

For detailed description of the preparation see [6]. Physical data of the compounds are shown in Table 1.

Table 1

Physical data of N-trimethylsilyl-aniline derivatives

	$C_6H_5NHSi(CH_3)_3$	$C_6H_5N[Si(CH_3)_3]_2$
b.p. °C/mm	96–98/15	70/2
d_4^{25} g/ml	0,9296	0,8978
n_D^{25}	1,5190	1,4835
MR_D (calculated)	52,64	75,37
MR_D (obtained)	53,97	75,61

2. Ultraviolet spectra

The ultraviolet absorption spectra of the compounds were recorded by a Spektromom 201 spectrophotometer in cyclohexane solutions of concentrations ranging from 10^{-2} to 10^{-5} mol/l using silica cells of 1 cm size. Our results show a good agreement with the data measured in iso-octane by PITT and FOWLER [7]. In order to evaluate the spectra above, the ultraviolet spectra of N-methyl-aniline and N,N-dimethyl-aniline were also determined in cyclohexane. The spectra are presented in Figs 1 and 2, the data of absorption peaks are compiled in Table 2.

Table 2

Ultraviolet absorption data of aniline derivatives

$C_6H_5NHSi(CH_3)_3$			$C_6H_5NHCH_3$		
λ nm	ν^* cm ⁻¹	ϵ	λ nm	ν^* cm ⁻¹	ϵ
241	41 494	11 780	244	40 984	12 640
287	34 845	1 790	294	34 014	2 110
299	33 445	1 300			
$C_6H_5N[Si(CH_3)_3]_2$			$C_6H_5N(CH_3)_2$		
λ nm	ν^* cm ⁻¹	ϵ	λ nm	ν^* cm ⁻¹	ϵ
235	42 553	3 980	251	39 841	15 690
266	37 594	470	298	33 557	2 400
272	36 765	450			

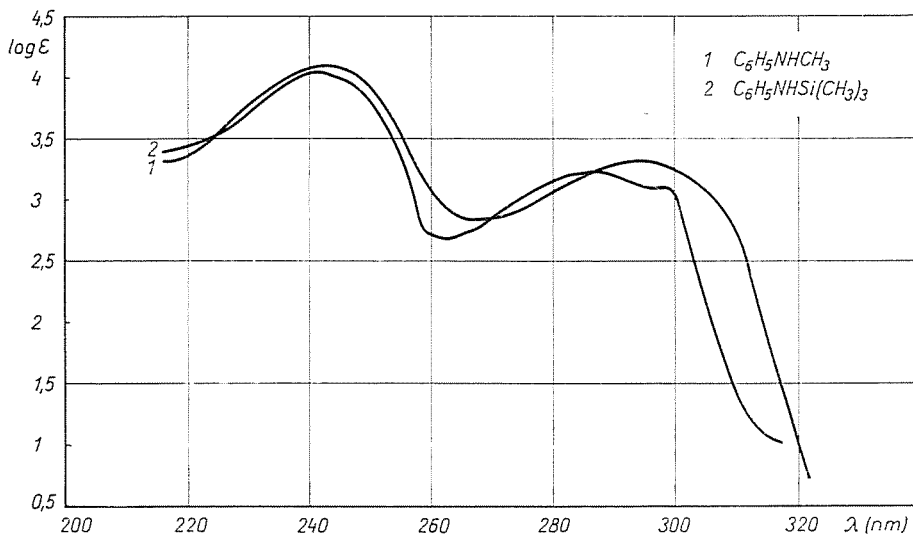


Fig. 1. Ultraviolet absorption spectra of N-methylaniline and trimethyl-phenylamino-silane

