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Journal of Organometallic Chemistry 484 (1994) 153–159

Journal of Organo metallic Chemistry

New refinement of the $Me_3E–E'Ph_3$ (E = Ge, E' = Sn; E = Sn, E' = Ge) isomeric compounds and the crystal structure of their solid solution

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Received 18 March 1994

Abstract

A new refinement of the isomeric pair of compounds $Me_3Ge–SnPh_3$ (**I**) and $Ph_3Ge–SnMe_3$ (**II**), using full sets of Friedel opposite reflections, is reported. The Ge–Sn bond length (**I**: 2.602(1) and **II**: 2.611(1) Å) difference was found to be significantly smaller (Δ = 0.009 Å) than reported previously (0.053 Å). A solid solution of the isostructural pair **I** and **II** was obtained by recrystallizing equimolar quantities of the isomer compounds and the disordered crystal structure was elucidated. The solid solution contains **I**:**II** in 0.375:0.625 ratio.

Keywords: Germanium; Tin; Crystal structure; X-ray diffraction

1. Introduction

The isomeric pair of compounds $Me_3Si–GePh_3$ and $Ph_3Si–GeMe_3$ possess significantly different Si–Ge bond lengths. We suggested that this difference might be due to the expansion and contraction of bonding orbitals caused by electron-donating and -withdrawing substituents that result in energetically more or less favourable overlap [1,2]. The crystal structures [3] of the isomeric pair of $Me_3E–E'Ph_3$ (E = Ge, E' = Sn [**I**]; E = Sn, E' = Ge [**II**]) molecules revealed that there is a considerable bond length difference between the Ge–Sn bonds (Δ(Ge–Sn) = 0.053 Å). Both compounds crystallize in the orthorhombic space group $Pna2_1$ (no. 33) with nearly identical unit cell parameters (Table 1). The Ge–Sn bond is fairly parallel with the *c*-axis, therefore in a given crystal all the molecules are uniformly oriented. Only unique data sets were collected for the published structures [3]. Because of the non-centrosymmetric space group and the special orientations of the molecules, serious polar dispersion errors were suspected that may have strongly influenced the experimental distances between the heavy atoms. New intensity data with full sets of Friedel opposites were collected for both $Me_3Ge–SnPh_3$ (**I**) and $Ph_3Ge–SnMe_3$ (**II**) using the very same specimen as for the original data collection and the refinements were repeated. With the refinement of the absolute structure parameter [4] the correct enantiomorph in each sample was determined and taken into account.

Because of the similar unit cell dimensions of **I** and **II**, and their isostructurality, these molecules could in principle substitute each other in the crystal lattice forming solid solutions. We attempted to obtain co-crystals by recrystallization of equal amounts of **I** and **II** from hexane. This crystallization yielded monoclinic crystals (a = 17.202(2), b = 9.350(1), c = 20.398(3) Å, β = 110.35(2)°, V = 3062.3 Å^3). Though the calculated density was extremely low (1.010 Mg m^{-3} for Z = 4), intensity data were collected for this co-crystal. Systematic absences and intensity statistics indicated space group $P2_1/n$ (no. 14), which must be a global average, with a centre of symmetry in the middle of the E(E')–E'(E) bond with partially occupied heavy atomic positions. The heavy atom sites could be located by the heavy atom method and subsequent difference Fourier syntheses showed phenyl rings at both ends of the E(E')–E'(E) bonds.

Refinement of two (EPh_3 and $E'Ph_3$) moieties, which constitute the asymmetric part, around the inversion centre converged to a conventional R 0.07

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0022-328X/94/$07.00
SSDI 0022-328X(94)24741-Z

(phenyl rings treated as rigid groups) but the occupation factors could not be clarified. No solvent molecules in the lattice (which could have compensated for the unusually low density) were detected. Crystal twinning was suspected and further attempts to complete this structure were abandoned. The co-crystallization was then repeated using CH_2Cl_2 with a few drops of acetone which yielded orthorhombic crystals (**III**) (space group $Pna2_1$ (no. 33)), the unit cell parameters closely related to those of **I** and **II** (Table 1). Melting point of a batch of crystals **III** was tested. No sharp melting point was, however, observed. The first crystallites seemed to undergo a phase transition (or melting) around 333 K and the rest melted between 364–369 K.

