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Cyclic 1,8-napththalenediyl compounds containing group 14 hetero atoms

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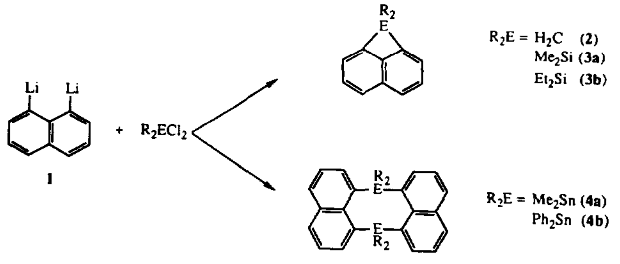
Abstract

Reaction of 1,8-naphthalenediylmagnesium with dimethylgermanium dichloride gave only dimethyl(1,8-naphthalenediyl) germanium (**7**), whereas use of 1,8-dilithionaphthalene gave a mixture of products, consisting mainly of **7** and its "dimer" 7,7,14,14-tetramethyldinaphtho[1,8-*bc*:1′, 8′-*fg*][1,5] digermocin (**8**). The silicon analogue (**12**) of **8** was prepared in a two-step procedure, starting from 1,8-dilithionaphthalene and 1,1,2,2-tetrachloro-1,2-dimethyl-disilane. The molecular structures of **8** and **12** were determined by single crystal X-ray diffraction studies. Both structures are centrosymmetric. The central eight-membered rings containing the $(CH_3)_2E$ moieties (E = Si, Ge) have a chair-like conformation. The naphthalene rings are quasi-coplanar and show strong out-of-plane distortions which are larger for **12** than for **8**.

Keywords: Naphthalenediyl; Lithium; Silicon; Germanium; Crystal structure

1. Introduction

We have been engaged for some time in the investigation of di-Grignard reagents with short carbon chains [1]. One of the most important applications of these reagents is their use in the synthesis of heterocyclic compounds. For instance, the reactions of Group 14 element dihalides with bifunctional organomagnesium (or organolithium) reagents have been used frequently as a route to heterocyclic compounds containing elements of Group 14 [2]. This is particularly true for ring sizes of five atoms and more, since the bifunctional organometallic reagents with four or more carbon atoms separating both metal atoms (Li or Mg) are readily available. The synthesis of four-membered heterocycles by this route requires a 1,3-dimetallated reagent. Reactions of 1,8-dilithionaphthalene (**1**) with Group 14 element dihalides provided early examples of such syntheses. The reaction of **1** with dichloromethane in the presence of TMEDA gave 1*H*-cyclobuta[*de*] naphthalene (**2**) [3]. When **1** was treated with dimethyl- or diethyl-dichlorosilane, (1,8-naphthalenediyl)dialkylsilanes such as **3** were obtained [4] (Scheme 1). In the present discussion, compounds of this type containing the hetero atom in a four-membered ring will be referred to as monomers. Dimeric counterparts such as **4** have been obtained from reactions of diorganyltin dihalides with **1** [5]. These species contain eight-membered rings containing two tin atoms (Scheme 1).



Scheme 1.

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* Corresponding author. Correspondence concerning the crystallography to Dr. A.L. Spek.

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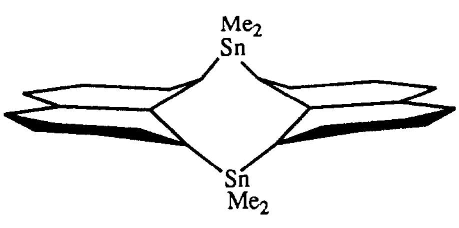

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Fig. 1. Schematic structure of **4a**.

Both the monomers and the dimers are strained compounds. This is obvious from the crystal structures of 1-bromo-1*H*-cyclobuta[*de*]naphthalene (**5**) [6] and that of 7,7,14,14-tetramethyl-dinaphtho[1,8-*bc*:1′,8′-*fg*][1,5]distannocin (**4a**) [5]. Large, in-plane distortions of the naphthalene moiety are observed in **5** because there is only a single carbon atom bridging the 1- and 8-position. In **4a**, the dimethyltin groups bridging both naphthalene moieties are placed above and below the plane of both naphthalenes, resulting in a chair-like conformation of the central eight-membered ring. This causes large out-of-plane distortions of the naphthalene moieties. The corresponding boat conformation, in which the naphthalene system would be planar and unstrained, has both Me_2Sn groups on the same side of the naphthalenes and would suffer from strong repulsions between the inner methyl groups. Therefore, the chair conformation is adopted, and like by necessity enforces distortions in the naphthalene fragments (Fig. 1).

To extend the investigations of the reactivity of Group 14 element dihalides toward 1,8-dimetallated naphthalene reagents, we have carried out reactions of **1** and the recently developed reagent 1,8-naphthalenediylmagnesium (**6**) [7] with dimethylgermanium dichloride, in order to see whether the behaviour of germanium is intermediate between that of silicon and tin by giving both the monomeric and the dimeric species. Furthermore a special synthetic route to the dimeric silicon species was developed in order to allow investigation of its structure.

