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ATRANES

VI. Infrared Absorption Spectra of Silatranes*

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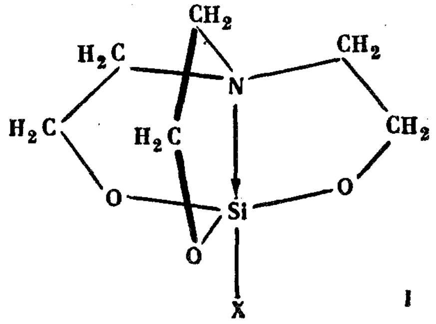
The infrared absorption spectra over the range 400-1700 cm^{-1} of ten organyl- and organoxysilatranes $XSi(OCH_2CH_2)_3N$ [X=H, CH_3, C_2H_5, $(CH_3)_2CH$, $CH_2{=}CH$, C_6H_5, C_2H_5O. n-$C_{14}H_{29}O$, C_6H_5O, p-$CH_3C_6H_4O$] are investigated. The Si←N coordinate link in these compounds is largely unreflected in the fundamental vibration frequencies of the bonds of the central silicon atom or the internal vibration frequencies of the substituents X linked to that atom. However, all the IR spectra have an absorption band in the 570 cm^{-1} region, related to the valence vibrations ν(Si←N), or manifesting itself as the frequency ν(Si—O) of the $XSi(O)_3$ group, substantially lowered because of interaction between the Si—O and Si—N bonds. Evidence in favor of this bond is shift of the ν(Si—H) frequency in the spectrum of silatrane (X = H).

The literature does not describe the IR absorption spectra of silatranes (I). A brief note [2] just indicates (without giving spectra and absorption maxima values) that the frequency of the Si—H valence vibrations in the IR spectrum of silatrane itself (I, X = H) does not lie in the region characteristic of the usual organosilicon compounds containing the $HSi(O)_3$ group (2190-2220 cm^{-1})** but is displaced towards the low-frequency side (2137 cm^{-1} in $CHCl_3$ solution, 2117 cm^{-1} in MeOH solution).



I

Figures 1-3 show, for the range 400-1700 cm^{-1}, the IR absorption spectra which have been studied, for ten organyl- and organoxysilatranes [7, 8] [I, X = H, CH_3, C_2H_5, $(CH_3)_2CH$, $CH_2{=}CH$, C_6H_5, C_2H_5O, n-$C_{13}H_{29}O$, p-$CH_3C_6H_4O$].

The IR spectra of methyltriethoxysilane $CH_3Si(OC_2H_5)_3$ (447, 645, 730, 780, 820, 855, 960, 1094, 1170, 1263, 1298, 1392, 1445, 1485 cm^{-1} and triethanolamine $(HOCH_2CH_2)_3N$ (885, 910, 1040, 1075, 1155, 1250, 1285, 1360, 1410, 1450, 1485 cm^{-1}), which are given in Fig. 4, were also determined to facilitate interpretation of the above.

The spectra were obtained with a UR-10 2-beam IR spectrophotometer over the range covered by NaCl and KBr prisms. For measurement the silatranes were tabletted with KBr, while $CH_3Si(OC_2H_5)_3$ and $(HOCH_2CH_2)_3N$ were used pure.

Molecules of I can be considered spectroscopically in parts. To the first, common to all the molecules, is related the actual cyclic silatrane skeleton (I), with an approximately C_{3v} symmetry. The substituents X (X = alkyl, alkenyl, aryl, alkoxy, aroxy groups) joined to the silicon atom are the second, variable part of the molecule. Making use of the characteristic nature of the spectra of silicon organic compounds, comparison of frequencies makes it possible to separate absorption bands corresponding to the ring system common to all the molecules (Table 1).

The absorption frequencies characteristic of the substituents X (Table 2) were identified from the literature data

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*For Part V see [1].

**It is known [3-6] that the vibration frequency of the Si—H bond in molecules of the type RR'R"SiH is a linear function of the total inductive effect of the substituents R, R', and R", and increases with increase of their electron-accepting capacity (when the polarity of the Si—H bond falls).

[9-12] with frequencies of known spectra.

