HETEROORGANIC DERIVATIVES OF FURAN.

68.* CALCULATION AND INTERPRETATION OF THE VIBRATIONAL SPECTRA OF FURAN DERIVATIVES OF GROUP IVB ELEMENTS

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

The vibrational spectra of heteroorganic derivatives of furan have been studied in a series of papers [2-5]. In order to obtain a more nearly complete interpretation of the vibrational spectra of heteroorganic derivatives of furan we calculated the frequencies and forms of the normal vibrations for trimethyl(2-furyl)-substituted silane, germane, and stannane molecules. As a zero approximation of the force field of the furyl fragment we used the force field of the furan molecule obtained in [6, 7]. This field was refined by solution of the inverse vibrational problem for the furan molecule and deuterium-substituted furan molecules by the method of successive congruence. Good agreement between the calculated and experimental frequencies of furan and six of its deuterium-substituted derivatives is observed. The maximum deviation is 19 cm^{-1}, and the mean deviation is ~4 cm^{-1}. The force fields of the $-M(CH_3)_3$ fragments (M = Si, Ge, Sn) were taken from [8-10].

For the calculation of the monofuryl-substituted compounds we used a system of natural independent coordinates (see Fig. 1): 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}, q_{25} – changes in the bond lengths: α_{10}, α_{11}, α_8, α_{41}, α_{43}, α_{44}, β_{12}, β_{13}, β_{14}, β_9, β_{33}, β_{42}, β_{45}, β_{46}, β_{47}, β_{28}, β_{29}, β_{30}, β_{31}, γ_{26}, γ_{27}, γ_7, γ_{32}, γ_{40}, ε_6, ε_{39} – the changes in the angles; ρ_{48}, ρ_{49}, ρ_{51}, ρ_{52} – coordinates that characterize the deviations of the corresponding bonds from the plane of the ring; $\varkappa_{50}$, $\varkappa_{53}$ – out-of-plane coordinates that characterize the bending of the furyl fragment. The rotations of the methyl groups relative to the M–C(Me) bonds and the rotation of the ring relative to the $M-C_r$ bond are disregarded. The designation of the coordinates corresponds to the designation used in studies from which the force fields of the fragments were borrowed. The coordinates were numbered in such a way that the symmetry of the molecules was taken into account in composing the matrix of the dynamic coefficients and instruction for the formation of the matrix of the kinematic coefficients. The vibrational problem was solved under the assumption that the molecules have C_s symmetry. The number of the atoms and the selected directions of the vectors of the bonds are presented in Fig. 2. The ring and the $M_{(1)}-C_{(14)}$ and $M_{(1)}-C_{(3)}$ bonds, as well as the $C_{(3)}-H_{(10)}$ bond, are located in the plane of symmetry. The $C_{(14)}-O_{(15)}$ and $M_{(1)}-C_{(3)}$ bonds are cis oriented. The geometrical parameters necessary for the calculation were taken from [11-13]. In the solution of the vibrational problem we used the method of fragmentary calculation. The calculations were made by means of programs [14] adapted for the Iskra-226 computer in BASIC language. An analysis of the vibrations and the distribution of the potential energy with respect to vibrational coordinates obtained in the solution of the vibrational problem for monofuryl-substituted compounds and the results of experimental measurements of the frequencies, intensities, and the degree of depolarization of the lines in the Raman spectra and the principal parameters of the bands in the IR absorption spectra of di-,

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*See [1] for Communication 67.

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TABLE 1. Interpretation of the Vibrational Spectra of the Trimethyl(2-furyl)silane Molecule

IR spectrum, ν, cm^{-1}	Raman spectrum, $\Delta\nu$, cm^{-1}	Type of symmetry	ν_{calc}, cm^{-1}	Form of vibration*	Distribution of the potential energy of the vibrations with respect to the symmetry coordinates, %
3148	3144	A'	3140	q_{23}(C—H), q_{25}(C—H)	$62q_{23}$, $36q_{25}$
3115	3113	A'	3115	q_{25}(C—H), q_{23}(C—H), q_{24}(C—H)	$54q_{25}$, $28q_{23}$, $17q_{24}$
3082	3083	A'	3087	q_{24}(C—H), q_{23}(C—H), q_{25}(C—H)	$81q_{24}$, $9q_{23}$, $8q_{25}$
2962	2960	$3A'$, $3A''$	3×2977, 3×2976	q(C—H) (**CH$_3$**)**	$100q$(C—H) (**CH$_3$**)
2902	2897	$2A'$, A''	2×2909, 2908	q(C—H) (**CH$_3$**)	$100q$(C—H) (**CH$_3$**)
1555	1552	A'	1560	β_{30}(C=C—H), β_{31}(C=C—H), β_{29}(C=C—H), Q_{22}(C=C), Q_{20}(C=C), γ_{26}(C=C—O), γ_{27}(C=C—O), Q_{17}(C$_r$—Si)	$46Q_{22}$, $22Q_{20}$, $15\beta_{30}$
1462	1458	A'	1463	β_{29}(C=C—H), Q_{20}(C=C), Q_{22}(C=C), γ_{26}(C=C—O), γ_{27}(C=C—O), β_{30}(C=C—H), β_{31}(C=C—H), Q_{19}(C—O)	$46Q_{20}$, $14Q_{22}$, $9\beta_{29}$
1410	1413	$3A'$, $3A''$	3×1410, 1409, 2×1408	α(H—C—H) (**CH$_3$**)	100α(H—C—H) (**CH$_3$**)
1362	1360	A'	1373	β_{30}(C=C—H), β_{29}(C=C—H), β_{31}(C=C—H), γ_{27}(C=C—O), Q_{18}(C—O), Q_{21}(C—C), Q_{22}(C=C)	$28Q_{18}$, $16\beta_{30}$, $15Q_{21}$, $12\beta_{29}$, $10Q_{22}$, $10\gamma_{27}$
1260 1252	1260 1252	$2A'$, A''	2×1260 1255	β(H—C—Si), α(H—C—H) (**CH$_3$**)	96β(H—C—Si) (**CH$_3$**)
1204	1203	A'	1205	β_{31}(C=C—H), β_{29}(C=C—H), γ_{26}(C=C—O), β_{30}(C=C—H), Q_{19}(C—O), Q_{21}(C—C), Q_{18}(C—O), γ_{27}(C=C—O)	$22\beta_{31}$, $22\gamma_{26}$, $17Q_{19}$, $12Q_{21}$, $11\gamma_{27}$
1150	1149	A'	1157	β_{29}(C=C—H), β_{31}(C=C—H), β_{30}(C=C—H), β_{28}(C=C—Si), Q_{18}(C—O)	$57\beta_{29}$, $9Q_{18}$, $7Q_{22}$, $5Q_{19}$, $5\gamma_{26}$
1109	1106	A'	1108	β_{30}(C=C—H), Q_{21}(C—C), Q_{18}(C—O), β_{31}(C=C—H), Q_{20}(C=C), Q_{19}(C—O)	$21Q_{18}$, $21Q_{20}$, $16Q_{21}$, $13Q_{19}$, $13\beta_{30}$
1074	1071	A'	1069	β_{31}(C=C—H), β_{30}(C=C—H), Q_{19}(C—O), Q_{21}(C—C), Q_{22}(C=C), γ_{26}(C=C—O)	$33\beta_{31}$, $22Q_{19}$, $12Q_{21}$, $11\beta_{30}$, $10Q_{22}$