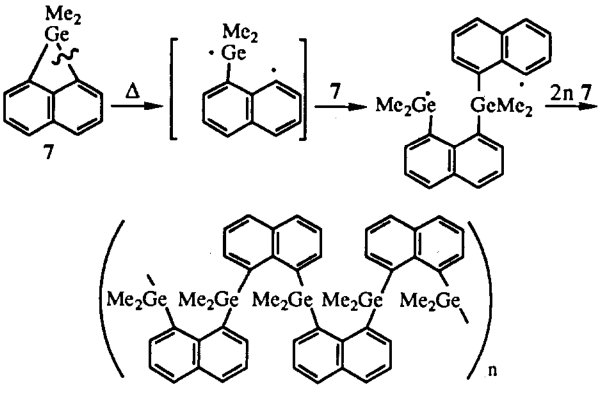
2. Results and discussion

2.1. Reactions of dimethylgermanium dichloride with 1 and 6

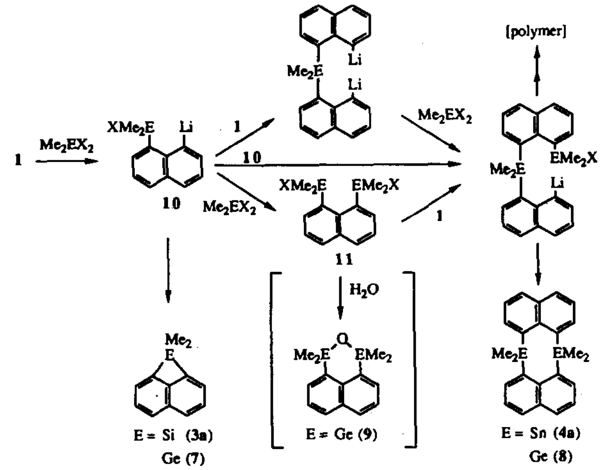
Dimethylgermanium dichloride (Me_2GeCl_2) was treated with **6** in THF at −20°C and the mixture was warmed to 5°C, removal of the solvent by distillation and subsequent extraction of the residue with pentane gave an oily substance. Its ^1H-NMR spectrum (C_6D_6) revealed only one signal assignable to a Ge–CH_3-group ($\delta = 0.58$ ppm). The ABC pattern in the aromatic region, expected for a symmetrically 1,8-disubstituted naphthalene, was only partially resolved, but the 1:1-relationship of the integrals of the signals in the aromatic region and the Ge–CH_3-signal suggested that only one compound had been formed. Because NMR spectroscopy cannot distinguish between the monomeric and the dimeric species, a GLC–MS analysis was performed. From the mass spectrum, it was concluded that the product was monomeric, i.e. that (1,8-naphthalenediyl)dimethylgermanium (**7**) had been formed.

It turned out that **7** was not stable in the perdeuterobenzene solution; at room temperature, in the dark and in the absence of oxygen and water, it decomposed. The white solid precipitate which formed during this thermal decomposition is insoluble in benzene or in chloroform, and is therefore assumed to be a polymer. However, GLC–MS analysis did not show even a trace of the dimeric species (7,7,14,14-tetramethyl-dinaphtho[1,8-*bc*:1′,8′-*fg*][1,5]digermocin, **8**). The thermal decomposition probably originates from homolytic Ge–C(naphthalene) bond cleavage, since this bond is the most strained in the molecule. Heterolytic cleavage of this bond cannot completely be excluded, but seems unlikely as the Ge–C bond is only weakly polarized. The propagation steps of the reaction can only be guessed at; they might proceed via S_H2 substitution at germanium, and in this case they would ultimately lead to the formation of a polymer as shown in Scheme 2. Analogous ring opening polymerizations, both radical and anionic, have been reported for silicon-bridged [1]ferrocenophanes [8].

The reaction of **1** with Me_2GeCl_2 was found to be more complex than that of **6**. It was carried out several times under different conditions in attempts to direct the reaction to either **7** or **8**. The reaction mixtures were analyzed by GLC–MS after hydrolytic workup and were found to contain several germanium compounds. After **7** and **8**, **9** was the most important product (ratios about 1:1:8); the latter compound is formed after hydrolysis of intermediate **11** (E = Ge, X = Cl) in Scheme 3. Attempts to control the course of



Scheme 2.



Scheme 3.

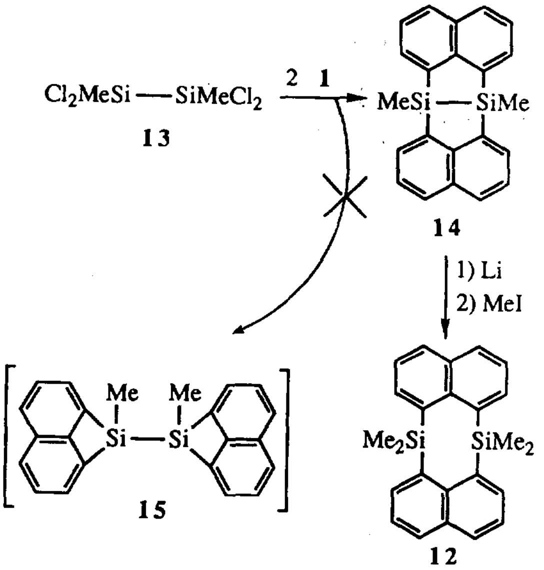
the reaction were not satisfactory, and **7** or **8** were never formed in appreciable purity or yield. Because **7** was readily available by the reaction of Me_2GeCl_2 with **6** (vide supra), we tried in particular to isolate **8** from the reaction mixture. After **7** had been allowed to polymerize and the polymeric material removed by filtration, crystallization from dichloromethane gave **8** in low yield; it was identified by ^{1}H-NMR and mass spectroscopy.

The general scheme according to which the reactions of **1** with Group 14 element dihalides may take place is shown in Scheme 3.

Whether monomers or dimers are formed in the reactions of **1** with Me_2ECl_2 probably depends on two factors namely the relative stabilities of the monomeric compounds, which is lower for the heavier elements, and the reactivity of the E–Cl bonds, which is higher for the heavier elements. These factors largely determine the relative rates of the reactions shown in Scheme 3, in particular the competition between the options for the primary intermediate **10**: ring closure to give a monomer (e.g. **3** or **7**) on the one hand and reaction with **1**, **10** or Me_2EX_2 on the other, leading to dimers or polymers. As a result, an optimum in respect of "monomer formation" is observed for germanium. This corresponds to previous experience with the formation of four-membered heterocycles of Group 14 elements [9].

