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ORGANOGERMANIUM COMPOUNDS
VII*. DIPOLE MOMENTS OF PHENYLMETHYLCHLOROGERMANES AND *p*-SUBSTITUTED PHENYLTRICHLOROGERMANES

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SUMMARY

The dipole moments of phenylmethylchlorogermanes of the general formula $C_6H_5(CH_3)_{3-n}GeCl_n$ and of *p*-substituted phenyltrichlorogermanes *p*-$XC_6H_4GeCl_3$ where X=H, F, Cl, CH_3, OCH_3 were determined in benzene at 25°. A comparison with analogous compounds of silicon and tin indicates that the germanium atom resembles silicon more than tin in its ability to accept π-electrons from the aromatic ring.

INTRODUCTION

We have discussed previously[2] the problem of the polarizability of a phenyl group attached to the silicon atom bearing different numbers of chlorine atoms. We showed that increase in the number of chlorine atoms was associated with a decrease in the polarity of the phenyl–silicon bond, as shown by the decrease in the corresponding group moment, which even reached negative values. This phenomenon was attributed to the increasing $-I$ effects of the methylchlorosilyl groups. A shift of the π-electrons of the phenyl group into the electron sphere of silicon, involving formation of a $(p \rightarrow d)\pi$ dative bond, is also assisted by electron-releasing substituents in the *para*-position of the phenyl group; halogen atoms[3-6], and methoxy[7], methyl[4,6], amino, dimethylamino[4] and nitro groups [4] have been used. Huang and Hui[6] measured the dipole moments of *p*-substituted trimethylphenyltin and found that whereas the methyl group and the methoxy group have the same effect as in analogous compounds of silicon, the halogen atoms show opposite effects in the two cases. The tin atom has a lower tendency to enter $(p \rightarrow d)\pi$ bonding with the phenyl group, and so halogen atoms (in this case of chlorine and bromine) act mainly through their $-I$ effects, the $+M$ effect which would assist the formation of a $(p \rightarrow d)\pi$ bond being of minor importance. It thus seemed of interest to study the effects of the chlorine atoms and of the *p*-substituents in phenylmethylchlorogermanes, the central atom of which lies between silicon and tin in the periodic system of elements.

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* For part VI, see ref. 1.

EXPERIMENTAL

Phenylmethylchlorogermanes[1] and *p*-substituted phenyltrichlorogermanes[9] were prepared as previously described. The purity of each compound was checked chromatographically. All the manipulations with derivatives of chlorogermanes were carried out in a dry-box.

As solvent we used reagent-grade benzene (Lachema), purified and dried as described before[10]. The dipole moments were determined from the dielectric constants and specific volumes of solutions over a range of concentrations from 10^{-3} to 10^{-2} mol/l.The dielectric constants were determined by the resonance method at a frequency of 0.5 MHz with an accuracy of $\Delta\varepsilon/\varepsilon = 1 \cdot 10^{-4}$. Densities were determined pycnometrically. All the measurements were at $25.00 \pm 0.05°$. Dipole moments were derived by Halverstadt and Kumler's method[11].

RESULTS AND DISCUSSION

The dipole moments of the compounds examined are shown in Table 1, together with the corresponding α and β coefficients, molar refractions and molar polarizations.

TABLE 1

DIPOLE MOMENTS OF ARYLGERMANIUM COMPOUNDS

Compound	α	β	P(cm^3)	MR (cm^3)	μ(D)
$C_6H_5Ge(CH_3)_3$	0.15	−0.232	50.57	43.66	0.58
$C_6H_5Ge(CH_3)_2Cl$	3.72	−0.455	227.08	53.73	2.91
$C_6H_5Ge(CH_3)Cl_2$	5.10	−0.446	274.62	53.66	3.28
$C_6H_5GeCl_3$	4.84	−0.832	256.82	53.59	3.15
p-$CH_3C_6H_4GeCl_3$	5.68	−0.472	342.39	59.72	3.71
p-$CH_3OC_6H_4GeCl_3$	6.57	−0.550	403.83	59.99	4.10
p-$ClC_6H_4GeCl_3$	1.45	−0.555	130.13	58.43	1.87
p-$FC_6H_4GeCl_3$	1.60	−0.561	130.23	53.62	1.93

Phenylmethylchlorogermanes all have larger dipole moments than the phenylmethylchlorosilanes[2] but the changes are analogous in both systems. Comparison with results for methylchlorogermanes[8] shows that there is an increasing difference between dipole moments in the two series as the number of chlorine atoms per molecule rises. For monochloro derivatives $\Delta\mu = 0.02$ D (which is within the limits of experimental error), for dichloro derivatives $\Delta\mu = 0.14$ D and for trichloro derivatives $\Delta\mu = 0.45$ D. These differences must be attributed to the presence of the phenyl group in one series. The phenyl group is much more polarizable than the methyl group, and its polarizability is markedly affected by chlorine atoms attached to germanium. The increase of dipole moments of phenylmethylchlorogermanes as compared with values of methylchlorogermanes corresponds to polarization of molecules in the direction $\overrightarrow{PhGeCl_n}$. This polarization is associated with interaction of the π-electrons of the phenyl group with the *d*-orbitals of the germanium atom and this interaction is greater the greater the —*I* effect of the methylchlorogermyl groups, so that the greatest differences between the moments of the methyl and phenyl compounds analogous occur in the organotrichlorogermanes.

If the hydrogen in the benzene ring at *para*-position with respect to the trichlorogermyl group is replaced with a substituent X, the dipole moment will change. If the value of the dipole moment of compound C_6H_5X is known, the moment of the rest of the molecule $C_{ar}GeCl_3$ may be calculated. The dipole moments of different *p*-substituted derivatives are shown in Table 1; *p*-Cl or *p*-F atoms lower the dipole moment of phenyltrichlorogermane whereas *p*-Me or *p*-MeO groups raise it. Table 2 shows the differences between the experimental dipole moment of p-$XC_6H_4GeCl_3$ and that of C_6H_5X. (Dipole moments used were: toluene, 0.34 D; anisole 1.30 D; chlorobenzene, 1.58 D; fluorobenzene, 1.50 D). It will be seen that the substituents all raise the dipole moment of the rest of the molecule $C_{ar}GeCl_3$ above that of phenyltrichlorogermane itself, the effect increasing in the sequence $CH_3 < F < Cl < OCH_3$. For the methyl group the effect is to be associated with inductive release of electrons, while the halogen atoms and the methoxy group release electrons by a conjugative effect and thus assist the shift of the π-electrons of the phenyl group toward the central germanium atom with the methoxy group as the most effective.

TABLE 2

DIFFERENCES BETWEEN THE DIPOLE MOMENTS OF p-$XC_6H_4GeCl_3$ AND C_6H_5X

Compound	$\mu_{exp}-\mu(C_6H_5X)$
$C_6H_5GeCl_3$	3.15
p-$CH_3C_6H_4GeCl_3$	3.37
p-$OCH_3C_6H_4GeCl_3$	3.50
p-$ClC_6H_4GeCl_3$	3.45
p-$FC_6H_4GeCl_3$	3.43

Comparison with the behaviour of the analogously substituted trimethylphenylsilicon and -tin compounds[6] indicates that germanium is closer to silicon than to tin in its ability to accept the π-electrons of the ring, and this is particularly evident for halogen substitution.

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