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A SPECTROSCOPIC STUDY OF THE STRUCTURE OF TRIMETHYLAROXYSILANES

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Summary

A number of trimethylaroxysilanes of general formula $\text{ArOSi}(\text{CH}_3)_3$ have been studied by the IR, Raman and UV spectroscopy methods and theoretical conformation analysis.

The UV spectra of these compounds in the 200–300 nm region are typical for molecules containing an ArO group and consist of bands attributed to the $\pi-\pi^*$ transitions of the oxygen-conjugated benzene ring. This is confirmed by higher 1600 cm^{-1} line intensity values in the Raman spectra compared to those for the corresponding benzene-monosubstituted compounds. The intensities of the 1600 cm^{-1} band in the IR spectra of trimethylaroxysilanes were used for the calculation of the $\text{OSi}(\text{CH}_3)_3$ constant as equal to -0.50 ± 0.03 . This points to a donating effect of the trimethylsiloxy group on the π -electron system of the benzene ring. There are indications that the molecules of trimethylaroxysilanes in the liquid and solution states have a conformation with the Ar—OSi dihedral angle not so high as to prevent oxygen—benzene ring conjugation. Theoretical conformational analysis of trimethyl-*p*-bromophenoxy-silane gave a dihedral angle value of 90° . Additional stabilisation of the conjugated conformation ($\vartheta < 90^\circ$) is assumed to occur in the liquid state through the internal field of the medium.

A dependence of the 830, 915 and 930 cm^{-1} band intensities on the dielectric constants of the medium has been found. The internal rotation potential around the C—O bond in trimethylaroxysilanes is suggested to have a “smoothed” appearance, that is a torsion vibration with a large amplitude.

Introduction

In physico-chemical investigations of trimethylaroxysilanes special attention is directed to the character of the conjugation of the trimethylsiloxy group with

the aromatic ring and to the relative orientation of this group [1-4]. The greater influence of substituent X on ^{29}Si NMR chemical shifts (δ) for these molecules as compared with the corresponding trimethylarylsilanes is of considerable interest [1]. This may be due to the conjugation of the oxygen atom with the benzene ring and does not agree, therefore, with the O—Si bond being in the plane normal to the aromatic ring [2]. According to the electron diffraction data, the $\vartheta(\text{SiO—C}_6\text{H}_5)$ dihedral angle in the phenoxysilane molecule is 68° [3].

The complicated character of the IR spectra of 4- and 2-substituted trimethylaroxysilanes suggests conformational inhomogeneity of the compounds of this series [5]. This hypothesis becomes more probable in connection with a possible existence of stable rotamers of alkylphenyl ethers [6,7]. In the series of 4- and 2,6-disubstituted trimethylphenoxysilanes, a linear dependence of $\delta(^{29}\text{Si})$ values on temperature is observed [1]. Here the slopes of this correlation for these two series are of opposite sign.

Using IR, Raman and UV spectroscopy and a theoretical conformational analysis we have studied the series of trimethylaroxysilanes of general formula $\text{ArOSi}(\text{CH}_3)_3$ where Ar = C_6H_5 (I), 4- FC_6H_4 (II), 4- ClC_6H_4 (III), 2,4,6- $\text{Cl}_3\text{C}_6\text{H}_2$ (IV), 2- BrC_6H_4 (V), 3- BrC_6H_4 (VI), 4- BrC_6H_4 (VII), 2,4,6- $\text{Br}_3\text{C}_6\text{H}_2$ (VIII), 4- IC_6H_4 (IX), 2- $\text{CH}_3\text{C}_6\text{H}_4$ (X), 3- $\text{CH}_3\text{C}_6\text{H}_4$ (XI), 4- $\text{CH}_3\text{C}_6\text{H}_4$ (XII), 2,6-($t\text{-C}_4\text{H}_9$) $_2\text{C}_6\text{H}_3$ (XIII), 2- $\text{NO}_2\text{C}_6\text{H}_4$ (XIV), 3- $\text{NO}_2\text{C}_6\text{H}_4$ (XV), 4- $\text{NO}_2\text{C}_6\text{H}_4$ (XVI).

