

# PREPARATION AND ULTRAVIOLET SPECTROPHOTOMETRIC INVESTIGATION OF PHENOXY-METHYL SILANES\*

By

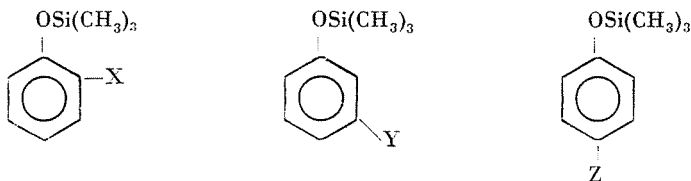
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In two previous papers [1, 2] the authors have already dealt with the molecular structure of compounds containing phenoxy silicon groups. The investigations have been expanded to phenoxy silanes substituted in the ortho-, meta- and para position. In the present paper the production and ultraviolet spectrophotometric investigation of these compounds will be treated.

The following compounds were prepared



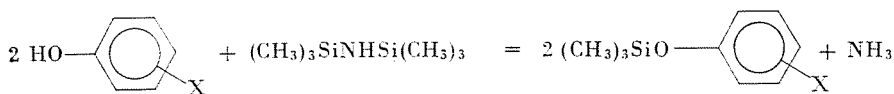
where

X = CH<sub>3</sub>, NO<sub>2</sub>, Cl;

Y = CH<sub>3</sub>, NO<sub>2</sub>;

Z = CH<sub>3</sub>, NO<sub>2</sub>, Cl, Br, F;

according to the following scheme:



According to literary data, the following methods have so far been used for preparing phenoxy trimethyl silanes:

1. Reaction of (CH<sub>3</sub>)<sub>3</sub>SiCl with the corresponding substituted phenol.
2. Reaction of (CH<sub>3</sub>)<sub>3</sub>SiCl with substituted phenol in the presence of pyridine.
3. Reaction of (CH<sub>3</sub>)<sub>3</sub>SiOSi(CH<sub>3</sub>)<sub>3</sub> with substituted phenol, in the presence of catalytic amount of benzene sulphonic acid.

\* Dedicated to Prof. Z. Csűrös on the occasion of his 70th birthday.

4. Reaction of  $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3$  with substituted phenol, in the presence of the sodium salt of the latter.

5. Reaction of  $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3$  with substituted phenol in the presence of  $(\text{CH}_3)_3\text{SiCl}$ .

The methods of preparation are summarized in Table 1 where also references are given.

**Table 1**  
Methods of preparation of phenoxy methyl silanes

Compound	Method				
	1	2	3	4	5
o- $(\text{CH}_3)_3\text{SiOC}_6\text{H}_4\text{CH}_3$	(3)	(3)	(10)	(11)	
m- $(\text{CH}_3)_3\text{SiOC}_6\text{H}_4\text{CH}_3$	(3)	(3)	(10)		
p- $(\text{CH}_3)_3\text{SiOC}_6\text{H}_4\text{CH}_3$	(3, 4)	(3)	(10)		
o- $(\text{CH}_3)_3\text{SiOC}_6\text{H}_4\text{Cl}$	(5)				
p- $(\text{CH}_3)_3\text{SiOC}_6\text{H}_4\text{Cl}$	(4, 5)		(10)		(12)
p- $(\text{CH}_3)_3\text{SiOC}_6\text{H}_4\text{Br}$	(4, 5, 6)	(8, 9)			
o- $(\text{CH}_3)_3\text{SiOC}_6\text{H}_4\text{NO}_2$				(11,7)	
p- $(\text{CH}_3)_3\text{SiOC}_6\text{H}_4\text{NO}_2$				(11,7)	
p- $(\text{CH}_3)_3\text{SiOC}_6\text{H}_4\text{F}$	(4)				

m-Nitrophenoxy-trimethyl silane has not yet been described in literature. Attempt was made also to prepare the p-carboxy, p-methoxy and p-amino derivatives from hexamethyl disilazane, which was, however, a failure. Neither could (p-hydroxyphenoxy)-trimethyl silane prepared, since the disubstituted product was invariably obtained.

The purity of the compounds was checked by gas-chromatography and by comparing theoretical and measured molar refractions. Gas-chromatographic measurements were made by means of a W. Giede 18.2 equipment. A column 1 m in length and 6 mm in diameter filled with 60–80 mesh Chromosorb W solid support wetted with 15% SE-30 methyl silicon polymer was used. The temperature of column was 150–300°C. Carrier gas was nitrogen, the volumetric flow rate of which was 55–98 ml/min.