2. Experimental section

2.1. Data collection

Compounds **I**, **II** and the solid solution **III** ($C_{21}H_{24}$-GeSn, Fwt.: 467.7) crystallize in the orthorhombic space group $Pna2_1$ (No. 33) with $Z = 4$, $F(000) = 928$. Crystal data, data collection and refinement details are shown in Table 1. Unit cell parameters for **I** were found to be identical within experimental error to those published [3], but the unit cell data of **II** significantly deviated from the published values ($\Delta a = 0.022$, $\Delta b = 0.015$, $\Delta c = 0.001$ Å, $\Delta V = 5.0$ Å^3). Unit cell parameters of **III** have values intermediate between **I** and **II**, but closer to those of **II**. Intensity data for **I**, **II** and **III** were collected at room temperature (293(2) K) with graphite monochromated Mo Kα($\lambda = 0.07107$ Å) radiation on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from the setting angles of 25 reflections in the θ-range of 15–30°. ω-θ scan technique was used for the data collections. The intensities of three check reflections were recorded every hour for each data collection and these remained constant within experimental error. Since **I**, **II** and **III** crystallize in a polar space group, polar axis restraints were applied [5]. Scattering factors, dispersion corrections and absorption coefficients were taken from Ref. [6]. The

Table 1
Crystal data, data collection and refinement summary

Compound	I	II	III
Unit cell dimensions:			
a, Å	20.626(3)	20.373(3)	20.741(3)
b, Å	12.389(2)	12.397(2)	12.393(2)
c, Å	8.035(1)	8.084(1)	8.064(1)
Volume, Å^3	2053.2(5)	2041.7(5)	2045.8(5)
Density (calc.), Mg/m^3	1.513	1.521	1.518
μ(Mo Kα), mm^{-1}	2.664	2.679	2.688
Crystal size, mm	Ref. 3		0.06 × 0.15 × 0.25
θ range, deg.	2.57–34.22	2.59–30.41	2.58–31.95
Index ranges:			
h	0 → 32	0 → 28	−30 → 30
k	0 → 19	0 → 17	−18 → 18
l	−12 → 12	−11 → 11	−12 → 12
Reflections collected	9551	7014	7677
Independent reflections	6342	5367	7066
R(int)	0.0121	0.0072	0.0176
Absorption correction (Psi scan):			
Max./min. transmission	99.3/87.5	99.4/88.3	100.0/84.5
Data/restraints/parameters	6080/1/210	5363/1/210	5081/93/385
Weighting scheme g_1, g_2	0.0263, 0.2119	0.0318, 0.4087	0.0371, 0.0
Goodness-of-fit S	1.024	1.083	0.970
Final R indices:			
$R1[I > 2\sigma(I)]$	0.0333	0.0266	0.0378
wR_2	0.0624	0.0627	0.0736
R indices (all data):			
R_1	0.0657	0.0377	0.1428
wR_2	0.0714	0.0680	0.0986
Absolute structure parameter, x	−0.012(9)	0.011(9)	chiral twin
Largest difference peak, e.Å^{-3}	0.451	0.451	0.163
Largest difference hole, e.Å^{-3}	−0.283	−0.378	−0.150

