MEASUREMENT AND CALCULATION OF DIPOLE MOMENTS FOR PHENOXYSILANES

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Introduction

Few papers have been published on the experimental and calculated dipole moments of phenoxysilanes with composition $XC_6H_4OSi(CH_3)_3$. MAURET et al. have dealt with the dipole moments of phenoxysilanes in two papers [1, 2]. They gave the experimental values for derivatives X=H and X=4-Cl (1.21 and 1.24 D; 2.38 and 2.39 D) and explained the increase of the SiOC bond angle on the basis of vectorial calculations by the formation of $d\pi-p\pi$ bond. In our earlier paper [3] the experimental dipole moments and vectorial calculations using group moment values were presented for derivatives X=H, o-, m-, p-$(CH_3)_3SiO$. This work deals with the measurements and calculations of dipole moments for the following compounds: X=H, 2-, 3-, 4-CH_3, Cl, NO_2, $(CH_3)_3SiO$, 4-F.

Measurement of Dipole Moment

The dipole moments of the investigated compounds were determined by ONSAGER's [4] or by HEDESTRAND's [5] method, for three compounds the measurements were carried out by both methods.

According to Onsager's method the required data for the calculation of the dipole moment of the investigated compound (relative permittivity density and refractive index) were determined by measuring the pure compound. The dipole moment values will be given in Debye units (D) in this paper. The conversion into coulombmeter used in the SI system of units can be carried out by the following equation:

$$1D = \frac{1}{3} \cdot 10^{-29} Cm .$$

The formula for the calculation of dipole moment is:

$$\mu = \sqrt{\frac{9kT}{4\pi N}} \cdot \sqrt{P^*}$$

The expression $\sqrt{\frac{9kT}{4\pi N}}$ is constant at a given temperature, its value at 25 °C is 0.22123. Since our measurements were performed at this temperature $\mu = 0.22123 \sqrt{P^*}$ and

$$P^* = (\varepsilon_0 - \varepsilon_{\mathrm{eff}}) \cdot V \cdot \frac{2\varepsilon_0 + \varepsilon_{\mathrm{eff}}}{\varepsilon_0(\varepsilon_{\mathrm{eff}} + 2)^2}$$

where ε_0 is the measured, relative permittivity of the compound,

$V = \frac{M}{d}$ is the molar volume of the compound

$$\varepsilon_{\mathrm{eff}} = \frac{2R + V}{V - R} \, .$$

In latter formula $R = P_A + P_e$, the sum of atompolarization and electron polarization, assumed to be $1.05\ MR_D$.

The measured date are summarized in Table 1.

Table 1

Dipole moments of phenoxysilanes with formula $XC_6H_4OSi(CH_3)_3$, determined by Onsager's method and the measured and calculated quantities required for the calculation ($t = 25$ °C)

X	n_D^{25}	d_4^{25} (gcm^{-3})	ε	$\varepsilon_{\mathrm{eff}}$	μ(D)
H	1.4753	0.9192	3.395	2.260	1.22
2-CH_3	1.4769	0.9158	3.219	2.265	1.17
3-CH_3	1.4767	0.9124	3.209	2.265	1.17
4-Cl	1.4927	1.0416	6.169	2.316	2.15
2-$(CH_3)_3SiO$					1.23 [3]
3-$(CH_3)_3SiO$					1.70 [3]

According to Hedestrand, the total polarization belonging to infinite dilution can be determined from data measured in diluted solutions of compounds:

$$P_\infty = \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\left(\frac{M_2}{d_1} - \frac{M_1}{d_1^2}\beta\right) + \frac{3M_1\alpha}{(\varepsilon_1 + 2)^2 d_1}$$

where M_1 and M_2 are the molecular mass of the solvent and the soluted, respectively,

d_1 is the density extrapolated to infinite dilution,

ε_1 is the relative permittivity extrapolated to infinite dilution,

Table 2

Dipole moments of phenoxysilanes with formula $XC_6H_4OSi(CH_3)_3$, determined by Hedestrand's method and the measured and calculated quantities required for the calculation ($t = 25$ °C)

