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ORGANOGERMANIUM COMPOUNDS
IV*. DIPOLE MOMENTS OF PROPYLCHLOROGERMANES, SOME ALKYLETHOXYGERMANES AND PROPYLETHOXYSILANES

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SUMMARY

The dipole moments of propylchlorogermanes, methylethoxygermanes, propylethoxygermanes and propylethoxysilanes in benzene have been determined at 25°. The experimental values are used for calculating the moments of the $GeCl_n$ groups and the moment of the Ge–O bond and their magnitude is compared with that of the $SiCl_n$ groups and of the Si–O bond. The polarizabilities of methyl and propyl groups attached to germanium and silicon are considered. The factors influencing the value of the dipole moments of alkylethoxysilanes and alkylethoxygermanes are discussed.

INTRODUCTION

As part of an extensive investigation of the character of the bonds of germanium and silicon in their organic compounds the present work was devoted mainly to the polarizability of germanium atoms with alkyl groups and further to the possible role of $p_\pi \rightarrow d_\pi$ dative character of Ge–Cl and Ge–O bonds. In comparison with analogous compounds of silicon one can expect in the germanium compounds a greater polarizability with a less pronounced $p_\pi \rightarrow d_\pi$ character of some of the bonds, but the available experimental material is rather poor. Of the compounds in which the above types of bond occur, the dipole moments of methylgermanes[2-5] and of some methylhalogermanes[2,6] and ethylhalogermanes[7] have been investigated. The moments of germanium bonds with other atoms are not yet known, but Kartsev[7] has attempted an assessment of the moments of Ge–Cl (3.0 D), Ge–H (1.0 D) and Ge–C (0.65 D).

As to the oxygen compounds of germanium, the dipole moments of methylmethoxygermanes[8,9] have been published. From a comparison of experimental and theoretical values the authors envisaged the role of free rotation of the terminal methyl groups about the Ge–O bonds in such compounds. The dipole moment of the $(CH_3)_3GeO$ group calculated from the dipole moment of trimethylmethoxygermane is 1.77 D.

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The dipole moments of methylchlorosilanes[10-13] and methylethoxysilanes[9,14-16] have been measured previously (see Table 2) and the moments of the $SiCl_n$ and $(CH_3)_3SiO$ groups were calculated therefrom. For the moment of the methyl group attached to silicon, the value of 0.2 D is commonly employed, this being practically constant in differently substituted methylsilanes. The moment of the $Si–C_3H_7$ has not yet been determined.

EXPERIMENTAL

The preparation of propylchlorogermanes, tetrapropylgermane, propylethoxygermanes, tetraethoxygermane, methylethoxygermanes and of propylethoxysilanes has been described in the first paper of this series[17] together with the results of analyses and physical constants.

The purity of all the compounds was checked chromatographically. All the manipulations with germanium derivatives were carried out in a dry box.

As solvent we used analytical-grade benzene (Lachema), dried and purified by a previously described procedure[18].

The dipole moments were determined on the basis of dielectric constants and specific volumes of solution of the compounds studied in benzene, over a concentration range from 10^{-2} to 10^{-3} M. The dielectric constants were determined by the resonance method at a frequency of 0.5 MHz, with an accuracy of $\Delta\varepsilon/\varepsilon = 1 \cdot 10^{-4}$. Density was determined pycnometrically. All the measurements were carried out at $25.00 \pm 0.05°$.

The dipole moments were calculated from the experimental data according to the procedure of Halverstadt and Kumler[19].

RESULTS AND DISCUSSION

The experimental results and the dipole moments of all the compounds described here were summarized in Table 1.

Using the value of 1.0 D for the bond moment of Ge–H[7] and the dipole moments of methylgermanes shown in Table 2, the group moments of $Ge–CH_3$ were calculated:

$CH_3GeH_3 : m(\overrightarrow{GeCH_3}) = 0.36$ D
$(CH_3)_2GeH_2 : \quad = 0.34$ D
$(CH_3)_3GeH : \quad = 0.33$ D

With the aid of the moments of the $Ge–CH_3$ groups found here the bond moments of the Ge–Cl bond were calculated for methylchlorogermanes (on the basis of the average values of the dipole moments of methylchlorogermanes determined by different authors and shown in Table 2):

$CH_3GeCl_3 : m(\overrightarrow{GeCl}) = 3.03$ D
$(CH_3)_2GeCl_2 : \quad = 3.07$ D
$(CH_3)_3GeCl : \quad = 3.17$ D

