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The Synthesis of a New Ring System, Germatrisilacyclobutane $[R_2Si]_3GeR'_2$ and Its Molecular Structure

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A new type of ring system, the first germatrisilacyclobutane $[R_2Si]_3GeR'_2$ ($R={}^iPr$, ${}^tBuCH_2$; $R'=Me_3SiCH_2$) was synthesized and characterized. The X-ray structure analysis revealed that the both Si_3Ge rings are nonplanar, and that the Si-Si and Si-Ge bond distances are considerably longer than those of the corresponding normal ones, respectively. The ring strain energy was estimated to be ca. 25 kcal/mol.

The chemistry of cyclopolysilanes containing a heteroatom such as oxygen, nitrogen, etc. is intriguing subject of a current interest because of their versatile physical and chemical properties. However, there are no reports on the four-membered ring system containing a germanium, Si_3Ge, although two studies on the syntheses of Si_4Ge 1) and Si_5Ge 2) systems have been described so far.

Recently, we reported some properties, including the photochemical behaviors, of cyclopolysilanes, $[R^1R^2Si]_n$ (n=3-7) 3) or $[R_2Si]_nO$ (n=3,4). 4,5) In connection with these compounds, we now wish to report the synthesis of germatrisilacyclobutane (**1**), $[R_2Si]_3GeR'_2$, and its molecular structure via X-ray analysis. Compounds **1a** and **1b** were obtained in good yields by the treatment of 1,3-dichlorohexaalkyltrisilanes and dialkyldichlorogermane with lithium in the presence (or absence) of biphenyl under mild conditions.

$$Cl(R_2Si)_3Cl + R'_2GeCl_2 \xrightarrow{Li} [R_2Si]_3GeR'_2 \quad \begin{array}{l}\textbf{1a};\ R={}^iPr,\ R'=Me_3SiCH_2\\ \textbf{1b};\ R={}^tBuCH_2,\ R'=Me_3SiCH_2\end{array}$$

Typically, a solution of $Cl({}^iPr_2Si)_3Cl$ (1.44 g, 3.49 mmol) in THF (14 cm^3) was added to a suspension of Li powder (0.13 g, 18.6 mmol) in THF (17

cm^3) at 0 °C under argon. The mixture was stirred at 0 °C until it turned to yellow in color. A solution of $(Me_3SiCH_2)_2GeCl_2$ 6) (1.33 g, 4.19 mmol) in THF (14 cm^3) was then added dropwise over 40 min to the mixture at 0 °C. After additional stirring for 3 h, the resulting mixture was worked up and recrystallized from EtOH to afford an analytically pure sample of **1a** (0.88 g, 44% yield) as colorless crystals: mp 77.0-77.5 °C (sealed capillary). Physical and spectral data 7) for the sample were consistent with the proposed structure. Compound **1b** 8) was also obtained by a similar treatment.

In order to obtain further confirmation, the structures of **1a** (Fig. 1) and **1b** were determined by X-ray diffraction 9,10) which showed the Si_3Ge four-membered rings to assume folded structures with dihedral angles of 24° in **1a** and 37° in **1b**, respectively. Table 1 lists bond distances and angles of the two ring systems of the compounds, together with the related data of the corresponding tetrasilacycles, $[^iPr_2Si]_4$ (**2a**) and $[(^tBuCH_2)_2Si]_4$ (**2b**). The Si-Si and Si-Ge bond distances of **1a** and **1b** are considerably longer than the corresponding normal ones (2.34 for Si-Si and 2.39 Å for Si-Ge bonds), respectively. However, the $C-Si_{ring}$ bonds (av. 1.916 in **1a** and 1.903 Å in **1b**) are shorter than the normal one (1.94 Å), and $C-Ge_{ring}$ bonds (av. 1.989 Å in **1a** and **1b**) almost the same as that of the normal (1.99 Å). The folded structure and bond elongation probably be interpreted generally in terms of the result of the compromise between two main factors, the ring strain in this system and the steric repulsion arising from the congestion of the bulky substituents, as shown previously. 3) Interestingly, the ∠SiGeSi in **1a** and **1b** are very close to the ∠SiSiSi in **2a** and **2b**, while the ∠SiSiSi in **1a** and **1b** are larger than those of **2a** and **2b** by ca. 2-3°, respectively. The difference between the Si-Ge and Si-Si bond distances in each pair (Table 1)