X	x_2	$\varepsilon_{1,2}$	$d_{1,2}$ (gcm^{-3})		μ(D)
2-CH_3	0.00840	2.025	0.7768	$\varepsilon_1 = 2.008$	1.19
	0.01135	2.028	0.7783	$d_1 = 0.7750$	
	0.02511	2.051	0.7805	$\alpha = 1.7694$	
	0.04545	2.086	—	$\beta = 0.2051$	
3-CH_3	0.00239	2.015	0.7759	$\varepsilon_1 = 2.011$	1.15
	0.01132	—	0.7767	$d_1 = 0.7741$	
	0.01109	2.032	—	$\alpha = 1.7647$	
	0.02254	—	0.7794	$\beta = 0.2535$	
	0.02280	2.052	—		
	0.03371	—	0.7828		
	0.03355	2.070	—		
	0.04470	—	0.7853		
	0.04430	2.090	—		
4-CH_3	0.00231	2.022	0.7746	$\varepsilon_1 = 2.008$	1.24
	0.01143	2.021	0.7767	$d_1 = 0.7744$	
	0.03353	2.086	0.7818	$\alpha = 1.9230$	
	0.05542	2.111	0.7862	$\beta = 0.2142$	
	0.07856	2.149	0.7911		
2-Cl	0.00922	2.051	—	$\varepsilon_1 = 2.017$	1.92
	0.00534	—	0.7765	$d_1 = 0.7742$	
	0.01429	2.075	—	$\alpha = 4.1660$	
	0.00562	—	0.7761	$\beta = 0.4440$	
	0.02004	2.110	—		
	0.01022	—	0.7790		
	0.02677	2.131	—		
	0.02876	—	0.7867		
	0.03140	2.146	—		
	0.03414	—	0.7891		
3-Cl	0.00804	—	0.7778	$\varepsilon_1 = 2.022$	2.20
	0.01014	2.076	—	$d_1 = 0.7735$	
	0.01415	2.098	0.7799	$\alpha = 5.3748$	
	0.02482	—	0.7851	$\beta = 0.4668$	
	0.02592	2.161	—		
	0.02844	2.174	0.7868		

Table 2 cont.

X	x_2	$\varepsilon_{1,2}$	$d_{1,2}$ (gcm^{-3})		μ(D)
4-Cl	0.00948	2.075	0.7776	$\varepsilon_1 = 2.018$	2.38
	0.01682	2.119	0.7807	$d_1 = 0.7744$	
	0.02513	2.154	0.7837	$\alpha = 6.1290$	
	0.03682	2.243	0.7900	$\beta = 0.4166$	
	0.04714	2.312	0.7937		
2-NO_2	0.00597	2.114	0.7778	$\varepsilon_1 = 2.005$	4.10
	0.00991	2.181	0.7802	$d_1 = 0.7736$	
	0.01347	2.211	0.7829	$\alpha = 17.647$	
	0.01531	2.283	—	$\beta = 0.6533$	
	0.01759	2.334	0.7850		
3-NO_2	0.00553	2.129	0.7758	$\varepsilon_1 = 2.013$	4.50
	0.00989	2.228	0.7782	$d_1 = 0.7724$	
	0.01084	2.248	0.7791	$\alpha = 21.052$	
	0.01432	2.318	0.7814	$\beta = 0.6226$	
	0.01748	2.379	0.7832		
4-NO_2	0.00597	2.173	0.7784	$\varepsilon_1 = 2.026$	4.86
	0.01014	2.253	0.7805	$d_1 = 0.7744$	
	0.01375	2.367	0.7828	$\alpha = 24.687$	
	0.01763	2.460	0.7846	$\beta = 0.6060$	
	0.01765	—	0.7854		
4-F	0.00161	2.028	0.7735	$\varepsilon_1 = 2.021$	2.14
	0.00449	2.042	0.7748	$d_1 = 0.7732$	
	0.00641	2.051	0.7753	$\alpha = 4.810$	
	0.00739	2.056	0.7752	$\beta = 0.313$	
	0.01378	2.087	0.7775		
4-$(CH_3)_3SiO$					1.61 [3]

α and β are the slopes of straight lines ε/x_2 and d/x_2, respectively, x_2 is the molar fraction of the solute.

