# Molecular Structure of Hexakis(trimethylelementyl)benzenes

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**Abstract:** Reaction of hexabromobenzene with chlorotrimethylgermane and magnesium affords hexakis(trimethylgermyl)benzene (**1c**) and 1,1,3,4,6,6-hexakis(trimethylgermyl)-1,2,4,5-hexatetraene. The synthesis of **1c** is the first of a hexakis(trimethylelementyl)benzene. Crystals of **1c** are orthorhombic, space group *Pnca* (no. 60), $a = 12.338$ (5) Å, $b = 14.175$ (4) Å, $c = 19.697$ (6) Å, and $Z = 4$. The molecule in the crystal has $C_2$ site symmetry. The benzene ring is very slightly puckered, and the six germaniums are located alternately above and below the average ring plane, with an average Ge–$C_{ar}$–$C_{ar}$–Ge torsion angle of 57.1°. The structures of 1,2,4,5-tetra-*tert*-butylbenzene and of the as yet unsynthesized hexa-*tert*-butylbenzene (**1a**) have been calculated by the empirical force field method. The structure of **1a** calculated with the MM2 force field has $D_3$ symmetry and closely resembles the structure of **1c**. Similar calculations with appropriately parametrized force fields yield $D_3$ ground-state conformations for hexakis(trimethylsilyl)benzene (**1b**) and for **1c**. The calculated and found structural parameters of **1c** are in good overall agreement. The force-field calculations also reveal the existence of higher energy conformers with $S_6$ symmetry for all three hexakis(trimethylelementyl)benzenes.

The study of hexaalkylbenzenes presents an opportunity to explore the effect of nonbonded interactions on molecular structure and internal mobility in sterically crowded molecules,[2] as previously demonstrated in work on hexaethylbenzene,[3] hexaisopropylbenzene,[4] and related hydrocarbons.[5] In this paper we report the effect of steric strain on the structures of hexakis(trimethylelementyl)benzenes.

**Synthesis and X-ray Structure of Hexakis(trimethylgermyl)benzene.** Neither the synthesis of the hexa-*tert*-butylbenzene (**1a**) nor that of any other hexakis(trimethylelementyl)benzene had been reported prior to our work. An attempted preparation[6] of hexakis(trimethylsilyl)benzene (**1b**) by reaction of hexabromobenzene with magnesium and chlorotrimethylsilane had resulted instead in the formation of 1,1,3,4,6,6-hexakis(trimethylsilyl)-1,2,4,5-hexatetraene (**2**) (eq 1). We found that reaction of hexabromobenzene with magnesium and chlorotrimethylgermane in tetrahydrofuran yielded hexakis(trimethylgermyl)benzene (**1c**) and 1,1,3,4,6,6-hexakis(trimethylgermyl)-1,2,4,5-hexatetraene (**3**) (eq 1), as well as a third product tentatively identified as 1,2,4,5-tetrakis(trimethylgermyl)benzene (**4**). The relative amounts of these products were found to depend on the reaction conditions employed.[7] Formation of **3** parallels the formation of **2**, for which a reaction mechanism has been suggested.[8]

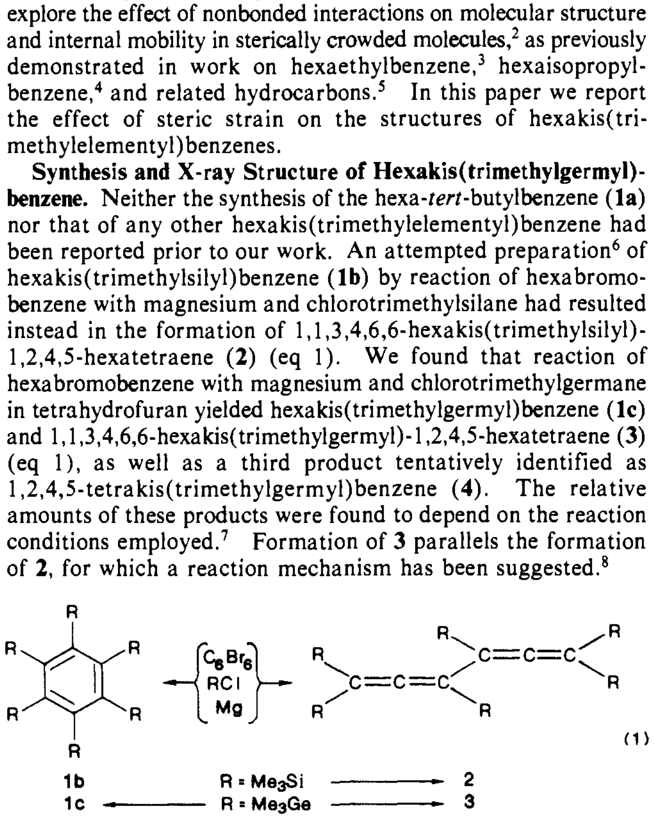

Table I. Final Atomic Parameters for **1c**[a,b]

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Ge(1) | 0.19389 (8) | 0.11901 (6) | 0.40205 (4) |
| Ge(2) | −0.00296 (8) | 0.07975 (7) | 0.26236 (5) |
| Ge(3) | 0.17963 (8) | 0.11528 (7) | 0.12014 (4) |
| C(1) | 0.2052 (6) | 0.0310 (4) | 0.3232 (3) |
| C(2) | 0.1550 (6) | 0.0571 (5) | 0.2616 (3) |
| C(3) | 0.2032 (6) | 0.0303 (5) | 0.1992 (3) |
| C(11) | 0.3449 (7) | 0.1513 (6) | 0.4215 (4) |
| C(12) | 0.1278 (8) | 0.0835 (6) | 0.4885 (4) |
| C(13) | 0.1312 (9) | 0.2379 (6) | 0.3736 (5) |
| C(21) | −0.0658 (7) | 0.0572 (7) | 0.3502 (5) |
| C(22) | −0.0633 (9) | 0.1973 (8) | 0.2278 (5) |
| C(23) | −0.0611 (9) | −0.0241 (7) | 0.2079 (6) |
| C(31) | 0.1838 (8) | 0.2424 (6) | 0.1585 (5) |
| C(32) | 0.0491 (8) | 0.1046 (7) | 0.0653 (5) |
| C(33) | 0.3052 (8) | 0.1154 (7) | 0.0598 (6) |

[a] Standard deviations in parentheses. [b] Anisotropic thermal parameters and final atomic parameters for hydrogen are given in the Supplementary Material.

