SPECTROSCOPIC STUDY OF ORGANOSILICON DERIVATIVES OF THIOPHENE

V.* IR SPECTRA OF MONO- AND DISUBSTITUTED THIOPHENES

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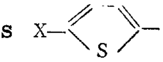
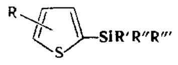
The IR spectra of organosilicon derivatives of thiophene were investigated. A comparison of the results with the literature data made it possible to isolate the characteristic absorption bands of the substituted thiophene ring and to reveal some regularities in the IR spectra of thienylsilanes. The σ^* inductive constants of substituted thienyl groups  were calculated from the experimental ν(Si−Cl) values. An analysis of the σ^* values shows that electron-donor substituents X lower the acceptor capacity of the thienyl substituent as a whole, while electron-acceptor substituents increase it.

In the present research we have investigated the IR spectra of thienylsilanes with the following structure:



I R=H, $R'=R''=R'''=CH_3$; II R=H, $R'=R''=R'''=C_2H_5$; III R=H, $R'=R''=R'''=Cl$; IV R=H, $R'=R''=Cl$, $R'''=CH_3$; V $R=R'=H$, $R''=R'''=CH_3$; VI $R=R'=H$, $R''=CH_3$, $R'''=Cl$; VII $R=R'=H$, $R''=CH_3$, $R'''=Br$; VIII $R=R'=R''=H$, $R'''=CH_3$; IX $R=R'=R''=H$, $R'''=Cl$; X $R=R'=R''=H$, $R'''=Br$; XI $R=R'=R''=R'''=H$; XII R=H. $R'=R''=CH_3$, R'''=2-thienyl XIII $R=R'=H$, $R''=C_2H_5$, R'''=2-thienyl XIV $R=R'=H$, $R''=C_6H_5$, R'''=2-thienyl XV $R=R'=H$, $R''=R'''$=2-thienyl XVI R=5-CH_3, $R'=R''=H$, $R'''=Cl$; XVII R=5-Cl, $R'=Cl$, $R''=R'''=H$; XVIII R=5-SiH_2CH_3, $R'=CH_3$, $R''=R'''=H$; XIX R=5-SiH_2Cl, $R'=Cl$, $R''=R'''=H$; XX R=5-SiH_2Br, $R'=Br$, $R''=R'''=H$; XXI R=5-CH_3, $R'=R''=R'''=H$; XXII R=5-SiH_3, $R'=R''=R'''=H$: XXIII R=5-Cl, $R'=R''=R'''=H$; XXIV R=5-SiH_2Cl, $R'=R''=R'''=H$; XXV R=5-SiH_2Br, $R'=R''=R'''=H$; XXVI R=5-Cl, $R'=H$, $R''=R'''=Cl$; XXVII R=5-$Si(CH_3)_2H$, $R'=H$. $R''=R'''=CH_3$; XXVIII R=5-Cl, $R'=Cl$, $R''=R'''=CH_3$; XXIX R=5-Cl. $R'=R''=R'''=CH_3$; XXX R=5-CH_3, $R'=R''=R'''=Cl$; XXXI R=5-Cl, $R'=R''=R'''=Cl$; XXXII R=3-CH_3, $R'=Cl$, $R''=R'''=CH_3$; XXXIII R=3-CH_3, $R'=CH_3$, $R''=R'''=Cl$; XXXIV R=3-CH_3, $R'=C_2H_5$, $R''=R'''=Cl$; XXXV R=3-CH_3. $R'=R''=R'''=Cl$.

A comparison of the results with the literature data makes it possible to determine the characteristic absorption frequencies of organosilicon derivatives of thiophene (Table 1) and to reveal some regularities in the IR spectra of these derivatives.

Stretching Vibrations of the Thiophene Ring C − H Bonds

Three absorption bands at 3065, 3080, and 3110 cm^{-1}, which correspond to ν(C−H) of the thiophene ring, are present in the IR spectra of thienylsilanes I-XV. When substituents with large −I effects (halogens) are bonded to the silicon atom, the frequencies of these bands increase by ~5-10 cm^{-1}. In addition, redis-

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[*] See [1] for communication IV.

