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DIPOLE MOMENTS OF $(CH_3)_3MX$ COMPOUNDS WITH BONDS BETWEEN HALOGENS AND GROUP IVA ELEMENTS: EVIDENCE FOR $p_X \rightarrow d_M$ BONDING

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Summary

The electric dipole moments of the two series of molecules $(CH_3)_3MX$ with M = C, Si, Ge, Sn and Pb, and X = Cl and Br have been determined. The two carbon compounds show behaviour different from that of the others, and this is interpreted as indicating that $p_X \rightarrow d_M$ back-bonding is present for the other elements of the series, and it is suggested that the extent of this back-bonding decreases with an increase in the atomic number of M.

Introduction

Continuing our studies of molecules containing elements of Group IVA*, we report the dipole moments of the compounds $(CH_3)_3MX$ with M = C, Si, Ge, Sn and Pb, and X = Cl and Br. The aim was to obtain information on the group moments and examine the relationship between these and the bonding and electronegativity of the atoms concerned. Several of the compounds were examined in early work on dipole moments in solution [2], but those studies were confined to comparisons between compounds containing the same central atom M and, furthermore, were carried out by various authors using different extrapolation procedures. Since this led to inconsistent results, we have remeasured all the compounds under one set of conditions and have interpreted the data in a way very different from that of the previous authors.

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* We previously considered the electric dipole moments of the series of compounds $C_6H_5SM(CH_3)_3$ and $[(CH_3)_3M]_2S$, where M = C, Si, Ge, Sn, Pb [1].

Results and discussion

Table 1 lists the observed properties of the benzene solutions and Table 2 the dipole moments deduced together with the parameters used to calculate them. The reproducibility of the dipole moments is ± 0.02 D for M = C, Si and Ge, and ± 0.03 D for M = Sn and Pb. $(CH_3)_3PbBr$ could not be studied because of very low solubility in benzene.

It has been shown, by electron diffraction studies [3], that tetramethyl-silicon, -germanium, -tin and -lead compounds have tetrahedral structures. It thus seems reasonable to assume that, if distortion or other effects are absent, the experimental moment for the compounds $(CH_3)_3MX$ is the vector sum of the moments $\mu(\overrightarrow{\text{M—CH}_3})$ and $\mu(\overrightarrow{\text{M—X}})$. The fact that the experimental moments for triphenyl-bismuth and -antimony [4] and trimethylsilane [5] are small indicates that the contribution by $\mu(\overrightarrow{\text{M—CH}_3})$ is likely to be small. It may thus be

TABLE 1

PHYSICAL PROPERTIES OF BENZENE SOLUTIONS OF $(CH_3)_3MX$ COMPOUNDS

$W_2 \times 10^3$	ϵ_{12}	$V_{12}{}^a$	n_{12}^2	$W_2 \times 10^3$	ϵ_{12}	$V_{12}{}^a$	n_{12}^2
$(CH_3)_3CCl$				*$(CH_3)_3CBr$*			
0 69	2.2756	1.1446	2.2432	1.22	2.2768	1.1442	2.2430
1.79	2.2814	1.1446	2.2429	2.82	2.2829	1.1437	2.2428
2.90	2.2873	1.1446	2.2426	4.16	2.2881	1.1433	2.2426
4.17		1.1446	2.2422	5.67	2.2938	1.1429	2.2424
5.78	2.3026	1.1447	2.2418	7.60	2.3012	1.1423	2.2421
7.36	2.3110	1.1447	2.2413	9.21	2.3073	1.1418	
$(CH_3)_3SiCl$				*$(CH_3)_3SiBr$*			
0.71	2.2758	1.1440	2.2428	0.88	2.2750	1.1443	2.2430
2.00	2.2812	1.1441	2.2423	2.32	2.2799	1.1439	2.2426
3.15	2.2860	1.1440	2.2419	3.19	2.2828	1.1437	
4.28	2.2908		2.2415	4.19		1.1434	2.2421
5.42		1.1440	2.2411	5.41	2.2904	1.1431	2.2418
7.24	2.3032	1.1440	2.2404	7.12	2.2962	1.1426	2.2413
$(CH_3)_3GeCl$				*$(CH_3)_3GeBr$*			
0.73	2.2767	1.1440	2.2429	0.86	2.2756	1.1449	2.2430
1.98	2.2840	1.1437	2.2426	2.31	2.2826	1.1442	2.2429
3.16	2.2908	1.1434	2.2424	3.15	2.2866	1.1438	2.2428
4.04	2.2959	1.1432	2.2422	4.24	2.2919	1.1433	2.2428
5.50	2.3044	1.1428	2.2420	5.72	2.2990	1.1426	2.2427
7.23		1.1424	2.2416	7.09	2.3056		2.2426
$(CH_3)_3SnCl$				*$(CH_3)_3SnBr$*			
2.15	2.2871	1.1437	2.2429	0.97	2.2776	1.1434	2.2433
3.38	2.2959	1.1430	2.2429	2.38	2.2859	1.1426	2.2434
4.94	2.3070	1.1423	2.2430	3.45	2.2921	1.1419	2.2435
6.69	2.3195	1.1414	2.2429	5.46		1.1407	2.2435
8.35	2.3327	1.1405	2.2429	7.09	2.3133	1.1396	2.2436
				8.10	2.3192	1.1390	2.2437
$(CH_3)_3PbCl$							
0.54	2.2777	1.1443	2.2428				
1.32	2.2846	1.1437	2.2429				
2.05	2.2911	1.1432	2.2429				
2.84	2.2981	1.1427	2.2430				
3.90	2.3074	1.1420	2.2430				
5.02	2.3173	1.1412	2.2431				