1008	1006	A'	1013	β_{30}(C=C—H), β_{31}(C=C—H), Q_{21}(C—C), β_{28}(C=C—Si)	$32\beta_{30}$, $31Q_{21}$, $25\beta_{31}$
902	903	A'	893	β_{29}(C=C—H), γ_{26}(C=C—O), β_{30}(C=C—H), γ_{27}(C=C—O)	$50\gamma_{26}$, $9\beta_{29}$, $9\beta_{30}$, $8\gamma_{27}$
887	886	A'	864	γ_{27}(C=C—O), Q_{18}(C—O), Q_{19}(C—O), β_{31}(C=C—H), β_{29}(C=C—H)	$46\gamma_{27}$, $25Q_{18}$, $22Q_{19}$
—	863	A''	852	ρ_{49}(C—H), ρ_{48}(C—H), ρ_{52}(C—H)	$64\rho_{49}$, $20\rho_{48}$, $15\rho_{52}$
843	843	$3A'$, $3A''$	2×870, 2×863, 2×824	β(H—C—Si) (**CH$_3$**)	90β(H—C—Si) (**CH$_3$**)
815	818	A''	802	ρ_{52}(C—H), ρ_{48}(C—H)	$81\rho_{52}$, $15\rho_{48}$
758	760	A'	759	Q_{15}(Si—C), Q_1(Si—C), β_{14}(H—C—Si), β_{13}(H—C—Si)	$49Q_{15}$, $25Q_1$, $11\beta_{13}$, $7\beta_{14}$
		A''	758	Q_{34}(Si—C), β_{42}(H—C—Si), β_{45}(H—C—Si)	$75Q_{34}$, $12\beta_{42}$, $5\beta_{45}$
745	748	A''	733	ρ_{48}(C—H), ρ_{49}(C—H)	$56\rho_{48}$, $34\rho_{49}$
—***	—***	A''	646	$\varkappa_{53}$, ρ_{51}(C—Si)	$90\varkappa_{53}$
633	632	A'	626	Q_1(Si—C), Q_{15}(Si—C), Q_{17}(Si—C)	$59Q_1$, $30Q_{15}$, $5Q_{17}$
597	—	A''	616	$\varkappa_{50}$, ρ_{49}(C—H)	$100\varkappa_{50}$
416	417	A'	406	Q_{17}(Si—$C_{\text{к}}$), γ_7(C_r—Si—C), ε_6(C—Si—C)	$61Q_{17}$, $11\gamma_7$, $9\gamma_{27}$
...	303	A'	313	β_{28}(C=C—Si), γ_{32}(C_r—Si—C)	$50\gamma_{32}$, $34\beta_{28}$, $15\varepsilon_6$
...	283	A''	301	γ_{40}(C_r—Si—C), ρ_{51}(C_r—Si), ε_{39}(C—Si—C), $\varkappa_{53}$	$45\gamma_{40}$, $20\varepsilon_{39}$, $15\rho_{51}$, $15\varkappa_{58}$
...	212	A'	222	ε_6(C—Si—C), γ_7(C_r—Si—C), γ_{32}(C_r—Si—C), Q_{17}(Si—C_r)	$47\gamma_7$, $22\gamma_{32}$, $12Q_{17}$, $10\varepsilon_6$
		A''	198	ε_{39}(C—Si—C), ρ_{51}(C_r—Si), γ_{40}(C_r—Si—C)	$74\varepsilon_{39}$, $11\rho_{51}$, $8\gamma_{40}$
		A'	197	ε_6(C—Si—C), β_{28}(C=C—Si), γ_{32}(C_r—Si—C), γ_7(C_r—Si—C)	$60\varepsilon_6$, $21\gamma_7$, $10\beta_{28}$
...	106	A'	125	β_{28}(C=C—Si), γ_{32}(C_r—Si—C), γ_7(C_r—Si—C)	$48\beta_{28}$, $35\gamma_{32}$, $16\gamma_7$
...	106	A''	113	ρ_{51}(C_r—Si), γ_{40}(C_r—Si—C)	$63\rho_{51}$, $37\gamma_{40}$

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*The coordinates that changed most markedly for the given vibration are indicated.

**Here and subsequently, the CH$_3$ group is distinguished by bold type.

***In the IR spectra of RSi(CH$_3$)$_3$ the band at 745 cm^{-1} is overlapped with the band of ν(Si—C)(CH$_3$) stretching vibrations.

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

Assignment	$RSi(CH_3)_3$			$R_2Si(CH_3)_2$			R_3SiCH_3			R_4Si		
	IR spectrum ν, cm^{-1}	Raman spectrum $\Delta\nu$, cm^{-1}	I_{rel}	IR spectrum, ν, cm^{-1}	Raman spectrum $\Delta\nu$, cm^{-1}	I_{rel}	IR spectrum, ν cm^{-1}	Raman spectrum, $\Delta\nu$, cm^{-1}	I_{rel}	IR spectrum, ν, cm^{-1}	Raman spectrum $\Delta\nu$, cm^{-1}	I_{rel}
q(C—H)	3148	3144	194	3148	3142	155	3150	3144	139	3150	3146	130
q(C—H)	3115	3113	74	3115	3111	70	3119	3113	59	3128	3117	80
q(C—H)	3082	3083	51	3087	3079	48	3087	3083	35	3086	—	—
q(C—H) (CH_3)	2962	2960	269	2966	2963	63	2968	2967	22	—	—	—
q(C—H) (CH_3)	2902	2897	623	2905	2901	143	2908	2903	80	—	—	—
β(C=C—H), Q(C=C)	1555	1552	31	1553	1551	30	1553	1554	30	1553	1552	57
β(C=C—H), Q(C=C)	1462	1458	809	1458	1453	725	1457	1453	600	1457	1449	800
α(H—C—H) (CH_3)	1410	1413	20	1410	1412	5	1410	1413	2	—	—	—
β(C=C—H), Q(C—O), Q(C—C)	1362	1360	100	1363	1361	100	1365	1362	100	1366	1362	100
α(H—C—H), β(H—C—Si) (CH_3)	1260	1260	26	1255	1256	15	1257	1256	4	—	—	—
	1252	1252										
β(C=C—H), Q(C—O), γ(C=C—O)	1204	1203	177	1205	1205	125	1207	1208	96	1208	1208	114
β(C=C—H)	1150	1149	57	1151	1152	35	1151	1153	35	1153	1153	50
Q(C—O), Q(C—C), Q(C=C)	1109	1106	11	1112	1111	10	1118	1113	4	1120	1120	18
β(C=C—H), Q(C—O), Q(C=C)	1074	1071	131	1072	1071	73	1072	1072	61	1069	1065	71
β(C=C—H), Q(C—C)	1008	1006	57	1008	1006	50	1009	1011	43	1008	1010	71
γ(C=C—O), β(C=C—H)	902	903	71	903	900	60	902	900	41	903	900	86
γ(C=C—O), Q(C—O)	887	886	40	887	886	40	886	886	28	886	886	79
ρ(C—H)	—	863	10	—	872	12	—	877	8	—	—	—
β(H—C—Si) (CH_3)	843	843	26	836	—	—	790	796	4	—	—	—
ρ(C—H)	815	818	14	—	822	8	822	824	9	829	831	21
β(H—C—Si) (CH_3)	—	—	—	810	—	—	—	—	—	—	—	—
Q(Si—C)	758	760	34	784	784	13	—	—	—	—	—	—
ρ(C—H)	745	748	17	747	747	5	748	748	7	753	758	11
Q(Si—C)	633	632	374	677	677	63	733	733	22	—	—	—
ϰ	—	—	—	650	649	8	651	651	4	652	656	21
ϰ	597	—	—	597	598	5	596	598	7	596	598	14
Q(Si—C_r)	—	—	—	475	—	—	503	503	2	535	—	—
Q(Si—C_r)	416	417	157	403	402	55	392	394	39	—	—	—
β(C=C—Si)	...	303	17	—	325	10	—	265	33	—	275	64
ε(C—Si—C)	...	283	17	—	270	25	—	240	22	—	260	50
γ(C_r—Si—C)	...	212	234	—	240	30	—	175	9	—	177	50
ρ(C_r—Si)	...	106	171	—	204	35	—	—	—	—	—	—
ε(C_r—Si—C_r)	...	—	—	—	146	20	—	—	—	—	—	—

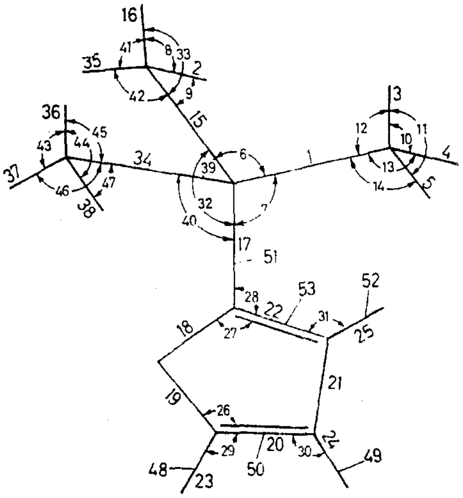

Fig. 1

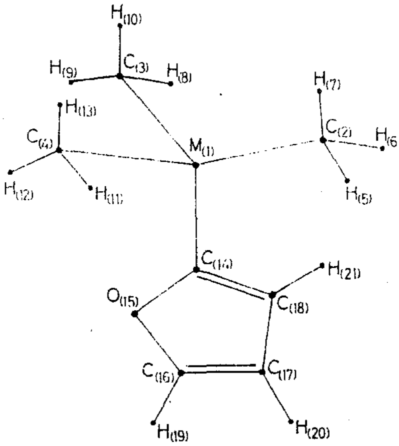

Fig. 2

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

tri-, and tetrafuryl-substituted silanes, germanes, and stannanes make it possible to perform an interpretation of the spectra of compounds of the indicated series.

