HETEROORGANIC DERIVATIVES OF SULFUR-CONTAINING HETEROCYCLES. 28.* CALCULATION AND INTERPRETATION OF VIBRATIONAL SPECTRA OF THIENYL DERIVATIVES OF GROUP IVB ELEMENTS

A. K. Kozyrev, K. I. Gur'ev,
R. G. Kutlubaev, N. P. Erchak,
and É. Lukevits

UDC 543.422.4'424:547.732'24

The frequencies and forms of the normal vibrations were calculated for trimethyl(2-thienyl)-substituted silane, germane, and stannane molecules. An interpretation of the results of an experimental study of the IR spectra and Raman spectra of compounds with the general formula R_nMMe_{4-n} (R = 2-thienyl, M = Si, Ge, Sn, n = 1...4) is given.

The vibrational spectra of heteroorganic derivatives of thiophene were investigated in [2-4]. In order to obtain the most nearly complete interpretation of the vibrational spectra of heteroorganic derivatives of thiophene we calculated the frequencies and forms of the normal vibrations for trimethyl(2-thienyl)-substituted silane, germane, and stannane molecules. The solution of the vibrational problem was accomplished using the method of fragmentary calculation by means of the programs from [5]. The force fields of the $-M(CH_3)_3$ fragments were taken from [6-8]. The force field of the thiophene molecule was used as the zero approximation of the force field of the thienyl fragment [9, 10]. The starting field was refined by solution of the inverse vibrational problem for the thiophene molecule and three of its deuterium-substituted compounds with C_{2v} symmetry by the method of successive congruence. Good agreement is observed between the experimental and calculated (by means of the force field obtained) frequencies in the series consisting of thiophene and six of its deuterium-substituted compounds; the average deviation was ∿6 cm^{-1}.

The numbers of the natural vibrational coordinates used in the calculations are indicated in Fig. 1. We introduced a total of 53 coordinates: Q_1, Q_{15}, Q_{34}, Q_{17}, Q_{18}, Q_{19}, Q_{20}, Q_{21}, Q_{22}, q_3, q_4, q_5, q_2, q_{16}, q_{35}, q_{36}, q_{37}, q_{38}, q_{23}, q_{24}, and q_{25} – the coordinates of stretching of the bonds; α_8, α_{10}, α_{11}, α_{41}, α_{43}, α_{44}, β_{12}, β_{13}, β_{14}, β_9, β_{33}, β_{42}, β_{46}, β_{47}, β_{28}, β_{29}, β_{30}, β_{31}, γ_{26}, γ_{27}, γ_7, γ_{32}, γ_{40}, ε_6, and ε_{39} – the coordinates of the change in the angles; ρ_{48}, ρ_{49}, ρ_{51}, and ρ_{52} – the out-of-plane coordinates of deviation of the bonds from the plane of the ring; χ_{50} and χ_{53} – the out-of-plane coordinates of the change in the dihedral angle that characterize the bending of the ring. The rotations of the methyl groups relative to the $M_{(1)}-C(Me)$ bonds and the rotation of the ring relative to the $M_{(1)}-C_r$ bond were not taken into account. The solution of the vibrational problem was carried out under the assumption that the molecules of the monothienyl derivatives have C_s symmetry. The numbering of the atoms and the selected directions of the vectors of the bonds are shown in Fig. 2. The thienyl fragment and the $M_{(1)}-C_{(14)}$. $M_{(1)}-C_{(3)}$. amd $C_{(3)}-H_{(10)}$ bonds lie in the plane of symmetry. The $M_{(1)}-C_{(3)}$ and $C_{(16)}-S_{(15)}$ bonds are cis oriented. The geometrical parameters of the molecules necessary for the calculation were taken from [11-13].

Vibrational Spectra of 2-Thienylsilanes $R_nSi(CH_3)_{4-n}$ (n = 1-4)

The IR and Raman spectra were measured for the mono- and dithienylsilanes; we have only the IR spectra at our disposal in the case of the tri- and tetrathienylsilanes. The vibrational problem was solved for the trimethyl(2-thienyl)silane molecule (see Table 1). The values of the experimental frequencies were determined for the liquid state of the substance.

The spectra of the entire series of 2-thienylsilanes (Table 2) were interpreted on the basis of the results of the solution of the vibrational problem and an analysis of the

---

*See [1] for communication 27.

K. A. Fedin Saratov State Pedagogical Institute, Saratov 410028. Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1467-1482, November, 1989. Original article submitted February 18, 1988.

0009-3122/89/2511-1224$12.50

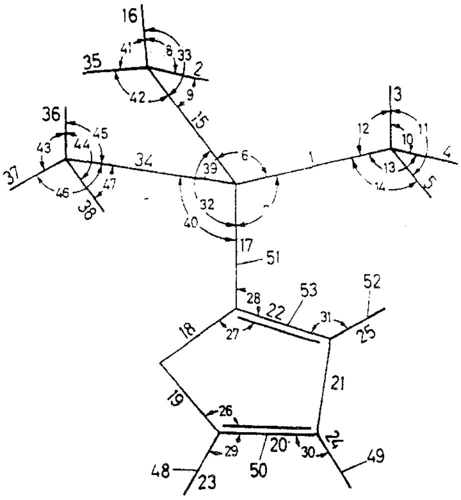

Fig. 1. Natural vibrational coordinates of monothienyl-substituted compounds of the $RM(CH_3)_3$ type.

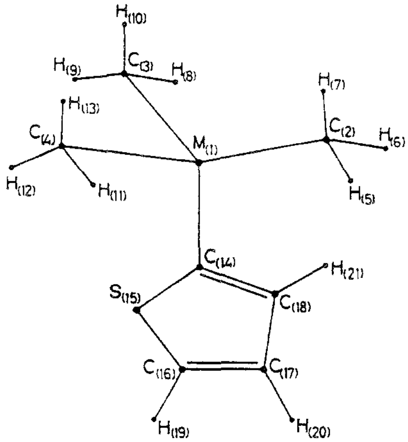

Fig. 2. Numbering of the atoms and selected directions of the vectors of the bonds in molecules of the $RM(CH_3)_3$ type.

experimental data from measurement of the standard intensities, the degree of depolarization of the lines in the Raman spectra, and the absolute intensities of the IR bands.

Three very weak overlapped bands that belong to the stretching vibrations of the C—H bonds of the thienyl fragment were recorded in the short-wave region of the IR spectra of 2-thienylsilanes. Their intensities increase with an increase in the number of rings in the molecules, while the frequencies change only slightly. The q_{23} and q_{24} coordinates change most markedly in the spectrum of trimethyl(2-thienyl)silane at the vibration with a frequency of 3106 cm^{-1}; the q_{23} coordinate makes the principal contribution to the potential energy of this vibration. In the Raman spectrum the line of this vibration is one of the most intense and is polarized. At the vibration with a frequency of 3078 cm^{-1} the hydrogen atom is shifted markedly along the $C_{(18)}$—$H_{(2)}$ bond; a considerably smaller shift is noted for the $H_{(20)}$ and $H_{(19)}$ atoms. The q_{25} coordinate makes the predominant contribution to the potential energy of the vibration. All three coordinates of stretching of the ring C—H bonds change markedly at the vibration with a frequency of 3062 cm^{-1}; the $H_{(20)}$ atom experiences the greatest shift.

Two intense bands with frequencies of 2898 and 2959 cm^{-1} belong to the stretching vibrations of the C—H bonds of the methyl groups. With a decrease in the number of methyl groups in the 2-thienylsilane series one observes a decrease in their intensities. In the Raman spectrum of trimethyl(2-thienyl)silane the $\nu(C—H)(CH_3)$ stretching vibrations show up in the form of two intense lines; the first line is polarized completely (ρ 0.03), while the second is depolarized (ρ 0.86).

