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DIPOLE MOMENTS AND MOLECULAR CONFORMATIONS OF $C_6H_5SM(CH_3)_3$ AND RELATED MOLECULES WITH BONDS BETWEEN SULFUR AND GROUP IVA ELEMENTS

S. SORRISO
Institute of Physical Chemistry, University of Perugia (Italy)
A. FOFFANI
Institute of Chemistry "G. Ciamician", University of Bologna (Italy)
A. RICCI and R. DANIELI
CNR Laboratory of Carbon Compounds Containing Heteroatoms, Ozzano, Bologna, (Italy)
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Summary

The dipole moments of compounds of the four series $C_6H_5SM(CH_3)_3$, *m*- and *p*-$ClC_6H_4SM(CH_3)_3$, $[(CH_3)_3M]_2S$ (M = C, Si, Ge, Sn, Pb) have been measured. From them, the $C\hat{S}M$ and $M\hat{S}M$ bond angles and the $\mu[(CH_3)_3M—S]$ group moments have been estimated. The bond angles increase significantly from diphenyl sulfide to the compounds of the series $C_6H_5SM(CH_3)_3$ and $[(CH_3)_3M]_2S$, mainly due to the steric influence of the bulkier $(CH_3)_3M$ groupings. The above group moments, which point to the sulfur atom, rise markedly with the atomic number of the Group IVA element, indicating a growing electron releasing ability of the element M on going to Pb. From the results for the *meta* derivatives it is inferred that the phenyl ring in the asymmetric compounds is forced almost 90° out of the plane containing the CSM atoms; this rules out a phenyl—sulfur conjugative interaction.

Introduction

The present work concerns the estimation of the dipole moments of the four series of compounds $C_6H_5SM(CH_3)_3$, *m*- and *p*-$ClC_6H_4SM(CH_3)_3$, $[(CH_3)_3M]_2S$(M = C, Si, Ge, Sn, Pb). Data were available [1] only for some symmetric derivatives $[(CH_3)_3M]_2S$, whose moments have been redetermined for the sake of internal comparison. These measurements are aimed to give information on the following points: (*a*) Value and direction of the $[(CH_3)_3$-M—S] group moment, and its dependence on the nature of the Group IVA elements. The knowledge of the group moment direction, ill-defined on the basis of the available data [1], is important to estimate the relative electron-releasing ability of the M elements in the series, about which there is some uncertainty [2], and to give evidence for the possible intervention of $p_\pi - d_\pi$ bonding between the filled sulfur *p* orbitals and the empty *d* orbitals of the M elements [3]. This information should also prove useful in interpreting the formation observed for some of these sulfur compounds [4] of charge transfer complexes with molecular iodine in CCl_4 solution. (*b*) $C\hat{S}M$ and $M\hat{S}M$ bond angles. Their estimation should allow one to distinguish whether they depend mainly on the steric influence of the $(CH_3)_3M$ groupings, or if a possible change along the series of the type of hybridization at the sulfur atom plays some role. (*c*) Molecular conformation of the asymmetric compounds above. Since it is known [5] that in diphenyl sulfide steric reasons force both rings out of the plane containing the CSC moiety by about 40°, an even greater distortion of the ring is to be expected in the present aromatic compounds. On this basis, one should possibly detect electronic effects still active between the ring and the rest of the molecule [6].

Experimental

Materials

The commercial di-tert-butyl sulfide (Schuchardt) was redistilled before use. The hexamethyldisilthiane [7] and the corresponding Ge, Sn and Pb derivatives [8, 9] were prepared following the literature methods. The m.p. of the latter is 40 - 41° (lit. [8] 98 - 100°), even after several recrystallizations from light petroleum; however, the analytical data are in good agreement with the calculated figures and the NMR spectrum is identical to that previously reported [10].

The syntheses of trimethyl(phenylthio)silanes and stannanes have been performed by previously reported procedures [2c]. The trimethyl(phenylthio) substituted derivatives of germanium and lead have been prepared in the same way used for the unsubstituted compounds.