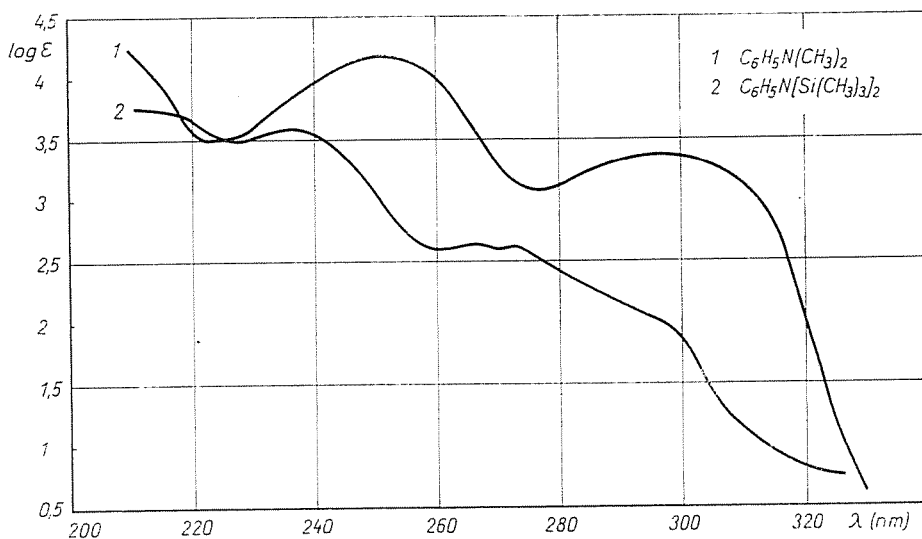


Fig. 2. Ultraviolet absorption spectra of N,N-dimethylaniline and hexamethyl-N-phenyl-disilazane

3. Infrared spectra

The infrared spectra were recorded by an UR-20 spectrophotometer, using a thin film between two plates. The infrared spectra are shown in Figs 3 and 4, and the data of spectra are given in Table 3.

Table 3
Data of infrared spectra
of N-trimethylsilyl-aniline derivatives

$C_6H_5NHSi(CH_3)_3$		$C_6H_5N[Si(CH_3)_3]_2$	
530	$\nu_s SiN$	525	$\nu_s SiN$
695	νCC	688	νCC
755	$\nu(=CH), \nu NH$	702	
782	$\nu SiCH_3$	768	$\nu(=CH)$
848		828	$\nu SiCH_3$
905	$\nu_{as} SiN$	841	
975		907	$\nu_{as} SiN$
1160	νNH	974	
1260	$\delta SiCH_3$	1158	$\delta SiCH_3$
1460	νCC	1258	
1490		1452	νCC
1515		1492	
1620		1510	
1635		1570	
3050	$\nu(=CH)$	1590	
3082		1604	
3100		1612	
3113		1630	
3222		3023	$\nu(=CH)$
3395	νNH	3038	
3480		3070	
		3082	

4. Dipole moments

The dipole moments of aniline derivatives were determined by a faradiometer of own construction [8]. Dielectric constant was calculated from the capacity values, then dipole moment was determined by the ONSAGER method [9] using the following equations:

$$R = 1.05 MR_D$$

$$\epsilon_{\text{eff}} = \frac{2R + V}{V - R},$$

$$P^* = (\epsilon_0 - \epsilon_{\text{eff}}) V \frac{2\epsilon_0 + \epsilon_{\text{eff}}}{\epsilon_0(\epsilon_{\text{eff}} + 2)^2}$$