[a] V_{12} in $cm^3\ g^{-1}$.

TABLE 2

OBSERVED DIPOLE MOMENTS OF $(CH_3)_3MX$ COMPOUNDS AND PARAMETERS USED IN CALCULATING THEM

Compound	ϵ_1	α	V_1 ($cm^3 g^1$)	β	n_1^2	γ	R_D (cm^3)	$P_{2\infty}$ (cm^3)	$\mu_{obs.}$ (D)	$\mu_{lit.}$ (D)
$(CH_3)_3CCl$	2.2720	5.300	1.1446	0.008	2.2434	−0.275	26.9	124.5	2.18	2.1 -- 2.17 [2a]
$(CH_3)_3CBr$	2.2722	3.820	1.1445	−0.294	2.2431	−0.137	30.5	133.1	2.24	2.23 [2b]
$(CH_3)_3SiCl$	2.2728	4.201	1.1440	0.000	2.2430	−0.350	29.9	122.8	2.13	2.09 [2c]
$(CH_3)_3SiBr$	2.2720	3.403	1.1445	−0.271	2.2432	−0.271	31.3	137.7	2.28	2.36 [2d]
$(CH_3)_3GeCl$	2.2725	5.800	1.1442	−0.255	2.2430	−0.194	34.3	207.5	2.91	
$(CH_3)_3GeBr$	2.2715	4.814	1.1453	−0.473	2.2430	−0.058	36.6	219.6	2.98	
$(CH_3)_3SnCl$	2.2718	7.137	1.1447	−0.501	2.2429	0.000	37.5	298.8	3.57	3.50 [2e]
$(CH_3)_3SnBr$	2.2720	6.834	1.1440	−0.620	2.2433	0.040	39.6	305.3	3.61	
$(CH_3)_3PbCl$	2.2730	8.841	1.1446	−0.680	2.2428	0.065	42.6	518 0	4.82	4.50 ± 0.15 [2f]