TABLE 1. Interpolation of the Vibrational Spectra of Trimethyl(2-thienyl)silane Molecules

IR spectrum, ν, cm^{-1}	Raman spectrum, Δν, cm^{-1}	Type of symmetry	ν_{calc}, cm^{-1}	Form of vibration[1*] (PED of the vibrations with respect to the symmetry coordinates, %)[2*]
1	2	3	4	5
3106	3102	A'	3099	q_{23}(C—H) (83), q_{24}(C—H) (14)
3078	3075	A'	3066	q_{25}(C—H) (75), q_{24}(C—H) (19)
3062	3062	A'	3054	q_{24}(C—H) (66), q_{25}(C—H) (24), (9q_{23})
2959	2957	$3A'$, $3A''$	3×2977 3×2976	q(C—H)(CH$_3$) (100)
2898	2893	$2A'$, A''	2×2909 2908	q(C—H)(CH$_3$) (100)
1502	1500	A'	1512	β_{30}(C=C—H) (19), β_{31}(C=C—H) (14), Q_{20}(C=C) (25), Q_{22}(C=C) (39)
1408	—[3*]	$3A'$, $3A''$	3×1410 1409 2×1408	α(H—C—H) (CH$_3$) (100)
1404	1404	A'	1397	β_{31}(C=C—H) (25), β_{30}(C=C—H) (23), Q_{21}(C—C) (17), Q_{20}(C=C), β_{29}(C=C—H) (12)
1326	1323	A'	1326	β_{29}(C=C—H) (31), Q_{20}(C=C) (33), Q_{19}(C—S) (10), Q_{22}(C=C) (12), β_{30}(C=C—H), β_{31}(C=C—H)
1265 1252	1265 1254	$2A'$, A''	1261 1260 1255	β(H—C—Si) (96), α(H—C—H)(CH$_3$)
1216	1217	A'	1227	β_{31}(C=C—H) (24), β_{29}(C=C—H) (11), β_{30}(C=C—H), β_{28}(C=C—Si), Q_{22}(C=C) (27), Q_{18}(C—S) (23)
1083	1088	A'	1080	β_{30}(C=C—H) (30), β_{29}(C=C—H) (25), β_{31}(C=C—H) (10), Q_{18}(C—S) (12), Q_{20}(C=C) (8)
1052	1057	A'	1050	β_{29}(C=C—H) (14), Q_{21}(C—C) (52), β_{31}(C=C—H) (11), Q_{20}(C=C) (13)
994	997	A'	997	γ_{27}(C=C—S) (35), β_{30}(C=C—H) (10), Q_{17}(C$_r$—Si) (7), Q_{18}(C—S), γ_{26}(C=C—S) (28), Q_{21}(C—C) (10)
900	905	A''	916	ρ_{52}(C—H) (70), ρ_{49}(C—H) (29)
860	860	A'	853	Q_{19}(C—S) (47), γ_{26}(C=C—S) (10), β_{31}(C=C—H), Q_{18}(C—S) (8), Q_{21}(C—C) (5), β_{12}(H—C—Si) (8)
—	846[4*]	A''	835	ρ_{49}(C—H) (49), ρ_{48}(C—H) (25), ρ_{52}(C—H) (26)
840	—	$3A'$, $3A''$	2×870 2×863 2×824	β(H—C—Si)(CH$_3$) (90)
		A'	761	Q_{15}(Si—C) (34), Q_1(Si—C) (17), Q_{18}(C—S) (10), β_{13}(H—C—Si) (8), β_{14}(H—C—Si)
758	755	A''	758	Q_{34}(Si—C) (76), β_{42}(H—C—Si) (12), β_{45}(H—C—Si) (5)
—	750	A'	756	β_{31}(C=C—H), β_{30}(C=C—H), Q_{18}(C—S) (21), Q_{15}(Si—C) (15), Q_{19}(C—S) (16), γ_{26}(C=C—S) (8), γ_{27}(C=C—S) (6)
705	702	A''	696	ρ_{48}(C—H) (78), ρ_{49}(C—H) (20)
642	647	A'	631	Q_1(Si—C) (45), Q_{15}(Si—C) (18), Q_{17}(Si—C) (11), γ_{26}(C=C—S) (12)
616	615	A'	602	γ_{26}(C=C—S) (34), γ_{27}(C=C—S) (24), β_{29}(C=C—H), Q_1(Si—C) (17), Q_{15}(Si—C) (10)
575	—	A''	583	$\varkappa_{53}$ (63), ρ_{51}, $\varkappa_{50}$ (36), ρ_{49}
484	486	A''	486	$\varkappa_{50}$ (73), ρ_{51}, ρ_{48}, $\varkappa_{53}$ (16), ρ_{49}
…	382	A'	382	Q_{17}(Si—C$_r$) (43), γ_{27} (C=C—S) (10), β_{28}(C=C—Si) (7), γ_7(C$_r$—Si—C) (15)
…	285	A'	295	β_{28}(C=C—Si) (24), γ_{32}(C$_r$—Si—C) (59)
…	280	A''	283	γ_{40}(C$_r$—Si—C) (38), ε_{39}(C—Si—C) (27), $\varkappa_{53}$ (22), ρ_{51}(C$_\kappa$—Si) (6)
		A'	214	ε_6(C—Si—C) (35), γ_7(C$_r$—Si—C) (29), γ_{32}(C$_r$—Si—C) (10), Q_{17}(C$_r$—Si) (12)

TABLE 1. (Continued)

1	2	3	4	5
...	212	A''	193	ε_{39}(C—Si—C) (67), γ_{40}(C$_r$—Si—C) (13), ρ_{51}(C$_r$—Si) (9), $\varkappa_{53}$ (5)
		A'	188	ε_{6}(C—Si—C) (45), γ_{7}(C$_r$—Si—C) (44), β_{28}(C=C—Si) (10), γ_{32}(C$_r$—Si—C)
...	...	A'	129	γ_{32}(C$_r$—Si—C) (40), β_{28}(C=C—Si) (40), γ_{7}(C$_r$—Si—C) (13)
...	...	A''	106	ρ_{51}(C$_r$—Si) (69), γ_{40}(C$_r$—Si—C) (31)

[1*] Here and in Tables 3 and 5, the coordinates that change most markedly for a given vibration are presented.

[2*] Here and in Tables 3 and 5, the results of calculation of the potential energy distribution (PED) of the vibrations with respect to the vibrational coordinates are presented in parentheses; when several equivalent coordinates exist, only one of them is indicated.

[3*] The umbrella vibrations of the methyl group are overlapped with the intense line with a frequency of 1404 cm^{-1}.

[4*] The weak depolarized line with a frequency of 846 cm^{-1} was assigned to the out-of-plane vibration of the C—H bonds of the thienyl fragment.

In the IR spectrum of $RSi(CH_3)_3$ the weak band with a frequency of 1502 cm^{-1} belongs to the in-plane deformation vibration of the thienyl fragment; the length of The C=C bonds and the angles that are formed by the C—H bonds with the skeleton of the ring change markedly at this vibration. The Q_{22} and Q_{20} coordinates make the principal contribution to the potential energy of the vibration. In the Raman spectrum the line of the described vibration is very weak and depolarized. On passing to dimethyldi(2-thienyl)silane the absolute intensity of the IR band increases by a factor of two, while a corresponding line is not recorded in the Raman spectrum.

The umbrella vibrations of the methyl groups in trimethyl(2-thienyl)silane have a frequency of 1408 cm^{-1}. In the IR spectrum the band of these vibrations is overlapped with the band of the ring in-plane vibration (1404 cm^{-1}). The intensity of the band with a frequency of 1408 cm^{-1} decreases with a decrease in the number of methyl groups in the examined series of molecules; in the spectrum of methyltri(2-thienyl)-silane the band with a frequency of 1404 cm^{-1} is considerably more intense, while the deformation vibrations of the CH_3 group show up in the form of a weak "shoulder" of the contour of this band. In the Raman spectrum of $RSi(CH_3)_3$ the line of the deformation vibrations of the methyl groups is completely overlapped by the most intense line with a frequency of 1404 cm^{-1}.

This line belongs to the in-plane deformation vibration of the ring at which the β_{31} and β_{30} angular coordinates and the coordinates of stretching of the double (Q_{20}) and single (Q_{21}) bonds change markedly. It follows from the calculation of the potential energy distribution (PED) that the angular coordinates make the principal contribution to the potential energy of this vibration, in agreement with the fact that the degree of depolarization of the line is rather high ($\rho = 0.5$); however the high value of the standard intensity of this line constitutes evidence for significant changes in the Q_{20} and Q_{22} coordinates. On passing to dimethyldi(2-thienyl)silane the standard intensity of the line of the vibration under discussion increases by a factor of more than two, its contour contracts, and the degree of depolarization changes only slightly ($\rho = 0.54$).

The strong polarized line ($\rho = 0.17$) with a frequency of 1323 cm^{-1} in the Raman spectrum of trimethyl(2-thienyl)silane belongs to an equal extent to both deformations of the C=C—H angles of the thienyl fragment and to changes in the lengths of the C=C and C—S bonds. The frequency of this ring vibration does not change with an increase in the number of thienyl fragments in the 2-thienylsilane series, the integral intensities of the bands in the IR absorption spectra increase additively, and the increase in the standard intensities of the lines does not obey the additivity rule and proceeds more rapidly.