Purity of the compounds was checked by elemental analyses and ^1H NMR spectra. The physical properties, yields and elemental analyses are collected in

TABLE 1

PHYSICAL PROPERTIES, YIELDS AND ELEMENTAL ANALYSES FOR $XC_6H_4SM(CH_3)_3$ COMPLEXES

X	M	M.p. (°C) [B.p.(°C/mmHg)][a]	Yield (%)	Analysis found (calcd.) (%) C	H
H	Ge	[59 - 60/0.3]	57	[b]	
*m*Cl	Ge	[79 - 80/0.3]	51	41.50 (41.36)	5.2 (5.01)
pCl	Ge	[88 - 89/0.4]	58	41.29 (41.36)	5.1 (5.01)
H	Pb	[105 - 107/0.2]	62	[b]	
*m*Cl	Pb	[c]	53	27.97 (27.30)	3.40 (3.28)
*p*Cl	Pb	59 - 60[d]	47	27.43 (27.30)	3.30 (3.28)

[a] M.p.'s and b.p.'s are uncorrected. [b] See ref. 2b. [c] Decomposes by distillation. [d] Crystallized from light petroleum.

Table 1. The benzene used for physical measurements was deaerated by flushing with nitrogen. The dipole moment of each compound was measured immediately after purification. The compounds were stable during the measurements.

Physical measurements

They were performed at 25 ± 0.1° as previously reported [11]. The deformation polarization ($P_E + P_A$) was put equal to the molar refraction R_D and evaluated from refraction index measurements. The dielectric constants (ϵ_{12}), the specific volumes (V_{12}) and the squares of the solution refractive indexes (n_{12}^2) were linear functions of the solute weight fraction (W_2) over the concentration range investigated. They are reported in Table 2.

The parameters used in calculating the solute total polarization at infinite dilution ($P_{2\infty}$) and its molar refraction (R_D) were obtained by the Halver-

TABLE 2

MEASURED PROPERTIES OF BENZENE SOLUTIONS

$W_2 \times 10^3$	ϵ_{12}	V_{12} ($cm^3 \cdot g^{-1}$)	n_{12}^2	$W_2 \times 10^3$	ϵ_{12}	V_{12} ($cm^3 \cdot g^{-1}$)	n_{12}^2
p-$ClC_6H_4SC(CH_3)_3$				$C_6H_5SC(CH_3)_3$			
1.22	2.2751	1.1438	2.2439	1.37	2.2751	1.1439	2.2436
2.41	2.2770	1.1437		3.06		1.1438	2.2438
3.64	2.2790	1.1435	2.2441	4.25	2.2795	1.1437	
4.80	2.2808	1.1433	2.2442	5.63	2.2816	1.1436	2.2441
6.00	2.2828	1.1431	2.2443	7.01	2.2837	1.1434	2.2442
7.91	2.2858	1.1428	2.2444	8.44	2.2859	1.1433	2.2444
$[(CH_3)_3C]_2S$				$C_6H_5SSi(CH_3)_3$			
1.22	2.2739	1.1445	2.2424	0.77	2.2734	1.1442	2.2435
2.12	2.2753	1.1446	2.2422	1.76	2.2753	1.1441	2.2436
3.93	2.2778	1.1448	2.2418	2.81	2.2774	1.1440	2.2438
5.77	2.2803	1.1451	2.2413	4.44	2.2805	1.1439	2.2439
8.11	2.2837	1.1454	2.2407	5.68	2.2829	1.1438	2.2440
9.00	2.2850	1.1455	2.2405	8.34	2.2880	1.1436	2.2443
p-$ClC_6H_4SSi(CH_3)_3$				m-$ClC_6H_4SSi(CH_3)_3$			
1.55	2.2754	1.1439	2.2435	1.03	2.2728	1.1442	2.2433
3.23	2.2788	1.1436	2.2436	2.24	2.2761	1.1438	2.2436
4.90	2.2821	1.1432	2.2437	3.12	2.2785	1.1436	2.2437
6.54	2.2854	1.1429	2.2438	4.61	2.2826	1.1432	2.2440
7.61	2.2875	1.1427	2.2439	5.58	2.2852	1.1429	2.2442
9.03	2.2903	1.1424	2.2439	7.22	2.2898	1.1427	2.2444
$[(CH_3)_3Si]_2S$				$C_6H_5SGe(CH_3)_3$			
0.41	2.2735	1.1445	2.2440	1.02	2.2749	1.1438	2.2442
2.10	2.2762	1.1446	2.2437	2.98	2.2795	1.1432	2.2446
4.05	2.2795	1.1447	2.2435	4.23	2.2825	1.1428	2.2448
5.61	2.2822	1.1448	2.2433	6.23	2.2873	1.1422	2.2452
7.40	2.2852	1.1449	2.2430	7.05	2.2892		2.2454
9.37	2.2886	1.1450	2.2428	8.49		1.1415	2.2456
p-$ClC_6H_4SGe(CH_3)_3$				m-$ClC_6H_4SGe(CH_3)_3$			
1.35	2.2760	1.1436	2.2430	1.51	2.2770	1.1444	2.2432
2.35	2.2786	1.1432	2.2432	2.98	2.2815	1.1439	2.2435
3.58	2.2818	1.1428	2.2434	5.62	2.2895	1.1431	2.2439
4.88	2.2852	1.1423	2.2436	6.44	2.2919	1.1428	2.2440
6.39	2.2892	1.1418	2.2439	8.06	2.2968	1.1423	2.2443
7.90	2.2931		2.2442	9.25	2.3004	1.1419	2.2445

