Molecular Structure of
1,8-Bis(trimethylelement)naphthalenes
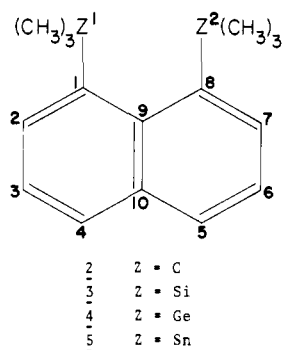
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Abstract: The X-ray structures of 1,8-bis(trimethylgermyl)naphthalene (**4**) and 1,8-bis(trimethylstannyl)naphthalene (**5**) have been determined. The structures of **4** and **5** are critically compared with those of 1,3,6,8-tetra-*tert*-butylnaphthalene (**1**) and 1,8-di-*tert*-butylnaphthalene (**2**). It is found that familial traits are shared by all the 1,8-bis(trimethylelement)naphthalenes: in each case a twist of the C1–C9–C8 and C4–C10–C5 planes about the C9–C10 axis imparts near C_2 symmetry to the molecule, and the trimethylelement groups in the peri positions are further deflected away from each other and out of the average molecular plane. In each case, the effects of internal strain, brought about by repulsion between the $(CH_3)_3Z$ groups, are felt most strongly near the peri positions, and it is there that the greatest distortions are localized. In this family of compounds, the skeletal distortion decreases in the order **1** (**2**) ≫ **4** > **5**, i.e., in the inverse order of the covalent radius of Z. The conformations adopted by the $(CH_3)_3Z$ groups in **4** and **5** are almost the same, but distinctively different from those in **1** (**2**). Empirical force field calculations yield structures in good agreement with those obtained by X-ray diffraction; these calculations also predict that the conformation of the as yet unknown 1,8-bis(trimethylsilyl)naphthalene (**3**) resembles **4** and **5** more closely than **1** (**2**)

Interest in the study of overcrowded molecules[2] remains active for a variety of reasons: such molecules pose synthetic challenges, they serve to test the limits of theoretical predictions, and they provide exceptional insights into the effect of intramolecular strain on ground-state structures and on internal mobility. A notable example is the 1,8-di-*tert*-butylnaphthalene system,[3-5] in which nonbonded repulsion between the bulky *tert*-butyl groups in the peri positions results in a warped naphthalene framework. As determined[5] for 1,3,6,8-tetra-*tert*-butylnaphthalene (**1**) by X-ray diffraction, and for 1,8-di-*tert*-butylnaphthalene (**2**) by empirical force field (EFF) calculations, a twist of the C1–C9–C8 and C4–C10–C5 planes about the C9–C10 bond imparts near C_2 symmetry to the molecule, with each benzene ring in the naphthalene nucleus distorted to a flattened half-chair and the peri *tert*-butyl groups further deflected to opposite sides of the average molecular plane.

Although an attempt[6] to synthesize the silicon analogue of **2**, 1,8-bis(trimethylsilyl)naphthalene (**3**), has been unsuccessful,[7] the germanium and tin analogues, 1,8-bis(trimethylgermyl)naphthalene (**4**)[8] and 1,8-bis(trimethylstannyl)naphthalene (**5**),[6] have recently become accessible. The material was therefore available for a comparative study of molecular deformations in the homologous series **2**, **4**, and **5**. The present paper describes the results of this study.

X-ray Structures

Compounds **4** and **5** were prepared as previously reported.[6,8] Crystals of **4** and **5** were obtained from methanol and are monoclinic, space group $P2_1/c$. For **4**, a = 13.045 (2) Å, b =

