

## DIPOLE MOMENTS OF THE ALCOHOLS $(\text{CH}_3)_3\text{M}(\text{CH}_2)_n\text{OH}$ (M = C, Si, Ge; $n = 1-4$ )\*

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Dipole moments of *t*-butyl, trimethylsilyl-, and trimethylgermyl-substituted alcohols were measured in the concentration range  $w \in \langle 0; 0.003 \rangle$  in cyclohexane and benzene solutions. The measurements in cyclohexane confirmed the similarity in the behaviour of silicon and germanium compounds and their difference from carbon analogues. The measurements in benzene solutions revealed a different character of the interaction of alcohols with the solvent. A statistical analysis of the measurement of dipole moment of  $\delta$ -trimethylgermyl-substituted butanol was made; the standard deviation of the dipole moment,  $S_{\mu}$ , was found to be 0.038 D.

Within the framework of a broader study of the preparation<sup>1,2</sup> and reactivity<sup>3,4</sup> of trimethylsilyl- and trimethylgermyl-substituted alcohols and their carbon analogues, we studied by <sup>1</sup>H NMR spectroscopy also their association in tetrachloromethane<sup>5</sup>. In continuation of this study in the present work we measured dipole moments of the above-mentioned alcohols.

Different values of dipole moments of the alcohols obtained by different authors for varying concentration ranges and solvents are due to the self-association and solvation of alcohols. Both phenomena are complicated by a number of factors, the quantitative calculation of which has not yet been satisfactorily solved. In order to suppress self-association, in the present work we measured dipole moments of these compounds in nonpolar solvents, using the concentration range as broad as possible.

### EXPERIMENTAL

*Alcohols studied* are summarised in Table I, along with their association equilibrium constants for dimerisation  $(K_2)_x$  in cyclohexane<sup>5</sup>. Their preparation, purification and physical properties were reported elsewhere<sup>1-3</sup>.

*Solvents.* Cyclohexane (analytical purity grade, Lachema, Brno) was fractionally distilled over

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sodium. A fraction boiling at  $80.5 \pm 0.25^\circ\text{C}$  was stored over a dried Nalsit 4 molecular sieve. Benzene (UV grade, Lachema, Brno) was purified in the same way. A fraction boiling at  $80 \pm 0.25^\circ\text{C}$  was collected and stored over the above molecular sieve. Both solvents contained less than  $3/\text{cm}^3$  of water.

*Preparation of samples.* Volumetric solutions were prepared by weighing individual components in air. Specific volumes of the solutions were measured with Ostwald pycnometer (c.  $5 \text{ cm}^3$ ) and calibrated with water at  $25^\circ\text{C}$ . Its volume was determined with the standard deviation of  $8 \cdot 10^{-5} \text{ cm}^3$ .

*Measurements of dielectric constants (relative permittivities) of solutions.* The apparatus used was the so-called dip-meter, also known as grid-dip oscillator<sup>6</sup>. Dielectric capacitor (c.  $24 \text{ cm}^3$ ) was thermostated at  $25^\circ\text{C}$  for 10 min. For each compound 8–12 solutions were measured. The dielectric constant of the solvent was measured twice, as the first and the last of the dipole moment measurements of each alcohol, in order to verify the accuracy of its determination. The difference between these two measurements did not exceed  $1.5 \cdot 10^{-4}$ . Both values were found by statistical test as undistinguishable on the 0.05 level of significance, so that the results can be regarded reproducible. This finding further indicates that no phenomena which would bring about a systematic error occurred during the measurements.

*Treatment of data.* With regard to the errors of the dipole moment determination arising from self-association of alcohols and with respect to the sensitivity of the instrument employed, the optimum range of the mass fraction for this apparatus was found to be  $w = 0-0.0025$ . Molar polarisations were calculated from Halverstadt-Kumler equation<sup>7</sup>. Resultant dipole mo-

TABLE I  
Alcohol Studied

Alcohol	Abbreviation	$(K_2)_x^a$	$\gamma^b$
$(\text{CH}_3)_3\text{CCH}_2\text{OH}$	C- $\alpha$	21.26	14
$(\text{CH}_3)_3\text{C}(\text{CH}_2)_2\text{OH}$	C- $\beta$	40.1	19
$(\text{CH}_3)_3\text{C}(\text{CH}_2)_3\text{OH}$	C- $\gamma$	62.1	23
$(\text{CH}_3)_3\text{C}(\text{CH}_2)_4\text{OH}$	C- $\delta$	32.1	14
$(\text{CH}_3)_3\text{SiCH}_2\text{OH}$	Si- $\alpha$	6.9	5
$(\text{CH}_3)_3\text{Si}(\text{CH}_2)_2\text{OH}$	Si- $\beta$	26.7	13
$(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{OH}$	Si- $\gamma$	— <sup>c</sup>	— <sup>c</sup>
$(\text{CH}_3)_3\text{Si}(\text{CH}_2)_4\text{OH}$	Si- $\delta$	41.4	16
$(\text{CH}_3)_3\text{GeCH}_2\text{OH}$	Ge- $\alpha$	13.4	65
$(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_2\text{OH}$	Ge- $\beta$	22.7	9
$(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_3\text{OH}$	Ge- $\gamma$	51.8	16
$(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_4\text{OH}$	Ge- $\delta$	60.2	17