The structure of **1c** was determined by X-ray crystallography. Crystals of **1c** belong to the orthorhombic system, space group *Pnca*. The four molecules in the unit cell have crystallographic twofold symmetry and approximate molecular $D_3$ symmetry. A stereoview of **1c** is shown in Figure 1, final atomic parameters are listed in Table I, and bond lengths, bond angles, and torsion angles are given in Table II, along with the corresponding values obtained by empirical-force-field (EFF) calculations (see below).

The twofold crystallographic axis passes through the midpoints of the C(1)–C(1′) and C(3)–C(3′) bonds. The benzene ring is very slightly puckered and assumes the conformation of a flattened chair. Four of the aromatic carbons, C(1′), C(2), C(2′), and C(3), are nearly coplanar, with an average deviation from the least-squares plane of 0.006 Å, while C(1) and C(3′) lie above and below that plane by +0.089 and −0.056 Å, respectively. The average bond distance between aromatic carbons ($C_{ar}$–$C_{ar}$), 1.418 Å, is significantly longer than that in benzene (1.39 Å). The average bond distance between germanium and methyl carbon atoms ($C_m$–Ge), 1.948 Å, conforms with the value of 1.945 Å reported for methylgermane[9] and is shorter than the average $C_{ar}$–Ge bond distance, 1.988 Å.

The $C_{ar}$–Ge vectors deviate markedly from their planes of attachment, $C_{ar}$(ortho)–$C_{ar}$(ipso)–$C_{ar}$(ortho). Thus, the angle between C(1)–Ge(1) and the plane defined by C(1′)–C(1)–C(2) is +22.5°; similar out-of-plane displacements are observed for C(2)–Ge(2) (−22.3°) and by C(3)–Ge(3) (+21.5°). Accordingly,

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[2] For an excellent review on the subject of steric crowding in organic molecules, see: Tidwell, T. T. *Tetrahedron* **1978**, *34*, 1855. A number of the "challenging goals" mentioned in this review have since been realized, e.g. tetra-*tert*-butyltetrahedrane (Maier, G.; Pfriem, S.; Schäfer, U.; Matusch, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 520. Maier, G.; Pfriem, S.; Schäfer, U.; Malsch, K.-D.; Matusch, R. *Chem. Ber.* **1981**, *114*, 3965) and permethylcyclohexane (Fitjer, L.; Scheuermann, H.-J.; Wehle, D. *Tetrahedron Lett.* **1984**, *25*, 2329).

[3] Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6073.

[4] Arnett, E. M.; Bollinger, J. M. *J. Am. Chem. Soc.* **1964**, *86*, 4729. Siegel, J.; Gutiérrez, A.; Schweizer, W. B.; Ermer, O.; Mislow, K. *Ibid.* **1986**, *108*, 1569.

[5] (a) Bar, I.; Bernstein, J.; Christensen, A. *Tetrahedron* **1977**, *33*, 3177. (b) Weissensteiner, W.; Gutiérrez, A.; Radcliffe, M. D.; Siegel, J.; Singh, M. D.; Tuohey, P. J.; Mislow, K. *J. Org. Chem.* **1985**, *50*, 5822.

[6] Brennan, T.; Gilman, H. *J. Organomet. Chem.* **1968**, *11*, 625.

[7] Accordingly, it seems conceivable that **1b** might be obtainable under conditions different from those previously employed.[6]

[8] Ballard, D.; Brennan, T.; Fearon, F. W. G.; Shiina, K.; Haiduc, I.; Gilman, H. *Pure Appl. Chem.* **1969**, *19*, 449.

[9] Laurie, V. W. *J. Chem. Phys.* **1959**, *30*, 1210.

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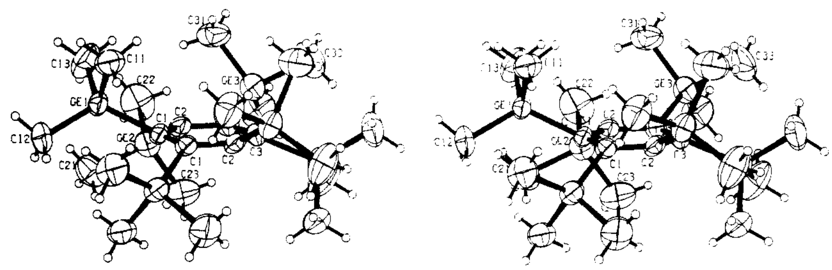

**Figure 1.** Stereoview of the X-ray structure of hexakis(trimethylgermyl)benzene (**1c**).

the six germaniums are located alternately above and below the average ring plane; the average out-of-plane displacement of 0.90 Å corresponds to an average Ge–$C_{ar}$–$C_{ar}$–Ge torsion angle of 57.1°. The six germanium atoms when connected thus describe a "super-chair", with edges averaging 3.67 Å. The $C_{ar}$–$C_{ar}$–Ge bond angles are all appreciably smaller than 120° (average 117.7°) as a result of these out-of-plane displacements; in contrast, the $C_{ar}$–$C_{ar}$–$C_{ar}$ angles do not deviate significantly from 120°. Although the alternating out-of-plane displacement of germanium atoms is precedented by similar displacements in other hexasubstituted benzenes,[10] the magnitude of the displacement in **1c** is considerably greater than that of any so far reported.[11]

Some of the bond angles subtended by germanium are grossly distorted from tetrahedral values. Thus, of the three $C_{ar}$–Ge–$C_m$ angles in each trimethylgermyl group, the one that corresponds to C(*n*)-Ge(*n*)-C(*n*2), *n* = 1, 2 or 3, is opened to an average of 121.5°. The plane defined by C(*n*)–Ge(*n*)–C(*n*2) makes a dihedral angle of 108.1° (the tilt angle) with the plane of attachment and bisects, approximately, the $C_m$–Ge–$C_m$ angle which corresponds to C(*n*1)-Ge(*n*)-C(*n*3) and which is compressed to an average of 102.9°. The average value of the remaining $C_m$–Ge–$C_m$ angles, 107.9°, is relatively normal.