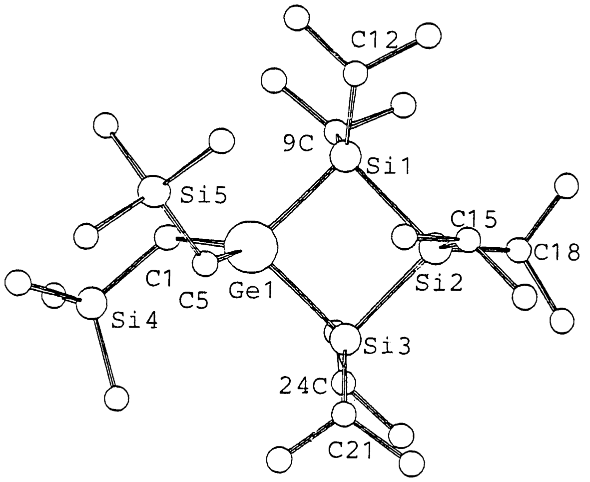

Fig. 1. Molecular structure of **1a**
Selected bond ditances (Å) and angles (°): Ge(1)-Si(1) 2.452(1), Si(1)-Si(2) 2.380(1), Si(2)-Si(3) 2.391(1), Si(3)-Ge(1) 2.462(1); Ge(1)-Si(1)-Si(2) 89.0 (1), Si(1)-Si(2)-Si(3) 90.4(1), Si(2)-Si(3)-Ge(1) 88.5(1), Si(3)-Ge(1)-Si(1) 87.1(1), C(1)-Ge(1)-C(5) 107.5(1): dihedral angle (°) between the two planes, Si(1)Ge(1)Si(3) and Si(1)Si(2)Si(3) 24.

Table 1. Comparisons of dihedral angles, bond distances, and bond angles of **1** and the related tetrasilacycles (**2**)

Compound	Dihedral angle/°	Bond distance/Å$^{a)}$		Bond angle/°	
		Si-Si	Si-Ge	∠SiSiSi	∠SiGeSi
$[{}^{i}Pr_2Si]_3Ge(CH_2SiMe_3)_2$ (**1a**)	24	2.386	2.457	90.4	87.1
$[({}^{t}BuCH_2)_2Si]_3Ge(CH_2SiMe_3)_2$ (**1b**)	37	2.393	2.444	88.7	86.4
$[{}^{i}Pr_2Si]_4{}^{b)}$ (**2a**)	37	2.377	–	87.0$^{a)}$	–
$[({}^{t}BuCH_2)_2Si]_4{}^{c)}$ (**2b**)	39	2.409	–	86.7$^{a)}$	–

a) Average value. b) See Ref. 3a. c) See Ref. 11.

appears to account for this angle difference. Consequently, the results mentioned above apparently reflect the difference between the silicon and germanium atomic diameters in the two ring systems, in all respects, and the latter system therefore holds a slightly deformed-rhombic structure.

Previously, we estimated the ring strain energies of a series of homopolysilacycles, $[R^1R^2Si]_n$ where n=2-6, by the comparisons of their lowest transition energies obtained from the longest-wavelength UV-absorption bands with the corresponding values for a series of linear permethylpolysilanes.[12] Similarly, the ring strain energies of the present compounds also can be estimated by using their UV-absorption bands of **1a** and **1b** at λ_{max} 300 and ca. 290 nm, respectively, since the factors controlling the spectral behaviors of the Si_3Ge system could be essentially identical with the factors in the Si_4 ring system. Thus, the ring strain energies were estimated to be ca. 27 and 23 kcal/mol in **1a** and **1b**, respectively (av. 25 kcal/mol). The two values agree well with that of the Si_4 ring system (av. 23 kcal/mol), as well as that of cyclobutane (26.5 kcal/mol),[12] but, it is worthy to note that **1a** bearing less bulky substituents, $Es({}^{i}Pr)=-0.47$,[13] than **1b**, $Es({}^{t}BuCH_2)=-1.74$,[13] holds a greater strain energy by 4 kcal /mol.