2.2. Synthesis of 7,7,14,14-tetramethyldinaphtho[1,8-bc: 1′,8′-fg][1,5]disilocin (12)

Unlike **4** and **8**, the "silicon dimer" **12** cannot be obtained by reaction of the appropriate Me_2ECl_2 with **1**, and **3a** being obtained as the only identified product. Therefore, a new route to it was developed, this is depicted in Scheme 4.

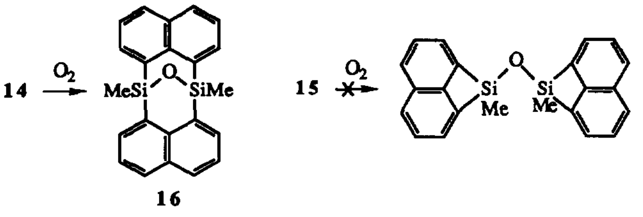


Scheme 4.

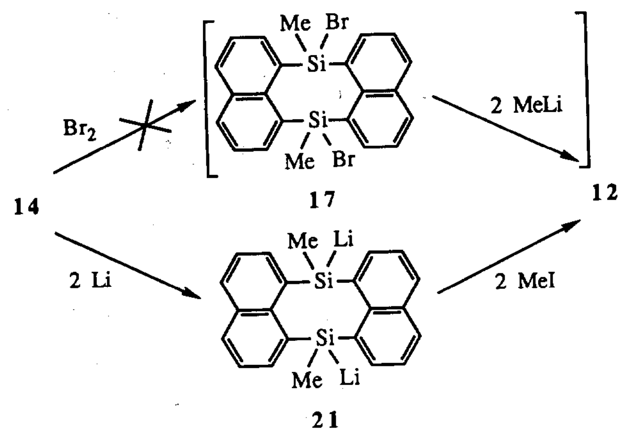
The reaction of 1,1,2,2-tetrachloro-1,2-dimethyldisilane (**13**) with two equivalents of **1** could in principle have given two (isomeric) products: the desired **14**, containing two condensed five-membered rings, and **15**, with two four-membered rings connected via a silicon-silicon bond. Only one of these two isomers was obtained from this reaction. From its ^{1}H-NMR and mass spectra it could not be concluded whether this compound was **14** or **15**. It was extremely air sensitive. Mass spectroscopy of the intermediate product and its oxidation product indicated the incorporation of an oxygen atom, presumably by oxidation of the Si–Si-bond. Scheme 5 shows the expected oxidation reactions for both isomers.

Such an oxidation by air is known for 1,2-disilacyclobutanes [10,11], whereas acyclic Si-Si bonds are not susceptible to air oxidation. Since the Si–Si-bond in **15** is not part of a cyclic system, **15** is not expected to undergo easy oxidation; on contact with (moist) air, it would probably be hydrolyzed more readily by cleavage of a Si–C bond, in analogy to the hydrolysis of **3a** [4], relief of strain in the four-membered rings being the driving force.

The Si–Si-bond in **14** is part of a strained (bi)cyclic system, which makes this bond more susceptible to oxidation than that in **15**. We take this as evidence that



Scheme 5.



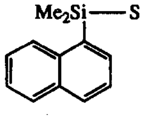
Scheme 6.

the intermediate product is in fact **14**. The preferential formation of **14** may be attributed to the fact that the formation of two five-membered rings (in **14**) is more favourable than that of two four-membered rings (in **15**).

Additional evidence for the structure of **14** came from the second step in the synthesis. In this step, the silicon-silicon bond was to be cleaved; **15** would give two fragments, while **14** would retain its skeleton upon cleavage of its Si–Si bond. Two ways of cleaving the Si–Si-bond were examined: reactions with bromine [11] or with lithium [11,12]; both are established procedures for this purpose.

Reaction of **14** with bromine was expected to give intermediate **17**, containing two Si–Br functionalities, which could be treated with methyllithium to give **12** (Scheme 6).

However, Si–Si-bond cleavage was not observed: GLC–MS analysis of the product mixture, obtained after reaction of **14** with bromine followed by addition of methyllithium, showed only the presence of compounds in which the Si–Si-bond was preserved. Instead, Si–C-bonds were cleaved, as indicated by the presence of **18**, **19** and **20**.



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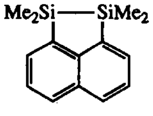

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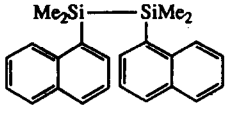

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The cleavage by lithium metal was more successful; reaction of **14** with a lithium suspension in THF at −25°C for 12 h apparently gave **21**; addition of an excess of methyl iodide at −50°C, yielded **12**, **19** and naphthalene as products. Crystallization from dichloromethane gave **12** (10% isolated yield based on **13**).

The ^1H NMR spectrum of **12** revealed a single Si–CH_3-signal at 0.53 ppm; the aromatic region showed a partially resolved ABC-pattern. The ratio of the integral of the aromatic signals to that of the Si-CH_3-signal of 1 : 1 is in accord with the assigned structure. High resolution mass spectroscopy showed that the compound had the correct elemental composition, confirming that **12** had been obtained.

