Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

INVESTIGATION OF THE MOLECULAR STRUCTURE OF PHENOXYSILANES

J. NAGY AND P. HENCSEI
Department of Inorganic Chemistry, Technical University, Budapest (Hungary)

(Received April 7th, 1970)

SUMMARY

The molecular structure of phenoxysilanes has been studied. From UV and IR spectral data conclusions were drawn on the nature of the silicon–oxygen bond. From dipole moment data, calculations were made on the steric arrangement of the molecules. The conclusions drawn were supported by approximative quantum chemical calculations. It was established that a d_π–p_π bond is formed between the silicon and the oxygen atom in phenoxysilanes, and this linkage extends also to the phenyl group.

INTRODUCTION

The silicon–oxygen bond has been studied in various phenoxysilanes. The UV and IR spectra and the dipole moments of the compounds prepared have been studied.

Data measured were evaluated qualitatively by approximation of quantum chemical calculations.

EXPERIMENTAL

The phenoxysilanes were prepared by reacting hexamethyldisilazane with the corresponding phenol. The purity of the compounds was checked by gas chromatography, and by a comparison of the theoretical and measured molecular refraction values. UV absorption spectra were determined in solutions in ethyl alcohol with a Spektromom 201 UV spectrophotometer. IR spectra were recorded with an UR-20 instrument. The dipole moments of the compounds were calculated by the method of Onsager and Hedestrand from capacitance values measured with a capacitance meter of our own construction. When measuring in solutions, cyclohexane was used as solvent.

RESULTS AND THEIR EVALUATION

For the evaluation of UV spectra, the maxima of the α-band have been studied. UV data of the phenyl ethers and the correspondingly substituted anisoles have also been used as a basis of comparison. UV absorption data for the phenoxysilanes and phenyl ethers are listed in Table 1.

It can be seen from data in Table 1 that there is only a slight difference, 1.2 to 5.5 nm, between the maxima of the corresponding organosilicon and organic compounds, with the exception of the nitro derivatives. Organosilicon compounds show partly a bathochromic, partly a hypsochromic shift, as compared to carbon compounds of the same composition. These shifts are attributed to the effect of the oxygen and silicon atoms. Besides the $-I$ (inductive) and $+M$ (mesomeric) effects of oxygen, the $+I$ and $-M$ effects of silicon are also present, and the relative magnitude of these four effects determines the shift observed in the spectrum. A comparison of the absorption maxima of compounds of the type C_6H_5O-M ($M=H$, C, Si, Na, P) proves experimentally the d_π–p_π character of the silicon–oxygen bond (see Table 2).

TABLE 1

UV ABSORPTION DATA FOR PHENOXYSILANES AND PHENYL ETHERS

Phenoxysilane	λ(nm)	ε	Phenyl ether	λ(nm)	ε
$(C_6H_5O)_4Si$[1]	273	5970			
$(C_6H_5O)_3SiCH_3$[1]	266	3100			
	273	2900			
$(C_6H_5O)_2Si(CH_3)_2$[1]	273	3060			
$C_6H_5OSi(CH_3)_3$[1]	273	1960	$C_6H_5OCH_3$[1]	271	1710
				278	1470
o-$C_6H_4[OSi(CH_3)_3]_2$[2]	272	1940	*o*-$C_6H_4(OCH_3)_2$[2]	275	2520
m-$C_6H_4[OSi(CH_3)_3]_2$[2]	272	1570	*m*-$C_6H_4(OCH_3)_2$[2]	274	2300
				280	2100
p-$C_6H_4[OSi(CH_3)_3]_2$[2]	293	2590	*p*-$C_6H_4(OCH_3)_2$[2]	289	3310
o-$CH_3C_6H_4OSi(CH_3)_3$[3]	270	930	*o*-$CH_3C_6H_4OCH_3$[4]	271.2	1725
	275	860		277	1725
m-$CH_3C_6H_4OSi(CH_3)_3$[3]	270	970	*m*-$CH_3C_6H_4OCH_3$[4]	272	1700
	275	960		278	1650
p-$CH_3C_6H_4OSi(CH_3)_3$[3]	274	1390	*p*-$CH_3C_6H_4OCH_3$[4]	277.5	2100
	279	1320		284.5	1800
o-$ClC_6H_4OSi(CH_3)_3$[3]	277	2400	*o*-$ClC_6H_4OCH_3$[4]	274	2100
				281	
p-$ClC_6H_4OSi(CH_3)_3$[3]	277	1180	*p*-$ClC_6H_4OCH_3$[4]	281.3	1850
				288	1600
p-$BrC_6H_4OSi(CH_3)_3$[3]	277	1210	*p*-$BrC_6H_4OCH_3$[4]	281.2	1500
				288	1300
p-$FC_6H_4OSi(CH_3)_3$[3]	275	1630			
	280	1550			
o-$O_2NC_6H_4OSi(CH_3)_3$[3]	273	5810	*o*-$O_2NC_6H_4OCH_3$[4]	258.5	3450
	348	3210		317.2	2850
m-$O_2NC_6H_4OSi(CH_3)_3$[3]	271	5330	*m*-$O_2NC_6H_4OCH_3$[4]	268	6400
	330	1960		325.2	2400
p-$O_2NC_6H_4OSi(CH_3)_3$[3]	314	10710	*p*-$O_2NC_6H_4OCH_3$[4]	305	13000