(continued)

TABLE 2 (continued)

$W_2 \times 10^3$	ϵ_{12}	v_{12} ($cm^3 \cdot g^{-1}$)	n^2_{12}	$W_2 \times 10^3$	ϵ_{12}	v_{12} ($cm^3 \cdot g^{-1}$)	n^2_{12}
$[(CH_3)_3Ge]_2S$				$C_6H_5SSn(C_6H_5)_3$			
1.47	2.2746	1.1436	2.2440	1.09	2.2744	1.1439	2.2434
3.05	2.2776	1.1430	2.2440	1.85	2.2757	1.1435	2.2437
4.20	2.2798	1.1427	2.2440	3.53	2.2783	1.1428	2.2444
5.50	2.2822	1.1422	2.2440	4.78	2.2803	1.1423	2.2449
7.03	2.2851	1.1418	2.2440	6.32	2.2828	1.1416	2.2455
9.21	2.2893	1.1411	2.2440	8.05	2.2855	1.1409	2.2462
$C_6H_5SSn(CH_3)_3$				p-$ClC_6H_4SSn(CH_3)_3$			
1.20	2.2758	1.1439	2.2435	0.80	2.2752	1.1441	2.2436
2.49	2.2793	1.1434	2.2436	2.64	2.2809	1.1433	2.2438
3.89	2.2832	1.1429	2.2438	3.85	2.2847	1.1427	2.2440
4.88	2.2859	1.1425	2.2439	5.52	2.2899	1.1420	2.2442
6.97	2.2916	1.1417	2.2441	7.14	2.2949	1.1413	2.2445
9.05	2.2973	1.1409	2.2443	8.91	2.3004	1.1405	2.2447
m-$ClC_6H_4SSn(CH_3)_3$				$[(CH_3)_3Sn]_2S$			
1.25	2.2770	1.1435	2.2438	2.04	2.2774	1.1430	2.2438
2.70	2.2818	1.1428	2.2440	3.91	2.2814	1.1420	2.2440
4.02	2.2861	1.1422	2.2441	5.75	2.2854	1.1411	2.2442
5.40	2.2906	1.1416	2.2443	7.20	2.2885	1.1404	2.2443
7.00	2.2959	1.1408	2.2446	8.12	2.2905	1.1399	2.2444
8.31	2.3001	1.1402	2.2447	9.84	2.2942	1.1390	2.2446
$C_6H_5SPb(CH_3)_3$				p-$ClC_6H_4SPb(CH_3)_3$			
1.19	2.2770	1.1432	2.2449	0.84	2.2757	1.1437	2.2436
2.40	2.2811	1.1425	2.2453	2.11	2.2806	1.1429	2.2438
3.56	2.2850	1.1417	2.2456	3.95	2.2877	1.1418	2.2440
5.17	2.2905	1.1416	2.2462	4.82	2.2911	1.1413	2.2442
6.90	2.2964	1.1395	2.2467	6.71	2.2984	1.1402	2.2446
8.36	2.3013	1.1386	2.2472				
m-$ClC_6H_4SPb(CH_3)_3$				$[(CH_3)_3Pb]_2S$			
1.42	2.2786	1.1433	2.2441	1.52	2.2758	1.1430	2.2440
2.63	2.2839	1.1425	2.2443	2.84	2.2784	1.1420	2.2441
3.89	2.2894	1.1417	2.2446	3.67	2.2801	1.1413	2.2442
5.06	2.2945	1.1409	2.2449	5.21	2.2831	1.1402	2.2443
6.20	2.2994	1.1402	2.2451	7.46	2.2876	1.1384	2.2445
7.53	2.3052	1.1393	2.2454	8.90	2.2905		2.2446

