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Communications

Tetrakis(trialkylsilyl)digermenes. Salient Effects of Trialkylsilyl Substituents on Planarity around the Ge=Ge Bond and Remarkable Thermochromism

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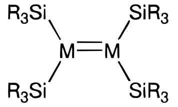
Summary: X-ray structural analyses of tetrakis(trialkylsilyl)digermenes have shown that the trialkylsilyl substituents enforce near-planar geometry around the Ge=Ge bonds, in accordance with theoretical predictions. A remarkable temperature dependence of the UV−vis spectra of tetrakis(triisopropylsilyl)digermene in solution was observed, suggesting an equilibrium between two different structures around the Ge=Ge bond.

One of the most intriguing structural characteristics of the doubly bonded group 14 metal compounds dimetalenes ($R_2M{=}MR_2$; M = Si, Ge, Sn)[1] is deformation from planarity around the double bonds. Theoretical calculations have shown that the parent dimetalenes ($H_2M{=}MH_2$) adopt trans-bent structures but the geometry is significantly affected by the electronic effects of the substituents; more electronegative and π-electron-donating substituents induce a larger bending deformation, while electropositive substituents favor a planar geometry.[2] However, it is difficult to detect the electronic effects of substituents on the geometry, because of the inevitable steric effects exerted by the bulky protecting groups. Although tetrasilyldimetalenes, $(H_3Si)_2M{=}M(SiH_3)_2$ (M = Si, Ge, Sn), have been predicted theoretically to be planar in the optimized geometry,[2a] in a recent study of tetrakis(trialkylsilyl)disilenes **1a**−**c**[3] we have found that the tetrasilyldisilenes show two modes of deformation, bending and twisting, in the solid state, depending on the alkyl substituents of the silyl groups.

We report herein the structure of novel tetrakis(trialkylsilyl)digermenes, **2a**−**c**, synthesized by reductive coupling of the corresponding bis(trialkylsilyl)dichlorogermanes by sodium in toluene at room temperature and isolated as thermally stable but air-sensitive crystals.[4]



1, M = Si; 2, M = Ge.
a, R_3Si = *i*-Pr_2MeSi;
b, R_3Si = *t*-$BuMe_2Si$;
c, R_3Si = *i*-Pr_3Si.

The molecular structures of **2a** and **2c** were deter-

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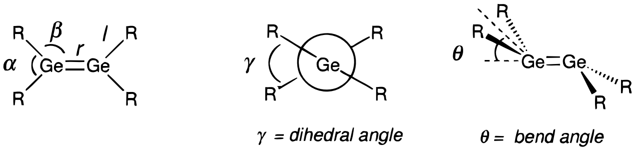
Table 1. Structural Parameters of Tetrasilyldigermenes[a]



digermene	*r*/pm	*l*/pm	α/deg	β/deg	γ/deg	θ/deg
2a (R = *i*-Pr_2MeSi)						
isomer 1	226.8(1)	240.2(2) 239.9(2)	118.2(0)	123.5(0) 117.9(0)	0.0	5.9(0)
isomer 2	226.6(1)	240.8(2) 239.9(2)	117.0(0)	120.9(0) 121.4(0)	0.0	7.1(0)
2c (R = *i*-Pr_3Si)	229.8(1)	242.6(2) 244.2(2)	115.3(0)	125.2(4) 116.5(5)	0.0	16.4(0)

[a] Standard deviations are shown in parentheses.