The wave number belonging to the maximum is plotted in Fig. 1 as a function of the electronegativity of the atom linked to oxygen.

It can be established from the first three data in Table 2 and from Fig. 1 that the electron density increases on the oxygen atom with decreasing electronegativity of

TABLE 2

UV ABSORPTION MAXIMA OF COMPOUNDS OF THE TYPE C_6H_5OM

C_6H_5OM	λ (nm)	ν^* (cm^{-1})	χ[a]
$C_6H_5OCH_3$[1]	271	36900	2.5
C_6H_5OH[5]	275	36363	2.1
$C_6H_5O^-Na^+$[5]	288	34722	0.9
$C_6H_5OSi(CH_3)_3$[1]	273	36630	1.8
$(C_6H_5O)_3PO$[6]	261	38314	2.1
$(C_6H_5O)_3P$[6]	270	37037	2.1

[a] Electronegativity.

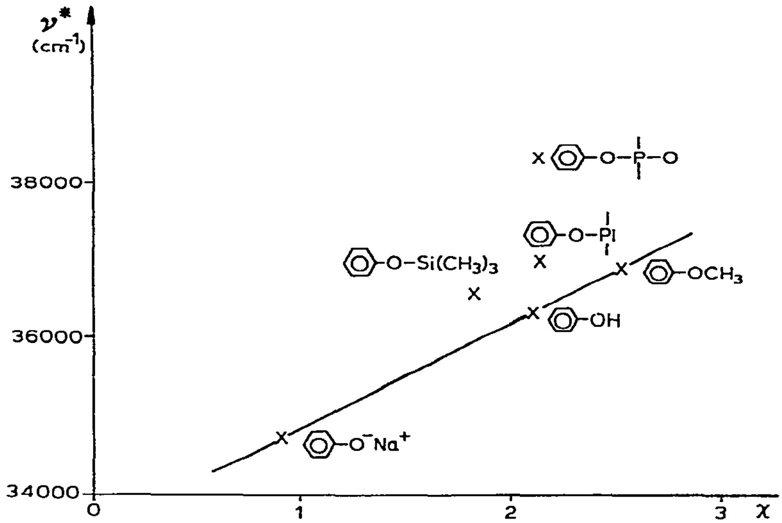

Fig. 1. UV absorption maxima of compounds of the type C_6H_5OM (M = H, C, Si, Na, P) as a function of the electronegativities

the atom linked to it, and this is manifested in the UV spectrum by a bathochromic shift. The silicon derivative and the two phosphorus derivatives do not fit into the sequence of electronegativity. Here, already an $-M$ effect asserts itself, and silicon and phosphorus attract the electron cloud. A d_π-p_π interaction is established, and instead of a system with seven centers, delocalisation will now involve eight atoms. Since phosphorus attracts electrons stronger than silicon, the $-M$ effect will manifest itself more strongly. Similarly, the electron attracting effect is stronger with P^{5+}, owing to the adjacent oxygen, than with compounds containing the P^{3+} atom.