stadt—Kumler method [12]. They are collected in Table 3 with the observed dipole moments, which were reproducible to ± 0.02 D, except for $[(CH_3)_3Pb]_2S$ (± 0.03 D).

Results and discussion

Group moments and bond angles

The $\mu[(CH_3)_3M—S]$ group moments previously reported [1b] were obtained in two different ways. (*i*) For M = Si and Ge they were estimated from the corresponding symmetrical molecules $[(CH_3)_3M]_2S$, assuming 97 and 108°, respectively, for the Si$\hat{S}$Si and Ge$\hat{S}$Ge bond angles. These were found for disilthiane by electron diffraction [13] and for digermthiane by IR and Raman [14] data; (*ii*) for M = C and Si they were deduced from the asymmetrical aliphatic compounds $CH_3SM(CH_3)_3$, assuming 99° for the C$\hat{S}$M bond angle and 1.12 D for the $\mu(CH_3—S)$ group moment both taken from data for dimethyl sulfide [1b, 15]. These assumptions do not seem altogether reliable, because (*i*), they do not account for possible steric interactions* between the two trimethyl groupings or between one of them and a methyl group, respectively, in the two classes of compound; (*ii*), they do not allow a meaningful internal comparison of the group moments, owing to the different origin of the bond angles employed for their estimation. In the method we used to evaluate the $C\hat{S}M$ bond angles and the $\mu[\overrightarrow{(CH_3)_3M-S}]$ group moments, the only assumption made is that the $\mu(C_6H_5-S)$ group moment can be transferred from diphenyl sulfide to the asymmetrical compounds $C_6H_5SM(CH_3)_3$**.

For $\mu(\overrightarrow{C_6H_5-S})$ a value of 1.3 D was used, as obtained from the moment observed for diphenyl sulfide (1.55 D) [16]; for the angle $C\hat{S}C$ a figure of 109°, as found for *p,p'*-dibromodiphenyl sulfide [5a, 17] was taken. $\overleftarrow{\mu(p\text{-}ClC_6H_4-S)}$ was assumed to be 0.3 D, by combining the moment above with that observed for chlorobenzene (1.59D) [18]. The following equations can be written:

$$\mu^2(\mathrm{I}) = \mu^2(C_6H_5-S) + \mu^2[(CH_3)_3M-S] + 2\mu(C_6H_5-S)\cdot\mu[(CH_3)_3M-S]\cdot\cos\theta$$

$$\mu^2(\mathrm{II}) = \mu^2(p\text{-}ClC_6H_4-S) + \mu^2[(CH_3)_3M-S] + 2\mu(p\text{-}ClC_6H_4-S)\mu[(CH_3)_3M-S]\cdot\cos(180°-\theta)$$

where μ(I) and μ(II) are the moments observed for $C_6H_5SM(CH_3)_3$ and p-$ClC_6H_4SM(CH_3)_3$, respectively. The acceptable solutions for this homogeneous system of the fourth degree, are reported in Table 4.