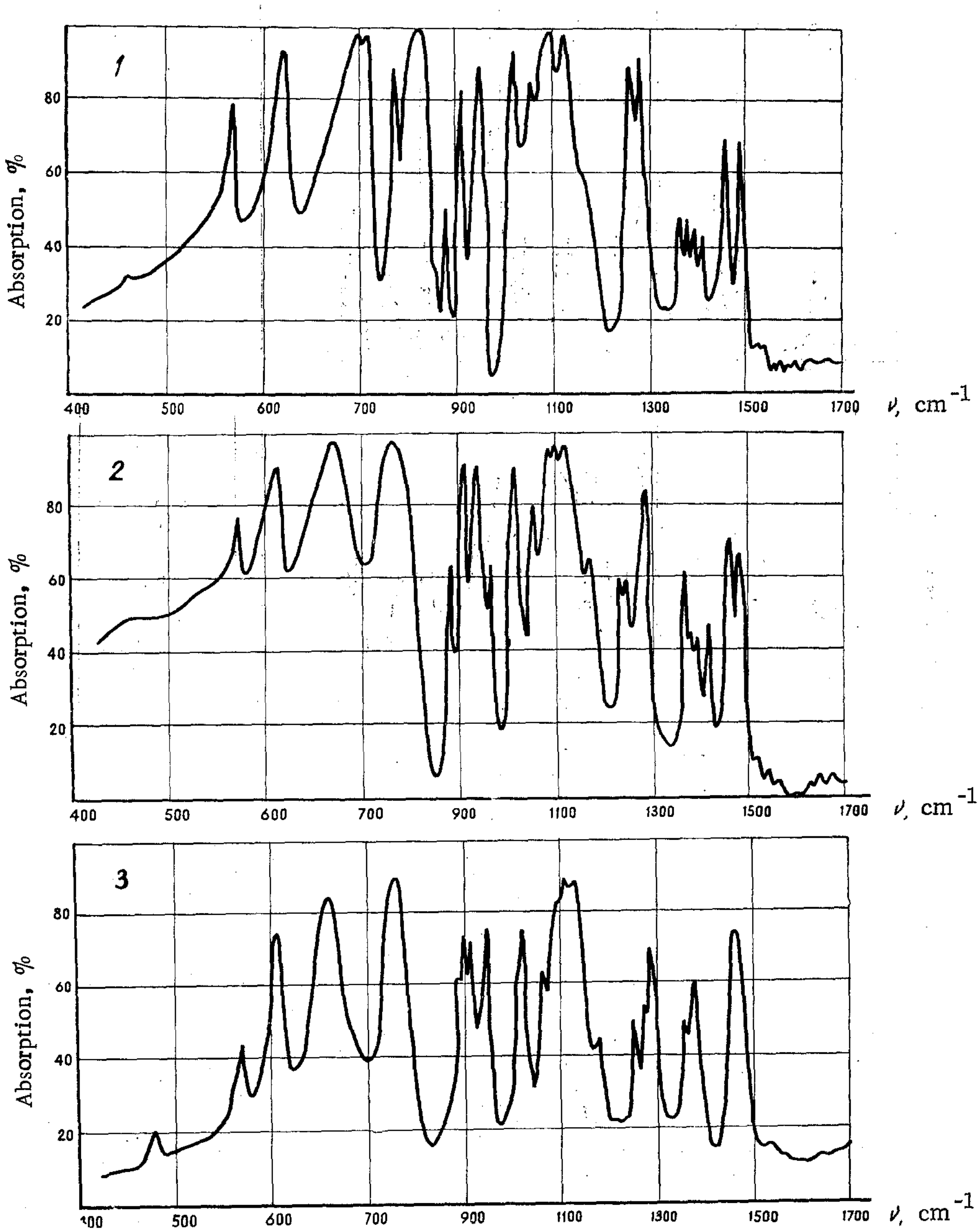

Fig. 1. IR absorption spectra of silatranes (I): X=CH_3 (1), C_2H_5(2), $(CH_3)_2CH$ (3).

From the structure of the skeleton I the spectra of the silatranes should have bands characteristic of vibrations involving participation of Si–O, C–O, C–C, C–H, and C–N bonds, as well as, possibly, the coordination link Si ←N. The presence of the latter in I molecules is conclusively shown by measurements of their dipole moments [15], and is supported by proton magnetic resonance data [1]. It was to be expected that the specific electronic state of the silicon atom in I must result in position and intensity changes in the bands ν (Si–O) and ν (Si–C).