Moreover, it becomes evident from data in Table 1 that the value of the absorption maximum, 273 nm, is the same in the series of methylphenoxysilanes, *i.e.* the position of the maximum is independent of the number of phenoxy groups. It may be assumed, therefore, as first approximation, that the conjugation between the silicon atom and the phenoxy groups does not involve all of the phenoxy groups, but these phenoxy groups form a conjugative bond with separate empty *d* orbitals, so that various phenoxysilanes consist of phenoxysilicon groups, practically independent from each other. Further, the following conclusions can be drawn from the UV spectral data: similar to the organic compounds, the absorption maxima of *ortho-* and *meta*-substituted organosilicon compounds containing identical groups are practically the same, while the *para*-substituted compounds exhibit a considerable shift. An examination of the effect of first order substituents shows that in the case of *para*-substituted compounds a bathochromic shift and a decrease in extinction value along the series $-CH_3$, $-F$, $-Cl$, $-Br$ is to be observed both with carbon and silicon compounds. *ortho*-Chloro derivatives, as compared to *ortho*-methyl derivatives, also show a bathochromic shift and a decrease in extinction values in both series. The effect of the second order $-NO_2$ group is manifested in both series by a hypsochromic shift in the direction *o*-, *m*-, *p*-. The different behaviour of *o*-nitroanisole may presumably be explained by steric effects. The comparison of the extinction values shows that *meta*-substituted compounds exhibit minimum values in both series, while *para*-nitro compounds show outstanding extinction values.

On comparing identically substituted members of the series of organic compounds and of the series of compounds containing silicon, the following observations can be made: unsubstituted phenoxymethylsilanes and the nitro compounds show a bathochromic shift, the other substituted phenoxysilanes show a hypsochromic shift, as compared to correspondingly substituted anisoles. Unsubstituted compounds show an increase, the other compounds a decrease in extinction value. For the explanation of these phenomena, the following approximative quantum chemical calculations were performed:

It is known from the literature[7] that the inductive effect of the substituent on the phenyl group changes primarily the coulomb integral of the carbon atom at the site of the linkage, and the changing of the extinction value is caused principally by the inductive effect. To study the effect of the silicon and the carbon atoms, approximative variational single-electron LCAO-MO calculations were made for the phenoxy group. Identical substituents in identical positions on the ring have been neglected, and the effect of the silicon and the carbon atom have been considered only by changing the coulomb integral of the carbon atom linked to oxygen. On the basis of our earlier work[3], the following coulomb and resonance integrals have been used:

$$\alpha_O = \alpha + 2.92\,\beta \qquad \beta_{CO} = 0.69\,\beta$$
$$\alpha_{C'} = \alpha + \delta \cdot \beta \qquad \beta_{CC'} = 0.93\,\beta$$
$$\alpha_C = \alpha \qquad \beta_{CC} = \beta$$

(The carbon atom marked by a (') is linked to the oxygen.) By the changing of the parameter δ, the transient dipole moment has been calculated. On the other hand, the oscillator strength can be determined from the following relationship:

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

where ν^* is the frequency of the UV maximum (this value is nearly identical with the compounds investigated), D is the transient dipole moment and G is the degree of degeneration (in our case 1).

It follows from the aforesaid that the transitional dipole moment is proportional to the oscillator strength, *i.e.* the intensity. Thus, the change in extinction value can be correlated with the transitional dipole moment. The relationship between the parameter δ and the transitional dipole moment has been plotted in Fig. 2.

Fig. 2 shows that an increase of the parameter δ in the region $\delta < -0.02$ results in a decrease of the transitional dipole moment, and is proportional to it, of the intensity, while in the region $\delta > 0$, higher D and ε values belong to a higher δ value. According to one of our earlier works[2], the partial charge of the carbon atom linked to the oxygen is larger in anisole than in trimethylphenoxysilane (0.0140 and 0.0118, respectively). Correspondingly, the coulomb integral (δ parameter) of the carbon atom is also larger in the carbon compound than in phenoxy silane. On the evidence of all these findings, the increase in the extinction value of unsubstituted phenoxysilanes, as compared to carbon compounds of the same composition, can be explained by the left side course of the curve, while the decrease in the extinction value of the substituted phenoxysilanes by the right side course of the curve. It should be mentioned that the effect of substituents has been neglected in these calculations, however, the symmetry of the π and π^* levels does not change with the increase in the number of atoms, the levels are only shifted. Therefore, in first approximation, the calculations used give qualitatively correct results.