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for *I* and **II**

	I				II			
	x	*y*	*z*	*U*(eq)	*x*	*y*	*z*	*U*(eq)
Sn	8343(1)	7899(1)	0(1)	43(1)	1631(1)	2056(1)	0(1)	46(1)
Ge	8357(1)	7908(1)	3237(1)	47(1)	1649(1)	2086(1)	3229(1)	42(1)
C1	7377(2)	8092(2)	−985(5)	45(1)	1086(2)	965(3)	4181(4)	49(1)
C2	7225(2)	8927(3)	−2075(5)	57(1)	1224(2)	−127(3)	3891(6)	63(1)
C3	6609(2)	9018(4)	−2741(6)	76(1)	850(2)	−927(4)	4616(7)	79(2)
C4	6137(2)	8299(4)	−2333(7)	77(1)	327(3)	−654(5)	5622(7)	92(2)
C5	6272(2)	7466(4)	−1247(7)	74(1)	172(2)	409(5)	5881(6)	88(2)
C6	6886(2)	7373(3)	−584(5)	59(1)	552(2)	1208(4)	5172(5)	67(1)
C7	8713(2)	6408(3)	−970(4)	44(1)	1329(2)	3475(3)	4038(5)	49(1)
C8	8348(2)	5769(3)	−2049(5)	57(1)	1701(2)	4097(3)	5157(5)	55(1)
C9	8599(3)	4800(3)	−2662(6)	74(1)	1462(3)	5078(4)	5735(6)	72(1)
C10	9211(3)	4479(4)	−2231(7)	83(1)	855(2)	5439(3)	5227(7)	79(1)
C11	9572(2)	5085(4)	−1218(8)	82(1)	493(2)	4854(4)	4161(7)	77(1)
C12	9328(2)	6051(3)	−577(6)	66(1)	726(2)	3877(3)	3555(5)	62(1)
C13	8928(2)	9165(3)	−1079(5)	48(1)	2541(2)	1859(3)	4062(4)	45(1)
C14	9449(2)	8942(4)	−2087(5)	61(1)	3051(2)	2530(3)	3557(5)	56(1)
C15	9801(2)	9749(5)	−2836(6)	85(2)	3675(2)	2405(4)	4159(7)	73(1)
C16	9635(2)	10810(5)	−2589(7)	88(2)	3813(2)	1578(4)	5262(7)	76(1)
C17	9122(3)	11059(4)	−1577(6)	81(2)	3323(2)	904(4)	5778(6)	74(1)
C18	8768(2)	10244(3)	−812(6)	63(1)	2690(2)	1035(3)	5168(5)	57(1)
C19	9089(2)	7075(3)	4063(6)	69(1)	825(2)	2987(3)	−936(6)	71(1)
C20	8411(2)	9384(3)	4017(6)	71(1)	2511(2)	2768(4)	−921(6)	74(1)
C21	7557(2)	7251(3)	4026(6)	72(1)	1561(2)	431(3)	−849(6)	70(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

absolute configuration for **I** and **II** was set as required by the refined absolute structure parameter *x*. Compound **III** was treated as a 'chiral twin' (after *x* refined to 0.34). The weighting scheme applied was $w = 1/[\sigma^2(F_o^2) + (g_1 P)^2 + g_2 P]$ where $P = (F_o^2 + 2F_c^2)/3$. Refinements were carried out on F^2 for all reflections with $F^2 > 0$. Weighted *R*-factors *wR* and all goodnesses of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*. The SHELXL-93 program [7] was used for refinement.

2.2. Refinement of I and II

The published atomic coordinates of **I** and **II** [3] were used as the starting model. Coordinates of molecule **I** had to be inverted, because the absolute structure parameter (*x*) refined to 1. Hydrogen atomic positions were generated from the assumed sp^2 and sp^3 geometry of the carbon atoms they were bonded to. Staggered conformations were assumed for the methyl groups. Positional parameters of the hydrogen atoms were not refined (riding model), but a common isotropic *U* was refined for the phenyl and the methyl hydrogen atoms. The same procedure was applied for the hydrogen atoms for **III**. The final atomic coordinates and the relevant bond lengths and angles are listed in Tables 2 and 3.

2.3. Structure elucidation and refinement of III

Patterson synthesis yielded two heavy atoms of equal weight juxtapositioned to the locations expected for the isostructural pair of isomers **I** and **II**. Subsequent difference maps showed phenyl rings and methyl peaks at