Rather a large number of papers have been published on the study of vibration spectra of organosilicon compounds containing the Si–O–C group [9-11, 16-26]. Analysis of these leads to the conclusion that the infrared absorption spectra of compounds with the Si–O–C atom grouping have a very intense absorption band in the 1100 cm^{-1} region, and bands of variable intensity over the range 620-840 cm^{-1}. In most of the papers the frequency ~ 1100 cm^{-1} belongs to the unsymmetric valence vibration of the Si–O–C group, with predominant stretching of the C–O link, and the 800-840 cm^{-1} frequency to Si–O symmetric valence vibrations. When one moves from the isolated Si–O–C grouping to molecules with several such, e.g., of the type XSi$(O-C)_3$, three skeleton frequencies arise in the spectra, one connected with the predominant stretching of the Si–X bond, and two (symmetric and degenerate) with the Si–O one.

Table 1

Absorption Frequencies Characteristic of the Cyclic Skeletons of the Silatranes (1) cm^{-1}.

H	CH_3	C_2H_5	$CH(CH_3)_2$	$CH{=}CH_2$	C_6H_5	OC_2H_5	$OC_{14}H_{29}$-*n*	OC_6H_5	$OC_6H_4CH_3$-*p*	Assignment
592 s	570	570	568	568	592	585	588	588	582	$\nu(Si{\leftarrow}N)$
	620 s	615 s	609 s	621 s						$\nu_s(Si{-}C)$
633 s	(675)	675	661	675	624	634	632	638	645	$\nu_s(Si{-}O)$
755 s	772 s	770 vs	768	767 vs	787 vs	770 vs	782 vs	775 vs	795 vs	$\nu_{as}(Si{-}O)$
865 s	880 m	880 m	885 w	880 m	880 m	880 m	880 s	895 vs	892 vs	$\nu(C{-}N)$
910 w	913 s	914 s	910 s	915 s	918 m	916 s	915 m	910 vw		
936 s	946 s	942 s	942 s	946 s	950 m	941 s	941 m	946 s	948 s	$\nu(C{-}C)$
1020 m	1020 s	1016 s	1015 s	1021 s	1027 m	1021 s	1020 s	1025 s	1022 s	$\nu(Si{-}O)$
1049 m	1055 m	1054 m	1057 w	1052 m	1052 w	1052 w	1054 w	1048 m	1050 m	$\nu(C{-}C)$
1085 vs	1095 vs	1085 vs	1083 vs	1086 vs	1097 vs	1085 vs	1085 vs	1100 vs	1095 vs	$\nu(C{-}O)$
1110 vs		1100 vs	1107 vs			1105 vs				
1126 vs	1126 vs	1126 vs	1127 vs	1125 vs	1113 vs	1115 vs	1115 vs	1125 vs	1130 vs	
1168 w	1175 vw	1175 w	1174 vw	1174 w	1170 w	1170 vw	1172 vw	1168 w	1172 vw	δCH_2
1270 s	1276 s	1284 s	1282 s	1278 s	1274 s	1275 s	1278 m	1272 s	1272 vs	
1349 w	1360 m	1360 w	1353 w	1360 m	1349 w	1360 w	1352 w	1355 m	1358 m	
1460 m	1456 s	1463 s	1455 s	1464 m	1453 s	1455 m	1455 m	1456 m	1462 m	

vw—very weak, w—weak, m—medium, s—strong, vs—very strong.

Review of formula I shows that the lower part of the silatrane skeleton is structurally similar to molecules $XSi(OMe)_3$ and $XSi(OEt)_3$ (X = alkyl). With the simplest of these $MeSi(OMe)_3$ [21, 25], the region below 900 cm^{-1} contains four frequencies: 620 $\nu(Si{-}C)$, 668 $\nu_s(Si{-}O)$, and the doublet 728 and 790 cm^{-1}, due to splitting of the secondary frequency $\nu_{as}(Si{-}O)$. In complete agreement with this, the spectrum of $MeSi(OEt)_3$ investigated by us has three frequencies 645, 730, and 780 cm^{-1}. Here the spectra of the silatranes have three unchanged frequencies: one 568-590, another 620-675, and a third 770-795 cm^{-1} (Table 3).