The $\mu[\overrightarrow{(CH_3)_3M-S}]$ group moments point in every case to the sulfur atom, and they are significantly higher than those previously reported [1b]. This is mainly due to the present choice of the $C\hat{S}M$ and $M\hat{S}M$ bond angles, higher than those previously assumed***. The substitution of phenyl for methyl should not appreciably influence these angles; this is apparent, e.g. from the behavior of the Si—S stretching frequency, which does not vary on going from $CH_3SSi(CH_3)_3$ to $C_6H_5SSi(CH_3)_3$ (461 and 459 cm^{-1}, respectively) [19].

As with the previous ones [1b], the new set of group moments shows a speedy increase with the atomic number of the group IVA element (see Table 4 and Fig. 1) †. Such behavior cannot be explained on the basis of the electronegativity change of M along the series alone (the values are 2.60, 1.90, 2.00, 1.95 and 2.45, respectively, for C, Si, Ge, Sn and Pb) [24]. Rather it points to a continuous increase of the electron releasing ability of the element M on going towards Pb††. This agrees fairly well with recent mass spectrometric

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[*] The dipole moments of $(CH_3)_2S$, $CH_3SC(CH_3)_3$ and $[(CH_3)_3C]_2S$ (1.45, 1.56 and 1.57 D, respectively, measured under the same experimental conditions) [1a] show that the steric influence of the tert-butyl groups significantly increases the $C\hat{S}C$ angle.

[**] This is correct for the first terms in the series, while for the last ones the group moments so estimated might be slightly lower than the effective ones; this is due to a prevailing inductive effect of the trimethyl grouping on the rest of the molecule (see below), only partially counterbalanced by its increased steric effect.

[***] Compare, e.g. the figure 99° cited above for the $C\hat{S}Si$ angle used in ref. 1b in the aliphatic compound $CH_3SSi(CH_3)_3$, with the value 114° presently estimated for the aromatic derivative $C_6H_5SSi(CH_3)_3$.

[†] The same trend is followed by, e.g. the structurally related chlorinated molecules $ClM(CH_3)_3$: (M, μ(D)): C, 1.96 - 2.1 [20]; Si, 2.09 [21]; Sn, 3.50 [22]; Pb, 4.50 [23].

[††] It is noteworthy, as from preliminary data [4], that the symmetrical carbon compound $[(CH_3)_3C]_2S$ shows evidence for the formation of a charge transfer complex with molecular iodine in anhydrous CCl_4 solution. Under the same conditions, no such evidence has been obtained so far with the compounds $C_6H_5SSi(CH_3)_3$, $[(CH_3)_3Ge]_2S$ and $C_6H_4SSn(CH_3)_3$. The absence in these cases of residual iodine suggests a rupture of the S—M bond, in agreement with its decreased bond dissociation energy [25].