mined by single-crystal X-ray diffraction.[5] The ORTEP representation of **2a** is shown in Figure 1. Selected structural parameters for **2a** and **2c** are given in Table 1. In a comparison of the structures among three open-chain digermenes whose solid-state structures have been determined,[6,7] $Dep_2Ge{=}GeDep_2$ (**3**; Dep = 2,6-diethylphenyl),[6a] $Dis_2Ge{=}GeDis_2$ (**4**; Dis = $CH[Si(CH_3)_3]_2$),[6b] and (*Z*)−Dip(Mes)Ge═Ge(Mes)Dip (**5**; Dip = 2,6-diisopropylphenyl, Mes = 2,4,6-trimethylphenyl),[6c] the geometries around the Ge═Ge bond of **4** and **5** are very similar to each other with large bending angles (θ = 32° and 36°, respectively), in good accord with the theoretical geometry of the parent digermene, while **3** is rather exceptionally twisted ($\gamma = 10°$) with a small bending angle ($\theta = 12°$). These results suggest that the geometry around the Ge═Ge bond is significantly dependent on the steric effects of substituents but the direction of the deformation is difficult to predict properly. The geometries of **2a** and **2c** are trans-bent with averaged bending angles of 6.5 and 16.4°, respectively; no twisting is observed. The small deformation from planarity found in **2a** should be a good indication of the electronic effects of trialkylsilyl substituents on the geometry around Ge═Ge bonds, as predicted by theoretical calculations. The ability of trialkylsilyl substituents to enforce the near-planar geometry of dimetalenes is actualized in **2a** and **2c**, because it is more difficult to bring digermene into a planar geometry than disilene, as indicated by the bending potential surface of these dimetalenes.[6b] However, the experimental results suggest that tetrakis(trialkylsilyl)digermenes should be slightly bent even if the steric effects of the trialkylsilyl groups are eliminated; though **2a** would be less congested than **1a**, the bending angle for **2a** is even larger than that for **1a** ($\theta = 5.4°$).[3] In conclusion, trialkylsilyl substituents exert significant effects to bring digermene into near-planar geometry.

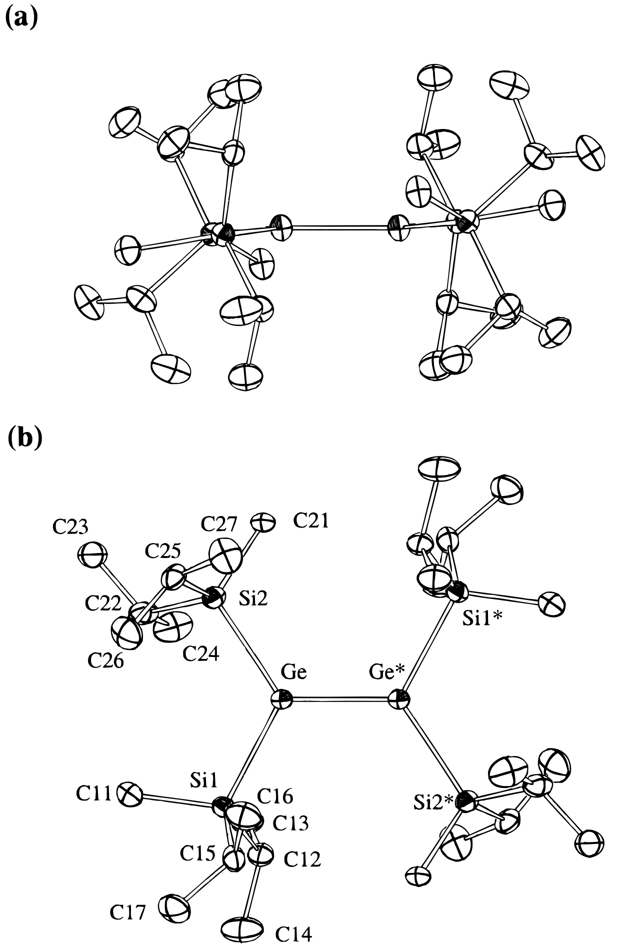


Figure 1. ORTEP drawing of **2a** (isomer 1): (a) side view; (b) top view. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity.

Interestingly, the Ge═Ge bond distances for **2a** and **2c** are even shorter than those for **4** and **5**, whereas the Si═Si bond distances for **1a**−**c** are significantly longer than those for most of the known tetraaryldisilenes.[3]