10.157 (1) Å, c = 12.701 (2) Å, β = 91.12 (1)°, and d_{calcd} = 1.427 g cm^{-3} for Z = 4 ($C_{16}H_{24}Ge_2$, mol wt 361.55). For **5**, a = 13.393 (2) Å, b = 10.185 (1) Å, c = 12.976 (2) Å, β = 92.99 (1)°, and d_{calcd} = 1.704 g cm^{-3} for Z = 4 ($C_{16}H_{24}Sn_2$, mol wt 453.75). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse height discrimination). For **4** and **5**, crystals measuring approximately 0.08 × 0.22 × 0.5 and 0.05 × 0.15 × 0.65 mm, respectively, were used for data collection; the data were corrected for absorption (μ = 46.8 and 231.6 cm^{-1}, respectively). A total of 2261 (**4**) and 2381 (**5**) reflections were measured for θ < 57°, of which 2028 (**4**) and 2111 (**5**) were considered to be observed (I > 2.5$\sigma(I)$). The structures were solved by Patterson and Fourier methods and were refined by full-matrix least squares. In the final refinements, anisotropic thermal parameters were used for the heavier 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 = 0.038 and wR = 0.048 for the 2028 observed reflections in **4**, and R = 0.030 and wR = 0.035 for the 2111 observed reflections in **5**. The final difference maps had no peaks greater than ±0.5 and ±1.0 e Å^{-3} for **4** and **5**, respectively. Stereoviews of the final structures are given in Figures 1 and 2.

Results and Discussion

From the stereoviews of the X-ray structures in Figures 1 and 2, it is immediately apparent that the germanium (**4**) and tin (**5**) compounds are distorted as described for **1** and **2** above: the twist of the C1–C9–C8 and C4–C10–C5 planes about the C9–C10 bond axis and the near C_2 symmetry of the molecules are plainly visible, as are the further deflections out of the mean molecular plane by the peri $(CH_3)_3Z$ groups. This familial resemblance between the members of the homologous series is borne out by a more detailed examination of the bonding parameters.

Tables I, II, and III list bond lengths, bond angles, and torsion angles for **1**, **4**, and **5**. Although the two halves of each molecule are crystallographically independent (since the molecules do not lie in crystallographic sites of C_2 symmetry), the deviations from molecular C_2 symmetry are in fact negligible. Thus, to a high degree of approximation, a molecular C_2
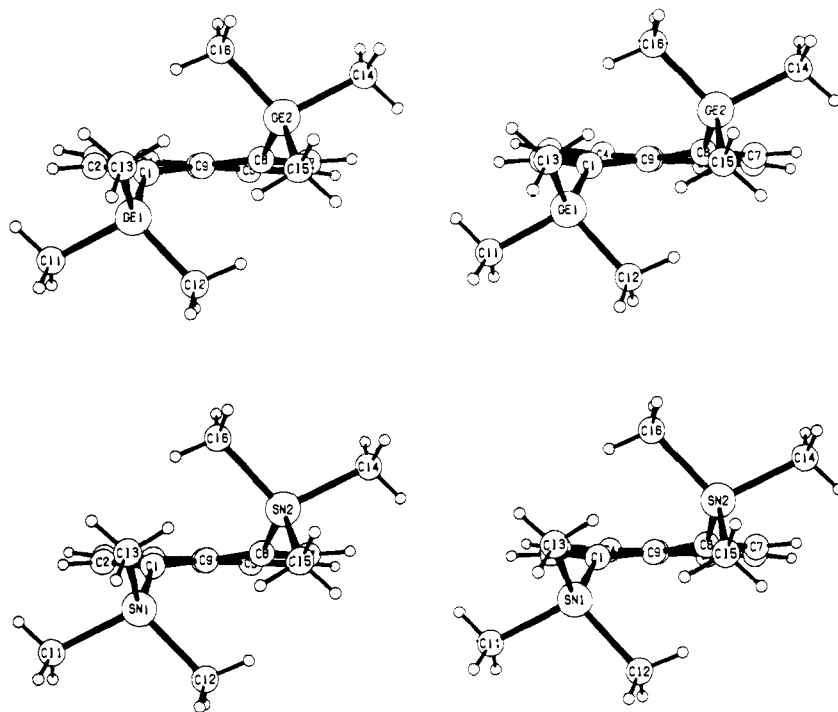
Figure 1. Stereoview of the X-ray structure of 1,8-bis(trimethylgermyl)naphthalene (**4**, top) and 1,8-bis(trimethylstannyl)naphthalene (**5**, bottom). The view is along the C9–C10 bond axis.
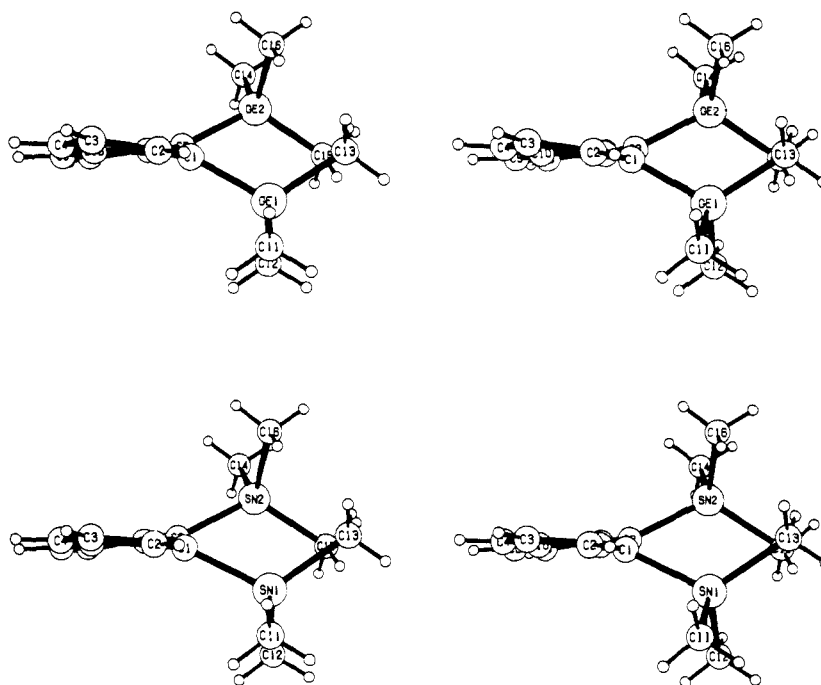

