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INVESTIGATIONS ON THE BOND STRUCTURE OF ALKYLPHENOXYSILANES USING ULTRAVIOLET SPECTROPHOTOMETRIC METHODS

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INTRODUCTION

Several authors have dealt with the bond structure of aromatic silicon compounds[1-3] but investigations on the structure of the phenoxy–silicon bond are relatively rare. Marchand and co-workers[4] recorded the characteristic frequencies of the Si–O–C bond in the phenoxysilanes. We have studied the phenoxy–silicon bond using an ultraviolet spectrophotometric method with calculations by the LCAO-MO one-electron method.

The compounds $(CH_3)_nSi(OC_6H_5)_{4-n}$, where $n = 0$–3 have been synthesized for experimental purposes. In the synthesis of trimethylphenoxysilane we have departed from the general method reviewed later because, owing to the close boiling points of the product and the unreacted phenol (178–179 and 181.8°), their separation would have been difficult. Therefore trimethylphenoxysilane was prepared from hexamethyldisilazane using Andrianov's method[5].

Anisole and tert-butylphenyl ether were used as standard substances.

RESULTS

The compounds listed above were synthesized by the method given in the literature[6-8] according to the following general equation:

$$(CH_3)_nSiCl_{4-n} + (4-n)\ C_6H_5OH = (CH_3)_nSi(OC_6H_5)_{4-n} + (4-n)\ HCl$$

where $n = 0$–2

Trimethylphenoxysilane was prepared partly by our own method according to the following reaction:

$$(CH_3)_3Si\text{–}NH\text{–}Si(CH_3)_3 + 2\ C_6H_5OH = 2\ (CH_3)_3SiOC_6H_5 + NH_3$$

Tert-butylphenyl ether was obtained by a published method[9]:

$$(CH_3)_3CCl + NaOC_6H_5 = (CH_3)_3C\text{–}O\text{–}C_6H_5 + NaCl$$

The compounds synthesized were of the grade of purity described in the literature references, as shown by the correspondence of calculated and experimentally obtained molar refraction values.

The spectra of the compounds prepared were obtained by means of a Spektromom 201 UV spectrophotometer. Alcoholic solutions at a concentration of 10^{-2}–

10^{-5} mole/l and quartz cuvettes of 1 cm thickness were used in the experimental work. The spectra obtained are shown in Figs. 1 and 2.

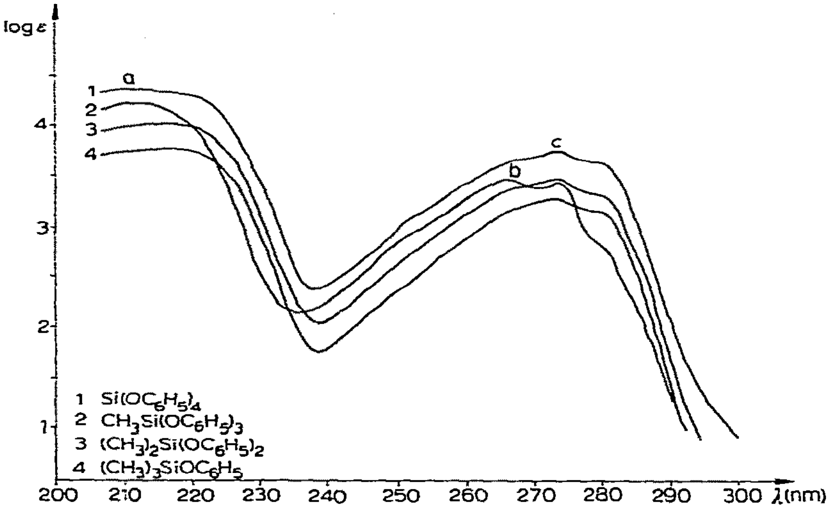


Fig. 1. Ultraviolet spectra of compounds of $(CH_3)_nSi(OC_6H_5)_{4-n}$ type (where $n = 0$–3). Solvent, 96% ethanol.