Table 3
Selected bond lengths (Å) and angles (°) for **I** and **II**

	I		II
Ge–Sn	2.6015(5)		2.6106(5)
Ge–C	1.946(4) (C19)		1.960(3) (C1)
	1.935(4) (C20)		1.954(3) (C7)
	1.947(4) (C21)		1.958(3) (C13)
Sn–C	2.156(3) (C1)		2.144(4) (C19)
	2.145(3) (C7)		2.133(4) (C20)
	2.161(3) (C13)		2.133(4) (C21)
C1–Sn–Ge	112.14(10)	C19–Sn–Ge	110.88(13)
C7–Sn–Ge	111.31(9)	C20–Sn–Ge	109.36(14)
C13–Sn–Ge	113.06(10)	C21–Sn–Ge	109.63(14)
C7–Sn–C1	106.94(13)	C20–Sn–C19	107.3(2)
C7–Sn–C13	106.28(14)	C20–Sn–C21	109.5(2)
C13–Sn–C1	106.71(13)	C21–Sn–C19	110.1(2)
C19–Ge–Sn	110.3(2)	C1–Ge–Sn	112.01(10)
C20–Ge–Sn	109.2(2)	C7–Ge–Sn	110.02(11)
C21–Ge–Sn	108.3(2)	C13–Ge–Sn	110.79(10)
C20–Ge–C19	110.2(2)	C7–Ge–C1	107.4(2)
C21–Ge–C19	109.0(2)	C7–Ge–C13	108.7(2)
C20–Ge–C21	109.8(2)	C13–Ge–C1	107.82(14)

both ends of the heavy atom bonds, showing that a pseudo inversion centre was present. Refinement carried out with the heavy atoms arbitrarily assigned as Ge and Sn eliminated one set of phenyl rings and methyl carbon atoms, retaining phenyl rings at one end and methyl carbons at the other end of the E–E′ bond. No such problems were encountered on the structure determinations of **I** and **II**. The absolute structure parameter x refined to 0.34, therefore the structure was considered a chiral twin. Since unit cell data indicated that this specimen of **III** was mainly built up with $Ph_3Ge–SnMe_3$ (if not exclusively so), final atomic parameters of **II** were introduced and the scale factor of the intensity data of **III** were refined. 3338 observed reflections were used in the refinement on F ($F_o \geq 4\sigma(F_o)$, $R = 0.083$).

A difference map was then calculated by subtracting the whole contribution of the $Ph_3Ge–SnMe_3$ molecule and the electron density was plotted on the plane of the C1, Ge and Sn atoms. All electrons in the unit cell of **II** (928) were taken as a difference $\Delta(F_{000})$, for scaling the map. The resulting difference map is shown in Fig. 1. It should have contained only insignificant peaks (errors) if the structure really was $Ph_3Ge–SnMe_3$. In the vicinity of each heavy atom location one large positive and one negative peak was found. The positive peaks (marked as (a) and (b) in Fig. 1) were 8.0 (a) and 5.5 eÅ^{-3} (b); the depths of the holes were −1.5 at Ge and −3.0 eÅ^{-3} at Sn. Positive peaks indicated that extra scattering power was present, holes and positive peaks indicated that the subtraction was perhaps carried out imperfectly, i.e. heavy atom positions in **III** did not match exactly with those of **II** and the thermal motion is also different. A similar map was computed for **II** with its own reflection set and it is also depicted in Fig. 1. This map had only insignificant positive

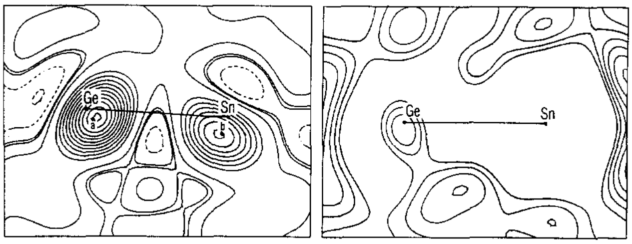

Fig. 1. Difference electron density map computed with the reflections of **III** and the atomic parameters of **II** (left; contour lines are drawn at 0.8 eÅ^{-3} intervals, dashed lines represent negative densities), and difference electron density for **II** (right; contour lines are drawn at 0.03 eÅ^{-3} intervals). Both maps are plotted on the plane of C1, Ge and Sn.

electron density peaks (the maximum was 0.87 eÅ^{-3}), with no negative regions near the heavy atom sites.