Figure 2. Same as Figure 1, except that the view is along the C2–C7 line.

axis, coextensive with the C9–C10 bond in **1, 4**, and **5**, leads to pairwise equivalence of Z1/2, C1/8, C2/7, C3/6, C4/5, and the $(CH_3)_3Z$ groups. In what is to follow, C_2 symmetry will therefore be assumed, and the parameters in Tables I–III are grouped in sets of symmetry-related pairs. Values cited in the text and Table IV refer to averages of values for symmetry-related parameters (e.g., C3/6–C4/5 = 1.356 Å is the average of the entries for C3–C4 and C6–C5 of **5** in Table I). The further assumption is made that the bonding parameters for **2** may be equated to the corresponding parameters for **1**. This assumption, i.e., that the presence of the *tert*-butyl groups in the 3 and 6 positions does not have a significant influence on

the conformation of the remainder of the molecule, is borne out by the agreement between selected parameters calculated for **2** by the EFF method and found for **1** by X-ray analysis[5] (see also Table IV).

Distortions in the Molecular Framework. The severe distortions brought about by the repulsion between the $(CH_3)_3Z$ groups are felt most strongly near the peri positions, and it is there that the greatest deformations are localized. In this respect the situation is similar to that encountered in other peri-substituted naphthalenes.[9]

The Z1/2–C1/8 bond distances of 1.558, 1.974, and 2.162 Å for Z = C, Ge, and Sn are each ca. 0.02 Å longer than the

Table I. Bond Lengths in 1,8-Bis(trimethylelement)naphthalenes[a]

atoms[b]	Z = C (1)[c,d]	Z = Ge (4)[e]	Z = Sn (5)[e]
Z1–C11	1.539	1.948	2.138
Z2–C14	1.550	1.960	2.140
Z1–C13	1.528	1.946	2.144
Z2–C15	1.544	1.968	2.153
Z1–C12	1.536	1.935	2.134
Z2–C16	1.534	1.943	2.129
Z1–C1	1.558	1.973	2.163
Z2–C8	1.557	1.975	2.160
C1–C9	1.454	1.435	1.433
C8–C9	1.443	1.448	1.426
C2–C3	1.417	1.407	1.401
C7–C6	1.420	1.405	1.405
C4–C10	1.415	1.400	1.410
C5–C10	1.417	1.425	1.408
C1–C2	1.377	1.381	1.381
C8–C7	1.376	1.375	1.383
C3–C4	1.362	1.370	1.363
C6–C5	1.361	1.332	1.349
C9–C10	1.433	1.439	1.444

a In angstroms. Estimated standard deviations for a typical C–C bond length are 0.002–0.003, 0.006, and 0.010 Å for Z = C,[5] Ge, and Sn, respectively. *b* Numbering as in Figures 1 and 2. *c* Values are taken from Table III in ref 5. *d* Atom indices C19/23, C22/25, C20/24, and C21/26 in ref 5 correspond to Z1/2, C11/14, C12/16, and C13/15, respectively, in the first column of this table. *e* Present work.

