SPECTROSCOPIC STUDY OF ORGANOSILICON DERIVATIVES OF THIOPHENE

IV.* PMR SPECTRA OF DI- AND TRISUBSTITUTED THIOPHENES

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Substituents in disubstituted thiophenes have an additive effect on the chemical shifts of the ring hydrogen atoms. The electronic effects of organosilicon substituents are transmitted via inductive and conjugation ($d_\pi - p_\pi$ interaction) mechanisms. The effect of $d_\pi - p_\pi$ interaction in the Si–ring bond is absent for $Si(OC_2H_5)$ and SiF_3 substituents.

In our preceding papers [1-3] we have demonstrated that thiophene derivatives are extremely convenient subjects for the study of the electronic effects of substituents. Thus, for example, the chemical shifts of the hydrogen in the 3 position of the thiophene ring (τ_3) in the PMR spectra of 2-substituted thiophenes are linearly related to the Hammett σ_p constants of the substituents in the 2 position [$\tau_3 = -1.44\sigma_p + 3.27$ (r = 0.95)]. The existence of a linear relationship between the experimental chemical shift and such an important characteristic of a substituent as its σ_p constant opens up the possibility for a study, from the PMR spectra, of the electronic effects of various (including organosilicon) substituents.

In the present paper we have investigated the regularities in the PMR spectra of di- and trisubstituted thiophenes. This investigation seemed of interest in two respects. First, we do not know of any data that prove or disprove the additivity of the effect of substituents in polysubstituted thiophenes. Second, the research seemed of promise from the point of view of a study of organosilicon substituents, the properties of which have still not been adequately studied.

The investigated compounds and chemical shifts in their PMR spectra are presented in Table 1. The compounds presented in Table 1 form several series: 2-X-5-chlorothiophenes (I-XI), 2-X-5-methylthiophenes (XII-XVII), 2-X-5-bromothiophenes (XVIII, XIX), 2-X-5-cyanothiophenes (XX, XXI), 2,5-disilyl derivatives of thiophene (XXII-XXXI), 2-X-3-methylthiophenes (XXXII-XXXVIII), and trisubstituted thiophenes (XXXVIII-XLII). In each of the series, the compounds are arranged in the order of increase of electron-acceptor properties of the substituents bonded to the silicon atom. It follows from Table 1 that the signals of the ring hydrogen atoms and the signals of the methyl groups are shifted regularly to weaker field (the τ_3, τ_4, τ_5, and τ_{CH_3} chemical shifts decrease) within the limits of each of the series as the series number of the compound increases, i.e., as the electron-acceptor properties of the $Si(R_i)_3$ fragments increase. Thus the character of the change in the chemical shifts in the PMR spectra of di- and trisubstituted thiophenes basically repeats the sequence of the change in the chemical shifts in the spectra of monosubstituted thiophenes. In all cases, the chemical shifts of the ring hydrogen atoms are primarily determined by the electronic effects of the substituents. Moreover, at first glance it appears that the contributions to the chemical shifts caused by the anisotropy of the magnetic susceptibility and the intramolecular electrical field are negligibly small. The latter is in agreement with the point of view adopted in the literature [4].

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*See [1] for communication III.

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TABLE 1. Chemical Shifts (τ) in the PMR Spectra of Substituted Thiophenes