At this stage, double atom positions (Ge, Snx; Sn, Gex) were introduced with 0.5–0.5 occupancy. The carbon part of the structure was still assumed to be ordered. The sums of occupancies were constrained to 1 for the Ge–Sn and Gex–Snx pairs. Full-matrix anisotropic least-squares was carried out against F^2. The occupancies refined to 0.627 (Ge, Sn) and 0.373 (Gex, Snx). The 0.627 value is close to the ratio of the Ge/Sn atomic numbers (32/50 = 0.64), therefore the heavy atom sites are occupied by heavy atoms mixed in the proportion of their electrons (i.e. scattering powers). Evidence was required that this was not a mere computational artefact arising from the weighted mixing of scattering power but a real solid solution. Four additional refinements were therefore performed. In the first two, atomic coordinates of **III** were refined against the intensity data of **I** (**A**) and **II** (**B**), and in the second two, the atomic parameters of **I** (**C**) and **II** (**D**) were refined against the intensity data of **III**. In terms of the conventional R-factors all four refinements gave

Table 4
The results of refinement of **III** against the intensity data of **I** (**A**) and **II** (**B**); refinements of **I** (**C**) and **II** (**D**) against the intensity data of **III** and the refinement of **II** against the intensity data of **I** (**E**)

	A	B	C	D	E
Number of reflections, all	6342	5487	7066	7066	6342
Number of reflections, obs.	6080	4635	3481	3481	6080
Observed criterion			$I \geq 2\sigma(I)$		
Number of parameters	229	229	210	210	211
R indices (obs):					
$R1$	0.0455	0.0428	0.0566	0.0469	0.0703
$wR2$	0.1262	0.1444	0.2164	0.1266	0.2176
R indices (all):					
$R1$	0.0773	0.0539	0.1640	0.1532	0.1013
$wR2$	0.1342	0.1444	0.1753	0.1541	0.2349
S (all)	0.783	0.709,	1.005	1.015	1.039
Site occupation factors:					
Sn,Ge	0.05(1)	0.92(1)	1.00	1.00	1.00
Snx,Gex	0.95(1)	0.08(2)	–	–	–
Distances (Å):					
Sn–Ge	2.79(1)	2.620(2)	2.574(1)	2.587(1)	2.622(1)
Snx–Gex	2.610(4)	2.56(9)	–	–	–

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **III**

	x	y	z	U(eq)		x	y	z	U(eq)
Ge	1646(2)	2110(4)	3238(4)	38(1)	Gex	1646(4)	2037(6)	44(8)	40(2)
Sn	1630(2)	2076(3)	19(2)	53(1)	Snx	1665(2)	2057(6)	3227(6)	58(2)
C1	1068(6)	989(9)	4202(17)	53(4)	C1x	1112(8)	827(11)	4311(26)	39(5)
C2	1215(9)	−113(12)	4114(2)	70(5)	C2x	1238(10)	−212(13)	3748(25)	56(6)
C3	854(9)	−913(10)	4896(18)	68(4)	C3x	874(12)	−1075(10)	4346(25)	58(5)
C4	321(9)	−588(12)	5842(23)	80(5)	C4x	384(11)	−899(12)	5507(29)	65(6)
C5	126(7)	483(12)	5944(21)	72(5)	C5x	257(8)	140(15)	6071(25)	50(5)
C6	513(5)	1250(10)	5136(15)	48(3)	C6x	622(8)	1003(10)	5473(22)	53(5)
C7	1349(8)	3548(10)	4039(25)	47(4)	C7x	1262(14)	3452(16)	4267(40)	46(5)
C8	739(7)	3932(13)	3542(21)	54(4)	C8x	635(12)	3807(17)	3903(35)	66(8)
C9	478(9)	4900(16)	4132(33)	97(8)	C9x	436(10)	4832(18)	4390(43)	65(7)
C10	817(10)	5428(13)	5371(30)	100(8)	C10x	866(11)	5501(13)	5241(41)	70(8)
C11	1416(9)	5097(14)	6002(24)	70(6)	C11x	1493(10)	5146(18)	5606(34)	50(5)
C12	1665(6)	4154(15)	5280(25)	58(5)	C12x	1692(10)	4121(22)	5119(41)	58(7)
C13	2526(5)	1899(16)	4203(26)	47(4)	C13x	2627(7)	1823(25)	4022(35)	37(5)
C14	3032(8)	2520(16)	3569(26)	64(5)	C14x	3113(11)	2595(22)	3825(33)	48(5)
C15	3675(7)	2417(16)	4109(22)	73(5)	C15x	3714(9)	2463(18)	4604(29)	51(6)
C16	3847(7)	1657(18)	5298(24)	83(6)	C16x	3828(7)	1558(18)	5581(29)	65(5)
C17	3344(9)	1023(13)	5928(27)	79(5)	C17x	3341(11)	786(15)	5779(31)	53(5)
C18	2704(7)	1116(12)	5354(21)	47(4)	C18x	2741(8)	918(20)	4999(33)	50(5)
C19	2488(6)	2783(13)	−876(21)	64(5)	C19x	2466(11)	2649(35)	−861(45)	129(18)
C20	1583(10)	482(6)	−832(15)	55(4)	C20x	1540(23)	516(14)	−665(56)	143(19)
C21	850(8)	2971(17)	−963(25)	63(5)	C21x	908(12)	2953(26)	−696(55)	101(13)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