In the knowledge of the total polarization, the dipole moment can be calculated by the following equation:

$$\mu = 0.22123 \sqrt{P_\infty - R},$$

where $R = P_A + P_e$, approximately taken as 1.05 MR_D.

Our measurements were carried out at 25 °C in solutions of the compounds, using cyclohexane as solvent.

Table 2 contains the measured and calculated data.

$\varepsilon_{1,2}$ and $d_{1,2}$ in Table 2 are the relative permittivities and densities of the solutions, respectively.

Calculation on the Basis of Group Moments

The dipole moment of molecules can be calculated by the vectorial summation of the group moments of substituents. This method is based on the approximation that the group moment of identical groups of atoms is identical in different compounds. As far as the aromatic compounds are concerned, the experimental dipole moment of the monosubstituted benzene derivatives were chosen as group moment values. If a molecule contains two freely rotating polar groups with given group moments, the resultant dipole moment according to FUCHS and TIGANIK [6, 7] is the following:

$$\mu = (\mu_1^2 + \mu_2^2 + 2\mu_1 \mu_2 \cos \theta_1 \cos \theta_2 \cos \omega)^{1/2}$$

where μ_1 and μ_2 are the group moments of the polar groups,

θ_1 and θ_2 are the angles between the direction of the rotation axes and the group moment vectors,

ω is the angle between the two rotational axes, its value is 60° for ortho substitution, 120° for meta substitution and 180° for para substitution (Fig. 1).

Values of μ_2 and θ_2 characteristic of the particular substituents were taken from the literature [8] and are summarized in Table 3. θ_1 value of the $(CH_3)_3SiO$ group was calculated from the experimental dipole moments. The

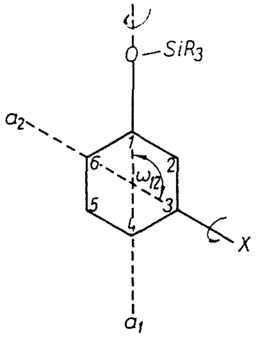

Fig. 1. Calculation of dipole moment from group moments

above mentioned equation was applied for p-bis-(trimethylsiloxy)-benzene assuming the free rotation of the $(CH_3)_3SiO$ groups and 69° was obtained for θ_1 [3].

Table 3

Values of group moments

$X-(C_6H_5)$	$\mu_1(D)$	θ_1	$\mu_2(D)$	θ_2
$(CH_3)_3SiO$	1.22	69°	—	—
CH_3			0.37	0
Cl			−1.59	0
NO_2			−4.01	0
F			−1.47	0

Quantumchemical Calculations

Del Re and iterative PPP methods were used for the calculation of the charge distribution of the investigated compounds. The applied equations and the parameters of the calculations were described in our previous paper [9]. The geometry data of the calculations were chosen on the basis of electron diffraction measurements of $C_6H_5OSiH_3$ [10]: R_{Si-O}: 164.8 pm, $R_{C-O} = 135.7$ pm, SiOC bond angle = 121°. The calculation of the π systems was carried out on planar models, in the case of the ortho and meta substitution the silicon atom was in trans position. For the C_2 and C_6 as well as for the C_3 and C_5 carbon atoms of the para substituted compounds, the mean values of the corresponding calculated partial charges were taken. The reason of averaging the charges mentioned was that the same results (charge distribution, dipole moment, electronic transitions) were provided in the calculations with planar model and with the silicon atom in perpendicular position, respectively. The partial charges σ and π obtained in the calculations are summarized in Table 4.