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

The vibrational problem for the trimethyl(2-furyl)-silane molecule was solved (Table 1). The experimental frequencies are presented for the liquid state of the substance. Assignments were made for the entire examined series of 2-furylsilanes (Table 2).

Three very weak bands related to the stretching vibrations of ring C—bonds were recorded in the short-wave region of the IR spectra; their intensities increase with an increase in the number of furyl groups in the molecule. In the Raman spectra the corresponding lines are quite intense [their relative intensities (I_{rel}) at the maxima are presented in Table 2]. The $H_{(19)}$ and $H_{(21)}$ atoms are displaced markedly in the vibration with a frequency of 3148 cm^{-1}. The q_{23} coordinate makes the greatest contribution to the potential energy of this vibration. The q_{25}, q_{23}, and q_{24} coordinates change simultaneously in the vibration with a frequency of 3115 cm^{-1}. The band with a frequency of 3082 cm^{-1} is very weak; in earlier studies dealing with the measurement of the IR spectra of 2-furylsilanes it was not observed; however, measurement of the Raman spectra and a more detailed study of the IR spectra for a greater thickness of the investigated sample made it possible to reliably record this vibration, which belongs primarily to the change in the q_{24} coordinate.

The bands at 2962 and 2902 cm^{-1} in the spectrum of trimethyl(2-furyl)silane are related to stretching vibrations of the C—H bonds of methyl groups. In the Raman spectrum the lines of these vibrations are among the most intense; the first of them is completely depolarized (ρ = 0.86) and very broad, while the second is polarized (ρ = 0.02). As the number of methyl groups in the $R_nSi(CH_3)_{4-n}$ series decreases their intensities decrease.

The vibration at 1555 cm^{-1} is characterized by a change in the angles formed by the C—H bonds with the skeleton of the furyl fragment and the lengths of the C═C bonds. In the Raman spectrum the line of this vibration is very weak and, as demonstrated by a qualitative evaluation, depolarized.

The B_{29}, Q_{20}, and Q_{22} coordinates change most markedly in the vibration at 1462 cm^{-1}. Lengthening of the C═C bonds is accompanied by an appreciable change in the internal angles (the γ_{26} and γ_{27} coordinates). In the investigated Raman spectra of 2-furylsilanes the line of this vibration is the most intense and polarized (ρ = 0.3-0.36). An increase in the number of furyl groups has virtually no effect on the frequency of this ring vibration, and the standard intensity of the lines increases; however, this increase does not obey the simple additivity rule.

The deformation vibrations of the methyl groups, which are associated primarily with a change in the α(H—C—H) angles, have a frequency of 1410 cm^{-1}; the corresponding line in the Raman spectrum is very weak and depolarized (ρ = 0.78).

All of the atoms of the furyl fragment are displaced appreciably in the complex in-plane vibration at 1362 cm^{-1}. Almost a third of the potential energy of the vibration goes into the Q_{18} coordinate, while the remainder is distributed rather uniformly among the β_{30}, Q_{21}, Q_{29}, Q_{22}, and γ_{27} coordinates. In the Raman spectra the line of this vibration has medium intensity, is depolarized (ρ = 0.78-0.83), and is not overlapped with other lines; it was used as the standard in the evaluation of the relative intensities at the maxima of the other lines.

Two markedly overlapped bands that belong to deformation vibrations of methyl groups are recorded at 1252-1260 cm^{-} in the IR spectrum of trimethyl(2-furyl)silane. The contour of the corresponding line in the Raman spectrum has two maxima. Similar splitting was noted in the spectra of trimethylchlorogemane [10] and trimethylbromogermane [10]. Lone bands, the intensities of which decrease with a decrease in the number of methyl groups, are recorded in the spectra of dimethyldi- and methyltri(2-furyl)silane in this region. In the Raman spectra the lines of deformation vibrations of methyl groups are weak and partially polarized.

A vibration with a frequency of 1204 cm^{-1} appears in the IR spectrum of trimethyl(2-furylsilane in the form of a narrow intense band. In the Raman spectrum the depolarized line of medium intensity corresponds to this vibration. The integral intensities of the IR bands increase additively as the number of furyl groups increases. The vibration under consideration is described by a marked change in the angular coordinates (β_{31}, β_{29}, β_{30}), which characterize the in-plane deformation vibration of the ring C—H bonds, as well as by a change in the internal angles (γ_{26}, γ_{27}) and the C—O (Q_{18}, Q_{19}) and C—C (Q_{21}) bond lengths of the furyl fragment.

The vibration with a frequency of 1150 cm^{-1} is related to in-plane deformation vibrations of the ring. The H_{19}, H_{20}, and H_{21} atoms are displaced most markedly. The B_{29} coordinate makes the principal contribution to the potential energy of this vibration. For the entire examined series of 2-furylsilanes the frequency of this vibration remains virtually unchanged; the lines in the Raman spectra are weak and depolarized.

The vibration with a frequency of 1109 cm^{-1} in the IR spectrum of trimethyl(2-furyl)silane show up in the form of a strong band. The intensities of the bands increase with an increase in the number of furyl groups, and a tendency toward an increase in the frequency with the addition of each furyl group is observed. A very weak broad line corresponds to the vibration under discussion in the Raman spectra. According to the results of calculation of the form of this vibration it should be assigned primarily to the vibration of the skeleton of the ring (pulsation of the ring); however, the external C═C—H angles also change appreciably. The Q_{18}, Q_{20}, Q_{21}, Q_{19}, and β_{30} coordinate makes the principal contribution to the potential energy.

The H_{21} and H_{20} atoms are very markedly displaced in the vibration with a frequency of 1074 cm^{-1}; the H_{19} atom is displaced to a considerably lesser extent. The β_{31}, Q_{19}, Q_{21}, and β_{30} coordinates make the principal contribution to the potential energy of this vibration. The band at 1074 cm^{-1} in the IR spectrum of trimethyl(2-furyl)silane is weak; in the Raman spectrum this vibration shows up in the form of a depolarized line of medium intensity.

Very strong bonds with a frequency of 1008 cm^{-1} are recorded in all of the investigated IR spectra of 2-furylsilanes. These bands serve as some of the indicators that make it possible to form a judgement regarding the presence of a 2- or 2,5-substituted furyl fragment in the molecule [15]. It is apparent from the results of the calculation presented above that the β_{30}, β_{31}, and Q_{21} coordinates change most markedly for this vibration and that they make the principal contribution to the potential energy of the vibration. The angles and bonds, the change in which determines the form of the vibration under consideration, are remote from the substitution positions, and the frequency of this in-plane vibration of the ring therefore changes only slightly on passing from 2-substituted to 2.5-substituted furans.

Two overlapped intense bands with frequencies of 902 and 887 cm^{-1} are also related to in-plane deformation vibrations of the furyl fragment. The β_{29}, β_{30}, γ_{26}, and γ_{27} coordinates change markedly in the vibration with a frequency of 902 cm^{-1}; the γ_{26} coordinate makes the principal contribution to the potential energy of this vibration. In the variation with a frequency of 887 cm^{-1} the hydrogen atoms of the furyl fragment are displaced to a lesser extent than in the preceding vibration, and the C—O bond lengths and the γ_{27}(C=C—O) internal angular coordinate change markedly. For the entire series of 2-furylsilanes the frequency of these vibrations remains unchanged, and two weak overlapped lines in the Raman spectra correspond to them.

The identification of the vibrations over the frequency range 880-800 cm^{-1} in the IR spectra of 2-furylsilanes is complicated, since the pendulum vibrations of the methyl groups appear in this region in the form of very strong broad bands.

A very weak line with a frequency of 863 cm^{-1}, which we assign to out-of-plane deformation vibrations of C—H bonds of the furyl fragment, was recorded in the Raman spectrum of trimethyl(2-furyl)silane. All three H_{19}, H_{20}, and H_{21} atoms are displaced perpendicularly relative to the plane of the ring. The ρ_{49} coordinate makes the principal contribution to the potential energy of this vibration. The frequency of this vibration increases with an increase in the number of furyl groups, and in the spectrum of tetra(2-furyl)silane the line of the examined vibration is overlapped with the line at 886 cm^{-1}.

As we have already noted, the pendulum vibrations of the methyl groups, which are characterized by a change in the β(H—C—Si) external angles, are very active in the IR spectra. The band at 843 cm^{-1} in the IR spectrum of trimethyl(2-furyl)silane belongs to them, while the weak depolarized line of the same frequency in the Raman spectrum belongs to them. We assign the very strong bands at 836 and 810 cm^{-1} in the IR spectrum of dimethyldi(2-furyl)silane to deformation vibrations of CH_3 groups. Corresponding lines do not appear in the Raman spectrum. In the spectra of methyltri(2-furyl)silane the pendulum vibrations of the methyl group have a frequency of 790 cm^{-1}.

