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X-RAY DIFFRACTION STUDY OF THE BONDING BETWEEN SULPHUR AND THE ELEMENTS OF GROUP IVB. THE CRYSTAL AND MOLECULAR STRUCTURES OF METHYLTHIOTRIPHENYL-METHANE, -SILICON, -GERMANIUM, -TIN AND -LEAD

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Summary

The X-ray analyses of the compounds methylthiotriphenyl-methane, -silicon, -germanium, -tin, and -lead were undertaken to see if the electronic interactions which affect the X–S bond could influence the molecular geometries. The five structures were solved or by direct methods or by Patterson and Fourier techniques and refined anisotropically to $R = 0.053$, 0.036, 0.031, 0.041, and 0.070 respectively. The central atom exhibits a distorted tetrahedral coordination; only the propeller shape orientation of the phenyl rings seems to be determined by differences in the electronic nature of the central atoms as well as by steric effects.

Introduction

The nature of the S–X bond (where X is Si, Ge, Sn, or Pb) has been investigated by UV [1], ^{13}C NMR, and ESCA spectroscopy [2], by electric dipole measurements [3,4], by kinetic studies [5,6], by UV and UV PE spectroscopy [7,8], by ionisation energie measurements [9], by mass spectrometry techniques [10] and by X-ray single crystal diffraction methods [11–13]. In an attempt to rationalize the features of various experimental properties, a perturbational molecular orbital treatment of hyperconjugation has been applied together with CNDO/2 calculations [14]. Some of the results were imprecise because of uncertainty about the conformation of the molecules; these were assumed in some cases on the basis of a combination of PE data and the results of CNDO/2 calculations [8], and in others they were selected to provide agreement with data for the carbon compounds [4]. The studies of UV photoelectron spectra [7] and of ionisation energies [9] showed that the replacement of a CH_3 group attached to S atom by a phenyl group did not influence the interactions between the S and the XR_3 group and, thus that the variation in the degree of p_π–d_π bonding between sulphur and the Group IVB elements is a direct consequence of the interaction of the filled *p* orbital of sulphur with the XC_3 orbitals (hyperconjugation) and with the empty *d* orbitals of X ($(p-d)_\pi$ interaction). In order to see whether this variation could be detected also in the solid state, an X-ray diffraction study of the compound $MeSXPh_3$ (X = C, Si, Ge, Sn, or Pb) was undertaken.

Experimental

Collection and reduction of X-ray data

Cell parameters, crystal and experimental data for the five $MeSXPh_3$ compounds are given in Table 1.

Preliminary cell parameters obtained by rotation and Weissenberg photographs were refined by least-squares fit to $(\theta,\chi,\phi)_{hkl}$ values of few reflections [10–15] carefully measured on a Siemens AED single crystal diffractometer. These parameters were further refined using a local version of the program CELFIT.

The reflections were measured at room temperature using the ω-2θ scanning method and the "five point" technique [15] with Zr-filtered Mo-K_α radiation. No absorption corrections were applied for compounds I and IV, but the data for the

TABLE 1

CRYSTAL PARAMETERS AND EXPERIMENTAL DATA OF COMPOUNDS I–V

	I	II	III	IV	V
Formula	$C_{20}H_{18}S$	$C_{19}H_{18}SiS$	$C_{19}H_{18}GeS$	$C_{19}H_{18}SnS$	$C_{19}H_{18}PbS$
a (Å)	27.619(6)	10.406(5)	10.422(5)	9.744(5)	9.651(5)
b (Å)	7.562(3)	9.625(5)	9.641(5)	18.866(9)	19.077(9)
c (Å)	7.535(3)	9.107(5)	9.118(5)	9.915(6)	9.895(6)
α (°)	90.0	81.3(1)	81.3(1)	90.0	90.0
β (°)	90.0	98.0(1)	97.8(1)	106.1(1)	106.8(1)
γ (°)	90.0	70.6(1)	71.1(1)	90.0	90.0
V (Å^3)	1573.5	832.9	839.9	1751.4	1744.0
Space group	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
W	290.4	306.5	351.0	396.5	485.6
D_c (g cm^{-3})	1.24	1.22	1.39	1.50	1.85
λ	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α
Z	4	2	2	4	4
μ (cm^{-1})	1.58	2.15	18.62	14.40	94.03
Final *R*	0.053	0.036	0.030	0.041	0.070
Temperature (°C)	23	23	23	23	23
Scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
Scan rate (° min^{-1})	$0.01/4.10^{-3}$	$0.01/8.10^{-3}$	$0.01/8.10^{-3}$	$0.01/4.10^{-3}$	$0.01/4.10^{-3}$
$\theta_{min}-\theta_{max}$ (°)	0–28	0–45	0–45	0–28	0–28
No reflections collected	2202	13563	13687	4096	11334 [a]
No reflections with $I > 2\sigma(I)$	1375	3488	3758	2047	1779
Solvent of crystallisation	chloroform	petroleum ether	n-hexane	petroleum ether	n-hexane
Forms		{1 0 0} {0 1 0} {0 0 1}	{1 0 0} {0 1 0} {0 0 1}		{1 1 0} {1 −1 0} {0 1 0} {−1 0 1}

[a] See Experimental.

other three were corrected using the SHELX program [16]. The data for compounds II and III were collected with special care: (a) the best crystal–pinhole distance of the collimator of the detector was determined in order to avoid the errors due to the tube characteristics, the collimation system, the mosaic dispersion of the crystal and the dispersion due to the separation α_1–α_2 of the employed radiation; (b) the count statistics were improved by increasing the scan rate to $8-10^{-3}$ min for 0.01° of θ. Collection of the experimental data for compound V required the use of six crystals that were used successively as a standard reflection, checked every 24 reflections, showed that the crystal had significantly deteriorated; the several sets of reflections were then combined by use of the SHELX program [16].