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TABLE 1. Absorption Bands of the Thienyl Grouping in the IR Spectra of Organosilicon Derivatives of Thiophene

Compound	Stretching vibrations of the thiophene ring C–H bonds, cm^{-1}			Stretching vibrations of the thiophene ring, cm^{-1}			Deformation vibrations of the C–H bond, cm^{-1}					
							in-plane			out-of-plane		
I	3110	3080	3067	1503	1410	1330	1220	1090	1000	865	765	710
II	3110	3080	3065	1505	1415	1330	1220	1090	1000	858	732	710
III	3115	3090	3070	1500	1408	1332	1225	1100	1020	865	760	725
IV	3112	3090	3075	1500	1410	1333	1224	1095	1010	860т	760	720
V	3110	3082	3065	1503	1410	1330	1220	1090	1000	870	770	710
VI	3112	3087	3068	1502	1410	1330	1222	1090	1013	860	755	715
VII	3115	3087	3063	1503	1410	1330	1223	1090	1015	860	750	720
VIII	3112	3085	3067	1502	1410	1330	1220	1090	1005	860	750	715
IX	3115	3090	3070	1503	1408	1332	1225	1095	1015	870	750	720
X	3115	3090	3070	1502	1410	1332	1225	1095	1015	870	760	720
XI	3110	3085	3070	1500	1410	1330	1220	1090	1015	870	770	715
XII	3110	3080	3065	1500	1410	1330	1220	1090	1000	860	783	710
XIII	3110	3080	3065	1500	1410	1330	1220	1090	1008	860	760	715
XIV*		—		1500	1405	1330	1220	1090	1008	860	770	715
XV	3110	3080	3070	1500	1408	1330	1220	1090	1010	860	750	715
XVI		3080		1495	1420	1315	1220		1020		810	700
XVII		3090		1515	1415	1300	1215		990		805	670
XVIII		3070		1495	1420	1277	1220		1023		760	710
XIX		3080		1490	1415	1280	1210		1030		820	680
XX		3075		1495	1410	1280	1210		1030		760	715
XXI		3087	3067	1495	1420	1315	1225		1012		805	680
XXII		3075		1495	1415	1280	1210		1020		815	680
XXIII		3090	3070	1510	1420	1300	1210		980		800	680
XXIV†		«—»		1493	1415	1280	1210		1030		815	680
XXV		3080	3065	1495	1410	1280	1210		1025		815	680
XXVI		3100	3070	1515	1415	1300	1215		980		805	670
XXVII		3070	3057	1495	1415	1273	1208		1020		810	670
XXVIII		3070		1518	1418	1300	1212		980		800	685
XXIX		3095	3070	1517	1420	1300	1210		975		800	700
XXX		3080		1530	—	1315	1223		1025		810	680
XXXI		«—»		—	1412	1300	1215		980		805	670
XXXII‡	3110		3073	1520	1395	—	1220	1108	—		—	
XXXIII	3110		3075	1520	1390	—	1222	1111	—		—	
XXXIV	3110		3075	1520	1388	1312	1222	1110	—		—	
XXXV	3112		3078	1520	1390	1318	1225	1112	—		—	

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*The thiophene ring ν(C–H) bands are overlapped by the C–H stretching vibrations of the C_6H_5 group.

†The dash denotes that the spectrum was not recorded in this region.

‡The absorption bands related to the out-of-plane deformation bands of the C–H bond were not isolated for XXXII-XXXV.

tribution of the intensities of these absorption bands is observed. This shows up quite graphically in the spectra of thiophenes that have such substituents as $(CH_3)Si$ (I), $(CH_3)_2HSi$ (V), $(CH_3)H_2Si$ (VIII), H_3Si (XI), and Cl_3Si (III). On passing from I to V and then to VIII, XI, and III, the intensity of the maximum of the low-frequency band decreases, while the intensity of the high-frequency band increases. While the low-frequency band has the maximum intensity and the high-frequency band has the minimum intensity for I, the reverse distribution of intensities of these bands is observed for III.

