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Synthesis and Structure of a Kinetically Stabilized 2-Germanaphthalene: The First Stable Neutral Germaaromatic Compound

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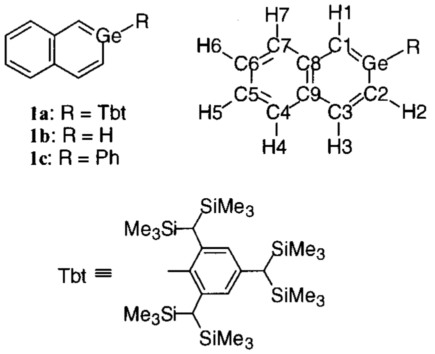
Summary: The first stable neutral germaaromatic compound, i.e., the 2-germanaphthalene ***1a*** *bearing an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt), was successfully synthesized by the reaction of the corresponding bromogermane* ***4*** *with lithium diisopropylamide. The molecular structure and aromaticity of* ***1a*** *were discussed on the basis of its NMR, UV−vis, and Raman spectra, X-ray crystallographic analysis, and theoretical calculations.*

In recent years much attention has been focused on germaaromatic compounds,[1] namely, Ge-containing [4*n* + 2]-π-electron ring systems, since they are among the heavier congeners of aromatic hydrocarbons,[2] which play very important roles in organic chemistry. As for ionic germaaromatic compounds, cyclotrigermenium cations[3] and germole dianions[4] have been successfully synthesized as stable compounds and fully characterized, while the synthesis of neutral germaaromatic compounds is little known. Märkl et al. have already reported the synthesis of 1,4-di-*tert*-butylgermabenzene,[5] but the generation was confirmed only by the formation of its [2 + 2] dimer and the trapping reaction with diene. Furthermore, they described the spectroscopic detection of 1,4-dialkylgermabenzenes in the gas phase by VTPES (variable-temperature photoelectron spectroscopy) experiments.[6] However, no isolation of a neutral germaaromatic compound has been reported, probably due to its high reactivity. On the other hand, we have recently succeeded in the synthesis and isolation of kinetically stabilized silabenzene[7] and 2-silanaphthalene,[8] the first examples of stable neutral silaaromatic compounds, by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). With these stable systems in hand, we have revealed their molecular structures and reactivities and have discussed the aromaticity of silaaromatic compounds. The successful results in the silaaromatic systems naturally prompted us to extend this chemistry to the heavier metallaaromatic systems of group 14 elements. Here, we report the synthesis and structure of the 2-germanaphthalene **1a** kinetically stabilized by the Tbt group, the first stable neutral germaaromatic compound (Chart 1).

Chart 1



1,2,3,4-Tetrahydro-2-germanaphthalene **2** was synthesized from homophthalic anhydride in four steps (Scheme 1).[9] Bromination of **2** with excess NBS followed by reduction with $LiAlH_4$ gave an inseparable mixture of the expected vinylgermane **3a** and overbrominated vinylgermane **3b**. Treatment of the mixture of vinylgermanes **3a** and **3b** with *t*-BuLi and successive addition of saturated aqueous NH_4Cl afforded the vinylgermane **3a** as a pure compound. Finally, careful bromination of **3a** with NBS (1 equiv) resulted in the quantitative formation of the corresponding bromogermane **4**, which is a suitable precursor of 2-germanaphthalene **1a** (Scheme 1).

2-Germanaphthalene **1a** was synthesized by the dehydrobromination of bromogermane **4** with LDA in THF at room temperature. 2-Germanaphthalene **1a** is thermally stable under an inert atmosphere either in the solid state (mp 143−145 °C) or in solution (benzene, at 100 °C for 1 h in a sealed tube), and no dimerization or decomposition was observed. However, **1a** is highly moisture sensitive and undergoes addition of water to

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[1] For reviews of germaaromatic compounds, see: (a) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283. (b) Lee, V. Y.; Sekiguchi, A.; Ichinohe, M.; Fukaya, N. *J. Organomet. Chem.* **2000**, *611*, 228.

[2] Minkin, V. J.; Glukhovtsev, M. N.; Simkin, Y. B. *Aromaticity and Antiaromaticity; Electronic and Structural Aspects*; Wiley: New York, 1994.