In the spectrum of trimethyl(2-furyl)silane the vibration with a frequency of 815 cm^{-1} is related to out-of-plane vibrations of the ring C—H bonds. All of the hydrogen atoms are displaced appreciably, the ρ_{52} and ρ_{48} coordinates change most markedly, and the ρ_{52} coordinate makes the preponderant contribution to the potential energy of this vibration. An increase in the frequency of this vibration to 829 cm^{-1} in the spectrum of tetra(2-furyl)silane is noted with an increase in the number of rings in the molecule. In the IR spectrum of dimethyldi(2-furyl)-silane the band of out-of-plane vibrations is overlapped by a more intense band belonging to pendulum vibrations of CH_3 groups.

The doubly degenerate (A' and A") stretching vibration of the Si—C(Me) bonds in the trimethyl(2-furyl)silane molecule and the unsymmetrical vibration of the Si—C(Me) bonds in the dimethyldi(2-furyl)silane molecule have frequencies of, respectively, 758 and 784 cm^{-1}. In the IR spectra the bands of the vibrations under discussion are very intense, whereas weak depolarized lines in the Raman spectra belong to them. For these vibrations, in addition to a change in the lengths of the Si—C(Me) bonds, one observes an appreciable change in the B(H—C—Si) angular coordinates.

In the spectrum of trimethyl(2-furyl)silane the out-of-plane deformation vibrations that are characterized primarily by a change in the ρ_{48} and ρ_{49} coordinates have a frequency of 745 cm^{-1}. The intensities of the IR bands increase additively with an increase in the number of furyl groups, and the frequencies remain virtually unchanged. The lines of out-of-plane deformation vibrations in the Raman spectra are very weak and depolarized.

The completely symmetrical stretching vibration of the Si—C(Me) bonds in the spectrum of trimethyl(2-furyl)silane has a frequency of 633 cm^{-1}. In the Raman spectrum the line of this vibration is very intense and polarized (ρ = 0.09). On passing to dimethyldi(2-furyl)-silane the frequency of the completely symmetrical vibration of the Si—C(Me) bonds increases to 677 cm^{-1}, the standard intensity of the line decreases additively with respect to the number of Si—C(Me) bonds, and the degree of depolarization changes only slightly (ρ = 0.11). In the Raman spectrum of methyltri(2-furyl)silane the line with a frequency of 733 cm^{-1} (ρ = 0.37) belongs to the ν(Si—C)(Me) stretching vibration.

The calculation of the frequencies in the vibrational spectrum of trimethyl(2-furyl)silane shows that one of the out-of-plane vibrations of the ring that is charcterized by a change in the coordinate of the $\varkappa$ type has a frequency of 646 cm^{-1}. We were unable to detect the corresponding line or band in the spectra of $RSi(CH_3)_3$, since the stretching vibration of the Si—C(Me) bonds shows up very actively in this region. But a weak broad band with a frequency of 650 cm^{-1} is observed in the Raman spectrum of dimethyldi(2-furyl)silane; its intensity in the 2-furylsilane series increases with the addition of furyl fragments, while the frequency does

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

IR spectrum, ν, cm⁻¹	Raman spectrum, Δν, cm⁻¹	Type of symmetry	ν_{calc}, cm⁻¹	Form of vibration	Distribution of the potential energy of the vibrations with respect to the symmetry coordinates, %
3142	3143	A'	3140	q_{23}(C—H), q_{25}(C—H)	$62q_{23}$, $36q_{25}$
3114	3111	A'	3115	q_{25}(C—H), q_{23}(C—H), q_{24}(C—H)	$54q_{25}$, $28q_{23}$, $17q_{24}$
—	3079	A'	3087	q_{24}(C—H), q_{23}(C—H), q_{25}(C—H)	$81q_{24}$, $8q_{23}$, $8q_{25}$
2978	2974	$3A'$, $3A''$	2982, 2981, 2×2979, 2×2978	q(C—H) **(CH$_3$)**	$100q$(C—H) (CH$_3$)
2910	2906	$2A'$, A''	3×2909	q(C—H) (CH$_3$)	$100q$(C—H) (CH$_3$)
1552	1547	A'	1560	β_{30}(C=C—H), β_{31}(C=C—H), β_{29}(C=C—H), Q_{22}(C=C), Q_{20}(C=C), γ_{26}(C=C—O), γ_{27}(C=C—O), Q_{17}($C_{\text{к}}$—Ge)	$46Q_{22}$, $22Q_{20}$, $15\beta_{30}$, $7\beta_{29}$, $6\beta_{31}$
1458	1456	A'	1461	β_{29}(C=C—H), Q_{20}(C=C), Q_{22}(C=C), γ_{26}(C=C—O), γ_{27}(C=C—O), β_{30}(C=C—H), β_{31}(C=C—H), Q_{19}(C—O)	$46Q_{20}$, $15Q_{22}$, $8\beta_{29}$, $7Q_{19}$, $7\gamma_{26}$
1414	1413	$3A'$, $3A''$	1396, 2×1398, 2×1402, 1403	α(H—C—H) **(CH$_3$)**	100α(H—C—H) **(CH$_3$)**
1362	1358	A'	1372	β_{30}(C=C—H), β_{29}(C=C—H), β_{31}(C=C—H), γ_{27}(C=C—O) Q_{18}(C—O), Q_{21}(C—C), Q_{22}(C=C), Q_{17}(C_{r}—Ge)	$28Q_{18}$, $16\beta_{30}$, $15Q_{21}$, $13\beta_{29}$, $10Q_{22}$, $10\gamma_{27}$
—* 1241	1245 1242	$2A'$, A''	1257, 1263, 1264	β(H—C—Si), α(H—C—H) **(CH$_3$)**	98β(H—C—Si) **(CH$_3$)**
1202	1201	A'	1203	β_{31}(C=C—H), β_{29}(C=C—H), γ_{26}(C=C—O), β_{30}(C=C—H), Q_{19}(C—O), Q_{21}(C—C), γ_{27}(C=C—O), Q_{18}(C—O), Q_{22}(C=C)	$22\beta_{31}$, $22\gamma_{26}$, $18Q_{19}$, $11Q_{21}$, $11\gamma_{27}$, $6Q_{22}$
1145	1146	A'	1156	β_{29}(C=C—H), β_{30}(C=C—H), β_{31}(C=C—H), β_{28}(C=C—Ge), Q_{18}(C—O), Q_{22}(C=C)	$58\beta_{29}$, $9Q_{18}$, $7Q_{22}$, $5\beta_{30}$, $5\gamma_{26}$