very good agreement, but **B** and **D** showed somewhat better fit than **A** and **C** (the major component of this mixed crystal specimen is probably $Ph_3Ge–SnMe_3$). Refinements **A** and **B** resulted in non-positive definite temperature factors for Sn and Snx respectively. The principal mean square atomic displacements for the Sn atom were approximately twice those of the Ge atom in refinements **C** and **D**. The multiplicities of the heavy atoms were permitted to refine freely in **A** and **B** and the refinement eliminated the major component heavy atoms in **A** and the minor component ones in **B** indicating again that **II** is the major component of **III**. Isostructurality of **I** and **II** is so strict that **II** can be refined against the intensity data of **I** (**E**) to a reasonable conventional R 0.0703 (4684 $F_o \geq 4.\sigma(F_o)$ and 0.1013 for all 6342 data. The weighted R-factor on intensities (wR_2) is, however, rather high (0.2176; 4684 data) showing that wR_2 is far more sensitive to the structural model (Table 4).

At the final stages of the refinement, double atoms were introduced for all carbon atoms. C–C distances were restrained to 1.400 Å and Ge–Sn, mean Ge–C and Sn–C distances were restrained to the values observed for **I** and **II**. Phenyl rings of the minor component were constrained to form regular hexagons. All atoms were refined anisotropically. C19x, C20x and C21x have high thermal motion coefficients pointing possibly to further disorder. The final occupancy factors were 0.625 and 0.375. The extinction coefficient was also refined using the following expression $F_c^* = kF_c[1 + cF_c^2 l^3/\sin(2\theta)]^{-1/4}$, where c was 0.0006(2).

At the end of refinement a comparison of the absolute (scaled) intensities of those reflections observed and present in both **II** and **III** data sets (4300), showed that although the intensities differ the intensity ratios agree approximately only for strong ($I > 1100$) reflections (I_{II} plotted against I_{III} gave an approximate straight line). Intensity ratios below this threshold deviate significantly.

Table 6
Selected bond lengths (Å) and angles (°) for **III**

Ge–Sn	2.596(4)	Gex–Snx	2.567(6)
Ge–C	1.984(7) C1	Gex–C	1.981(8) C19x
	1.991(7) C7		1.983(8) C20x
	1.979(7) C13		1.982(8) C21x
Sn–C	2.092(7) C19	Snx	2.091(7) C1x
	2.093(6) C20		2.091(7) C7x
	2.099(7) C21		2.091(7) C13x
C13–Ge–C(1)	107.3(7)	C19x–Gex–C21x	109(2)
C13–Ge–C(7)	105.6(8)	C19x–Gex–C20x	111(2)
C1–Ge–C(7)	108.5(7)	C21x–Gex–C20x	112(2)
C13–Ge–Sn	113.8(7)	C19x–Gex–Snx	110.6(12)
C1–Ge–Sn	111.9(4)	C21x–Gex–Snx	107.9(14)
C7–Ge–Sn	109.6(6)	C20x–Gex–Snx	107.4(14)
C19–Sn–C20	108.7(7)	C7x–Snx–C13x	111.3(12)
C19–Sn–C21	106.7(8)	C7x–Snx–C1x	102.8(10)
C20–Sn–C21	109.9(8)	C13x–Snx–C1x	106.3(11)