[3] (a) Sekiguchi, A.; Tsukamoto, M.; Ichinohe, M. *Science* **1997**, *275*, 60. (b) Ichinohe, M.; Fukaya, N.; Sekiguchi, A. *Chem. Lett.* **1998**, 1045. (c) Sekiguchi, A.; Fukaya, N.; Ichinohe, M. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1999**, *59*, 150. (d) Sekiguchi, A.; Fukaya, N.; Ichinohe, M.; Ishida, Y. *Eur. J. Inorg. Chem.* **2000**, 1155.

[4] (a) West, R.; Sohn, H.; Powell, D. R.; Müller, T.; Apeloig, Y. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1002. (b) Choi, S.-B.; Boudjouk, P.; Qin, K. *Organometallics* **2000**, *19*, 1806.

[5] Märkl, G.; Rudnick, D. *Tetrahedron Lett.* **1980**, *21*, 1405.

[6] Märkl, G.; Rudnick, D.; Schulz, R.; Schweig, A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 221.

[7] (a) Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 634. (b) Wakita, K.; Tokitoh, N.; Okazaki, R.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2000**, *122*, 5648.

[8] (a) Tokitoh, N.; Wakita, K.; Okazaki, R.; Nagase, S.; Schleyer, P. v. R.; Jiao, H. *J. Am. Chem. Soc.* **1997**, *119*, 6951. (b) Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S.; Schleyer, P. v. R.; Jiao, H. *J. Am. Chem. Soc.* **1999**, *121*, 11336.

[9] Fang, X.; Larson, D. L.; Portoghese, P. S. *J. Med. Chem.* **1997**, *40*, 3064.

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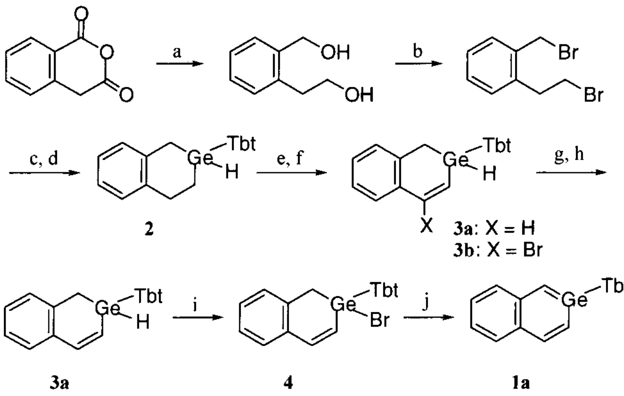
Scheme 1[a]



[a] Conditions: (a) $LiAlH_4$, THF, 0 °C, 96%; (b) Ph_3P, CBr_4, Et_2O, room temperature, 68%; (c) $TbtGeCl_3$, Mg, THF, room temperature; (d) $LiAlH_4$, THF, 0 °C, 33% for two steps; (e) NBS (7.1 equiv), BPO (cat.), benzene, reflux; (f) $LiAlH_4$, THF, 0 °C; (g) *t*-BuLi, THF, −78 °C; (h) saturated aqueous NH_4Cl, room temperature, 62% for four steps; (i) NBS, (1.0 equiv), BPO (cat.), benzene, reflux, 99%; (j) LDA (1.3 equiv), THF, room temperature, ca. 98%.

Scheme 2

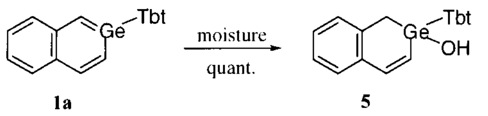


Table 1. Observed and Calculated ^{1}H and ^{13}C NMR Chemical Shifts (ppm) for 2-Germanaphthalenes[a]

	1a (R = Tbt, obsd[a])	**1b** (R = H, calcd[b])	**1c** (R = Ph, calcd[b,c])
H1	8.24	8.13	7.62
H2	7.85	7.48	7.18
H3	8.55	8.50	8.40
H4	7.60	7.49	7.44
H5	7.03	7.02	6.92
H6	7.20	7.22	7.10
H7	7.65	7.45	7.36
C1	127.69	135.55	127.46
C2	130.45	128.34	125.74
C3	145.89	145.51	145.09
C4	133.71	133.17	132.48
C5	120.75	120.94	119.43
C6	126.26	125.53	124.80
C7	128.40	127.15	127.08
C8	145.15	145.61	145.20
C9	128.12	127.69	126.43

[a] See Chart 1. [b] Measured in benzene-d_6. [c] Calculated at the GIAO−B3LYP/6-311G(d)(6-311G(3d) on Ge)//B3LYP/6-31G(d) level. [d] The phenyl group is fixed in such a way that it is perpendicular to the 2-germanaphthalene.

its Ge═C moiety, giving the corresponding hydroxygermane **5** in a quantitative yield (Scheme 2).