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7) Anal. Found: C, 52.26; H, 10.67%. Calcd for $C_{26}H_{64}Si_5Ge$: C, 52.95; H, 10.94%. UV (cyclohexane) λ_{max} 300 nm (ε 320 dm^3 mol^{-1} cm^{-1}). ^1H NMR (C_6D_6) δ 0.26 (s, 18H, $SiCH_3$), 0.53 (s, 4H, $GeCH_2Si$), 1.33 (m, 36H, $SiCH(C\underline{H}_3)_2$), 1.59 (m, 6H, $SiCHMe_2$); ^{13}C NMR (C_6D_6) δ 0.70 ($GeCH_2Si$), 2.37 ($SiCH_3$), 14.99 (Si^2CHMe_2), 15.60 ($Si^{1,3}CHMe_2$), 22.71 ($SiCH(\underline{C}H_3)_2$); ^{29}Si NMR (C_6D_6) δ 1.13 (Si^2), 2.23 (SiMe), 5.78 ($Si^{1,3}$). MW 590 by MS (Calcd 590).

8) Colorless crystals (23% yield) mp 368-374 °C (sealed capillary). Anal. Found: C, 60.04; H, 11.68%. Calcd for $C_{38}H_{88}Si_5Ge$: C, 60.20; H, 11.70%. UV (cyclohexane) λ_{max} 286 nm (ε 590 dm^3 mol^{-1} cm^{-1}). ^1H NMR (C_6D_6) δ 0.31 (s, 18H, $SiCH_3$), 0.67 (s, 4H, $GeCH_2Si$), 1.22 (s, 18H, Si^2CH_2-$C(C\underline{H}_3)_3$), 1.24 (s, 36H, $Si^{1,3}CH_2C(C\underline{H}_3)_3$), 1.51 (s, 4H, $Si^2CH_2{}^tBu$), 1.57 (s, 8H, $Si^{1,3}CH_2{}^tBu$); ^{13}C NMR (C_6D_6) δ 2.93 ($SiCH_3$), 3.46 ($GeCH_2Si$), 32.13 ($Si^2CH_2\underline{C}Me_3$), 32.34 ($Si^{1,3}CH_2\underline{C}Me_3$), 32.21 ($Si^{1,3}CH_2{}^tBu$), 32.43 ($Si^2CH_2{}^tBu$), 34.28 ($Si^2CH_2C(\underline{C}H_3)_3$), 34.43 ($Si^{1,3}CH_2C(\underline{C}H_3)_3$); ^{29}Si NMR (C_6D_6) δ -23.45 (Si^2), -11.82 (SiMe), 1.83 ($Si^{1,3}$). MW 758 by MS (Calcd 758).

9) Crystal data for **1a**: $C_{26}H_{64}Si_5Ge$, M=589.844, monoclinic, $P2_1/a$, a=12.131 (2), b=19.102(2), c=16.132(2) Å, β=99.39(1)°, U=3688(1) $Å^3$, Z=4, Dc= 1.062 g cm^{-3}, μ(Cu Kα)=28.3 cm^{-1}. R=4.7, Rw=5.7%.

10) Crystal data for **1b**: $C_{38}H_{88}Si_5Ge$, M=758.159, monoclinic, $P2_1/n$, a=11.299 (4), b=19.019(1), c=23.850(4) Å, β=98.31(1)°, U=5072(2) $Å^3$, Z=4, Dc= 0.997 g cm^{-3}, μ(Cu Kα)=13.3 cm^{-1}. R=5.7, Rw=7.3%.

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