It should be noted that in the spectrum of I where X = =Me, the frequency 675 cm^{-1} is hidden in the background of a wide band extending from 700 to 635 cm^{-1}.

With alkoxy and aroxysilatranes, as well as where X = H, the first frequency is substantially higher than with alkylsilatranes. This tendency also exists for the third of the frequencies. On the other hand the second frequency for these silatranes is lower. In the stated region the alkylsilatranes have, further, a single frequency 609-620 cm^{-1}, relating to the $\nu_s(Si{-}C)$ vibration.

According to the literature, [20, 22, 23], frequencies lying over 700 cm^{-1}, relate to degenerate (antisymmetric) vibrations of the Si—O bond of the silicon-oxygen skeleton, and those below 700 cm^{-1} to symmetric ones. The frequency which can be related to the degenerate one, occupies a region close to that expected, i.e., about 800 cm^{-1}. Then the second symmetric frequency probably occurs in the region 620-675 cm^{-1}.

With such a formulation of the problem, the frequency in the region 568-590 cm^{-1} can belong to $\nu(Si{-}N)$ vibration of the coordinate link. Moving over to silatrane itself (X = H) an irregular shift of the skeleton frequencies under consideration is observed. Evidently this is due to change in the form of the vibrations due to the small mass of the substituent X, which is a hydrogen atom.

Actually the above assignment of skeleton frequencies must be regarded as only probable. In particular, the possibility is not excluded that due to interaction between Si—O and Si—N bonds, the $\nu_s(Si{-}O)$ frequency will be situated not at 620-675 cm^{-1}, but at 568-590 cm^{-1}. It should be added that the literature does not contain any information on the vibration frequency of the $Si \leftarrow N$ coordination link. It is known that valence vibrations of the Si—N bond lie in the region 920-980 cm^{-1} (in silazanes) and 790-830 cm^{-1} (in aminosilanes) [9,29-31]. From these results and values of the force constants it follows that the Si—N frequency lies lower than the C—N one. The frequency of the $Si \leftarrow N$ coordinate link itself should lie even lower than that of the ordinary Si—N bond, i.e., the higher range attributed to it is quite possible.

In the KBr region, further deserving of attention is the frequency of the Si—C bond fully symmetric valence vibration [23, 27, 28], and for X = $CHMe_2$, Et, Me, $CH{=}CH_2$ this is respectively 609, 615, 620, and 621 cm^{-1}. The fully symmetric ν_s(Si−C) vibration depends but little on the mass of the group, but its value is greatly influenced by the nature of the substitution at the given silicon atom.