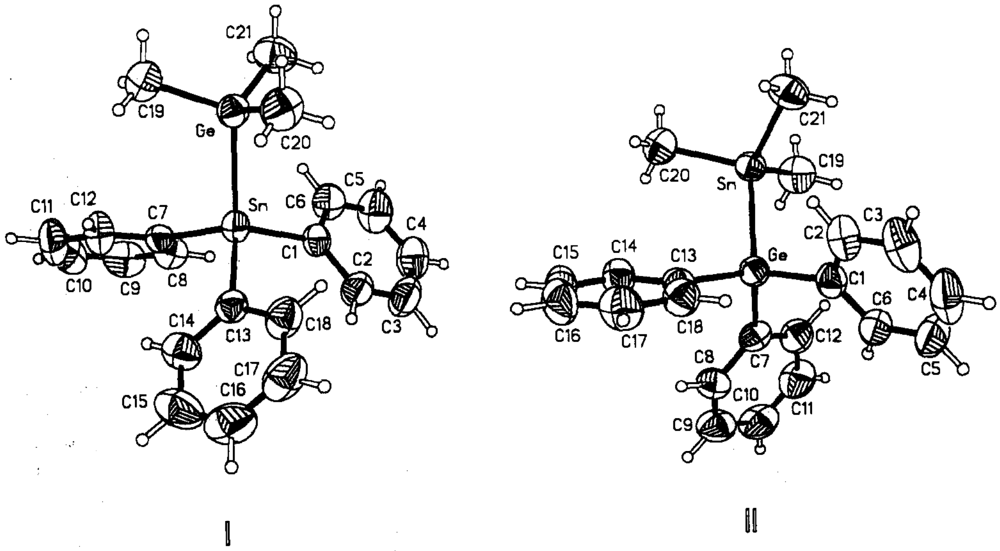

Fig. 2. The molecular diagrams of I and II. Thermal ellipsoids represent 50% probabilities.

The final atomic coordinates and relevant bond distances and angles are listed in Tables 5 and 6.

3. Discussion

The conformations of I, II and III are identical (Figs. 2 and 3). The Ge–Sn bond length (I: 2.602(1) and II: 2.611(1) Å) difference is significantly smaller ($\Delta = 0.009$ Å) than reported previously (0.053 Å, [3]), thus neglecting the polar dispersion error results in an approximately six-fold deviation. Despite the significant difference between these Ge–Sn bond distances and those we published previously, the new data conform to our premise concerning the effect of relatively electron-withdrawing and -donating groups on the two group 14 elements. When Sn has the phenyl group and Ge the methyl group substituents, a shorter bond is observed.

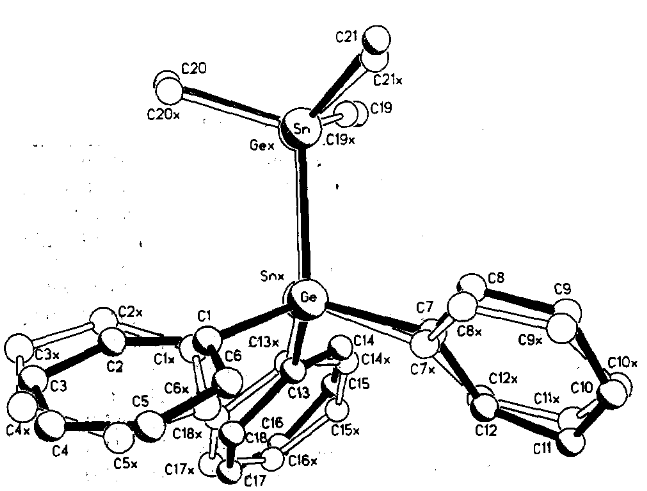

Fig. 3. The molecular diagram of III. The bonds between major component atoms are drawn with full lines and they are represented as shaded balls.

