Close Packing and Isostructuralism of Analogous Ph$_3$E–E'R$_3$ Compounds (R = Me, E, E' = Si, Ge, Sn; R = Ph, E, E' = Si, Ge, Sn, Pb): Crystal Structure of Ph$_3$Ge–GeMe$_3$

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Introduction

Kitaigorodskii[1] observed that the solid phases of molecules will be approximately isomorphous if their structures are obtained by an atom for atom replacement that does not diminish an already high packing coefficient (defined as $\eta = ZV_m/V$ where Z is the number of molecules in the unit cell, V_m is the volume of the molecule, and V is the unit cell volume). If this coefficient does decrease significantly, a new packing motif is adopted, termed by Kitaigorodskii a morphotropic step. When these ideas were promulgated, there were a relatively small number of organic molecules that could illustrate the concept; thus although morphotropic transitions are associated with the size of the core atoms, the extent of the size change required is unclear.

Group 14 organometallic compounds present an attractive series for investigating the features of size, electron-withdrawing/attracting substituents, and possible isomer formation that affect the structures of molecules. It is known that a conformational degree of freedom is needed for a morphotropic transition since the essentially spherical tetraphenyl group 14 derivatives (Ph$_4$M, M = C,[2] Si,[3] Ge,[4] Sn,[5] Pb[6]) each crystallize in the tetragonal space group $P\bar{4}2_1c$ (No. 114). A series of group 14 compounds that have progressive changes in central atom size and conformational freedoms, thereby permitting further examination of these problems, is Ph$_3$E–E'Me$_3$ (E, E' = Si, Ge, Sn) (series A, Chart 1). It has been shown that replacement of a Si nucleus in Ph$_3$Si–SiMe$_3$ (I)[7] with a Ge atom results in two isomers Ph$_3$Ge–SiMe$_3$ (II)[8] and Ph$_3$Si–GeMe$_3$ (III),[9] which crystallize in similar unit cells in the trigonal space group $P\bar{3}$ (No. 147); thus the trio of I, II, and III are isomorphous and isostructural although this is not immediately obvious.[9] The charged sizes of the two group 14 central atoms do not change a high packing coefficient, and the values are almost identical at $\eta = 0.73$ (Table 1). The Si–Ge bond distances in II and III are significantly different (2.384(1) (II) and 2.394(1) Å (III)), resulting from the effect of substitution of electron-withdrawing/donating groups on the energy levels and radial distributions of the bonding orbitals of Si and Ge.

Chart 1

Ph$_3$M—M'R$_3$

A R=Me	B R=Ph
I: M=M'=Si	VII: M=M'=Si
II: M=Ge, M'=Si	VIII: M=M'=Ge
III: M=Si, M'=Ge	IX: M=M'=Sn
IV: M=M'=Ge	X: M=M'=Pb
V: M=Sn, M'=Ge	XI: M=Ge, M'=Pb
VI: M=Ge, M'=Sn	XII: M=Sn, M'=Pb

Table 1. Molecular Volumes V_m (Å^3) and Packing Coefficients η for I–VI[a]

	V_m	η		V_m	η
I	357.2	0.731	IV	363.9	0.732
II	360.4	0.730	V	372.4	0.726
III	361.4	0.733	VI	373.0	0.731

[a] The following atomic radii (Å) were used: C, 1.80; H, 1.35; Si, 1.90; Ge, 2.10; Sn, 2.30. The applied packing radii to a first approximation were inferred from the van der Waals radii suggested by Allinger[10] with corrections made on the basis of a comparison with the original values given by Pauling.[11] The value for carbon was taken from ref 1.