Results

Figure 1 shows IR and Raman spectra of trimethylphenoxysilane (I) in the 200—3200 cm^{-1} region. The assignment of some bands was made earlier [2,4,9]. The 920 and 1254 cm^{-1} lines were assigned to symmetric and asymmetric $\nu(\text{Si—O}(\text{C}))$ vibrations, respectively. Although this assignment is a rather widespread one [10-13], it has not been confirmed and is in some doubt. In particular, known data [2,4,9] suggest that the Si—O bond in trimethylaroxysilanes may be more rigid than in trimethylalkoxysilanes, although this is unlikely. Nevertheless, in the IR spectrum of trimethylphenoxysilane the band at 920 cm^{-1} ranks among the most intense ones and it can be assumed that the corresponding vibration would include deformation of a Si—O—C fragment.

In the spectra of 4- and 2-substituted trimethylphenoxysilanes the band in the 910—920 cm^{-1} region has a shoulder within the 925—935 cm^{-1} range (excluding compounds I and XVI). The presence of this doublet suggests conformational inhomogeneity of 4- and 2-substituted trimethylphenoxysilanes. In this connection, IR spectra of solutions of compounds II, III, VII and XII in solvents with different dielectric constant values, ϵ , were measured. An increase in the ϵ value decreases the intensity of the high-frequency component of the doublet (Fig. 2). The correlation of $\lg D_1/D_2$ (optical densities in the 910—920 cm^{-1} and 925—935 cm^{-1} regions, respectively) with $(\epsilon - 1)(2\epsilon + 1)$ is linear and

Compound III: $D_1/D_2 = 2.10(\pm 0.30)(\epsilon - 1)(2\epsilon + 1) + 0.15(\pm 0.09)$

$$r = 0.970, s_0 = 0.06$$

Compound XII: $D_1/D_2 = 1.44(\pm 0.08)(\epsilon - 1)(2\epsilon + 1) + 0.03(\pm 0.03)$