TABLE 3

OBSERVED DIPOLE MOMENTS, AND THE PARAMETERS USED IN CALCULATION

Compound	ϵ_1	α	V_1 (cm^3·g^{-1})	β	n_1^2	γ	R_D(cm^3)	$P_{2\infty}$(cm^3)	μ(D)[a]	μ(D)[b]
$C_6H_5SC(CH_3)_3$	2.2730	1.528	1.1440	−0.085	2.2435	0.110	55.2	100.5	1.49	
p-$ClC_6H_4SC(CH_3)_3$	2.2732	1.600	1.1440	−0.157	2.2438	0.077	60.9	119.4	1.69	
$[(CH_3)_3C]_2S$	2.2722	1.426	1.1443	0.128	2.2427	−0.250	47.5	94.6	1.52	1.57[c]
$C_6H_5SSi(CH_3)_3$	2.2720	1.922	1.1442	−0.075	2.2435	0.102	60.8	124.3	1.76	
p-$ClC_6H_4SSi(CH_3)_3$	2.2724	1.991	1.1442	−0.200	2.2435	0.053	62.2	142.0	1.97	
m-$ClC_6H_4SSi(CH_3)_3$	2.2700	2.747	1.1444	−0.240	2.2432	0.186	65.1	170.4	2.26	
$[(CH_3)_3Si]_2S$	2.2727	1.696	1.1445	0.055	2.2440	−0.136	58.1	120.5	1.75	1.85[d]
$C_6H_5SGe(CH_3)_3$	2.2725	2.379	1.1441	−0.307	2.2440	0.199	64.2	160.6	2.18	
p-$ClC_6H_4SGe(CH_3)_3$	2.2725	2.619	1.1440	−0.345	2.2428	0.177	70.1	190.9	2.43	
m-$ClC_6H_4SGe(CH_3)_3$	2.2725	3.024	1.1448	−0.316	2.2430	0.168	71.8	213.0	2.63	
$[(CH_3)_3Ge]_2S$	2.2718	1.901	1.1440	−0.323	2.2440	0.000	64.3	161.0	2.18	2.15[d]
$C_6H_5SSn(C_6H_5)_3$	2.2728	1.580	1.1443	−0.430	2.2430	0.407	131.6	208.3	1.94	
$C_6H_5SSn(CH_3)_3$	2.2725	2.750	1.1443	−0.380	2.2434	0.104	66.5	203.3	2.58	
p-$ClC_6H_4SSn(CH_3)_3$	2.2728	3.100	1.1444	−0.445	2.2435	0.141	71.2	243.2	2.90	
m-$ClC_6H_4SSn(CH_3)_3$	2.2730	3.270	1.1440	−0.460	2.2436	0.140	69.7	251.5	2.98	
$[(CH_3)_3Sn]_2S$	2.2730	2.162	1.1440	−0.509	2.2436	0.102	73.9	214.9	2.62	
$C_6H_5SPb(CH_3)_3$	2.2730	3.391	1.1440	−0.653	2.2445	0.326	74.4	283.4	3.20	
p-$ClC_6H_4SPb(CH_3)_3$	2.2725	3.864	1.1442	−0.610	2.2434	0.212	77.8	350.8	3.65	
m-$ClC_6H_4SPb(CH_3)_3$	2.2725	4.351	1.1442	−0.655	2.2438	0.222	78.3	385.7	3.88	
$[(CH_3)_3Pb]_2S$	2.2728	1.991	1.1441	−0.767	2.2439	0.077	76.6	298.8	3.08	

[a] This work. [b] Literature values for benzene solutions. [c] Ref. 1a. [d] Ref. 1b.

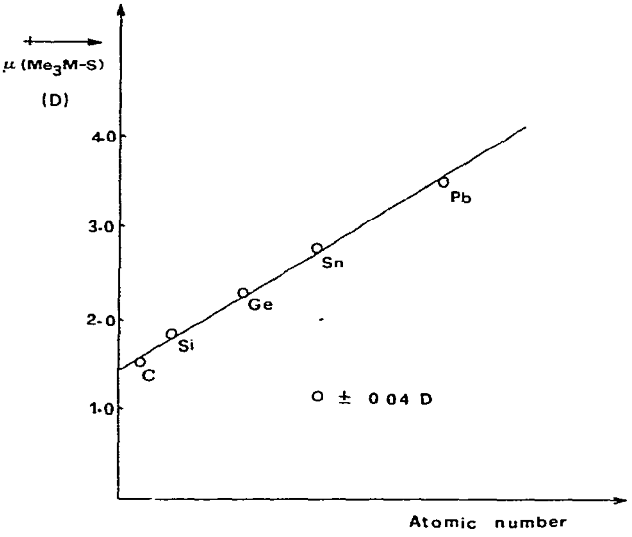
TABLE 4

ANGLES (°) AND GROUP DIPOLE MOMENTS (D)

Compound	$C\hat{S}M$ and $M\hat{S}M$ angles	$\mu[\overrightarrow{(CH_3)_3M—S}]$		
		This work	Literature	
$C_6H_5SC(CH_3)_3$	116	1.53	1.28[a]	
$C_6H_5SSi(CH_3)_3$	114	1.83	1.44	1.44[b]
$C_6H_5SGe(CH_3)_3$	113	2.30		1.67
$C_6H_5SSn(CH_3)_3$	112	2.77		
$C_6H_5SPb(CH_3)_3$	114	3.50		
$[(CH_3)_3C]_2S$	120			
$[(CH_3)_3Si]_2S$	122			
$[(CH_3)_3Ge]_2S$	123			
$[(CH_3)_3Sn]_2S$	124			
$[(CH_3)_3Pb]_2S$	128			