TABLE 1

MOLAR POLARIZATION, REFRACTION AND DIPOLE MOMENTS OF COMPOUNDS DESCRIBED IN THE TEXT

Compound	α^a	β^b	MR^c	$(P_2)_0{}^d$	μ_{298}
n-$C_3H_7GeCl_3$	4.52	−0.513	44.66	231.317	3.01
(n-$C_3H_7)_2GeCl_2$	6.34	−0.364	57.00	299.099	3.42
(n-$C_3H_7)_3GeCl$	3.83	−0.235	69.34	236.034	2.82
(n-$C_3H_7)_4Ge$	−0.09	−0.055	81.68	75.884	0
$Ge(OC_2H_5)_4$	1.29	−0.285	61.12	126.761	1.75
n-$C_3H_7Ge(OC_2H_5)_3$	1.38	−0.248	66.26	132.844	1.76
(n-$C_3H_7)_2Ge(OC_2H_5)_2$	1.11	−0.206	71.40	122.246	1.52
(n-$C_3H_7)_3GeOC_2H_5$	1.03	−0.129	76.54	123.222	1.45
$CH_3Ge(OC_2H_5)_3$	1.45	−0.259	53.94	120.152	1.76
$(CH_3)_2Ge(OC_2H_5)_2$	1.21	−0.251	46.76	95.719	1.51
$(CH_3)_3GeOC_2H_5$	1.55	−0.192	39.54	94.099	1.60
n-$C_3H_7Si(OC_2H_5)_3$	1.43	−0.017	55.71	125.41	1.80
(n-$C_3H_7)_2Si(OC_2H_5)_2$	0.61	+0.010	59.38	93.17	1.22
(n-$C_3H_7)_3SiOC_2H_5$	0.36	+0.082	63.45	88.18	1.03
n-$C_3H_7Si(CH_3)_3$	−0.31	+0.308	39.42	43.86	0.34

[a] Slope of the concentration dependences of dielectric constants. [b] Slope of the concentration dependences of specific volumes. [c] Molar refraction. [d] Molar polarization of the compound studied extrapolated to infinite dilution.

TABLE 2

DIPOLE MOMENTS OF METHYLGERMANES, METHYLCHLOROGERMANES, METHYLCHLOROSILANES AND METHYLETHOXYSILANES

Compound	μ(D)
CH_3GeH_3	0.64[2]
$(CH_3)_2GeH_2$	0.76[2]
$(CH_3)_3GeH$	0.67[2]
CH_3GeCl_3	2.70[2]; 2.63[7]
$(CH_3)_2GeCl_2$	3.14[2]; 3.11[7]
$(CH_3)_3GeCl$	2.89[2]; 2.78[6]
CH_3SiCl_3	1.93[10]; 1.87[12]
$(CH_3)_2SiCl_2$	2.28[10]; 1.89[12]
$(CH_3)_3SiCl$	2.09[10]; 2.02[11]; 2.08[13]
$CH_3Si(OC_2H_5)_3$	1.70[15]; 1.72[9]; 1.678[16]
$(CH_3)_2Si(OC_2H_5)_2$	1.36[14]; 1.39[9]; 1.358[16]
$(CH_3)_3SiOC_2H_5$	1.18[14]; 1.17[9]; 1.146[16]

These bond moments were used for calculating the group moment of the propyl group attached to the germanium atom in propylchlorogermanes, under the assumption that the replacement of the methyl groups with propyl groups has no apparent effect on the magnitude of m(GeCl):

$$\text{n-}C_3H_7GeCl_3\colon\ m(\overrightarrow{GeC_3H_7}) = 0.02\ \text{D}$$

$$(\text{n-}C_3H_7)_2GeCl_2\colon\ = 0.09\ \text{D}$$

$$(\text{n-}C_3H_7)_3GeCl\colon\ = 0.36\ \text{D}$$

It is understood that the moments calculated here represent only approximate values since a tetrahedric arrangement about the germanium atom is assumed and only negligible changes of the bond moment of Ge–H in the methylgermane series are postulated. Moreover, it must be assumed that the moment of the Ge–CH_3 group remains constant upon transition from methylgermanes to methylchlorogermanes just as do the moments of Ge–Cl upon transition from methylchlorogermanes to propylchlorogermanes.