$$r = 0.989, s_0 = 0.04$$

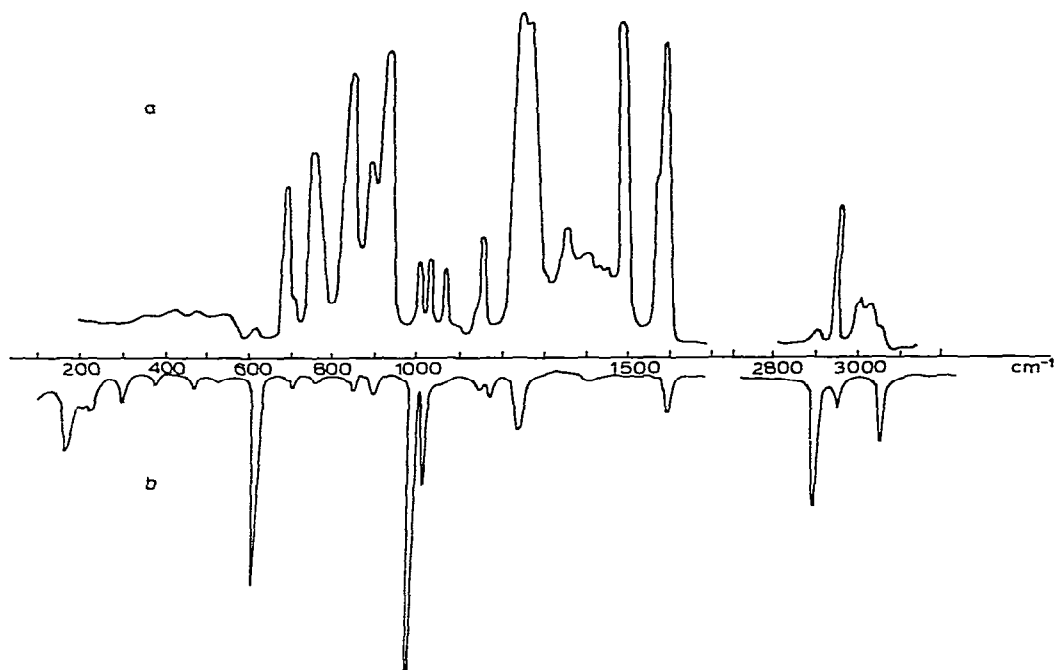


Fig.1. The vibrational spectra of trimethylphenoxysilane: a) IR; b) Raman.

subjects to the regression equations for compounds III and XII.

The optical density of the $\sim 830 \text{ cm}^{-1}$ band in the spectra of compounds III and XII also depends on the solvent. When trimethylaroxysilanes, II, III and XII, change from the liquid into the gaseous state their IR spectra display some changes, most pronounced for compound II. A higher intensity of the high-frequency component of the doublet ($915\text{--}930 \text{ cm}^{-1}$) and a lower intensity of the $\sim 830 \text{ cm}^{-1}$ band (relative to the $\sim 850 \text{ cm}^{-1}$ band) are characteristic of IR spectra of compounds II, III and XII in the gaseous state as compared with the absorption of these compounds dissolved in CCl_4 .

The integral intensity of the 1600 cm^{-1} stretching vibration (A_{1600}) of the benzene ring in the spectra of mono- and disubstituted benzenes may be used

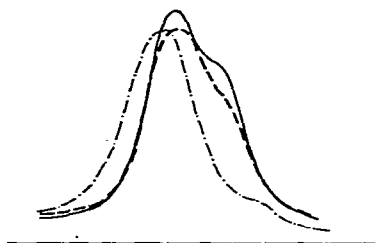


Fig. 2. The $\nu(\text{SiO}(\text{C}))$ absorption bands in compound XII in solution of heptane (solid line), triethylamine (dashed line), acetonitrile (broken line).

TABLE 1

THE 1600 cm^{-1} LINE INTENSITY IN THE IR AND RAMAN SPECTRA OF TRIMETHYLAROXY-SILANES

X	$A_{\Sigma 1600}$	$\sigma_{\text{R}}^0(\text{X})$	$\sigma_{\text{R}}^1(\text{OSi}(\text{CH}_3)_3)$	$\sigma_{\text{R}}^2(\text{OSi}(\text{CH}_3)_3)$	L_{1600} (dioxane)
H	3864	0.00	-0.48	0.48	48
<i>p</i> -CH ₃	2171	-0.10	-0.47	0.27	50
<i>p</i> -F	564	-0.34	-0.50	0.18	25
<i>p</i> -Cl	1476	-0.22	-0.52	0.08	65
<i>p</i> -Br	1824	-0.23	-0.56	0.10	59
<i>p</i> -I	2171	-0.22	-0.59	0.15	69
<i>m</i> -CH ₃	6253	-0.10	-0.50	0.60	35
<i>o</i> -CH ₃	2342	-0.10	-0.44	0.34	48
<i>m</i> -Br	5688	-0.23	-0.61	0.38	56
<i>o</i> -Br	2084	-0.23	-0.42	0.20	65

for the determination of the resonance constants of the substituents, σ_{R}^0 [14]. On the basis of experimental values of A_{1600} and σ_{R}^0 for the second substituent, we have calculated, using the Katritzky equation, the σ_{R}^0 constant for the OSi(CH₃)₃ group in trimethylaroxysilanes (Table 1). For each case, two σ_{R}^0 -OSi(CH₃)₃ values have been obtained, a positive and a negative one. We chose the negative values since the positive ones attaining +0.60 are unreal. Thus, in the series of 3- and 4-substituted trimethylaroxysilanes the $\sigma_{\text{R}}^0(\text{OSi}(\text{CH}_3)_3)$ constant ranges from -0.47 to -0.61, which exceeds the absolute σ_{R}^0 value for the methoxy group (-0.43) [14].