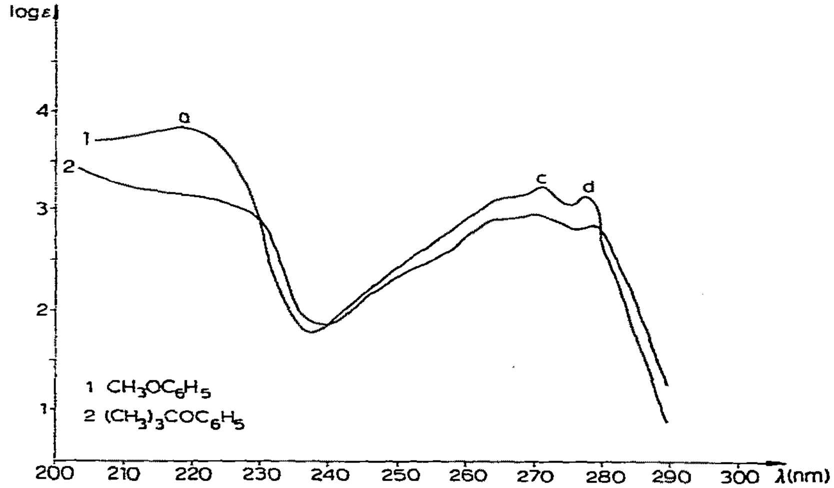


Fig. 2. Ultraviolet spectra of anisole and tert-butylphenyl ether. Solvent, 96% ethanol.

The positions of the absorption maxima are marked as a, b, c and d and the corresponding wave lengths (λ), wave numbers (ν^*) and extinction values (ε) are tabulated in Table 1.

DISCUSSION

In evaluating the ultraviolet spectra, the maxima marked c (band α) have been selected for consideration. It can be seen from Table 1 and from Figs. 1 and 2 that

TABLE 1

UV ABSORPTION MAXIMA OF METHYLPHENOXYSILANES AND PHENYLETHERS

	λ_a (*nm*)	ν^* (*cm*$^{-1}$)	ε	λ_c (*nm*)	ν^* (*cm*$^{-1}$)	ε	λ (*nm*)	ν^* (*cm*$^{-1}$)	ε
$Si(OC_6H_5)_4$	211	47393	24340	273	36630	5970			
$CH_3Si(OC_6H_5)_3$	211	47393	17550	273	36630	2900	266	37594	3100(b)
$(CH_3)_2Si(OC_6H_5)_2$	218	45871	10600	273	36630	3060			
$(CH_3)_3SiOC_6H_5$	218	45871	6200	273	36630	1960			
$CH_3OC_6H_5$	219	45662	6760	271	36900	1710	278	35971	1470(d)
$(CH_3)_3COC_6H_5$				270	37037	950	279	35842	740(d)

the phenoxysilanes show a limited bathochromic shift when compared with anisole and tert-butylphenyl ether chosen for comparison. It is also evident from the experimental data that the frequency of the absorption maximum is the same, for each methylphenoxysilane compound (273 nm = 36630 cm^{-1}) investigated, *i.e.*, the position of the maximum is independent of the number of phenoxy groups. It can therefore be assumed that the conjugation between the phenoxy groups and the silicon atom does not extend to each phenoxy group, but that these phenoxy groups are in conjugative contact with single empty *d*-orbitals; the phenoxysilanes can thus be divided into phenoxysilicon groups practically independent of one another. On the basis of these considerations, quantum-chemical calculations have been performed for tetraphenoxysilane which is completely symmetrical thus reducing the calculation problem to a single phenoxysilicon group.

First, the quantum-chemical calculation of the standard carbon analogue compounds was performed by the LCAO-MO one-electron molecular orbital calculation method.

In the case of anisole and tert-butylphenyl ether, the inductive ($+I$) and hyperconjugative effects of the $-CH_3$ group as well as the inductive ($+I$) effect of the $-C(CH_3)_3$ group were not taken into consideration and in our calculations the 7-center system shown in Fig. 3 was used.

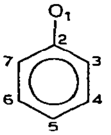


Fig. 3. Numbering of the atoms of the phenoxy group in the quantum-chemical calculation.

As the phenoxy group, C_6H_5O-, has C_{2v} symmetry, when solving the problem the seven different eigen-values are calculated from two matrix equations, utilizing the group theory. The calculation was performed by Hückel's method[10].

The Coulomb integrals of all carbon atoms in the phenyl ring were chosen to be identical (α) as well as the resonance integrals of the carbon–carbon bonds (β). The literature data[11] indicated the Coulomb integral for oxygen as $\alpha+2\beta$ and the resonance integral of the oxygen–carbon bond as 0.8 β.