TABLE 2

ATOMIC COORDINATES ($\times 10^4$) FOR COMPOUND I

Atom	x/a	y/b	z/c
C(C)	1410(4)	6835(13)	5258(12)
S	1892(1)	5586(4)	6418(3)
C(1)	1090(3)	5628(14)	4102(12)
C(2)	873(5)	6265(22)	2564(17)
C(3)	547(5)	5290(24)	1629(19)
C(4)	424(5)	3624(21)	2214(24)
C(5)	644(5)	2952(21)	3679(27)
C(6)	964(4)	3935(18)	4606(20)
C(11)	1701(3)	8020(12)	3994(13)
C(12)	2025(3)	7241(14)	2783(14)
C(13)	2291(4)	8284(16)	1679(17)
C(14)	2235(4)	10108(16)	1625(16)
C(15)	1916(4)	10847(15)	2807(14)
C(16)	1654(4)	9834(13)	3963(14)
C(21)	1104(3)	7870(11)	6585(13)
C(22)	1330(4)	8900(15)	7855(13)
C(23)	1051(5)	9876(15)	9039(15)
C(24)	565(5)	9780(16)	9025(15)
C(25)	339(4)	8762(20)	7770(16)
C(26)	613(4)	7816(14)	6584(14)
CM	1630(4)	4777(15)	8444(15)
H(2)	815(51)	7289(152)	2634(193)
H(3)	363(38)	5669(154)	718(136)
H(4)	258(37)	2958(142)	1569(145)
H(5)	552(63)	1760(244)	3985(232)
H(6)	1111(34)	3739(123)	5614(122)
H(12)	2181(24)	5765(114)	2913(93)
H(13)	2444(44)	7837(146)	682(165)
H(14)	2425(35)	10768(141)	895(136)
H(15)	1887(28)	12132(104)	2850(99)
H(16)	1412(29)	10208(106)	4597(101)
H(22)	1716(35)	9064(134)	7860(127)
H(23)	1227(26)	10386(102)	9773(96)
H(24)	429(30)	10604(129)	9809(116)
H(25)	−1(34)	8641(109)	7934(111)
H(26)	458(31)	7058(112)	5855(105)
HM(1)	1867(4)	3881(15)	9154(15)
HM(2)	1315(4)	4060(15)	7971(15)
HM(3)	1514(4)	5825(15)	9329(15)

Solution and refinement of the structures

Compound I. The data were put on an absolute scale by Wilson's method [17] and normalized structure factors amplitudes were derived. The structure was solved using the MULTAN program [18], and an E map computed using the most consistent set of signs revealed the position of all non-hydrogen atoms with the exception of two benzene carbons. Structure factor calculations at this stage gave $R = 0.32$. After two cycles of refinement the remaining two carbons were located in a ΔF map. The refinement was carried out by least-squares full-matrix cycles using the SHELX system of programs [16] with initially isotropic and then anisotropic thermal

TABLE 3

ATOMIC COORDINATES ($\times 10^4$) FOR COMPOUND II

Atom	x/a	y/b	z/c
Si	1828(1)	1593(1)	1179(1)
S	2834(1)	2967(1)	2106(1)
C(1)	1474(2)	2050(2)	−936(2)
C(3)	147(2)	2871(2)	−1767(2)
C(3)	−125(3)	3261(3)	−3333(3)
C(4)	928(3)	2832(3)	−4100(3)
C(5)	2245(3)	2016(3)	−3318(3)
C(6)	2521(3)	1622(3)	−1750(3)
C(11)	195(2)	2093(2)	1923(2)
C(12)	−192(2)	1012(2)	2740(2)
C(13)	−1370(2)	1408(3)	3349(3)
C(14)	−2189(2)	2884(3)	3155(3)
C(15)	−1850(2)	3981(3)	2338(3)
C(16)	−676(2)	3584(2)	1731(2)
C(21)	2905(2)	−439(2)	1891(2)
C(22)	2801(2)	−1495(2)	1051(3)
C(23)	3511(3)	−3017(3)	1609(3)
C(24)	4360(3)	−3510(3)	3008(3)
C(25)	4491(3)	−2501(3)	3855(3)
C(26)	3767(3)	−979(3)	3313(3)
CM	4391(4)	2544(5)	1323(6)
H(2)	−557(23)	3178(24)	−1224(24)
H(3)	−1046(27)	3848(28)	−3908(28)
H(4)	687(28)	3081(30)	−5165(32)
H(5)	2977(28)	1720(29)	−3757(29)
H(6)	3403(24)	1071(25)	−1199(25)
H(12)	385(21)	21(23)	2887(22)
H(13)	−1577(23)	663(25)	3857(25)
H(14)	−2992(25)	3134(25)	3561(26)
H(15)	−2399(23)	4989(26)	2244(25)
H(16)	−421(21)	4273(23)	1282(23)
H(22)	2273(25)	−1139(26)	70(27)
H(23)	3496(29)	−3795(33)	1060(32)
H(24)	4850(26)	−4575(29)	3383(28)
H(25)	5000(28)	−2768(30)	4679(30)
H(26)	3850(24)	−281(25)	3816(26)
HM(1)	4744(36)	1546(40)	1711(39)
HM(2)	4840(36)	3259(40)	1611(38)
HM(3)	4160(45)	2579(49)	341(48)

parameters. The hydrogens were put in their theoretical position and refined isotropically. The final agreement R value was 0.053.