For the estimation of the extent of conjugation between the oxygen atom and the benzene ring in methylaroxysilanes the relative integral intensities of the 1600 cm^{-1} band (I_{1600}) in the Raman spectra have been measured. The I_{1600} values depend on the character of the substituent at the benzene ring, varying from 25 to 69 units. These values for monosubstituted benzenes are within the 26-42 unit range [15], varying from 43 to 117 units for arylvinyl ethers with the same set of substituents in the ring [16]. The I_{1600} value for anisole is 50 units [15]. Thus, the high I_{1600} values in the Raman spectra are due to the presence of the OSi(CH₃)₃ group in trimethylaroxysilanes. However, this increase relative to monosubstituted benzene is 1.5-2.0 times as low as that for aryl vinyl esters. The I_{1600} values for isomeric nitro derivatives of trimethylphenoxy-silane (XIV, XV, XVI) were measured using the 6328 Å exciting line of a He-Ne laser. The I_{1600} ratio in the series 2-, 3- and 4-O₂NC₆H₄OSi(CH₃)₃, equal to 1 : 1.7 : 6.7, unambiguously confirms the conjugation between the OSi(CH₃)₃ group and the benzene ring.

Table 2 shows the main parameters for two long-wave UV bands in the spectra of trimethylaroxysilanes, (aroxymethyl)triethylsilanes, ArOCH₂Si(C₂H₅)₃, and methyl aryl ethers, ArOCH₃. The first absorption band (the α -band) has its maximum in the 265-295 nm region. The position of the maximum depends on the type of substitution of the benzene ring. The maximum extinction of the α -band ranges from 1×10^3 to 3×10^3 l mol⁻¹ cm⁻¹. In the spectra of (aroxymethyl)triethylsilanes the α -band is displaced slightly to the red region. This may be explained by the positive inductive effect of the triethylsilyl group. The

TABLE 2
LONGWAVE ABSORPTION BANDS IN THE UV SPECTRA OF *p*-XC₆H₄OX'

X	X' = CH ₃ [22]			X' = Si(CH ₃) ₃			X' = CH ₂ Si(C ₂ H ₅) ₃		
	λ_{\max} (nm)	$\xi \times 10^{-3}$ (l mol ⁻¹ cm ⁻¹)	λ_{\max} (nm) ^a	$\xi \times 10^{-3}$ (l mol ⁻¹ cm ⁻¹)	<i>f</i>	λ_{\max} (nm) ^b	$\xi \times 10^{-3}$ (l mol ⁻¹ cm ⁻¹)	λ_{\max} (nm) ^c	$\xi \times 10^{-3}$ (l mol ⁻¹ cm ⁻¹)
OCH ₃	226	9.70	—	—	—	—	—	227	12.80
	290	3.20	—	—	—	—	—	295	3.00
	222	8.60	214	6.93	—	214	7.00	225	9.00
CH ₃	276	—	222	—	—	221	9.00	—	—
	276	2.20	275	1.35	0.019	275	1.30	281	2.00
H	220	7.50	217	7.20	—	—	—	222	9.70
	269	2.10	268	1.15	0.017	—	—	272	1.90
F	216	5.40	217	4.63	—	216	5.40	220	7.50
	278	3.20	276	2.40	0.033	274	2.30	283	3.00
Cl	228	11.90	226	10.70	—	226	10.20	230	14.50
	279	1.90	278	1.22	0.018	287	1.00	285	1.70
Br	226	12.50	226	13.02	—	225	13.50	229	16.70
	279	1.75	279	1.20	0.017	278	1.10	285	1.80
I	233	19.00	233	17.14	—	—	—	237	24.00
	278	1.60	279	13.78	—	—	—	285	1.30

^a Solution in C₆H₁₂. ^b Solution in CH₃CN. ^c Solution in *n*-C₆H₁₄.