average of the six corresponding Z–CH₃ bond distances (1.539, 1.950, and 2.140 Å, respectively), and, for a given Z, longer than any individual Z–CH₃ bond distance, in contrast to the expected ordering $r(Z-C_{sp3}) > r(Z-C_{sp2})$. Evidently, the severe congestion in the neighborhood of the peri positions is partly relieved by bond stretching. Similar stretching seems to occur in the ring system itself, where the C1/8–C2/7, C1/8–C9, and C9–C10 bond lengths of ca. 1.38, 1.44, and 1.43 Å, respectively, significantly exceed the corresponding C–C bond lengths of 1.361, 1.425, and 1.410 Å in naphthalene.[10] On the other hand, in regions further removed from the peri positions, bond distances are normal, to judge by the C2/7–C3/6, C3/6–C4/5, and C4/5–C10 bond lengths of ca. 1.41, 1.36, and 1.41 Å, which are comparable to the corresponding C–C bond lengths of 1.421, 1.361, and 1.425 Å in naphthalene.[10]

As in the case of bond lengths, the effect of internal strain on bond angles is also most strongly felt in the neighborhood of the peri positions, specifically at C2/7, C3/6, C9, and C1/8. By comparison with the C–C–C bond angles in naphthalene (119–121°),[10] bond angles subtended at these four carbon centers are distinctly abnormal. In contrast, the bond angles at C4/5 and C10, i.e., C3/6–C4/5–C10, C4–C10–C5, and C4/5–C10–C9, are in a relatively strain-free region and fall into the normal 119–121° range.

The extent of bond-angle deformation is manifestly dependent on the nature of Z. Thus, in the cases of C1/8–C2/7–C3/6 (124.6, 123.4, and 122.6° for Z = C, Ge, and Sn, respectively) and C2/7–C3/6–C4/5 (116.0, 118.5, and 119.3° for Z = C, Ge, and Sn, respectively), the effect of strain seems to be most pronounced for the carbon system. Similarly, the spread in the C1–C9–C8 angle (129.9, 126.1, and 125.6° for Z = C, Ge, and Sn, respectively) and the corresponding compression of the C1/8–C9–C10 angle (115.1, 117.0, and 117.2° for Z = C, Ge, and Sn, respectively) is more pronounced for **1** (**2**) than for the higher homologues.

Of particular interest are the angle deformations at C1/8. While the Z1/2–C1/8–C9 angle of ca. 125.5° seems to be

Table II. Bond Angles in 1,8-Bis(trimethylelement)naphthalenes[a]

atoms[b]	Z = C (1)[c,d]	Z = Ge (4)[e]	Z = Sn (5)[e]
C1–Z1–C13	113.3	117.9	119.4
C8–Z2–C15	112.9	119.3	120.6
C1–Z1–C12	115.5	107.8	108.2
C8–Z2–C16	113.6	108.8	108.0
C1–Z1–C11	104.5	106.4	104.5
C8–Z2–C14	106.6	106.7	104.7
C12–Z1–C13	108.7	114.8	113.1
C16–Z2–C15	111.9	112.0	111.8
C11–Z1–C12	105.3	104.9	107.1
C14–Z2–C16	104.7	105.8	107.5
C11–Z1–C13	108.9	103.9	103.4
C14–Z2–C15	106.5	103.1	103.2
Z1–C1–C9	125.6	125.4	125.4
Z2–C8–C9	125.8	125.0	125.6
Z1–C1–C2	114.3	112.7	112.1
Z2–C8–C7	114.5	113.0	112.2
C2–C1–C9	117.4	118.5	119.2
C7–C8–C9	117.6	118.4	118.9
C1–C2–C3	124.5	123.6	122.8
C8–C7–C6	124.6	123.1	122.4
C2–C3–C4	116.2	117.7	119.2
C7–C6–C5	115.8	119.3	119.3
C3–C4–C10	121.8	121.3	120.7
C6–C5–C10	121.7	121.5	121.3
C1–C9–C10	115.1	116.8	116.9
C8–C9–C10	115.0	117.1	117.4
C4–C10–C9	120.5	120.6	120.5
C5–C10–C9	120.6	119.6	119.7
C1–C9–C8	129.9	126.1	125.6
C4–C10–C5	118.9	119.8	119.8
Z1–C1–C4	150.7[f]	154.8	155.8
Z2–C8–C5	151.0[f]	156.7	156.7

a In degrees. Estimated standard deviations for a typical C–C–C bond angle are 0.1–0.2, 0.4, and 0.7° for Z = C,[5] Ge, and Sn, respectively. *b-e* See Table I. *f* See ref 11.