Ultraviolet spectra were measured by means of a Spektromom 201 ultraviolet spectrophotometer, using solutions in ethylalcohol and 1 cm silica cells. Concentrations varied between  $10^{-2}$  and  $10^{-5}$  mole/l. The spectra of the compounds studied are presented in Figs 1, 2, 3 and 4, while the data of absorption peaks are summarized in Table 2.

To the evaluation of the spectra the data of the ultraviolet absorption spectrum of anisole, determined by BURAWOY and CHAMBERLAIN [13] have been used. These data are given in Table 3.

The following conclusion can be drawn from the spectra in Figs 1, 2, 3 and 4, and the data in Table 3. The spectrophotometric properties of silicon

Table 2  
Ultraviolet absorption data of phenoxy methyl silanes

	$\lambda_{\max}$ (nm)	$\nu^*$ ( $\text{cm}^{-1}$ )	$\epsilon$	$\lambda_{\max}$ (nm)	$\nu^*$ ( $\text{cm}^{-1}$ )	$\epsilon$	$\lambda_{\max}$ (nm)	$\nu^*$ ( $\text{cm}^{-1}$ )	$\epsilon$	$\lambda_{\max}$ (nm)	$\nu^*$ ( $\text{cm}^{-1}$ )	$\epsilon$
o-(CH <sub>3</sub> ) <sub>2</sub> SiOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	215	46512	6470	270	37037	930	275	36364	860			
m-(CH <sub>3</sub> ) <sub>2</sub> SiOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	217	46083	6270	270	37037	970	275	36364	960			
p-(CH <sub>3</sub> ) <sub>2</sub> SiOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	221	45249	7160	274	36496	1390	279	35842	1320			
o-(CH <sub>3</sub> ) <sub>2</sub> SiOC <sub>6</sub> H <sub>4</sub> Cl	217	46083	6460	277	36101	2400						
p-(CH <sub>3</sub> ) <sub>2</sub> SiOC <sub>6</sub> H <sub>4</sub> Cl	226	44248	10200	277	36101	1180						
p-(CH <sub>3</sub> ) <sub>2</sub> SiOC <sub>6</sub> H <sub>4</sub> Br	226	44248	12900	277	36101	1210						
o-(CH <sub>3</sub> ) <sub>2</sub> SiOC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	213	46948	11660	273	36630	5810	348	28736	3210			
m-(CH <sub>3</sub> ) <sub>2</sub> SiOC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	211	47393	12440	229	43668	8740	271	36900	5330	330	30303	1960
p-(CH <sub>3</sub> ) <sub>2</sub> SiOC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	226	44248	7250	314	31847	10710						
p-(CH <sub>3</sub> ) <sub>2</sub> SiOC <sub>6</sub> H <sub>4</sub> F	210	47619	4470	275	36364	1630	280	35714	1550			