Compound II. A trial structure consisting of all non-hydrogen atoms was obtained by direct methods using the SHELX program [16]. Isotropic and anisotropic refinement using unit weight full-matrix least-squares gave $R = 0.067$. All hydrogen atoms were located in a ΔF map and included in the refinement with isotropic temperature factors. The final agreement value, obtained using variable weights, was $R = 0.036[w_h = 1.0/\sigma^2(F_h) + 0.004(F_h)^2]$.

Compound III. Since the cell parameters of this compound were practically identical to those of compound II we assumed that these two compounds were isostructural, and consequently the coordinates of compound II were used to refine the compound III. The weights used in the refinement were $w_h = 1.0/\sigma^2(F_h) +$

TABLE 4

ATOMIC COORDINATES ($\times 10^4$) FOR COMPOUND III

Atom	x/a	y/b	z/c
Ge	1813(0)	1585(0)	1161(0)
S	2889(1)	2993(1)	2121(1)
C(1)	1461(2)	2072(2)	−1022(2)
C(2)	136(3)	2891(3)	−1820(3)
C(3)	−137(3)	3284(3)	−3373(3)
C(4)	905(4)	2855(3)	−4147(3)
C(5)	2220(4)	2039(0)	−3385(3)
C(6)	2505(3)	1638(3)	−1825(3)
C(11)	125(2)	2104(2)	1942(2)
C(12)	−243(3)	1022(3)	2769(3)
C(13)	−1414(3)	1425(3)	3381(3)
C(14)	−2219(3)	2887(3)	3180(3)
C(15)	−1887(3)	3981(3)	2354(3)
C(16)	−725(3)	3590(3)	1732(3)
C(21)	2920(2)	−508(2)	1910(2)
C(22)	2810(3)	−1556(3)	1051(3)
C(23)	3518(3)	−3071(3)	1610(4)
C(24)	4363(3)	−3545(3)	3001(4)
C(25)	4496(3)	−2528(4)	3850(4)
C(26)	3773(3)	−1004(3)	3313(3)
CM	4382(4)	2588(6)	1256(6)
H(2)	−577(29)	3193(33)	−1223(34)
H(3)	−1096(37)	3943(40)	−3939(41)
H(4)	743(33)	3089(35)	−5083(39)
H(5)	3031(31)	1670(34)	−3854(36)
H(6)	3491(32)	1016(32)	−1318(34)
H(12)	319(27)	25(31)	2938(30)
H(13)	−1553(35)	686(40)	3893(40)
H(14)	−2902(33)	3121(35)	3606(37)
H(15)	−2421(30)	4952(35)	2165(34)
H(16)	−466(30)	4333(34)	1236(35)
H(22)	2301(31)	−1311(33)	1(35)
H(23)	3484(36)	−3717(43)	974(42)
H(24)	4938(32)	−4639(37)	3248(35)
H(25)	5096(39)	−2847(41)	4662(43)
H(26)	3856(29)	−318(34)	3821(34)

$0.0022(F_h)^2$. The hydrogens of methyl group were not located and the final agreement value was 0.030.

Compound IV. The Sn atom was located by direct methods using the SHELX system [16]. An electron density calculation phased with the coordinates of this atom revealed the sulphur, while the carbons were located in a subsequent ΔF map computed after one cycle of refinement of these two atoms. The refinement was carried out by means of full-matrix least-squared using at the beginning isotropic and then anisotropic thermal parameters. At the end of anisotropic refinement ($R = 0.049$) significant residual peaks present in a ΔF map were interpreted as being

TABLE 5

ATOMIC COORDINATES ($\times 10^4$) FOR COMPOUND IV

Atom	x/a	y/b	z/c
Sn	3683(1)	1478(0)	5402(1)
S	3380(3)	617(1)	7064(3)
C(1)	2683(8)	1104(4)	3329(8)
C(2)	1227(10)	1144(5)	2715(10)
C(3)	578(12)	932(5)	1330(12)
C(4)	1421(14)	673(6)	569(11)
C(5)	2902(12)	616(5)	1164(11)
C(6)	3523(10)	833(5)	2546(9)
C(11)	5948(8)	1591(4)	5847(7)
C(12)	6555(12)	2231(5)	5687(10)
C(13)	8042(14)	2306(7)	6030(12)
C(14)	8928(13)	1755(9)	6565(13)
C(15)	8331(12)	1113(8)	6738(14)
C(16)	6875(10)	1034(5)	6372(10)
C(21)	2728(7)	2438(4)	5775(7)
C(22)	2807(9)	2659(5)	7129(8)
C(23)	2262(12)	3301(5)	7353(11)
C(24)	1619(10)	3739(5)	6235(11)
C(25)	1514(10)	3521(5)	4904(10)
C(26)	2074(10)	2880(5)	4667(9)
CM	1691(13)	246(8)	6220(15)
H(2)	620(85)	1320(41)	3178(83)
H(3)	−357(105)	929(49)	1025(100)
H(4)	1154(96)	490(53)	−303(100)
H(5)	3502(83)	437(4)	558(81)
H(6)	4496(101)	783(43)	2967(88)
H(12)	6141(83)	2548(46)	5225(85)
H(13)	8357(100)	2679(55)	5941(98)
H(14)	10038(130)	1788(60)	6990(122)
H(15)	8870(118)	700(60)	7018(113)
H(16)	6466(83)	543(44)	6379(82)
H(22)	3304(74)	2380(38)	7926(77)
H(23)	2414(102)	3428(45)	8286(109)
H(24)	1276(87)	4206(44)	6394(86)
H(25)	965(94)	3793(47)	4091(95)
H(26)	2024(57)	2728(29)	3723(61)
HM(1)	1543(13)	−183(8)	6885(15)
HM(2)	1611(13)	45(8)	5180(15)
HM(3)	877(13)	642(8)	6161(15)

due to most hydrogen atoms. The other five hydrogens were put in their theoretical positions and all refined isotropically. The final R factor was 0.041.