When the silicon atom in II and III is replaced by tin, Ph$_3$Sn–GeMe$_3$ (V) and Ph$_3$Ge–SnMe$_3$ (VI), a morphotropic phase transition terminates their isostructuralism with the Si–Si and Si–Ge analogs. Thus V and VI crystallize in pseudohexagonal orthorhombic unit cells with a common space group $Pna2_1$ (No. 33), related to the trigonal cells as follows: $\sqrt{3}a' \approx b$, $b' \approx a$, $c' \approx c$ (where a, b, and c are the unit cell parameters of the orthorhombic cell (V, VI) and a', $b' = a'$, c' are the trigonal cell axes (I–III)).[12] The new molecular arrays maintain an optimum close packing with coefficients identical to I, II, and III (Table 1). The infinite columns of the head-to-tail associated molecules are arranged such that the ridges of the molecules are fitted in the clefts of the adjacent columns (oriented in the same direction) *via* glide planes are depicted in Figure 1. The bond lengths of V and VI exhibit the same relationship as those of II and III; however, our published data (2.599(3) (V) and 2.652(2) Å (VI)) are incorrect. We omitted collection of opposite Friedel pair data; thus polar dispersion errors significantly affected the heavy-atom positions and proper Ge–Sn bond lengths are 2.601(1) (V) and 2.611(1) Å (VI). The difference between the two isomers is now much less but still comparable to the trends noted for the pair II and III. With respect to the structural discussion that is the essence of this publication, the omission of Friedel pair collection is not relevant. A new refinement of the data for V and VI is the subject of a separate publication. To discover where the morphotropic step occurs in series A (I–VI), we have synthesized the missing link of the series, Ph$_3$Ge–GeMe$_3$ (IV), and determined its structure.

Experimental Section

Compound IV was synthesized in 65% yield using the literature procedure of Marchand and Gerval.[13]

X-ray Structure. Crystallographic data are given in Table 2. A transparent prism crystal grown in hexane (0.20 × 0.38 × 0.40 mm) was mounted on an Enraf-Nonius CAD4 single-crystal diffractometer. Data were collected by graphite-monochromated Mo α radiation at room temperature. The ω–2θ scan technique was applied ($2.0 \le \theta \le 38.3°$; variable scan speed 2.00–30.00°/min in ω; scan range $\Delta\omega = 0.51 + 0.46$

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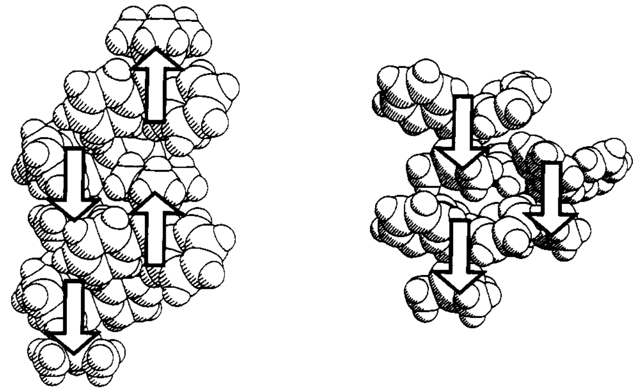

Figure 1. Packing motifs for compounds I–III and V–VI.

Table 2. Crystallographic Data for $Ph_3Ge–GeMe_3$ (IV)

formula $C_{21}H_{24}Ge_2$	fw 421.6
a = 11.335(1) Å	space group $P\bar{3}$ (No. 147)
c = 8.939(1) Å	λ(Mo Kα) = 0.710 69 Å
V = 994.6(2) Å^3	ρ_{calcd} = 1.408 g cm^{-3}
Z = 2	μ = 2.979 mm^{-1}
T = 298 °C	$R(F_o)$, $R_w(F_o)$ = 0.036, 0.036[a]

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

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	y	z	U(eq)[a]
Ge1	$^1/_3$	$^2/_3$	3384(1)	36(1)
Ge2	$^1/_3$	$^2/_3$	6090(1)	49(1)
C1	5161(2)	7236(2)	2625(2)	40(1)
C2	5371(2)	6702(2)	1315(2)	50(1)
C3	6672(2)	7084(2)	831(3)	59(1)
C4	7776(2)	7982(2)	1639(3)	63(1)
C5	7597(2)	8536(3)	2915(3)	69(1)
C6	6301(2)	8169(2)	3407(2)	57(1)
C7	3788(3)	8454(3)	6839(3)	98(2)
H2	4602	6059	739	
H3	6797	6716	–84	
H4	8676	8220	1315	
H5	8376	9185	3474	
H6	6191	8569	4306	
H7a	3785	8442	7913	
H7a	4676	9119	6489	
H7a	3128	8684	6489	