The intense band at 1252-1265 cm^{-1} in the IR spectrum of trimethyl(2-thienyl)silane has an unsymmetrical contour, and the corresponding line in the Raman spectrum also has an

TABLE 2. Principal Frequencies in the Vibrational Spectra of 2-Thienylsilanes

Assignment	RSi(CH$_3$)$_3$			R$_2$Si(CH)$_2$			R$_3$SiCH$_3$	R$_4$Si
	IR spectrum, ν, cm^{-1}	Raman spectrum, Δν, cm^{-1}	I$_{rel}$	IR spectrum, ν, cm^{-1}	Raman spectrum, Δν, cm^{-1}	I$_{rel}$	IR spectrum, ν, cm^{-1}	Raman spectrum, ν, cm^{-1}
q(C—H)	3106	3102	100	3103	3098	80	3103	3088
q(C—H)	3078	3075	65	3078	3071	55	3077	3077
q(C—H)	3062	3062	30	3063	3058	30	3062	3064
q(C—H) (CH$_3$)	2959	2957	90	2961	2956	35	2958	—
q(C—H) (CH$_3$)	2898	2893	190	2900	2895	65	2900	—
β(C=C—H), Q(C=C)	1502	1500	2	1501	—	—	1498	1491
α(H—C—H) (CH$_3$)	1408	—	—	1406	—	—	—	—
β(C=C—H), Q(C—C)	—	1404	220	—	1402	260	1404	1402
β(C=C—H), Q(C=C)	1326	1323	100	1326	1323	100	1326	1324
α(H—C—H),	1265	1265	5	—	—	—	—	—
β(H—C—Si) (CH$_3$)	1252	1254	10	1253	1252	5	1257	—
β(C=C—H), Q(C=C), Q(C—S)	1216	1217	40	1216	1214	40	1217	1212
β(C=C—H)	1083	1088	30	1087	1083	35	1087	1082
Q(C—C), β(C=C—H)	1052	1057	30	1053	1051	30	1057	1056
γ(C=C—S), Q(C—C)	994	997	10	998	994	8	1001	1001
ρ(C—H)	900	905	2	900	898	2	904	912
Q(C—S), γ(C=C—S)	860	860	25	853	853	35	852	851
ρ(C—H)	—	846	20	830	834	8	836	837
β(H—C—Si) (CH$_3$)	840	—	—	840	—	—	783	—
β(H—C—Si) (CH$_3$)	—	—	—	807	—	—	—	—
Q(Si—C)	758	755	20	780	779	8	—	—
Q(C—S), γ(C=C—S)	—	750	20	750	748	25	749	748
ρ(C—H)	705	702	25	708	706	10	710	717
Q(Si—C)	642	647	15	677	676	20	725	—
γ(C=C—S)	616	615	260	623	622	155	640	650
ϰ	575	—	—	577	576	2	577	577
ϰ	484	486	2	487	486	4	495	507
Q(Si—C$_r$)	—	—	—	433	—	—	448	453
Q(Si—C$_r$)	—	382	50	—	362	30	—	—
β(C=C—Si)	—	285	25	—	303	8	—	—
ε(C—Si—C)	—	280	20	—	250	15	—	—
γ(C$_r$—Si—C)	—	212	80	—	233	30	—	—
ρ(C$_r$—Si)	—	—	—	—	207	35	—	—
ε(C$_r$—Si—C$_r$)	—	—	—	—	142	10	—	—

unsymmetrical contour; this is due to splitting of the deformation vibrations of the CH$_3$ groups. The intensity of the band of deformation vibrations decreases with a decrease in the number of methyl groups, and the contour becomes symmetrical.

We assign the intense band with a frequency of 1216 cm^{-1} in the IR spectrum of RSi(CH$_3$)$_3$ to the complex in-plane deformation vibration of the thienyl fragment; the H$_{(21)}$, H$_{(19)}$, and H$_{(20)}$ atoms, as well as the C$_{(14)}$, C$_{(18)}$, and C$_{(17)}$ atoms of the skeleton of the ring, are shifted markedly at this vibration. Three coordinates — Q_{22}, β_{31}, and Q_{18} —make approximately equal contributions to the potential energy of this vibration, while the contribution of the β_{29} coordinate is appreciably lower. In the Raman spectrum a narrow partially polarized line corresponds to this vibration. The frequency of the vibration under consideration does not change in the entire series of 2-thienylsilanes.

The vibration with a frequency of 1083 cm^{-1} belongs primarily to deformation vibrations of ring C—H bonds; at this vibration the β_{30}, β_{29}, and β_{31} angular coordinates change most markedly, and the principal part of the potential energy of vibration belongs to them.

The weak band with a frequency of 1052 cm^{-1} in the IR spectrum of RSi(CH$_3$)$_3$ belongs to the complex in-plane vibration of the ring. The H$_{(19)}$ and H$_{(21)}$ atom and the C$_{(16)}$, C$_{(17)}$, and C$_{(18)}$ atoms of the thienyl fragment are shifted appreciably. The Q_{21} coordinate experiences the greatest change, and it makes the principal contribution to the potential energy of this vibration. In the Raman spectrum the line of this vibration is weak and has a rather low degree of depolarization ($\rho \sim 0.3$). With an increase in the number of thienyl fragments in molecules of the R$_n$Si(CH$_3$)$_{4-n}$ series the absolute intensity of the IR band of the vibration under discussion increases, but it remains the weakest among the bands of the in-plane vibrations of the ring.

A change in the internal angles of the coordinates of the ring occurs at the vibration with a frequency of 994 cm^{-1}, and the ν_{27}(C=C—S) coordinate changes most markedly. The $C_{(14)}$ atom is shifted appreciably, which leads to a change in the length of the $C_{(14)}$—Si bond; the Q_{17} coordinate makes a small contribution to the potential energy of this vibration. The band of this vibration in the IR spectra of 2-thienylsilanes is intense, while the line in the Raman spectra is very weak and depolarized.

A very weak band that lies on the wing of the intense band of pendulum vibrations of methyl groups was recorded in the IR spectrum of trimethyl(2-thienyl)silane at 900 cm^{-1}. In the Raman spectrum in this region one observes a very weak line with a frequency of 905 cm^{-1}. According to the results of the calculation, the out-of-plane vibration of the thienyl fragment, which is characterized by deviation of the $C_{(18)}$—$H_{(21)}$ and $C_{(17)}$—$H_{(20)}$ bonds from the plane of the ring, should appear in this region. The ρ_{52} coordinate makes the greatest contribution to the potential energy of this vibration. In the spectrum of tetra(2-thienyl)silane has a frequency of 912 cm^{-1}.

The vibration with a frequency of 860 cm^{-1} is related to the number of in-plane vibrations of the thienyl fragment. The band of this vibration in the IR spectrum of trimethyl(2-thienyl)silane is overlapped with the band of pendulum vibrations of the CH_3 groups; in the Raman spectrum the line of this vibration is partially polarized and weak. The Q_{19} coordinate makes the principal contribution to the potential energy of vibration. A small ($\Delta\nu \sim$ 10 cm^{-1}) decrease in the frequency of the vibration under consideration is noted with an increase in the number of thienyl fragments.

In the Raman spectrum of trimethyl(2-thienyl)silane the weak depolarized line with a frequency of 846 cm^{-1} was assigned to the out-of-plane vibration of the C—H bonds of the thienyl fragment; in the IR spectrum the band of this vibration is completely overlapped by the more intense band of pendulum vibrations of methyl groups; a band of medium intensity is recorded in this region in the IR spectra of the remaining compounds of the series. The ρ_{49} coordinate makes the principal contribution to the potential energy of vibration; the ρ_{48} and ρ_{52} coordinates make approximately equal contributions. All three hydrogen atoms $H_{(20)}$, $H_{(21)}$, and $H_{(19)}$ are shifted perpendicularly to the plane of the ring.

The very intense band with a frequency of 840 cm^{-1} in the IR spectra of $RSi(CH_3)_3$ belongs to the pendulum vibrations of the methyl groups. In the Raman spectra this vibration does not appear. In the IR spectrum of dimethyldi(2-thienyl)silane we assign the two intense bands with frequencies of 840 and 807 cm^{-1} to the deformation vibrations of methyl groups, while in the spectrum of methyltri(2-thienyl)silane we assign the band with a frequency of 783 cm^{-1} to them.

The doubly degenerate stretching vibration of the Si—C(Me) bonds in the vibrational spectrum of trimethyl(2-thienyl)silane has a frequency of 758 cm^{-1}; the band of this vibration is very intense and has an unsymmetrical contour, since it is superimposed on the band on the inplane vibrations of the thienyl fragment. The corresponding line in the Raman spectrum is weak and completely depolarized. In the spectrum of dimethyldi(2-thienyl)silane the unsymmetrical vibration of the Si—C(Me) bonds has a frequency of 780 cm^{-1}. The band of this vibration in the IR spectrum is very intense, while the line in the Raman spectrum is very weak and depolarized.