Compound	Substituents in positions			Chemical shifts of the ring hydrogen atoms, τ, ppm					τ_{CH_3}, ppm
	2	3	5	τ_3		τ_4		τ_5	
				exptl	calc.	exptl	calc.		
I	CH_3	—	Cl	3,63		3,48		—	7,78
II	Cl	—	Cl	3,47		3,47		—	—
III	$Si(CH_3)_3$	—	Cl	3,12		3,20		—	9,69 ($Si—CH_3$)
IV	SiH_3	—	Cl	3,05		3,22		—	—
V	$Si(CH_3)_2Cl$	—	Cl	2,94		3,14		—	9,38 ($Si—CH_3$)
VI	SiH_2Cl	—	Cl	2,83		3,12		—	—
VII	$Si(OC_2H_5)_3$	—	Cl	2,84		3,08		—	—
VIII	$Si(CH_3)Cl_2$	—	Cl	2,74		3,06		—	9,03 ($Si—CH_3$)
IX	$SiHCl_2$	—	Cl	2,74		3,08		—	—
X	$SiCl_3$	—	Cl	2,66		3,09		—	—
XI	SiF_3	—	Cl	2,62		3,06		—	—
XII	SiH_3	—	CH_3	2,99	3,05	3,37	3,38	—	7,68
XIII	$Si(CH_3)_2Cl$	—	CH_3	2,84	2,94	3,24	3,30	—	7,63; 9,39 ($Si—CH_3$)
XIV	SiH_2Cl	—	CH_3	2,77	2,83	3,25	3,28	—	7,63
XV	$Si(OC_2H_5)_3$	—	CH_3	2,77	2,84	3,23	3,24	—	7,59
XVI	$Si(CH_3)Cl_2$	—	CH_3	2,72	2,74	3,22	3,22	—	7,59; 9,07 ($Si—CH_3$)
XVII	$SiCl_3$	—	CH_3	2,64	2,66	3,24	3,25	—	7,57
XVIII	$Si(CH_3)Cl_2$	—	Br	2,80	—	2,97	—	—	9,02 ($Si—CH_3$)
XIX	$SiCl_3$	—	Br	2,65	2,58	2,91	2,82	—	—
XX	$Si(OC_2H_5)_3$	—	CN	2,53	—	2,25	—	—	—
XXI	$SiCl_3$	—	CN	2,26	2,35	2,13	2,26	—	—
XXII	$Si(CH_3)_3$	—	$Si(CH_3)_3$	2,81	2,85	2,81	2,85	—	9,71 ($Si—CH_3$)
XXIII	SiH_3	—	SiH_3	2,65	2,80	2,65	2,80	—	—
XXIV	SiH_2Br	—	SiH_3	2,60	—	2,71	—	—	—
XXV	SiH_2Cl	—	SiH_3	2,56	2,58	2,65	2,70	—	—
XXVI	$Si(CH_3)_2Cl$	—	$Si(CH_3)_2Cl$	2,55	2,61	2,55	2,61	—	9,33 ($Si—CH_3$)
XXVII	SiH_2Br	—	SiH_2Br	2,42	2,51	2,42	2,51	—	—
XXVIII	SiH_2Cl	—	SiH_2Cl	2,48	2,48	2,48	2,48	—	—
XXIX	$Si(OC_2H_5)_3$	—	$Si(OC_2H_5)_3$	2,46	2,45	2,46	2,45	—	—
XXX	$Si(CH_3)Cl_2$	—	$Si(CH_3)Cl_2$	2,41	2,33	2,41	2,33	—	9,01 ($Si—CH_3$)
XXXI	$SiCl_3$	—	$SiCl_3$	2,30	2,28	2,30	2,28	—	—
XXXII	Cl	CH_3	—	—	—	3,46	—	3,27	7,94
XXXIII	$Si(CH_3)_2Cl$	CH_3	—	—	—	3,12	—	2,66	7,65
XXXIV	$Si(OC_2H_5)_3$	CH_3	—	—	—	3,12	—	2,61	7,62
XXXV	$Si(C_2H_5)Cl_2$	CH_3	—	—	—	3,09	—	2,60	7,59
XXXVI	$Si(CH_3)Cl_2$	CH_3	—	—	—	3,08	—	2,60	7,61
XXXVII	$SiCl_3$	CH_3	—	—	—	3,09	—	2,59	7,56
XXXVIII	Cl	CH_3	Cl	—	—	3,61	—	—	7,98
XXXIX	Cl	Cl	Cl	—	—	3,43	—	—	—
XL	$SiCl_3$	CH_3	Cl	—	—	3,28	—	—	7,61
XLI	Cl	CH_3	$SiCl_3$	—	—	2,72	—	—	7,84
XLII	$SiCl_3$	CH_3	$SiCl_3$	—	—	2,40	—	—	7,44

