5,52 | 0,98 |
| VII | $SiH_3$ | 2,64 | 3,04 | 2,75 | — | — | 5,72 | 1,47 |
| VIII | $Si(CH_3)_2(OC_2H_5)$ | 2,67 | 2,92 | 2,48 | 9,61[c] | — | — | 1,5 |
| IX | $Si(CH_3)_2Cl$ | 2,60 | 3,01 | 2,70 | 9,41 | — | — | 2,9 |
| X | $Si(CH_3)BrH$ | 2,53 | 2,98 | 2,64 | 9,20 | — | 4,68 | 3,29 |
| XI | $Si(CH_3)ClH$ | 2,50 | 2,95 | 2,60 | 9,37 | — | 4,65 | 3,39 |
| XII | $SiBrH_2$ | 2,53 | 3,00 | 2,65 | — | — | 4,98 | 3,78 |
| XIII | $SiClH_2$ | 2,55 | 3,00 | 2,65 | — | — | 4,81 | 3,88 |
| XIV | $Si(OC_2H_5)_3$ | 2,53 | 2,85 | 2,36 | 8,79[d] | 6,13[d] | — | 4,5 |
| XV | $Si(CH_3)Cl_2$ | 2,40 | 2,90 | 2,48 | 9,06 | — | — | 5,8 |
| XVI | $SiCl_3$ | 2,35 | 2,96 | 2,50 | — | — | — | 8,7 |
| XVII | $SiF_3$ | 2,37 | 2,88 | 2,46 | — | — | — | 9,3 |

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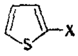
[a] Signals of the hydrogen atoms of the $C_2H_5Si$ group.

[b] These are the $\sigma^*$ constants taken from [4].

[c] In the spectrum of the ethoxy group, $\tau_{CH_3}$ is 8.87 ppm, and $\tau_{CH_2}$ is 6.37 ppm.

[d] Signals of the hydrogen atoms of the ethoxy group.

TABLE 2. $\Delta\tau$ Values Caused by $d_\pi - p_\pi$ Conjugation, in Several 2-Substituted Thiophenes



| X | $Si(CH_3)_3$ | $SiCl(CH_3)_2$ | $SiCl_2CH_3$ | $Si(OC_2H_5)(CH_3)_2$ |
|---|---|---|---|---|
| $\Delta\tau$, ppm | 0,07 | 0,39 | 0,69 | 0,28 |
| $\Delta\tau_{add}$, ppm | — | 0,30 | 0,54 | 0,36 |

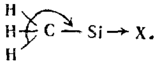
TABLE 3. Frequencies of the Stretching Vibrations of the Si−H Bond in the IR Spectra of Some 2-(Organosilyl)thiophenes

| Comp. | Compound | $\nu_{cal}$, $cm^{-1}$ | exp, $cm^{-1}$ | $\Delta\nu$, $cm^{-1}$ | $\Delta\nu_{add}$, $cm^{-1}$ |
|---|---|---|---|---|---|
| V | $(C_4H_3S)(CH_3)_2SiH$ | 2142 | 2135 | 7 | — |
| XI | $(C_4H_3S)(CH_3)ClSiH$ | 2209 | 2182 | 27 | 29 |
| X | $(C_4H_3S)(CH_3)BrSiH$ | 2207 | 2182 | 25 | 23 |
| XIII | $(C_4H_3S)ClSiH_2$ | 2229 | 2194 | 35 | 39 |
| XII | $(C_4H_3S)BrSiH_2$ | 2227 | 2195 | 32 | 33 |
| XVIII | $(C_4H_3S)_2(C_2H_5)SiH$ | 2170 | 2136 | 34 | — |
| XIX | $(C_4H_3S)_2(C_6H_5)SiH$ | 2186 | 2142 | 44 | 42 |
| XX | $(C_4H_3S)_3SiH$ | 2202 | 2149 | 53 | — |

Calculation of the $\sigma_C = \sigma_n - \sigma_I$ constants can be performed only for $Si(C_2H_5)_3$, $Si(CH_3)_3$, and $SiCl_3$ substituents, for which the $\sigma^* = 6.23\sigma_I$ constants are known and are, respectively, −1.1, −0.9 [7], and 1.55 [8]. We found that the $\sigma_C$ constant of the $SiCl_3$ group (0.39) is appreciably lower than the constants of the $Si(C_2H_5)_3$ (0.53) and $Si(CH_3)_3$ (0.52) groups. This fact is explained as follows. The magnitude of the $\sigma_C$ constant of the silyl group reflects the effectiveness of using the d orbitals of silicon in $d_\pi - p_\pi$ conjugation with the ring. In the case of $Si(C_2H_5)_3$ and $Si(CH_3)_3$ substituents, the silicon atom maximally utilizes its possibility for $d_\pi - p_\pi$ bonding. The d orbitals of silicon in the $SiCl_3$ group are involved to a considerable extent in $d_\pi - p_\pi$ conjugation with the unshared p electrons of the chlorine atoms. Consequently, $d_\pi - p_\pi$ conjugation with the ring $\pi$ electrons in 2-(trichlorosilyl)thiophene becomes less effective than the analogous conjugation in 2-(trialkylsilyl) thiophenes.