2.3. *Crystal structures of 8 and 12*

The molecular structures of **8** and **12** were determined by X-ray crystallography. As the structures are

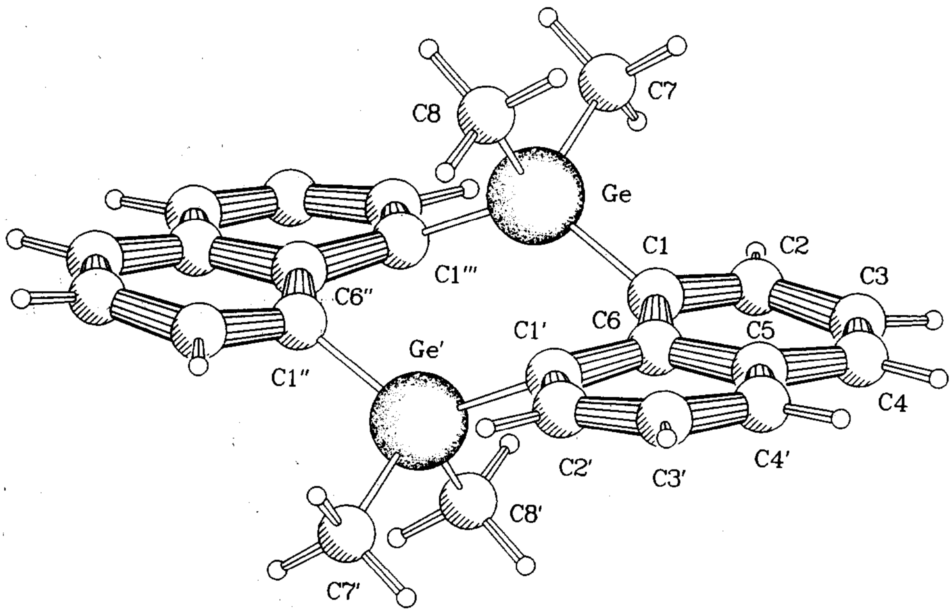

Fig. 2. PLUTON drawing of **8** with the adopted atom labeling.

Table 1
Selected bond distances (Å), angles (°) and torsional angles (°) of **8**

Ge(1)–C(1)	1.969(3)	C(2)–C(3)	1.410(4)
Ge(1)–C(7)	1.962(5)	C(3)–C(4)	1.363(4)
Ge(1)–C(8)	1.962(5)	C(4)–C(5)	1.417(4)
C(1)–C(2)	1.378(4)	C(5)–C(6)	1.422(7)
C(1)–C(6)	1.434(4)		
C(1)–Ge(1)–C(7)	105.47(11)	C(1)–C(2)–C(3)	121.9(3)
C(1)–Ge(1)–C(8)	106.73(11)	C(2)–C(3)–C(4)	119.6(3)
C(1)–Ge(1)–C(1 ^{b})	125.80(13)	C(3)–C(4)–C(5)	120.8(3)
C(7)–Ge(1)–C(8)	105.0(2)	C(4)–C(5)–C(6)	119.5(2)
C(1 ^{b})–Ge(1)–C(7)	105.47(11)	C(4)–C(5)–C(4 ^{a})	120.9(4)
C(1 ^{b})–Ge(1)–C(8)	106.73(11)	C(4 ^{a})–C(5)–C(6)	119.5(2)
Ge(1)–C(1)–C(2)	116.4(2)	C(1)–C(6)–C(5)	118.4(2)
Ge(1)–C(1)–C(6)	121.4(2)	C(1)–C(6)–C(1 ^{a})	123.2(4)
C(2)–C(1)–C(6)	118.9(3)	C(1 ^{a})–C(6)–C(5)	118.4(2)

[a] Indicates symmetry operation: $-x, -y, z$.
[b] Indicates symmetry operation: $x, y, -z$.

very similar, only that of **8** is depicted in Fig. 2; selected bond lengths, and bond and torsional angles of **8** and **12** are given in Tables 1 and 2. The structures are also quite similar to that of the analogous tin compound **4a** [5]: the two naphthalene moieties are approximately in the same plane, and the bridging Me_2Ge groups are situated above and below this plane, respectively. This results in a chair-like conformation of the central eight-membered ring in which the two methyl groups on each Group 14 element atom are in principle different; one occupies a pseudo-axial and the other a pseudo-equatorial position. However, this difference could not be observed in the ^{1}H-NMR spectrum (just one E–CH_3-signal was present!), indicating that in solution, there is probably a chair-to-chair ring inversion that is fast on the NMR time scale. Lowering the temperature of the NMR sample to −60°C did not cause any changes.

Table 2
Selected bond distances (Å), angles (°) and torsional angles (°) of **12**

Si–C(1)	1.886(5)	Si–C(1)–C(6)	122.5(5)
Si–C(7)	1.883(12)	C(2)–C(1)–C(6)	117.6(5)
Si–C(8)	1.870(12)	C(1)–C(2)–C(3)	121.8(6)
C(1)–C(2)	1.380(9)	C(2)–C(3)–C(4)	119.7(6)
C(1)–C(6)	1.457(7)	C(3)–C(4)–C(5)	120.0(6)
C(2)–C(3)	1.429(9)	C(4)–C(5)–C(6)	120.5(4)
C(3)–C(4)	1.365(10)	C(4)–C(5)–C(4 ^{a})	119.0(6)
C(4)–C(5)	1.420(8)	C(1)–C(6)–C(5)	119.2(4)
C(5)–C(6)	1.390(12)	C(1)–C(6)–C(1 ^{a})	121.5(7)
C(1)–Si–C(1 ^{b})	123.4(3)	Si–C(1)–C(6)–C(5)	−147.1(3)
C(1)–Si–C(7)	105.9(3)	C(2)–C(3)–C(4)–C(5)	−4.6(10)
C(1)–Si–C(8)	107.5(2)	C(3)–C(4)–C(5)–C(6)	−3.6(7)
C(7)–Si–C(8)	105.4(5)	C(4)–C(5)–C(6)–C(1)	−11.6(4)
Si–C(1)–C(2)	116.5(5)	C(4 ^{a})–C(5)–C(6)–C(1)	168.4(4)

[a] Indicates symmetry operation: $-x, -y, z$.
[b] Indicates symmetry operation: $x, y, -z$.