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Bond Lengths (Å) and Bond Angles (deg)

Bond Lengths					
Ge1–Ge2	2.418(1)	C1–C2	1.393(3)	C3–C4	1.360(3)
Ge1–C1 (3×)	1.957(2)	C1–C6	1.382(2)	C4–C5	1.365(4)
Ge2–C7 (3×)	1.943(4)	C2–C3	1.382(3)	C5–C6	1.384(3)

Bond Angles			
Ge2–Ge1–C1 (3×)	110.3(1)	C2–C1–C6	117.4(2)
C1–Ge1–C1 (3×)	108.6(1)	C1–C2–C3	121.0(2)
Ge1–Ge2–C7 (3×)	110.2(1)	C2–C3–C4	120.4(2)
C7–Ge2–C7 (3×)	108.7(1)	C3–C4–C5	119.6(2)
Ge1–C1–C2	122.1(1)	C4–C5–C6	120.5(2)
Ge1–C1–C6	120.5(1)	C1–C6–C5	121.1(2)

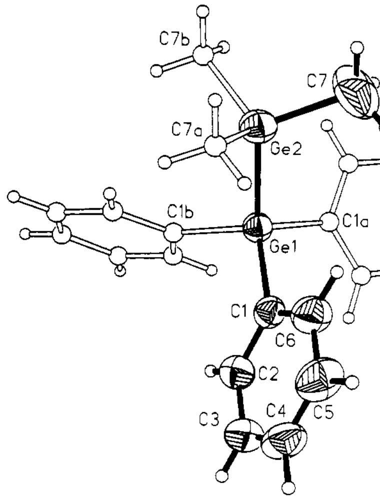

Figure 2. Molecular diagram with the numbering of atoms. Thermal ellipsoids represent 50% probability.

tan θ). The intensities of three standard reflections were measured every 60 min, and these remained constant throughout data collection. A total of 3707 reflections were collected ($-9 \le h \le 19$, $-19 \le k \le 0$, $0 \le l \le 15$) of which 2849 were independent (R_{int} = 0.0158). Empirical absorption corrections (ψ scan) were applied to the data (the minimum, maximum, and average transmission factors were 75.06, 99.98, and 89.00%). The structure was solved by the heavy-atom method and Fourier techniques (SHELXS-86[14]) and was refined by full-matrix least-squares procedures using the SHELX-76 program.[15] A total of 1870 observed reflections ($F_o > 4.0\sigma(F_o)$) were used in the refinement. The quantity minimized was $\sum w(F_o - F_c)^2$. Hydrogen atoms were included as riding atoms, and common isotropic U's were refined for the phenyl (0.078(4) Å^2) and the methyl (0.17(1) Å^2) hydrogen atoms. The weighting scheme applied was $w^{-1} = \sigma^2(F) + 0.0002F^2$. A total of 72 parameters were refined. Final R indices: R = 0.036, R_w = 0.036 (obs data); R = 0.073, R_w = 0.039 (all data); goodness-of-fit 1.42. The largest and mean Δ/σ were 0.004 and 0.001; the data-to-parameter ratio was 26:1. The largest difference peak and difference hole in the final difference map were 0.50 and –0.29 e Å^{-3}. Final atomic parameters, bond lengths, and bond angles are listed in Tables 3 and 4.

Results and Discussion

The structure of $Ph_3Ge–GeMe_3$ (IV) is illustrated in Figure 2, a stereoview of the molecular packing is given in Figure 3, and the bond lengths and angles are presented in Table 4. The compound is isostructural with I, II, and III. An overlap diagram of the least-squares fit for all 23 non-hydrogen atoms is shown in Figure 4. A 0.58° rotation was required when IV was fit to I (rms deviation 0.081 Å). The highest deviations from the assumed model were observed for the C7 methyl carbon atoms (Δ = 0.149 Å) due to a rotation about the Ge–Ge bond (C1–Ge1–Ge2–C7 = 31.9(1)°; C1–Si1–Si2–C7 = 34.2(1)°) and the difference in Si–C(methyl) and Ge–C(methyl) bond distances (Ge–C = 1.943(4) and Si–C = 1.862(2) Å). This result clearly states that the morphotropic step occurs between IV and V upon introduction of the tin atom into the series of compounds. The packing coefficient of IV remains identical to those exhibited by I, II, III, V, and VI (Table 1).