The X-ray structure of **1c** thus reveals that nonbonded interactions between ortho- and meta-related trimethylgermyl moieties result in major deviations from normal bonding parameters, most strikingly in large out-of-plane displacements of the trimethylgermyl groups that resemble those previously observed in 1,8-bis(trimethylgermyl)naphthalene.[12] Given the shorter covalent radii of carbon and silicon, as compared to germanium, one would expect overcrowding in **1a** and **1b** to be at least as severe as in **1c**. To explore the consequences of such steric strain on the molecular geometry and steric energy of these as yet unsynthesized molecules, we resorted to EFF calculations.

## Empirical Force Field Calculations

**A Test of the Method: 1,2,4,5-Tetra-*tert*-butylbenzene (5).** EFF calculations have proven to be highly successful in modeling structures of hydrocarbons.[13] As a further test of the reliability of this method, we compared the calculated structure of 1,2,4,5-tetra-*tert*-butylbenzene (**5**), a compound closely related to **1a**, with the reported[14] X-ray structure. With use of Allinger's MM2 force field,[15] these calculations[16] yielded two energy minima, corresponding to structures with $C_{2h}$ and $D_2$ symmetry, that

**Table II.** Experimental and Calculated Structural Parameters for Hexakis(trimethylgermyl)benzene (**1c**)[a]

| atoms[b] | exptl (X-ray)[c] | calcd (EFF)[d] |
|---|---|---|
| | Bond Lengths | |
| Ge(1)-C(1) | 1.998 (6) | 1.983 |
| Ge(1)-C(11) | 1.956 (9) | 1.990 |
| Ge(1)-C(12) | 1.954 (8) | 1.935 |
| Ge(1)-C(13) | 1.938 (9) | 1.971 |
| Ge(2)-C(2) | 1.976 (7) | 1.983 |
| Ge(2)-C(21) | 1.923 (9) | 1.971 |
| Ge(2)-C(22) | 1.948 (11) | 1.935 |
| Ge(2)-C(23) | 1.958 (10) | 1.990 |
| Ge(3)-C(3) | 1.991 (7) | 1.983 |
| Ge(3)-C(31) | 1.955 (9) | 1.990 |
| Ge(3)-C(32) | 1.945 (10) | 1.935 |
| Ge(3)-C(33) | 1.953 (11) | 1.971 |
| C(1)-C(2) | 1.411 (9) | 1.407 |
| C(1)-C(1′) | 1.412 (13) | 1.409 |
| C(2)-C(3) | 1.417 (9) | 1.409 |
| C(3)-C(3′) | 1.439 (14) | 1.407 |
| | Bond Angles | |
| C(1)-Ge(1)-C(11) | 103.5 (3) | 103.5 |
| C(1)-Ge(1)-C(12) | 123.1 (3) | 121.8 |
| C(1)-Ge(1)-C(13) | 110.3 (3) | 113.9 |
| C(11)-Ge(1)-C(12) | 106.7 (4) | 109.2 |
| C(11)-Ge(1)-C(13) | 103.5 (4) | 96.7 |
| C(12)-Ge(1)-C(13) | 108.0 (4) | 108.5 |
| C(2)-Ge(2)-C(21) | 112.2 (3) | 113.9 |
| C(2)-Ge(2)-C(22) | 120.9 (4) | 121.8 |
| C(2)-Ge(2)-C(23) | 103.6 (4) | 103.5 |
| C(21)-Ge(2)-C(22) | 107.6 (4) | 108.5 |
| C(21)-Ge(2)-C(23) | 102.8 (4) | 96.7 |
| C(22)-Ge(2)-C(23) | 108.2 (4) | 109.2 |
| C(3)-Ge(3)-C(31) | 104.6 (3) | 103.5 |
| C(3)-Ge(3)-C(32) | 120.5 (3) | 121.8 |
| C(3)-Ge(3)-C(33) | 111.1 (4) | 113.9 |
| C(31)-Ge(3)-C(32) | 108.0 (4) | 109.2 |
| C(31)-Ge(3)-C(33) | 102.3 (4) | 96.7 |
| C(32)-Ge(3)-C(33) | 108.6 (4) | 108.5 |
| Ge(1)-C(1)-C(2) | 118.3 (5) | 118.6 |
| Ge(1)-C(1)-C(1′) | 116.3 (4) | 118.0 |
| C(2)-C(1)-C(1′) | 120.5 (4) | 120.0 |
| Ge(2)-C(2)-C(1) | 118.0 (5) | 118.6 |
| Ge(2)-C(2)-C(3) | 117.6 (5) | 118.0 |
| C(1)-C(2)-C(3) | 119.4 (6) | 120.0 |
| Ge(3)-C(3)-C(2) | 117.1 (5) | 118.0 |
| Ge(3)-C(3)-C(3′) | 118.6 (3) | 118.6 |
| C(2)-C(3)-C(3′) | 119.8 (4) | 120.0 |
| | Torsion Angles[e] | |
| C(1)-C(2)-C(3)-C(3′) | 6.8 | 4.0 |
| C(2)-C(1)-Ge(1)-C(11) | −116.6 | −117.1 |
| C(2)-C(1)-Ge(1)-C(12) | 122.3 | 119.8 |
| C(2)-C(1)-Ge(1)-C(13) | −6.7 | −13.4 |
| Ge(1)-C(1)-C(2)-Ge(2) | −57.1 | −46.8 |

[a] Bond lengths in angstroms, angles in degrees. [b] Atom numbers are given in Figure 1. [c] Standard deviations in parentheses. [d] Based on a $D_3$ conformation. See text. [e] Average values.

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(10) (a) Hexakis(bromomethyl)benzene: Marsau, M. P. *Acta Crystallogr.* **1965**, *18*, 851. (b) Hexanitrobenzene: Akopyan, Z. A.; Struchov, Y. T.; Dashevskii, V. G. *J. Struct. Chem.* (*USSR*) **1966**, *7*, 385. (c) Hexaphenylbenzene: Bart, J. C. J. *Acta Crystallogr., Sect. B* **1968**, *B24*, 1277. (d) Hexaiiodobenzene: Steer, R. J.; Watkins, S. F.; Woodward, P. *J. Chem. Soc. C* **1970**, *403*. (e) Hexacyclopropylbenzene: ref 5a. (f) Hexakis(trifluoromethyl)benzene: Couldwell, M. H.; Penfold, B. R. *J. Cryst. Mol. Struct.* **1976**, *6*, 59. (g) Hexakis(phenylthio)benzene: Hardy, A. D. U.; MacNicol, D. D.; Wilson, D. R. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1011. (h) Hexakis(benzylthiomethyl)benzene: Hardy, A. D. U.; MacNicol, D. D.; Swanson, S.; Wilson, D. R. *Ibid.* **1980**, 999. (i) Hexaethylbenzene: ref 3.

