DETERMINATION OF DIPOLE MOMENTS OF SILATRANES

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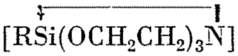
Introduction

The first paper related to the dipole moments of silatranes



$$[RSi(OCH_2CH_2)_3N]$$

was published in 1965 [1]. Since that time only a few papers have dealt with the dipole moment of these type of compounds, which can be explained by the rather poor solubility of the silatranes in solvent generally used for dipole moment measurements. In this work informations on the dipole moment determination of five different silatrane compounds are given.

Experimental

The compounds were prepared by reesterification reactions known from the literature [2]. The products were purified by recrystalization. The most important data for the preparation of silatranes are summarized in Table 1

Table 1

Data of preparation of silatranes $RSi(OCH_2CH_2)_3N$

R	Reagent	Solvent	Catalyst	Exp. m.p.(°C)	M.p. from lit [2] (°C)
C_6H_5	$C_6H_5Si(OC_2H_5)_3$	toluene	KOH	203 – 205	210,3 – 211,3
CH_3	$CH_3Si(OC_2H_5)_3$	benzene	KOH	140 – 142	142 – 143
C_2H_5O	$Si(OC_2H_5)_4$	xylene	KOH	100.4	102 – 103
C_6H_5O	$Si(OC_2H_5)_4 + C_6H_5OH$	xylene	—	224 – 225	228 – 229.5
$p\text{-}ClC_6H_4O$	$Si(OC_2H_5)_4 + p\text{-}ClC_6H_4OH$	xylene	—	164	166 – 167
$p\text{-}NO_2C_6H_4O$	$Si(OC_2H_5)_4 + p\text{-}NO_2C_6H_4OH$	xylene	—	175 – 178	182.5 – 184

Experiments on dipole moment determination of silatranes were carried by Voronkov and al. Their measurements were carried out at 25 °C mostly in benzene solutions and in some cases in chloroform and ethylacetate. The dipole moment was calculated from the measured data by HEDESTRAND method [3], the sum of atompolarization and electronpolarization was taken as 1,15 times the experimental molar refraction (MR_D). The experimental dipole moments of silatranes available from the literature are summarized in Tables 2 and 3 (1 Debye = $3.33563 \cdot 10^{-30}$ Cm).

Table 2

Experimental dipole moments of silatranes (in Debye)

R	In benzene	In chloroform [4]	In ethylacetate [4]
CH_3	5.30 [1]	7.57	5.65
	5.46 [5]		
C_6H_5	5.98 [1]	7.53	
$CH_2{=}CH$	5.88 [1]	7.39	6.04
C_2H_5O	6.29 [1]	8.31	
C_6H_5O	7.13 [1]	9.23	7.00
$(CH_3)_2CH$	5.55 [1]	—	
C_2H_5		7.07	
H		9.01	
$3\text{-}CH_3C_6H_4O$		9.02	
$3\text{-}NO_2C_6H_4O$		11.46	9.72
$4\text{-}ClC_6H_4O$		10.09	
$4\text{-}(CH_3)_3CC_6H_4O$		8.63	
$5\text{-}CH_3\text{-}2\text{-}(CH_3)_2CHC_6H_3O$		8.35	
$(CH_2)_4NCH_2$	5.40 [6]		
$(CH_2)_5NCH_2$	5.56 [6]		
$(CH_2)_6NCH_2$	5.62 [6]		
$(CH_2)_4N(CH_2)_3$	5.23 [6]		
$(CH_2)_5N(CH_2)_3$	5.28 [6]		
$(CH_2)_6N(CH_2)_3$	5.08 [6]		
$Cl(CH_2)_3$	6.99 [7]		
$Br(CH_2)_3$	6.91 [7]		
$I(CH_2)_3$	6.99 [7]		
$C_2H_5SCH_2$	5.83 [7]		
$C_2H_5SCH_2CH_2$	6.86 [8]		

We determined the dipole moment of silatranes under the following conditions. Series of solutions were made from the investigated compounds. The relative permittivity of solutions was determined by a WTW Dipolmeter DM 01 instrument, the measurement of density was carried out in dilatometers, the refractive index was measured with Abbe refractometer. The dipole moment was calculated from the measured data by HEDESTRAND method, the experimental molar refraction values multiplied by 1,10 were considered as the sum of atompolarization and electronpolarization. For three compounds (R = CH_3, C_6H_5O, p-ClC_6H_4O) the dipole moment was determined in various temperatures between 20 and 70 °C, in the case of two compounds (R = C_6H_5, C_2H_5O), measurement were carried out only at 25 °C. The dipole of p-nitrophenoxysilatrane could not be measured because of its extremely poor solubility.