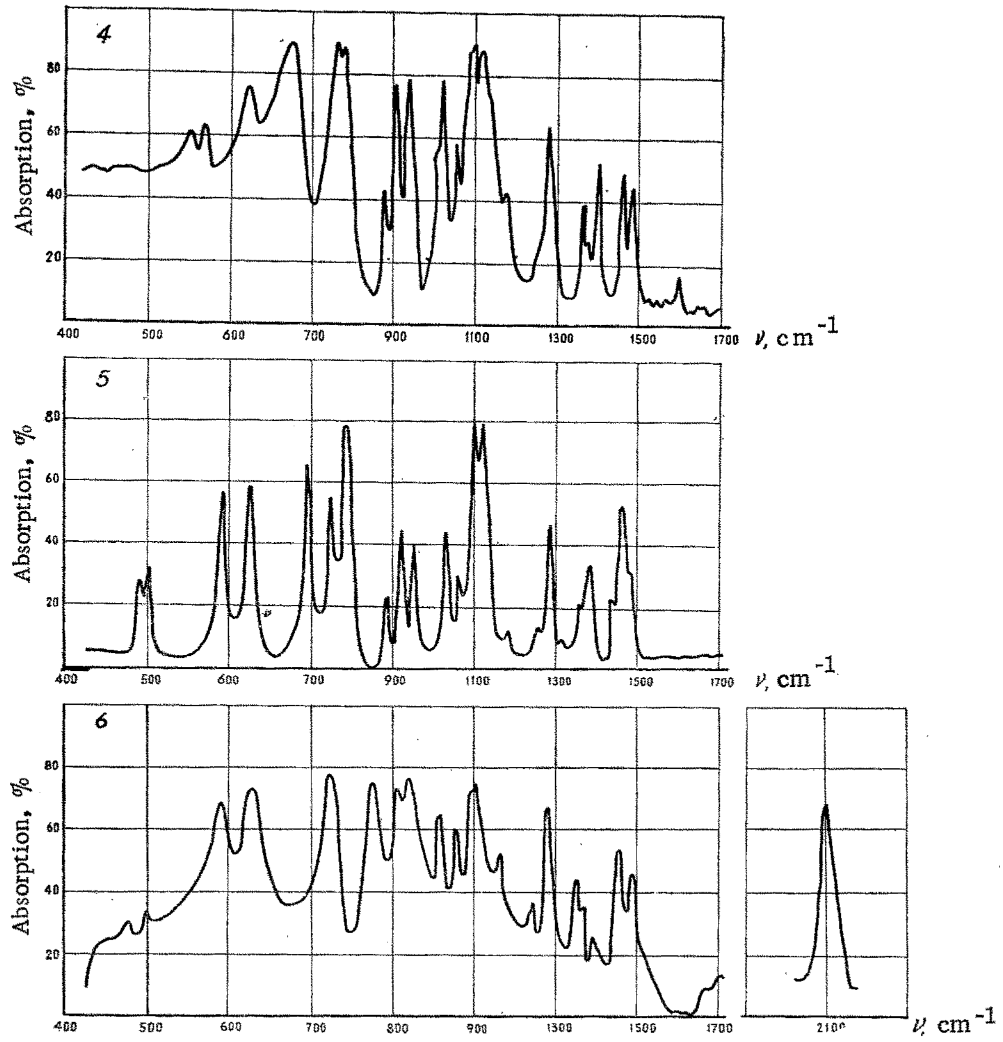

Fig. 2. IR spectra I: X = CH_2 = CH (4), C_6H_5 (5), H (6).

Table 2

Absorption Frequencies Characteristic of Substituents X in I, cm^{-1}

CH_3	C_2H_5	$CH(CH_3)_2$	$CH{=}CH_2$	C_6H_5	OC_2H_5	$OC_{14}H_{29}$-n	OC_6H_5	$OC_6H_4CH_3$-p
720 VS	962 m	432 VW	550 m	488 m	684 S	705 m	500 m	450 m
815 VS	1010—1025	477 W	945 S	498 m	740 m	722 W	545 m	462 m
855 VW	1236 W	896 S	1005 VW	695 S	782 VS	755 W	700 VS	482 W
1256 S	1418 m		1270—1280	709 m	1145 VW	850 VW	788 S	538 S
1410 m	1453		1404 m	750 S	1465 W	902 VW	809 VS	645 m
			1592 W	1020 S		995 VW	835 VW	675 VS
				1113 VS		1142 VW	988 VW	845 VS
				1427 W			1000 m	1515 VW
							1155 VW	1550 VW
							1288 S	1560 VW
							1598 VS	1582 VW

vw–very weak, w–weak, m–medium, s–strong, vs–very strong.

One of us has established [27] a relationship between the nature of the hydrocarbon radical attached to the central silicon atom, i.e., between the state of the electron cloud of the Si−C bond, and the ν_A(Si−C) frequency, where increase in substituent electronegativity increases the ν_A(Si−C) frequency. The notably lower ν_A(Si−C) frequencies of alkylsilatranes compared with that for $MeSi(OEt)_3$ (609-620 cm^{-1} and 645 cm^{-1} respectively) agree with the value of this frequency in molecules such as, for example, Me_3SiPh, or $Me_3SiCH{=}CHCH_3$, while the general −I effect of the