1093	1093	A'	1106	$\beta_{30}(C{=}C{-}H)$, $Q_{21}(C{-}C)$, $Q_{18}(C{-}O)$, $Q_{20}(C{=}C)$, $Q_{19}(C{-}O)$, $\gamma_{26}(C{=}C{-}O)$	$22Q_{18}$, $20Q_{20}$, $17Q_{21}$, $14Q_{19}$, $12\beta_{30}$, $5\gamma_{2}$
1067	1066	A'	1068	$\beta_{31}(C{=}C{-}H)$, $\beta_{30}(C{=}C{-}H)$, $Q_{19}(C{-}O)$, $Q_{21}(C{-}C)$, $\gamma_{26}(C{=}C{-}O)$, $Q_{22}(C{=}C)$, $Q_{20}(C{=}C)$	$34\beta_{31}$, $21Q_{19}$, $12\beta_{30}$, $11Q_{21}$, $10Q_{22}$, $5Q_{20}$
1003	1003	A'	1012	$\beta_{30}(C{=}C{-}H)$, $\beta_{31}(C{=}C{-}H)$, $Q_{21}(C{-}C)$, $\beta_{28}(C{=}C{-}Ge)$	$32\beta_{30}$, $31Q_{21}$, $25\beta_{31}$, $6Q_{19}$
895	896	A'	889	$\beta_{29}(C{=}C{-}H)$, $\gamma_{26}(C{=}C{-}O)$, $\beta_{30}(C{=}C{-}H)$, $\gamma_{27}(C{=}C{-}O)$	$54\gamma_{26}$, $9\beta_{29}$, $8Q_{21}$, $7\gamma_{27}$, $5\beta_{30}$
885	882	A'	870	$\gamma_{27}(C{=}C{-}O)$, $Q_{18}(C{-}O)$, $Q_{19}(C{-}O)$, $Q_{17}(Si{-}C_r)$, $\beta_{21}(C{=}C{-}H)$, $\beta_{29}(C{=}C{-}H)$	$47\gamma_{27}$, $26Q_{18}$, $21Q_{19}$
—*	—*	A''	852	$\rho_{49}(C{-}H)$, $\rho_{48}(C{-}H)$, $\rho_{52}(C{-}H)$	$64\rho_{49}$, $20\rho_{43}$, $15\rho_{52}$
830	—	$2A'$, A''	840, 2×837	$\beta(H{-}C{-}Ge)$ **(CH_3)**	$90\beta(H{-}C{-}Si)$ **(CH_3)**
810	808	A''	802	$\rho_{52}(C{-}H)$, $\rho_{48}(C{-}H)$	$81\rho_{52}$, $15\rho_{48}$
764	—	A', $2A''$	2×771, 744	$\beta(H{-}C{-}Ge)$ **(CH_3)**	$90\beta(H{-}C{-}Si)$ **(CH_3)**
740	741	A''	733	$\rho_{48}(C{-}H)$, $\rho_{49}(C{-}H)$	$56\rho_{48}$, $34\rho_{49}$
637*	—	A''	647	$\varkappa_{53}$, $\rho_{51}(C_r{-}Ge)$, $Q_{34}(Ge{-}C)$	$90\varkappa_{53}$
		A'	612	$Q_{15}(Ge{-}C)$, $Q_{1}(Ge{-}C)$	$59Q_{15}$, $40Q_{1}$
608	608	A''	620	$Q_{34}(Ge{-}C)$, $\varkappa_{53}$	$80Q_{34}$
—*	600	A''	614	$\varkappa_{50}$, $\rho_{49}(C{-}H)$	$95\varkappa_{50}$
575	575	A'	563	$Q_{1}(Ge{-}C)$, $Q_{15}(Ge{-}C)$	$60Q_{1}$, $32Q_{15}$
...	320	A'	319	$Q_{17}(Ge{-}C_r)$	$80Q_{17}$, $11\gamma_{27}$
...	264	A'	249	$\beta_{28}(C{=}C{-}Ge)$, $\gamma_{32}(C_r{-}Ge{-}C)$	$62\beta_{28}$, $33\gamma_{32}$
...	248	A''	240	$\rho_{51}(C_r{-}Ge)$, $\gamma_{40}(C_r{-}Ge{-}C)$	$43\gamma_{40}$, $40\rho_{51}$, $14\varkappa_{53}$
		A''	197	$\varepsilon_{39}(C{-}Ge{-}C)$	$94\varepsilon_{39}$
...	186	A'	196	$\varepsilon_{6}(C{-}Ge{-}C)$	$99\varepsilon_{6}$
		A'	186	$\gamma_{7}(C_r{-}Ge{-}C)$, $\varepsilon_{6}(C{-}Ge{-}C)$, $\gamma_{32}(C_r{-}Ge{-}C)$	$73\gamma_{7}$, $27\gamma_{32}$
...	100	A'	111	$\gamma_{32}(C_r{-}Ge{-}C)$, $\beta_{28}(C{=}C{-}Ge)$, $\gamma_{7}(C_r{-}Ge{-}C)$	$50\gamma_{32}$, $35\beta_{28}$, $13\gamma_{7}$
...	100	A''	103	$\rho_{51}(C_r{-}Ge)$, $\gamma_{40}(C_r{-}Ge{-}C)$	$51\rho_{51}$, $49\gamma_{40}$

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*The band is overlapped with the band of deformation vibrations of the methyl groups.

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

Assignment	RGe(CH$_3$)$_3$			R$_2$Ge(CH$_3$)$_2$			R$_3$GeCH$_3$		
	IR spectrum, ν, cm^{-1}	Raman spectrum, Δν, cm^{-1}	I_0	IR spectrum, ν, cm^{-1}	Raman spectrum Δν, cm^{-1}	I_0	IR spectrum ν, cm^{-1}	Raman spectrum Δν, cm^{-1}	I_0
q(C—H)	3142	3143	120	3145	3148	144	3150	3145	115
q(C—H)	3114	3111	54	3112	3109	67	3116	3112	60
ς(C—H)	—	3079	35	—	3079	47	3085	3078	41
ι(C—H) (**CH$_3$**)	2978	2974	140	2983	2982	81	2980	2980	50
q(C—H) (**CH$_3$**)	2910	2906	656	2910	2908	342	2920	2920	212
β(C=C—H), Q(C=C)	1552	1547	31	1550	1554	26	1550	1550	25
β(C=C—H), Q(C=C)	1458	1456	769	1456	1456	1055	1460	1461	923
α(H—C—H) (**CH$_3$**)	1414	1413	26	1412	1416	23	1418	—	—
β(C=C—H), Q(C—O), Q(C—C)	1362	1358	100	1361	1360	100	1361	1360	100
α(H—C—H), β(H—C—Ge) (**CH$_3$**)	—	1245	80	1245	1248	39	1249	1250	23
	1241	1242	62	—	—	—	—	—	—
β(C=C—H), Q(C—O), γ(C=C—O)	1202	1201	120	1204	1205	114	1206	1207	110
β(C=C—H)	1145	1146	49	1149	1149	49	1151	1151	45
Q(C—O), Q(C=C), Q(C—C)	1093	1093	16	1098	1103	13	1102	1100	15
β(C=C—H), Q(C—O), Q(C—C)	1067	1066	124	1066	1065	111	1064	1065	120
β(C=C—H), Q(C—C)	1003	1003	45	1004	1004	54	1005	1005	43
γ(C=C—O), β(C=C—H)	895	896	96	897	899	103	897	898	90
γ(C=C—O), Q(C—O)	885	882	38	884	884	50	885	890	44
ρ(C—H)	—	—	—	—	870	6	870	—	—
β(H—C—Ge) (**CH$_3$**)	830	—	—	837	—	—	838	—	—
ρ(C—H)	810	808	6	810	810	6	806	—	—
β(H—C—Ge) (**CH$_3$**)	764	—	—	753	753	11	753	—	—
ρ(C—H)	740	741	14	744	745	26	745	740	20
ϰ	637	—	—	640	639	11	640	642	15
Q(Ge—C)	608	608	328	617	616	87	—	—	—
ϰ	—	—	—	597	—	—	598	—	—
Q(Ge—C)	575	575	939	590	588	350	611	610	87
Q(Ge—C$_r$)	—	—	—	—	340	6	—	—	—
Q(Ge—C$_r$)	...	320	147	...	315	104	...	...	...
β(C=C—Ge)	...	264	35	...	258	23	...	255	20
ε(C—Ge—C)	...	248	20	...	233	11	...	222	13
γ(C$_r$—Ge—C)	...	186	350	...	220	24	...	170	5
ρ(C$_r$—Ge)	...	100	35	...	184	76	...	120	18

not change. In the Raman spectra very weak depolarized lines correspond to this vibration. In addition to the $\varkappa_{53}$ coordinate, which makes the principal contribution to the potential energy of this deformation vibration of the furyl skeleton (90%), the $\rho_{51}(C_r—Si)$ coordinate changes appreciably.

The vibration with a frequency of 597 cm^{-1} is one of the characteristic vibrations in the spectra of furan derivatives. This vibration is described primarily by a change in the $\varkappa_{50}$ coordinate; the hydrogen atoms of the furyl fragment are displaced only slightly perpendicular to the plane of the ring. In the IR spectra of 2-furylsilanes the bands with a frequency of 597 cm^{-1} are intense, while the lines in the Raman spectra are very weak and depolarized.

In the spectrum of trimethyl(2-furyl)silane the stretching vibration of the $Si—C_r$ bond has a frequency of 416 cm^{-1}. The $\gamma_7(C_r—Si—C)$ and $\gamma_{40}(C_r—Si—C)$ and $\varepsilon_6(C—Si—C)$ and $\varepsilon_{39}(C—Si—C)$ angular coordinates change appreciably simultaneously with the $Q_{17}(Si—C_r)$ coordinate. The Q_{17} coordinate makes the principal contribution to the potential energy of this vibration. In the Raman spectrum the line of the stretching vibration is intense and polarized ($\rho = 0.04$). In the spectrum of dimethyldi(2-furyl)silane the completely symmetrical stretching vibration of the $Si—C_r$ bonds appears at 403 cm^{-1}; the line of the completely symmetrical vibration is intense and polarized ($\rho = 0.16$), and its contour is almost twice as broad as the contour of the line at 416 cm^{-1} in the Raman spectrum of $RSi(CH_3)_3$. An unsymmetrical vibration does not appear in the Raman spectrum, whereas the intense band at 475 cm^{-1} in the IR spectrum corresponds to it. A decrease in the completely symmetrical vibration of the $Si—C_r$ bonds to 392 cm^{-1} is observed on passing to methyl tri(2-furyl)silane, and the very strong band at 503 cm^{-1} is related to the doubly degenerate unsymmetrical vibration of these bonds. In the Raman spectrum of tetra(2-furyl)silane a line of the completely symmetrical vibration of the $Si—C_r$ bonds is observed at 370-380 cm^{-1}; unsymmetrical vibrations do not appear in the Raman spectrum, while the most intense and broadest band with a frequency of 535 cm^{-1} corresponds to it in the IR spectrum.