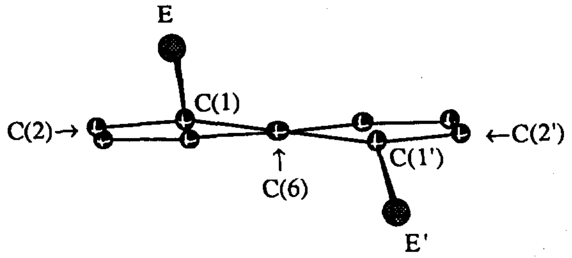

Fig. 3. Distortion of a naphtalene moiety viewed from C(6').

An interesting aspect of the structures of **8** and **12** is the deformation of the naphthalene fragments. This is the result of the chair-like conformation of the molecule; the naphthalene carbon atoms bonded to germanium (C(1)) are "pulled" out of the plane of the naphthalene in the direction of the bridging Me_2Ge-group. To a lesser extent, this is also true for C(2). The distortion can be described as a rotation of C(1) and C(1') with respect to the axis defined by C(5) and C(6) (Fig. 3).

Carbon atoms C(2) and C(2') are also drawn out of the naphthalene plane by this rotation, but the other carbon atoms (C(3), C(4), C(5), C(6), C(3') and C(4')) all remain in the original plane. The angle by which C(1) and C(1') are rotated around C(5)–C(6) (i.e. the torsional angle C(4)–C(5)–C(6)–C(1)) is a good quantitative indication of the distortion of the naphthalene moiety. By this criterion, **12** shows a slightly larger distortion than **8** (11.6(4)° and 10.0(2)°, respectively).

The absolute values of these torsion angles and the difference between those of **8** and **12** are smaller than the corresponding values for 1,8-bis(trimethylsilyl)naphthalene (**22**, 15.5°) [13] and 1,8-bis(trimethylgermyl)naphthalene (**23**, 11.5°) [14]. (These compounds show a distortion of the naphthalene fragment which is similar to that found in **8** and **12**). This can be rationalized on the basis of the factors responsible for the distortions. In **22** and **23**, nonbonding interactions between the two peri-substituents are responsible; each element (Si or Ge) bears three methyl groups, and it is the interaction between the methyls on the two peri-elements which determines the amount of distortion. This results in a larger distortion for **22** since the Si–C bonds are shorter than the Ge–C bonds, and so there is a smaller distance between the methyl groups and increasing steric interaction between them.

The distortions in **8** and **12** are caused mainly by the bonding situation; the fact that the peri-positions of two naphthalenes are doubly bridged by tetrahedrally coordinated atoms (Si, Ge) in a chair-like conformation enforces the distortion. Therefore, the angle at the bridging atoms C(1)–E(1)–C(1') is inversely correlated with the degree of the distortion. These angles are 125.80(13) for **8** and 123.4(3)° for **12** (cf. 127.5(6)/126.6(6) in **3**); the small difference between them reflects the small difference in the distortion of the naphthalene fragments in **8** and **12**. The reason for the decrease in the value of the C(1)–E–C(1‴) in the order E = Sn, Ge, Si, is the decrease in the order of the ability of the element to form large C–E–C bond angles. Since the atomic orbitals of the valence electrons of the heavier elements in a group are more diffuse and softer, larger bond angles around them are accepted.

Secondly, steric factors have to be considered. The non-bonding interactions in **8** and **12** are considerably less than those in **22** and **23**, because only two methyl groups are situated on the silicon and germanium atoms. Furthermore, the chair-like conformation provides such a distance between the methyl groups that the steric interaction between them is reduced. Two other possible interactions may be considered: the direct interaction between both elements and the interaction between one element and the nearest methyl group on the other element. The first interaction does not seem very likely, in view of the E–E distances in **4a**, **8** and **12** which are 3.56, 3.43 and 3.47 Å, respectively (cf. the sum of the Van der Waals radii: 4.32, 3.96 and 3.86 Å, respectively). If steric interactions between both elements were important, this should have resulted in different E–E distances, but they are essentially equal in the three compounds. A similar comment can be made for the second interaction. The shortest non-bonding E–CH_3 distance in **8** is 3.760(5) Å, in **12** it is 3.774(11) Å. Again, if the steric interactions between the element and the nearest methyl were important, this should have resulted in a longer E–CH_3 distance in **8**. Thus we conclude that it is not steric congestion so much as the imposed chair geometry which causes the distortion of the naphthalene system.

3. Experimental section

3.1. General

Apart from the reaction of **6** with Me_2GeCl_2, which was carried out in evacuated and fully sealed glass apparatus, all reactions were carried out in conventional glassware under nitrogen; solvents were dried and distilled before use. Reagent **6** [7] and 1,1,2,2-tetrachloro-1,2-dimethyldisilane (**13**) [15] were prepared according by published procedures.

NMR spectra were recorded on Bruker WM 250 and AC 200 NMR spectrometers. GLC–MS analyses were performed on a Hewlett Packard 5970 Mass Selective Detector linked to a Hewlett Packard 5890 gas chromatograph. Direct inlet mass spectra were recorded on a Finnigan MAT 90 mass spectrometer.