In [2] it was shown that the line at 3110 cm^{-1} belongs to vibrations with primary participation of the α-C–H bonds of the thiophene ring, while the lines at 3073 and 3086 cm^{-1} are affiliated primarily with the β-C–H bonds. Our data confirm this. In fact, the band at 3110 cm^{-1}, which is absent in the IR spectra of 2,5-disubstituted thiophenes (XVI-XXXI), shows up distinctly in the spectra of 2,3-disubstituted thiophenes (XXXII-XXXV). One broad low-intensity band is usually observed in the spectra of XVI-XXX in the region of the C–H stretching vibrations. On the whole, the ν(C–H) bands of the thiophene ring are of low intensity. The examined regularities may therefore have only limited application for the identification of the thienyl group in organosilicon derivatives of thiophene from the IR spectra.

Skeletal Vibrations of the Thiophene Ring

The absorption bands at ~1500-1540, 1400-1445, and 1335-1365 cm^{-1} [3, 4] correspond to the stretching vibrations of the thiophene ring in 2-substituted thiophenes. Absorption bands at 1503 ± 3, 1410 ± 2, and 1332 ± 2 cm^{-1} are observed for 2-thienylsilanes I-XV. The most intense band is at 1410 cm^{-1}. The intensities of the maxima of the other two bands are comparable and have about half the intensity of the band at 1410 cm^{-1}. These three absorption bands can be used as analytical bands for the identification of 2-thienylsilanes.

2,5-Disubstituted thiophenes XVI-XXXI have absorption bands at 1490-1520, 1390-1420, and 1275-1318 cm^{-1}. The intensities of these absorption bands are primarily determined by the nature of the substituents in the thiophene ring. Thus, if two silyl substituents are attached to the thiophene ring in the 2- and 5-positions, the ratio of the intensities of the maxima of the bands at 1495, 1410, and 1280 cm^{-1} is 3:1:2 (XIX, XX, and XXV) or 2:1:2 (XXII and XXIV), i.e., the 1410 cm^{-1} band is the least intense band. Replacement of one of the organosilicon substituents by a chlorine atom leads to a certain shift in the band at 1410 cm^{-1} to the high-frequency side and a sharp increase in its intensity with a simultaneous decrease in the intensities of the maxima of the bands at 1280 and 1495 cm^{-1} (XVII, XXIX, and XXIII). The introduction of methyl and silyl substituents into the 2- and 5-positions of the thiophene ring leads to a decrease in the intensity of the maxima of all three of the examined absorption bands to extremely low values (XVI, XXI, and XXX).

The absorption bands at 840-870, 740-770, 545-570, and 440-470 cm^{-1} are related to the deformation vibrations of the thiophene ring [4, 5]. However, these bands are of low intensity and are frequently overlapped by the bands that correspond to the vibrations of the substituents in the thiophene ring. We made a completely unambiguous identification of the deformation vibrations only for I-XV, in the IR spectra of which weak bands at 570 ± 5 and 480 ± 5 cm^{-1} are observed.

We did not isolate the absorption band related to the ring pulsation vibration [3, 5], inasmuch as it is overlapped by one of the deformation vibrations of the C−H bonds [6].

Deformation Vibrations of the Thiophene Ring C − H Bonds

The absorption bands at 1215-1240, 1075-1085, and 1030-1050 cm^{-1} are related to the in-plane vibrations of the C−H bonds of the 2-substituted thiophene ring [3, 4]. Narrow intense bands at ~1220, 1090, and 1010 ± 10 cm^{-1} are observed in the spectra of monosubstituted thiophenes I-XV. For 2,5-disubstituted thiophenes the absorption maxima at 1210-1225 and 975-1030 cm^{-1} correspond to this vibration, while the two absorption bands at 1222 ± 3 and 1110 ± 2 cm^{-1} correspond to this vibration for 2,3-disubstituted thiophenes (XXXII-XXXV).

The absorption bands at 890-915, 780-855, and 670-725 cm^{-1} correspond to the out-of-plane deformation vibrations of the C−H bonds of the 2-substituted thiophene ring [3, 4]. In the spectra of I-XV, the three bands at 865 ± 5, 760 ± 10, and 715 ± 5 cm^{-1} correspond to this vibration. Absorption is observed at wider ranges (750-820 and 670-715 cm^{-1}) in the spectra of 2,5-disubstituted thiophenes XVI-XXXI. The small number of investigated compounds, which have many absorption bands over the examined range, made it impossible for us to isolate the absorption bands related to the out-of-plane vibrations of the C−H bonds in 2,3-disubstituted thiophenes (XXXII-XXXV). It has been noted [7] that the out-of-plane deformation vibrations of the C−H bonds in thiophene derivatives are less sensitive to the effect of substituents than the analogous vibrations in substituted benzenes.