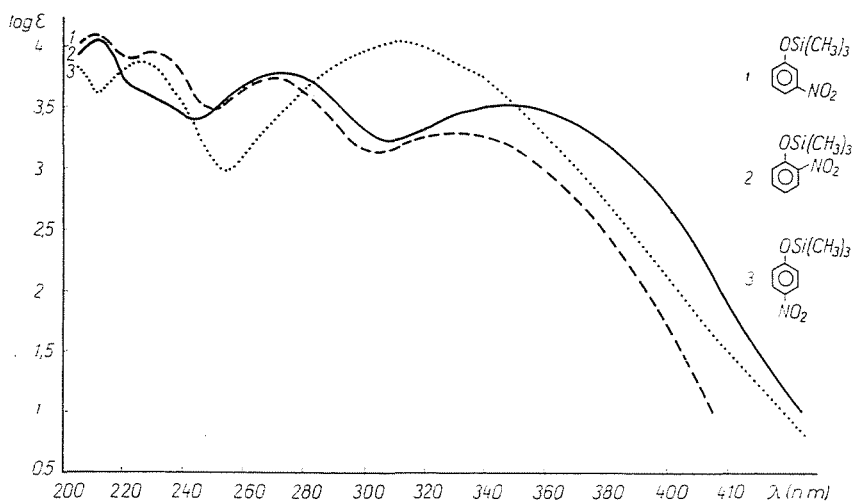


Fig. 1. Ultraviolet absorption spectra of nitrophenoxy trimethyl silanes

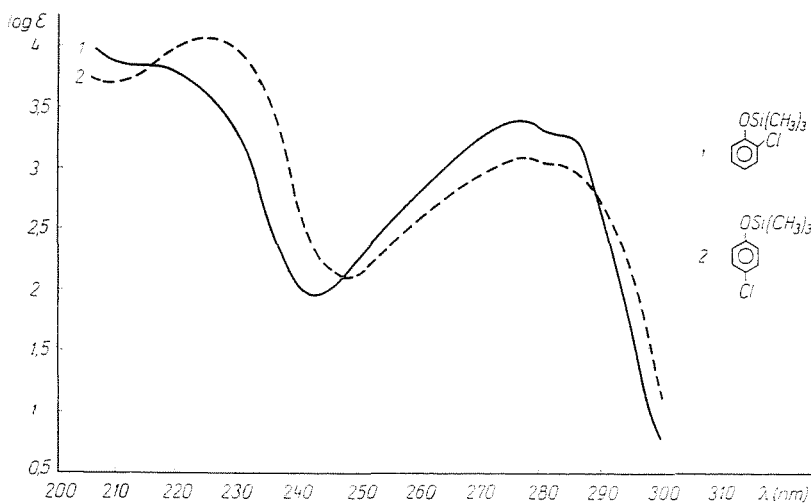


Fig. 2. Ultraviolet absorption spectra of chlorophenoxy trimethyl silanes

compounds were found to be similar to those of organic compounds. The absorption maxima of ortho and meta substituted compounds are nearly at the same wave number, while those of the para derivatives are remarkably shifted. This is due to the higher symmetry of the latter. Studies on the effect of 1st-order-substituents have led to the following conclusions: In the case of compounds substituted in the para position, a bathochromic shift (increase in the wave-length) and a reduction in the optical density of the peak in the order  $-\text{CH}_3$ ,  $-\text{F}$ ,  $-\text{Cl}$  and  $-\text{Br}$  can be observed with both carbon and silicon