[a] From $CH_3SM(CH_3)_3$. [b] From $[(CH_3)_3M]_2S$.

results [25] which show for the asymmetrical and symmetrical compounds used, a systematic decrease of the molecular ionization potentials on going from Si to Pb, with higher values in the symmetrical series. Correspondingly, the neutral S—M bond dissociation energies decrease continuously from C to Pb in the asymmetrical series, roughly reflecting the varied tendency of these molecules to interact with electron acceptors to give charge transfer complexes (see footnote above). The singular behavior of the ionization potentials of the carbon compounds, which reflects a superposed $p_\pi—d_\pi$ contribution to the S—M bond from Si to Pb, is not revealed in the trend of the group moments. This might be due to a lower sensitivity, in the present cases, of the group moments to the mesomeric effect, which anyhow should play a minor role in comparison with the inductive one. Parallel indications [2a, b] come from IR, NMR and kinetic data. On the other hand, electron spectroscopy results in the



solid state [2d] point to a decrease of the global electron density at the sulfur atom on going towards Pb in the asymmetric series. This supports the existence of some π character at the S—M bond, likely to cause the electron distribution at that bond to have its maximum somewhere between the S and M atoms.

The $M\hat{S}M$ bond angles reported in Table 3 were estimated by transferring to the symmetrical compounds $[(CH_3)_3M]_2S$ the group moments obtained above. It is apparent that some steric hindrance exists between the trimethyl groupings; it grows, as expected, with the atomic number of M.

Molecular conformation of the aromatic compounds

Vector analysis of the *m*-Cl derivatives of $C_6H_5SM(CH_3)_3$ shows, as the most reliable alternative, that in these molecules the phenyl ring should be forced by about 100° and 95°, respectively for M = Si and Ge, Sn, Pb, out of the plane containing the CSM moiety, assuming a 0° value when the chlorine atom is in *cis* position to the trimethyl grouping. In these conditions any steric or dipolar field interaction between the Cl atom and the $M(CH_3)_3$ grouping should be minimized. The same situation should be active in the unsubstituted asymmetric compounds $C_6H_5SM(CH_3)_3$ and in their *p*-Cl derivatives. As a consequence, the phenyl—sulfur mesomeric interaction should be almost absent, leaving only the possibility of inductive perturbations on the sulfur atom from substituents in the phenyl ring.

Such a molecular conformation agrees with the observed variation of the angle at the sulfur atom on going from diphenyl sulfide (109° $C\hat{S}C$ angle assumed here) to $C_6H_5SM(CH_3)_3$ (116, 114, 113, 112, and 114°, respectively for M = C, Si, Ge, Sn and Pb) and to $[(CH_3)_3M]_2S$ (120, 122, 123, 124 and 128°). In fact, the first trimethyl grouping takes the place of a phenyl ring rotated for steric reasons in diphenyl sulfide by about 36—46° [5] out of the CSC plane; so it does not contribute much additional angular deformation at the sulfur atom; in agreement with the fact (see above) that the residual phenyl ring arranges itself much more rotated out of that plane, i.e., in a condition of minimum steric hindrance. Now, the introduction of a second trimethyl grouping must cause, particularly for M = Sn and Pb, a much greater angular deformation at the sulfur atom, since it is not possible to release its steric hindrance in any other way.

The conformational alternative involving the phenyl ring almost coplanar to the CSM molecular moiety is, for the reasons above, structurally less valid*, although it cannot be ruled out on the basis of dipole moment data alone.

References

1 (a) C.W.N. Cumper, J.F. Read and A.I. Vogel, J. Chem. Soc., (1965) 5323.
(b) C.W.N. Cumper, A. Melnikoff and A.I. Vogel, J. Chem. Soc. A, (1966) 246.
2 (a) R.W. Bott, C. Eaborn and D.R.M. Walton, J. Organometal. Chem., 2 (1964) 154.
(b) O.J. Scherer and M. Schmidt, J. Organometal. Chem., 1 (1964) 490.
(c) G. Pirazzini, R. Danieli, A. Ricci and C.A. Boicelli, J. Chem. Soc., to be published.
(d) S. Pignataro, L. Lunazzi, C.A. Boicelli, R. Di Marino, A. Ricci, A. Mangini and R. Danieli, Tetrahedron Lett., 52 (1972) 5341.