The chemical shifts of the hydrogen atoms of the methyl groups bonded to the silicon atom ($\tau_{CH_3}$) also convey information regarding $d_\pi - p_\pi$ conjugation between the d orbitals of silicon and the ring $\pi$ electrons. We have previously demonstrated [3] that the isolation of the contribution of the $d_\pi - p_\pi$ conjugation to $\tau_{CH_3}$ in $(CH_3)_{4-n}SiX_n$ compounds requires prior separation of the following effects: the inductive effect of X (1), the effect of anisotropy of the magnetic susceptibility (2), the effect of the intramolecular electrical field of the bonds of the $SiX_n$ fragment (3), and $d_\pi - p_\pi$ conjugation in the Si−X bonds (4). The first effect is easily taken into account, since the $\tau_{CH_3}$ values are associated with the sums of the inductive substituent constants ($\Sigma\sigma^*$) by the linear equation $\tau_{CH_3} = 10.00 - 0.140\Sigma\sigma^*$ [9]. We have described in detail methods for quantitative evaluation of effects 2 and 3 in [3]. As in the case of trimethylphenylsilane [3], it was assumed that the anisotropic contribution to $\tau_{CH_3}$ of 2-(trimethylsilyl)thiophene is due only to the effect of the ring current of the thiophene ring [10]. In this case, it was assumed that effect 3 is negligibly small in 2-(trimethylsilyl)thiophene. The contribution of $d_\pi - p_\pi$ conjugation to $\tau_{CH_3}$ of 2-(trimethylsilyl)-thiophene obtained in this way is 0.07 ppm, which is extremely close to the corresponding contribution to trimethylphenylsilane (0.08 ppm).

In [3] we made quantitative estimates of effects 2 and 3 for the $CH_3-Si-Cl$ and $CH_3-Si-OAlk$ fragments. This provides a possibility for calculation of the contributions of $d_\pi - p_\pi$ conjugation ($\Delta\tau$) to VIII, IX, and XV (Table 1). The $\Delta\tau$ values are presented in Table 2 and compared with the $\Delta\tau_{add}$ values. The calculation of $\Delta\tau_{add}$ can be illustrated by the following example. It is assumed that the contribution of $d_\pi - p_\pi$ conjugation to $\tau_{CH_3}$ in 2-(dimethylchlorosilyl)thiophene is additively assembled from the contributions in 2-(trimethylsilyl)thiophene (0.07 ppm) and trimethylchlorosilane (0.23 ppm [3]). It is apparent from Table 2 that the $\Delta\tau$ values differ somewhat from $\Delta\tau_{add}$. In our opinion, the reason for this is the fact that the dipole moments of the Si−Cl and $Si-OC_2H_5$ bonds that are necessary for evaluating effect 3 have different values in the compounds of Table 2 and in compounds of simpler structure (of the trimethylchlorosilane type). It is known, for example, that the dipole moments of $CF_nCl_{4-n}$ have lower values than those calculated from data on fluoro- and chloromethane [11]. A similar phenomenon is also observed in the buildup of the number of diverse substituents in organosilicon compounds [12]. Allowance for the decrease in the magnitudes of the dipole moments of Si−Cl in $(C_4H_3S)SiCl_n(CH_3)_{3-n}$ groups ($n = 1$-$3$), which are adjacent to the thiophene ring, should bring the $\Delta\tau$ values close to the $\Delta\tau_{add}$ values. However, in 2-(alkoxydimethylsilyl)thiophenes, this sort of consideration would increase the difference between $\Delta\tau$ and $\Delta\tau_{add}$ even more. This apparently is evidence for the suppression of the capacity of the silicon atom for $d_\pi - p_\pi$ conjugation after introduction of one alkoxy group into the tetraalkylsilane molecule, which we have already noted in a study of the IR spectra of alkoxysilanes [13].