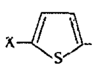
Vibrations of Silyl Groups Attached to the Thiophene Ring

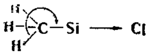
It is known that the vibrational spectra of organosilanes display a characteristic peculiarity called [8] the "barrier effect of the silicon atom." A theoretical calculation of the vibrational spectra of ethylchlorosilanes [9, 10] shows that for substances of the $RSi(R_i)_3$ type, where R is a fixed organic grouping, but R_i is a variable substituent, the set of frequencies and the forms of the normal vibrations of R is almost completely independent of the nature of R_i. Any silyl grouping can therefore be characterized by the appropriate set of absorption bands. No difficulties are encountered in the assignment of the bands characteristic for the $Si-CH_3$, $Si-C_2H_5$, Si−Hal, and Si−H bonds [11].

Let us examine thienylsilanes that contain an Si−Cl bond in somewhat greater detail (Table 2). It is known that the stretching vibration usually associated with the presence of an Si−Cl bond in a molecule has a complex form [11, 12]. In view of this, it might have been expected that the frequency of this vibration, ν(Si−Cl), depends on a large number of intramolecular factors. However, it has been shown experimentally [13] that ν(Si−Cl) for $(R_i)_3SiCl$ compounds is linearly related to $\Sigma\sigma^*$ of substituents R_i, i.e., at least for this type of compound the chief reason for the change in the position of ν(Si−Cl) is the inductive effect of substituents R_i. On the basis of this, the increase in ν (Si−Cl) on passing from XVI and then to (IX, XIX, XXIV) can be explained principally by an increase in the electron-acceptor properties of the thienyl group-

TABLE 2. Frequencies of the Symmetrical (ν_s) and Asymmetrical (ν_{as}) Stretching Vibrations of the Si−Cl Bond in the IR Spectra of the Investigated Compounds

Compound	ν_s, cm^{-1}	ν_{as}, cm^{-1}
III	530	590
IV	512	552
VI	516	
IX	535	
XVI	530	
XVII	545	
XIX	540	
XXIV	540	
XXVI	545	580
XXVIII	517	
XXX	510	585
XXXI	562	590
XXXII	495	
XXXIII	505	550
XXXIV	510	575
XXXV	512	585

ing. The increase in ν_s(Si−Cl) from 510 to 562 cm^{-1} (XXX, II, and XXXI) also attests to an increase in the −I effect of the thienyl group. Taking into account the data in [13] and the fact that the σ^* constant of the 2-thienyl group is 0.93 [14], one can approximately evaluate the σ^* constants of substituted thienyl groups X—  —. Calculations have shown that the σ^* values are 0.63, 0.95, 0.95, and 1.13, respectively, for X=CH_3, SiH_2Cl, SiH_3, and Cl. Thus, the same tendency is followed in thiophene derivatives as in phenyl derivatives: electron-donor groupings lower the acceptor capacity of the thienyl substituent as a whole, while electron-acceptor groupings raise it.

The ν(Si−Cl) frequencies are depressed in thienylchlorosilanes VI, XXXII, and XXXIII, which contain one or two methyl groups attached to the silicon atom. Replacement of the ethyl group by a methyl group in similarly constructed XXXIV and XXXIII leads to a decrease in ν_{as}(Si−Cl) by 25 cm^{-1}. The reason for the decrease in the frequencies of the stretching vibrations of the Si−Cl bond is the effect of σ,σ conjugation — . We examined this effect in detail in a study of methyl(ethyl)chlorosilanes by IR and NMR spectroscopy [15].

We examined the effect of $d_\pi - p_\pi$ interaction in the Si-thienyl fragment and the dependence of this effect on the nature of three other substituents attached to the silicon atom in [1, 16-19]. We note here only that the capacities of the thienyl and phenyl groups for $d_\pi - p_\pi$ interaction with the silicon atom are approximately identical.

EXPERIMENTAL

The IR spectra of pure liquid samples of the organosilicon derivatives of thiophene were obtained with a UR-20 spectrometer.

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