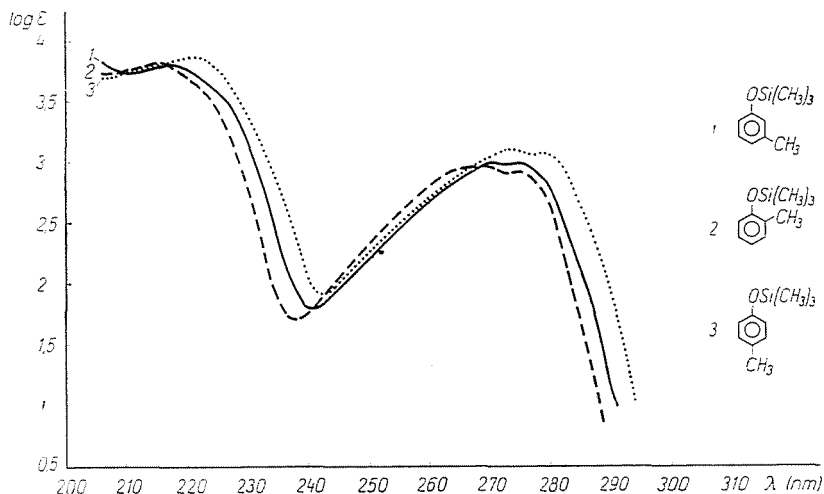


Fig. 3. Ultraviolet absorption spectra of methylphenoxy trimethyl silanes

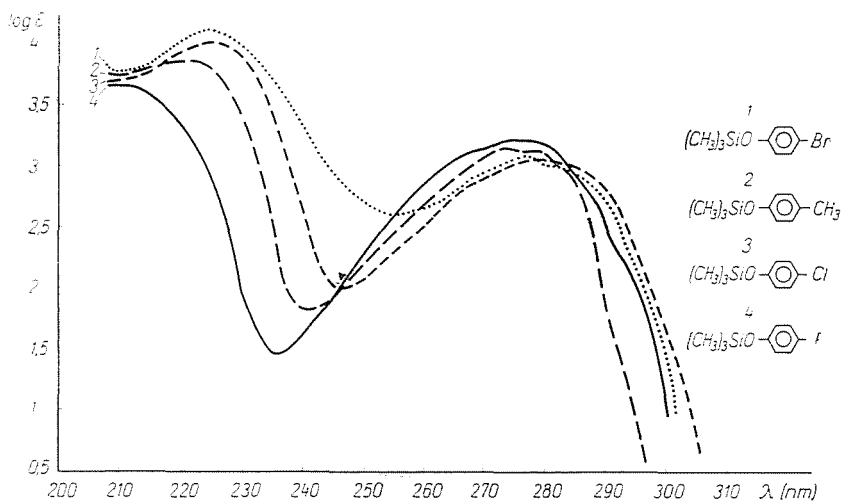


Fig. 4. Ultraviolet absorption spectra of  $p\text{-X-C}_6\text{H}_4\text{O-Si(CH}_3)_3$  type compounds (where  $X = \text{F, Cl, Br, CH}_3$ )

compounds. Ortho-chloro phenoxy derivatives exhibit a bathochromic shift and an increase in the optical density in comparison with ortho-methyl phenoxy derivatives, in the case of both series.

The effect of the 2nd-order substituent  $\text{NO}_2$  can be summarized as follows. A hypsochromic effect (decrease in the wave-length) can be observed in the order o-, m-, p-. In the case of the corresponding carbon compounds the ortho-nitro compound behaves differently, probably due to steric effects. In

**Table 3**  
Ultraviolet absorption data of substituted anisoles

	$\lambda_{\max}$ (nm)	$\nu^*$ ( $\text{cm}^{-1}$ )	$\epsilon$	$\lambda_{\max}$ (nm)	$\nu^*$ ( $\text{cm}^{-1}$ )	$\epsilon$
o- $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_3$	271.2	36873	1725	277	36101	1725
m- $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_3$	272	36765	1700	278	35971	1650
p- $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_3$	277.5	36036	2100	284.5	35149	1800
o- $\text{CH}_3\text{OC}_6\text{H}_4\text{Cl}$	274	36496	2100	281	35587	2100
p- $\text{CH}_3\text{OC}_6\text{H}_4\text{Cl}$	281.3	35549	1850	288	34722	1600
p- $\text{CH}_3\text{OC}_6\text{H}_4\text{Br}$	281.2	35562	1500	288	34722	1300
o- $\text{CH}_3\text{OC}_6\text{H}_4\text{NO}_2$	258.5	38685	3450	317.2	31526	2850
m- $\text{CH}_3\text{OC}_6\text{H}_4\text{NO}_2$	268	37313	6400	325.2	30750	2400
p- $\text{CH}_3\text{OC}_6\text{H}_4\text{NO}_2$	305	32787	13000			

both series meta derivatives exhibit the lowest optical densities, while the optical density of para-nitro derivatives is very high.

Comparing similarly substituted members of the series of organic and silicon-organic compounds the following conclusions can be drawn. With the exception of the nitro compounds, all substituted phenoxy-methyl silanes exhibit a hypsochromic shift and optical density decrease as compared to the corresponding substituted anisoles. With nitro compounds a bathochromic shift can be observed.

These results are best demonstrated on the basis of the comparison method by KARAPETIAN [14]. In Fig. 5 the wave numbers ( $\nu^*$ ), in Fig. 6 the

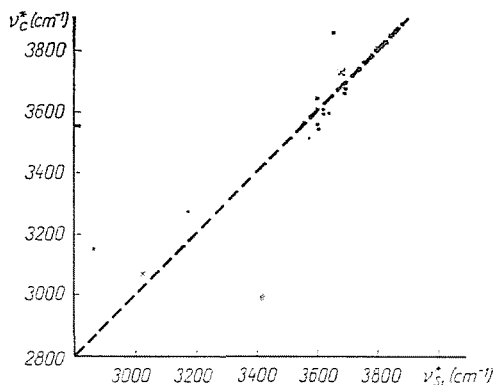


Fig. 5. Relationship between the wave numbers of the absorption maxima of phenoxy trimethyl silanes and substituted anisoles

optical densities ( $\epsilon$ ) of the absorption maxima of compounds of identical composition are plotted.

The points in Fig. 5 fall below the  $45^\circ$  line — except for nitro compounds —, i.e. they show a hypsochromic shift. The points for nitro compounds

are above the  $45^\circ$  line owing to the bathochromic shift. Similarly, the points in Fig. 6 are above the  $45^\circ$  line due to the reduction in optical density.