Independent conclusions regarding the presence of $d_\pi - p_\pi$ conjugation in organosilicon derivatives of thiophene can be drawn in a study of the frequencies ($\nu$) of the stretching vibrations of the Si−H bond in the IR spectra (Table 3). In [14, 15] it was established that in tri- and disubstituted silanes these frequencies are associated with inductive constants of substituents that are incapable of $d_\pi - p_\pi$ conjugation by linear equations $\nu = 23.1\Sigma\sigma^* + 2112$ and $\nu = 23.1\Sigma\sigma^* + 2121$. For silanes that have substituents that are capable of forming $d_\pi - p_\pi$ bonds with the silicon atom, the experimental frequencies are too low as compared with the values calculated from these equations, which is explained by the decrease in the −I effect of the substituents under the influence of the oppositely directed effect of $d_\pi - p_\pi$ conjugation. Thus the $\Delta\nu = \nu_{cal} - \nu_{exp}$ values may be a measure of the effect of $d_\pi - p_\pi$ conjugation. Let us consider the $\Delta\nu$ values in the compounds in Table 3. Compounds XVIII and XX have, respectively, two and three thienyl groups that enter into $d_\pi - p_\pi$ conjugation with the silicon atom. Since the $\Delta\nu$ values in these compounds are 34 and 53 $cm^{-1}$, each of the thienyl groups accounts for $\Delta\nu$ of 17 $cm^{-1}$. However, $\Delta\nu$ in thienyldimethylsilane is not 17 $cm^{-1}$ but only 7 $cm^{-1}$. Similarly, the $\Delta\nu$ values are too low by about 10 $cm^{-1}$ in X and XI, which, in contrast to XII and XIII, have methyl groups. This peculiarity of the IR spectra of methylsilanes can be explained on the basis of $\sigma,\sigma$ conjugation  $H_3C-Si\rightarrow X$. The effect of $\sigma,\sigma$ conjugation acts in a direction opposite to the effect of $d_\pi - p_\pi$ conjugation in the Si−X bond (in this case, X is a thienyl group). The ethyl group is capable of considerably less $\sigma,\sigma$ conjugation. Consequently, $\sigma,\sigma$ conjugation in the ethyl derivatives cannot be detected in the IR spectrum. We made a detailed examination of the appearance of the effect of $\sigma,\sigma$ conjugation in the IR and PMR spectra of methylchlorosilane in [3]. The $\Delta\nu$ values in XII, XIII, and XIX reflect $d_\pi - p_\pi$ conjugation with chlorine, bromine, or the phenyl group, as well as with the thienyl group. We calculated the $\Delta\nu_{add}$ values for these compounds. It was assumed that $\Delta\nu_{add}$ is the additive sum of the independent contributions to $d_\pi - p_\pi$ conjugation from the thienyl group ($\Delta\nu = 17$ $cm^{-1}$), and the chloro ($\Delta\nu = 22$ $cm^{-1}$) [16], bromo ($\Delta\nu = 16$ $cm^{-1}$) [16], and phenyl ($\Delta\nu = 8$ $cm^{-1}$) [14] groups. The corresponding additive contributions for allowance for $\sigma,\sigma$ conjugation for methyl derivatives X and XI were reduced by 10 $cm^{-1}$. As follows from Table 3, the $\Delta\nu$ and $\Delta\nu_{add}$ values practically coincide. This is evidence that competition between several groups, each of which participates in $d_\pi-p_\pi$ conjugation, holds for compounds in Table 3. However, as noted above, no such competition occurs in 2-(trifluorosilyl)thiophene and 2-(dimethylethoxysilyl)thiophene). These conclusions are in complete agreement with the results obtained in an analysis of the IR spectra of halosilanes [16] and alkoxysilanes [13].

In conclusion, we will compare some data on $d_\pi-p_\pi$ conjugation obtained by PMR and IR spectroscopy. Close $\Delta\nu$ values (17 and 22 $cm^{-1}$, respectively) were obtained by IR spectroscopy for the thienyl and chloro groups. However, the $\Delta\tau$ values obtained from the PMR spectra for the thienyl group (0.07 ppm) are considerably lower than those obtained for the chloro group (0.23 ppm). In evaluating the two methods that we used to study $d_\pi-p_\pi$ conjugation, it should be acknowledged that IR spectroscopy is a more accurate method, since the assumptions that are inevitable in calculating intramolecular contributions to chemical shifts in the PMR spectra are absent in it. Thus neglect of the effect of the intramolecular electrical field on $\tau_{CH_3}$ apparently leads to a lowering of the $\Delta\tau$ values of the thienyl group in 2-(trimethylsilyl)thiophene. However, this had no effect whatsoever on the fundamental aspect of the problems examined in this paper.

## EXPERIMENTAL

The PMR spectra were obtained with a YaMR-5535 spectrometer (40 MHz). The compounds were studied in solutions in cyclohexane (volume ratio 1 : 2), which simultaneously served as the internal standard. The chemical shifts ($\tau$) of the hydrogen atoms of the thiophene ring were determined with an accuracy of about ±0.05 ppm; the $\tau$ values of the other hydrogen atoms were determined with an accuracy of ± (0.01-0.02) ppm. The accuracy in the determination of the $\tau$ values of the ring hydrogens was low because of errors associated with the method we used to analyze the spectra of the ABC type, with which these atoms are affiliated. We analyzed these spectra by comparison with the spectra of a large number of 2-substituted thiophenes, the complete analysis of which was performed in [17]; data on the $\tau_3$ values were also taken from [17]. The effect of the current of the thiophene ring on $\tau_{CH_3}$ in 2-(trimethylsilyl)-thiophene was calculated allowing for the free rotation of the methyl groups and trimethylsilyl groups as a whole about the bond of the silicon atom with the ring. The geometrical parameters of the thiophene ring were taken from [18], while those for the trimethylsilyl group were taken from [3]. Data from the calculation of the contributions of the ring current to the chemical shifts in the PMR spectra of thiophene derivatives [9] and the tables in [19] were used for the calculations.

The IR spectra of dilute solutions of the compounds in carbon tetrachloride were recorded with a UR-20 spectrometer.

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