3.2. *Synthesis of dimethyl(1,8-naphthalenediyl)germanium(IV) (7)*

A solution of **6** in THF (9.5 ml, 0.021 M) was added to one of Me_2GeCl_2 (0.2 mmol in 2.5 ml diethyl ether) at room temperature. The mixture was stirred overnight. After removal of the solvent by distillation, the mixture was worked up in two ways: either extraction of the residue with pentane or direct sublimation from the residue. The sublimation was carried out at room temperature in high vacuum (circa 10^{-5} mbar) using a liquid nitrogen cooled trap. Compound **7** was obtained as a colorless oil. When its solutions in perdeuterated benzene were kept at room temperature, a finely divided precipitate formed, which was insoluble in benzene and chloroform. The signals in the NMR spectrum of **7** slowly disappeared; no new signals were observed.

7: ^{1}H-NMR (90 MHz, C_6D_6, ref. $C_6D_5H = 7.17$ ppm) δ 7.7–7.3 (6H, H(2,3,4,5,6,7)), 0.58 ppm (s, 6H, Ge–CH_3). ^{1}H-NMR (200 MHz, $CDCl_3$, ref. $CHCl_3 = 7.27$ ppm) δ 7.73 (dd, ^3J(H–H) = 7.7 Hz, ^4J(H–H) = 1.4 Hz), 2H, H(2,7)), 7.6–7.4 (4H, H(3,4,5,6)), 0.92 ppm (s, 6H, Ge–CH_3).

$^{13}C\{^1H\}$-NMR (50.32 MHz, $CDCl_3$, ref. $CDCl_3 = 77.0$ ppm) δ 149.5 (C(1,8)), 127.8 (C(2,7)), 126.3 (C(3,6)), 124.5 (C(4,5)), 2.0 ppm ($GeCH_3$). Other quaternary carbon atoms were not observed.

GLC–MS: m/z (rel. intensity): 232 (7), 231 (4), 230 (28, $M^{+\cdot}$), 229 (12), 228 (18), 227 (5), 226 (12), 215 (100, $(M\text{-}Me)^+$), 200 (25), 141 (47).

Molecular ion cluster, calculated for $C_{12}H_{12}Ge$ (rel. intensity of the m/z 230 (M^+) is 28%): 232 (6), 231 (4), 230 (28), 229 (8), 228 (20), 227 (2), 226 (15).

3.3. *Reaction of Me_2GeCl_2 with 1*

A solution of *n*-butyllithium in hexane (3.85 ml, 6.87 mmol) was slowly added to a solution of 1,8-diiodonaphthalene (3.43 mmol, 1.30 g) in diethyl ether (40 ml) at 0°C. After 1 h stirring at room temperature the solution was cooled to 0°C and a solution of Me_2GeCl_2 (2.75 mmol, 0.32 ml) in diethyl ether (5 ml) was slowly added. The mixture was allowed to warm to room temperature, to give after 1 h, a brownish solution with an off-white precipitate. The solvents and butyl iodide were removed by vacuum distillation. The residue was extracted with pentane. The pentane extract was examined by GLC–MS and the products observed were **7**, **8** and **9** (relative yields: 79, 10 and 11%). The pentane was removed by distillation and the residue was dissolved in dichloromethane. After several days, an amorphous precipitate separated (polymerization of **6**), and was removed by filtration. Slow evaporation overnight of the filtrate gave a small amount of **8** as colorless crystals.

8: ^{1}H-NMR (250 MHz, $CDCl_3$, ref. $CHCl_3 = 7.27$ ppm) δ 7.79 (dd, ^3J(HH) = 8.1 Hz, ^4J(HH) = 1.2 Hz), 4H, H(2,7)), 7.71 (dd, ^3J(H–H) = 6.8 Hz, ^4J(H–H) = 1.3 Hz), 4H, H(4,5)), 7.39 (dd, ^3J(H–H) = 8.1 Hz, ^3J(H–H) = 6.8 Hz), 4H, H(3,6)), 0.65 ppm (s, 12H, Ge–CH_3). HRMS: calculated for $C_{24}H_{24}Ge_2$: 460.0302; observed: 460.0315. Mass spectrum (EI): m/z (rel. intensity) 462

(2), 461 (2), 460 (7, M$^{+\cdot}$), 459 (4), 458 (10), 457 (3), 456 (9), 455 (2), 454 (4), 445 (5), 341 (20), 252 (100).

9: ^{1}H-NMR (250 MHz, $CDCl_3$, ref. $CHCl_3 = 7.27$ ppm) δ 7.90–7.47 (m, 6H, H(arom)), 0.68 ppm (s, 12H, Ge–CH_3). GLC–MS: m/z (rel. intensity): 352 (2), 351 (1), 350 (6), 349 (3), 348 (7, M$^{+\cdot}$), 347 (2), 346 (6), 345 (2), 344 (3), 342 (1), 333 (100, (M-Me)$^+$), 303 (7), 213 (13), 215 (13), 141 (13). Molecular ion cluster, calculated for $C_{14}H_{18}Ge_2O$ (rel. intensity of the m/z 348 is 7%): 352 (2), 351 (1), 350 (5), 349 (3), 348 (7), 347 (2), 346 (7), 345 (1), 344 (3), 342 (1).

3.4. Synthesis of 14

Diiodonaphthalene (2.5 mmol, 0.95 g) was dissolved in diethyl ether (20 ml). At 0°C, a solution of n-butyllithium in hexane (2.8 ml, 5.0 mmol) was added. After 1 h stirring at room temperature, the mixture was cooled to 0°C and 1,1,2,2-tetrachloro-1,2-dimethyldisilane (**13**, 1.25 mmol, 0.285 g) in 3 ml of diethyl ether was slowly added. The mixture was allowed to warm to room temperature; after 1 h the solvent was removed by distillation and the residue was washed with pentane (30 ml), and then extracted with 30 ml of toluene. The toluene extract was found to contain **14** (81%) and 1-iodonaphthalene (15%, relative yields by (GLC–MS). Crystallization gave pure **14** could be obtained as colorless crystals. The isolated yield was very low, and so in experiments, aimed at the synthesis of **12**, the toluene extract was used without further workup.

