Notes

Iso- and Homeostructuralism of Analogous Ph$_4$E and Ph$_3$E−E′R$_3$ Compounds (E = C, Si, Ge, Sn, Pb; E′ = Si, Ge, Sn; R = Me, Ph): Crystal Structure of 1,1,1-Trimethyltriphenyldistannane

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Introduction

The strict rules[1] limiting the formation of similar packing arrays restrict organic crystals from exhibiting isostructurality, which along with crystal polymorphism is governed by the effort to gain the maximum of close packing. Molecular associations strive for attainment of the maximum density by bringing the bumps of the molecules of irregular shape into the hollows of the adjacent molecules *via* the optimum symmetry operations permitted within the seven crystal systems.[2] In principle, only isometric molecules can form isostructural crystals; otherwise, only relaxed relationships, termed as homeostructural, can be expected.

The quadrivalent C, Si, Ge, Sn, and Pb atoms screened by their alkyl and/or aryl substituents can be replaced by each other without altering the outer shape of the molecules, presenting an attractive series for investigating the conditions of isostructurality. The substantial change of the covalent radii of C to Pb ($r_e = 0.77$ *vs* 1.40 Å) may lead to phase transitions. The tetraphenyl derivatives (Ph$_4$E) of the group 14 elements crystallize in the tetragonal space group $P\bar{4}2_1c$, (No. 114).[3] The increasing radii of the core atoms do not terminate their identical close packing. The analogous Ph$_3$E−E′Ph$_3$ derivatives (E = E′ = Ge, Sn, Pb) also exhibit isostructuralism, but their packing relationship is modulated by additional pseudosymmetries and disorder.[4]

Isostructurality is also a recurrent phenomenon among the Ph$_3$E−E′Me$_3$ derivatives (E = Si, Ge, Sn). Group a complexes (**I**, Ph$_3$Si−SiMe$_3$;[5] **IIa**, Ph$_3$Si−GeMe$_3$;[6] **IIb**, Ph$_3$Ge−SiMe$_3$;[7] **III**, Ph$_3$Ge−GeMe$_3$)[8] crystallize in space group $P\bar{3}$ (No. 147). The high index[1] of isostructurality ($I_i(23) = 95\%$) between Ph$_3$Si−SiMe$_3$ and Ph$_3$Ge−SiMe$_3$ is also observed between its isomers Ph$_3$Si−GeMe$_3$ and Ph$_3$Ge−GeMe$_3$ (94%). When one of the core atoms of Ph$_3$Ge−GeMe$_3$ is replaced by the larger Sn atom, the new isomers **IVa**, Ph$_3$Ge−SnMe$_3$, and **IVb**, Ph$_3$Sn−GeMe$_3$ (group b, space group $Pna2_1$ (No. 33)),[9] are no longer isostructural with group a. Kitaigorodskii expected such "morphotropic" phase transitions whenever the atomic replacement diminishes the existing packing coefficient.[2] The Ge−Sn isomers remain isostructural and can substitute one another in the crystal lattice, forming solid solutions.[10] In the new pseudohexagonal unit cells ($Pna2_1$), the bumps of the Ph$_3$Ge−SnMe$_3$ and Ph$_3$Sn−GeMe$_3$ molecules stacked with similar orientations along the polar *c* axis fit perfectly into the hollows of the adjacent columns generated by the glide planes.[11] No structural data have been reported for the series Ph$_3$E−E′Me$_3$ (E = E′ = C, Sn, Pb); therefore the reason for this grouping is not apparent. It may depend on the size (radius) of the core atoms and/or on their radius difference. The present work on the structure determination of Ph$_3$Sn−SnMe$_3$ (**V**) aims to fill in, at least in part, this gap.

Table 1. Crystal Data and Structure Refinement Details for **V**

empirical formula = $C_{21}H_{24}Sn_2$
fw = 513.78
$a = 11.739(3)$ Å
$c = 8.871(4)$ Å
$V = 1058.7(6)$ Å^3
$Z = 2$
$\mu = 23.57$ cm^{-1}

space group $P\bar{3}$ (No. 147)
$T = 20(2)$ °C
$\lambda = 0.710\,73$ Å
$\rho_{calcd} = 1.612$ g cm^{-3}
R1[a] = 0.0301
wR2[b] = 0.0651

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)^2]^{1/2}$.