Compound V. The structure was solved employing the coordinates of compound IV. The hydrogens were put a distance of 1.08 Å from carbons and refined isotropically. The final R factor was 0.070.

The scattering factors used throughout the analyses were from ref. 19.

The atomic coordinates for the five compounds are reported in Tables 2–6. Lists of observed and calculated structure factor amplitudes and of thermal parameters are available from the authors on request.

TABLE 6

ATOMIC COORDINATES ($\times 10^4$) FOR COMPOUND V

Atom	x/a	y/b	z/c
Pb	3717(1)	1502(0)	5432(1)
S	3358(6)	626(3)	7167(6)
C(1)	2652(18)	1108(7)	3293(15)
C(2)	1155(21)	1169(10)	2713(21)
C(3)	536(27)	955(11)	1338(21)
C(4)	1470(33)	669(13)	583(29)
C(5)	2864(27)	600(12)	1190(22)
C(6)	3502(19)	805(9)	2517(20)
C(11)	6064(20)	1611(7)	5924(18)
C(12)	6653(24)	2244(0)	5703(20)
C(13)	8178(31)	2301(13)	6120(29)
C(14)	9037(26)	1750(20)	6655(34)
C(15)	8423(26)	1128(16)	6822(30)
C(16)	6969(21)	1056(11)	6484(22)
C(21)	2731(17)	2481(8)	5837(16)
C(22)	2785(20)	2695(9)	7127(18)
C(23)	2232(31)	3336(11)	7368(23)
C(24)	1555(25)	3744(11)	6240(24)
C(25)	1477(19)	3552(10)	4903(21)
C(26)	2073(17)	2920(10)	4670(20)
CM	1709(25)	218(11)	6153(28)
H(2)	497(21)	1379(10)	3335(21)
H(3)	−616(27)	996(11)	841(21)
H(4)	1021(33)	519(13)	−508(29)
H(5)	3514(27)	358(12)	594(22)
H(6)	4655(19)	743(9)	2986(20)
H(12)	5974(24)	2688(10)	5274(20)
H(13)	8649(31)	2798(0)	5966(29)
H(14)	10196(26)	1816(20)	6939(34)
H(15)	9114(26)	686(16)	7244(30)
H(16)	6500(21)	562(11)	6648(22)
H(22)	3279(20)	2364(9)	8020(18)
H(23)	2317(31)	3512(11)	8428(23)
H(24)	1080(25)	4236(11)	6418(24)
H(25)	959(19)	3891(10)	4028(21)
H(26)	2032(17)	2758(10)	3613(20)
HM(1)	1817(25)	−140(11)	7022(28)
HM(2)	1321(25)	−62(11)	5168(28)
HM(3)	950(25)	626(11)	6199(28)

All the calculations were performed on the CDC CYBER 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna) with the financial support of the University of Parma.

Results and discussion

The drawings of the molecules projected on the plane formed by the C(1), C(11), C(21) atoms with arbitrary numbering scheme used in the analyses are showed in Figs. 1–3.

Bond distances and valency angles are given in Tables 7 and 8, respectively. Table 9 gives some mean planes for the molecules and the dihedral angles between them.

Molecular geometries

A distorted tetrahedral coordination around the central atom is a common feature for this series of derivatives: the greatest distortion from a regular tetrahedral geometry involves the S–X–C(11) angle, which is close to 102° for the first three compounds and to 104° for the other two. The other two S–X–C angles are closer to the ideal value of 109.5°, and show a significant reduction on going from compound I through compound V.

All phenyl rings are planar within experimental error (maximum deviations from ring planes are 0.020, 0.007, 0.009, 0.011 and 0.022 Å for the five compounds, respectively) with distances and angles in the range generally observed, for this type of group. The C–C distances are not equivalent: if we assume that the aromatic ring has a *mm*2 symmetry (cf. ref. 20), then the C(*i*1)–C(*i*2) [≡C(*i*1)–C(*i*6)] mean bond is 1.384(1) Å, the mean C(*i*2)–C(*i*3) [≡C(*i*5)–C(*i*6)] is 1.379(1) Å and C(*i*3)–C(*i*4) [≡C(*i*4)–C(*i*5)] is 1.362(1) Å (*i* = 0,1,2). The significant shortening of the C(*i*3)–C(*i*4)

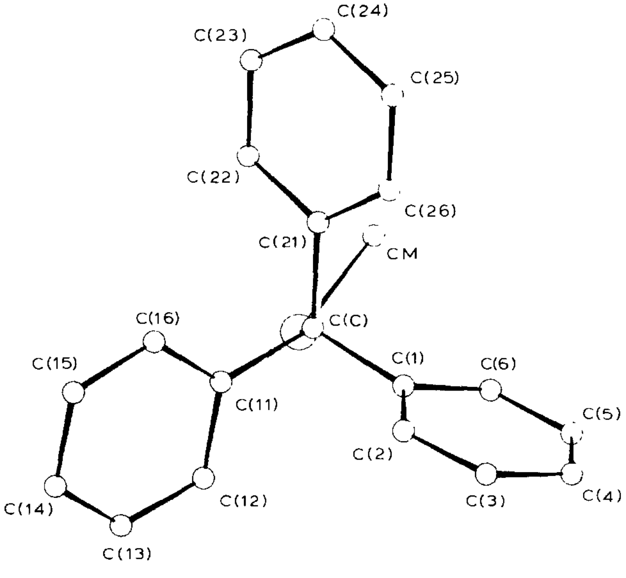

Fig. 1. Projection on the C(1),C(11),C(21) plane of the structure of Ph_3CSMe (I), with numbering scheme.