<sup>a</sup> Equilibrium constant of dimerisation (in units of molar fractions) for solutions in cyclohexane;

<sup>b</sup> degree of association for the molar fraction  $w = 0.0025$ ; <sup>c</sup> solution diverged.

ments  $\mu$  were calculated according to the equation

$$\mu = \sqrt{0.01281(P_2 - 1.05R_m)}, \quad (1)$$

where  $R_m$  is the molar refraction of a polar substance 2. The  $R_m$  values were calculated from reported bond refractions<sup>8,9</sup>. The values of dipole moments so obtained are given in Tables II and III, along with some sub-results.

The calculation of the errors, presented in Table IV, was performed only for the measurement of  $\delta$ -trimethylgermylbutanol, which has the lowest dipole moment, using the relations derived on the basis of Student's distribution<sup>10</sup>. The dispersion variance of dipole moment is caused above all by the dispersion variance of the instrument and by the effect of thermostat. The inaccuracy in determination of  $v_1$  and  $\beta$  is not critical, and from the values of  $S_{\mu, T}$  it follows that temperature adjustment of the thermostat plays negligible role. The difference between the values of the dipole moment obtained by statistical and by graphical treatment of experimental results is about 0.02 D, *i.e.* it is smaller than the standard deviation, which justifies the use of graphical treatment of experimental results. If  $n$  is the number of the solutions measured, than the degree of freedom of the random quantity  $\alpha$  is  $n - 2 = 7$ . As the dispersion variance of the slope  $\alpha$  contributes to the variance of dipole moment most significantly, the same degree of freedom can be also ascribed to the random quantity  $\mu$ , and the experimental dipole moment of the  $\delta$ -germyl alcohol lies with 95% probability within the interval  $\mu = 1.46 \pm 0.09$  D.

TABLE II  
Experimental Dipole Moments Measured in Cyclohexane and Important Sub-Results

Alcohol	$R_M^a$	Concentration range	$\alpha$	$\beta$	$P_2^a$	$\mu$ (D)
C- $\alpha$	26.83	0.0—4.8	2.4325	0.040	81.19	1.61
C- $\beta$	31.46	0.0—2.1	2.2304	0.035	88.10	1.64
C- $\gamma$	36.09	0.0—4.0	1.9168	0.016	90.94	1.61
C- $\delta$	40.72	0.0—4.0	1.8051	-0.038	97.71	1.64
Si- $\alpha$	31.71	0.0—2.0	2.6624	-0.025	100.06	1.81
Si- $\beta$	36.34	0.0—3.0	1.8939	-0.032	91.41	1.61
Si- $\gamma$	40.97	0.0—2.0	2.7195	-0.049	128.04	2.04
Si- $\delta$	45.60	0.0—4.0	1.6332	-0.076	102.26	1.55
Ge- $\alpha$	34.03	0.0—2.5	2.0008	-0.323	107.91	1.88
Ge- $\beta$	38.66	0.0—3.0	1.6333	-0.329	103.44	1.75
Ge- $\gamma$	43.29	0.0—2.0	1.8725	-0.327	122.63	1.94
Ge- $\delta$	47.92	0.0—3.0	1.0601	-0.318	95.48	1.48

<sup>a</sup> In  $\text{cm}^3 \text{mol}^{-1}$ .

## RESULTS AND DISCUSSION

As follows from statistical analysis, the experimental error of the measurement of dipole moments is not greater than 0.09 D. In solution of alcohols with the concentration range  $w = 0-0.0025$ , which was taken as the standard range for determination of dipole moment, dimerisation takes place at 0-20% analytical concentration. The influencing of experimental dipole moment cannot be quantitatively evaluated, since dielectric measurements provide no information about the type of this association. Resulting from the knowledge of association constant, only an estimate can be made of the range within which the experimental dipole moment  $\mu$  can differ from the actual dipole moment  $\mu_0$ .