The dipole moments of molecules can be calculated from the partial charges given by the quantumchemical calculations. In the calculations it was assumed that the $(CH_3)_3SiO$ group could freely rotate along the $C_{ar}-O$ axis, the rest of the molecules was fixed and characterized by a constant vector. The average value of the dipole moment for a freely rotating molecule was calculated by integration from the summation of the constant and rotating vector:

$$\bar{\mu}^2 = \frac{1}{2\pi}\int_0^{2\pi} [(a \cos \alpha \cos \varphi - x)^2 + (a \sin \alpha - y)^2 + (a \cos \alpha \sin \varphi)^2]\, d\varphi .$$

Table 4

Partial charges σ and π of phenoxysilanes $XC_6H_4OSi(CH_3)_3$

X=H	σ	π
Si	.4193	-.1234
O	-.4283	.2191
C_1	.0711	-.0369
C_2	-.0204	-.0270
C_3	-.0389	.0017
C_4	-.0405	-.0082
C_{Si}	-.0834	—
$H(C_{Si})$	.0155	—
H_2	.0424	—
H_3	.0410	—
H_4	.0409	—

X=2-Cl	σ	π
Si	.4200	-.1243
O	-.4239	.2188
C_1	.1072	-.0488
C_2	.0858	-.0412
C_3	.0003	-.0124
C_4	-.0369	-.0048
C_5	-.0381	.0006
C_6	-.0162	-.0221
Cl	-.1565	.0342
C_{Si}	-.0834	—
$H(C_{Si})$	.0155	—
H_3	.0440	—
H_4	.0412	—
H_5	.0411	—
H_6	.0427	—

X=3-NO_2	σ	π
Si	.4193	-.1158
O	-.4280	.2199
C_1	.0727	-.0261
C_2	-.0137	-.0088
C_3	.1011	-.0543
C_4	-.0309	-.0109
C_5	-.0379	.0148
C_6	-.0200	-.0062
N	-.0850	.5464
O_N	-.0180	-.2904
C_{Si}	-.0834	—
$H(C_{Si})$	.0155	—
H_2	.0439	—
H_4	.0417	—
H_5	.0411	—
H_6	.0424	—

X=2-CH_3	σ	π
Si	.4194	-.1237
O	-.4274	.2189
C_1	.0774	-.0400
C_2	-.0400	-.0226
C_3	-.0320	-.0023
C_4	-.0396	-.0077
C_5	-.0389	.0019
C_6	-.0194	-.0245
C_{Si}	-.0834	—
$H(C_{Si})$	.0155	—
C_{Me}	-.0171	—
$H(C_{Me})$	.0208	—
H_3	.0416	—
H_4	.0409	—
H_5	.0410	—
H_6	.0424	—

X=3-Cl	σ	π
Si	.4193	-.1235
O	-.4278	.2198
C_1	.0774	-.0340
C_2	.0188	-.0434
C_3	.0686	-.0119
C_4	-.0016	-.0220
C_5	-.0351	.0054
C_6	-.0198	-.0271
Cl	-.1590	.0367
C_{Si}	-.0834	—
$H(C_{Si})$	.0155	—
H_2	.0453	—
H_4	.0438	—
H_5	.0413	—
H_6	.0425	—

X=4-NO_2	σ	π
Si	.4193	-.1126
O	-.4282	.2222
C_1	.0712	-.0175
C_2	-.0180	-.0164
C_3	-.0155	.0159
C_4	.0503	-.0501
N	-.0723	.5426
O_N	-.0165	-.2918
C_{Si}	-.0834	—
$H(C_{Si})$	.0155	—
H_2	.0425	—
H_3	.0427	—

X=3-CH_3	σ	π
Si	.4193	-.1235
O	-.4282	.2193
C_1	.0716	-.0363
C_2	-.0133	-.0326
C_3	-.0575	.0074
C_4	-.0334	-.0117
C_5	-.0384	.0030
C_6	-.0202	-.0256
C_{Si}	-.0834	—
$H(C_{Si})$	.0155	—
C_{Me}	-.0191	—
$H(C_{Me})$	.0207	—
H_2	.0429	—
H_4	.0414	—
H_5	.0411	—
H_6	.0424	—