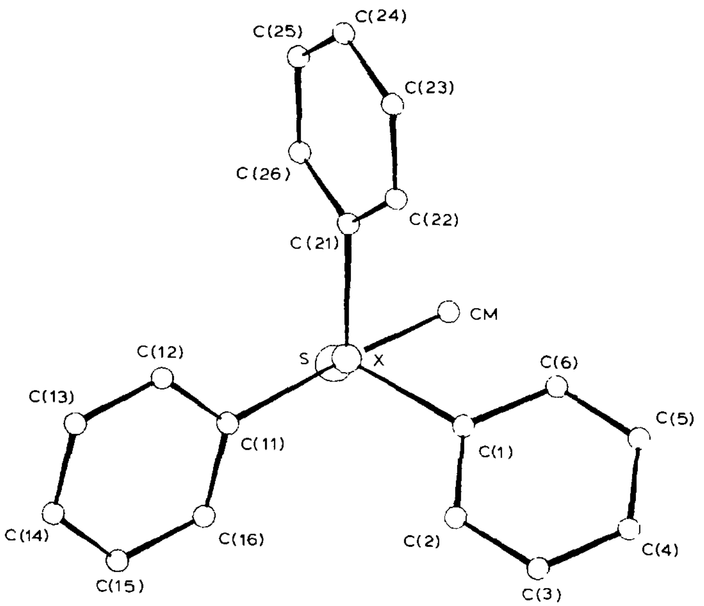

Fig. 2. Projection on the C(1),C(11),C(21) plane of the structures of the compounds Ph_3XSMe (X = Si (II) or Ge (III)), with numbering scheme.

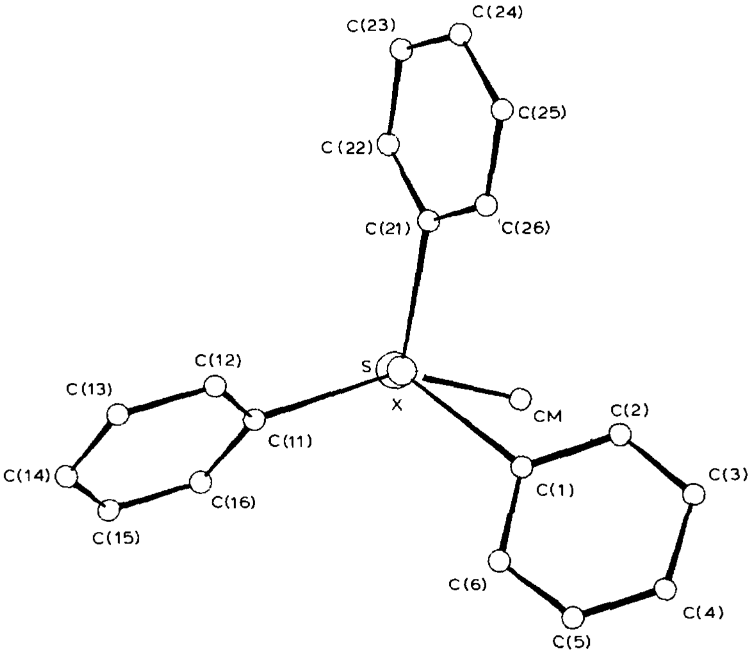

Fig. 3. Projection on the C(1),C(11),C(21) plane of the structures of the compounds Ph_3XSMe (X = Sn (IV) or Pb (V)), with arbitrary numbering scheme.

distance has frequently been observed in such derivatives and has been ascribed to thermal motion [21].

The phenyl rings are oriented in a propeller fashion with dihedral angles with respect to the C(1),C(11),C(21) plane ranging between 23.1–65.8°. From Figs. 2–4 and the values reported in Table 9c for compounds II–V it can be seen that the changes in the geometry of the compounds affect only the orientation of the C(11)–C(16) ring. In fact the change in the S–CM bond direction with respect the