In Table 2 are tabulated the values of the Coulomb and resonance integrals used in the calculations of the seven-centre system, the calculated eigen-values, the

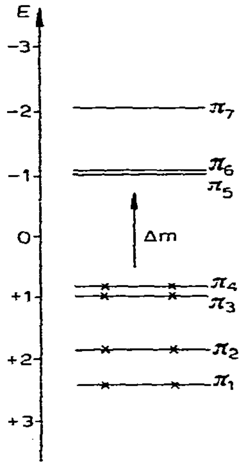
TABLE 2

QUANTUM-CHEMICAL CALCULATION DATA OF THE PHENOXY GROUP IN PHENYL ETHERS

Number of atoms	1	2	3	4	5	6	7
Coulomb integrals	$\alpha+2\beta$	α	α	α	α	α	α
Resonance integral	0.8β	β	β	β	β	β	
Eigen-values	*Linear coefficients*						
$\varepsilon_1=\alpha+2.4623\beta$	0.7847	0.4535	0.2445	0.1488	0.1208	0.1488	0.2445
$\varepsilon_2=\alpha+1.8090\beta$	0.4831	−0.1153	−0.2975	−0.4228	−0.4676	−0.4228	−0.2975
$\varepsilon_3=\alpha+1.0000\beta$	0.0000	0.0000	0.5000	0.5000	0.0000	−0.5000	−0.5000
$\varepsilon_4=\alpha+0.8274\beta$	0.3468	−0.5082	−0.3490	0.2195	0.5306	0.2195	−0.3490
$\varepsilon_5=\alpha-1.0000\beta$	0.0000	0.0000	0.5000	0.5000	0.0000	0.5000	0.5000
$\varepsilon_6=\alpha-1.0700\beta$	0.1496	−0.5739	0.2472	0.3094	−0.5783	0.3094	0.2472
$\varepsilon_7=\alpha-2.0286\beta$	0.0873	−0.4396	0.4109	−0.3941	0.3885	−0.3941	0.4109
Δm	1.8274β					$(\pi\rightarrow\pi^*$ transition)	

linear coefficients, and the Δm energy differences belonging to the $\pi\rightarrow\pi^*$ transition (in β-units).

The eigen-values of the molecular orbitals are shown in Fig. 4, and the partial charge distribution calculated from the linear coefficients and the bond orders are shown in Fig. 5.



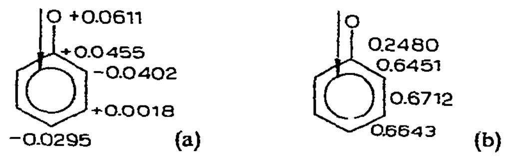


Fig. 4. Eigen-values of the molecular orbitals of the phenoxy group in phenyl ethers.

Fig. 5. Partial charge distribution (a) and bond orders (b) of the phenoxy group in phenyl ethers.

In the phenoxy group the oxygen atom connected with the aromatic ring has a $-I$ and a $+M$ effect. In consequence of its $-I$ effect, the oxygen atom attracts electrons from the aromatic ring and will therefore be richer in electrons; its electronegativity decreases and its Coulomb integral also decreases proportionally. At the same time, as a result of the $-I$ and $+M$ effects, the distance between the oxygen and carbon atoms will be shorter, the overlap of the atomic orbits increases and, consequently, the resonance integral, β(CO), also increases.

The absorption maxima tabulated in Table 3 are taken partly from the literature[12] and partly from our measurements.

TABLE 3

UV ABSORPTION MAXIMA OF COMPOUNDS OF TYPE C_6H_5O–M (M = CH_3, Si≡, H, Na)

	λ (nm)	ν^* (cm^{-1})	
Anisole $C_6H_5OCH_3$	271	36900	1.8274 β
Phenoxy-Si $C_6H_5OSi\equiv$	273	36630	1.8140 β
Phenol C_6H_5OH	275	36363	1.8008 β
Phenolate ion $C_6H_5O^-$ (Na^+)	288	34722	1.7195 β

The increase of the bathochromic effect in the sequence given can be seen in Table 3. This may be connected with the fact that, because of the electron repulsing effect of the substituents, the electron density of oxygen increases; also, the resonance integral of the carbon–oxygen atoms increases with the $+M$ effect, from anisole to the phenolate ion.