The results have been compared to those of methyl silanes presented in an earlier paper [1]. Trimethyl phenoxy silane has shown a small bathochromic shift and increase in optical density in comparison with anisole, while

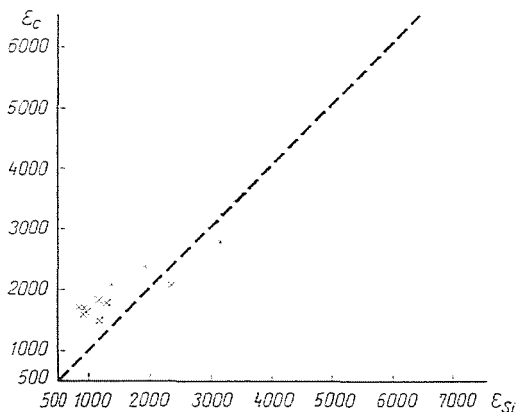


Fig. 6. Relationship between the maximum ultraviolet optical densities of phenoxy trimethyl silanes and substituted anisoles

substituted derivatives — as already mentioned — a hypsochromic effect and reduction in optical density. The data of the ultraviolet spectra can be accounted for by the  $+I$  (inductive) and  $-M$  (mesomeric) effect of the silicon atom, and by the  $-I$  and  $+M$  effect of the oxygen atom. The combination of these four effects results in small bathochromic or hypsochromic shifts.

It has been shown by ROBERTSON and MATSEN [15] that the inductive effect of the substituent on the phenyl group changes mainly the coulomb integral of the substituted carbon atom, and the inductive effect is also responsible for the changes in the intensity of absorption. Similarly to the quantum-chemical calculations made for the series of phenyl silanes [16], variation calculations have been carried out for the phenoxy group. The oscillator strength can be determined by means of the following equation:

$$f = 1.085 \cdot 10^{-5} \cdot \nu^* \cdot D \cdot G$$

where

- $\nu^*$  wave number of the ultraviolet absorption maximum (the value of which was similar in the case of all the compounds studied);
- $D$  transition dipole moment;
- $G$  degree of degeneration (in this case 1).

According to the above-said, the transition dipole moment is proportional to the oscillator strength, and intensity, respectively. Thus the change in optical density is related to the transition dipole moment.

In order to study the effect of silicon and carbon atom, one-electron LCAO-MO approximation calculations were made for the  $C_6H_5O$ -(phenoxy)

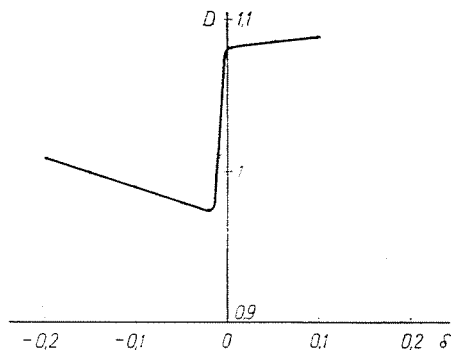


Fig. 7. Variation of transition dipole moment as a function of coulomb parameter

group. The effect of identical substituents at equivalent positions in the ring has been neglected, and the effect of silicon and carbon atom has been taken into consideration by varying the coulomb integral of the carbon atom attached to oxygen. On the basis of the earlier experience of the authors [2] the following coulomb and resonance integrals have been used:

$$\begin{aligned} \alpha_O &= \alpha + 2.92\beta & \beta_{CO} &= 0.69\beta \\ \alpha'_C &= \alpha + \delta\beta & \beta'_{CC} &= 0.93\beta \\ \alpha_C &= \alpha & \beta_{CC} &= \beta \end{aligned}$$

(Carbon atom denoted by ' is attached to oxygen.)

By changing the parameter  $\delta$  the transition dipole moment has been calculated. The obtained relationship is demonstrated in Fig. 7.

As shown by the figure, the increase of the parameter  $\delta$  in the range  $\delta < -0.02$  leads to the reduction in transition dipole moment and consequently in the intensity. In the range  $\delta > 0$ ,  $D$  and  $\epsilon$  increase with increasing  $\delta$ . As shown by earlier results [2], the partial charge on the carbon atom attached to oxygen is higher in anisole than in trimethyl phenoxy silane (0.0140 and 0.0119, respectively). Accordingly, the coulomb integral ( $\delta$  parameter) of carbon atom is higher in the carbon compound than in phenoxy silane. The higher intensity of the ultraviolet absorption of trimethyl phenoxy silane as compared to that of anisole can be interpreted by the assumption that the conditions are suitable on the left side of the absorption band. The lower intensity of the absorption of substituted phenoxy silanes as compared to substituted anisoles can be explained by the shape of the curve on the left side



of the maximum. It is to be stressed that in this case the effect of substituents has been neglected, although the symmetry of the  $\pi$  and  $\pi^*$  orbitals does not change as the number of atoms increases, the orbitals are only shifted. Accordingly, as a first approximation, the calculations gave qualitatively correct results. Precise quantumchemical calculations of the molecular structure of phenoxy silanes will be presented later.