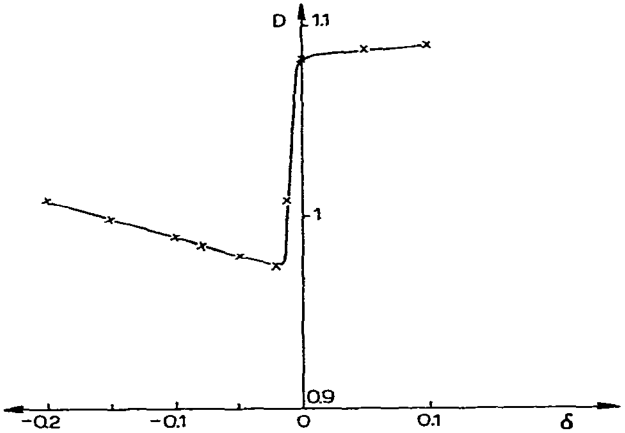

Fig. 2. The change of the transitional dipole moment as a function of the δ coulomb parameter.

The ν_s(Si–O) frequency values of the IR spectra of phenoxysilanes are listed in Table 3. For comparison, Table 3 also contains the corresponding data for trimethylmethoxysilane and trimethyl(benzyloxy)silane.

TABLE 3

IR SPECTRAL DATA OF PHENOXYSILANES

Phenoxysilane	ν_s(Si–O) (cm^{-1})
$C_6H_5OSi(CH_3)_3$[8]	925 vs
$(C_6H_5O)_2Si(CH_3)_2$[8]	940 vs
o-$C_6H_4[OSi(CH_3)_3]_2$[8]	938 vs
m-$C_6H_4[OSi(CH_3)_3]_2$[8]	998 s
p-$C_6H_4[OSi(CH_3)_3]_2$[8]	9320 s
$CH_3OSi(CH_3)_3$[9]	719
$C_6H_5CH_2OSi(CH_3)_3$[10]	870

The results show that the ν_s value of the Si–O–C bond varies between 940 and 925 cm^{-1} in the case of phenoxysilanes with the exception of the *meta* derivative. Moreover, it will be seen that the frequency values are higher than the frequency of the Si–O bond in trimethylmethoxysilane and in trimethyl(benzyloxy)silane. The increase in frequency can be attributed to the fact that in the phenoxysilanes the π-electrons of the oxygen atom participate in the delocalization extending to the Si–O–C_6H_5 system. The electronegativity of oxygen increases thereby, and this shifts ν_s(Si–O) towards higher frequencies.

TABLE 4

DIPOLE MOMENTS OF PHENOXYSILANES

Phenoxysilane	Temp. (°C)	μ (D) (Onsager)	μ (D) (Hedestrand)
$(C_6H_5O)_2Si$[8]	60	1.586	
$(C_6H_5O)_3SiCH_3$[8]	25	1.417	1.446
$(C_6H_5O)_2Si(CH_3)_2$[8]	0	1.212	
	15	1.246	
	25	1.278	1.216
	40	1.309	
	60	1.353	
	80	1.399	
$C_6H_5OSi(CH_3)_3$[8]	25	1.215	
o-$C_6H_4[OSi(CH_3)_3]_2$[8]	25	1.228	
	50	1.273	
m-$C_6H_4[OSi(CH_3)_3]_2$[8]	25	1.703	
	50	1.726	
p-$C_6H_4[OSi(CH_3)_3]_2$[8]	25		1.606

Dipole moments measured for the phenoxysilanes are listed in Table 4.