To prove this supposition, a variation calculation has been performed for the $\pi \rightarrow \pi^*$ transition where the Coulomb integral of oxygen and the resonance integral of the carbon–oxygen bond has been changed. The result of this calculation is shown in Fig. 6.

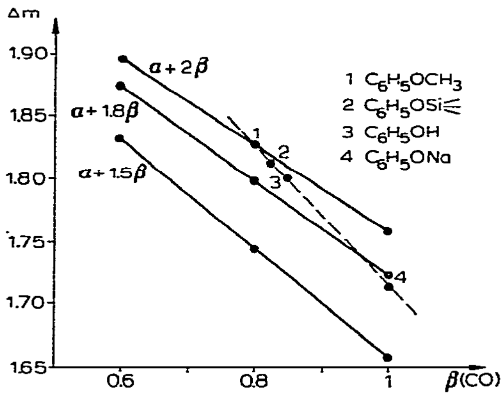


Fig. 6. $\pi \rightarrow \pi^*$ transition of compounds of C_6H_5O–M type (where M = CH_3, Si≡, H, Na) in the function of the Coulomb integral of oxygen and resonance integral of the carbon–oxygen bond.

If the 271-nm maximum value for anisole is taken as a basis and an approximately linear proportionality between the Δm energy change and the ν^* wave number is supposed, the Δm-values for each of the other three groups can be calculated (in β-units):

$$\Delta m_i = \frac{\nu_i^*}{\nu_0^*} \cdot \Delta m_0 \, ,$$

where Δm_0 = energy difference belonging to the $\pi \to \pi^*$ transition of anisole, in β-units; ν_0^* = wave number of the absorption maximum of anisole; ν_i^* = wave number of the absorption maximum of phenol, phenolate ion and the phenoxysilicon group; Δm_i = energy difference, in β-units, of the $\pi \to \pi^*$ transition of the above substances.

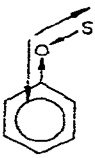
Since the resonance integral of the carbon–oxygen bond is higher in the phenolate ion (in sodium phenolate) than in anisole, its value has been chosen to be 1 β; in the previous calculation in the case of anisole, a value of 0.8 β was used.

When these two points were fixed, the dotted line in Fig. 6 was obtained. Using the Δm-values from Table 3, the points corresponding to phenol and the phenoxysilicon group were marked on this line. In this way the supposition is proved, *i.e.*, the bathochromic effect increases from anisole to the phenolate ion with increase of the resonance integral of the carbon–oxygen bond and decrease of the Coulomb integral of oxygen.

Here an apparent contradiction with the electronegativity order appears, *viz.*, on the basis of an electronegativity value of 1.8 for the silicon atom, a smaller $\pi \to \pi^*$ transition can be expected in the phenoxysilicon system than in the case of phenol (the electronegativity of H is 2.1). This fact can be explained as follows.

In the phenoxy-silicon system the electron shift effects shown in Fig. 7 are realized. As with anisole, the $-I$ and $+M$ effects of the oxygen will act with the addition of the $+I$ and $-M$ effects of silicon. The outcome of these four effects taken one with another will cause the limited bathochromic shift, derived from the experimental results. It can be explained by the fact that from the side of the silicon not only a large $+I$, but also, to a smaller extent, a $-M$ effect appears which decreases the degree of the bathochromic shift. This explanation was substantiated by our quantum-chemical calculations. Because of the reasons mentioned above the LCAO-MO one-electron calculation has been performed for the C_6H_5OSi group on the basis of the Hückel-principle[10].

The $C_6H_5OSi\equiv$-system, similarly to the C_6H_5O-system, has a C_{2v} symmetry, the eight different eigen-values can therefore be calculated with the aid of the group theory from two matrix equations (Fig. 8). In agreement with the previous calculation



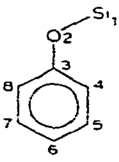


Fig. 7. Electron shift effects in the phenoxy–silicon system.

Fig. 8. Numbering of the atoms of the phenoxysilicon group in the quantum-chemical calculation.

the Coulomb integral of the carbon and the resonance integral of the carbon–carbon bond were chosen as α and β, respectively, and the Coulomb integral of the oxygen as $\alpha+2\ \beta$. The $\alpha-2\ \beta$ value published previously[1] was accepted for the Coulomb integral of silicon.