(11) Average out-of-plane displacements of X groups in $C_6X_6$[10] are 0.03 Å (X = Et, $NO_2$), 0.04 Å (X = I), 0.08 Å (X = Ph, $CH_2SCH_2Ph$), 0.09 Å (X = SPh), 0.12 Å (X = c-Pr), and 0.34 Å (X = $CF_3$). The torsion angles associated with the last two displacements are $(C_2H_5)C–C_{ar}–C_{ar}–C(C_2H_5)$ = 7.8° and $(F_3)C–C_{ar}–C_{ar}–C(F_3)$ = 25.1° (calculated from the atomic coordinates reported in ref 5a and 10f, respectively).

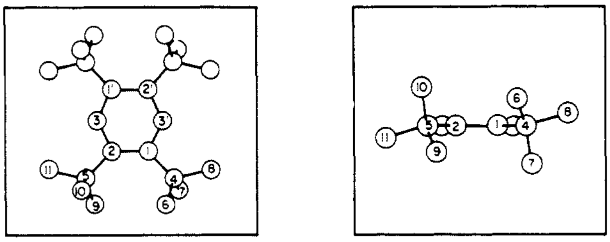
(12) Blount, J. F.; Cozzi, F.; Damewood, J. R.; Jr.; Iroff, L. D.; Sjöstrand, U.; Mislow, K. *J. Am. Chem. Soc.* **1980**, *102*, 99.

(13) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, D.C., 1982.

(14) Stam, C. H. *Acta Crystallogr., Sect. B* **1972**, *B28*, 2715.

(15) Allinger, N. L.; Yuh, Y. H. *QCPE* **1981**, *13*, 395. Two modifications were used for $C_{ar}$–$C_{ar}$ bonds, $l^0$ = 1.3937 Å and $k_s$ = 8.0667 mdyn Å$^{-1}$. All torsional parameters for $C_{ar}$ were taken to be the same as for C(sp$^2$). See: Ōsawa, E.; Onuki, Y.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 7475.

**Table III.** Experimental and Calculated Structural Parameters for 1,2,4,5-Tetra-*tert*-butylbenzene (**5**)[a]

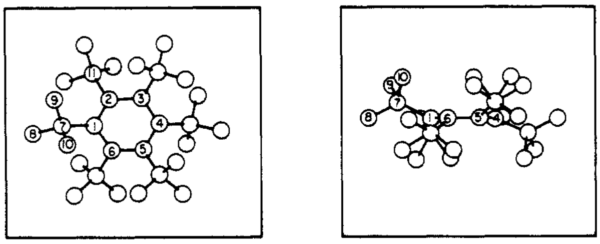


| atoms[b] | exptl (X-ray)[c] | calcd (EFF) |
|---|---|---|
| Bond Lengths | | |
| C(1)-C(2) | 1.425 (5) | 1.418 |
| C(1)-C(3') | 1.395 (4) | 1.407 |
| C(1)-C(4) | 1.567 (5) | 1.561 |
| C(2)-C(3) | 1.402 (4) | 1.407 |
| C(2)-C(5) | 1.572 (4) | 1.561 |
| C(4)-C(6) | 1.560 (2) | 1.546 |
| C(4)-C(7) | 1.515 (5) | 1.545 |
| C(4)-C(8) | 1.554 (6) | 1.568 |
| C(5)-C(9) | 1.525 (6) | 1.546 |
| C(5)-C(10) | 1.519 (6) | 1.545 |
| C(5)-C(11) | 1.581 (7) | 1.568 |
| Bond Angles | | |
| C(2)-C(1)-C(3') | 115.0 (3) | 114.0 |
| C(2')-C(3')-C(1) | 129.9 | 130.3 |
| C(2)-C(1)-C(4) | 130.3 (2) | 130.3 |
| C(3')-C(1)-C(4) | 114.7 (3) | 115.7 |
| C(1)-C(2)-C(3) | 115.1 (2) | 114.0 |
| C(1)-C(2)-C(5) | 130.8 (3) | 130.3 |
| C(3)-C(2)-C(5) | 114.0 (3) | 115.7 |
| C(1)-C(4)-C(6) | 112.6 (4) | 115.0 |
| C(1)-C(4)-C(7) | 109.7 (3) | 109.1 |
| C(1)-C(4)-C(8) | 112.0 (3) | 114.4 |
| C(6)-C(4)-C(7) | 112.9 (4) | 113.8 |
| C(6)-C(4)-C(8) | 101.6 (4) | 100.2 |
| C(7)-C(4)-C(8) | 107.8 (4) | 103.6 |
| C(2)-C(5)-C(9) | 115.0 (3) | 115.0 |
| C(2)-C(5)-C(10) | 110.0 (3) | 109.1 |
| C(2)-C(5)-C(11) | 111.3 (3) | 114.4 |
| C(9)-C(5)-C(10) | 113.2 (4) | 113.8 |
| C(9)-C(5)-C(11) | 100.8 (3) | 100.2 |
| C(10)-C(5)-C(11) | 105.9 (4) | 103.6 |
| Torsion Angles[d] | | |
| C(3')-C(1)-C(2)-C(3) | -1.2 | -1.5 |
| C(1)-C(2)-C(3)-C(1') | 1.4 | 1.8 |
| C(2)-C(1)-C(4)-C(7) | 80.9 | 83.1 |
| C(2)-C(1)-C(4)-C(6) | -45.6 | -46.1 |
| C(2)-C(1)-C(4)-C(8) | -159.4 | -161.4 |
| C(1)-C(2)-C(5)-C(9) | -44.8 | -46.1 |
| C(1)-C(2)-C(5)-C(10) | 84.3 | 83.1 |
| C(1)-C(2)-C(5)-C(11) | -158.6 | -161.4 |

[a] Bond lengths in angstroms, angles in degrees. [b] Atom numbers are those given in ref 14 for the X-ray structure (crystallographic $C_i$ symmetry) and are shown above in renderings of the calculated $C_{2h}$ structure. [c] Standard deviations in parentheses. [d] Torsion angles for the X-ray structure were calculated from the atomic coordinates given in ref 14.

differed by only 0.1 kcal mol$^{-1}$ in steric energy. The X-ray structure ($C_i$ site symmetry) has approximate $C_{2h}$ symmetry;[14] the comparison was therefore made between the two centrosymmetric structures. The results (Table III) indicate excellent overall agreement between calculated and observed structural parameters. The calculated results are also in accord with the conclusion,[14] based on the observation of crystal disorder and the occurrence of a noncentrosymmetric vibration in the IR spectrum of **5**, that the energy difference between the $C_{2h}$ and $D_2$ conformations must be quite small.