A   **B**
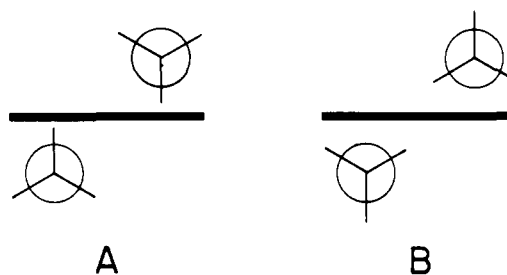
Figure 3. A schematic representation of idealized conformations of (CH₃)₃Z groups in 1,8-bis(trimethylelement)naphthalenes, viewed down the C9–C10 bond axis: A, **4** (Z = Ge) and **5** (Z = Sn); B, **1** (**2**) (Z = C).

independent of Z, the range of angles for Z1/2–C1/8–C2/7 (from 114.4° for Z = C to 112.2° for Z = Sn) and for C2/7–C1/8–C9 (from 117.5° for Z = C to 119.1° for Z = Sn) reveals a small but unmistakable dependence on Z. The artificial torsion angle Z1–C1–C8–Z2, which reflects the pyramidality at the C1/8 center, shows a similar dependence on Z (Table III). This structural feature is plainly visible in the stereoviews of **1**,[5] **4**, and **5** (Figures 1 and 2).

These stereoviews also display the twist of the C1–C9–C8 and C4–C10–C5 planes about the C9–C10 axis. As required

Table III. Torsion Angles in
1,8-Bis(trimethylelement)naphthalenes[a]

atoms[b]	Z = C (1)[c,d]	Z = Ge (4)[e]	Z = Sn (5)[e]
C9-C1-Z1-C11	−101.1	−141.8	−143.3
C9-C8-Z2-C14	−111.9	−144.6	−146.1
C9-C1-Z1-C12	14.1	−29.7	−29.5
C9-C8-Z2-C16	2.9	−30.8	−31.8
C9-C1-Z1-C13	140.4	102.3	101.8
C9-C8-Z2-C15	131.7	99.3	98.4
C2-C1-Z1-C11	51.9	16.9	15.7
C7-C8-Z2-C14	51.0	13.9	12.8
C2-C1-Z1-C12	175.1	129.0	129.5
C7-C8-Z2-C16	165.8	127.7	127.2
C2-C1-Z1-C13	−58.6	−99.1	−99.3
C7-C8-Z2-C15	−65.5	−102.2	−102.6
Z1-C1-C9-C8	−42.1	−34.7	−33.7
Z2-C8-C9-C1	−41.8	−31.6	−29.1
Z1-C1-C8-Z2	−68.6	−54.3	−53.1
C10-C9-C1-C2	−23.1	−12.0	−8.8
C10-C9-C8-C7	−23.6	−9.3	−9.4
C1-C9-C10-C4	19.3	11.5	7.8
C8-C9-C10-C5	19.2	11.0	10.8
C9-C1-C2-C3	11.4	3.1	3.4
C9-C8-C7-C6	11.7	1.1	1.4
C1-C2-C3-C4	5.8	7.0	3.5
C8-C7-C6-C5	6.5	5.8	5.7
C2-C3-C4-C10	−10.3	−7.5	−4.6
C7-C6-C5-C10	−11.6	−4.0	−4.3
C3-C4-C10-C9	−2.5	−1.7	−1.1
C6-C5-C10-C9	−1.5	−4.5	−4.1

[a] In degrees. Estimated standard deviations for a typical C-C-C-C torsion angle are 0.5° for Ge and 0.8° for Sn. [b] See Table I. [c] See ref 11. All signs were inverted to achieve correspondence with the data for Z = Ge and Sn. [d,e] See Table I.

by the model of the molecule, in which the C9-C10 bond coincides with the C_2 axis, C9 and C10 lie in the planes of their respective bonding neighbors. This is borne out by the data in Table II, which show that the angles subtended by C9 and C10

sum to 360° within experimental error. The absolute values of the angles of twist C1/8-C9-C10-C4/5 (Table III) are 19.3, 11.2, and 9.3° for Z = C, Ge, and Sn, respectively. The conclusion that the skeletal distortion decreases in the order **1 (2)** ≫ **4** > **5** is supported by the magnitudes of the angle Z1/2-C1/8-C4/5 (150.9,[11] 155.8, and 156.3° for Z = C, Ge, and Sn, respectively); this parameter combines the effect of pyramidality at C1/8 with that of the twist about the C9-C10 axis.