From the dipole moment values, the following conclusions have been drawn on the molecular structure and the steric arrangement of the phenoxysilanes. The trimethylphenoxysilane molecule was selected as basic compound. We assumed for this compound a full rotation, and selected an angle of 120° for the Si–O–C bonding angle with regard to oxygen in sp^2 hybrid state. Starting from these conditions, we determined the bond moment *m*(Si–O) of phenoxysilanes, using the following data:

$m(Si–CH_3) = 0.2$ D[11]

$m(C_6H_5–O) = 1.1067$ D[8] (determined from the dipole moment of diphenyl ether and from the bond angle)

$\mu[C_6H_5OSi(CH_3)_3] = 1.215$ D

$\angle$C–Si–O = 109°28′ (valence angle corresponding to the sp^3 hybrid state of silicon)

From these data, the bond moment *m*(Si–O) is 1.5002 D.

With the aid of the Si–O bond moment calculated, the free rotational dipole moments of the other phenoxysilanes have also been calculated. Calculated and experimental values are compared in Table 5.

It can be seen from data listed in Table 5 that the *p*-bis(trimethylsiloxy)benzene

TABLE 5

CALCULATED AND EXPERIMENTAL DIPOLE MOMENTS OF PHENOXYSILANES

Phenoxysilane	μ_{rot} (D)	μ_{exp} (D)	Difference (D)
$C_6H_5OSi(CH_3)_3$	1.215	1.215	0
$(C_6H_5O)_4Si$	1.917	1.586	0.331
$(C_6H_5O)_3SiCH_3$	1.820	1.417	0.403
$(C_6H_5O)_2Si(CH_3)_2$	1.607	1.278	0.329
o-$C_6H_4[OSi(CH_3)_3]_2$	1.772	1.228	0.544
m-$C_6H_4[OSi(CH_3)_3]_2$	1.663	1.703	0.040
p-$C_6H_4[OSi(CH_3)_3]_2$	1.592	1.606	0.014

molecule rotates freely, while the rotation of the other phenoxysilanes is hindered, as proved by the difference between the calculated and measured dipole moment values. Hindered rotation is proved also by the fact that the dipole moments of dimethyldiphenoxy silane, *o*- and *m*-bis(trimethylsiloxy)benzene are dependent on temperature. Our results further show that it was correct to assume free rotation for trimethylphenoxysilane, and select a bond angle of 120° for Si–O–C, since the *m*(Si–O) bond moment calculated with these values resulted in the further calculations of realistic data, corresponding to expectations.

With the object to study the molecular structure of phenoxysilanes, various quantum chemical calculations were also carried out, partly by the method of Hückel, and partly by the method of Pariser–Parr–Pople. Results of these calculations support the UV, IR and dipole moment data measured, and the conclusions drawn from them. For the silicon–oxygen bond the π-bond order of 0.3–0.4 has been calculated, which proves the d_π–p_π bond formed. Our quantum chemical calculations will be described in detail in a following publication.

REFERENCES

1 J. Nagy and P. Hencsei, *J. Organometal. Chem.*, 9 (1967) 57.
2 P. Hencsei and J. Nagy, *Period. Polytech., Chem. Eng. (Budapest)*, 13 (1969) 351.
3 J. Nagy, P. Hencsei, A. Borbély-Kuszman, and R. Farkas, *Period. Polytech., Chem., Eng. (Budapest)*, in print.
4 A. Burawoy and J. T. Chamberlain, *J. Chem. Soc.*, (1952) 2310.
5 H. H. Jaffé and M. Orchin, *Theory and applications of UV spectroscopy*, Wiley, New York, 1962.
6 J. Nagy, I. Barta and J. Réffy, *Period. Polytech., Chem. Eng. (Budapest)*, 11 (1967) 33.
7 W. W. Robertson and F. A. Matsen, *J. Amer. Chem. Soc.*, 72 (1950) 5252.
8 J. Nagy, P. Hencsei, S. Ferenczi-Gresz and T. Gábor, *Acta Chim. Acad. Sci. Hung.*, in print.
9 R. Forneris and E. Funck, *Z. Elektrochem.*, 62 (1958) 1130.
10 I. Földesi and F. Török, *Acta Chim. Acad. Sci. Hung.*, 53 (1967) 1.
11 A. P. Altshuler and R. Rosenblum, *J. Amer. Chem. Soc.*, 77 (1955) 272.