Intense bands with a frequency of $\sim$750 cm^{-1} are recorded in the IR spectra of 2-thienylsilanes; partially polarized lines, which we assign to in-plane vibrations of the thienyl fragments of the molecules, are observed in the Raman spectrum in this region. In the IR spectrum of trimethyl(2-thienyl)silane the band of this in-plane deformation vibration is completely overlapped with the band of stretching vibrations of Si—C(Me) bonds. Calculations shows that the coordinates of stretching of the C—S bonds, viz., Q_{18} and Q_{19}, make the principal contribution to the potential energy of the vibration under discussion. Because the frequency of the deformation vibration of the ring skeleton (756 cm^{-1}, type A') is close to the frequency of the stretching vibration of Si—C(Me) bonds (761 cm^{-1}, type A') "mixing of the forms" of vibrations occurs, which distorts the pattern of distribution of the potential energy over the vibrational coordinates.

The very strong band with a frequency of 705 cm^{-1} in the IR spectra of $RSi(CH_3)_3$ belongs to the out-of-plane deformation vibrations of the C—H bonds of the thienyl fragment; in the Raman spectra the weak depolarized line belongs to this vibration. The $H_{(19)}$ and $H_{(20)}$ atoms are shifted perpendicularly to the plane of the ring, and the contribution of the ρ_{48} coordinate

TABLE 3. Interpretation of the Vibrational Spectra of the Trimethyl(2-thienyl)germane Molecule

IR spectrum, ν, cm⁻¹	Raman spectrum, Δν, cm⁻¹	Type of symmetry	ν_{calc}, cm⁻¹	Form of vibration (PED of the vibrations with respect to the symmetry coordinates, %)
1	2	3	4	5
3107	3106	A'	3108	q_{23}(C—H) (83), q_{24}(C—H) (14)
3079	3075	A'	3075	q_{25}(C—H) (74), q_{24}(C—H) (20)
3061	3060	A'	3062	q_{24}(C—H) (65), q_{25}(C—H) (24), q_{23}(C—H) (9)
2978	2977	$3A'$, $3A''$	2982 2981 2×2979 2978 2977	q(C—H)(CH_3) (98)
2910	2907	$2A'$, A''	3×2909	ρ(C—H)(CH_3) (98)
1502	—	A'	1508	β_{30}(C=C—H) (18), β_{31}(C=C—H) (15), Q_{22}(C=C) (39), Q_{20}(C=C) (25)
1408*¹	—	$3A'$, $3A''$	1399 2×1398 2×1394 1392	α(H—C—H)(CH_3) (92)
—*¹	1404	A'	1404	β_{30}(C=C—H) (22), β_{31}(C=C—H) (23), β_{29}(C=C—H) (10), Q_{21}(C—C) (17), γ_{26}(C=C—S), γ_{27}(C=C—S), Q_{20}(C=C) (8)
1326	1324	A'	1326	β_{29}(C=C—H) (33), Q_{20}(C=C) (31), Q_{19}(C—S) (11), Q_{22}(C=C) (12), β_{30}(C=C—H) (5), β_{31}(C=C—H)
— 1242	1251 1245	$2A'$, A''	1261 1260 1254	β(H—C—Ge) (98), α(H—C—H) (CH_3)
1216	1217	A'	1222	β_{31}(C=C—H) (25), β_{29}(C=C—H) (11), β_{30}(C=C—H), β_{28}(C=C—Ge), Q_{22}(C=C) (27), Q_{18}(C—S) (22)
1082	1083	A'	1077	β_{30}(C=C—H) (33), β_{29}(C=C—H) (21), β_{31}(C=C—H) (11), Q_{18}(C—S) (12), γ_{27}(C=C—S), Q_{20}(C=C) (6), Q_{21}(C—C) (9)
1045	1048	A'	1048	β_{29}(C=C—H) (17), β_{31}(C=C—H) (10), Q_{21}(C—C) (47), Q_{20}(C=C) (15)
970	971	A'	977	γ_{27}(C=C—S) (34), Q_{17}(C_r—Ge) (8), γ_{26}(C=C—S) (23), β_{30}(C=C—H) (7), Q_{18}(C—S) (8), Q_{21}(C—C) (12), β_{29}(C=C—H), β_{31}(C=C—H)
895*²	—	A''	903	ρ_{52}(C—H) (60), ρ_{49}(C—H) (39)
849	851	A'	853	Q_{19}(C—S) (58), γ_{26}(C=C—S) (16), β_{31}(C=C—H), Q_{21}(C—C) (5), Q_{18}(C—S) (5)
—	834*³	A''	829	ρ_{52}(C—H) (37), ρ_{49}(C—H) (39), ρ_{48}(C—H) (24)
828	—	$2A'$, A''	837 2×835	β(H—C—Ge)(CH_3) (90)
762	760	A', $2A''$	2×769 742	β(H—C—Ge)(CH_3) (90)
747	748	A'	756	β_{31}(C=C—H), β_{30}(C=C—H) (5), Q_{18}(C—S) (30), Q_{19}(C—S) (22), γ_{26}(C=C—S) (16), γ_{27}(C=C—S) (9)
703	—	A''	696	ρ_{48}(C—H) (78), ρ_{49}(C—H) (20)
629	630	A'	632	γ_{26}(C=C—S) (44), γ_{27}(C=C—S) (28), Q_{17}(Ge—C_r) (10), β_{29}(C=C—H), Q_{18}(C—S) (8)
606	607	A' A''	612 620	Q_{15}(Ge—C) (60), Q_1(Ge—C) (39) Q_{34}(Ge—C) (80)
573	573	A'	563	Q_1(Ge—C) (60), Q_{15}(Ge—C) (31)
—*⁴	—*⁴	A''	577	$\varkappa_{53}$ (60), $\varkappa_{50}$ (40), ρ_{51}(C—H)
480	476	A''	478	$\varkappa_{50}$ (69), $\varkappa_{53}$ (24), ρ_{51}(C—H) (6)
...	292	A'	295	Q_{17}(Ge—C_r) (56), β_{28}(C=C—Ge) (20), γ_{27}(C=C—S) (8)
...	237	A'	223	γ_{32}(C_r—Ge—C) (41), β_{28}(C=C—Ge) (38), Q_{17}(C_r—Ge) (10), γ_{27}(C=C—S) (5)

TABLE 3. (Continued)

1	2	3	4	5
...	*5	A''	221	$\rho_{51}(C_r—Ge)$ (28), $\gamma_{40}(C_r—Ge—C)$ (42), $\varkappa_{53}$ (20), $\varepsilon_{39}(C—Ge—C)$ (8)
		A''	196	$\varepsilon_{39}(C—Ge—C)$ (89), $\gamma_{40}(C_r—Ge—C)$ (5)
...	190	A'	194	$\varepsilon_6(C—Ge—C)$ (98), $\gamma_{32}(C_r—Ge—C)$
		A'	181	$\gamma_7(C_r—Ge—C)$ (81), $\varepsilon_6(C—Ge—C)$, $\gamma_{32}(C_r—Ge—C)$ (15)
...	109	A'	115	$\gamma_{32}(C_r—Ge—C)$ (54), $\beta_{28}(C{=}C—Ge)$ (27), $\gamma_7(C_r—Ge—C)$ (13)
...	109	A''	97	$\rho_{51}(C_r—Ge)$ (57), $\gamma_{40}(C_r—Ge—C)$ (43)

[1*] The band of the umbrella vibrations of the methyl group at 1408 cm^{-1} is overlapped with the band of the in-plane deformation vibrations of the thienyl fragment.

[2*] On passing from monothienylgermane to tetrathienylgermane the frequency of the vibration increases to 908 cm^{-1}.

[3*] On passing from monothienylgermane to tetrathienylgermane the frequency of the out-of-plane vibrations remains unchanged.

[4*] Overlapped by the stretching vibrations of the Ge—C(Me) bond.

[5*] Overlapped by the line with a frequency of 237 cm^{-1}.

to the potential energy of vibration is the principal one. With an increase in the number of rings in the series of 2-thienylsilanes one notes a certain increase in the frequency of this vibration; in the IR spectrum of tetra(2-thienyl)silane the corresponding band has a frequency of 717 cm^{-1}.

The completely symmetrical stretching vibration of the Si—C(Me) bonds in the spectrum of trimethyl(2-thienyl)silane has a frequency of 642 cm^{-1}. The integral intensity of the IR band of this vibration is somewhat lower than the intensity of the band of the analogous vibration in the spectrum of trimethyl(2-furyl)silane; the standard intensity of the line of the completely symmetrical ν(Si—C)(Me) vibration in the spectrum of trimethyl(2-thienyl)silane is an order of magnitude lower than in the spectrum of trimethyl(2-furyl)silane [14]. On passing to dimethyldi(2-thienyl)silane the frequency of the completely symmetrical vibration of the Si—C(Me) bonds increases to 677 cm^{-1}; the line of this vibration in the Raman spectrum is very weak and polarized. The ν(Si—C)(Me) stretching vibration in the spectrum of methyltri(2-thienyl)silane has a frequency of 725 cm^{-1}.