Providing that only dimers are formed and that, according to Table I, the average degree of association is 10%, i.e.  $\gamma_1 = 0.9$  and  $\gamma_2 = 0.1$ , then Frohlich correlation factor<sup>11</sup>  $g$  can acquire all values within the limits  $g = 1 \pm 0.1$ . Dipole moments of alcohols do not exceed generally 1.7 D, so that the difference between the experimental and actual dipole moments would not be greater than 0.085 D. Limit values

TABLE III  
Experimental Dipole Moments Measured in Benzene and Important Sub-Results

Alcohol	$R_M^a$	Concentration range	$\alpha$	$\beta$	$P_2^a$	$\mu$ , D
C- $\alpha$	26.83	0.0-0.7	3.899	0.1507	97.65	1.84
		0.0-6.0	2.998		83.68	1.64
C- $\beta$	31.46	0.0-4.7	2.9375	0.1722	96.58	1.76
C- $\gamma$	36.09	0.0-0.6	2.7559	0.1413	104.32	1.80
		0.0-2.5	2.4806		94.22	1.67
C- $\delta$	40.72	0.0-1.7	2.7272	0.1330	116.27	1.89
		1.7-4.2	1.9322	0.1332	96.82	1.63
Si- $\alpha$	31.71	0.0-1.0	2.6217	0.0925	89.71	1.66
Si- $\beta$	36.34	0.0-2.6	2.8362	0.1528	108.63	1.85
Si- $\gamma$	40.97	0.0-0.3	2.8254	0.0417	116.89	1.92
		0.0-1.2	2.4401		106.65	1.76
Si- $\delta$	45.60	0.0-1.7	2.6133	0.1267	127.18	1.96
Ge- $\alpha$	34.03	0.0-3.0	1.8912	-0.2657	91.77	1.65
Ge- $\beta$	38.66	0.0-2.0	1.8717	-0.1893	103.25	1.75
Ge- $\gamma$	43.29	0.0-2.0	1.6332	-0.1852	104.20	1.69
Ge- $\delta$	47.92	0.0-1.8	2.1457	-0.1899	131.06	1.97
		0.0-8.6	1.6002		111.63	1.73

<sup>a</sup> In  $\text{cm}^3 \text{mol}^{-1}$ .

are however least probable. The error of the determination of dipole moment does not exceed 0.15 D, providing that only dimers are formed. If two experimental values of dipole moments differ by 0.3 D, this does not necessarily mean that dipole moments of both alcohols are different.

From the results of the measurements of dipole moments in cyclohexane solutions, presented in Table II, it is seen that experimental values for silicon derivatives agree well with those for germanium analogues, and both series differ from the series of carbon compounds. The dipole moments of individual carbon derivatives differ only within experimental errors and equal to the dipole moments of higher alcohols reported by Ibbitson and Moor<sup>12</sup> for the same concentration range.

TABLE IV

Results of Statistical Treatment of the Measurement of  $\delta$ -Trimethylgermyl-Substituted Butanol in Cyclohexane

Quantity	$S_x^a$	$S_{\mu, X}$
$\alpha = 1.033_5$	$S_\alpha = 0.048_4$	$S_{\mu, \alpha} = 0.037_1$
$\beta = -0.320_3 \text{ cm}^3 \text{ g}^{-1}$	$S_\beta = 0.010_6 \text{ cm}^3 \text{ g}^{-1}$	$S_{\mu, \beta} = 0.008_5$
$T = 298.1 \text{ K}$	$S_T = 0.1^\circ\text{C}$	$S_{\mu, T} = 2.2 \cdot 10^{-4}$
$v_1 = 1.2907_2 \text{ cm}^3 \text{ g}^{-1}$	$S_{v_1} = 0.00014_4 \text{ cm}^3 \text{ g}^{-1}$	$S_{\mu, v_1} = 0.006_5$
$\mu = 1.46_3$	$S_\mu = 0.038_6 \text{ D}$	—

<sup>a</sup> Standard deviation of the random quantity X, <sup>b</sup> standard deviation of the dipole moment  $\mu$  due to the dispersion of the random quantity X.

TABLE V

Comparison of Values of  $\mu$  (in D) for Low Concentration of Alcohols in Benzene with  $\Delta\tilde{\nu}(\text{OH})$  (in  $\text{cm}^{-1}$ ) in Tetrahydrofuran

Alcohol	$\mu$			$\Delta\tilde{\nu}(\text{OH})$		
	C	Si	Ge	C <sup>a</sup>	Si <sup>b</sup>	Ge <sup>a</sup>
$\alpha$	1.84	1.66	1.65	154	145	150
$\beta$	1.76	1.85	1.75	151	149	151
$\gamma$	1.80	1.92	1.69	155	155	153
$\delta$	1.89	1.96	1.96	157	154	153

<sup>a</sup> Ref.<sup>4</sup>; <sup>b</sup> ref.<sup>3</sup>.

Providing that  $m_2 = m_{\text{CH}_2 \rightarrow \text{O}} = 1.14$ ,  $m_3 = m_{\text{O} \rightarrow \text{H}} = 1.51$  (ref.<sup>13</sup>), and bond angle  $\omega = \angle \text{COH} = 105^\circ$  (ref.<sup>13</sup>), the dipole moments of carbon alcohols should have the value of 1.64 D, which is in an excellent agreement with experimental values.