**Table IV.** Structural Parameters Calculated for Hexa-*tert*-butylbenzene (**1a**) and Hexakis(trimethylsilyl)benzene (**1b**)[a]



| atom[b] | **1a** | **1b** |
|---|---|---|
| Bond Lengths | | |
| C(1)-C(2) | 1.422 | 1.410 |
| C(2)-C(3) | 1.426 | 1.413 |
| C(1)-X(7) | 1.605 | 1.885 |
| X(7)-C(8) | 1.547 | 1.859 |
| X(7)-C(9) | 1.563 | 1.890 |
| X(7)-C(10) | 1.569 | 1.906 |
| Bond Angles | | |
| C(1)-C(2)-C(3) | 119.9 | 120.0 |
| C(2)-C(1)-X(7) | 117.6 | 118.3 |
| C(6)-C(1)-X(7) | 117.5 | 117.4 |
| C(1)-X(7)-C(9) | 114.3 | 114.5 |
| C(1)-X(7)-C(10) | 104.5 | 104.2 |
| C(1)-X(7)-C(8) | 124.7 | 121.8 |
| C(8)-X(7)-C(9) | 104.8 | 107.1 |
| C(8)-X(7)-C(10) | 108.7 | 109.4 |
| C(9)-X(7)-C(10) | 96.1 | 96.7 |
| Torsion Angles[c] | | |
| C(1)-C(2)-C(3)-C(4) | 7.0 | 4.3 |
| C(2)-C(1)-X(7)-C(8) | 119.4 | 120.3 |
| C(2)-C(1)-X(7)-C(9) | -11.4 | -11.3 |
| C(2)-C(1)-X(7)-C(10) | -115.1 | -115.6 |
| X(7)-C(1)-C(2)-X(11) | -58.4 | -52.1 |

[a] Bond lengths in angstroms, angles in degrees. [b] Atom numbers are shown above in renderings of the calculated $D_3$ structure. X = C in **1a** and Si in **1b**. [c] Average values.

Results with the MMPI force field[19] were less satisfactory. Thus, the observed[14] deviations of C(1), C(2), and C(3) from the best plane through the benzene ring are -0.005, +0.005, and -0.005 Å, respectively. These values are well reproduced by the deviations calculated with MM2 parameters, -0.006, +0.006, and -0.006 Å, respectively. In contrast, MMPI calculations give deviations of -0.076, +0.076, and -0.082 Å, respectively, i.e., they grossly exaggerate the distortion of the benzene ring. In this connection, we note that MMPI calculations have also been reported[20] to yield a structure of 1,2-di-*tert*-butylbenzene in which the conformations of the *tert*-butyl groups differ substantially from those observed in **5**. In contrast, we found that MM2 calculations give a $C_2$ structure of 1,2-di-*tert*-butylbenzene which accords in all significant respects with the corresponding moiety of **5**, including major in-plane deformations.[21]

The satisfactory agreement between X-ray and calculated structures of **5** encouraged our belief that the ground-state structure of **1a** might be reliably assessed by MM2/BIGSTRN-3

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(16) Input geometries were based on standard bond lengths and bond angles. These structures were then optimized[17] by the program BIGSTRN-3.[18] Final structurs were characterized as minima by the absence of negative eigenvalues in the matrix of analytical second derivatives.

(17) Geometry optimizations were routinely begun with the variable-metric method and concluded with the full-matrix Newton-Raphson method; analytical second derivatives were used at both stages. The final convergence criteria for the Newton-Raphson stage were as follows: rms gradient less than $10^{-6}$ kcal mol$^{-1}$ Å$^{-1}$ and rms atom movement less than $10^{-6}$ Å.

(18) BIGSTRN-3 (Nachbar, R. B., Jr.; Mislow, K.) is available as QCPE No. 514 from QCPE, Department of Chemistry, Indiana University, Bloomington, IN 47405.

(19) Allinger, N. L.; Yuh, Y. H. *QCPE* **1978**, *10*, 318.

(20) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893.

(21) Selected structural parameters found for **5** by X-ray crystallography[14] and calculated in the present work for the $C_{2h}$ and $D_2$ conformations are as follows: C(2)-C(1)-C(4)-C(7) = 82.6° (av), 83.1°, and 83.6°, respectively; C(2)-C(1)-C(4) = 130.5° (av), 130.3°, and 130.4°, respectively; C(2')-C(3')-C(1) = 129.9°, 130.3°, and 132.0°, respectively; C(1)-C(2) = 1.425, 1.418, and 1.417 Å, respectively. The corresponding structural parameters calculated for 1,2-di-*tert*-butylbenzene are 83.1°, 129.8°, 126.0°, and 1.433 Å, respectively.

EFF calculations.[15,16] The results of these calculations are reported in the next section.

**Hexa-*tert*-butylbenzene (1a).** Two energy minima for **1a** were found by the EFF calculations, one corresponding to a ground-state structure with $D_3$ symmetry and the other, 18.4 kcal mol$^{-1}$ higher in energy, to one with $S_6$ symmetry. The structural parameters of the calculated $D_3$ conformation are listed in Table IV. The $C_{ar}-C_q$ bond length of 1.605 Å is comparable to the $C_1-C_q$ bond length of 1.611 Å in tri-*tert*-butylmethane[22] and is indicative of the considerable internal strain in **1a**.