1 β was chosen for the resonance integral of the carbon–oxygen bond since, on the basis of previous considerations due to the $+I$ effect of silicon, the resonance integral of the carbon–oxygen bond would be larger than for anisole (0.8 β).

The resonance integral of the silicon–oxygen bond was calculated (based on the proportionality of the overlap and the resonance integrals) as follows:

$$\beta(\mathrm{SiO}) = \frac{S(\mathrm{SiO})}{S(\mathrm{CC})} \cdot \beta(\mathrm{CC}),$$

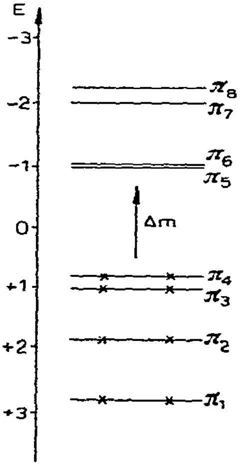
where $\beta(\mathrm{CC})$ and $S(\mathrm{CC})$ are the resonance and overlap integral values of the carbon atoms of benzene, and $S(\mathrm{SiO})$ is the overlap integral of the silicon–oxygen bonds. A value of 1.1 β was obtained for $\beta(\mathrm{SiO})$. A more detailed discussion of the calculation will be given in another paper.

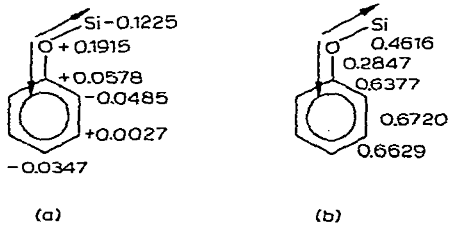
Table 4 gives the Coulomb and resonance integral values used in the calculations, the eigen-values obtained, the linear coefficients, and the Δm-values corresponding to the transition $\pi \rightarrow \pi^*$.

TABLE 4

QUANTUM-CHEMICAL CALCULATION DATA OF THE $C_6H_5OSi\equiv$-GROUP IN PHENOXYSILANES (Fig. 8)

Number of atoms	1	2	3	4	5	6	7	8
Coulomb integral	$\alpha-2\beta$	$\alpha+2\beta$	α	α	α	α	α	α
Resonance integral	1.1β	β	β	β	β	β	β	
Eigen-values	*Linear coefficients*							
$\varepsilon_1 = \alpha+2.7780\,\beta$	0.1903	0.8265	0.4337	0.1891	0.0917	0.0642	0.0917	0.1891
$\varepsilon_2 = \alpha+1.8389\,\beta$	0.1011	0.3529	−0.1681	−0.3310	−0.4405	−0.4793	−0.4405	−0.3310
$\varepsilon_3 = \alpha+1.0000\,\beta$	0.0000	0.0000	0.0000	0.5000	0.5000	0.0000	−0.5000	−0.5000
$\varepsilon_4 = \alpha+0.8071\,\beta$	0.1218	0.3108	−0.5047	−0.3591	0.2149	0.5325	0.2149	−0.3591
$\varepsilon_5 = \alpha-1.0000\,\beta$	0.0000	0.0000	0.0000	0.5000	0.5000	0.0000	0.5000	0.5000
$\varepsilon_6 = \alpha-1.0766\,\beta$	0.1557	0.1307	−0.5735	0.2434	0.3115	−0.5631	0.3115	0.2434
$\varepsilon_7 = \alpha-2.0000\,\beta$	0.3478	0.0000	−0.3826	0.3826	−0.3826	0.3833	−0.3826	0.3826
$\varepsilon_8 = \alpha-2.3475\,\beta$	0.8911	−0.2815	0.2438	−0.1451	0.0969	−0.0796	0.0969	−0.1451
Δm	$1.8071\,\beta$						($\pi \rightarrow \pi^*$ transition)	





(a) (b)

Fig. 9. Eigen-values of the molecular orbitals of the phenoxysilicon group in methylphenoxysilanes.
Fig. 10. Partial charge distribution (a) and bond orders (b) of the phenoxysilicon group in methylphenoxysilane.

The eigen-values of the $C_6H_5OSi\equiv$-system are shown in Fig. 9 and in Fig. 10 the partial charge distribution calculated from the linear coefficients and the bond orders. The following conclusions can be drawn from the results.