The molecular structure of **1a** was confirmed by ^{1}H and ^{13}C NMR spectroscopy using 2D NMR techniques together with NOE and decoupling experiments. The assignments of ^{1}H and ^{13}C NMR signals are listed in Table 1 along with the calculated values for some model compounds, i.e., 2-germanaphthalene **1b** and 2-phenyl-2-germanaphthalene **1c**, where the observed values are in good agreement with the calculated ones.[10] Thus, these results clearly indicate the delocalized π-electronic system of **1a**. All the ^{1}H NMR signals of the 2-germanaphthalene ring protons (7.03−8.55 ppm) of **1a** were observed in the aromatic region, and the ^{13}C NMR signals of the germanaphthalene ring carbons (120.75−145.89 ppm) were located in the sp^2 region.

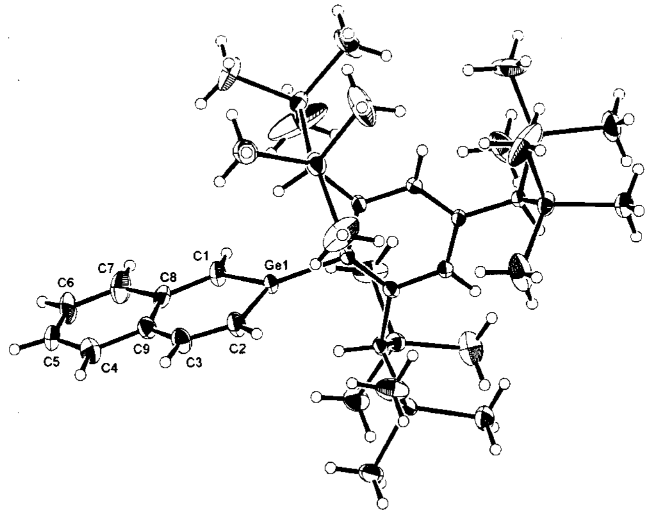


Figure 1. ORTEP drawing of 2-germanaphthalene **1a** (major fragment, 30% probability).

The molecular geometry of **1a** was finally determined by X-ray crystallographic analysis (Figure 1),[11] in which the structure was successfully refined more adequately by the separation of the overlapped disorder of the 2-germanaphthalene moieties (2:1 ratio).[12] The structural analysis revealed the planarity of the 2-germanaphthalene ring and the completely trigonal planar geometry around the germanium atom. In addition, the benzene ring of the Tbt group is almost perpendicular to the 2-germanaphthalene ring, and hence it is considered that there is very little conjugative interaction between the two aromatic rings. The bond lengths of the two Ge−C bonds in the 2-germanaphthalene ring (1.803(5) and 1.859(5) Å) are between those of calculated Ge−C double (1.767 Å) and single bonds (1.908−2.001 Å).[13] In particular, the former Ge−C bond length is close to the Ge−C double bond length of the previously reported germene $Mes_2Ge{=}CR_2$ (CR_2 = fluorenylidene; 1.803(4) Å),[14] which is stabilized by the conjugation of

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(10) Calculations were carried out using the Gaussian 98 program: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(11) Crystal data of **1a**: Rigaku/MSC Mercury CCD, Mo Kα radiation, graphite monochromator, reflections recorded at 93 K from a colorless prismatic crystal with dimensions 0.40 × 0.40 × 0.35 mm^3 to $2\theta_{max}$ = 50°, structure solved by direct methods (SIR97)[17] and refined by full-matrix least-squares procedures on F^2 (SHELX-97),[18] formula $C_{36}H_{66}GeSi_6$, mol wt 740.02, triclinic, space group $P\bar{1}$, $Z = 2$, a = 11.033(4) Å, b = 12.112 (5) Å, c = 17.851(6) Å, α = 72.423(15)°, β = 86.91(2)°, γ = 75.064(9)°, V = 2196.6(14) Å^3, D_{calcd} = 1.119 g cm^{-3}, μ = 0.883 mm^{-1}; R1($I > 2\sigma(I)$) = 0.053, wR2(all data) = 0.138 for 7709 reflections, 479 parameters, and 50 restraints.