$$\mu = 0.22123 \sqrt{P^*} \quad (\text{at } 25^\circ \text{C})$$

where R sum of atom and electron polarizations

MR_D molar refraction calculated from the density and the refractive index

ϵ_{eff} effective dielectric constant

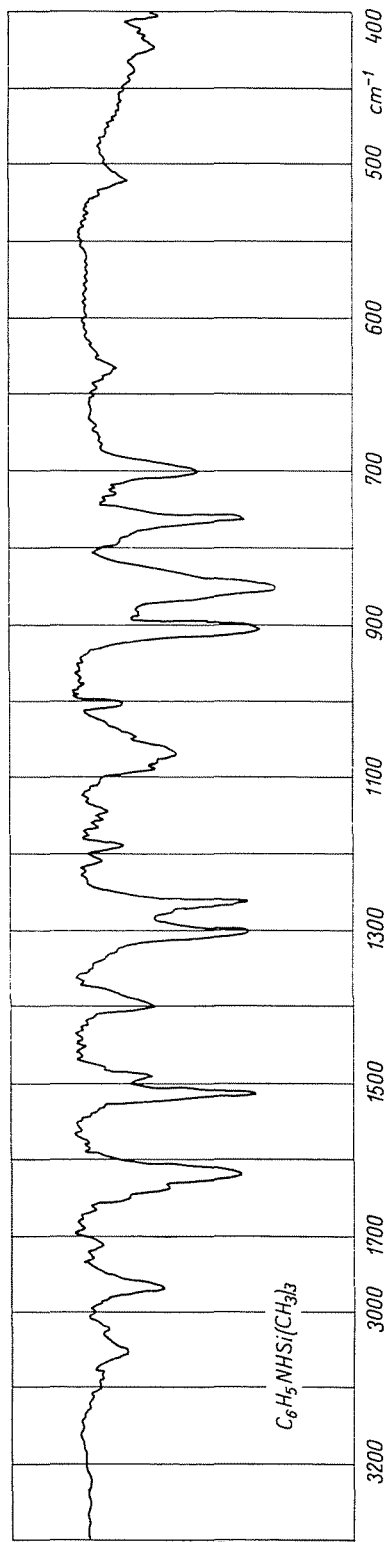


Fig. 3. Infrared spectrum of trimethyl-phenylamino-silane

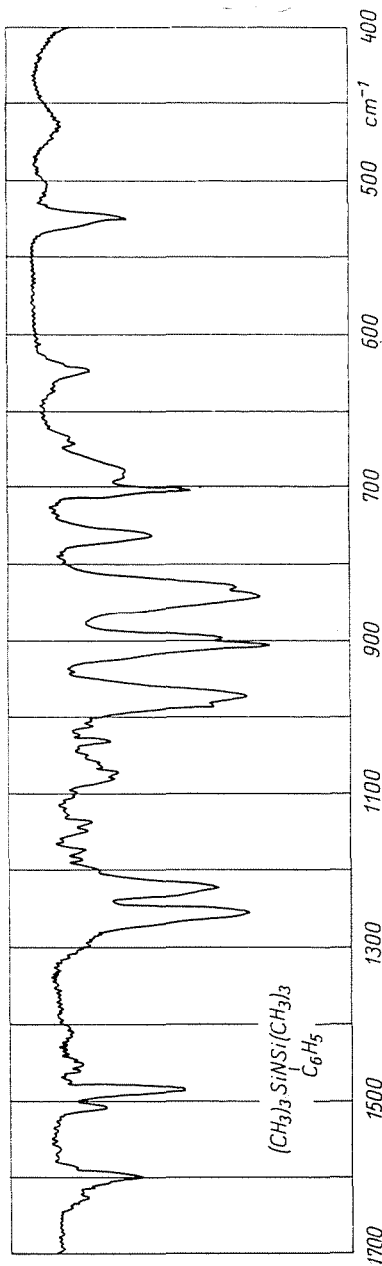


Fig. 4. Infrared spectrum of hexamethyl-N-phenyl-disilazane

- V molecular volume
 P^* orientation polarization
 ϵ_0 measured dielectric constant
 μ dipole moment in Debye units.

The dipole moments of the compounds are shown in Table 4.

Table 4

Dipole moments of N-trimethylsilyl-aniline derivatives

	$C_6H_5NHSi(CH_3)_3$	$C_6H_5N[Si(CH_3)_2]_2$
R	56.669	79.391
ϵ_0	3.9056	2.4361
ϵ_{eff}	2.4032	2.2866
P^*	36.0376	6.3243
μ [D]	1.328	0.556

5. Hydrolysis investigations

Hydrolysis tests were intended to investigate the stability of silicon-nitrogen bond. Silicon derivatives reacted with alcohol containing hydrochloric acid at 2.3 mol/l concentration were applied to determine the ultraviolet absorption spectra, compared in turn with the spectrum of aniline. The resulting ultraviolet spectra are shown in Fig. 5.

In order to examine the effect of the solvent the ultraviolet spectra of these compounds has been determined in absolute alcohol and no important difference has been found between tests in absolute alcohol and cyclohexane, i.e. the spectra recorded in cyclohexane and alcohol containing hydrochloric acid are comparable.