The calculated values still show quite clearly that the moment of the Ge–C_3H_7 group, in contrast with the Ge–CH_3 group decreases pronouncedly with an increasing number of chlorine atoms in the molecule. This points to a greater polarizability of the propyl group attached to germanium as compared with the methyl group. In view of this fact one must exercise caution in applying the moment of the Ge–C_3H_7 group calculated from propylchlorogermanes to propylethoxygermanes whereas the error incurred on applying the Ge–CH_3 group moment in methylethoxygermanes should be negligible. For the sake of comparison we have determined the moments of Ge–C_3H_7 also in propylethoxygermanes by establishing first the contribution of the ethoxy groups to the overall dipole moment of methylethoxygermanes:

$CH_3Ge(OC_2H_5)_3$: $m[Ge(OC_2H_5)_3] = 2.12$ D
$(CH_3)_2Ge(OC_2H_5)_2$: $m[Ge(OC_2H_5)_2] = 1.90$ D
$(CH_3)_3GeOC_2H_5$: $m(GeOC_2H_5) = 1.89$ D

These values and the experimental dipole moments of propylethoxygermanes were then used for calculating the values of the group moment of Ge–C_3H_7 in dependence on the number of ethoxy groups in the molecule:

n-$C_3H_7Ge(OC_2H_5)_3$: $m(\overrightarrow{GeC_3H_7}) = 0.36$ D
(n-$C_3H_7)_2Ge(OC_2H_5)_2$: $= 0.33$ D
(n-$C_3H_7)_3GeOC_2H_5$: $= 0.56$ D

It is assumed in this connection that the contributions of the ethoxy groups in methyl- and propylethoxygermanes are the same, the dipole moments of methyl- and propylethoxygermanes are the same and hence the group moments of the methyl and propyl groups are identical. An exception is formed here by tripropylethoxygermane, the dipole moment of which is slightly lower than that of the corresponding trimethyl derivative. This corresponds to a smaller contribution of the $(C_3H_7)_3GeO$ group as compared with the $(CH_3)_3GeO$ group, apparently due to mutual steric repulsion of the propyl groups. Contributions of these groups to the overall dipole moments have been estimated.

To calculate the moments of the $(CH_3)_3GeO$ group in trimethylethoxygermane the following values were used: $m(OC_2H_5) = 1.10$ D, for the angle of GeOC 113°, the other angles being of a tetrahedron. By a vector sum the value of 1.67 D was found. Cumper, Melnikoff and Vogel[8] published for this group in trimethylmethoxygermane the value of 1.77 D. If the inaccuracy of such results is taken into account the agreement is fair. An analogous calculation for tripropylethoxygermane yields the group moment for (n-$C_3H_7)_3GeO$ equal to 1.47 D.

Since $m[(CH_3)_3GeO] = m(GeO) - m[(CH_3)_3Ge]$, one should be able to use the moment of the trimethylgermyl group (0.33 D) for calculating directly the moment of the Ge–O bond: $m(\text{GeO})=2.00$ D.

If this type of calculation is applied to tripropylethoxygermane, using for the $(n\text{-}C_3H_7)_3Ge$ group moment the value obtained from tripropylchlorogermane (0.35 D) one obtains the value of 1.82 D for the moment of the Ge–O bond. In view of the more pronounced $+I$ effect of the propyl group as compared with that of the methyl group one might rather expect a greater bond moment $m(\text{GeO})$ in tripropylethoxygermane. It thus appears that due to the inconstancy of the moment of the $Ge{-}C_3H_7$ group one cannot use the value obtained from one compound for obtaining the value in a compound of another type.

In addition to the values of group moments the overall dipole moments of alkylethoxygermanes are affected by the possibility of rotation of the terminal alkyl groups. For this reason the theoretical dipole moments of methylethoxygermanes and propylethoxygermanes were calculated using Eyring's formula[20] which is valid on the assumption that only free rotation takes place in the molecule. The values obtained (Table 3) are in all cases higher than the experimentally found ones which points to the fact that free rotation in these compounds can be very probably excluded and that the existence of certain conformations or mixtures of various conformations must be assumed.