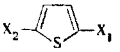
The presence of a large number of thiophene derivatives of diverse structure makes it possible to evaluate the contribution of different substituents to the chemical shifts of the ring hydrogen atoms. We made this sort of evaluation in the following way. The τ_3 and τ_4 chemical shifts in I and III-XI were compared with the chemical shift of 2,5-dichlorothiophene (II) (3.47 ppm). The $\Delta\tau_3$ and $\Delta\tau_4$ values obtained in this case are the differences in the τ_3 and τ_4 chemical shifts that arise when a chlorine atom in the 2 position of the ring is replaced by substituent X (Table 2). (In principle, $\Delta\tau_3$ and $\Delta\tau_4$ can also be obtained by a comparison of the chemical shifts of 5-X-thiophenes with the chemical shifts of thiophene. However, because of the considerable errors in the measurement of the chemical shifts in monosubstituted thiophenes, the $\Delta\tau$ values in this case will be less accurate.) With the use of the $\Delta\tau_3$ and $\Delta\tau_4$ values, the τ_3 and τ_4 chemical shifts in a disubstituted thiophene of the  type can be determined from the formulas $\tau_3 = 3.47 + (\Delta\tau_3)_{X_1} + (\Delta\tau_4)_{X_2}$ and $\tau_4 = 3.47 + (\Delta\tau_3)_{X_2} + (\Delta\tau_4)_{X_1}$, where the subscripts X_1 and X_2 denote that the $\Delta\tau$ values pertain to substituents X_1 and X_2 in the ring. The chemical shifts calculated via this path

TABLE 2. Contributions to the Chemical Shifts in the 3 ($\Delta\tau_3$) and 4 ($\Delta\tau_4$) Positions of the Thiophene Ring That Arise from Substituents X in the 2 Position

X	$\Delta\tau_3$, ppm	$\Delta\tau_4$, ppm	$\Delta\tau_{corr}$, ppm
CH_3	+0,16*	0,00	—
Cl	0,00	0,00	—
Br	−0,18	−0,01	—
$Si(CH_3)_3$	−0,35	−0,27	−0,39
SiH_3	−0,42	−0,25	−0,40
$Si(CH_3)_2Cl$	−0,53	−0,33	−0,53
SiH_2Br	−0,62	−0,34	−0,62
SiH_2Cl	−0,64	−0,35	−0,64
$Si(OC_2H_5)_3$	−0,63	−0,39	−0,40
$Si(CH_3)Cl_2$	−0,73	−0,41	−0,73
$SiCl_3$	−0,81	−0,38	−0,84
SiF_3	−0,85	−0,41	−0,68
CN	−0,96	−0,40	—

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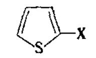
*A comparison of the chemical shifts in XXXII-XXXVIII, XL-XLII, and 2-substituted [2] or 2,5-disubstituted thiophenes demonstrates that the contributions of the CH_3 group as a substituent in the 3 position to the chemical shifts of the hydrogen atoms in the 4 and 5 positions amount to only about +0.15 ppm.

TABLE 3. Contributions ($\Delta\tau_{tot} = \Delta\tau_{an} + \Delta\tau_{el}$) to the Chemical Shifts of the Hydrogen Atoms of the Thiophene Ring in 2-Substituted Thiophenes

Substituent	Δ_{tot}, ppm		
	τ_3	τ_4	τ_5
$Si(CH_3)_3$	+0,04	+0,05	+0,04
SiH_3	−0,02	−0,01	+0,01
$SiCl_3$	+0,03	+0,01	+0,01
SiF_3	−0,17	−0,04	−0,05
$Si(OCH_3)_3$	−0,23	−0,04	−0,02

TABLE 4. Lengths of Some Bonds, Dipole Moments (μ), and $\Delta\chi$ Values of Bonds* in Silylthiophenes



[$X = Si(CH_3)_3$, SiH_3, SiF_3, $SiCl_3$, $Si(OCH_3)_3$]

Bond	Bond length, Å	μ, D	$10^6 \cdot \Delta\chi$, cm^3/ mole
Si—C	1,84	0,6	1,2
Si—H	1,48	1,0	—
Si—F	1,57	1,9	—
Si—Cl	2,06	2,07	4,85
Si—O	1,63	1,23	0,8
C—O	1,43	0,7	1,23
C—H	1,09	0,4	0,9

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* From the data in [9].