Experimental Section

Synthesis.[12] A solution of 1.93 g (5 mmol) of Ph$_3$SnCl in 15 mL of THF was added to Li, 0.35 g (50 mmol), stirred in 15 mL of THF. After 1 h, the color changed, and after 12 h, a dark green solution was obtained. This was transferred *via* canula to a dropping funnel and added dropwise to a cooled solution of Me$_3$SnCl, 0.99 g (5 mmol). Upon slow addition, the color disappeared, and after 30 min of stirring, the solvent was removed in vacuo. Recrystallization from hexane/methylene chloride resulted in crystals of Ph$_3$SnSnMe$_3$ suitable for X-ray analysis.

X-ray Structure. A transparent prism crystal (0.60 × 0.40 × 0.20 mm) was mounted on a Siemens R3m/V four-circle diffractometer using graphite-monochromated Mo *K*α radiation at room temperature. Crystallographic data and refinement details are given in Table 1. Intensities of three standard reflections were measured after each 100 reflections, and these remained constant throughout the data collection. The structure was solved by the heavy-atom method. Full-matrix anisotropic least-squares refinement was carried out on F^2 using the

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Table 2. Bond Lengths (Å) and Angles (deg)[a]

Sn1−C1	2.152(4)	C2−C3	1.380(7)
Sn1−Sn2	2.7820(14)	C3−C4	1.360(8)
Sn2−C7	2.138(5)	C4−C5	1.382(8)
C1−C2	1.373(6)	C5−C6	1.368(7)
C1−C6	1.384(6)		
C1−Sn1−C1^{i}	105.48(12)	C6−C1−Sn1	122.2(3)
C1−Sn1−Sn2	113.21(10)	C3−C2−C1	121.4(4)
C7−Sn2−C7^{ii}	108.1(2)	C4−C3−C2	120.2(5)
C7−Sn2−Sn1	110.8(2)	C3−C4−C5	119.6(5)
C2−C1−C6	117.4(4)	C6−C5−C4	119.5(5)
C2−C1−Sn1	120.4(3)	C5−C6−C1	121.9(5)

[a] Symmetry transformations used to generate the complete molecule: (i) $-y + 1, x - y + 1, z$; (ii) $-x + y, -x + 1, z$.

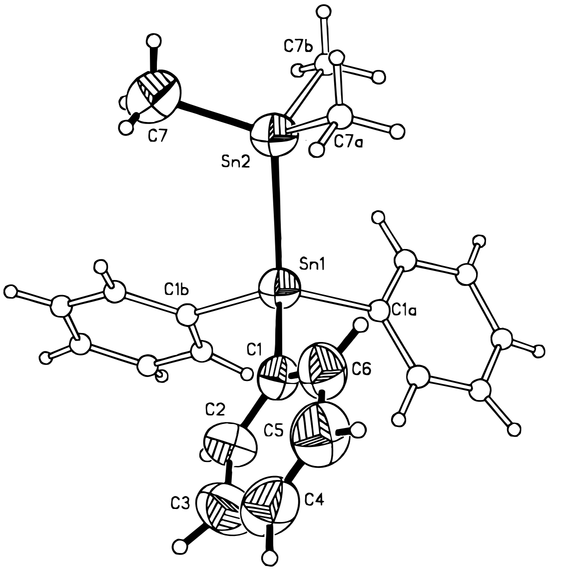

Figure 1. Molecular diagram with the numbering of atoms. Thermal ellipsoids represent 50% probabilities.

SHELXL program.[13] Atomic positions for the hydrogen atoms were calculated from assumed geometries, and they were treated as riding atoms. A common *U*(iso) temperature factor was refined for the phenyl hydrogens, and another, for the methyl hydrogen atoms. The scattering factors used were taken from ref 14. Selected bond lengths and angles are given in Table 2, and the structure is depicted in Figure 1.

Discussion

Molecular Geometry and Packing. **V** crystallizes in space group $P\bar{3}$ (group a), and the unit cell indicates that it might be isostructural with other members of this group. The atomic coordinates, however, testify only a relaxed relationship, since the molecule adopts a different position in the unit cell. Placing the title compound and **III** in the unit cell of disilane **I**, one can see the difference in the relative positions of the two molecules as shown in Figure 2. This comparison reveals that molecule **V** is no longer isometric with **I**, **IIa**, **IIb**, and **III** (group a). While the E−E′ distance for group a varies 1% about the mean 2.388(26) Å, the Sn−Sn bond distance [2.782(1) Å] is longer by 16.5%. Consequently, the packing relationship of **V** with **I**−**III** is a *par excellence* case of homeostructuralism.[1]