TABLE 3

THE THEORETICAL DIPOLE MOMENTS OF ALKYLETHOXYSILANES AND ALKYLETHOXYGERMANES

Compound	$\bar{\mu}_{theor}$	μ_{exp}
$CH_3Si(OC_2H_5)_3$	1.85	1.70
$(CH_3)_2Si(OC_2H_5)_2$	1.59	1.36
$CH_3Ge(OC_2H_5)_3$	2.09	1.76
$(CH_3)_2Ge(OC_2H_5)_2$	2.00	1.51
$n\text{-}C_3H_7Si(OC_2H_5)_3$	1.88	1.80
$(n\text{-}C_3H_7)_2Si(OC_2H_5)_2$	1.53	1.22
$n\text{-}C_3H_7Ge(OC_2H_5)_3$	2.11	1.76
$(n\text{-}C_3H_7)_2Ge(OC_2H_5)_2$	2.03	1.52

In order to compare the polarity of the bonds of the propyl groups attached to germanium and to silicon the moments of the $n\text{-}C_3H_7Si$ group were calculated by a procedure analogous to that described for germanium derivatives. For the calculation we used the following values: $m(C_2H_5O)=1.10$ D, $m(SiCH_3)=0.2$ D, the angle of SiOC being 113°, the other angles being of a tetrahedron. The contributions of the $SiOC_2H_5$, $Si(OC_2H_5)_2$ and $Si(OC_2H_5)_3$ groups to the overall moments of methylethoxysilanes are 1.29 D, 1.59 D and 1.90 D, respectively. If it is assumed that these contributions change only negligibly on replacing methyl by propyl groups, one can calculate the moment of the propyl group attached to silicon:

$n\text{-}C_3H_7Si(OC_2H_5)_3$: $m(\overrightarrow{Si{-}C_3H_7}) = 0.08$ D
$(n\text{-}C_3H_7)_2Si(OC_2H_5)_2$: $= 0.32$ D
$(n\text{-}C_3H_7)_3SiOC_2H_5$: $= 0.58$ D

The moment of the propyl group calculated from trimethylpropylsilane is 0.54 D.

In trimethylethoxysilanes we found the value of 1.03 D for the moment of $(CH_3)_3SiO$ group which is in agreement with the value published for this moment in trimethylmethoxysilane[8]. Hence the moment of the Si–O bond is equal to 1.23 D. In comparison with the Ge–O bond the Si–O one is thus much less polarized.

Similarly to alkylethoxygermanes, the moment of the $(n\text{-}C_3H_7)_3SiO$ group in alkylethoxysilanes (0.65 D) is much lower than $(CH_3)_3SiO$ (1.03 D). An explanation may be sought in the steric effect of voluminous propyl groups which is even more marked in silicon derivatives in comparison with germanium derivatives in view of the smaller volume of the central atom.

As to the possibility of rotation of the ethyl groups in alkylethoxysilanes one can assume, on the basis of temperature dependences found by Ferenczi-Gresz[21], free rotation to occur only in trimethylethoxysilane. In the other methylethoxysilanes, and even more so in propylethoxysilanes, the possibility of free rotation of the ethyl groups is nil. This is indicated also by a comparison of the experimental dipole moments with the theoretical ones. The dipole moments calculated are shown in Table 3.

The lower polarity of silicon bonds as compared with germanium is evident in the moments of the Si–Cl bonds in methylchlorosilanes. These bond moments were computed from a vectorial calculation from the dipole moments of the methylchlorosilanes:

$$CH_3SiCl_3: m(\overrightarrow{Si\text{–}Cl}) = 2.13 \text{ D}$$
$$(CH_3)_2SiCl_2: \quad = 2.21 \text{ D}$$
$$(CH_3)_3SiCl: \quad = 2.29 \text{ D}$$

The bond moments of the Ge–Cl and Si–Cl bonds in the analogous methylchloro derivatives correspond to the ratio 1.38–1.42. Since the moments of the Ge–O and Si–O bonds cannot be calculated for the di- and triethoxy derivatives they were expressed by the quotients of dipole moments of methyl- and propylethoxygermanes and the corresponding methyl- and propylethoxysilanes. Their values (from the mono- to the triethoxy derivatives) are the following: 1.36, 1.11 and 1.04 for the methyl derivatives, and 1.41, 1.21 and 0.98 for the propyl derivatives. In view of the fact that both the covalent radii and the electronegativities of silicon and germanium atoms are very similar[7] one can account for the high quotients by assuming that the $p_\pi \rightarrow d_\pi$ interaction plays a much greater role in the Si–Cl and Si–O bonds than in the corresponding germanium ones. A decrease of the quotients with increasing number of the ethoxy groups in the molecule indicates that the role of the $p_\pi \rightarrow d_\pi$ interaction is greatest in monoethoxysilanes and then gradually decreases.

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