X=4-Cl	σ	π
Si	.4193	-.1248
O	-.4282	.2193
C_1	.0716	-.0388
C_2	-.0166	-.0236
C_3	.0	-.0118
C_4	.0672	-.0209
Cl	-.1592	.0360
C_{Si}	-.0834	—
$H(C_{Si})$	.0155	—
H_2	.0427	—
H_3	.0439	—

X=2-$OSi(CH_3)_3$	σ	π
Si	.4196	-.1268
O	-.4259	.2171
C_1	.0901	-.0624
C_3	-.0182	-0.233
C_4	-.0386	-.0046
C_{Si}	-.0834	—
$H(C_{Si})$	.0155	—
H_3	.0426	—
H_4	.0411	—

X=4-$OSi(CH_3)_3$	σ	π
Si	.4193	-.1277
O	-.4282	.2208
C_1	.0714	-.0443
C_2	-.0184	-.0244
C_{Si}	-.0834	—
$H(C_{Si})$	.0155	—
H_2	.0425	—

X=4-CH_3	σ	π
Si	.4193	-.1237
O	-.4282	.2192
C_1	.0710	-.0374
C_2	-.0197	-.0264
C_3	-.0318	-.0017
C_4	-.0590	-.0020
C_{Si}	-.0834	—
$H(C_{Si})$	.0155	—
C_{Me}	-.0193	—
$H(C_{Me})$	.0207	—
H_2	.0424	—
H_3	.0415	

X=2-NO_2	σ	π
Si	.4196	-.1098
O	-.4261	.2266
C_1	.0900	-.0214
C_2	.0807	-.0727
C_3	-.0188	.0164
C_4	-.0387	.0040
C_5	-.0384	.0227
C_6	-.0182	-.0144
N	-.0734	.5424
O_N	-.0166	-.2969
C_{Si}	-.0834	—
$H(C_{Si})$	.0155	—
H_3	.0426	—
H_4	.0411	—
H_5	.0410	—
H_6	.0425	—

X=3-$OSi(CH_3)_3$	σ	π
Si	.4193	-.1250
O	-.4280	.2208
C_1	.0727	-.0359
C_2	.0003	-.0604
C_4	-.0199	-.0321
C_5	-.0370	.0048
C_{Si}	-.0834	—
$H(C_{Si})$	.0155	—
H_2	.0439	—
H_4	.0424	—
H_5	.0412	—

X=4-F	σ	π
Si	.4193	-.1226
O	-.4282	.2197
C_1	.0714	-.0336
C_2	-.0177	-.0235
C_3	-.0116	.0017
C_4	.1609	-.0473
F	-.2253	.0274
C_{Si}	-.0834	—
$H(C_{Si})$	.0155	—
H_2	.0426	—
H_3	.0430	—

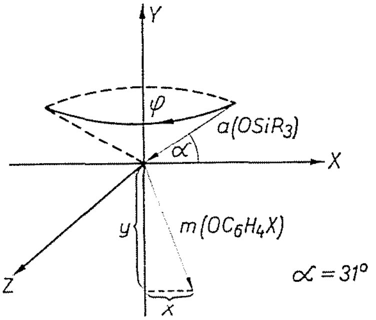

Fig. 2. Calculation of dipole moment from charge distribution, assuming free rotation

The positions of the vectors are illustrated in Fig. 2. In the calculations, the charge distribution of the molecules was regard as constant during rotation.

The dipole moments of phenoxysilanes, calculated on the basis of group moments and from the charge distributions are summarized in Table 5.