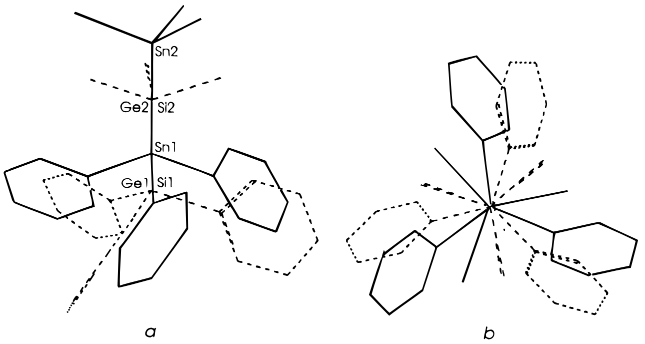

Figure 2. Relative positions of **I**, **III**, and **V** (full line) in the unit cell of **I**: (a) view perpendicular to the 3-fold axis; (b) view down the 3-fold axis.

The Sn−Sn bond length falls in the range of bonds reported for linear Sn−Sn bonds (2.77−2.89 Å). The shortest bond (2.770(4) Å) was observed in the hexaphenyl derivative.[15] An extremely long Sn−Sn bond of 3.034(1) Å was reported for tetra-*tert*-butyl-1,2-bis(2,4,6-triisopropylphenyl)distannane, which adopts an unusual conformation in the crystal with all bulky aryl moieties in the *syn* orientation and eclipsed Sn−C bonds.[16] The Sn−Sn bond length in the hexa-*tert*-butyl compound is 2.894(1) Å.[17] The E−E bond length difference between the corresponding Ph_3E-EMe_3 and $t\text{-}Bu_6E_2$ compounds decreases with the increasing E−E bond length (Δ(Si−Si) = 0.34, Δ(Ge−Ge) = 0.28, Δ(Sn−Sn) = 0.11 Å), showing a significant reduction of steric crowding.[17−19]

The lack of isometricity between the molecules of group a and **V** is equally responsible for the shifting of **V** along the 3-fold axis and a rotation of the molecule by 23° with reference to the disilane (Figure 2b). The best planes of the phenyl rings also turn by 24.5°, forming a smaller dihedral angle (52.7°) with the 3-fold axis (**I**: 57.1°).

Isostructuralism and Morphotropic Phase Transitions. The systematic replacement of the core atoms in the $Ph_3E-E'Me_3$ series from Si−Si to Sn−Sn gives rise to two morphotropic phase transitions as presented in Figure 3.

The *c* crystallographic axis slightly elongates upon going from the disilane to the digermane (Δc(**III**−**I**) = 0.122 Å), and it shortens from digermane to distannane (Δc(**V**−**III**) = −0.068 Å), yielding a value that is close to the *c* axis of the disilane (Δc(**V**−**I**) = 0.054 Å). The greatest change is perceivable in the lengths of the *a* axes (Δa(**III**−**I**) = 0.022, Δa(**V**−**I**) = 0.426, Δa(**V**−**III**) = 0.404 Å). The unit cell volume differences are as follows: ΔV(**III**−**I**) = 17.3, ΔV(**V**−**I**) = 81.4 ΔV(**V**−**III**) = 64.1 $Å^3$.

In contrast, the tetragonal unit cells assumed by the isostructural Ph_4E homologs (with two molecules in the asymmetric unit) are flattened in a stepwise mode as if pressed along the principal *c* axis. The change in the *a/c* ratio seems to be proportional to the increase of the atomic radii, showing the greatest difference between the C and Pb homologues. This phenomenon underscores our earlier conclusion concerning the relationship between the unit cells of the isostructural pairs expressed by eq 1 given in ref 1.

In the crystal structures of Ph_4E and $Ph_3E-E'Me_3$ derivatives (except **IVa** and **IVb** with Sn−Ge cores), the molecular

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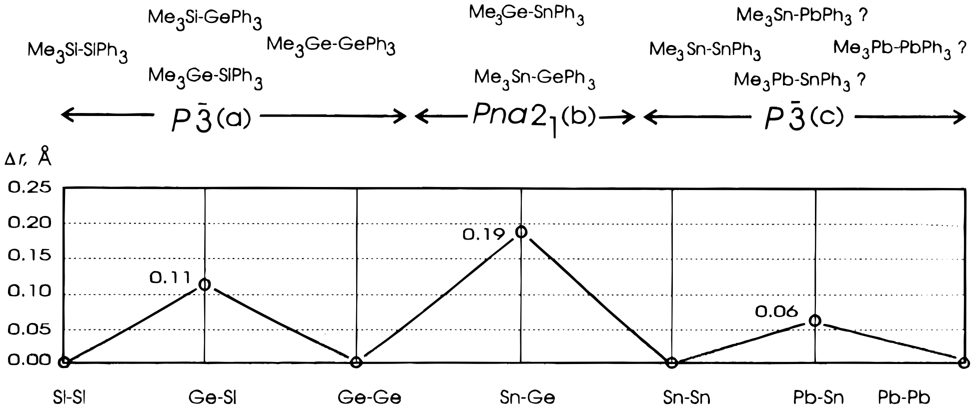