TABLE 7

BOND DISTANCES (Å) IN COMPOUNDS I–V

	I	II	III	IV	V [a]
X–S	1.852(10)	2.138(2)	2.224(1)	2.391(2)	2.489(6)
X–C(1)	1.540(11)	1.865(2)	1.931(1)	2.135(7)	2.201(13)
X–C(11)	1.535(10)	1.859(3)	1.930(2)	2.139(7)	2.185(18)
X–C(21)	1.525(10)	1.860(3)	1.932(1)	2.115(7)	2 186(16)
S–CM	1.797(9)	1.809(5)	1.796(4)	1.770(12)	1.795(22)
C(1)–C(2)	1.391(11)	1.381(3)	1.381(3)	1.383(11)	1.398(24)
C(1)–C(6)	1.380(10)	1.388(4)	1.381(3)	1.373(13)	1.400(27)
C(2)–C(3)	1.360(16)	1.382(3)	1.374(3)	1.401(14)	1.380(27)
C(3)–C(4)	1.377(12)	1.363(5)	1.361(4)	1.352(18)	1.436(42)
C(4)–C(5)	1.358(14)	1.359(4)	1.363(4)	1.403(16)	1.311(37)
C(5)–C(6)	1.350(15)	1.384(4)	1.380(3)	1.398(12)	1.338(26)
C(11)–C(12)	1.407(10)	1.388(3)	1.380(3)	1.373(12)	1.379(19)
C(11)–C(16)	1.378(9)	1.388(3)	1.387(3)	1.389(11)	1.382(24)
C(12)–C(13)	1.361(12)	1.378(3)	1.376(3)	1.401(17)	1.412(36)
C(13)–C(14)	1.389(12)	1.362(4)	1.356(3)	1.359(19)	1.349(41)
C(14)–C(15)	1.372(13)	1.370(4)	1.366(4)	1.376(21)	1.354(32)
C(15)–C(16)	1.367(12)	1.373(3)	1.373(4)	1 372(14)	1.385(27)
C(21)–C(22)	1.383(10)	1.384(3)	1.382(3)	1.387(10)	1.327(24)
C(21)–C(26)	1.357(14)	1.384(4)	1.373(3)	1 385(10)	1.420(23)
C(22)–C(23)	1.391(13)	1 379(3)	1.383(3)	1.365(13)	1.382(29)
C(23)–C(24)	1.344(20)	1.362(4)	1.362(4)	1.385(13)	1.362(29)
C(24)–C(25)	1.370(20)	1.357(5)	1.367(5)	1.358(14)	1.354(32)
C(25)–C(26)	1.372(13)	1.379(4)	1.390(4)	1.373(13)	1.385(27)
C(2)–H(2)	0.79(8)	0.94(2)	0.98(3)	0.91(9)	
C(3)–H(3)	0.90(9)	0.96(3)	1.01(3)	0.88(10)	
C(4)–H(4)	0.83(9)	0.94(3)	0.83(3)	0.90(10)	
C(5)–H(5)	0.97(11)	0.90(3)	0.99(3)	1.01(9)	
C(6)–H(6)	0.87(7)	0.92(2)	1.01(3)	0.93(9)	
C(12)–H(12)	1.20(7)	0.92(2)	0.93(3)	0 79(8)	
C(13)–H(13)	0.92(9)	0.90(3)	0.86(4)	0.78(11)	
C(14)–H(14)	0.92(8)	0.94(3)	0.84(4)	1.05(12)	
C(15)–H(15)	0.97(5)	0.93(2)	0.90(3)	0.94(11)	
C(16)–H(16)	0.87(7)	0.86(2)	0.92(4)	1.01(8)	
C(22)–H(22)	1.08(11)	0.93(3)	0.98(3)	0.96(7)	
C(23)–H(23)	0.84(6)	0.96(3)	0.92(4)	0.93(11)	
C(24)–H(24)	0.93(6)	0.97(3)	1.00(3)	0.97(9)	
C(25)–H(25)	0.95(8)	0.81(3)	0.85(4)	0.98(8)	
C(25)–H(26)	0.90(6)	0.89(3)	0.88(4)	0.97(6)	
CM–HM(1)	1.09(4)	0.90(3)		1.08(2)	
CM–HM(2)	1.08(5)	1.00(4)		1.08(2)	
CM–HM(3)	1.09(3)	0.89(4)		1.08(2)	

[a] The C–H bond distances are fixed at 1.08 Å.

C(1)–X–C(21) angle causes no significant change in the orientation of the C(1)–C(6) and C(21)–C(26) rings but does affect that of the C(11)–C(16) ring. It thus seems that the orientation of the rings is influenced not only by steric effects but also by differences in the electronic states of the atoms in the molecules.

In compound I the C(C)–C(Ph) bond distances (1.542(13), 1.535(13), 1.527(13) Å) are comparable with those in triphenylmethane [22] (1.524(16), 1.527(9) Å) but shorter than those in tetraphenylmethane [33] (1.550(3) Å), while the two S–C(C) and S–CM bond distances are in the range previously observed for this type of bond. The Si–C distances span the range 1.858(1) to 1.865(1) Å, which is consistent with those found in other similar compounds: e.g. 1.864(8) Å in $Ph_3SiCOCH_3$ [24] and 1.860(13) Å in $Ph_3SiC(N_2)Ph$ [25].

The average value of the Ge–C distances (1.931(1) Å) is fairly close to those observed in $Ph_3GeSC_6H_4$-t-Bu-*p* (1.938(7) Å) [11], $Ph_3GeCOCH_3$ (1.945(8) Å) [26], and $O[Ge(PH)_3]_2$ (mean value 1.942(3) Å) [27].