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* See, e.g. ref. 5c for theoretical reasons favoring phenyl rotation rather than $C\hat{S}C$ angle deformation in diphenyl sulfide.

(e) C.J. Attridge, Organometal. Chem. Rev. Sect. A, 5 (1970) 323 and references therein; P.M. Kuznesoff, F.B.T. Pessini and R.E. Bruns, J. Amer. Chem. Soc., 94 (1972) 9087; A.J. Smith, W. Adcock and W. Kitching, J. Amer. Chem. Soc., 92 (1970) 6140.

3 E.W. Abel and D.A. Armitage, in Advances in Organometallic Chemistry, Vol. 2, 1965, p. 1, and references therein.

4 S. Sorriso and S. Santini, unpublished results from this laboratory.

5 (a) W.R. Blackmore and S.C. Abrahams, Acta Crystallogr., 8 (1955) 329.
(b) R.J.W. Le Fèvre and J.D. Saxby, J. Chem. Soc. B, (1966) 1064.
(c) V. Galasso, G. De Alti and A. Bigotto, Tetrahedron, 27 (1971) 6151.

6 R. Danieli and A. Ricci, J.Chem. Soc., Perkin II, in press.

7 E.W. Abel, J. Chem. Soc., (1961) 4933.

8 E.W. Abel, D.A. Armitage and D.B. Brady, Trans. Faraday Soc., 62 (1966) 3459.

9 T. Haroda, Bull. Chem. Soc. Japan, 17 (1942) 281.

10 E.W. Abel and D.B. Brady, J. Organometal. Chem., 11 (1968) 145.

11 S. Sorriso, G. Cardaci and S.M. Murgia, Z. Naturforsch. B, 27 (1972) 1316.

12 I.F. Halverstadt and W.D. Kumler, J. Amer. Chem. Soc., 64 (1942) 2988.

13 A. Almenningen, K. Hedberg and R. Seip, Acta Chem. Scand., 17 (1963) 2264.

14 J.D. Goldfarb and S. Sujishi, J. Amer. Chem. Soc., 86 (1964) 1679.

15 L. Pierce and M. Hayashi, J. Chem. Phys., 35 (1961) 479.

16 J. De Vries and W.H. Rodebush, J. Amer. Chem. Soc., 53 (1931) 2888; M. Gomel, N. Marziano and R. Passerini, Bull. Soc. Chim. France, (1959) 1908; C.W.N. Cumper, J.F. Read and A.I. Vogel, J. Chem. Soc., (1965) 5860.

17 J. Toussaint, Helv. Chim. Acta, 28 (1945) 1233; Bull. Soc. Chim. Belg. 13 (1944) 111.

18 A.L. McClellan, Tables of Experimental Dipole Moments, W.H. Freeman and Co., San Francisco and London, 1963.

19 K.A. Hoaton and A.L. Allred, Inorg. Chem., 4 (1965) 671.

20 G.R. Paranjpe and M.B. Vijidar, Ind. J. Phys., 20 (1946) 197; A.E. Van Arkel, Rec. Trav. Chim. Pays-Bas, 52 (1933) 719.

21 K. Schaarschmidt, Z. Anorg. Allg. Chem., 310 (1961) 78.

22 E.G. Klays, G.P. Van der Kelen and Z. Eeckhaut, Bull. Soc. Chim. Belg. 70 (1961) 462.

23 G.L. Lewis, P.F. Oesper and C.P. Smyth, J. Amer. Chem. Soc., 62 (1940) 3243.

24 A.L. Allred and E.G. Rochow, J. Inorg. Nucl. Chem., 5 (1958) 269.

25 G. Distefano, A. Ricci, R. Danieli, A. Foffani, G. Innorta and S. Torroni, J. Organometal. Chem., 65 (1974) 205.