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Communications

Synthesis and Characterization of Two Isomers of 14π-Electron Germaaromatics: Kinetically Stabilized 9-Germaanthracene and 9-Germaphenanthrene

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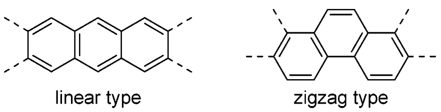
Summary: The first stable 9-germaanthracene and 9-germaphenanthrene were successfully synthesized by taking advantage of kinetic stabilization utilizing effective steric protection groups, Tbt and Bbt groups (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl). The similarities and differences of the structures and properties between the two isomers of germaaromatics are discussed.

There has been much interest in the chemistry of "*heavy aromatics*", [4*n*+2] π-electron ring systems containing a heavier group 14 element (Si, Ge, Sn, Pb),[1] from the standpoint of comparison with the parent aromatic hydrocarbon compounds, which play very important roles in organic chemistry. Although *heavy* aromatics have been known to be highly reactive and undergo ready dimerization or oligomerization under ambient conditions so far, we have succeeded in the synthesis of the first stable neutral sila- and germaaromatics,[1g] i.e., silabenzene,[2] 1- and 2-silanaphthalenes,[3,4] 9-silaanthracene,[5] germabenzene,[6] and 2-germanaphthalene,[7] by taking advantage of kinetic stabilization using efficient steric protection groups, Tbt and Bbt. The experimental and theoretical studies on the structures, spectroscopic properties, and reactivities of these kinetically stabilized sila- and germaaromatics evidenced the high aromaticity of the monosila- and monogermaaromatic systems.[1g] Very recently, the stable stannaaromatics,[8] 2-stannanaphthalene, was also isolated and fully characterized, suggesting the considerable aromaticity of a 10π-electron ring system containing a much heavier group 14 atom, an Sn atom.[9] Thus, the concept of kinetic stabilization is evidenced to be of great use for the construction of stable *heavy aromatics*. On the other hand, anthracene and phenanthrene are attractive 14π-electron aromatic systems due to their unique electrochemical and photochemical properties from the viewpoint of material science.[10] Hence, it should be of great importance to elucidate the similarities and differences between two types of extended π-electron aromatic systems containing a heavier group 14 atom, i.e., the linear type (acene system) and the zigzag type (phen system) such as anthracene and phenanthrene (Scheme 1). We report here the synthesis of the two structural isomers of 14π-electron germaaromatic systems, 9-germaanthracene **1** and 9-germaphenanthrene **2**, utilizing a Tbt or Bbt group as a steric protection group.

Scheme 1



In consideration of previous reports,[1g] the reactions of the corresponding precursors bearing a leaving group (halogeno or

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(8) This is the first example of neutral stannaaromatics, although ionic stannaaromatic compounds such as stannole dianion derivatives have been already synthesized and characterized; see ref 1i and: Todorov, I.; Sevov, S. C. *Inorg. Chem.* **2005**, *44*, 5361.

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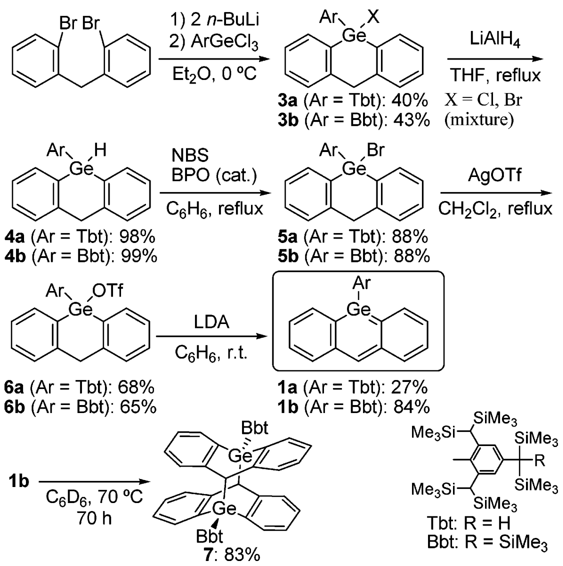
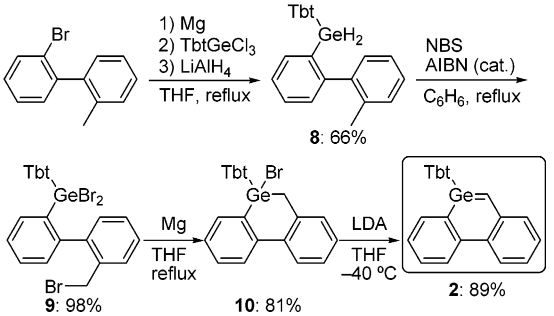
Scheme 2