(τ_{calc}) are presented in Table 1. The data in Table 1 show that the τ_{calc} values for XII-XXXI are extremely close to the experimental chemical shifts for these compounds. These results attest to the fact that in disubstituted thiophenes, as in disubstituted benzenes and polysubstituted furans [5], the contributions of different substituents to shielding of the ring hydrogen atoms are additive.

Let us examine the $\Delta\tau_3$ and $\Delta\tau_4$ values (Table 2) in greater detail. It follows from what was set forth above that, to a first approximation, the $\Delta\tau$ values characterize the electron-acceptor properties of the corresponding substituents. In fact, in estimating the contribution of the anisotropy of the magnetic susceptibility to the chemical shifts of the ring hydrogen atoms of thiophene derivatives having organic substituents, it was found that this contribution is practically negligibly small [4].

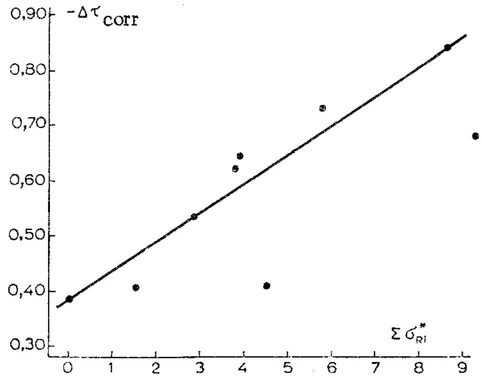

Fig. 1. Relationship between the $\Delta\tau_{corr}$ values in organosilicon derivatives of thiophene $[(C_4H_3S)Si(R_i)_3]$ and the sums of the Taft inductive constants of the three substituents bonded to the silicon atom $(\Sigma\sigma^*_{R_i})$.

For the correct estimate of the electronic effects of silyl substituents in organosilicon derivatives of thiophene, one needs data on the magnitude of the contributions of the anisotropy of the magnetic susceptibility and intramolecular electrical field to the chemical shifts of the ring hydrogen atoms for those cases in which the source of such contributions are the organosilicon fragments. In view of the absence of literature data on this problem, we undertook calculations of the magnitudes of these contributions for several molecules having typical organosilicon substituents (Table 3). The effect of the anisotropy of the magnetic susceptibility and the intramolecular electrical field of $Si-C_{thienyl}$, $Si-C_{alkyl}$, Si−Cl, Si−H, Si−F, Si−O, C−O, and C−H bonds to the chemical shifts of the hydrogen atoms in the 3,4, and 5 positions of the thiophene ring of a number of silylthiophenes was calculated. The anisotropic contribution to the chemical shifts ($\Delta\tau_{an}$) was calculated from the formula [6]

$$\Delta\tau_{an}=\frac{\Delta\chi}{3N}\left\langle\frac{1-3\cos^2\theta}{R^3}\right\rangle,$$

where $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ is the anisotropy of the molar magnetic susceptibility of the above-indicated bonds, and θ is the angle between the axis of symmetry of these bonds and radius vector R, drawn from the center of the dipole to the shielded proton.

The contribution to the chemical shifts due to the effect of the electrical field of the Si−X, C−O, and C−H dipoles was calculated from the formula [7]

$$\Delta\tau_{el}=-3.1\cdot10^{-12}2\mu\left\langle\frac{\cos\theta}{R^3}\right\rangle,$$

where μ is the dipole moment of the bond, and θ is the same angle as in the computation of $\Delta\tau_{an}$.

The geometrical factors $\langle(1-3\cos^2\theta)/R^3\rangle$ and $\langle\cos\theta/R^3\rangle$ were calculated with allowance for the possibility of free rotation of the silyl groups (SiX_3) about the Si−ring bonds. Moreover, it was assumed that all of the possible configurations that arise during free rotation are equally probable. It was assumed that the center of the dipole coincides with the middle of the Si−X, C−O, and C−H bonds. The geometrical parameters of the thiophene ring were taken from [8]. The other geometrical parameters, the $\Delta\chi$ values, and the dipole moments of the bonds are presented in Table 4.