Table 5

Dipole moments of phenoxysilanes ($XC_6H_4OSi(CH_3)_3$) calculated from group moments μ_m and charge distribution μ_δ [in Debye units]

X	μ_m	μ_δ
H	—	1.089
2-CH_3	1.332	1.123
3-CH_3	1.206	1.074
4-CH_3	1.137	1.051
2-Cl	2.166	1.767
3-Cl	1.822	2.017
4-Cl	2.319	2.098
2-NO_2	3.978	3.990
3-NO_2	4.392	4.253
4-NO_2	4.585	4.611
4-F	2.215	2.414
2-$(CH_3)_3SiO$	1.772	1.503
3-$(CH_3)_3SiO$	1.663	1.477
4-$(CH_3)_3SiIO$	1.606	1.431

Discussion

In Fig. 3 the dipole moments calculated on the basis of group moments are shown as a function of the experimental dipole moments. A linear regression line is drawn in the figure, the regression coefficient is 0.986. In Fig. 4

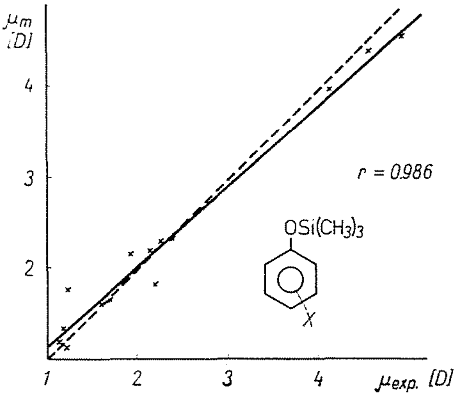

Fig. 3. Dipole moments of phenoxysilanes calculated from group moments vs. experimental values

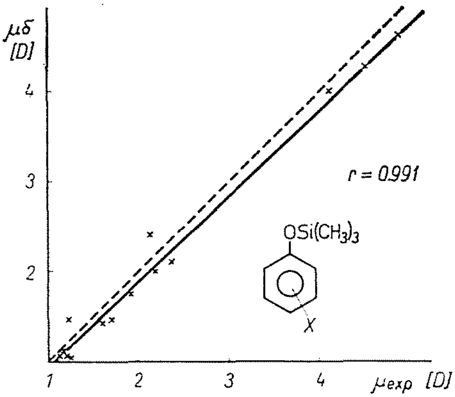

Fig. 4. Dipole moments of phenoxysilanes calculated from charge distribution vs. ex per mental values

the connection between the dipole moments calculated from the charge distributions and the experimental dipole moments is illustrated, regression coefficient $r = 0.991$.

The agreement between the experimental and the calculated dipole moment is good in both cases: the standard deviation is 0.156 D (8.61%) in the first case and 0.188 D (9.88%) in the second case. Prominent difference between the calculated and measured values is observed only for one compound: for the ortho-bis(trimethylsiloxy)-benzene. This significant deviation can be explained by the hindered rotation structure of the compound. The good agreement in other cases shows that in the series of phenoxysilanes the group moment of the same substituents is nearly identical for substitutions in different positions and the effect of the substituents on the π systems of the molecules is not significant. The effect of the nitro group is more marked, specially in the case of para substitution. The good agreement of the dipole moments calculated from the charge distribution with the experimental values proves the free rotation structures of the compounds with the exception of the above mentioned ortho-bis-(trimethylsiloxy)-benzene. The greater deviation observed for the para-fluoro derivative can be explained by the enhanced effect of the fluor atom on the charge distribution.

At the same time the good agreement between experimental and calculated data proves the applied quantumchemical methods, parameters and geometrical data to be adequate and the choice of planar model to be reasonable.

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Summary

In this paper the experimental and calculated dipole moments of phenoxysilanes with formula $XC_6H_4OSi(CH_3)_3$ (X = H, 2-, 3-, 4-CH_3, Cl, NO_2, $(CH_3)_3SiO$, 4-F) are given. The measurements of dipole moments were carried out at 25 °C in liquid state by ONSAGER's method and in cyclohexane solutions by HEDESTRAND's method. The calculated values were determined on the basis of the group moment method and from the charge distribution provided by Del Re and IPPP methods. Based on the good agreement between experimental and calculated data, the $(CH_3)_3SiO$ groups were found to freely rotate along the $C_{ar}-O$ axis in phenoxysilanes (with the exception of the ortho-bis-(trimethylsiloxy)-benzene).

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