Regarding the full set of isomers and parent molecules ($Ph_3E–E'Me_3$, E, E′ = Si, Ge, Sn, Pb), the existence of two isostructural groups is now established (**a**) Si–Si, Si–Ge, Ge–Ge; (**b**) Ge–Sn. Clearly, this conclusion excludes the C–C, C–Si and Sn–Sn, Sn–Pb, Pb–Pb systems from this grouping since to date they are not reported. It is possible that further morphotropic steps occur with these compounds especially for the C–C and C–Si systems where a larger break in sequential atomic radii exists. However, there are two additional factors that should be addressed: (1) We may have two distinct series, E = E′ (parent) and E ≠ E′ (isomers), which (with respect to their crystallographic symmetry) coincide at moderate difference in atomic radii of the core atoms. The E = E′ compounds (zero radius difference) might always be isostructural and isomorphous. The possibility of polymorphism of the Ge–Sn isomers cannot re ruled out; i.e., they may have a crystal form with the $P\bar{3}$ space group.

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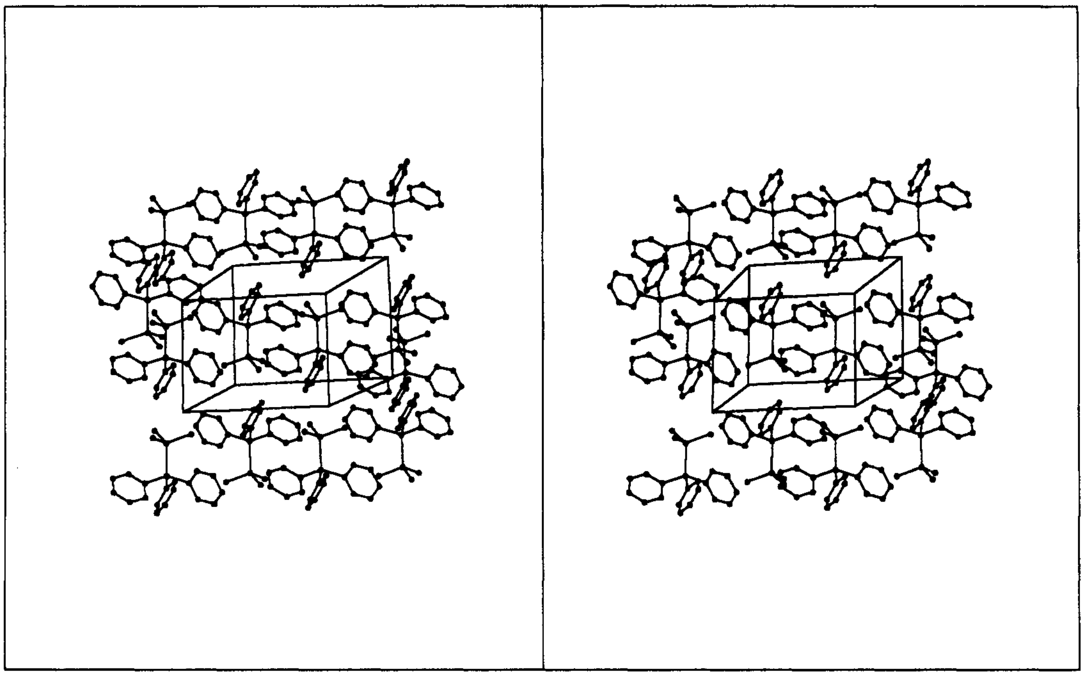

Figure 3. Stereoview of the molecular packing in **IV** (hydrogen atoms are omitted for clarity).