The total contributions ($\Delta\tau_{tot}$), which are the algebraic sums of the $\Delta\tau_{an}$ and $\Delta\tau_{el}$ values calculated from the formulas presented above, are given in Table 3. It is apparent from Table 3 that the $\Delta\tau_{tot}$ contributions to the chemical shifts of the ring protons are small, except for the contributions to the τ_3 chemical shift of fluoro and methoxy derivatives. The small $\Delta\tau_{tot}$ value makes it possible to conclude that, as in the organic derivatives of thiophene, the change in the chemical shifts in the ring of organosilicon derivatives is determined principally by the electronic effects of the variable substituents. However, it is necessary to introduce corrections ($\Delta\tau_{tot}$) to the $\Delta\tau$ values presented in Table 2 for some substituents. The thus corrected ($\Delta\tau_{corr}$) $\Delta\tau_3$ values are presented in Table 2. It is clear from what has been set forth above that the $\Delta\tau_{corr}$ values are a measure of the electronic effects of silyl substituents, which are transmitted via both inductive and conjugation mechanisms. On the basis of the above it is also clear that the $\Delta\tau_{corr}$ values are proportional to the Hammett σ_p constants of the corresponding silyl substituents. It is known that σ_p is the sum of the σ_I constants (which characterize the inductive effect) and the σ_c constants (which characterize the conjugation effect) [10]. If, therefore, it is assumed that the magnitude of the effect of conjugation of the silyl substituents $[Si(R_i)_3]$ with the thiophene ring is independent of the nature of the other substituents (R_i) attached to the silicon atom, one may expect the existence of a proportionality between $\Delta\tau_{corr}$ and the sum of the Taft inductive constants (σ^*) of the three substituents R_i. It follows from Fig. 1 that this sort of proportionality actually exists for most of the silyl substituents. However, the points corresponding to the $Si(OC_2H_5)_3$ and SiF_3 substituents deviate sharply from this dependence. The reason for this deviation is the sharp decrease in the acceptor properties of the silicon atom with respect to the ring when three alkoxy groups or three fluorine atoms are attached to the silicon atom. Conjugation between the ring and the silyl substituent is realized via a $d_\pi - p_\pi$ interaction mechanism, which includes the vacant 3d orbitals of the silicon atom and the ring π electrons [1-3]. As we have previously shown (for example [9, 11]), the overall effect of the $d_\pi - p_\pi$ interaction in the molecule increases as the number of chlorine atoms added to the silicon atom builds up. An increase in the number of chlorine atoms therefore does not decrease the degree of $d_\pi - p_\pi$ interaction of silicon with the ring very sharply [2]. However, the buildup of alkoxy groups or fluorine atoms on the silicon atom very markedly decreases the $d_\pi - p_\pi$ interaction in the molecule as a whole [11-13]. In this case, the energically weaker $d_\pi - p_\pi$ interaction in the silicon–ring bond (as compared with the analogous interaction in the Si–O and Si–F bonds) is not realized at all. The electronic effect of $Si(OC_2H_5)_3$ and SiF_3 substituents is therefore realized only via an inductive mechanism, and the electron-acceptor properties of these substituents prove to be relatively low.

EXPERIMENTAL

The PMR spectra of cyclohexane solutions of the compounds (volume ratios from 1 : 2 to 2 : 1) were obtained with a YaMR-5535 spectrometer (40 MHz). Cyclohexane also served as the internal standard. The accuracy in the determination of the chemical shifts was ±0.01-0.03 ppm. The signals of the ring hydrogen atoms of disubstituted thiophenes constitute spectra of the AB type. The spin–spin coupling constants (J_{AB}), which were 4 ± 0.4 and 4.6 ± 0.4 Hz, respectively, for 2,5- and 2,3-disubstituted thiophenes, confirm the type of substitution in these compounds.

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