For the low-frequency region of the spectra of 2-furylsilanes we have experimental data only from the Raman spectra. The deviation between the experimental and calculated frequencies for this region of the spectrum of trimethyl(2-furyl)silane does not exceed 18 cm^{-1}. An additional correction of the force field in order to decrease this difference was not made.

The $\beta_{28}(C{=}C—Si)$ and $\gamma_{32}(C_r—Si—C)$ coordinates, which characterize the changes in the angles that lie in the plane of symmetry of the molecule, change most markedly for the vibration with a frequency of 303 cm^{-1}, and the $\varepsilon_6(C—Si—C)$ and $\varepsilon_{39}(C—Si—C)$ coordinates change appreciably. The γ_{32} coordinate makes the greatest contribution to the potential energy of this vibration.

In the vibration with a frequency of 283 cm^{-1}, in addition to the coordinates that describe the vibration of the $—SiC_3(Me)$ skeleton, the coordinates that characterize the out-of-plane vibrations of the ring, viz., $\rho_{51}(C_r—Si)$ and $\varkappa_{53}$, also change. The line of this vibration is very weak and depolarized.

The very strong, broad, and depolarized line with a frequency of 212 cm^{-1} in the spectrum of trimethyl(2-furyl)silane belongs to deformation vibrations of the $—SiC_3(Me)$ fragment.

We assign the intense depolarized line with a frequency of 106 cm^{-1} to a vibration associated with a change in the $\beta_{28}(C{=}C—Si)$ and $\gamma_{32}(C_r—Si—C)$ angular coordinates.

A vibration that is characterized by deviation of the $C_r—Si$ bond from the plane of the ring and a change in the $\gamma_{40}(C_r—Si—C)$ and $\gamma_7(C_r—Si—C)$ angular coordinates was not observed in the experimental spectrum.

Vibrational Spectra of 2-Furylgermanes

The vibrational problem was solved for the trimethyl(2-furyl)germane molecule (Table 3). For the spectra of a number of 2-furylgermanes $R_nGe(CH_3)_{4-n}$ (n = 1-3) we assigned the principal frequencies (Table 4) on the basis of the solution of the vibrational problem. It is apparent from a comparison of the results of measurement of the spectra of 2-furylgermanes and 2-furylsilanes that the frequencies of the stretching vibrations of the ring C—H bonds coincide within the limits of the experimental error. The frequencies of the stretching vibrations of the C—H bonds of the methyl groups in the spectra of 2-furylgermanes are 10-20 cm^{-1} higher than in the corresponding 2-furylsilanes.

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

IR spectrum ν, cm^{-1}	Raman spectrum, $\Delta\nu$, cm^{-1}	Type of symmetry	ν_{calc}, cm^{-1}	Form of vibration	Distribution of the potential energy of the vibrations with respect to symmetry, %
3145	3141	A'	3140	q_{23}(C—H), q_{25}(C—H)	$62q_{23}$, $36q_{25}$
3110	3113	A'	3115	q_{25}(C—H), q_{23}(C—H), q_{24}(C—H)	$54q_{25}$, $28q_{23}$, $16q_{24}$
—	3075	A'	3087	q_{24}(C—H), q_{23}(C—H), q_{25}(C—H)	$82q_{24}$, $8q_{23}$, $8q_{25}$
2985	2987	$3A'$, $3A''$	2991, 2990, 2989, 2988, 2987, 2986	q(C—H) (**CH$_3$**)	$100q$(C—H) (**CH$_3$**)
2918	2919	$2A'$, A''	2918, 2×2917	q(C—H) (**CH$_3$**)	$100q$(C—H) (**CH$_3$**)
1546	1547	A'	1549	β_{30}(C=C—H), β_{31}(C=C—H), β_{29}(C=C—H), Q_{22}(C=C), Q_{20}(C=C), γ_{26}(C=C—O), γ_{27}(C=C—O), Q_{17}(C_r–Sn)	$48Q_{22}$, $23Q_{20}$, $12\beta_{30}$, $8\beta_{29}$, $7\beta_{31}$
1445	1443	A'	1452	β_{29}(C=C—H), Q_{20}(C=C), Q_{22}(C=C), γ_{26}(C=C—O), Q_{19}(C—O), Q_{18}(C—O), γ_{27}(C=C—O)	$47Q_{20}$, $14Q_{22}$, $8\beta_{29}$, $8\gamma_{26}$, $7Q_{19}$, $5Q_{18}$, $5\gamma_{27}$
1400	—	$3A'$, $3A''$	1401, 2×1399, 2×1396, 1394	α(H—C—H) (**CH$_3$**)	100α(H—C—H) (**CH$_3$**)
1357	1355	A'	1355	β_{30}(C=C—H), β_{29}(C=C—H), β_{31}(C=C—H), γ_{27}(C=C—O), Q_{21}(C—C), Q_{18}(C—O), Q_{22}(C=C), Q_{17}(C_r—Sn)	$28Q_{18}$, $18Q_{21}$, $14\beta_{29}$, $12Q_{22}$, $12\beta_{30}$, $9\gamma_{27}$
1201	1203	A'	1203	β_{31}(C=C—H), γ_{26}(C=C—O), Q_{19}(C—O), β_{29}(C=C—H), Q_{21}(C—C), γ_{27}(C=C—O), Q_{18}(C—O)	$23Q_{19}$, $23\gamma_{26}$, $22\beta_{31}$, $12\gamma_{27}$, $9Q_{21}$
1198*¹	—	$2A'$, A''	2×1220, 1216	β(H—C—Sn), α(H—C—H) (**CH$_3$**)	100β(H—C—Sn) (**CH$_3$**)
1142	1146	A'	1152	β_{29}(C=C—H), β_{30}(C=C—H), β_{31}(C=C—H), β_{28}(C=C—Sn), Q_{18}(C—O), γ_{27}(C=C—O), Q_{22}(C=C)	$58\beta_{29}$, $11Q_{18}$, $8Q_{22}$, $5\gamma_{27}$
1076	1079	A'	1084	β_{30}(C=C—H), Q_{21}(C—C), Q_{18}(C—O), γ_{26}(C=C—O), Q_{20}(C=C), Q_{19}(C—O)	$29Q_{21}$, $21Q_{18}$, $15Q_{20}$, $12Q_{19}$, $8\gamma_{26}$, $5\beta_{30}$