The most intense line in the Raman spectrum of trimethyl(2-thienyl)silane is the line with a frequency of 615 cm^{-1}; we assign at which the internal angular coordinates γ_{26} and γ_{27} change most markedly. The frequency of the deformation vibration increases with an increase in the number of thienyl groups in the molecule and reaches 650 cm^{-1} in the spectrum of tetra-(2-thienyl)silane; the relative intensity of the line of the vibration under discussion decreases.

We assign the weak band with a frequency of 575 cm^{-1} in the IR spectrum of trimethyl(2-thienyl)silane to the out-of-plane deformation vibration of the thienyl skeleton. The χ_{53}, ρ_{51}, χ_{50}, and ρ_{49} coordinates change most markedly at this vibration; the χ_{53} and χ_{50} coordinates make the greatest contribution to the potential energy. A corresponding line was not observed in the Raman spectrum. The frequency of the vibration under discussion remains unchanged with the addition of thienyl fragments.

The band with a frequency of 484 cm^{-1} in the IR spectra of $RSi(CH_3)_3$ was also assigned to the out-of-plane vibration of ring, which is characterized by a significant change in the χ_{50}, ρ_{51}, ρ_{48}, and χ_{53} coordinates. The χ_{50} coordinate makes the principal contribution to the potential energy of vibration. A very weak depolarized line corresponds to this vibration in the Raman spectra. With an increase in the number of thienyl fragments in the molecules of the examined series one notes an increase in the frequency of the out-of-plane deformation vibrations to 507 cm^{-1} in the spectrum of tetra(2-thienyl)silane.

The stretching vibration of the $Si—C_{(14)}$ $(Si—C_r)$ bond appears in the Raman spectrum of trimethyl(2-thienyl)silane with a frequency of 382 cm^{-1}. The line of this vibration is rather intense, broad (δ 9.5 cm^{-1}), and polarized (ρ 0.17). An analysis of the form of this vibration shows that, in addition to the $Q_{17}(Si—Cr)$ coordinate, the internal angular coordinate of the thienyl fragment γ_{27}(C=C—S) and the angular coordinates γ_7(C_r—Si—C) and γ_{40}(C_r—Si—C) of the trimethylsilyl fragment change appreciably. The Q_{17} coordinate makes the principal contribution to the potential energy of this vibration. On passing to dimethyldi(2-thienyl)silane the frequency of the completely symmetrical vibration of the Si—C_r bonds decreases to 362 cm^{-1}, the half width of the line increases by a factor of more than two (δ 24.7 cm^{-1}), and the degree of depolarization changes only slightly (ρ 0.13). Similar broadening of the line of the completely symmetrical vibration of the Si—C_r bonds was also observed in the previously investigated spectrum of dimethyl(2-furyl)silane [14]. The unsymmetrical vibration of the Si—C_r bonds appears only in the IR spectrum of dimethyldi(2-thienyl)silane with a frequency of 433 cm^{-1} in the form of an intense band; a line of an unsymmetrical vibration is not observed in the Raman spectrum. The unsymmetrical doubly degenerate vibration of the Si—C_r bonds in the vibrational spectrum of methyltri(2-thienyl)-silane has a frequency of 448 cm^{-1}. We assign the band with a frequency of 453 cm^{-1} in the IR spectrum of tetra(2-thienyl)-silane to an unsymmetrical vibration of Si—C_r bonds.

The weak depolarized line with a frequency of 285 cm^{-1} in the Raman spectrum of trimethyl-(2-thienyl)silane belongs to the deformation vibration, which is characterized by a change in the C=C—Si and C_r—Si—C angles, which lie in the plane of symmetry of the molecule. The γ_{32} coordinate makes the principal contribution to the potential energy of this vibration.

A complex vibration with a frequency of 280 cm^{-1} appears in the Raman spectrum in the form of a weak depolarized line. The angular coordinates of the —Si—$C_{(3)}$ skeleton (γ_7, γ_{40}, ε_6, ε_{39}) and the out-of-plane coordinates of the ring fragment ($\varkappa_{53}$, $\varkappa_{51}$) change at this vibration; 65% of the potential energy is associated with the angular coordinates, while 28% is associated with the out-of-plane coordinates.

The broad, intense, depolarized line with a frequency of 212 cm^{-1} belongs to the deformation vibrations of the trimethylsilyl fragment.

The calculation shows that yet another two lines, one of which belongs to the deformation vibration characterized by a change in the β_{28} (C=C—Si) and γ_{32}(C_r—Si—C) coordinates, the other of which belongs to a vibration characterized by deviation of the C_r—Si bond from the plane of the ring (ρ_{51}), should be observed in the low-frequency region of the spectra of $RSi(CH_3)_3$; however, we were unable to record the corresponding lines in the experimental Raman spectrum.

Vibrational Spectra of 2-Thienylgermanes $R_nGe(CH_3)_{4-n}$ (n = 1...4)

The Raman and IR absorption spectra of mono- and dithienylgermanes were measured, and the IR spectra were obtained for tetrathienylgermanes. The vibrational problem was solved for the trimethyl(2-thienyl)germane molecule (see Table 3). Using the results of the solution of the vibrational problem and the experimental data obtained we assigned the principal frequencies in the spectra of 2-thienylgermanes (Table 4).

Stretching vibrations of C—H bonds of the thienyl fragment appear in the high-frequency region of the spectra. The frequencies of the lines of these three vibrations in the spectra of 2-thienylgermanes and 2-thienylsilanes coincide within the limits of experimental error.

The stretching vibrations of the C—H bonds of the methyl groups in the spectra of 2-thienylgermanes appear with frequencies of 2910 and 2980 cm^{-1}, which is 10-20 cm^{-1} higher than in the corresponding 2-thienylsilanes. The frequencies of the umbrella vibrations of the methyl groups in the spectra of 2-thienylgermanes and 2-thienylsilanes are identical. In the IR spectrum of trimethyl(2-thienyl)germane the band of umbrella vibrations has a frequency of 1408 cm^{-1} and is markedly overlapped with the band of in-plane deformation vibrations of the thienyl fragment, whereas in the spectra of dimethyldi(2-thienyl)- and methyltri(2-thienyl)germane it is completely overlapped by the band of ring vibrations. In the Raman spectra the line of the ring vibration (1404 cm^{-1}) is one of the most intense and completely overlaps the line of the deformation vibrations of the CH_3 groups. In the IR spectra of $RGe(CH_3)_3$ the band with a frequency of 1242 cm^{-1} is also related to the deformation vibrations of the methyl groups, and the contour of this band is unsymmetrical. Similar splitting was also observed in the spectra of $RSi(CH_3)_3$. With a decrease in the number of methyl groups in the examined series of molecules splitting vanishes, the intensity of the band of deformation vibrations decreases, and the frequency increases to 1248 cm^{-1}.

The frequencies of the in-plane deformation vibrations of the thienyl fragment at 1045-1502 cm^{-1} in the spectra of 2-thienylgermanes and 2-thienylsilanes are close to one another.

TABLE 4. Principal Frequencies in the Vibrational Spectra of 2-Thienyl germanes

Assignment	$RGe(CH_3)_3$			$R_2Ge(CH_6)_2$			R_3GeCH_3	R_4Ge
	IR spectrum, ν, cm^{-1}	Raman spectrum, Δν, cm^{-1}	I_{rel}	IR spectrum, ν, cm^{-1}	Raman spectrum, Δν, cm^{-1}	I_{rel}	IR spectrum, ν, cm^{-1}	IR spectrum, ν, cm^{-1}
q(C—H)	3107	3106	85	3105	3098	90	3103	3090
q(C—H)	3079	3075	60	3077	3073	55	3076	3077
q(C—H)	3061	3060	30	3062	3060	30	3061	3067
q(C—H) (CH$_3$)	2978	2977	85	2980	2981	40	2981	—
q(C—H) (CH$_3$)	2910	2907	220	2910	2905	100	2911	—
β(C=C—H), Q(C=C)	1502	—	—	1501	1498	5	1500	1496
α(H—C—H) (CH$_3$)	1408	—						
β(C=C—H), Q(C—C)	—	1404	215	1404	1402	320	1402	1400
β(C=C—H), Q(C=C)	1326	1324	100	1326	1324	100	1326	1326
α(H—C—H)	—	1251	25	—	—	—	—	—
β(H—C—Ge) (CH$_3$)	1242	1245	20	1243	1247	15	1248	—
β(C=C—H), Q(C=C), Q(C—S)	1216	1217	35	1215	1215	35	1215	1215
β(C=C—H)	1082	1083	40	1082	1081	40	1081	1079
β(C=C—H), Q(C—C)	1045	1048	25	1052	1048	20	1052	1052
γ(C=C—S), Q(C—C)	970	971	10	975	973	10	978	982
ρ(C—H)	895	—	—	898	900	2	901	908
Q(C—S), γ(C=C—S)	849	851	55	849	850	55	849	850
ρ(C—H)	—	834	5	832	834	5	832	834
β(H—C—Ge) (CH$_3$)	828	—	—	808	—	—	800	—
β(H—C—Ge) (CH$_3$)	762	—	—	755	—	—	—	—
Q(C—S), γ(C=C—S)	747	748	15	747	748	25	747	748
ρ(C—H)	703	—	—	705	708	5	708	714
γ(C=C—S)	629	630	100	630	629	75	631	633
Q(Ge—C)	606	607	80	614	613	30	—	—
Q(Ge—C)	573	573	335	587	587	120	603	—
ϰ	—	—	—	573	—	—	572	571
ϰ	480	476	5	482	481	2	481	475
Q(Ge—C$_r$)	—	292	70	—	284	25	—	—
γ(C$_r$—Ge—C)	—	237	40	—	255	7	—	—
β(C=C—Ge)	—	190	160	—	217	20	—	—
ε(C—Ge—C)	—	109	10	—	200	25	—	—
ρ(C$_r$—Ge)	—	—	—	—	185	25	—	—