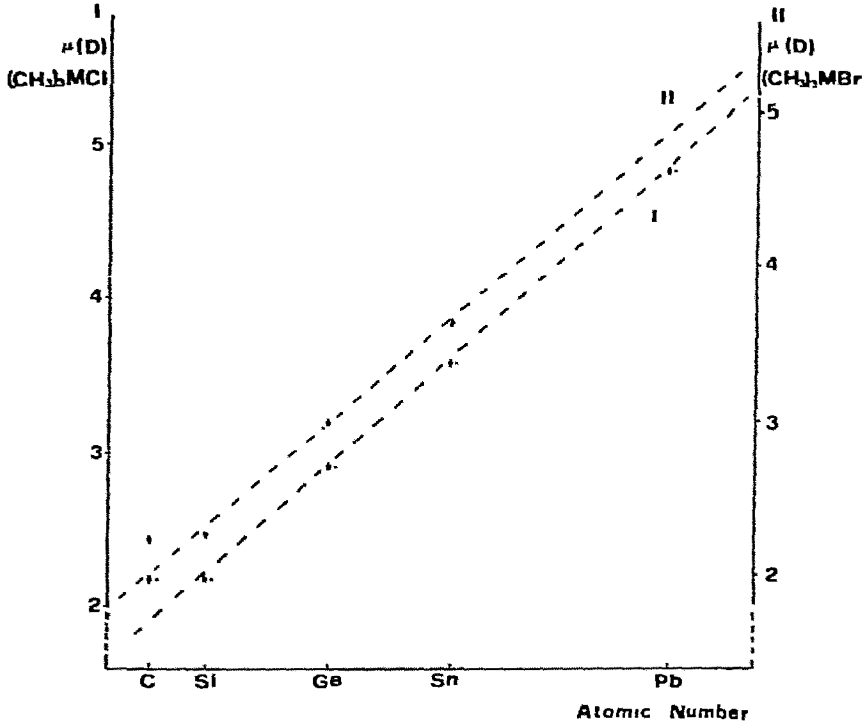

Fig. 1.

assumed that the variation in experimental dipole moment of the compounds under investigation, on going through each series from the carbon to the lead compound, is due mainly to variation in the bond moment $\mu(\overrightarrow{\text{M}-\text{X}})$. A plot of dipole moment against atomic number of M is shown in Fig. 1. From this it is seen that the chloro and bromo derivatives show similar behaviour. There is a virtually linear behaviour on going from silicon to lead whilst the moments of the two t-butyl derivatives are significantly above this line. These results cannot be explained solely in terms of differences in the electronegativity of the atoms M. It is possible that in the compounds with M = Si, Ge, Sn and Pb there is back-donation between the full *p* orbitals of the halogen and empty *d* orbitals of M. Thus an increase in moment from silicon to lead will then be due not only to the increase in the electron donor power, but also to the decrease in the acceptor power of M in the same sequence. In fact, for X = Cl and Br, the degree of overlap between the atomic orbitals involved in this back-bonding is more favourable for silicon and germanium than for tin and lead. The $p_X \rightarrow d_M$ bond must, of course, be absent in the two t-butyl compounds. This absence of a π-contribution would explain the fact that the experimental moments for the two carbon derivatives are of the same order as those for the silicon derivatives.

The dipole moments for the bromo derivatives are always greater than those for the chloro analogues. The reason for this is not clear. For tetramethylsilane and the trimethylsilicon halides it has been observed that chemical shifts decrease, and coupling constants (J) increase, in the order CH_3, F, Cl, Br, I [6]. This has been explained by assuming that there is a systematic decrease in the $p \rightarrow d$ bond between silicon and halogen, and that the extent of this decrease depends on the relative sizes of the atomic radii of the two atoms. Further measurements are in progress to clarify the nature of the bond between halogens and Group IV elements.

Experimental

Materials

t-Butyl-chloride and -bromide, trimethylchlorosilane, trimethylchlorotin and trimethylbromogermane were commercial products. They were purified by several distillations through a fractionating column packed with Fenske rings. The purity of the products was checked by NMR spectra or, where possible, by GLC on an SE 30 column at various temperatures. The remaining compounds were prepared as follows:

Trimethylbromosilane. This compound was prepared by the reaction of hexamethyldisiloxane with PBr_3 [7].

Trimethylchlorogermane. 2 g of commercial trimethylbromogermane and 1 g of dry, freshly prepared silver chloride were heated at ca. 100°C for 8 h in a sealed Carius tube. After this period the reaction mixture was washed with ether. Evaporation of the ether followed by distillation of the residue gave 0.7 g of trimethylchlorogermane [8], b.p. 114°C/760 mmHg.

Trimethylbromotin. This was obtained as previously described [9] in 80% yield by adding to tetramethyltin the stoichiometric amount of AR (analytical grade) bromine, dropwise and with stirring at 0°C. After 30 min at room temperature the reaction mixture was fractionated on a Vigreux column and the fraction with b.p. 165°C/760 mmHg collected.

Trimethyllead chloride. This was prepared by treating commercially available tetramethyllead with dry hydrochloric acid [10]. After recrystallization from ligroin, 5.2 g of trimethylchlorolead were obtained (m.p. 187-189°C) [11].

Trimethylbromolead. This was prepared as described in ref. 11.

Physical measurements

Measurements were performed at 25.0 ± 0.1°C. The apparatus and method used in calculating the electronic and total molar polarizations have been described previously [12]. Deaerated dry benzene was used.

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