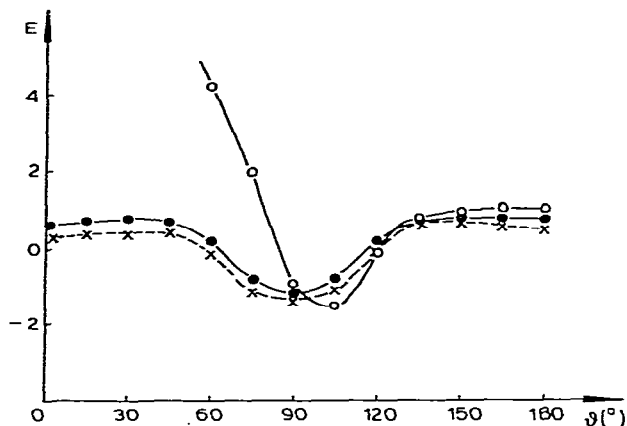


Fig. 3. Plot of conformation energy in *p*-, *m*-, *o*-bromotrimethylphenoxysilanes, E , versus dihedral angle value, ϑ . (●) *para*-derivative, (X) *meta*-derivative, (○) *ortho*-derivative).

α -band position in the spectra of trimethylaroxysilanes and anisoles having analogous substituents in the benzene ring, is in fact, coincident but the extinction in the maxima of the latter is 1.5–2.0 times higher.

The second, *p*-band is observed in the 210–235 nm region for all the compounds studied. In the spectra of trimethylaroxysilanes the maximum of this band lies at 3–5 nm shorter wave-lengths relative to the above two groups of compounds. Hence, the UV spectra of trimethylaroxysilanes are fairly typical for the compounds having an aroxy group as a chromophore. For such molecules the absorption in the 200–300 nm region consists of bands due to π – π^* transitions in the benzene ring conjugated with the oxygen atom.

Theoretical conformation analysis

The geometry of bromo derivatives V, VI and VII was calculated using the approximation of the Westheimer-Kitaigorodsky method. The optimization of the structure was done with ϑ angle values from 0 to 180°. The C–O bond conjugation energy was assumed to be equal to that in the phenol molecule. This value was calculated as the difference between the internal rotation barrier and the steric energy of the planar phenol molecule. The resulting dependence of the conformation energy of molecules V, VI and VII on the ϑ angle value is shown in Fig. 3. The ϑ angles of 90° (VI and VII) and 95° (V) and the stabilization energy of approximately 1.5 kcal/mol correspond to the stable conformations.

Discussion

The most important properties of compounds of general formula C_6H_5OR are determined by the presence or absence of conjugation between the oxygen atom and the benzene ring. Trimethylaroxysilanes should be no exception in this respect. The characteristic structure of the latter allows the data obtained to be characterized.

The conjugation in the molecule is described by several parameters. These are the energy of additional stabilization, the degree of electron polarizability and the distribution of electronic charges. These parameters do not change together in general, and owing to this fact the conjugation effect is not manifested in the same way in the different physico-chemical properties of the molecules.

The UV absorption spectra of trimethylaroxysilanes are typical for all the compounds having an ArO group. In this regard, the lower intensity and the small hypsochromic shift of the *p*-band as compared to that in the spectra of (aroxymethyl)triethylsilanes is noteworthy. If the dihedral angle ϑ were constant, one would expect the *p*-bands to have a bathochromic shift due to the greater inductive effect of the silicon atom. From quantum-chemical calculations, the withdrawing properties of the silicon atom may explain the hypsochromic shift seen, provided the second lone electron pair of the oxygen atom is involved in conjugation [17]. However, the photoelectron spectral data show that the second lone electron pair of the oxygen atom in vinyl- and arylalkyl ethers has a relatively high ionisation potential and *p*-character [18]. Another reason for the hypsochromic shift of the *p*-band may be an increase in the ϑ angle. The latter suggestion is in agreement with the $\nu_{(1600)}$ line intensities in the Raman spectra. The narrower I_{1600} range on varying the substituents in position 4 of the benzene ring is probably indicative of a lower polarizability of the π -electron system in trimethylaroxysilanes in comparison with that of aryl vinyl ethers, although a higher one than in the corresponding monosubstituted benzenes.