### Experimental

The required amount of the substituted phenol was placed into a three-necked flask equipped with a mercury-sealed stirrer, reflux cooler and tap-funnel and hexamethyl disilazane was added dropwise. Then the mixture was boiled until  $\text{NH}_3$  evolution ceased. The product was purified by vacuum distillation.

#### *Cresoxy trimethyl silanes*

54.0 g (0.5 mole) of cresol were allowed to react with 44.3 g (0.275 mole) of hexamethyl disilazane. Yield: 85–90%.

#### *Chlorophenoxy trimethyl silanes*

64.3 g (0.5 mole) of chlorophenol were allowed to react with 44.3 g (0.275 mole) of hexamethyl disilazane. Yield: 85–90%.

#### *Nitrophenoxy trimethyl silanes*

69.6 g (0.5 mole) of nitrophenol were allowed to react with 44.3 g (0.275 mole) of hexamethyl disilazane. Yield: o-: 81%, m: 70%, p-: 79%.

#### *p-Bromophenoxy trimethyl silane*

96.5 g (0.5 mole) of p-bromophenol were allowed to react with 44.3 g (0.275 mole) of hexamethyl disilazane. Yield: 87%.

#### *p-Fluorophenoxy trimethyl silane*

56.0 g (0.5 mole) of p-fluorophenol were allowed to react with 44.3 g (0.275 mole) of hexamethyl disilazane. Yield: 82%. The physical data of the compounds prepared are presented in Table 4.

Table 4

Physical data of trimethyl phenoxy silanes

Compound	b.p.C° (Hgmm)	$d_4^{25}$ (gml <sup>-1</sup> )	$n_D^{25}$	MR <sub>D</sub> (measured) (ml)	MR <sub>D</sub> (calculated) (ml)
o-(CH <sub>3</sub> ) <sub>3</sub> SiOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	83–84 (15)	0.9158	1.4769	55.62	55.84
m-(CH <sub>3</sub> ) <sub>3</sub> SiOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	86 (15)	0.9124	1.4767	55.81	55.84
p-(CH <sub>3</sub> ) <sub>3</sub> SiOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	84–85 (16)	0.9127	1.4770	55.82	55.84
o-(CH <sub>3</sub> ) <sub>3</sub> SiOC <sub>6</sub> H <sub>4</sub> Cl	95–96 (15)	1.0451	1.4921	55.73	55.33
p-(CH <sub>3</sub> ) <sub>3</sub> SiOC <sub>6</sub> H <sub>4</sub> Cl	102–103 (15)	1.0415	1.4927	55.98	55.33
p-(CH <sub>3</sub> ) <sub>3</sub> SiOC <sub>6</sub> H <sub>4</sub> Br	110 (15)	1.2498	1.5122	58.88	58.21
o-(CH <sub>3</sub> ) <sub>3</sub> SiOC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	131 (14)	1.0922	1.5062	57.49	58.39
m-(CH <sub>3</sub> ) <sub>3</sub> SiOC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	131 (15)	1.0890	1.5078	57.82	58.39
p-(CH <sub>3</sub> ) <sub>3</sub> SiOC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	143 (13)	1.0994	1.5261	59.00	58.39
p-(CH <sub>3</sub> ) <sub>3</sub> SiOC <sub>6</sub> H <sub>4</sub> F	73–74 (15)	0.9954	1.4591	50.61	50.26

### Summary

Compounds of the general composition  $(\text{CH}_3)_2\text{SiOC}_6\text{H}_4\text{X}$  (where  $\text{X} = \text{CH}_3, \text{Cl}, \text{NO}_2, \text{Br}, \text{F}$ ) have been prepared from hexamethyl disilazane. The ultraviolet absorption spectra of these compounds were considered. Approximation variation quantum-chemical calculations have been made for the  $\text{C}_6\text{H}_5\text{O}$  group, then the shifts and optical density changes in the spectra have been estimated qualitatively.

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