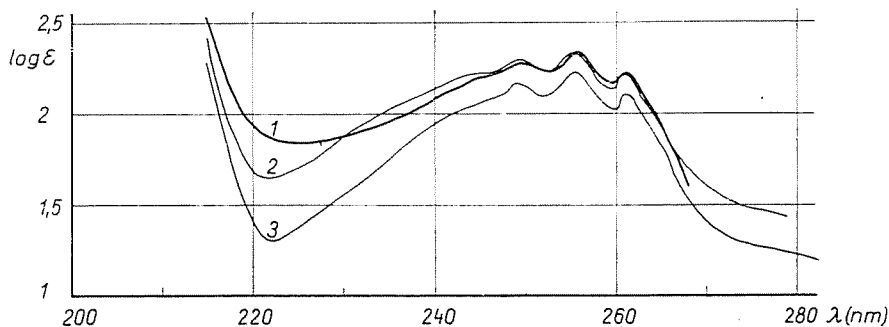


Fig. 5. Ultraviolet absorption spectra of aniline, trimethyl-phenylamino-silane and hexamethyl-N-phenyl-disilazane in alcohol containing hydrochloric acid

The hydrolysis of hexamethyl-N-phenyl-disilazane was investigated in another way, too. The silicon derivatives were boiled for one hour in 0.1 n hydrochloric acid solution used ten times in excess. After boiling the solvent was distilled and the solid residue was pointed out to contain an about theoretical quantity of anilino-hydrochloride. The product was identified by determining the melting point after recrystallization.

Discussion

Data in Figs 1, 2 and Table 2 show the ultraviolet spectra of the compounds containing silicon to exhibit a hypsochromic shift referred to the corresponding carbon compounds. There is also a hypsochromic shift between spectra of hexamethyl-N-phenyl-disilazane and of trimethyl-anilino-silane. These effects can be explained with the electron withdrawing character of silicon. The silicon draws away electrons from the nitrogen and the phenyl-ring and that is why the molecule can be excited by a radiation of shorter wavelength and higher energy. This effect causes the loss of intensity in the ultraviolet spectrum.

The relation between electron withdrawing effect and hypsochromic shift is clearly illustrated by the comparison of the spectra of aniline and aniline cation ($C_6H_5NH_3^+$). If an aniline molecule without charge is transformed to cation by adding a proton, a hypsochromic shift in the ultraviolet spectrum can be observed (230 and 280 nm, 203 and 254 nm, respectively [10]). The same effect appears if an organic aniline derivative is transformed to a silicon derivative.

The values of dipole moments can also be attributed to the electron withdrawal by silicon. If one hydrogen of an aniline molecule is substituted by a $(CH_3)_3Si$ -group, the dipole moment slightly decreases (1.48 *D* [11] and 1.328 *D*, respectively). Namely there is no serious difference between the moments of NH and SiN bonds. If two silicon atoms are attached to the nitrogen of aniline, the dipole moment decreases significantly (0.556 *D*). The silicon atoms draw away the electron pair of nitrogen and electrons of nitrogen-carbon bond, therefore the value of the NC_{Ar} bond moment will increase and the dipole moment decrease because of the opposite vector directions.

The assignments of infrared spectra of the compounds concerned are shown in Table 3. ν_{SiN} and ν_{ASiN} stretching frequency values are seen to be practically equal in either compound. As the spatial structures of the two silicon derivatives differ significantly, no direct and unambiguous relation between frequencies and bond orders can be established. The ν_{CC} and $\nu_{(=CH)}$ vibrations characterizing aromatic rings appear at a higher frequency in the spectrum of trimethyl-anilino-silane than of hexamethyl-N-phenyl-disilazane. This fact

can be explained by the withdrawal of the electron cloud from the aromatic ring by the two silicon atoms, thereby the bond order in the ring decreases.

Curves in Fig. 5 are seen to be about the shape, i.e. hydrochloric acid the silicon-nitrogen bond causes for both silicon derivatives to split and a hydrolysis to take place producing aniline hydrochloride. This hypothesis was supported by our second hydrolytic investigation, identifying the product as aniline hydrochloride.

Our results will be more comprehensively evaluated by means of quantum chemical calculations in a subsequent publication.

Summary

N-trimethylsilyl-aniline derivatives were prepared for determining their ultraviolet and infrared spectra and dipole moments together with hydrolysis investigations. The shifts in the spectra were evaluated qualitatively. The silicon atom was seen to draw away electrons from the nitrogen atom and the phenyl rings to develop delocalized molecules consisting of 8 or 9 atoms.

A further statement was that the silicon-nitrogen bond splitted in the presence of hydrochloric acid to form aniline hydrochloride.

References

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