The intensity of the $\nu_{(1600)}$ line in the IR spectra of substituted benzenes is related to the charge transfer function between the substituent and the benzene ring [14]. The calculated $\sigma_{\text{R}}^0(\text{OSi}(\text{CH}_3)_3)$ constant shows that the electron-donating ability of the trimethylsiloxy group is not lower than that of the methoxy group ($\sigma_{\text{R}}^0 = -0.43$). A significant difference is observed in the $\sigma_{\text{R}}^0(\text{OSi}(\text{CH}_3)_3)$ values calculated for trimethylaroxysilanes having different aromatic substituents; in most cases, however, this constant is equal to -0.50 ± 0.03 . A similar value of $\sigma_{\text{R}}^0(\text{OSi}(\text{CH}_3)_3)$ has been obtained by the NMR method [1].

Some known dipole moments of trimethylaroxysilanes [10,19] also suggest a significant charge transfer from the oxygen atom to the aromatic ring. The dipole moment, $\vec{\mu}$, of 4-substituted trimethylphenoxy silane may be represented as

$$\vec{\mu} = \vec{\mu}_0 - \vec{\mu}(C_{sp^2}-H) + \vec{\mu}(C_{sp^2}-X)$$

where X is the substituent, $\vec{\mu}_0$ is the dipole moment of trimethylphenoxy silane, $\vec{\mu}(C_{sp^2}-H)$ and $\vec{\mu}(C_{sp^2}-X)$ are dipole moments of the corresponding bonds. The $|\vec{\mu}|$, $|\vec{\mu}_0|$, $|\vec{\mu}(C_{sp^2}-X)$ values are known. Thus it is possible to calculate the α and α_0 angles between directions $\vec{\mu}$, $\vec{\mu}_0$ and the benzene ring axis passing across positions 1 and 4 (assuming retainment of the equilibrium molecular configuration). The data obtained are given in Table 3. Using the dipole moment data of molecules II, III, VII gave similar $\alpha(\vec{\mu}_0)$ values equal, on average, to 62° ($\vec{\mu}_0 = 1.215$ D [10]) or 80° ($\vec{\mu}_0 = 1.53$ D [19]). The corresponding angle for the anisole molecule is 72° . This suggests that the electronic distribution in the phenoxy group of the molecules studied and anisole does not differ much. The

TABLE 3
THE DIPOLE MOMENTS OF SOME TRIMETHYLAROXYSILANES

X	$ \mu $ (D)	$\mu(C_{sp^2}-X)$ (D)	$\alpha(\vec{\mu}_0)$ (°) ($ \vec{\mu} =$ 1.53 D)	$\alpha(\mu_0)$ (°) ($ \mu =$ 1.53 D)	$\alpha'(\vec{\mu}_0)$ (°) ($ \vec{\mu} =$ 1.215 D)	$\alpha'(\vec{\mu})$ (°) ($ \vec{\mu} =$ 1.215 D)
H	1.53 [20] 1.215 [10]	-0.63	—	80	—	62
F	2.31 [20]	0.84	79	41	63	29
Cl	0.96 [20]	0.96	81	40	66	29
Br	2.39 [20]	0.94	79	39	57	28
CH ₃	1.29 [20]	-1.00	44	56	—	—
NO ₂	5.12 [20]	3.38	50	13	30	7

results for molecules XII and XVI lead to even smaller $\alpha(\vec{\mu}_0)$ angle values.