It had previously been assumed[6] that, as the distance of the $(CH_3)_3Z$ substituent from the naphthalene ring in the series **2–5** increases (with an increase in the covalent radius of Z), the magnitude of the deflection of the substituent out of the aromatic plane also increases. However, as demonstrated in the present work, the trend is in fact in the opposite direction, i.e., the larger the covalent radius of Z, the smaller the deflection out of the aromatic plane.

Conformation of the $(CH_3)_3Z$ Groups. We saw that although some bond and torsion angle deformations are slightly greater for **4** than for **5**, such distortions are far more pronounced in **1 (2)** than in **4**. Nowhere is the difference between **1 (2)** and the other two systems more in evidence than in the conformations of the two peri $(CH_3)_3Z$ groups.

One pair of symmetry-equivalent methyl groups (C13 and C15) in **4** and **5** points in a direction roughly perpendicular to the average plane of the naphthalene ring (Figure 1). As schematically shown in Figure 3, although a similar situation exists for **1 (2)**, the out-of-plane bending of the $(CH_3)_3Z$ groups results in the perpendicular methyls being proximal to each other in **4** and **5** (Figure 3A) and distal in **1 (2)** (Figure 3B). Rotation of the *tert*-butyl groups of **1 (2)** by ca. 40° would result in the conformation exhibited by **4** and **5** (see Table III).

It is also noteworthy that all bond angles terminating in methyl groups C13/15 of **4** and **5** have abnormal values: C1/8-Z1/2-C13/15 is exceptionally enlarged (to ca. 119°), and the other two angles are also significantly distorted (C12/16-Z1/2-C13/15 and C11/14-Z1/2-C13/15 are ca. 113 and 103°, respectively). The remaining bond angles in the $(CH_3)_3Z$ groups do not deviate as markedly from normal values.

On the assumption that the ground-state conformations (Figure 3) of **1 (2)**, **4**, and **5** in solution closely resemble those

Table IV. Selected Calculated Structural Parameters for 1,8-Bis(trimethylelement)naphthalene[a]

	Z = C (2)	Z = Si (3)	Z = Ge (4)	Z = Sn (5)
		Bond Lengths		
Z1/2-C$_{methyl}$[b]	1.551	1.883	1.991	2.155
Z1/2-C1/8	1.554	1.868	1.969	2.130
		Bond Angles		
Z1/2-C1/8-C9	127.9	126.4	125.9	125.4
C1/8-C2/7-C3/6	122.2	121.1	120.9	120.4
C1/8-C9-C10	126.1	124.1	123.5	122.7
Z1/2-C1/8-C4/5	151.0	157.7	159.0	160.4
		Torsion Angles		
C9-C1/8-Z1/2-C11/14	−107.2	−142.5	−145.1	−147.4
C9-C1/8-Z1/2-C12/16	4.7	−34.2	−37.2	−39.2
C9-C1/8-Z1/2-C13/15	136.3	102.3	99.7	97.4
C2/7-C1/8-Z1/2-C11/14	55.7	23.9	21.6	19.8
C2/7-C1/8-Z1/2-C12/16	167.5	132.1	129.5	128.0
C2/7-C1/8-Z1/2-C13/15	−60.9	−91.5	−93.7	−95.4
Z1/2-C1/8-C9-C8/1	−40.7	−30.0	−28.3	−26.2
Z1-C1-C8-Z2	−64.7	−48.4	−45.8	−42.8
C10-C9-C1/8-C2/7	−22.6	−15.3	−14.1	−12.6
C1/8-C9-C10-C4/5	15.0	9.9	9.1	8.3

[a] Symmetry-related values are reported as averages. Bond lengths in angstroms, angles in degrees. [b] Average of the six Z-C$_{methyl}$ bond lengths.