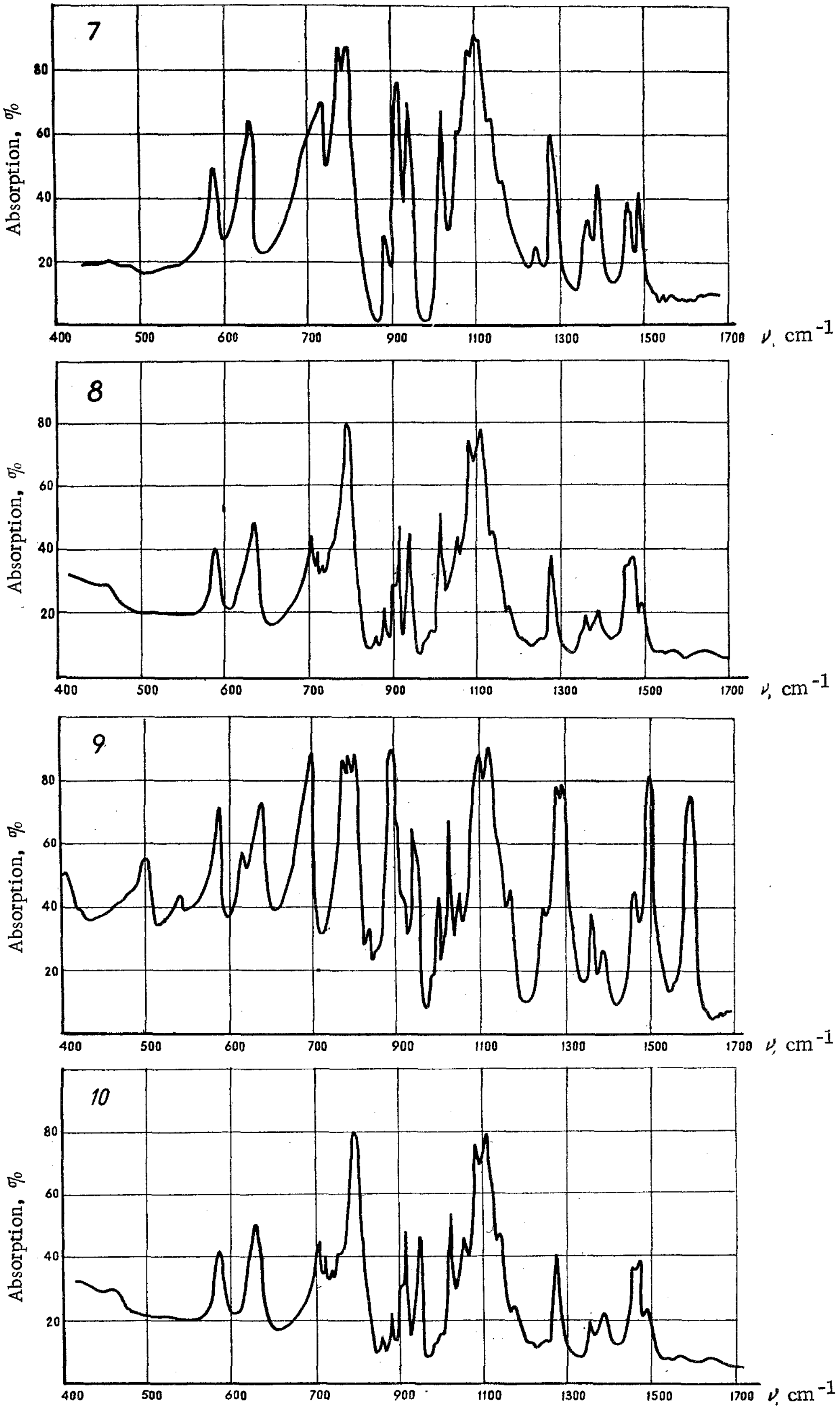

Fig. 3. IR spectra I: X = C_2H_5O (7), n-$C_{14}H_{29}O$ (8), C_6H_5O (9), p-$CH_3C_6H_4O$ (10).

group $(OCH_2CH_2)_3N$ (when the Si ← N bond is lacking) must be even greater than for the group $(OEt)_3$. This fact, as well as the shift, described in the literature [2] of the ν(Si–H) absorption band for silatrane itself (I, X = H) in the low frequency direction (we found for I where X = H, ν(Si–H) = 2100 cm^{-1}), is added evidence that I contains an intramolecular coordination link Si ← N, which lowers the electronegativity of the central silicon atom and thus increases the polarities of its links with C and H atoms.