The average $C_m-C_q$ bond length in **1a**, 1.560 Å, is shorter by 0.045 Å than the $C_{ar}-C_q$ bond length. Recall that the average $C_m$–Ge bond length in **1c** was also found to be 0.040 Å shorter than the average $C_{ar}$–Ge bond length. In this as in most other respects, the X-ray structure of **1c** bears a strong resemblance to the calculated structure of **1a**, as shown by a comparison between the average structural parameters found by X-ray diffraction for **1c** (Table II) with the corresponding calculated parameters for **1a** (Table IV).

The benzene ring in the $S_6$ conformation is almost planar ($C_{ar}-C_{ar}-C_{ar}-C_{ar} = 2.9°$), and one of the methyl carbons almost eclipses the plane ($C_{ar}-C_{ar}-C_q-C_m = 5.4°$), thus imparting approximate $C_{6h}$ symmetry to this structure. Substantial internal strain in this conformer is manifested by exceptionally large bond length and angle deformations ($C_{ar}-C_{ar} = 1.450$ Å, $C_{ar}-C_q = 1.645$ Å, $C_{ar}-C_q-C_m$ (eclipsed) = 134.2°).

**Hexakis(trimethylsilyl)benzene (1b).** The MM2 force field contains all but two of the parameters necessary to calculate the structure of this compound. The two missing parameters, for Si–$C_{ar}-C_{ar}$–Si and $C_{ar}-C_{ar}-C_{ar}$–Si torsion, were supplied by optimizing correspondence with the crystal structure of tetrakis(trimethylsilyl)ethylene.[23] With the inclusion of the new parameters,[24] the MM2 force field yields a calculated structure of the ethylene ($D_2$ symmetry) that reproduces the X-ray structure ($C_1$ site symmetry, approximately $D_2$) with reasonable accuracy.[25]

The calculated ground state of **1b** has $D_3$ symmetry, with structural parameters listed in Table IV. Comparison of the corresponding parameters for **1a** and **1b** shows that the two structures closely resemble each other. As in the case of **1a**, the higher energy $S_6$ conformation of **1b** has approximate $C_{6h}$ symmetry ($C_{ar}-C_{ar}-C_{ar}-C_{ar} = 1.7°$, $C_{ar}-C_{ar}-Si-C_m = 4.2°$). The internal strain in this conformation is manifested by deformations ($C_{ar}-C_{ar} = 1.429$ Å, $C_{ar}-Si = 1.907$ Å, $C_{ar}-Si-C_m$ (eclipsed) = 131.7°) similar to those calculated for the $S_6$ conformation of **1a**.

**Hexakis(trimethylgermyl)benzene (1c).** No germanium parameters are implemented in the MM2 force field. In a previous study of the sterically crowded 1,8-bis(trimethylgermyl)naphthalene,[12] it had been noted that the $C_{ar}$–Ge and $C_m$–Ge bond lengths found by EFF calculations,[26] 1.969 and 1.991 Å, were in the reverse order when compared to the bond lengths found experimentally, 1.974 and 1.950 Å, respectively.[27] To avoid this difficulty in the present work, a new set of parameters was developed, as follows. The complete set of silicon parameters, including the two introduced in the present work,[24] was used for the corresponding germanium parameters, except for the C–Ge bond stretching force constant, $k_s$, and the "preferred" C–Ge bond lengths, $r_0$. Following Ouellette,[29] a value of 2.700 mdyn Å$^{-1}$ molecule$^{-1}$ was adopted for $k_s$. The best values of $r_0$, 1.948 and 1.943 Å for C(sp$^3$)–Ge and C(sp$^2$)–Ge, respectively, were obtained by optimizing correspondence with the crystal structure of 9,9,10,10-tetramethyl-9,10-digermadihydroanthracene.[30,31]

When the new and modified parameters were used in conjunction with the MM2 force field to calculate the structure of 1,8-bis(trimethylgermyl)naphthalene, it was found that the calculated $C_{ar}$–Ge and average $C_m$–Ge bond lengths, 1.976 and 1.965 Å, were now matched correctly to the corresponding experimental values. In addition, the calculated $C_{ar}$–Ge bond length of 1.956 Å for tetraphenylgermane correctly reproduced the reported values of 1.957 (4)[32a] and 1.954 Å.[32b] The structure of **1c** was then calculated in the same way.

As in the case of **1a** and **1b**, two conformers were found, one with $D_3$ symmetry and another, 16.3 kcal mol$^{-1}$ higher in energy, with $S_6$ symmetry. Table II lists the calculated structural parameters for the $D_3$ conformer along with the corresponding experimental values. The good overall agreement between the two sets of values may be taken as evidence that the deformations in **1c** are not merely the result of crystal packing forces. In particular, torsion angles (i.e., molecular shape) are well matched, including the calculated tilt angle of 108.1°, and the calculated $C_{ar}$–Ge and average $C_m$–Ge bond lengths, 1.983 and 1.965 Å, are in good correspondence with the experimental values. The Ge–$C_{ar}-C_{ar}$–Ge torsion angle, however, is underestimated by ca 10°, and it seems likely that the corresponding torsion angles in **1a** and **1b** are similarly underestimated.

The $S_6$ conformation has approximate $C_{6h}$ symmetry ($C_{ar}-C_{ar}-C_{ar}-C_{ar} = 1.5°$, $C_{ar}-C_{ar}-Ge-C_m = 5.0°$) and exhibits structural deformations ($C_{ar}-C_{ar} = 1.422$ Å, $C_{ar}-Ge = 1.999$ Å, $C_{ar}-Ge-C_m$ (eclipsed) = 130.8°) that are similar to those described for the $S_6$ conformations of **1a** and **1b**.