The frequency of the complex deformation vibration of the ring, which is characterized by a change in internal angular coordinates γ_{27} and γ_{26}, decreases appreciably; it is 20-25 cm^{-1} lower in the spectra of 2-thienylgermanes than in the spectra of 2-furylsilanes. The integral intensities of the corresponding bands in the IR spectra and the standard intensities of the lines in the Raman spectra that belong to in-plane vibrations differ only slightly in the spectra of 2-thienyl-substituted germanes and silanes.

The out-of-plane deformation vibration of the $C_{(18)}$—$H_{(21)}$ and $C_{(17)}$—$H_{(20)}$ bonds in the IR spectrum of trimethyl(2-thienyl)germane appears with a frequency of 895 cm^{-1}; with the addition of thienyl fragments one notes an additive increase in the frequency of this vibration to 908 cm^{-1} in the spectrum of tetra(2-thienyl)germane.

The band with a frequency of 849 cm^{-1} in the IR spectra of $RGe(CH_3)_3$ belongs to the in-plane deformation vibration of the thienyl fragment, at which the Q_{19}(C—S) and γ_{26}(C=C—S) coordinates change most markedly. With an increase in the number of rings in the molecules of the examined series of 2-thienylgermanes the frequency of this vibrations remains unchanged, in contrast to the series of 2-thienylsilanes.

The band of the out-of-plane deformation vibration in the IR spectrum of trimethyl(2-thienyl)germane is overlapped completely by the intense broad band of pendulum vibrations of the methyl groups; in the Raman spectrum, in which pendulum vibrations do not appear, the weak depolarized line with a frequency of 834 cm^{-1} belongs to the out-of-plane vibration. In the spectra of the remaining compounds of the series of 2-thienylgermanes the frequency of the out-of-plane vibration under discussion remains unchanged.

Pendulum vibrations of CH_3 groups appear only in the IR spectra of 2-thienylgermanes. The two intense broad bands with frequencies of 828 and 762 cm^{-1} in the spectrum of

TABLE 5. Interpretation of the Vibrational Spectra of the Trimethyl(2-thienyl)stannane Molecule

IR spectrum, ν, cm^{-1}	Raman spectrum, Δν, cm^{-1}	Type of symmetry	ν$_{\mathrm{calc}}$, cm^{-1}	Form of vibration (PED of the vibrations with respect to the symmetry coordinates, %)
	2	3	4	5
3105	3100	A'	3108	q_{23}(C—H) (83), q_{24}(C—H) (14)
3073	3069	A'	3075	q_{25}(C—H) (74), q_{24}(C—H) (20), q_{23}(C—H)
3052	3052	A'	3062	q_{24}(C—H) (65), q_{25}(C—H) (24), q_{23}(C—H) (9)
2984	2981	$3A'$, $3A''$	2991 2990 2989 2988 2987 2986	q(C—H)(CH$_3$) (98)
2918	2913	$2A'$, A''	2918 2×2917	q(C—H)(CH$_3$) (98)
1497	1496	A'	1503	β_{30}(C=C—H) (19), β_{31}(C=C—H) (14), Q_{22}(C=C) (38), Q_{20}(C=C) (28)
1405*	—	$3A'$, $3A''$	1397 2×1395 1393 1392 1390	α(H—C—H)(CH$_3$) (98)
1398	1395	A'	1401	β_{31}(C=C—H) (24), β_{30}(C=C—H) (22), β_{29}(C=C—H) (11), Q_{21}(C—C) (18), Q_{20}(C=C) (6), Q_{22}(C=C), γ_{26}(C=C—S), γ_{27}(C=C—S)
1320	1319	A'	1323	β_{29}(C=C—H) (32), Q_{20}(C=C) (30), β_{30}(C=C—H) (5), β_{31}(C=C—H), Q_{22}(C=C) (14), Q_{19}(C—S) (11)
1213	1213	A'	1222	β_{31}(C=C—H) (22), β_{29}(C=C—H) (10), β_{30}(C=C—H), Q_{22}(C=C) (23), Q_{18}(C—S) (19), β_{28}(C=C—Sn)
1191	1194	$2A'$, A''	2×1215 1213	β(H—C—Sn) (98), α(H—C—H)(CH$_3$)
1078	1078	A'	1075	β_{30}(C=C—H) (36), β_{29}(C=C—H) (20), β_{31}(C=C—H) (9), Q_{18}(C—S) (11), Q_{21}(C—C) (11), γ_{27}(C=C—S), Q_{20}(C=C) (6)
1048	1046	A'	1048	β_{29}(C=C—H) (18), β_{31}(C=C—H) (10), Q_{21}(C—C) (46), Q_{20}(C=C) (15)
945	947	A'	948	γ_{27}(C=C—S) (35), γ_{26}(C=C—S) (28), Q_{17}(C$_r$—Sn), Q_{18}(C—S) (12), Q_{21}(C—C) (9), Q_{22}(C=C), (5), β_{30}(C=C—H) (5), β_{29}(C=C—H)
—	900	A''	901	ρ_{49}(C—H) (70), ρ_{52}(C—H) (30)
845	846	A'	852	Q_{19}(C—S) (58), Q_{21}(C—C) (6), γ_{26}(C=C—S) (14), Q_{18}(C—S) (7)
823	—	A''	819	ρ_{52}(C—H) (60), ρ_{48}(C—H) (17), ρ_{49}(C—H) (17)
774	—	$2A'$, A''	790 2×782	β(H—C—Sn)(CH$_3$) (90)
745	748	A'	756	β_{31}(C=C—H), β_{30}(C=C—H), Q_{18}(C—S) (30), Q_{19}(C—S) (23), γ_{26}(C=C—S) (16), γ_{27}(C=C—S) (9)
720**	—	A', $2A''$	2×726 700	β(H—C—Sn)(CH$_3$) (90)
703	697	A''	698	ρ_{48}(C—H) (80), ρ_{49}(C—H) (17)
—	623	A'	613	γ_{26}(C=C—S) (42), γ_{27}(C=C—S) (38), Q_{17}(Sn—C$_r$) (6), Q_{18}(C—S) (5)
570	—	A''	577	$\varkappa_{53}$ (60), $\varkappa_{50}$ (40)
534	535	A' A''	542 542	Q_1(Sn—C) (33), Q_{15}(Sn—C) (67) Q_{34}(Sn—C) (100)
515	515	A'	512	Q_1(Sn—C) (67), Q_{15}(Sn—C) (33)
473	478	A''	474	$\varkappa_{50}$ (66), ρ_{51}(C—H) (5), $\varkappa_{53}$ (29)
—	247	A'	252	Q_{17}(Sn—C$_r$) (50), β_{28}(C=C—Sn) (34), γ_{32}(C$_r$—Sn—C) (5)
—	—	A''	199	ρ_{51}(C$_r$—Sn) (37), γ_{40}(C$_r$—Sn—C) (43), $\varkappa_{53}$ (18)
—	190	A'	194	γ_{32}(C$_r$—Sn—C) (16), β_{28}(C=C—Sn) (31), Q_{17}(Sn—C) (35), γ_{27}(C=C—S) (9), Q_{18}(C—S) (5)
		A'	144	ε_6(C—Sn—C) (5), γ_7(C$_r$—Sn—C) (68), γ_{32}(C$_r$—Sn—C) (27)

TABLE 5. (Continued)

1	2	3	4	5
—	152	A'	142	ε_6(C—Sn—C) (89), γ_7(C_r—Sn—C) (10), γ_{32}(C_r—Sn—C)
		A''	142	ε_{30}(C—Sn—C) (96)
—	90	A'	101	γ_{32}(C_r—Sn—C) (58), β_{28}(C=C—Sn) (24) γ_7(C_r—Sn—C) (9)
—	—	A''	89	ρ_{51}(C_r—Sn) (50), γ_{40}(C_r—Sn—C) (48)

---

*In the spectra of dimethyl- and di(2-thienyl)stannane and methyltri(2-thienyl)stannane the umbrella vubrations of the methyl group are overlapped with the bands of the in-plane deformation vibrations of the ring.