trifluoromethanesulfonyl group) with an appropriate base should be effective for the construction of *heavy aromatics*. 9-Trifluoromethanesulfonyl-9-Tbt-9,10-dihydro-9-germaanthracene (**6a**) was prepared as a precursor for 9-germaanthracene **1a** according to Scheme 2. Treatment of **6a** with 1.1 equiv of lithium diisopropyl amide (LDA) in benzene at rt afforded germaanthracene **1a** as red crystals in 27% isolated yield. The similarity of the spectroscopic data (^{1}H NMR and UV/vis) to those of 9-Tbt-9-silaanthracene[5] supported the structure of **1a**. However, 9-germaanthracene **1a** undergoes gradual decomposition at ambient temperature to afford an insoluble colorless solid, in contrast to 9-Tbt-9-silaanthracene,[5] which is stable up to 100 °C in C_6D_6. Therefore, further investigation on the properties of **1a** could not be performed. Next, we introduced a Bbt group on the central germanium atom instead of a Tbt group.[11] Thus, triflate **6b**, prepared by the same method as that for **6a**, was treated with 1.1 equiv of LDA to gave 9-Bbt-9-germaanthracene (**1b**) as red crystals in 84% yield. 9-Germaanthracene **1b** possesses sufficient stability at ambient temperature to be handled under an inert atmosphere, although it is slightly light-sensitive. Heating of the C_6D_6 solution of **1b** at 70 °C for 70 h gave [4+4] head-to-tail dimer **7** in 83% yield. Hence, 9-germaanthracene **1b** is less stable than 9-Tbt-9-silaanthracene, which undergoes dimerization in C_6D_6 at 110 °C for 15 days to afford the corresponding [4+4] dimer.[5] On the other hand, the dehydrobromination reaction of 9-bromo-9-Tbt-9,10-dihydro-9-germaphenanthrene (**10**), which was prepared according to Scheme 3, using LDA in THF afforded 9-Tbt-9-germaphenanthrene (**2**) as pale yellow crystals in 89% yield. It should be noted that **2** is stable up to 100 °C in C_6D_6 in contrast to 9-Tbt-9-stannaphenanthrene, which undergoes ready [2+2] dimerization at room temperature.[12] The structures of **1b** and **2** were identified by spectroscopic analyses (NMR, UV/vis, mass, and Raman spectra) and finally established by X-ray crystallographic analysis.[13]

Scheme 3



The X-ray crystallographic analyses (Figure 1) of **1b** and **2** show a completely planar geometry for their central germaaromatic moieties, which are almost perpendicular to the aromatic rings of the Bbt (86° for **1b**) and Tbt (87° and 86° for **2**) groups, indicating that there is almost no conjugative stabilization effect between the substituents and the central germaaromatic rings. It should be noted that 9-germaphenanthrene **2** has two independent molecules in the unit cell. Two types of intermolecular C−H π-interactions are confirmed between the two molecules, forming a unique tetrameric packing structure, as shown in Figure 2; one is between the two 9-germaphenanthrene rings (the distance between the C atom and the aromatic ring is ca. 3.54 Å), and the other is between the methyl group and the 9-germaphenanthrene ring (the distance between the C atom and the aromatic ring is ca. 3.41 Å).[14] In contrast, 9-germaanthracene **1b** shows no apparent intermolecular interactions in its packing structure. In Figure 3 are shown selected structural parameters of **1b** and **2** together with calculated ones for the model compounds bearing a Dmp (2,6-dimethylphenyl) group.[13] In the case of both **1b** and **2**, the C−C and Ge−C bond lengths are the middle values between the corresponding single- and double-bond lengths,[15] indicating the existence of π-electron delocalization on their germaaromatic rings, as in the case of 1-Tbt-germabenzene[6] and 2-Tbt-2-germanaphthalene.[7] The observed structural parameters of **1b** and **2** are in good agreement with those calculated for their model compounds and show bond alternations in the central germaaromatic ring reflecting the corresponding canonical structures[16] as in the case of anthracene and phenanthrene, respectively. While the two Ge−C bond lengths [1.855(2) and 1.862(2) Å] of the 9-germaanthracene ring of **1b** are close to each other due to its bilateral symmetry, those of the 9-germaphenanthrene skeleton of **2** are different from each other [1.797(3) and 1.883(3) Å for molecule **A**; 1.792(3) and 1.886(3) Å for molecule **B**], reflecting the most contributory

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[11] It has been reported that 1-Bbt-1-silanaphthalene is more stable than 1-Tbt-1-silanaphthalene toward [4+2] dimerization; see ref 4b. In the course of our studies on kinetic stabilization of the double-bond compounds between heavier group 15 elements, it was found that the central moieties of BbtE═EBbt (E = P, Sb, Bi) are slightly more congested than those of TbtE═ETbt; see: (a) Sasamori, T.; Arai, Y.; Takeda, N.; Okazaki, R.; Furukawa, Y.; Kimura, M.; Nagase, S.; Tokitoh, N. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 661. (b) Sasamori, T.; Takeda, N.; Tokitoh, N. *J. Phys. Org. Chem.* **2003**, *16*, 450.