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(4) Typically, **2a** was synthesized by the following procedure. To a mixture of sodium dispersion (167 mg, 7.26 mmol) and toluene (10 mL) was added dichlorobis(diisopropylmethylsilyl)germane (929 mg, 2.31 mmol) in toluene (8 mL), and the mixture was stirred for 41.5 h. Removal of the inorganic salts and condensation of the filtrate in vacuo gave crystals of **2a**. The other digermenes were prepared by similar procedures. **2a**: yellow crystals; 20.4% yield; mp 140 °C dec; ^1H NMR (300 MHz, C_6D_6) δ 0.40 (s, 12 H), 1.15 (d, ^3J(H,H) = 7.2 Hz, 24 H), 1.21 (d, ^3J(H,H) = 7.2 Hz, 24 H), 1.35−1.47 (m, 8 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ −6.3, 16.5, 19.3, 21.0; ^{29}Si NMR (59.6 MHz, C_6D_6) δ 21.5; UV (3-methylpentane) λ_{max}/nm (ϵ) 361 (2900), 413 (16 100); HRMS calcd for $C_{28}H_{68}{}^{74}Ge_2Si_4$ 664.2822, found 664.2793. **2b**: orange crystals; mp 163 °C dec; 30% yield; ^1H NMR (300 MHz, C_6D_6) δ 0.51 (s, 24 H), 1.08 (s, 36 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 1.1, 19.8, 28.3; ^{29}Si NMR (59.6 MHz, C_6D_6) δ 16.0; UV (3-methylpentane) λ_{max}/nm (ϵ) 266 (5300), 295 (2600), 362 (3100), 421 (7000). **2c**: pale yellow crystals; 21% yield; mp 145 °C dec; ^1H NMR (300 MHz, C_6D_6) δ 1.35 (d, ^3J(H,H) = 7.5 Hz, 72 H), 1.58−1.73 (m, 12 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 17.7, 21.2; ^{29}Si NMR (59.6 MHz, C_6D_6) δ 26.6; MS (14 eV, EI) *m/z* (%) 774 (1.1, M^+), 158 (12.7), 131 (100); UV (3-methylpentane) λ_{max}/nm (ϵ) 472 (2000), 432 (2100), 367 (2200), 332 (1200, sh), 277 (3500).

(5) The data collection and structural analysis for **2a** and **2c** were carried out as follows. The reflection intensities were collected on a Rigaku AFC-5R diffractometer with a rotating anode (45 kV, 200 mA) using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) for **2a** and Cu Kα radiation (λ = 1.518 Å) for **2c**. Crystal data for **2a** (150 K): triclinic, space group $P\bar{1}$, *a* = 11.948(3) Å, *b* = 16.352(4) Å, *c* = 11.168(4) Å, α = 104.73(2)°, β = 117.79(2)°, γ = 81.88(2)°, *V* = 1866.0(10) $Å^3$, *Z* = 2, D_{calcd} = 1.18 g cm^{-3}. A total of 10 071 reflections was measured, and of these 6273 reflections ($F_o > 3\sigma(F_o)$) were used in refinement. *R* = 0.061, R_w = 0.067. Crystal data for **2c** (150 K): monoclinic, space group *C*2/*c*, *a* = 19.221(3) Å, *b* = 14.438(1) Å, *c* = 16.979(4) Å, β = 110.76(1) °, *V* = 4406(1) $Å^3$, *Z* = 4, D_{calcd} = 1.17 g cm^{-3}. A total of 3669 reflections was measured, and of these 2703 reflections ($F_o > 3\sigma(F_o)$) were used in refinement; *R* = 0.051, R_w = 0.057. The molecules of **2a** and **2c** have a crystallographic center of symmetry. All calculations were performed by an ACOS-3900 computer at Tohoku University with the applied library program UNICS III system and RANTAN81 program.

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(7) Very recently, an interesting cyclic digermene, tetrakis(tri-*tert*-butylsilyl)cyclotrigermene, has been prepared and found to have a planar ring structure: Sekiguchi, A.; Yamazaki, H.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1995**, *117*, 8025.

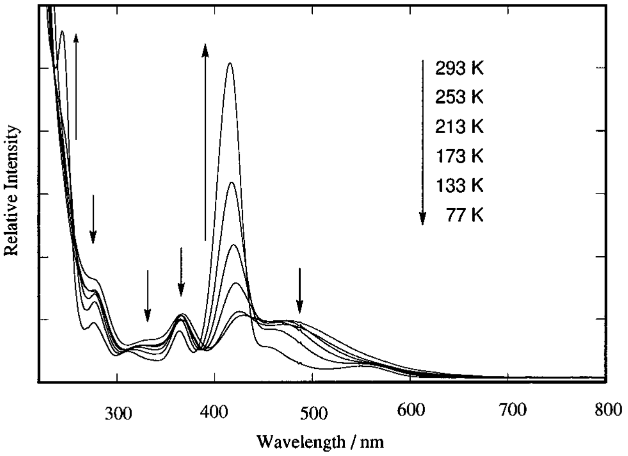

Figure 2. Temperature-dependent UV−vis spectra of **2c** in 3-methylpentane.