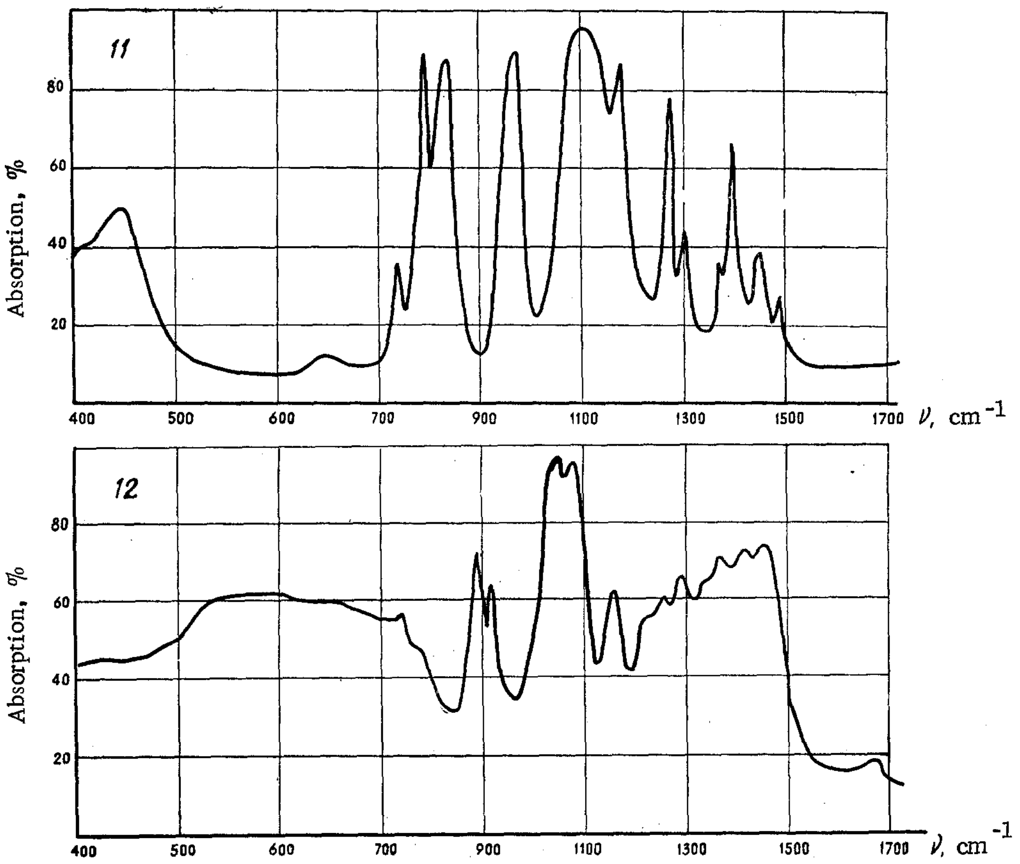

Fig. 4. IR spectra of methyltriethoxysilane $CH_3Si(OC_2H_5)_3$ (11) and triethanolamine $N(CH_2CH_2OH)_3$ (12).

Table 3

Vibration Frequencies of the Silicon-Oxygen Skeleton I, cm^{-1}

X	ν(Si ← N)	ν_s(Si—O)	ν_{as}(Si—O)	ν(Si—C)
H	592	633	755	—
CH_3	570	(675)	772	620
CH_2CH_3	570	675	770	615
$CH(CH_3)_2$	568	661	768	609
$CH{=}CH_2$	568	675	767	621
C_6H_5	592	624*	787	624*
OC_2H_5	585	634	770	—
$OC_{14}H_{29}$-*n*	588	632	782	—
OC_6H_5	588	638	775	—
$OC_6H_4CH_3$-*p*	582	645	795	—

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*In the case of phenylsilatrane, the ν(Si—O) and ν_A(Si—C) frequencies overlap.