[12] Mizuhata, Y.; Takeda, N.; Sasamori, T.; Tokitoh, N. *Chem. Lett.* **2005**, *34*, 1088.

[13] The experimental procedures and spectral data for **1b** and **2** and theoretical calculations for their model compounds are shown in the Supporting Information.

[14] Although the degree of T-shaped CH−π interaction should be discussed on the basis of the distance between the center of the aromatic ring and the aromatic plane, it is somewhat difficult to define the center of the 9-germaphenanthrene ring due to the slight deformation of the skeleton. It was reported that the T-shaped CH−π interaction in a benzene dimer should be highly effective when the distance between the center of the aromatic ring and the aromatic plane is ca. 5.0 Å; that is, that between the C atom at the edge and the aromatic plane is ca. 3.6 Å, see: (a) Pawliszyn, J.; Szczesniak, M. M.; Scheiner, S. *J. Phys. Chem.* **1984**, *88*, 1726. (b) Felker, P. M.; Maxton, P. M.; Schaeffer, M. W. *Chem. Rev.* **1994**, *94*, 1787. (c) Sinnokrot, M. O.; Sherrill, C. D. *J. Am. Chem. Soc.* **2004**, *126*, 7690. (d) Sinnokrot, M. O.; Sherrill, C. D. *J. Phys. Chem. A* **2004**, *108*, 10200. (e) Sato, T.; Tsuneda, T.; Hirao, K. *J. Chem. Phys.* **2005**, *123*, 104307.

[15] The calculated Ge−C single and double bond lengths are ca. 1.91−2.00 and ca. 1.77 Å, respectively. See: Grev, R. S.; Schaefer, H. F. *Organometallics* **1992**, *11*, 3489.

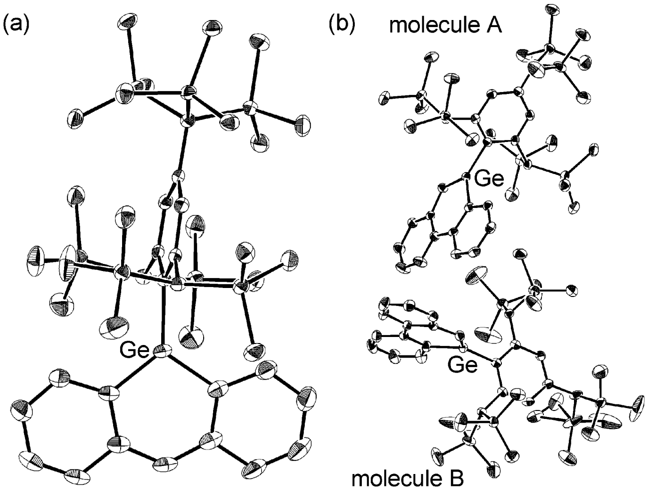

Figure 1. ORTEP drawing of **1b** (a) and **2** (b) with thermal ellipsoid plots (50% probability). Hydrogen atoms are omitted for clarity.

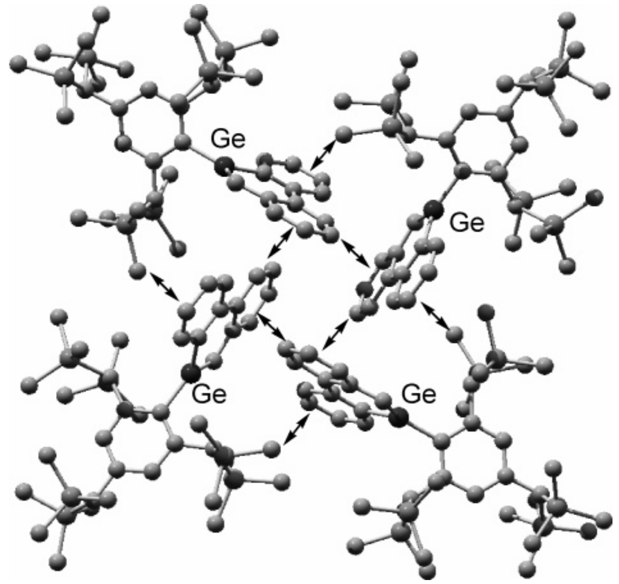

Figure 2. Tetrameric packing structure of 9-germaphenanthrene **2**.

canonical structure of a 9-germaphenanthrene skeleton.[16] Thus, the Ge−C bond of the 9,10-position of 9-germaphenanthrene **2** features higher double-bond character than the other Ge−C bond of **2**.