Elongation of the Ge═Ge bonds for **4** and **5** would be a consequence of the severe steric congestion around the double bonds.

The UV−vis spectra of **2a**−**c** varied significantly as a function of temperature. Especially, a remarkable thermochromism was observed for **2c**, which was red at room temperature but yellow at 77 K in 3-methylpentane; the temperature-dependent UV spectra are shown in Figure 2. The absorbance of the band maximum at 420 nm increased with decreasing temperature, while the maximum at 492 nm decreased. Two apparent isosbestic points were observed in the temperature-dependent spectra, which may imply that the bent structure in the solid state is not kept in solution but that there exists an equilibrium between two different structures. The enthalpy difference between the two structures was estimated to be 0.7 kcal/mol from the slope of the straight line obtained from a plot of log [absorbance at 513 nm]/[absorbance at 393 nm] vs 1/*T*. The following two mechanisms are suggested as the origin of the remarkable thermochromism: (1) a dissociation−recombination equilibrium between the digermene and the corresponding germylene and (2) an equilibrium between the bent structure and another deformed structure such as a twisted structure. We have found the n(Ge)−4p(Ge) transition band of phenyl(trimethylsilyl)germylene at 610 nm, compared with the band maximum of phenyl(trimethylsilyl)silylene at 660 nm.[8] Since the n(Si)−3p(Si) absorption for disilylsilylene is predicted to appear at 987 nm by recent ab initio MO calculations,[9] we can estimate the maximum for disilylgermylene at longer than 850 nm, which is far longer than the maximum observed for **2c** (492 nm) at higher temperatures. The maximum at 492 nm did not shift in THF, while silylenes and germylenes have been known to blue-shift significantly by complexation with bases.[10] No germylene was trapped during the reaction of **2c** with 2,3-dimethylbutadiene, an efficient germylene trapping reagent.[11] These experimental results preclude the first mechanism and support the second mechanism for the thermochromism. A similar mechanism has been proposed for bianthrone, while the enthalpy difference for **2c** is much smaller than that for bianthrone (3.0 kcal/mol).[12] The thermochromic behavior of **2c** is quite different from the temperature dependence of the spectrum of **1c**; although at higher temperatures, **1c** shows a UV spectral pattern similar to that of **2c**, the major spectral feature for **1c** is retained at low temperatures.

Further works are in progress.

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Supporting Information Available: A plot of log [absorbance at 513 nm]/[absorbance at 393 nm] vs 1/*T* and tables of crystallographic data, including all bond lengths, bond angles, and thermal and positional parameters, for **2a** and **2c** (27 pages). Ordering information is given on any current masthead page.

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[11] No adducts of the digermene or the germylene with the butadiene were observed. On the other hand, the reaction of **2b** with 2,3-dimethyl-1,3-butadiene in benzene-d_6 at room temperature gave the corresponding Diels−Alder adduct, 1,1,2,2-tetrakis(*tert*-butyldimethylsilyl)-3,4-dimethyl-1,2-digerma-4-cyclohexene, in quantitative yield: colorless oil; ^{1}H (C_6D_6, 300 MHz) δ 0.30 (s, 12 H), 0.31 (s, 12 H), 1.01 (s, 36 H), 1.75 (s, 6 H), 2.12 (s, 4 H); ^{13}C NMR (C_6D_6, 75.5 MHz) δ −0.31, 0.23, 20.4, 21.0, 26.3, 28.6, 127.9; ^{29}Si NMR (C_6D_6, 59.6 MHz) δ 6.6; MS (14 eV, EI) *m/z* 606 (14.8, $M^+ - 82$), 573 (7.2), 304 (19.1), 84 (100).

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