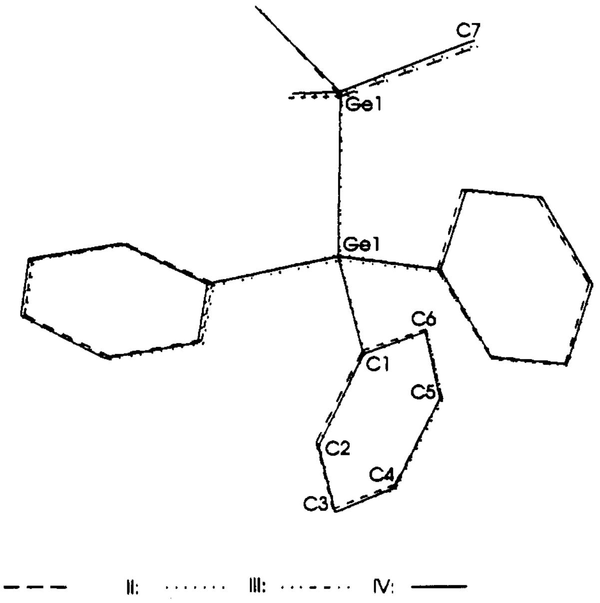

Figure 4. Overlap diagram of I–IV.

The symmetric shape of the group 14 hexaphenyl series **B**, $Ph_3E–E'Ph_3$, the resulting positional disorder of the core heavy atoms, and cocrystallization make **VII–XII** a less useful series for studying isostructuralism. The structure of **VII** (E = E′ = Si) is only available from a sample cocrystallized with **X** (E = E′ = Pb) in space group $P\bar{1}$ (No. 2).[16] In its pure form, **X** crystallizes in space group $P2_1/c$ (No. 14)[17] and it is perfectly isostructural with **XII** (E = Sn, E′ = Pb);[16] however, **XII** is disordered and the heavy-atom sites are occupied with Sn and Pb in 1:1 ratio. **VIII** (E = E′ = Ge) exhibits two crystal forms;[18] **VIIIa** crystallizes in space group $P\bar{1}$ (No. 2), while **VIIIb** crystallizes with two molecules of benzene in space group $R3$ (No. 146).[19] **VIIIb** is pseudo-isostructural with the solvate crystal **IXb** (E = E′ = Sn),[20] which crystallizes in the centrosymmetric space group $R\bar{3}$ (No. 148). **VIIIa** has no structural relationship to the unsolvated **IXa** (space group $P2_1/c$, No. 14).[21] **XI** (E = Ge, E′ = Pb) (space group $P\bar{1}$, No. 2) is pseudo-isostructural with **VIIIa** (space group $P1$, No. 1),[16] a relationship similar to that of the **VIIIb–IXb** solvates noted above. The heavy-atom sites in the crystal structure of **XI** are statistically filled with Ge and Pb in a 1:1 ratio.

Germanium-Germanium Bond Distances in Linear Germanes. A search of the Cambridge Crystallographic Data files retrieved 14 linear germane structures with an average Ge–Ge bond distance of 2.46(8) Å.[22] The Ge–Ge bond lengths vary as a function of the electron-withdrawing and/or steric properties of the various substituents. Thus, the bond length of $PhCl_2Ge–GePhCl_2$ (2.413 Å) is one of the shortest and responds to the electron-withdrawing nature of the substituents.[23] On the other hand, the six electron-donating and bulky *tert*-butyl substituents of $t\text{-}Bu_6Ge_2$ result in the longest Ge–Ge bonds, 2,708(2) Å,[24] a result that parallels the case of the corresponding hexa-*tert*-butyldisilane, 2.697(3) Å.[25] The bond length of **IV** (2.418(1) Å) is shorter than that of the hexaphenyl analog, Ph_6Ge_2 (2.432 Å),[26] a response to the relatively less sterically demanding methyl groups. This result parallels the difference reported on changing from $Ph_3Ge–GePh_2–GePh_3$ (2.440 Å)[27] to $Ph_3Ge–GeMe_2–GePh_3$ (2.429 Å),[28] where a related Ph to Me substitution occurs.

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Supplementary Material Available: For complex **IV**, a table of anisotropic thermal parameters (1 page). Ordering information is given on any current masthead page.

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