in the solid state, it may therefore be anticipated that the effect of the naphthalene ring on the chemical shifts of the three diastereotopic methyl groups in **4** and **5** at the slow exchange limit will differ markedly from those of the peri *tert*-butyl methyls in **1** (three singlets in the ^{1}H NMR spectrum at δ 0.61, 1.40, and 1.78 ppm).[4]

Empirical Force Field Calculations on 1,8-Bis(trimethylelement)naphthalenes. The EFF approach[12] has recently been used to study the dynamic stereochemistry of **2, 3,** and **5**.[13,14] It therefore seemed of interest to compare calculated structures with those determined by X-ray analysis.

The ground states of **2–5** were each calculated[12,15] using the approximations previously described.[13,16] Salient features of the calculated structures are presented in Table IV. Comparison with the appropriate entries in Tables I–III reveals satisfactory overall agreement between calculated and X-ray structures. In particular, the structural deformations, as reflected in the values of Z1–C1–C8–Z2, C1/8–C9–C10–C4/5, and Z1/2–C1/8–C4/5, are well reproduced. Most notably, the (CH$_3$)$_3$Z groups exhibit the conformations found in the crystal, i.e., conformation A for **4** and **5** and conformation B for **1** (**2**) (Figure 3).

The Z–C bond lengths in **1** (**2**) are reasonably well reproduced. However, the expected reversal of the Z–C$_{sp^3}$ and Z–C$_{sp^2}$ bond lengths is not reproduced for **4** and **5**; the approximations used in calculations on the higher homologues may be responsible for this discrepancy.

Since the bonding parameters for Si are closer to those of Ge[16] than to those of C, it may be predicted that the structure of **3** more closely resembles that of **4** than that of **2** (**1**). This prediction is supported by the EFF calculations (Table IV). While those parameters which reflect the pyramidality at C1/8 and the twist of the C1–C9–C8 and C4–C10–C5 planes (see above) are very similar for **3, 4,** and **5**, there is a significant gap between the values for **2** (**1**) and those found in the higher homologues. Furthermore, the (CH$_3$)$_3$Si groups adopt conformation A (Figure 3), which is also preferred by **4** and **5**, in contrast to conformation B, which is adopted by **2** (**1**).

Thus it appears that molecular deformations in the homologous series of 1,8-bis(trimethylelement)naphthalenes follow the order **2** ≫ **3** > **4** > **5**. A test of this prediction awaits the synthesis of **3**.

References and Notes

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(14) The ground state of **2** has also been calculated[5] using the MMPI force field.
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(16) The naphthalene ring was simulated by two fused benzene rings.[13] Parameters for silicon, germanium, and tin were those of carbon with the following longer preferred bond lengths for the stretching functions: Z–C$_{sp^3}$, 1.87, 1.98, and 2.15 Å; Z–C$_{sp^2}$, 1.85, 1.955, and 2.12 Å, for Z = Si, Ge, and Sn, respectively.

Conditions Favoring Retention of Configuration in S$_N$2 Reactions. A Perturbational Study

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Abstract: Salem's frontier orbital treatment of the Walden inversion may be extended to show that retention of configuration is favored by (a) a reaction center Z of low electronegativity, (b) a leaving group X of high electronegativity and/or with contracted valence orbitals, (c) a high percentage of s character in the hybrid atomic orbital of Z in the ZX bond, (d) a "hard" nucleophile. Condition (b) applies rigorously to homologous series, i.e., to comparisons of X's belonging to the same column of the periodic table. At least for the case of silicon compounds, it is *not* necessary in order to reproduce the experimental trends to introduce in the calculations either d orbitals for the reaction center or pseudorotations for the transition state.

Although many theoretical studies have been devoted to the S$_N$2 reaction over the last few years,[2] its stereochemistry remains an intriguing problem. To the best of our knowledge, there is still no proven example of an S$_N$2 reaction with retention of configuration[3] if the reaction center is a saturated carbon atom.[4] However, if the reaction center is a silicon atom, it is possible, depending on the nature of the substrate and of the nucleophilic reagent, to obtain highly stereoselective reactions with either predominant retention or inversion of configuration.[5,6] It is interesting to note that all these various stereochemistries may be rationalized with the help of one single perturbational scheme.