Table 3

Experimental dipole moments of silatranes substituted in ring (in Debye)

R	3	7	10	μ(D)	Lit.
Cl_2CH	CH_3	H	H	7.50	[5]
Cl_2CH	CH_3	CH_3	H	7.93	[5]
Cl_2CH	CH_3	CH_3	CH_3	8.19	[5]
CH_3CHCl	CH_3	H	H	5.95	[5]
CH_3CHCl	CH_3	CH_3	H	6.47	[5]
CH_3CHCl	CH_3	CH_3	CH_3	6.69	[5]
ICH_2	CH_3	CH_3	CH_3	6.77	[5]
C_6H_5	CH_3	CH_3	H	6.03	[8]
CH_3	CH_3	CH_3	CH_3	4.92	[7]
$C_2H_5SCH_2$	CH_3	CH_3	CH_3	5.23	[7]
$C_2H_5SCH_2CH_2$	CH_3	CH_3	CH_3	6.31	[7]

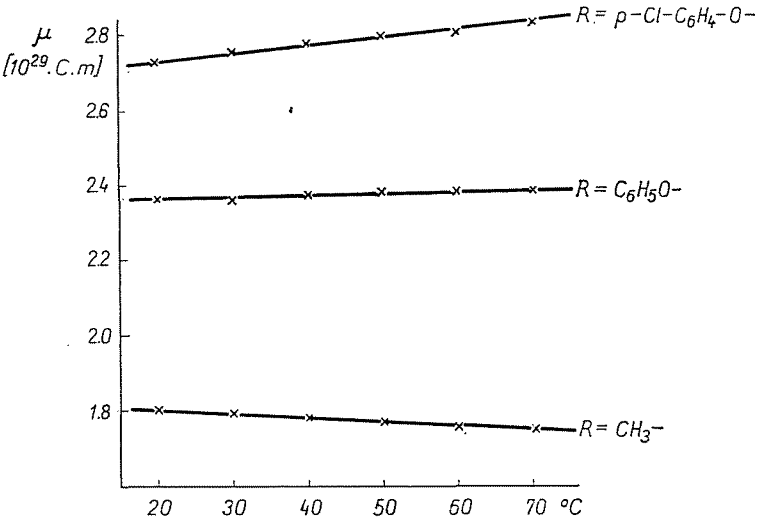


Fig. 1. Change of dipole moments for silatranes as a function of temperature

For the solutions of a given compound with various concentrations, the change of relative permittivity and density in the function of temperature was calculated by a parabolic relation: $y(t) = a + b \cdot t + c \cdot t^2$. In Tables 4 and 5 the measured data and calculated values required for the determination of the dipole moments of the investigated compounds are presented. Table 6 contains the experimental dipole moment of silatranes. The designations in

Table 4

Dipole moments of silatranes and the measured and calculated data necessary for the calculations ($t = 25$ °C)

R	$10^3 \cdot x$	$d(gcm^{-3})$	ε	n_D	
C_6H_5	0.1002	0.87432	2.2785	1.49822	$MR_D = 62.93$ cm^3
	0.5764	0.87470	—	—	$\mu = 1.92 \cdot 10^{-29}$ Cm
	0.7723	0.87490	2.3088	1.49858	
	1.5829	0.87564	2.3500	1.49905	
	2.2490	0.87630	2.3799	1.49950	
C_2H_5O	1.259	0.87701	2.3359	1.49771	$MR_D = 47.84$ cm^3
	2.474	0.87790	2.3953	1.49770	$\mu = 1.96 \cdot 10^{-29}$ Cm
	4.969	0.88005	2.5126	1.49765	
	6.593	0.88138	2.5916	1.49763	

Table 5

The measured and calculated data necessary for the calculations of dipole moments of silatranes