(12) Recently, we reported the analogous separation by overlapped disorder of a 2-silanaphthalene bearing a Tbt group: Wakita, K.; Tokitoh, N.; Okazaki, R. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2157.

(13) Grev, R. S.; Schaefer, H. F., III. *Organometallics* **1992**, *11*, 3489.

(14) Lazraq, M.; Escudié, J.; Couret, C.; Satgé, J.; Dammel, R. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 828.

Table 2. Observed and Calculated Bond Lengths (Å) of 2-Germanaphthalenes

	1a (R = Tbt, obsd[a])	**1b** (R = H, calcd[b])	**1c** (R = Ph, calcd[b])
C1−Ge1	1.803(5)	1.810	1.812
Ge1−C2	1.859(5)	1.851	1.853
C2−C3	1.368(7)	1.374	1.374
C3−C9	1.429(8)	1.433	1.433
C9−C4	1.416(8)	1.423	1.422
C4−C5	1.337(12)	1.376	1.376
C5−C6	1.391(15)	1.414	1.414
C6−C7	1.368(9)	1.374	1.375
C7−C8	1.413(8)	1.429	1.429
C8−C1	1.450(8)	1.421	1.421
C8−C9	1.430(7)	1.446	1.446

[a] The major fragment; two overlapped fragments were restrained to have the same structure. [b] Calculated at the B3LYP/6-31G(d) level.

the Ge−C double bond with the fluorenylidene moiety. The C−C bond lengths (1.337(12)−1.450(8) Å) of the 2-germanaphthalene ring are also roughly intermediate between those of C−C double and single bonds. These results suggest that the π-electrons in the 2-germanaphthalene ring system of **1a** are delocalized. Furthermore, theoretical calculations for the model compounds **1b** and **1c** were also performed for comparison (Table 2).[10] The experimentally obtained bond lengths are in fairly good agreement with those theoretically calculated.

The Raman spectrum of **1a** showed the most intense Raman signal at 1363 cm^{-1}, which corresponds to the most intense signals of 1382 and 1368 cm^{-1} for naphthalene and 2-silanaphthalene,[8] respectively. This strongest vibrational frequency observed for **1a** is in good agreement with the theoretically calculated one (1356 cm^{-1} for **1c**, computed at the B3LYP/6-31G(d) level and scaled by 0.96).[15] Furthermore, the calculated vibration modes of **1c** considerably resemble those of naphthalene, suggesting the structural similarity between 2-germanaphthalene **1a** and naphthalene.

The UV−vis spectrum of **1a** in hexane showed three absorption maxima (269 (ϵ 2 × 10^4), 335 (ϵ 1 × 10^4), and 386 nm (ϵ 2 × 10^3)) most likely assignable to the E1, E2, and B bands, respectively. These are red-shifted compared to those for naphthalene (221 (ϵ 1.33 × 10^5), 286 (ϵ 9.3 × 10^3), and 312 nm (ϵ 2.9 × 10^2))[16] and 2-silanaphthalene (267 (ϵ 2 × 10^4), 327 (ϵ 7 × 10^3), and 387 nm (ϵ 2 × 10^3)),[8] respectively, suggesting the aromatic character of this conjugated ring system containing the germanium atom similar to that of naphthalene and 2-silanaphthalene.

In summary, we have succeeded in the synthesis and characterization of 2-germanaphthalene **1a**, the first example of a stable neutral aromatic compound containing a germanium atom. Further investigations on the physical and chemical properties of **1a** are currently in progress.

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Supporting Information Available: Text and tables giving physical properties of compounds **1a** and **2**−**5**, crystallographic data with all bond lengths, bond angles, and thermal and positional parameters for **1a**, and the observed Raman shifts for **1a** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] For the scaling factor of 0.96, see: Bauschlicher, C. W., Jr.; Partridge, H. *J. Chem. Phys.* **1995**, *103*, 1788.

[16] Silverstein, R. M.; Bassler, G. C.; Morril, T. C. In *Spectrometric Identification of Organic Compounds*, 5th ed.; Wiley: New York, 1991.

[17] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. SIR97: a New Tool for Crystal Structure Determination and Refinement. Submitted for publication.

[18] Sheldrick, G. M. SHELX-97, Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.