The structure of the fragment Si—O—C—C is characterized by typical frequencies 940-950 cm^{-1}, 1015-1020 cm^{-1}, and by splitting of the group of bands in the 1080-1130 cm^{-1} region. The silatranes with X = Et, OEt, CH=CH_2, $CHMe_2$ have the following frequencies in the range 1080-1130 cm^{-1}: 1085, 1095, and 1125 cm^{-1}. Two frequencies 1095 and 1125 cm^{-1} are found with silatranes for which X = Me, Ph, OPh, $OC_{14}H_{29}$—n, and OPhMe—p.

In the IR spectra of I the frequency 1055 cm^{-1} occurs at the edge of a very strong band at 1095 cm^{-1}. Taking into account existing data [24], it may presumably be ascribed to valence vibrations of the C—C bond of the silatrane skeleton. Comparison of IR spectra of I with that of $N(CH_2CH_2OH)_3$ showed that a 911 cm^{-1} general frequency is inherent in it. Obviously it can be ascribed to C—N bond vibrations. The 944 cm^{-1} band lies in the region of C—C valence vibrations. However, its high intensity indicates possible overlap of other Si—O—C—C group frequencies. The frequency 880-895 cm^{-1}, which is present in the spectra of all organyl- and alkoxysilatranes, as well as of $N(CH_2CH_2OH)_3$, is interesting. This frequency is of medium intensity in the spectra of the silatranes mentioned, while in the spectrum of triethanolamine its intensity is far greater. This absorption band is displaced to 895 cm^{-1} in the spectra of the aroxysilatranes, and is very intense. It may be considered that the frequencies at 880-895 cm^{-1} and 910 cm^{-1} are characteristic of the C—N bond.

Frequencies 1360 and 1460 cm^{-1}, characteristic of CH_2 group deformation vibrations, are also specific for the cyclic skeleton of I. The fact that the spectrum of $N(CH_2CH_2OH)_3$ also shows frequencies at 1360 and 1462 cm^{-1}, in particular favors this view.

Bands relating to substituents X in I are easily interpreted (Table 2), as the number of relevant investigations [9-13] is adequate, while the actual frequencies of the internal vibrations of X are characteristic.

It is clear that the frequencies of the substituents X are generally substantially undisplaced, although substituents which are also joined to the silicon atom, are additionally coordinationally linked to the nitrogen atom. Even the frequencies of the nonplanar vibrations of the vinyl group, which are sensitive to inductive effects, have the usual values (945 and 1010 cm^{-1}).

A number of frequencies of substituents X is overlapped by frequencies for the skeleton, as is shown by corresponding absorption bands of varying intensity. Thus according to [31], the Et group is related to frequencies 1012, 1380, and 1460 cm^{-1}. In the case of I with X = Et, these bands are superimposed on the skeleton absorption frequencies (respectively 1016, 1366, and 1460 cm^{-1}). The characteristic frequencies [12] for the vinyl group are 955 and 1270-1280 cm^{-1}. They overlap with the absorption bands for the skeleton of I (respectively 945 and 1283 cm^{-1}). The frequencies belonging to the C_6H_5group are [28, 32] 1435, 1190, 1125, and 1032 cm^{-1}. The spectrum of I with X = C_6H_5shows 1427, 1170, 1113, and 1027 cm^{-1}. Bands at 1113 and 1027 cm^{-1} overlap with the I skeleton absorption bands. Again the frequency 740 cm^{-1} belongs to the C_6H_5group. I with X = Ph has a band at 750 cm^{-1}.

According to [11, 23], the deformation vibrations of Si-Me in polymethylsiloxanes appear at 804 ±10 cm^{-1}, and are also characterized by a frequency at 1256 ±4 cm^{-1}. I with X = Me is characterized by bands at 815 and 1259 cm^{-1}, the first of these belonging to rocking oscillation in the Me group, and the second to Si-Me deformation vibrations.

I with X = Et has characteristic frequencies at 963 and 1016 cm^{-1} (valence vibrations of the ethyl group C—C at the silicon atom) [13]). The 1412 cm^{-1} frequency corresponds to CH_2 deformation vibrations, the 1370 cm^{-1} one to Me symmetric deformation vibrations, the 1453 cm^{-1} one to Me antisymmetric deformation vibrations in the Et group.

Finally we mention the substantial changes in intensity and position undergone by bands in the C—H valence vibrations region when I is dissolved in various solvents.

Special research is required on this point, and it will be discussed further.

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