Figure 3. Phase transitions in the $Ph_3E-E'Me_3$ series and the covalent radius (Δr) differences.

symmetries (S_4 and C_3) are the principal operators. This rule is relaxed in the crystals of the bulkier hexaphenyl molecules. Only hexaphenyldigermane has a metastable hexagonal form (space group $P6_322$; No. 182).[20] Its dominant form crystallizes in triclinic unit cell (space group $P1$; No. 1) built up by achiral bipropellers. If one of the Ge atoms is replaced by Pb, then the asymmetric Ge$-$Pb group bearing six phenyl groups exhibits orientational disorder in a triclinic unit cell isomorphous with that of $Ph_3Ge-GePh_3$.[4] The orientational disorder of the Ge$-$Pb ↔ Pb$-$Ge dumbbells generates inversion centers (space group $P\bar{1}$; No. 2) that result in the shrinkage of the observed Ge$-$Pb distances. This distance is still 7.6% longer than the Ge$-$Ge bond of 2.437(7) Å, resulting in a homeostructural packing scheme. When the second Ge atom in $Ph_3Pb-GePh_3$ is replaced by a tin atom, a morphotropic phase transition occurs again. In the monoclinic unit cell ($P2_1/c$; No. 14), there are two symmetry-independent molecules providing the optimum of close packing.[4] The small ($\Delta = 0.06$ Å) difference between the atomic radii of Sn and Pb provides ideal conditions for an orientational disorder developed by $Ph_3Pb-SnPh_3$ molecules. Since the E$-$E′ distances for Sn and Pb vary only 1% about 2.82(3) Å, these molecules are isometric, as substantiated by the isostructuralisms of $Ph_3Sn-SnPh_3$[4] and $Ph_3Pb-PbPh_3$[21] with $Ph_3Pb-SnPh_3$.

Conclusions

(A) The compact and relatively small Ph_4E and $Ph_3E-E'Me_3$ molecules reach their bump-in-hollow packing with a relatively high packing coefficient about 0.73 by inducing their own molecular symmetry (either S_4 or C_3) in the crystal lattice. For long E$-$C bonds, the close packing of Ph_4E homologues tolerates even the accommodation of the bulky methyl group in an *ortho* position (Sn derivative) without altering their symmetry.[3d] Even the *m*- and *p*-tolyl derivatives crystallize in closely related space groups, $I4_1/a$ (No. 88) and $I\bar{4}$ (No. 82), but they are no longer isostructural. Only the asymmetric Sn$-$Ge dumbbell brings the $Ph_3Sn-GeMe_3$ and $Ph_3Ge-SnMe_3$ pair into an isostructural orthorhombic packing.

(B) The bulky hexaphenyl derivatives cannot develop the optimum packing around their S_6 molecular symmetry; they accommodate themselves in unit cells of lower (triclinic and monoclinic) symmetries instead. The presence of more than one molecule in the asymmetric units of $Ph_3E-E'Ph_3$ with E = Sn, Sn, Pb and E′ = Sn, Pb, Pb, combined with positional disorder of the asymmetric E$-$E′ core, seems to serve the same goal.

(C) An isostructural packing array can be expected among the $Ph_3E-E'R_3$ molecules if they are closely isometric; *i.e.*, E/E′ is either Si/Ge or Sn/Pb (*i.e.*, the unknown Sn$-$Pb isomers and the Pb$-$Pb compound are expected to be isostructural with **V**). This is also shown by bulky molecules of the Si/Ge pair even without any molecular symmetry (*e.g.*, (perchloro-2,2′-biphenylylene)diphenylsilane and -germane,[22] (η^5-C_5H_5)Fe(CO)$_2$SiMe$_2-$SiPh$_3$,[23] and (η^5-C_5H_5)Fe(CO)$_2$SiMe$_2-$GePh$_3$[7]).

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Supporting Information Available: For compound **V**, tables of anisotropic thermal parameters, full crystal data and structure refinement data, atomic coordinates and equivalent isotropic displacement parameters, complete bond lengths and angles, and H atoms at calculated coordinates (5 pages). Ordering information is given on any current masthead page.

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