In the ^{1}H and ^{13}C NMR spectra of **1b** and **2**, all of the signals corresponding to the central 9-germaanthracene and 9-germaphenanthrene skeletons were observed within the aromatic region, 7−8 ppm for the ^{1}H NMR spectra and 110−150 ppm for the ^{13}C NMR spectra. In particular, the protons of the 10-positions of **1b** and **2** appeared as characteristic singlet signals at 7.73 and 8.13 ppm, respectively, which are apparently lower than those of olefins (ca. 4.5−7.0 ppm).[17] In addition, the calculated chemical shifts for the model compounds bearing less hindered substituents on the Ge atoms are in good agreement with the observed values, indicating that the steric effect of Tbt and Bbt on the central germaaromatic rings should be negligible.[13] Thus, the NMR spectral properties of **1b** and **2** are similar to each other. Electronic spectra should be of great use in the evaluation of the extension of π-electrons on the aromatic rings. In the UV/vis spectra in hexane, the longest absorption maxima (λ_{max}) corresponding to the HOMO−LUMO electron transitions of **1b** (520 nm) and **2** (409 nm) are red-shifted as compared with those of 1-Tbt-germabenzene[6] (326 nm) and 2-Tbt-2-germanaphthalene[7] (386 nm), respectively. That is, the π-electron conjugation can be extended as the n value of $[4n+2]$ π-electron aromatic systems increases.[18] Furthermore, the longest λ_{max} of 9-germaanthracene **1b** is apparently longer than that of **2**, reflecting their colors in solution (red for **1b** and pale yellow for **2**; see Figure S6 in the Supporting Information). Hence, it is evidenced that the 14π-electron systems of germaaromatics can be extensively conjugated in the linear type but not so effectively in the zigzag type.

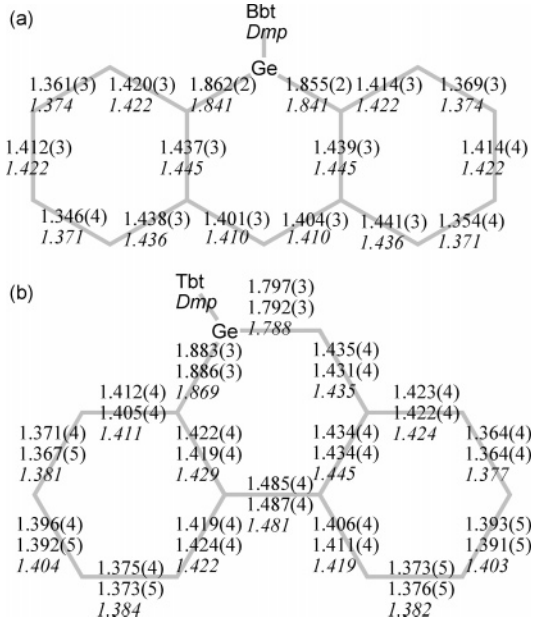

Figure 3. Observed and calculated (*italic*) bond lengths (Å) for (a) 9-germaanthracenes and (b) 9-germaphenanthrenes. The calculated values are obtained for the Dmp (2,6-dimethylphenyl)-substituted model compounds at the B3LYP/6-31G(d) level.

In conclusion, two isomers of 14π-electron germaaromatic systems, 9-germaanthracene **1b** and 9-germaphenanthrene **2**, were synthesized as stable crystalline compounds. Their similarities and differences are revealed on the basis of the structural and spectroscopic analyses. Further investigations on their photochemical and electrochemical properties, reactivities, and applications as arene ligands to transition metals are currently in progress.

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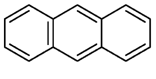
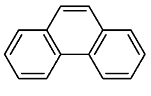
(16) In the case of anthracene and phenanthrene, the slight bond alternations can be seen, reflecting their most dominant canonical structures as shown below. Similarly, one can see their slight bond alternations in the germaaromatic rings of **1b** and **2**, which should be reasonably explained in terms of their dominant canonical structures as well as their all-carbon analogues.


anthracene


phenanthrene

(17) For example, the olefinic proton of triphenylethylene is observed at 6.96 ppm [SDBSWeb: http://www.aist.go.jp/RIODB/SDBS/(National Institute of Advanced Industrial Science and Technology, 2006)].

(18) The longest absorption maxima of silaaromatic systems are apparently red-shifted as compared with those of the corresponding all-carbon systems. However, those of germaaromatic systems are observed in the region similar to that for the corresponding silaaromatic systems. The systematic comparisons of the longest absorption maxima between the kinetically stabilized sila- and germaaromatic systems with all-carbon systems are shown in the Supporting Information.

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Supporting Information Available: X-ray crystallographic data of **1** and **15** in CIF format, experimental procedures, and spectral data. These materials are available free of charge via the Internet at http://pubs.acs.org.

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