$10^3 \cdot x$	Relative permittivity			Density			n_D^{25}
	$a \cdot 10^6$	$b \cdot 10^3$	c	$a \cdot 10^5$	$b \cdot 10^3$	c	
$R = CH_3$ $MR_D = 48.60$ cm^3							
1.2623	0.54	−2.326	2.3818	0.19	−1.118	0.9054	1.50127*
2.9776	2.83	−2.895	2.4644	−0.52	−1.039	0.9046	1.50124*
4.7045	3.50	−2.335	2.5457	−0.40	−1.047	0.9057	1.50117*
4.8285	2.30	−2.250	2.5487	0.31	−1.098	0.9061	1.50116*
$R = C_6H_5O$ $MR_D = 65.69$ cm^3							
0.0000	0.82	−2.053	2.3242	−0.96	−1.000	0.8984	1.49766
0.3261	0.54	−2.139	2.3503	0.30	−1.076	0.9009	1.49770
0.6800	−0.41	−2.186	2.3774	−0.98	−0.963	0.8990	1.49778
0.9125	0.55	−2.304	2.3964	−0.79	−0.984	0.8999	1.49783
1.0007	1.23	−2.402	2.4029	0.62	−1.100	0.9019	1.49789
$R = p\text{-}ClC_6H_4O$ $MR_D = 68.24$ cm^3							
0.3186	0.38	−2.198	2.3614	−0.51	−1.011	0.8999	1.49776
0.5804	0.56	−2.311	2.3899	−0.24	−1.049	0.9013	1.49777
1.1669	−0.59	−2.426	2.4489	−0.68	−1.000	0.9010	1.49793
1.5764	1.15	−2.665	2.4901	−0.35	−1.016	0.9014	1.49795
1.9369	—	—	—	−0.33	−1.027	0.9024	1.49799

* at 19.2 °C

the tables are the following: x: molar fraction, d: density, ε: relative permittivity, n_D: refractive index, MR_D: molar refraction, μ: dipole moment. In Fig. 1 the change of dipole moments are plotted against the temperature.

Table 6

Experimental dipole moments of silatranes $\mathrm{R\overset{\downarrow}{Si}(OCH_2CH_2)_3N}$ in various temperatures (in 10^{29} Cm)

t (°C)	$R{=}CH_3$	C_6H_5O	p-ClC_6H_4O	C_6H_5	C_2H_5O
20	1.80	2.36	2.72		
25	1.80	2.36	2.73	1.92	1.96
30	1.79	2.36	2.75		
40	1.78	2.37	2.77		
50	1.77	2.38	2.79		
60	1.76	2.38	2.80		
70	1.75	2.38	2.82		

Discussion

The dipole moment values determined by us show good agreement with the data of measurement carried out by other researchers also in benzene solutions [1, 5].

The dipole moment of p-chlorophenoxysilatrane earlier was reported [4] based on measurements in chloroform, and this value is larger by about 2 Debye than our results obtained from benzene solutions. The difference is nearly the same as observed in the cases of other silatranes (Table 2).

Considering the dipole moment values, it was found that their change showed similar trend than the increase in the electron withdrawing effect of substituent R ($CH_3 < C_6H_5 < C_2H_5O < C_6H_5O <$ p-ClC_6H_4O). As it is known, the large dipole moment of silatranes can be explained by the formation of Si ← N dative bond.

Figure 1 illustrates the dipole moments of 3 compounds in the function of temperature in a range between 20 and 70 °C. In the case of methylsilatrane the dipole moment decreases in a small degree with the rise of temperature, an increase can be observed in the dipole moment of p-chlorophenoxysilatrane, and the dipole moment of phenoxysilatrane is nearly constant with the rising temperature. On the basis of the results it can be assumed that in the case of the methyl derivative the rise of temperature is accompanied by the increase of the Si ← N bond length, but the effect of the diminution of partial charges is of larger extent. On the other hand, in p-chlorophenoxysilatrane the bond distance is likely shorter (the partial charge is larger) than in methylsilatrane, and the increase of bond distance following the rise of temperature still does not cause the lowering of partial charges in a degree to result in the decrease of the dipole moment. In the case of the phenoxy derivative the effect two opposite effects compensate each other.

We intend to determine the structure of the investigated compounds by X-ray diffraction and in the knowledge of the experimental geometrical data dipole moment calculations will be carried out by the use of bond moments and group moments.

Summary

We have dealt with the determination of experimental dipole moments of silatranes with general formula $\mathrm{R}\,\overline{\overset{\downarrow}{\mathrm{Si}}\,(\mathrm{OCH_2CH_2})_3\mathrm{N}}$. For three compounds ($R{=}CH_3$, C_6H_5O, p-ClC_6H_4O) our measurements in benzene solutions were carried out in various temperatures between 20 and 70 °C, in the case of two compounds ($R{=}C_6H_5$, C_2H_5O) the dipole moments were determined at 25 °C. In all cases Hedestrand method was used. The change of the experimental values was explained on the basis of some considerations on the bond structure of the investigated compounds.

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