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DIPOLE MOMENTS OF METHYLGERMANIUM FLUORIDES

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SUMMARY

Successive halogen substitution in methylgermanium fluorides and chlorides leads to different observed trends in the dipole moments of the various compounds. These trends may be explained in terms of hybridisation and polarisability effects. If π bonding exists it is small in the fluorine compounds but possibly somewhat larger in the chlorine compounds.

INTRODUCTION

In previous studies of bonding in some organometallic compounds of Group IVa elements, the dipole moments of molecules of general formula Me_nMX_{4-n} ($X = Cl, Br$; $M = Sn$ or Ge and $n = 1$–3) have been measured.

From a simple additive relationship for the bond dipole moments[1] and assuming tetrahedral angles, the following ratios would be expected to be observed: $\mu(Me_2MX_2)/\mu(Me_3MX) = 1.16$ and $\mu(MeMX_3)/\mu(Me_3MX) = 1$. In fact, in the Sn–Br[2], Ge–Cl[3] and Ge–Br[4] series the measured values of these ratios are lower than those predicted from theory whereas for the Sn–Cl[2] series the corresponding ratios are higher (see Table I).

One possible explanation for this behaviour could be the greater difference in electronegativity between Sn and Cl relative to the other metal–halogen bonds. To test this hypothesis measurement has been made of the dipole moments of the Me_nGeF_{4-n} series of compounds in which the difference in electronegativity between

TABLE 1

DIPOLE MOMENTS OF SOME GROUP IVa METHYL HALIDES

M	*X*	$\mu(R_3MX)$ (*D*)	$\mu(R_2MX_2)$ (*D*)	$\mu(RMX_3)$ (*D*)	$\mu(R_2MX_2)/\mu(R_3MX)$	$\mu(RMX_3)/\mu(R_3MX)$
Ge	F	2.61 (2.51)[9]	3.39	3.49 (3.80)[10]	1.30	1.33
Ge	Cl	2.89	3.14	2.70	1.08	0.94
Sn	Cl	3.50	4.10	3.64	1.17	1.04
Sn	Br	3.45	3.86	3.24	1.12	0.94

Ge and F is also high. A similar result to that observed for the Me_nSnCl_{4-n} series may be expected.

EXPERIMENTAL

Compounds in the series Me_nGeF_{4-n} were prepared by a Swarts reaction. Thus, in a typical experiment, freshly sublimed SbF_3 (10% excess) and $MeGeBr_3$ were mixed together with stirring. After refluxing for 1 h the reaction product was crudely separated by gradually lowering the pressure during a distillation in order to obtain as much volatile material as possible. A carefuly conducted second distillation using a Widmer column gave the pure products with yields which were always greater than 50%. The observed physical constants agreed well with those[5] indicated by Panemarenko.

All measurements necessary to obtain dipole moment data by the Debye method were made at 25° in benzene solution. The dipole moments were calculated using the formula $\mu = 0.01281\sqrt{(P_{2\infty}-R_{2\infty})\cdot T}$. The molar refraction $R_{2\infty}$ was measured using the D line of sodium. No correction was made to the molecular polarisation $P_{2\infty}$ for the atomic polarisation P_a.

DISCUSSION

The results obtained are listed in Table 1 together with the corresponding literature values for the same compounds. For comparison, the dipole moments of some other methyltin and methylgermanium halides are also included in the table.

In view of the large separation between the CH bond and the electronegative halogen atom, only minor changes might be expected in the dipole moment of the CH bond. In addition, the relatively small CH bond moment [0.4 D ($C^- - M^+$)] relative to the $M \rightarrow X$ and $M \rightarrow C$ moments led to the assumption that the dipole moment variation is mainly attributable to variations in the corresponding moments of the M–X and M–C bonds.

If we consider the molecule Me_3GeF, it is possible to assume that the strongly electronegative F atom will cause rehybridisation involving the Ge atom, resulting in large percentage *s* character for the orbital directed toward each carbon atom and large percentage *p* character for the orbital directed toward fluorine. This assumption is consistent with the ^2J(Sn–H) and ^2J(Si–H) values obtained from NMR data[6] for various methylmetal halides. The net effect of this rehybridization is that an increase in the C–Ge–C angle will result.

Introduction of a second F atom (as in Me_2GeF_2) will reduce the percentage *p* character of the Ge orbitals directed toward fluorine. Nevertheless the percentage *p* character per Ge–F bond is still greater than 75%, the value assumed for $GeMe_4$. The ensuing isovalent rehybridisation will result in a decrease in the F–Ge–F bond angle to a value less than the tetrahedral value. Hence, two compensating effects will determine the group moment of the GeF_2 group: a reduction in the individual Ge–F bond moment, which will be small due to the weak polarisability of the Ge–F bond, and an increase in the resultant GeF_2 moment to a value greater then the theoretical value of 1.16 times the individual Ge–F bond moments through a decrease in the F–Ge–F angle. If pure *p* orbitals are assumed for the Ge–F bonds (giving a 90° angle for the

GeF_2 group) and if the bond moment is the same as in the monofluoride, the GeF_2 group moment would increase by a factor of $2 \cos 45° = 1.42$ as against $2 \cos 54.44° = 1.16$ for tetrahedral angles.

The increase in the percentage s character of the Ge orbital directed towards carbon will give rise to two additional effects, both acting in the same direction. First, an increase in the C–Ge–C angle, which gives rise to a decrease in the resultant C_2Ge group moment, and second an increase in the electronegativity of the Ge hybrid orbital[7] which will result in a decrease of each individual Ge–C bond moment. These two effects will enhance the increase in the molecular dipole moment already increased by an increase in the GeF_2 group moment caused by the GeC_2 group moment acting in the opposite direction to that of the GeF_2 group.

With $MeGeF_3$, all the effects described above would lead to a very large dipole moment relative to that of Me_3GeF, in agreement with the observed values.

In the Me_nGeCl_{4-n} series, since the difference in electronegativity between Ge and Cl is much smaller both rehybridisation and the variation in the Ge–C partial bond moment will be much smaller, leading to ratios for the dipole moments much closer to those predicted theoretically. Nevertheless, the larger polarisability of the Ge–Cl bond* relative to that of the Ge–F bond will lead to a drastic decrease in the partial moment of the Ge–Cl bond on further introduction of Cl atoms. These two effects should lead to the dipole moment ratios being smaller than those predicted theoretically, in agreement with the observed values.

The observed values for the dipole moments in the Me_nGeF_{4-n} series indicate that $(p-d)\pi$ bonding between Ge and F is unlikely, or at least very small. Since further introduction of electronegative substituents should lead to a contraction of the *d* orbitals of Ge, the largest amount of π bonding would be expected in Me_3GeF_3. This would lead to a lower dipole moment than that found in Me_3GeF, in contradiction to the experimental findings. If π bonding exists, it should be somewhat larger in the chlorine series, although π bonding is not necessary to explain the observed dipole moment ratios.

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* The larger value of the polarisability may be deduced from a comparison with the halogenomethanes for which the values were calculated using the method of Smith[8].