14: ^{1}H-NMR (250 MHz, $CDCl_3$, ref. $CHCl_3 = 7.27$ ppm) δ 7.94 (dd, ^3J(H–H) = 6.6 Hz, ^4J(H–H) = 1.1 Hz), 4H, H(2, 7)), 7.75 (dd, ^3J(H–H) = 8.2 Hz, ^4J(H–H) = 1.1 Hz), 4H, H(4,5)), 7.47 (dd, ^3J(H–H) = 8.2 Hz, ^3J(H–H) = 6.6 Hz), 4H, H(3,6)), 1.06 ppm (s, 6H, Si–CH_3). EI mass spectrum: m/z (rel. intensity) 341 (2), 340 (11), 339 (34), 338 (100, M$^{+\cdot}$), 337 (16), 323 (21), 295 (8), 169 (7), 167 (9). Calculated for $C_{22}H_{18}Si_2$: 341 (3), 340 (12), 339 (35), 338 (100). On the exposure of a toluene solution of **14** to air, oxidation occurred; crystallization of the product gave diamond shaped crystals of **16**, which were identified by ^{1}H-NMR and mass spectroscopy.

16: ^{1}H-NMR (250 MHz, $CDCl_3$, ref. $CHCl_3 = 7.27$ ppm) δ 7.8–7.7 (8H, H(2,4,5,7)), 7.45 (dd, ^3J(H–H) = 8.0 Hz, ^3J(H–H) = 6.8 Hz), 4H, H(3,6)), 1.14 ppm (s, 6H, Si–CH_3). EI mass spectrum: m/z (rel. intensity) 357 (2), 356 (13), 355 (36), 354 (100, M$^{+\cdot}$), 353 (29), 339 (26) 338 (30), 323 (9), 295 (11), 252 (5), 177 (4), 169 (8), 167 (4). Calculated for $C_{22}H_{18}Si_2O$: 357 (3), 356 (13), 355 (35), 354 (100, M$^{+\cdot}$).

3.5. Synthesis of 7,7,14,14-tetramethyl-dinaphthol[1,8-bc:1′,8′-fg][1,5]disilocin (12)

A suspension of lithium metal in mineral oil (1.3 g, 25 weight-% Li, 47 mmol) was washed with THF (3 × 10 ml) to remove the oil and THF was then added to give a total volume of 10 ml and the mixture was cooled to −50°C. The toluene extract containing **14** as described above was evaporated and the residue was dissolved in 30 ml of THF. This solution was slowly added to the lithium metal and stirring was continued for 12 hours at −25°C. The green/black mixture was cooled to −50°C and methyl iodide (7.1 g, 50 mmol) was added. The mixture was allowed to warm to room temperature. The solvent and the excess of methyl iodide were distilled off and 20 ml of THF were added. This solution was poured into water. After neutralization of the basic solution with 5% aqueous HCl, it was extracted with diethyl ether (3 × 75 ml). Drying of the combined ethereal layers over $MgSO_4$ and evaporation of the solvent gave 0.74 g of a yellow solid. Crystallization from dichloromethane yielded 45 mg of **12** (10%).

12: ^{1}H-NMR (250 MHz, $CDCl_3$, ref. $CHCl_3 = 7.27$ ppm) δ 7.9–7.7 (8H, H(2,4,5,7)), 7.39 (dd, ^3J(H–H) = 7.6 Hz, ^3J(H–H) = 7.6 Hz, 4H, H(3,6)), 0.53 ppm (s, 12H, Si–CH_3).

^{13}C-NMR (50.32 MHz, $CDCl_3$, ref. $CDCl_3 = 77.0$ ppm) δ 142.5 (bs, C(1,8)), 139.1 (bs, C(9)), 135.9 (dm ^1J(C–H) = 160 Hz, C(2,7)), 132.6 (t, ^2J(C–H) = 8 Hz, C(10)), 130.4 (dm, ^1J(C–H) = 160 Hz, C(3,6)), 124.1 (dm, ^1J(C–H) = 162 Hz, C(4,5)), 5.0 ppm (qd, ^1J(C–H) = 121 Hz, ^4J(C–H) = 2.3 Hz, $SiCH_3$). HRMS: calculated for $C_{24}H_{24}Si$: 368.1417; observed: 368.142. EI mass spectrum: m/z (rel. intensity) 371 (4), 370 (9), 369 (45) 368 (100, M$^{+\cdot}$), 367 (13), 356 (3), 355 (8), 354 (19), 353 (26), 309 (18), 296 (10), 295 (58), 293 (41), 252 (26), 215 (27), 167 (11), 149 (12). Calculated for $C_{24}H_{24}Si_2$: 371 (3), 370 (13), 369 (37) 368 (100, M$^{+\cdot}$).

