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CHARGE DISTRIBUTION, DIPOLE MOMENTS AND MOLECULAR STRUCTURE OF SOME ORGANOGERMANIUM COMPOUNDS

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Summary

Formal charge distributions in, and the electric dipole moments of, a few simple organogermanium compounds have been evaluated by the method of R.P. Smith et al. [J. Amer. Chem. Soc., 73(1951) 2263]. The difference between the experimental and calculated moments in the case of alkylhalogermanes is explained in terms of the p_π—d_π back bonding effect outweighing the electron releasing effect. In unsaturated compounds, the differences are attributed to possible mesmeric effects involving the expansion of the germanium valence shell.

Introduction

In many organogermanium compounds, the shortening of the Ge—X bond (where X is a π-electron donor group), inferred from various physical studies [1—5], has been attributed to p_π—d_π back bonding. On the other hand, dipole moment studies on alkylgermanes have substantiated the view that alkyl groups release electrons more readily towards germanium than towards carbon or silicon [7, 9]. In this paper, the charge distribution and the dipole moments of a few organogermanium compounds have been theoretically evaluated using the scheme of Smith et al. [10], and compared with the experimental data with a view to assessing the nature of electromeric effects operating in these molecules. The dipole moments and structure of organogermanium compounds are of considerable interest since relatively little is known about them.

Calculation

The method of Smith et al. [10] was used. The parameters used for the evaluation of the formal charge distribution are listed in Table 1. The charge distributions for the various organogermanium compounds are given in Table 2,

TABLE 1

PARAMETERS USED IN THE CALCULATION OF THE CHARGE DISTRIBUTIONS AND DIPOLE MOMENTS

Bond (a—b)	β_{ab}	γ_{ab}	Bond distance (Å)
H—C	0.13	0.00	1.090
Cl—C	0.71	—1.49	1.762
C—C	$\beta_C^C = 0.718$	$\alpha_{CC} = 0.00$	1.541
C=C	$\beta_C^C = 1.700$		1.337
C≡C	$\beta_C^C = 2.840$		1.204
H—Ge	0.053	0.00	1.530
Cl—Ge	0.267	—1.146	2.210
C—Ge	$\beta_C^{Ge} = 0.500$ $\beta_{Ge}^C = 0.200$	$\alpha_{CGe} = 0.456$	1.992

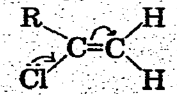
while the calculated and the experimental values are presented in Table 3. A zero value is chosen for γ_{HGe} in all cases.

Discussion

Examination of Table 3 reveals that in the case of alkylhalogermanes, substitution of chlorine for the alkyl group gives rise to a change in direction of the difference between the calculated and the observed moments, this being from +0.14 to —0.15 D from Me_2GeCl_2 to $MeGeCl_3$. In simple halogermanes both the electron releasing effect of the alkyl group and the $p_\pi - d_\pi$ back bonding effect contribute to the observed moment. The fact that the calculated moments are higher than the experimental values, suggests that the $p_\pi - d_\pi$ effect outweighs the other effect. But in the case of *gem*-alkylhalogermanes, the calculated moments are lower than the observed moments. This is probably due to the fact that the R_2Ge group is much more polarizable than the H_2O, H_2Si or R_2C groups. This suggests an increased contribution of the structure $H^+C{=}Ge^-$ in dialkyldihalogermanes. This is in line with the observations of Curran et al. [14] in the case of dihalodialkylsilanes.

The difference between the calculated and the experimental values in the case of dichlorodimethyl- and trichloromethyl-germanes (+0.14 and —0.15 D, respectively) can be attributed to the observation that a more electronegative outer group enhances the electronegativity of the central atom and hence decreases the effective radius [15]. Such substitutions must be expected to reduce the polarity of the metal—halogen bond. This is also in qualitative agreement with Gordy's expression for electronegativity and that successive substitutions of halogen decrease the effective radius of the central atom [16, 17].

In the case of $Me_3GeCH{=}CHCl$ and $Cl_3GeCH{=}CHCl$ the presence of geometrical isomers precludes an assessment of the above effects. For $Me_3GeCl{=}CH_2$, a mesomeric effect of the type shown:



can account for the fact that the experimental value is lower than that calculated (Table 3).