**The band of pendulum vibrations of the methyl groups is overlapped by the band of out-of-plane vibrations.

trimethyl(2-thienyl)germane belong to them. In the spectrum of dimethyldi(2-thienyl)germane the bands of pendulum vibrations are shifted in the long-wave direction and are recorded with frequencies of 808 and 755 cm^{-1}. In the spectrum of methyltri(2-thienyl)germane the band with a frequency of 800 cm^{-1} belongs to the vibrations under discussion.

The in-plane deformation vibration of the ring, at which the coordinates of stretching of the C—S bonds and angular coordinates γ_{26} and γ_{27} change most markedly, in the spectra of $RGe(CH_3)_3$ has a frequency of 747 cm^{-1}. With the addition of thienyl fragments the frequencies of the corresponding lines and bands remain unchanged.

The out-of-plane vibration, at which the $H_{(19)}$ and $H_{(20)}$ atoms are shifted perpendicularly to the plane of the ring, has a frequency of 703 cm^{-1} in the spectrum of monothienylgermane; the very strong broad band in the IR spectrum belongs to this vibration, while a corresponding line is not observed in the Raman spectrum.

In the Raman spectrum of trimethyl(2-thienyl)germane the line of in-plane deformation vibration of the ring, which is characterized by a change in the γ_{26}(C=C—S) and γ_{27}(C=C—S) angular coordinates, is one of the most intense. This vibration has a frequency of 629 cm^{-1}, which is 13 cm^{-1} higher as compared with the frequency of the ring vibration in trimethyl(2-thienyl)silane; the frequency of the vibration remains virtually unchanged with an increase in the number of ring fragments in the series of 2-thienylgermanes, while this change is 34 cm^{-1} in the 2-thienylsilane series.

We assign the intense depolarized line (ρ 0.86) with a frequency of 607 cm^{-1} in the Raman spectrum of trimethyl(2-thienyl)germane to the doubly degenerate stretching vibration of the Ge—C(Me) bonds. In the spectrum of dimethyldi(2-thienyl)germane the unsymmetrical vibration of the Ge—C(Me) bonds shows up in the form of a weaker, depolarized (ρ 0.86), broad ($\delta \sim$ 10 cm^{-1}), line with a frequency of 613 cm^{-1}.

The very intense polarized (ρ 0.09) line with a frequency of 573 cm^{-1} belongs to the completely symmetrical stretching vibration of Ge—C(Me) bonds in the Raman spectra of $RGe(CH_3)_3$. In the spectrum of dimethyldi(2-thienyl)germane the symmetrical vibration of the Ge—C(Me) bonds has a frequency of 587 cm^{-1}, and the line of this vibration is very intense and polarized (ρ 0.16). We assign the ν(Ge—C)(Me) stretching vibration in the IR spectrum of methyltri(2-thienyl)germane to the band with a frequency of 603 cm^{-1}.

According to the calculation, the out-of-plane deformation vibration of the thienyl skeleton, which is characterized by a change in the $\varkappa_{53}$ and $\varkappa_{50}$, coordinates, in the spectra of $RGe(CH_3)_3$ has a frequency of 577 cm^{-1}; however, stretching vibrations of Ge—C(Me) bonds show up very actively in this region of the experimental Raman and IR absorption spectra, which hinders the assignment. On passing to $R_2Ge(CH_3)_2$ the bands of the stretching vibration are shifted to the short-wave region, while the out-of-plane vibration is recorded in the IR spectra in the form of a weak band with a frequency of 573 cm^{-1}. A corresponding line was not observed in the Raman spectra. The frequency of this out-of-plane vibration does not change with an increase in the number of rings in the molecules of the 2-thienylgermane series.

A second out-of-plane vibration, which is associated with bending of the thienyl skeleton, in the spectra of 2-thienyl-germanes is recorded with a frequency of $\sim$480 cm^{-1}. In contrast to 2-thienylsilanes, the frequency of this vibration in the spectra of 2-thienylgermanes does not depend on the number of thienyl rings.

TABLE 6. Principal Frequencies in the Vibrational Spectra of 2-Thienylstannanes

Assignment	$RSn(CH_3)_3$			$R_2Sn(CH_3)_2$			R_3SnCH_3	R_4Sn
	IR spectrum, ν, cm^{-1}	Raman spectrum, Δν, cm^{-1}	I_{rel}	IR spectrum, ν, cm^{-1}	Raman spectrum, Δν, cm^{-1}	I_{rel}	IR spectrum, ν, cm^{-1}	IR spectrum, ν, cm^{-1}
q(C—H)	3105	3100	110	3103	3098	85	3102	3090
q(C—H)	3073	3069	80	3073	3069	55	3073	3073
q(C—H)	3052	3052	40	3056	3052	30	3058	3060
q(C—H) (CH_3)	2984	2981	70	2988	2983	20	2990	—
q(C—H) (CH_3)	2918	2913	200	2922	2921	45	2925	—
β(C=C—H), Q(C=C)	1497	1496	8	1496	1494	5	1493	1493
α(H—C—H) (CH_3)	1405	—	—	—	—	—	—	—
β(C=C—H), Q(C—C)	1398	1395	240	1397	1395	270	1394	1393
β(C=C—H), Q(C=C)	1320	1319	100	1321	1320	100	1320	1322
β(C=C—H), Q(C=C), Q(C—S)	1213	1213	50	1214	1213	35	1214	1215
β(H—C—Sn), α(H—C—H) (CH_3)	1191	1194	125	1195	1199	35	1202	—
β(C=C—H)	1078	1078	50	1079	1079	40	1078	1076
Q(C—C), β(C=C—H)	1048	1046	25	1049	1047	20	1049	1050
γ(C=C—S)	945	947	20	948	947	15	952	959
ρ(C—H)	—	900	5	900	900	5	903	907
Q(C—S), γ(C=C—S)	845	846	65	845	846	50	844	847
ρ(C—H)	823	—	—	827	—	—	828	833
β(H—C—Sn) (CH_3)	774	—	—	762	—	—	757	—
Q(C—S), γ(C=C—S)	745	748	20	744	748	20	743	745
β(H—C—Sn) (CH_3)	720	—	—	—	—	—	—	—
ρ(C—H)	703	697	10	705	700	2	707	713
γ(C=C—S)	—	623	120	623	624	140	625	627
ϰ	570	—	—	570	—	—	568	567
Q(Sn—C)	534	535	190	540	540	50	—	—
Q(Sn—C)	515	515	640	524	525	190	536	—
ϰ	473	478	8	473	476	5	473	473
Q(Sn—C_r)	—	—	—	—	255	20	—	—
Q(Sn—C_r)	—	247	120	—	245	45	—	—
ε(C—Sn—C)	—	190	60	—	198	5	—	—
γ(C_r—Sn—C)	—	152	280	—	174	20	—	—
β(C=C—Sn)	—	—	—	—	144	10	—	—
ρ(C_r—Sn)								

The stretching vibration of the Ge—C_r bond in trimethyl(2-thienyl) germanes has a frequency of 292 cm^{-1}. The line in the Raman spectrum is weak, broad (δ 8.9 cm^{-1}), and polarized (ρ 0.16). In the Raman spectrum of dimethyldi(2-thienyl)germane the very broad (δ 21.8 cm^{-1}) polarized (ρ 0.12) line with a frequency of 284 cm^{-1} belongs to the symmetrical stretching vibration of Ge—C_r bonds. A line of unsymmetrical vibration could not be recorded; it is possibly located in the wing of the line of the symmetrical vibration (approximate frequency $\Delta\nu \sim$ 300 cm^{-1}).

In the Raman spectrum of trimethyl(2-thienyl)germane the line with a frequency of 237 cm^{-1} can be assigned to a deformation vibration associated with a change in angular coordinates γ_{32} and β_{28}. The calculation shows that a line of a complex vibration described both by a change in the angular coordinates of the skeleton of the $GeC_3(Me)$ group and by a change in the out-of-plane coordinates of the thienyl fragment should be found in the same region ($\Delta\nu_{calc}$ = 221 cm^{-1}). It is possible that the line with a frequency of 237 cm^{-1} in the experimental spectrum is a "double" line.

The very intense, broad, depolarized line with a frequency of 190 cm^{-1} undoubtedly belongs to the deformation vibration of the $GeC_3(Me)$ skeleton.

We assign the weak line with a frequency of 109 cm^{-1} to a deformation vibration associated with a change in the C=C_r—Ge and C_r—Ge—C(Me) angles, which lie in the plane of symmetry of the molecule.

A line of an out-of-plane vibration characterized by deviation of the C_r—Ge bond from the plane of the ring could not be detected in the wing of the exciting line.