1057	1056	A'	1056	$\beta_{31}(C{=}C{-}H)$, $\beta_{30}(C{=}C{-}H)$, $Q_{19}(C{-}O)$, $\gamma_{26}(C{=}C{-}O)$, $Q_{20}(C{=}C)$, $Q_{22}(C{=}C)$	$49\beta_{31}$, $25Q_{19}$, $8Q_{22}$, $7\gamma_{26}$, $6Q_{20}$
999	998	A'	991	$\beta_{30}(C{=}C{-}H)$, $\beta_{31}(C{=}C{-}H)$, $Q_{21}(C{-}C)$, $\beta_{28}(C{=}C{-}Sn)$	$52\beta_{30}$, $26Q_{21}$, $12\beta_{31}$
888	889	A'	879	$\beta_{29}(C{=}C{-}H)$, $\beta_{30}(C{=}C{-}H)$, $\gamma_{26}(C{=}C{-}O)$, $\gamma_{27}(C{=}C{-}O)$, $Q_{18}(C{-}O)$, $Q_{21}(C{-}C)$	$52\gamma_{26}$, $14Q_{18}$, $10\beta_{30}$, $7Q_{19}$, $6Q_{21}$, $6\beta_{29}$
—	885[*2]	A'	870	$\gamma_{27}(C{=}C{-}O)$, $\beta_{29}(C{=}C{-}H)$, $\beta_{31}(C{=}C{-}H)$, $Q_{19}(C{-}O)$, $Q_{17}(Sn{-}C_r)$	$60\gamma_{27}$, $17Q_{19}$, $15Q_{18}$
870	—	A''	852	$\rho_{49}(C{-}H)$, $\rho_{48}(C{-}H)$, $\rho_{52}(C{-}H)$	$64\rho_{49}$, $20\rho_{48}$, $15\rho_{52}$
805	—	A''	802	$\rho_{52}(C{-}H)$, $\rho_{48}(C{-}H)$	$81\rho_{52}$, $15\rho_{48}$
776	—	$2A'$, A''	792, 2×784	$\beta(H{-}C{-}Sn)(CH_3)$	$90\beta(H{-}C{-}Sn)(CH_3)$
740	—	A''	733	$\rho_{48}(C{-}H)$, $\rho_{49}(C{-}H)$	$56\rho_{48}$, $34\rho_{49}$
720[*3]	—	A', $2A''$	2×728, 700	$\beta(H{-}C{-}Sn)\ (CH_3)$	$90\beta(H{-}C{-}Sn)(CH_3)$
627	—	A''	637	$\varkappa_{53}$, $\rho_{51}(C_r{-}Sn)$	$93\varkappa_{53}$, $7\varkappa_{50}$
599	601	A''	614	$\varkappa_{50}$, $\rho_{49}(C{-}H)$	$99\varkappa_{50}$
534	531	A' A''	542 541	$Q_{15}(Sn{-}C)$, $Q_1(Sn{-}C)$ $Q_{34}(Sn{-}C)$	$67Q_{15}$, $33Q_1$ $100Q_{34}$
516	513	A'	512	$Q_1(Sn{-}C)$, $Q_{15}(Sn{-}C)$	$67Q_1$, $33Q_{15}$
—	267	A'	265	$Q_{17}(Sn{-}C_r)$, $\beta_{28}(C{=}C{-}Sn)$	$85Q_{17}$, $8\gamma_{27}$
—	217	A'	224	$\beta_{28}(C{=}C{-}Sn)$, $\gamma_{32}(C_r{-}Sn{-}C)$	$67\beta_{28}$, $21\beta_{32}$, $6\gamma_7$
—	—[*4]	A''	217	$\rho_{51}(C{-}Sn)$, $\gamma_{40}(C_r{-}Sn{-}C)$	$48\rho_{51}$, $40\gamma_{40}$, $12\varkappa_{53}$
—	145	A' A' A''	145 142 142	$\varepsilon_6(C{-}Sn{-}C)$, $\gamma_7(C_r{-}Sn{-}C)$, $\gamma_{32}(C_r{-}Sn{-}C)$ $\varepsilon_6(C{-}Sn{-}C)$ $\varepsilon_{39}(C{-}Sn{-}C)$	$70\gamma_7$, $30\gamma_{32}$ $95\varepsilon_6$ $96\varepsilon_{39}$
—	90	A'	101	$\gamma_{32}(C_r{-}Sn{-}C)$, $\beta_{28}(C{=}C{-}Sn)$, $\gamma_7(C_r{-}Sn{-}C)$	$56\gamma_{32}$, $29\beta_{28}$, $11\gamma_7$
—	—	A''	94	$\rho_{51}(C_r{-}Sn)$, $\gamma_{40}(C_r{-}Sn{-}C)$	$54\gamma_{40}$, $44\rho_{51}$

[*1] Overlapped with the more intense band of the in-plane ring vibration, which has a frequency of 1201 cm^{-1}.

[*2] Overlapped with the complex vibration at 889 cm^{-1}.

[*3] Overlapped with the more intense band of out-of-plane vibrations of the ring C–H bonds.

[*4] Overlapped with the deformation vibration with a band at 217 cm^{-1}.

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

Assignment	$RSn(CH_3)_3$			$R_2Sn(CH_3)_2$			$R_3Sn(CH_3)$		
	IR spectrum, ν, cm^{-1}	Raman spectrum, Δν, cm^{-1}	I_0	IR spectrum, ν, cm^{-1}	Raman spectrum, Δν, cm^{-1}	I_0	IR spectrum, ν, cm^{-1}	Raman spectrum, Δν, cm^{-1}	I_0
q(C—H)	3145	3141	91	3148	3145	65	3150	3145	76
q(C—H)	3110	3113	68	3115	3115	42	3125	—	—
q(C—H)	—	3075	45	—	3075	15	—	3078	30
q(C—H) (CH_3)	2985	2987	77	2994	2994	21	3005	—	—
q(C—H) (CH_3)	2918	2919	127	2928	2931	35	2930	2925	15
β(C=C—H), Q(C=C)	1546	1547	36	1545	1545	10	1549	1550	5
β(C=C—H), Q(C=C)	1445	1443	481	1445	1446	262	1445	1448	380
α(H—C—H) (CH_3)	1400	—	—	1405	—	—	1412	—	—
β(C=C—H), Q(C—O), Q(C—C)	1357	1355	100	1358	1358	100	1360	1360	100
β(C=C—H), Q(C—O), γ(C=C—O)	1201	1203	272	1202	1203	110	1202	1205	130
α(H—C—H), β(H—C—Sn) (CH_3)	1198	—	—	—	—	—	—	—	—
β(C=C—H)	1142	1146	91	1145	1146	41	1145	1150	55
Q(C—C), Q(C—O), Q(C=C)	1076	1079	32	1081	1082	18	1084	1086	27
β(C=C—H), Q(C—O), Q(C=C)	1057	1056	86	1057	1058	60	1058	1060	73
β(C=C—H), Q(C—C)	999	998	32	1001	1000	23	1000	1002	28
γ(C=C—O), β(C=C—H)	888	889	100	889	891	78	890	890	84
γ(C=C—O), Q(C—O)	—	885	45	885	885	35	885	885	38
ρ(C—H)	870	—	—	—	870	5	—	—	—
ρ(C—H)	805	—	—	810	—	—	815	—	—
β(H—C—Sn) (CH_3)	776	—	—	775	—	—	—	—	—
ρ(C—H)	740	—	—	745	—	—	745	—	—
β(C—H—Sn) (CH_3)	720	—	—	—	—	—	—	—	—
ϰ	627	—	—	627	—	—	628	630	5
ϰ	599	601	5	598	600	3	597	600	5
Q(Sn—C)	534	531	432	544	545	95	—	—	—
Q(Sn—C)	516	513	910	527	528	258	541	543	33
Q(Sn—C_r)	—	—	—	—	281	48	—	293	39
Q(Sn—C_r)	—	267	141	—	269	80	—	270	70
β(C=C—Sn)	—	217	45	—	227	25	—	230	23
ε(C—Sn—C)	—	—	—	—	189	25	—	198	15
γ(C_r—Sn—C)	—	145	523	—	145	36	—	150	12
ρ(C_r—Sn)	—	90	205	—	—	—	—	—	—
r(C_r—Sn—C)									

Of the 10 bands of in-plane vibrations of the furyl fragment that appear at 880-1560 cm^{-1} in the spectrum of trimethyl(2-furyl)germane, only the band of a complex vibration for which virtually all of the lengths of the ring bonds change (the pulsation vibration) was shifted extremely markedly to the long-wave region ($\Delta\nu$ = 16 cm^{-1}) as compared with the spectrum of trimethyl(2-furyl)silane; for the remaining bands the shift in the same direction does not exceed 7 cm^{-1}. The character of the change in the frequencies of the ring vibrations with the addition of furyl fragments is approximately the same as in the case of 2-furylsilanes.

The deformation vibrations of the methyl groups in 2-furylgermanes appear at 1410-1420 and 1240-1250 cm^{-1}. In the spectrum of trimethyl(2-furyl)germane the contour of the band at 1241 cm^{-1} is unsymmetrical, while two markedly overlapped lines are recorded in the Raman spectrum. A similar pattern is observed in the spectrum of trimethyl(2-furyl)silane.

The frequencies of the five out-of-plane vibrations of the furyl fragment in the spectrum of $RGe(CH_3)_3$ lie at 590-870 cm^{-1}. As compared with the spectrum of $RSi(CH_3)_3$, a 5-10 cm^{-1} decrease in the frequencies of four vibrations was noted, while the frequency of the vibration that is characterized by a change in the $\varkappa_{50}$ coordinate remained unchanged (597 cm^{-1}).

Pendulum vibrations of methyl groups are recorded in the IR spectra of 2-furylgermanes in the form of very intense broad bands at 830-840 and 750-765 cm^{-1}, where they are overlapped with no less intense bands of out-of-plane vibrations of the ring. In the Raman spectra the pendulum vibrations are either inactive or show up in the form of very weak depolarized lines.