We have shown [9] that contrary to the change of space group from $P\bar{3}$ (no. 147; $Me_3Si{-}SiPh_3$, $Me_3Ge{-}SiPh_3$ $Ph_3Ge{-}SiMe_3$ and $Ph_3Ge{-}GeMe_3$, $Z = 2$) to $Pna2_1$ (no. 33; I and II, $Z = 4$), the high packing coefficient $\eta = 0.73$ (defined as $Z * V_{mol}/V_{cell}$) is maintained. The $P\bar{3} \rightarrow Pna2_1$ morphotropic step [10], involving the violation of the strict three-fold molecular symmetry, may be attributable to the long Ge–Sn bond leading to greater conformational freedom. To test the conformational difference between the two series, the coordinates of I and II were orthogonalized and each GeC_3 moiety was fitted to $Me_3Ge{-}SiPh_3$ [1] and $Ph_3Ge{-}SiMe_3$ [2] (weighted *rms* deviations: 0.0378 (I) and 0.0087 (II)). Only the phenyl *ipso* atoms were used in the least-squares fit for II. Two coordinate sets, referring to the trigonal $P\bar{3}$ space group of the silyl structures, were derived this way. Fixing one carbon at each germanium and tin atom, the remaining four carbon atomic positions were generated assuming ideal three-fold symmetry (I: x − y, 1 − x, z; 1 − y, 1 + x − y, z; II: 1 − x, x − y, z; 1 − x + y, 1 − x, z). The *rms* deviations from the idealized positions (Table 7) indicate that the three-fold symmetry is fairly retained in I and II. The phenyl ring planes, however, are rotated by ca. 90° with respect to those of the Si–Ge derivatives. The mean dihedral angles are 91.1(2.5)° (I, (Sn)Ph/

Table 7
RMS deviations ($\times 10^{-5}$) from the idealized threefold symmetry

Compund	RMS deviation C(Me)	RMS deviation C(Ph)	Fitted moiety
I	1.47	23.0	GeC_3(Me)
II	12.9	0.061	GeC_3(Ph)

(Si)Ph) and 91.7(3.8)° (**II**, (Ge)Ph/(Ge)Ph[$P\bar{3}$]). Crystal packing is identical within each series.

The Ge–Sn bond distances in **III** are 2.596(4) (Ge–Sn) and 2.568(6) Å (Gex–Snx) with a difference of 0.028 Å, though bond lengths are less reliable in this case, since this structure is a result of averaging and the e.s.d.'s are rather high. This is also apparent from the mean Sn–C and Ge–C bond distances. The mean Sn–C distances in **III** are shorter (2.093(1) Å) with respect to **I** and **II** (2.154(4) Å) and Ge–C bonds are longer (1.984(2) vs. 1.950(4) Å [**I**, **II**]). The rigid group treatment of the phenyl groups introduced a further bias in the C(*ipso*) positions since it does not allow the distortion of the endocyclic *ipso* bond angle that should deviate significantly from 120° [8]. The disordered heavy atoms (Sn ··· Gex and Snx ··· Ge) are 0.062(8) and 0.076(8) Å apart.

The phenyl ring least-squares planes form the following dihedral angles with their counterpart: 14.4(2)° (C1 ··· C6/C1x ··· C6x); 15.3(5)° (C7 ··· C12/C7x ··· C12x); 15.0(4)° (C13 ··· C18/C13x ··· C18x). Superimposing **I** with **II**, the dihedral angles between the corresponding phenyl rings is in the range of 1–3°. The overlapping two molecules are slightly rotated with respect to each other.

4. Supplementary data

Atomic parameters and bond lengths, hydrogen coordinates and isotropic displacement parameter listings have been deposited with the Cambridge Crystallographic Data Centre. Any request for copies of this material should include the full literature citation for this paper.

Acknowledgements

This research was supported by the Hungarian Research Fund, Grant no. OTKA 1805 and the National Science Foundation grants nos. RII-88-02973 and CHE-91-16934.

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