The Sn–C bond distances (2.135(7), 2.139(7), 2.115(7) Å) agree well with those in $Ph_3SnSC_6H_4$-t-Bu-*p* [12], Ph_4Sn [28], $(CO)_3Mn–C_5Ph_4–O–SnPh_3$ [29],

(Continued on p. 44)

TABLE 8

BOND ANGLES (°) IN COMPOUNDS I–V

	I	II	III	IV	V
X–S–CM	106.6(4)	102.6(2)	101.4(3)	102.6(8)	100.5(12)
S–X–C(1)	112.2(5)	111.2(2)	110.6(1)	109.1(4)	108.4(8)
S–X–C(11)	102.4(6)	102.4(2)	102.8(1)	104.0(4)	104.6(10)
S–X–C(21)	110.5(5)	110.6(2)	109.6(1)	108.5(4)	107.0(8)
C(1)–X–C(11)	107.2(5)	111.9(2)	112.1(2)	113.6(6)	114.4(13)
C(1)–X–C(21)	110.9(7)	109.8(2)	110.6(1)	110.3(6)	111.2(12)
C(11)–X–C(21)	113.5(4)	110.8(2)	110.9(2)	111.0(6)	110.8(14)
X–C(1)–C(2)	120.9(7)	121.0(3)	119.8(2)	123.0(9)	120.4(17)
X–C(1)–C(6)	122.6(6)	122.2(3)	121.9(3)	118.9(9)	118.9(19)
C(2)–C(1)–C(6)	116.2(7)	116.8(2)	118.4(4)	118.1(15)	120.6(31)
C(1)–C(2)–C(3)	121.9(8)	121.7(4)	121.0(4)	123.1(15)	118.8(23)
C(2)–C(3)–C(4)	119.6(9)	120.1(4)	120.0(5)	118.1(18)	117.9(40)
C(3)–C(4)–C(5)	119.5(10)	119.7(3)	120.2(5)	120.5(20)	121.0(45)
C(4)–C(5)–C(6)	120.5(9)	120.3(5)	120.3(5)	120.3(16)	122.8(38)
C(1)–C(6)–C(5)	122.3(7)	121.4(5)	120.2(4)	120.0(15)	118.8(31)
X–C(11)–C(12)	119.5(4)	122.1(4)	121.3(3)	121.1(10)	119.8(19)
X–C(11)–C(16)	122.8(7)	121.2(3)	120.5(3)	121.9(9)	120.7(19)
C(12)–C(11)–C(16)	117.8(7)	116.6(4)	118.1(4)	116.9(14)	119.5(25)
C(11)–C(12)–C(13)	119.8(7)	121.4(4)	120.4(4)	120.7(18)	117.5(34)
C(12)–C(13)–C(14)	122.2(9)	120.3(4)	120.4(4)	121.3(20)	121.7(42)
C(13)–C(14)–C(15)	117.2(8)	119.9(5)	120.5(5)	118.5(23)	119.3(49)
C(14)–C(15)–C(16)	121.7(7)	119.7(4)	119.5(5)	120.3(21)	121.1(45)
C(11)–C(16)–C(15)	121.2(7)	122.0(4)	121.1(4)	122.3(16)	120.9(34)
X–C(21)–C(22)	119.5(8)	120.8(2)	119.8(3)	121.2(9)	122.8(19)
X–C(21)–C(26)	122.6(6)	122.1(3)	121.4(2)	120.3(9)	118.1(17)
C(22)–C(21)–C(26)	117.9(7)	116.9(4)	118.7(4)	118.4(12)	119.0(28)
C(21)–C(22)–C(23)	119.5(9)	121.6(3)	120.8(4)	120.3(15)	122.0(33)
C(22)–C(23)–C(24)	121.3(8)	119.9(4)	119.8(4)	120.5(15)	118.7(32)
C(23)–C(24)–C(25)	119.4(10)	119.8(4)	120.1(6)	119.7(15)	121.7(36)
C(24)–C(25)–C(26)	119.4(9)	120.5(3)	120.7(5)	120.3(17)	119.3(35)
C(21)–C(26)–C(25)	122.4(8)	121.1(3)	119.9(4)	120.8(14)	119.2(27)

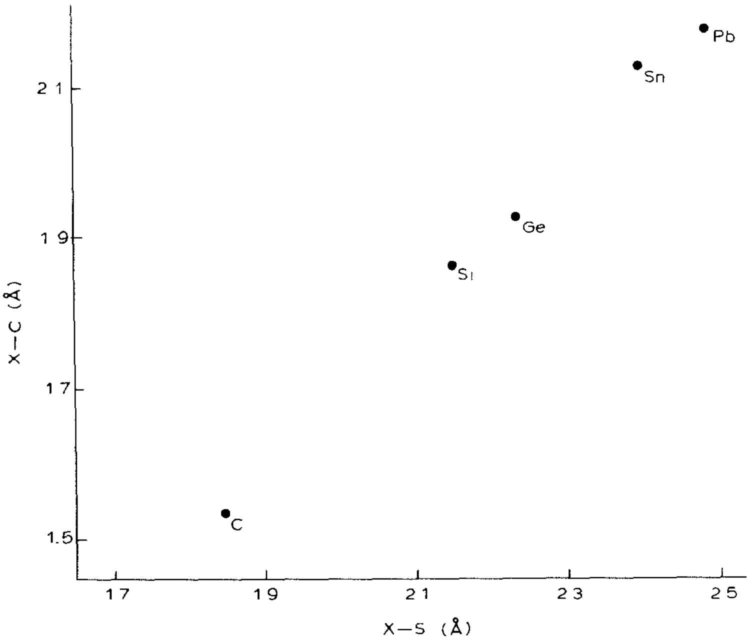

Fig. 4. Plot of X–S vs. X–C distances in compounds I–V.