The most intense polarized (ρ = 0.07) line with a frequency of 575 cm^{-1} in the Raman spectrum of trimethyl(2-furyl)germane belongs to the completely symmetrical stretching vibration of the Ge—C(Me) bonds. The unsymmetrical vibration of these bonds has a frequency of 608 cm^{-1}; the line in the Raman spectrum is intense and depolarized (ρ = 0.78), while in the IR spectrum the band of this vibration is overlapped with the band of the ring deformation vibration, which has a frequency of 600 cm^{-1}. On passing to dimethyldi(2-furyl)germane the frequencies of the completely symmetrical and unsymmetrical vibrations of the Ge—C(Me) bonds are shifted to the short-wave region and are equal to 590 and 617 cm^{-1}, respectively. In the spectrum of methyltri(2-furyl)germane we assign the band with a frequency of 611 cm^{-1} to the ν(Ge—C) stretching vibration.

In the spectrum of the trimethyl(2-furyl)germane molecule the $\nu(Ge—C_r)$ stretching vibration has a frequency of 320 cm^{-1}. In the Raman spectrum the line of this vibration is quite intense and polarized (ρ = 0.13). In the spectrum of dimethyldi(2-furyl)germane the line of the completely symmetrical vibration of the $Ge—C_r$ bonds shows up with a frequency of 315 cm^{-1}, and the very weak depolarized line with a frequency of 340 cm^{-1} can be assigned to the unsymmetrical vibration of these bonds.

Vibrational Spectra of 2-Furylstannanes

The vibrational problem for the trimethyl(2-furyl)stannane molecule was solved (Table 5). The principal frequencies in the vibrational spectra of compounds of the $R_nSn(CH_3)_{4-n}$ series (n = 1-3) were assigned (Table 6). The frequencies of the stretching vibrations of the C—H bonds of the furyl fragment remain virtually unchanged on passing from 2-furylgermanes to 2-furylstannanes. Stretching vibrations of the C—H bonds of methyl groups are recorded at 2995-3005 and 2918-2930 cm^{-1}; this is 7-25 cm^{-1} higher than in the case of the corresponding 2-furylgermanes.

In the case of the in-plane vibrations of the ring fragment one observes a tendency for a decrease in the frequencies on passing from M = Ge to M = Sn; the maximum shift to the long-wave direction was noted for the band of the pulsation vibration of the ring ($\Delta\nu$ = 17 cm^{-1}).

In the IR spectrum of trimethyl(2-furyl)stannane the band of deformation vibrations of the methyl groups (1198 cm^{-1}) is overlapped with the more intense band of the in-plane ring vibration, which has a frequency of 1201 cm^{-1}; in the spectra of dimethyldi(2-furyl)stannane and methyltri(2-furyl)stannane the frequencies of these vibrations evidently coincide, and the contour of the band becomes symmetrical. Umbrella vibrations of the methyl groups are observed at 1400-1412 cm^{-1} only in the IR spectra of 2-furylstannanes.

Pendulum vibrations of methyl groups were not recorded in the Raman spectra of 2-furylstannanes, while the broad intense bands at 776 and 720 cm^{-1} correspond to them in the IR spectra.

In the Raman spectrum of trimethyl(2-furyl)stannane we assign the powerful polarized ($\rho = 0.08$) line with a frequency of 513 cm^{-1} to the completely symmetrical stretching vibration of Sn—C(Me) bonds; the line of unsymmetrical vibrations is completely depolarized ($\rho = 0.82$) and broad with a frequency of 531 cm^{-1}. In the spectrum of dimethyldi(2-furyl)stannane the frequency of the completely symmetrical stretching vibration of the Sn—C(Me) bonds increases to 528 cm^{-1}, and the broad depolarized ($\rho = 0.86$) line with a frequency of 545 cm^{-1} belongs to an unsymmetrical vibration. In the spectrum of methyltri(2-furyl)stannane the frequency of the stretching vibration fo the Sn—C(Me) bond is equal to 543 cm^{-1}.

We assigned the broad polarized line with a frequency of 267 cm^{-1} in the Raman spectrum of trimethyl(2-furyl)stannane to the stretching vibration fo the $Sn—C_r$ bond. In the spectrum of dimethyldi(2-furyl)stannane the completely symmetrical $\Delta\nu(Sn—C_r)$ vibration has a frequency of 269 cm^{-1}, while the unsymmetrical vibration has a frequency of 281 cm^{-1}; these vibrations show up in the Raman spectrum in the form of overlapped broad lines, the first of which is polarized ($\rho = 0.18$), while the second has a degree of depolarization of 0.41. We assign the weak lines with frequencies of 270 and 293 cm^{-1} in the spectrum of methyltri(2-furyl)stannane to stretching vibrations of the $Sn—C_r$ bonds.

Thus we have interpreted the frequencies in the vibrational spectra of 10 heteroorganic furan derivatives. It was noted that a 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 ring. The frequency of the pulsation vibration decreases most appreciably ($\Delta\nu = 33$ cm^{-1}). The methyl groups in the investigated compounds are rather fixed in space, the eigenfunctions corresponding to the vibrational levels of the CH_3 groups are degenerate, and one line for each of the symmetrical and unsymmetrical vibrations is, as a rule, observed in the spectra. The frequency of the stretching vibrations of the $M—C_r$ bonds is considerably smaller than the frequency of the vibrations of the M—C(Me) bonds; this is due not only to the kinematic factor but also to the smaller degree of rigidity of the $M—C_r$ bond.

EXPERIMENTAL

The IR absorption spectra of KBr pellets of the crystalline compounds were obtained with a UR-20 spectrometer.

The Raman spectra were obtained with DFS-12 and DFS-24 spectrometers. The lines of cadmium (440 nm) or argon (488 nm) lasers were used as the exciting lines. The samples of the powdery substances were first pulverized and then placed in capillaries. The relative intensities (I_0) of the Raman lines are presented with allowance for the sensitivity of the photomultiplier (FEU-17, FEU-79).

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2,2-DIMETHYL-5-(5-R-FURFURYLIDENE)-1,3-DIOXANE-4,6-DIONES.

3.* SELECTIVE HYDROGENATION OF THE EXOCYCLIC DOUBLE BOND AND THREE-DIMENSIONAL STRUCTURES OF THE REACTION PRODUCTS

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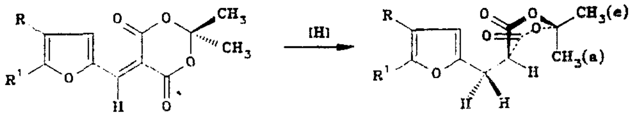
The reaction of 2,2-dimethyl-5-(5-R-furfurylidene)-1,3-dioxane-4,6-diones with sodium borohydride in alcohol leads exclusively to products of hydrogenation of the exocyclic double bond. The three-dimensional structure of one of them — 2,2-dimethyl-5-(5-methyl-furfuryl)-1,3-dioxane-4,6-dioxane — was investigated by x-ray diffraction analysis (XDA).

In [2] on the basis of an analysis of the PMR spectra of substituted 5-benzyl-2,2-dimethyl-1,3-dioxane-4,6-diones it was concluded that the molecules of these compounds are folded into a "sandwich" in which the benzene ring is situated almost parallel to the planar dioxanedione ring. However, recent x-ray diffraction studies of Meldrum's acid and its 5-ethyl and 5-phenyl derivatives [3, 4] have shown that in the crystal the dioxanedione ring has a boat conformation, while the substituent in the 5 position is equatorially oriented. These data cast doubt on the possibility of the formation of the "sandwich" structures proposed in [2].

The present research was carried out to shed some light on the problem of the three-dimensional structures of compounds that are, in principle, capable of forming intramolecular complexes of this type. We selected furfuryldioxanediones as the subjects of our investigation. These compounds are of interest, first, from the point of view of the study of the chemical properties of furfurylidenedioxanediones [5] — particularly the possibility of the selective hydrogenation of the exocyclic C=C bond of the latter — and, second, for a comparison of the three-dimensional structures of the molecules before and after hydrogenation of the ylidene bond.



I a-f II a-f

I, II a-e R=H, f R=Br; a R^1=H, b R^1=Me, c R^1=C≡CPh, d R^1=Br, e,f R^1=I

Various methods exist for the hydrogenation of alkylidene and benzylidene derivatives of Meldrum's acid on both a heterogeneous catalyst [6] and under homogeneous conditions (lithium aluminum hydride [7], sodium borohydride [8], the borane—dimethylamine complex [9]). Our investigations showed that the catalytic hydrogenation of furfurylidenedioxanediones I on Raney nickel and on palladium on carbon at increased and atmospheric pressure leads to complex and difficult-to-separate mixtures of products. Hydrogenation on inactivated (with water and then with dilute acetic acid until the pyrophoric character in the dry state vanishes) Raney nickel in a stream of hydrogen at atmospheric pressure and room temperature makes it possible to ob-

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*See [1] for Communication 2.

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