3.6. Structure determination and refinement of 8

A colorless block shaped crystal was glued on top of a glass fibre and transferred immediately to the cold nitrogen stream of an Enraf-Nonius CAD4F diffractometer for data collection at 100 K. Unit cell parameters were determined from a least squares treatment of the SET4 setting angles of 25 reflections with $12.4 < \theta < 20.9°$. Unit cell parameters were checked for the presence of higher lattice symmetry [16]. Data were corrected for Lp, for absorption (DIFABS [22]; correction range 0.755–1.137) and for a linear decay of 1.5% of the intensity control reflections during the 10 h of X-ray exposure time. The structure was solved with standard Patterson methods (SHELXS86, [17]) and subsequent difference Fourier analyses. Refinement on F was carried out by full matrix least squares techniques. Hydrogen atoms were introduced on calculated positions [C–H = 1.08 Å] and included in the refinement riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters, hydrogen atoms with one common isotropic thermal pa-

Table 3
Crystal data and details of the structure determination for **8** and **12**

a) Crystal data		
Compound	**8**	**12**
Formula	$C_{24}H_{24}Ge_2$	$C_{24}H_{24}Si_2$
Mol. wt.	457.67	368.63
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnnm* (No. 58)	*Pnnm* (No. 58)
a, b, c (Å)	6.383(1), 9.892(1), 15.428(2)	6.464(1), 9.976(2), 15.277(2)
V (Å^3)	974.1(2)	985.1(3)
Z	2	2
D_{calc} (g cm^{-3})	1.560	1.243
F(000) (electrons)	464	392
μ (cm^{-1})	30.5	16.5
Crystal size (mm^3)	0.50 × 0.33 × 0.20	0.12 × 0.12 × 0.50
b) Data collection		
Temperature (K)	100	295
θ_{min}, θ_{max}	1.32, 27.50	2.89, 75
Radiation	Mo Kα(Zr), 0.71073 Å	Cu Kα(Ni), 1.5418 Å
Scan type	$\omega/2\theta$	$\omega/2\theta$
$\Delta\omega$(°)	0.70 + 0.35 tan θ	0.60 + 0.15 tan θ
Hor. and vert. aperture (mm)	3.0, 5.0	3.0, 3.0
Dist. cryst. to detector (mm)	173	173
Reference reflections	0 2 −2; −1 2 0; −1 0 1	1 2 0; 0 −2 2; 1 0 −1
Data set	h −8:0; k 0:12; l 0:20	h 0:8; k −12:12; l −19:19
Total data	1792	5019
Total unique data	1110	1055
Observed data	878 [$I > 2.5\sigma(I)$]	957 [$I > 3\sigma(I)$]
c) Refinement		
No. of refined refls./pars.	878, 66	957, 77
Weighting scheme	$w = 1.0/[\sigma^2(F) + 0.000074\ F^2]$	$w = 1/\sigma^2(F)$
Final R/R_w S	0.0313, 0.0307, 1.30	0.098, 0.11, 1.67
$(\Delta/\sigma)_{av}$ and max. in final cycle	0.0003, 0.0014	0.02, 0.12
Min. and max. resd. dens. e Å^{-3}	−0.50, 0.55	−0.67, 1.07

rameter [$U = 0.035(5)$ Å^2]. Weights were introduced in the final refinement cycles, convergence was reached at $R = 0.0313$, $R_w = 0.0307$, $w = 1/[\sigma^2(F) + 0.000074F^2]$. Crystal data and details of the structure determination are given in Table 3. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 4.

3.7. Structure determination and refinement of 12

X-ray data were collected for a colorless transparent crystal glued on top of a glass fibre on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were derived from the SET4 setting angles of 25 reflections in the range 18 < θ < 30°. The data were corrected for Lp effects but not for absorption. No decay during data collection was observed. The structure was solved by direct methods (SHELXS 86 [17]) and refined on F by full matrix least squares (SHELX 76 [20]) with anisotropic displacement parameters for the non-hydrogen atoms. Hydrogen atoms were located from a difference map and their positions and isotropic displacement parameters refined.

Table 4
Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for $C_{24}H_{24}Ge_2$ (**8**)

Atom	x	y	z	U_{eq} (Å^2) [a]
Ge(1)	0.07388(9)	0.16676(5)	0	0.0113(1)
C(1)	0.1432(5)	0.0879(3)	0.1136(2)	0.0117(8)
C(2)	0.2963(5)	0.1529(3)	0.1608(2)	0.0156(9)
C(3)	0.3106(5)	0.1398(3)	0.2516(2)	0.0172(10)
C(4)	0.1609(5)	0.0690(3)	0.2953(2)	0.0160(9)
C(5)	0	0	0.2500(3)	0.0125(11)
C(6)	0	0	0.1578(3)	0.0120(11)
C(7)	0.2018(8)	0.3471(5)	0	0.0170(12)
C(8)	−0.2291(8)	0.1999(5)	0	0.0180(14)

[a] U_{eq} = one-third of the trace of the orthogonalized U.

Table 5
Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for $C_{24}H_{24}Si_2$ (**12**)

Atom	x	y	z	U_{eq} (Å^2) [a]
Si(1)	0.0737(4)	0.1672(2)	0	0.0334(6)
C(1)	0.1410(10)	0.0889(6)	0.1087(3)	0.0360(17)
C(2)	0.2936(11)	0.1516(7)	0.1568(4)	0.047(2)
C(3)	0.3080(11)	0.1365(7)	0.2496(4)	0.051(2)
C(4)	0.1595(11)	0.0661(6)	0.2935(4)	0.047(2)
C(5)	0	0	0.2463(5)	0.042(3)
C(6)	0	0	0.1553(6)	0.037(2)
C(7)	0.200(2)	0.3373(12)	0	0.062(4)
C(8)	−0.2109(18)	0.2007(11)	0	0.052(3)

[a] U_{eq} = one-third of the trace of the orthogonalized U.

Convergence was reached at $R = 0.098$. The relatively high R factor is ascribed to the effects of the poor quality of the best available crystal (i.e. crystals are not pure single crystals). Crystal data and details of the structure determination are listed in Table 3. Final positional parameters are given in Table 5.

Neutral atom scattering factors for **8** and **12** were taken from [18] and corrected for anomalous dispersion [19]. All calculations for **8** and **12** were performed with SHELX76 [20] and PLATON [21] (geometrical calculations and illustration) on a DEC-5000 cluster. Full lists of bond lengths and angles, and tables of hydrogen atom coordinates and isotrophic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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