TABLE 9a

DISTANCES (Å) OF RELEVANT ATOMS FROM MEAN PLANES THROUGH THE MOLECULES IN COMPOUNDS I–V

		I	II	III	IV	V
Plane 1	C(1)	−0.007	−0.003	−0.003	0.005	0.012
C(1)–C(6)	C(2)	0.010	0.001	0.004	−0.004	−0.015
	C(3)	−0.003	0.000	−0.001	−0.001	−0.001
	C(4)	−0.020	−0.002	−0.002	−0.004	0.019
	C(5)	0.011	0.000	−0.002	−0.003	0.004
	C(6)	0.004	0.004	0.003	−0.001	−0.011
	X	−0.171	−0.059	−0.043	0.106	0.120
Plane 2	C(11)	−0.003	−0.007	−0.005	−0.001	−0.006
C(11)–C(16)	C(12)	0.012	0.005	0.003	−0.005	0.014
	C(13)	−0.019	0.002	0.002	0.011	−0.017
	C(14)	0.010	−0.006	−0.006	−0.004	−0.003
	C(15)	0.002	0.002	−0.001	−0.008	0.016
	C(16)	−0.002	0.005	0.007	0.007	−0.002
	X	0.007	−0.094	−0.101	−0.100	−0.088
Plane 3	C(21)	0.004	−0.001	−0.003	−0.003	0.006
C(21)–C(26)	C(22)	−0.010	0.004	0.009	0.005	0.005
	C(23)	0.013	−0.007	−0.008	0.000	−0.022
	C(24)	−0.009	0.001	−0.001	−0.008	0.013
	C(25)	0.004	0.005	0.004	0.009	0.006
	C(26)	−0.001	−0.004	−0.001	−0.002	−0.009
	X	0.013	−0.126	−0.114	−0.125	−0.080
Plane 4	X	0.001	−0.577	−0.587	−0.630	−0.628
C(1),C(11),C(21)						
Plane 5						
X,S,CM						

TABLE 9b

NORMAL EQUATIONS OF PLANES IN THE FORM $lX + mY + nZ = p$ (X, Y and Z are in Å, referred to orthogonal axes x, y and z^*)

Plane	I				II				III			
	l	*m*	*n*	*p*	*l*	*m*	*n*	*p*	*l*	*m*	*n*	*p*
1	0.7443	−0.3739	−0.5533	−1.0538	0.1597	0.9860	0.0479	2.5376	0.1727	0.9837	0.0493	2.5448
2	0.7289	0.0804	0.6799	5.9572	0.3720	0.3945	0.8403	2.2851	0.3805	0.4013	0.8332	2.2796
3	−0.0201	0.7747	−0.6320	1.4103	0.8688	0.2888	−0.4021	1.7515	0.8646	0.2896	−0.4107	1.7263
4	−0.6405	0.5757	−0.5082	−1.0487	0.4665	0.8201	0.3313	2.4125	0.4706	0.8165	0.3345	2.3802
5	0.2849	0.8355	0.4698	7.2908	−0.3338	0.5115	−0.7918	−0.1592	−0.3601	0.5254	−0.7709	−0.1517

Plane	IV				V			
	l	*m*	*n*	*p*	*l*	*m*	*n*	*p*
1	0.2143	0.9214	−0.3241	1.2516	0.2469	0.9094	−0.3346	1.2664
2	0.2632	−0.2594	−0.9292	−4.8520	0.2685	−0.2843	−0.9204	−4.9167
3	0.8991	0.4337	0.0596	3.2828	0.8910	0.4465	0.0820	3.4338
4	0.3630	0.6799	−0.6371	0.0120	0.3682	0.6775	−0.6367	0.0412
5	0.5843	−0.6884	−0.4298	−2.9034	0.6563	−0.6710	−0.3450	−2.3629

TABLE 9c

ANGLES BETWEEN PLANES (°)

	I	II	III	IV	V
1–2	97.8	60.7	59.9	83.2	83.4
1–3	87.4	66.2	65.5	55.0	53.2
2–3	67.5	84.3	84.1	86.1	87 9
4–5	86.6	89.9	89.9	89.0	89.6
1–4	65.8	26.0	25.7	24.4	23.1
2–4	40.0	39.2	38.2	59.3	60.5
3–4	38.8	59.4	59.6	54.3	54.7

$Ph_3SnSC_6H_2(CH_3)_2$ [13], Ph_3SnCl [30], $(C_6F_5)_4Sn$ [31], Ph_3SnOH [32] and $(3\text{-}CH_3\text{-}C_6H_4)_4Sn$ [33], which range between 2.126(8) and 2.150(3) Å.

The Pb–C distance that we observed (2.201(13), 2.185(18), 2.186(16) Å) is close to those in $PbPh_4$ (2.19(3) Å) [34] and in $Pb(CH_3)_4$ (2.203(10) Å) [35].

The Si–S distance (2.139(1) Å) agrees well with that reported in ref. 36 (2.143(3) Å) while the Ge–S bond length (2.224(1) Å) is rather less than the sum of covalent radii (2.25 Å) [37] but in close agreement with the value observed in ref. 11 (2.229(2) Å). The Sn–S bond length we observed (2.391(2) Å) is similarly rather less than the sum of covalent radii (2.44 Å) [38] and below previously observed values, (2.434(5) Å) [13] and (2.413(3) Å) [12]. The lowering of the Pb–S bond length below the sum of covalent radii (2.50 Å) [38] is less marked, but still evident.

It is noteworthy that a plot of the X–S distance against the mean X–C distance (Fig. 4) gives a straight line with only small deviations. While compound I has a crystal structure, different from that of the other compounds, the isostructurality proposed on the basis of similarities of cell parameters for compounds II and III and also for compounds IV and V, is confirmed by the crystal structures.

The crystal packings for II and III, which are determined mainly by Van der Waals interactions, are very similar to one another. The same is true for IV and V.

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