## Experimental Section

Solution 250.13-MHz $^1$H and 62.83-MHz $^{13}$C NMR spectra were recorded at ambient temperature in CDCl$_3$, unless otherwise specified, on a Bruker WM-250 spectrometer. Melting points are corrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

**Hexakis(trimethylgermyl)benzene (1c).** Chlorotrimethylgermane (5.0 g, 0.033 mol, Strem Chemicals) and dry tetrahydrofuran (4 mL, distilled from sodium benzophenone ketyl) were added to magnesium turnings (0.83 g, 0.034 mol) in a 25-mL three-necked flask. The flask and magnesium had been predried at above 100 °C, and the addition was carried out under an inert (argon) atmosphere. The mixture was stirred vigorously, and one-third of a slurry of hexabromobenzene (1.5 g, 0.0027 mol, Aldrich) in 15 mL of dry tetrahydrofuran was added without external heating. After 0.5 h of vigorous stirring, a crystal of iodine was introduced, and a slightly exothermic reaction ensued. After about 15 min, the remainder of the hexabromobenzene slurry was added slowly. The reaction mixture was stirred vigorously for an additional hour and then heated gently over a 12-h period. At the end of this period the solution had turned dark brown and much of the magnesium had been consumed. The reaction mixture was cooled and poured into about 20 mL of 2.4 M HCl to decompose excess magnesium, and the resulting mixture was extracted with several portions of ether. The combined ether extracts were washed until neutral with several portions of water and then with saturated sodium chloride solution, and they were finally dried over

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(22) Bürgi, H.-B.; Bartell, L. S. *J. Am. Chem. Soc.* **1972**, *94*, 5236. The corresponding bond distance in tri-*tert*-butylmethyl *p*-nitrobenzoate is 1.618 Å. See: Cheng, P.-T.; Nyburg, S. C. *Acta Crystallogr., Sect. B* **1978**, *B34*, 3001. Wong-Ng, W.; Cheng, P.-T.; Nyburg, S. C. *Acta Crystallogr., Sect. C* **1984**, *C40*, 92.

(23) Sakurai, H.; Nakadaira, Y.; Tobita, H.; Ito, T.; Toriumi, K.; Ito, H. *J. Am. Chem. Soc.* **1982**, *104*, 300.

(24) The following values of $V_n$ (kcal mol$^{-1}$) were employed for Si–$C_{ar}-C_{ar}$–Si and $C_{ar}-C_{ar}-C_{ar}$–Si torsions, respectively: $V_0$ = 10.40, 10.23; $V_1$ = –0.10, –0.27; $V_2$ = –10.5, –10.5; $V_3$ = 0.0, 0.0.

(25) Thus, for the torsion angle Si–C(sp$^2$)–C(sp$^2$)–Si, calcd 30.3°, found[23] 29.5° (av). For the bond angle $C_m$–Si–$C_m$, calcd 98.8°, found[23] 101.8° (av). The only significant discrepancy was in the C(sp$^2$)–Si bond length (calcd 1.864 Å, found 1.915 Å).

(26) In this study,[12] parameters for germanium were taken to be those of carbon, with bond length parameters $r^0$ of 1.98 and 1.955 Å for C(sp$^3$)–Ge and C(sp$^2$)–Ge, respectively, and were used in conjunction with the AM force field. See: Andose, J. D.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 2168.

(27) A similar reversal had been noted[12] for 1,8-bis(trimethylstannyl)naphthalene: $C_{ar}$–Sn, calcd 2.130 Å, found 2.162 Å; $C_m$–Sn, calcd 2.155 Å, found 2.140 Å. A recent determination of the crystal structure of 1,8-bis(trimethylsilyl)naphthalene[28] has revealed yet a third reversal: $C_{ar}$–Si, calcd[12] 1.868 Å, found[28] 1.895 Å; $C_m$–Si, calcd[12] 1.883 Å, found[28] 1.866 Å.

(28) Sooriyakumaran, R.; Boudjouk, P.; Garvey, R. G. *Acta Crystallogr., Sect. C* **1985**, *C41*, 1348.

(29) Ouellette, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 7674.

(30) D'yachenko, O. A.; Soboleva, S. V.; Atovmyan, L. O. *Zh. Strukt. Khim.* **1976**, *17*, 496; *J. Struct. Chem. (USSR)* **1976**, *17*, 426.

(31) This molecule and 1,8-bis(trimethylgermyl)benzene are the only ones listed in the Cambridge Crystallographic Database (updated to 1985) that contain both C(sp$^3$)–Ge and C(sp$^2$)–Ge bonds and no atoms other than C, H, and Ge, and whose crystal structure has an *R* factor of less than 10%.

(32) (a) Karipides, A.; Haller, D. A. *Acta Crystallogr., Sect. B* **1972**, *B28*, 2889. (b) Chieh, P. C. *J. Chem. Soc. A* **1971**, 3243.

(33) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.

anhydrous magnesium sulfate. The solvent was removed and the residual heavy, yellow oil was dissolved in hot methanol–ethyl acetate. On prolonged standing, the cooled solution deposited 0.16 g (7.6%) of yellow, transparent plates: mp 261–264.5 °C. $^1$H NMR $\delta$ 0.41 ($CH_3$). $^{13}$C NMR ($CDCl_3$ containing 10% w/w $Cr(acac)_3$) $\delta$ 5.14 ($C_m$), 162.46 ($C_{ar}$). Low-resolution MS *m/e* (intensity found, calcd relative to *m/e* 778 = 100) 787 (11.8, 10.6), 786 (23.6, 23.6), 785 (20.6, 24.3), 784 (43.9, 47.2), 783 (40.6, 43.2), 782 (74.6, 74.6), 781 (59.6, 60.6), 780 (92.7, 95.4), 779 (63.0, 68.5), 778 (100, 100), 777 (65.7, 62.9), 776 (86.0, 86.6), 775 (45.8, 46.9), 774 (63.4, 62.1), 773 (29.7, 28.4), 772 (37.9, 36.7), 771 (16.0, 13.6), 770 (20.2, 17.7), 769 (11.2, 5.1), 768 (12.3, 6.9). Decomposition pattern *m/e* (intensity relative to *m/e* 119 = 100) 778 (25.2, $M^+$), 661 (6.5, $M^+ - Ge(CH_3)_3$), 529 (18.4, $M^+ - 2Ge(CH_3)_3 - CH_3$), 513 (8.4, $M^+ - 2Ge(CH_3)_3 - 2CH_3$). High-resolution mass spectrum, *m/e* 773.9570 (773.9551 calcd for $C_{24}H_{54}{}^{72}Ge_6$).

Anal. Calcd for $C_{24}H_{54}Ge_6$: C, 37.02; H, 7.00. Found: C, 36.87; H, 6.94.

Evaporation of the mother liquors from the crystallization of **1c** left an oily residue containing a mixture of **1c**, **3**, and **4**. Solutions of **1c** in $C_6H_6$ showed no evidence of decomposition on standing. Solutions of **1c** in $CHCl_3$ showed signs of decomposition after standing for several hours at room temperature. One of the products of decomposition is **4**, but there was no indication of the presence of **3** ($^1$H NMR).