The calculations show that the resonance integral of the carbon–oxygen bond increases because of the $+I$ effect of silicon, this being proved by the increase in the bond order of the carbon–oxygen bond as compared with anisole. Also, at the same time the Δm-values of the phenoxy group in anisole and of the phenoxysilicon group in tetraphenoxysilane (1.8274 β and 1.8071 β) agrees with the bathochromic effect observed experimentally. The difference between the two values is very small which proves convincingly that silicon not only has a $+I$ but also a $-M$ effect and, thus, in spite of the electronegativity order, the bathochromic effect of the phenoxysilicon group in phenoxysilanes is smaller than that of phenol.

Our calculations show that the bond order of the carbon atoms in the aromatic ring shows a slight change when compared with benzene (0.6670), the two systems discussed differ only in the bond order of the substituted carbon atom. In the matter of partial charge distribution, the charge of oxygen is higher in the phenoxy-silicon system than in the phenoxy group. The charge of the carbon atoms in *ortho*- and *para*-positions is negative in both cases, *i.e.*, in agreement with other observers the oxygen and the oxygen–silicon group can be regarded as substituents of the first order.

EXPERIMENTAL

Tetraphenoxysilane. This was obtained from silicon tetrachloride and phenol. The product was purified by vacuum distillation and recrystallization from glacial acetic acid.

Methyltriphenoxysilane. This was prepared from methyltrichlorosilane (CH_3SiCl_3) and phenol (in 20–30% excess) and purified by vacuum distillation.

Dimethyldiphenoxysilane. Dimethyldichlorosilane [$(CH_3)_2SiCl_2$] was reacted with phenol (in 20–30% excess) and the product obtained purified by vacuum distillation.

Trimethylphenoxysilane. Hexamethyldisilazane was reacted with phenol in 1 : 1

TABLE 5

PHYSICAL DATA OF METHYLPHENOXYSILANES AND PHENYL ETHERS

	M.p. (°C)	*B.p.* °C (*mm*)	d^{25} (*g ml*$^{-1}$)	n_D^{25}	*MR* (*calcd.*)	*MR* (*measured*)
$Si(OC_6H_5)_4$	47–48° (48° lit.)	260–262° (12)		1.5578[a] (1.5583 lit.)		
$CH_3Si(OC_6H_5)_3$		210–211° (12)	1.1297	1.5575	91.84	91.94
$(CH_3)_2Si(OC_6H_5)_2$		150–153° (12)	1.0566	1.5299	71.42	71.43
$(CH_3)_3SiOC_6H_5$		178–179° (760)	0.9448	1.4884	50.80	50.71
$CH_3OC_6H_5$		153–154° (760) (153.8° lit.)		1.5154 (1.5150 lit.)		
$(CH_3)_3COC_6H_5$		72–74° (12) [70–71° (11) lit.]		1.4885 (1.4880 lit.)		

[a] At 54.7°C.

molar ratio in a three-neck test-tube with constant stirring and boiling. The reaction was assumed to be completed when NH_3 ceased to be evolved. The product was purified by repeated distillation. Yield: 75%.

Tert-butylphenyl ether. This was obtained from tert-butyl chloride and sodium phenolate in absolute ethanol. The product was purified by vacuum distillation.

Anisole. The commercial product of analytical grade was purified by distillation.

The physical constants of the substances listed above are tabulated in Table 5.

SUMMARY

1. Substances of formula $(CH_3)_nSi(OC_6H_5)_{4-n}$, where $n = 0$–3 have been investigated by an ultraviolet spectrophotometric method. The compounds were prepared partly as described in the literature and partly by our own method.

2. It has been found that the phenoxy–silicon bond of phenoxysilanes shows a small bathochromic effect as compared with the phenoxy group of the phenyl ethers. The position of the absorption maximum is independent of the number of phenoxy groups.

3. The spectra observed indicate that besides the $-I$ and $+M$ effects of oxygen, silicon has $+I$ and $-M$ effects. These four effects together cause the bathochromic shift which is of a lower degree than would be expected from the order of electronegativity.

4. The $\pi \rightarrow \pi^*$ transitions of the phenoxy groups in the phenyl ethers and of the phenoxysilicon groups in the phenoxysilanes have been calculated (1.8274 β and 1.8071 β) by the LCAO-MO one-electron method. The results are in accordance with the absorption maxima (271 nm and 273 nm) observed.

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