The Raman and IR spectra were measured for trimethyl(2-thienyl)- and dimethyldi(2-thienyl)stannane, while the IR spectra were obtained for methyltri(2-thienyl)- and tetra(2-thienyl)stannane. The vibrational problem was solved for the trimethyl(2-thienyl)stannane molecule; the results of the solution are presented in Table 5. The principal frequencies in the vibrational spectra of the entire series of 2-thienylstannanes were assigned (Table 6).

As compared with 2-thienylsilanes and 2-thienylgermanes, for the frequencies of the vibrations of the C—H bonds of the thienyl fragment in 2-thienylstannanes one should note a slight tendency for a decrease ($\Delta\nu$ = 2-9 cm^{-1}).

The stretching vibrations of the C—H bonds of the methyl groups in 2-thienylstannanes are recorded with frequencies of ∿2920 and 2985 cm^{-1}, which is 10-15 cm^{-1} higher than for the corresponding 2-thienylgermanes.

We assigned the weak band with a frequency of 1405 cm^{-1} in the IR spectrum of trimethyl(2-thienyl)stannane to the deformation vibration of the methyl groups. Umbrella vibrations of CH_3 groups were not identified in the spectra of dimethyldi(2-thienyl)stannane and methyltri(2-thienyl)stannane; the band of these vibrations is evidently overlapped with the band of the in-plane deformation vibration of the ring (ν ∿ 1404 cm^{-1}). The deformation vibrations characterized by a change in external angles β(H—C—Sn) in the spectra of 2-thienylstannanes have a frequency of 1191-1202 cm^{-1}. Pendulum vibrations of methyl groups do not appear in the Raman spectra of 2-thienylstannanes. We assign the bands with frequencies of 774 and 720 cm^{-1} in the IR spectrum of trimethyl(2-thienyl)stannane to these vibrations, while we assign the bands with frequencies of 762 and 757 cm^{-1} in the IR spectra of dimethyldi(2-thienyl)- and methyltri(2-thienyl)stannane, respectively, to these vibrations.

For the in-plane deformation vibrations of the ring at 1045-1500 cm^{-1} on passing from 2-thienylgermanes to 2-thienylstannanes one notes a decrease in the frequency of the vibrations that does not exceed 8 cm^{-1}. As in the case of the transition from M = Si to M = Ge, just as when Ge is replaced by Sn, a substantial shift to the low-frequency region ($\Delta\nu$ = 25-30 cm^{-1}) is observed for the bands of the complex deformation vibration of the ring, which is associated primarily with a change in the internal angles (coordinates γ_{26} and γ_{27}).

For the bands of the in-plane and out-of-plane vibrations of the thienyl fragment that have a frequency below 945 cm^{-1} one also notes a slight shift of 3-8 cm^{-1} in the long-wave direction.

In the IR spectrum of trimethyl(2-thienyl)stannane the band of pendulum vibrations of the methyl groups with a frequency of 720 cm^{-1} is almost completely overlapped by the more intense band of the out-of-plane vibration with a frequency of 703 cm^{-1}. An in-plane deformation vibration of the ring with a frequency of 623 cm^{-1} does not appear in the IR spectra of $RSn(CH_3)_3$; the intensities of the corresponding bands increase with an increase in the number of thienyl fragments. One of the most intense lines in the Raman spectra of 2-thienylstannanes belongs to this vibration.

The very intense polarized line (ρ = 0.1) with a frequency of 515 cm^{-1} in the Raman spectra of $RSn(CH_3)_3$ undoubtedly belongs to the symmetrical stretching vibration of Sn—C(Me) bonds. The completely depolarized (ρ 0.86) rather intense line with a frequency of 535 cm^{-1} belongs to the unsymmetrical doubly degenerate vibration of these bonds. On passing to $R_2Sn(CH_3)_2$ the frequency of the symmetrical stretching vibration of the Sn—C(Me) bonds increases to 525 cm^{-1}, while that of the unsymmetrical vibration increases to 540 cm^{-1}. The line of the symmetrical vibration is polarized (ρ 0.17), while the line of the unsymmetrical vibration is depolarized (ρ 0.86). The overall standard intensity of the lines of these vibrations decreases virtually additively with respect to the number of Sn—C(Me) bonds on passing from mono- to di(2-thienyl)stannane. We assign the band with a frequency of 536 cm^{-1} in the IR spectra of R_3SnCH_3 to the stretching vibration of the Sn—C(Me) bond.

The weak polarized line (ρ 0.23) with a frequency of 247 cm^{-1} in the Raman spectrum of trimethyl(2-thienyl)stannane belongs to the stretching vibration of the Sn—C_r vibration. In the Raman spectrum of dimethyldi(2-thienyl)stannane the line of the symmetrical stretching vibration of the Sn—C_r bonds has a frequency of 245 cm^{-1}; it is polarized (ρ 0.20) and very broad (δ 16.5 cm^{-1}), and its standard intensity is more than twice the intensity of the ν(Sn—C_r) line in the spectra of $RSn(CH_3)_3$. The partially polarized (ρ 0.5) line with a frequency of 255 cm^{-1} belongs to the unsymmetrical vibration of the Sn—C_r bonds.

Thus we have interpreted the vibrational spectra of 12 heteroorganic derivatives of thiophene. A slight tendency for a decrease in the frequency in the order M = Si, Ge, Sn is observed for the bulk of the in-plane and out-of-plane vibrations of the thienyl fragment. The greatest shift in the long-wave direction ($\Delta\nu = 50\ cm^{-1}$) was noted for the bands of the in-plane deformation vibration, which is characterized by a change in the angles (coordinates γ_{26} and γ_{27}). The form of the heteroring has a slight effect on the frequency of the vibrations of the $M(CH_3)_{4-n}$ fragment, and the observed frequencies of the CH_3 groups in the corresponding spectra of the heteroorganic derivatives of thiophene and furan virtually coincide. The frequencies of the stretching vibrations of the $M-C_r$ bonds in the 2-thienyl derivatives are lower than in the 2-furyl derivatives; this is explained primarily by a kinematic factor.

EXPERIMENTAL

The IR spectra were obtained with a UR-20 spectrometer at 400-4000 cm^{-1}. The crystalline compounds were investigated in the form of potassium bromide pellets. The Raman spectra were obtained with DFS-12 and DFS-24 spectrometers. The lines of a cadmium (440 nm) or argon (488 nm) laser were used as the exciting lines. Samples of powdery substances were first ground and placed in capillaries. The relative intensities of the Raman lines (I_{rel}) are presented with allowance for the sensitivity of the photomultiplier (FÉU-17, FÉU-79).

LITERATURE CITED

1. S. Rozite, I. Mazheika (Mazeika), A. Gaukhman, N. Erchak, and E. Lukevits (Lukevics), J. Organomet. Chem., 348, 169 (1988).
2. A. K. Kozyrev and I. F. Kovalev, Summaries of Papers Presented at the First All-Union Conference on Organometallic Chemistry [in Russian], Part 1, Izd. GNIIKhTÉOS, Moscow (1979), p. 41.
3. A. K. Kozyrev and I. F. Kovalev, Summaries of Papers Presented at the 16th Conference on the Chemistry and Technology of Organic Compounds of Sulfur and Sulfurous Petroleum Oils [in Russian], Zinatne, Riga (1984), p. 277.
4. A. K. Kozyrev, Spectroscopic Properties of Compounds of Group IVB Elements [in Russian], Izd. Saratovsk. Gos. Ped. Inst., Saratov (1981), p. 63.
5. L. A. Gribov and V. A. Dement'ev, Methods and Algorithms for Calculations in the Theory of the Vibrational Spectra of Molecules [in Russian], Nauka, Moscow (1981), p. 356.
6. I. F. Kovalev, Dokl. Akad. Nauk SSSR, 134, 559 (1960).
7. I. F. Kovalev, Opt. Spektrosk., 10, 707 (1961).
8. V. S. Dernova and I. F. Kovalev, Vibrational Spectra of Compounds of Group IVB Elements [in Russian], Izd. Saratovsk. Gos. Univ., Saratov (1979).
9. É. N. Bolotina and L. M. Sverdlov, Opt. Spektrosk., 3, 150 (1967).
10. É. N. Bolotina, Master's Dissertation, Saratov State University, Saratov (1967).
11. A. Karipides, A. T. Reed, D. A. Haller, and F. Hayes, Acta Cryst., 33B, 950 (1977).
12. A. Karipides, A. T. Reed, and R. H. P. Thomas, Acta Cryst., 30B, 1372 (1974).
13. É. Ya. Lukevits, O. A. Pudova, and R. Ya. Strukovich, Molecular Structures of Organosilicon Compounds [in Russian], Zinatne, Riga (1988).
14. A. K. Kozyrev, Spectroscopic Properties of Heteroorganic Compounds [in Russian], Izd. Saratovsk. Gos. Ped. Inst., Saratov (1978), p. 41.