TABLE 2

FORMAL CHARGE DISTRIBUTIONS IN ORGANOGERMANIUM COMPOUNDS

Compound	H_1	C_1	Ge	C_2	H_2	C_3	H_3	Cl_1	Cl_2
H_3GeCl	0.0426		0.8037					0.9315	
H_2GeCl_2	0.0741		1.3970					0.7729	
H_3GeCH_3									
$H_2Ge(CH_3)_2$	−0.0254	0.1905	−0.4792		0.0248				
$HGe(CH_3)_3$	−0.0357	0.1701	−0.6726		0.0221				
H_3CGeCl_3	0.0533	0.4100	1.5920					−0.7209	
$(H_3C)_2GeCl_2$	0.0436	0.3352	0.8867					−0.9093	
$(H_3C)_3GeCl$	0.0325	0.2500	0.8820					−1.1240	
$(H_3CCH_2)GeCl_3$	0.0160	0.1227	1.5630	0.3602	0.0468			−0.7289	
$(H_3CCH_2)_2GeCl_2$	0.0129	0.0995	0.8347	0.2920	0.0380			−0.9232	
$(H_3C)_3GeCH_2Cl$	0.0223	0.1705	−0.6680	0.7342	0.0955			−0.9682	
Cl_3GeCH_2Cl	0.1205	0.9272	1.7230					−0.6862	−0.8315
$(H_3C)_3GeCCl{=}CH_2$	0.0216	0.1662	−0.7092	0.5995	0.0448	0.3443		−1.0160	
$(H_3C)_3GeCH{=}CHCl$	0.0208	0.1599	−0.7682	0.4058	0.0527	0.6157	0.0800	−1.0530	
$Cl_3GeCH{=}CHCl$	0.0775	0.5964	1.6401	0.7072	0.0919			−0.7082	0.9878
$(H_3C)_3GeC{\equiv}CH$	0.0196	0.1608	−0.8540	0.1245	0.0160	0.0890			
$H_3GeC{\equiv}CH$	−0.0144	0.1741	−0.2717	0.1246	0.0162				

TABLE 3

CALCULATED AND OBSERVED MOMENTS FOR SOME ORGANOGERMANIUM COMPOUNDS

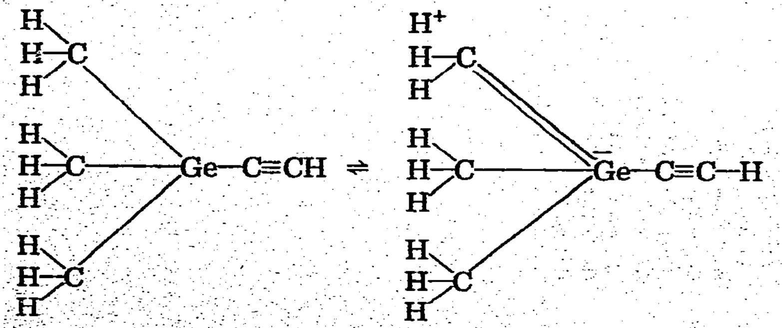
(Experimental values are taken from McClellan's tables [11]).

Compound	Dipole moment (D)		$D_{obs}-D_{calc.}$
	Obs.	Calc.	
H_3GeCl	2.06		
H_2GeCl_2	2.20	2.09	+0.11
$MeGeH_3$	0.64		
Me_2GeH_2	0.76	0.59	+0.17
Me_3GeH	0.67	0.55	+0.12
$MeGeCl_3$	2.63	2.79	−0.16
Me_2GeCl_2	3.11	2.97	+0.14
Me_3GeCl	2.90	3.21	−0.31
$EtGeCl_3$	2.87	2.92	−0.05
Et_2GeCl_2[a]	3.19	3.12	+0.07
		3.48	
		3.84	
Me_3GeCH_2Cl	1.85	2.03	−0.18
Cl_3GeCH_2Cl	2.10	2.32	−0.22
$Me_3GeCH{=}CHCl$[a]	1.86	1.98	
		2.20	
$Me_3GeCCl{=}CH_2$	1.82	2.28	−0.46
$Cl_3GeCH{=}CClH$[a]	1.86	0.72	
		3.87	
$H_3GeC{\equiv}CH$	0.14	0.84	−0.70
$Me_3GeC{\equiv}CH$	0.79	0.14	+0.65

[a] Rotational isomers are also considered.

In the case of germylacetylene, the difference between the calculated and the experimental moments (−0.70 D) can possibly be attributed to a mesomeric effect as follows:

From microwave studies, Thomas et al. [18] have suggested that a mesomeric effect of this type operates in this molecule. Trimethylgermylacetylene presents an interesting case. Here the difference between the calculated and experimental moments is positive, and the net moment acts in a direction opposite to that in the case of germylacetylene. A possible explanation is that a hyperconjugative effect arising from the three methyl groups probably outweighs other probable electromeric shifts. One of the possible hyperconjugative structures is:



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