The above implies the presence of oxygen atom—benzene ring conjugation and this is inconsistent with the conclusion [2] that the angle in I is close to 90° as well as with calculations of the optimum conformation of molecule VII. The additional stabilisation by the halogen atom in position 4 does not seem to be significant since it never exceeds 0.3 kcal/mol in the corresponding halogen anisoles [21]. The data obtained by us for trimethylaroxysilanes may be correlated with the results of theoretical conformation analysis of molecule VII and electron diffraction studies [3], as the additional stabilisation of the conformation with $\vartheta = 0^\circ$ is approximately 3 kcal/mol in the series of anisoles in the liquid state as compared with those in the gaseous state. This permits one to conclude that trimethylaroxysilane molecules in the liquid and solution states display conformations with a dihedral angle not too large to prevent the oxygen atom—aromatic ring conjugation.

The second aspect of the problem of trimethylaroxysilane structure is the number of stable conformers. The observed dependence of the intense absorption bands at $\sim 830, 910-925, 925-935 \text{ cm}^{-1}$ on the dielectric constant of the medium, ϵ , is in accord with the assumption of two isomeric forms of these molecules. However, the absence of doublets attributed to conformational isomerism in the IR spectra of trimethylphenoxysilane and its *meta*-substituted derivatives is not predicted. And the hypothesis under consideration is not completely consistent with the fact that the A_{1600} values for compounds I, II, III and XII remain constant with variation in temperature of the samples and dielectric constants of the medium (solvents: CCl₄, n-C₇H₁₆, CH₃CN). The data listed in Table 2 show that ζ in the α -band maximum for compounds II, III, VII and XII in cyclohexane and acetonitrile are coincident, in fact; the changes in the p -band parameters are not systematic and may be considered negligible. The IR spectroscopic study of compounds I, II, III, VI and XII within the -100 to $+100^\circ \text{C}$ range did not allow any temperature dependence to be established. This indicates that any conclusion on the conformational inhomogeneity of trimethylaroxysilanes seems to be premature.

The observed changes in the IR absorption spectra of trimethylaroxysilanes in different solvents can be explained, if the internal rotation potential around the C—O bond axis is assumed to have a "smoothed" appearance which gives rise to

the possibility of torsional vibrations of a large amplitude. The mode of the potential function depends, in this case, on the solvent and, due to the relatively low rotational barrier, on the character of the benzene ring substitution. Vibrations exhibiting a considerable displacement relative to the equilibrium position cause the appearance of bands corresponding to the combined transitions prohibited for the equilibrium state. The spectrum pattern should depend on the properties of the medium.

In conclusion, we find it necessary to point to one possibility which should be taken into consideration in the analysis of mutual effects of molecular fragments in compounds of the type of trimethylaroxysilanes. If the dihedral angle, ϑ , in such molecules is not equal to 0° or 90° , the most probable configuration of the molecule will depend on both the medium properties and the ring-substitution character. This may account for the influence of the medium on the substituent effects and the change in the character of their action on the reaction centre of the molecule.

Experimental

All the trimethylaroxysilanes studied were prepared as described earlier [8]. Their purity was checked by GLC. IR spectra of trimethylaroxysilanes in different solvents and in the liquid state were obtained on UR-20 and Specord IR-75 spectrophotometers in the $400\text{--}3200\text{ cm}^{-1}$. Measurements within the $200\text{--}400\text{ cm}^{-1}$ range were carried out on a Perkin-Elmer model 577 spectrophotometer. Integral intensities of IR absorption band were measured on $0.1\text{--}0.8\text{ M}$ solutions using a $0.002\text{--}0.025\text{ cm}$ cell. The results are listed in Table 1 in IUPAC units. UV absorption spectra of solutions of trimethylaroxysilanes in C_6H_{12} and CH_3CN and (aroxymethyl)triethylsilanes in $n\text{-C}_6\text{H}_{14}$ were measured on a Specord UV-vis spectrophotometer. Raman spectra were recorded on a DFS-12 spectrophotometer with the 4358 \AA Hg line as exciting radiation from the Toronto-type arc. Integral intensities were measured by the internal standard method. The 1445 and 1454 cm^{-1} bands of dioxane (the solvent) served as the standard. 1% of the 313 cm^{-1} 1 M CCl_4 intensity was taken as a unit.

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