**1,1,3,4,6,6-Hexakis(trimethylgermyl)-1,2,4,5-hexatetraene (3).** Chlorotrimethylgermane and magnesium in dry tetrahydrofuran were mixed as described above. A slurry of hexabromobenzene (1.5 g) in 11 mL of dry tetrahydrofuran was added all at once, a crystal of iodine was introduced to initiate the reaction, and the mixture was heated under reflux for about 15 h. At the end of this period the greenish yellow solution was cooled, poured into 20 mL of 2.4 N HCl, and extracted with ether. The combined ether extracts were washed with several portions of water and then with saturated sodium chloride and dried over anhydrous magnesium sulfate. The solvent was removed and the residual oil was dissolved in methanol–ethyl acetate. On standing, 0.133 g (6.4%) of crude **3** precipitated. Recrystallization from methanol–ethyl acetate yielded 0.109 g of **3** as a white powder: mp 141.2–142.8 °C. $^1$H NMR $\delta$ 0.20 (18 H, $Ge(CH_3)_3$ protons on C(3) and C(4) of the hexatetraene skeleton), 0.25 (36 H, accidentally isochronous $Ge(CH_3)_3$ protons on C(1) and C(6)). $^{13}$C NMR $\delta$ –0.053 (accidentally isochronous $Ge(CH_3)_3$ carbons on C(1) and C(6)), 0.026 ($Ge(CH_3)_3$ carbons on C(3) and C(4)), 79.16 and 81.41 (C(1), C(6), C(3), and C(4)), 200.12 (C(2) and C(5)). Low-resolution MS *m/e* (intensity found, calcd relative to *m/e* 778 = 100) 790 (2.74, 2.64), 789 (3.27, 3.49), 788 (8.94, 9.14), 787 (11.06, 10.62), 786 (23.63, 23.65), 785 (24.87, 24.34), 784 (47.79, 47.19), 783 (43.45, 43.15), 782 (75.93, 74.62), 781 (60.62, 60.62), 780 (97.08, 95.42), 779 (69.65, 68.49), 778 (100, 100), 777 (64.51, 62.87), 776 (89.47, 86.58), 775 (48.85, 46.91), 774 (64.69, 62.06), 773 (30.62, 28.36), 772 (39.47, 36.71), 771 (15.22, 13.62), 770 (19.91, 17.74), 769 (6.73, 5.07), 7.68 (8.41, 6.89), 767 (3.45, 1.36), 766 (3.54, 2.06). Decomposition pattern *m/e* (intensity relative to *m/e* 119 = 100) 778 (11.3, $M^+$), 661 (7.3, $M^+ - Ge(CH_3)_3$), 529 (23.0, $M^+ - 2Ge(CH_3)_3 - 2CH_3$), 395 (5.4, $M^+ - 3Ge(CH_3)_3 - 2CH_3$), 119 (100, $^{74}Ge(CH_3)_3$), 117 (77.3, 75.1 calcd, $^{72}Ge(CH_3)_3$), 115 (58.5, 56.2 calcd, $^{70}Ge(CH_3)_3$).

Anal. Calcd for $C_{24}H_{54}Ge_6$: C, 37.02; H, 7.00. Found: C, 36.60; H, 7.16.

Workup of the mother liquor from the crystallization of **3** by evaporation of the solvent and further recrystallization from methanol–ethyl acetate gave 0.0316 g (2.1%) of white plates: mp 164.0–174.5 °C. $^1$H NMR $\delta$ 7.73 (s, 2 H, $C_{ar}$–H), 0.45 (s, 36 H, $CH_3$). $^{13}$C NMR $\delta$ 1.32 ($CH_3$), 146.93, 140.23 ($C_{ar}$). Low-resolution MS *m/e* (relative to *m/e* 28 = 100) 531 (50.0, $M^+ - CH_3$), 395 (8.1, $M^+ - 3Ge(CH_3)_3 - 2CH_3$), 119 (44.4, $^{74}Ge(CH_3)_3$). These characteristics are consistent with those expected for **4**.

The corresponding bis-allene **2** was prepared as previously outlined,[6] by a procedure analogous to the one described above for the preparation of **3**. Crystals of **2** from methanol–ethyl acetate had mp 107.8–109.9 °C. $^1$H NMR $\delta$ 0.11 (18 H, $Si(CH_3)_3$ protons on C(3) and C4)), 0.13 (36 H, accidentally isochronous $Si(CH_3)_3$ protons on C(1) and C(6)). $^{13}$C NMR $\delta$ 0.02 ($Si(CH_3)_3$ carbons on C(3) and C(4)), 0.56 (accidentally isochronous $Si(CH_3)_3$ carbons on C(1) and C(6)), 74.67 and 79.65 (C(1), C(6), C(3), and C(4)), 206.42 (C(2) and C(5)).

**Crystallography.** Crystals of **1c** are orthorhombic, space group *Pnca*, with $a = 12.338$ (5) Å, $b = 14.175$ (4) Å, $c = 19.697$ (6) Å, and $d_{calcd} = 1.501$ g cm$^{-3}$ for $Z = 4$ ($C_6[Ge(CH_3)_3]_6$, $M = 778.23$). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu K$\alpha$ radiation, $\theta$–$2\theta$ scans, pulse-height discrimination). The size of the crystal used for data collection was approximately 0.12 × 0.75 × 0.85 mm; the data were corrected for absorption ($\mu = 66.1$ cm$^{-1}$). A total of 2334 independent reflections were measured for $\theta < 57°$, of which 1847 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple-solution procedure[33] and was refined by full-matrix least squares. Four reflections which were strongly affected by extinction were excluded from the final refinement and difference map. In the final refinement, anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indices are $R = 0.055$ and $wR = 0.061$ for the remaining 1843 observed reflections. The final difference map has a number of small peaks, none greater than ±0.8 e Å$^{-3}$, about the germanium atoms.

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**Registry No.** **1a**, 103240-49-9; **1b**, 103240-52-4; **1c**, 103240-48-8; **3**, 103240-50-2; **4**, 103240-51-3; **5**, 796-97-4; chlorotrimethylgermane, 1529-47-1; hexbromobenzene, 87-82-1.

**Supplementary Material Available:** Final anisotropic thermal parameters and atomic parameters for hydrogen for **1c**, with standard deviations (Tables V and VI) (2 pages). Ordering information is given on any current masthead page.