Surprisingly alternating changes of dipole moments in the silicon and germanium series may be due to a different orientation of bond moments of the  $(\text{CH}_3)_3\text{Si}-\text{CH}_2$  or  $(\text{CH}_3)_3\text{Ge}-\text{CH}_2$  bond with respect to bond moments of  $\text{CH}_2-\text{O}$  and  $\text{O}-\text{H}$  bonds, which could arise from different intramolecular interaction of oxygen atoms with silicon and concurrent intermolecular association.

Under the assumption of free rotation round all bonds, according to the Eyring relation

$$\mu^2 = \sum_{j=1}^n m_j^2 + 2 \sum_{j=1}^n \sum_{s_j} \sum_{k=j}^{s_j-1} \cos \theta m_j m_s, \quad (2)$$

where  $\mu$  is the resultant dipole moment and  $\theta$  is the angle formed by dipole moments  $m_k$  and  $m_{k+1}$ , the silyl- and germyl-substituted alcohols should have dipole moments

$$\mu^2 = m_1^2 + m_2^2 + m_3^2 - 2m_2m_3 \cos(180 - \omega) = 2m_1 \cos^n(180 - \theta) \cdot [m_2 - m_3 \cos(180 - \omega)], \quad (3)$$

where  $m_1 = m_{\text{Me}_3\text{M}-\text{CH}_2} = 0.28$  D,  $\text{M} = \text{Si}, \text{Ge}$  (refs<sup>14-16</sup>);  $\theta = \angle \text{SiCC}$  resp.  $\angle \text{CCC} = 109^\circ 28'$ . After evaluation of  $\mu^2 = 2.76703 + 0.41954 \cdot 0.3333^n$  the following constants of dipole moments can be obtained for  $n = 1, 2, 3, 4$ : 1.71 D, 1.67 D, 1.66 D, and 1.66 D. The difference observed between the calculated and experimental values indicate the presence of above mentioned phenomena.

The increase in the values of dipole moments of  $\alpha$ -alcohols could be explained by steric hindrance toward the rotation of the trimethylsilyl group around the  $\text{C}-\text{O}$  bond with respect to the hydrogen of the  $\text{O}-\text{H}$  group. The values of dipole moments of  $\beta$ -alcohols corroborates within experimental errors (due to association) the assumption of free rotation.

Discussion of experimental dipole moments of  $\gamma$ - and  $\delta$ -alcohols is practically impossible because of the lack of the knowledge about an eventual interaction of oxygen with silicon or germanium. It can only be stated that similar effects are observed with both silyl- and germyl-substituted alcohols.

Experimental dipole moments determined in benzene solutions, which significantly differ from those obtained by measurements in cyclohexane, speaks for solvent effect which suppresses the effects occurring in cyclohexane. Contrary to measurements in cyclohexane, the dependences of dielectric constants of benzene solutions on the concentration of alcohols markedly deviated from linearity. This speaks for the existence of an effect which does not play a role in cyclohexane and arise probably

from the formation of hydrogen bridges of the type  $\text{RO}\dots\text{H}\dots\text{C}_6\text{H}_6$ . Nonlinearity of dependences, most distinct for  $w = 0.0002 - 0.002$ , strongly reduces the reliability of the values of dipole moments. Because of the dispersion of experimental data, the slope  $\alpha = (d\epsilon/dw)_{w=0}$  could not be reliably determined, so that the arithmetic mean of the interval  $w \in \langle 0; 0.0025 \rangle$  was taken as decisive. The dipole moments so obtained show a tendency to increase with increasing number of carbon atoms. Only  $\gamma$ -alcohols have lower values. If dipole moments (given in Table III in parentheses) for several experimental points in the lowest concentrations measured (the reliability of which is, of course, very low) are calculated, then their sequence corresponds qualitatively to the decrease of wavenumbers of the OH stretching vibrations of alcohols measured in tetrahydrofuran (Table V). The decrease of the wavenumbers is proportional to the acidity of the hydroxyl group hydrogen, similarly as the equilibrium constant of the formation of the hydrogen bridge  $\text{RO}\dots\text{H}\dots\text{C}_6\text{H}_6$ ; also proportional is dipole moment which increases with hydrogen bonding. Only the result of the measurement of the  $\gamma$ -trimethylgermylpropanol deviates from this correlation.

Dependences found for silyl- and germyl-substituted alcohols can be therefore explained by the predominant +I effect of trimethylsilyl or trimethylgermyl groups; this effect decreases with lengthening of the carbon chain, which brings about an increase of the acidity of the hydrogen of the hydroxyl group.

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