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Crystal and Molecular Structures of Octaisopropylcyclotetragermane, $[(i\text{-Pr})_2\text{Ge}]_4$

Kunio MOCHIDA,* Yuko KAWAJIRI, and Midori GOTO*,†
Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Tokyo 171
† National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305

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Synopsis. The crystal and molecular structures of octaisopropylcyclotetragermane, $[(i\text{-Pr})_2\text{Ge}]_4$ have been determined by X-ray diffraction at room temperature. The triclinic structure was refined by the full matrix least-squares method to a final $R=0.049$ for 5091 reflections. The Ge–Ge distances are in the range 2.47—2.48 Å. The Ge_4 ring is nonplanar with a dihedral angle of ca. 17°. The Ge–Ge–C and C–Ge–C bond angles appear to bend away due to the steric repulsion of the isopropyl group.

The chemistry of the cyclic polygermanes has been a subject of interest in recent years because of their unique physical and chemical properties arising from electronic delocalization and bond strength in the Ge–Ge σ-bond framework. However, there have been few reports on the crystal structures of these cyclic polygermanes.[1—9] Most recently, we reported on the photochemistry of octaisopropylcyclotetragermane, $[(i\text{-Pr})_2\text{Ge}]_4$, which involved both ring contraction to hexaisopropylcyclotrigermane, $[(i\text{-Pr})_2\text{Ge}]_3$, with extrusion of diisopropylgermylene, $(i\text{-Pr})_2\text{Ge:}$, and conversion to tetraisopropyldigermene, $(i\text{-Pr})_2\text{Ge=Ge}(i\text{-Pr})_2$.[10] A good relationship between the reactivity and the structure was suggested for cyclic polysilanes and polygermanes.[11] Under these circumstances, we have undertaken the first structural studies of alkyl-substituted cyclic tetragermanes, $[(i\text{-Pr})_2\text{Ge}]_4$, in order to clarify the photodecomposition mechanism of $[(i\text{-Pr})_2\text{Ge}]_4$.

Experimental

The title compound, $[(i\text{-Pr})_2\text{Ge}]_4$ was prepared by the reaction of diisopropyldichlorogermane and Mg–MgBr_2 in THF as previously described.[12] A 0.27×0.1×0.07 mm crystal cut from a larger one was used. The crystal data and diffraction intensities were measured on a four-circle diffractometer (Enraf–Nonius CAD-4) using Cu $K\alpha$ ($\lambda=1.5418$ Å) radiation with a graphite monochrometer.

Crystal data: $\text{C}_{24}\text{H}_{56}\text{Ge}_4$, $M_r=635.1$, triclinic, $P\bar{1}$, $a=10.511(2)$, $b=10.784(2)$, $c=15.534(3)$ Å, $\alpha=82.64(1)$, $\beta=74.94(1)$, $\gamma=68.92(1)$°, $V=1585.3(5)$ Å^3, $Z=2$, $\rho=1.334$, λ (Cu $K\alpha$)=1.5418 Å, $T=298$ K, $R=0.049$ for 5091 observed $[|F_o|\geqq 3\sigma|F_o|]$ reflections.

The unit-cell parameters were refined by the least-squares method using the 2θ values of 5091 reflections with $25°<2\theta<35°$. Data were collected for $4°<2\theta<130°$, with a θ/ω-scan, $\omega=(1.2+0.15\tan\theta)°$. A total of 5389 reflections were collected and 5091 ($|F_o|\geqq 3\sigma|F_o|$) reflections were used. Corrections for Lorenz, polarization, an empirical absorption correction using ψ scans (transmission factors 0.8544/0.9995, $\mu=49.02$ cm^{-1}), and linear decay correction were applied. (The total loss in intesity was 30%).

Table 1. Fractional Atomic Coordinates and Thermal Parameters for Non-Hydrogen Atoms

Atom	x	y	z	B_{eq} (Å^2)
Ge(1)	0.88007(5)	0.59169(4)	0.26743(3)	3.62(1)
Ge(2)	0.64529(5)	0.63104(4)	0.24177(3)	3.87(2)
Ge(3)	0.59504(5)	0.87374(4)	0.24278(3)	3.95(2)
Ge(4)	0.84493(5)	0.83070(4)	0.23417(3)	3.87(2)
C(1)	0.8987(6)	0.5407(5)	0.3935(3)	5.6(2)
C(2)	0.9074(11)	0.3963(7)	0.4194(5)	9.7(4)
C(3)	0.7836(7)	0.6335(7)	0.4604(4)	7.2(2)
C(4)	1.0465(5)	0.4699(5)	0.1876(4)	5.5(2)
C(5)	1.1824(6)	0.4578(7)	0.2135(6)	8.2(3)
C(6)	1.0370(8)	0.3347(7)	0.1809(6)	9.3(3)
C(7)	0.5197(5)	0.5571(5)	0.3368(4)	6.5(2)
C(8)	0.3747(8)	0.6100(10)	0.3306(8)	11.6(4)
C(9)	0.5680(10)	0.4094(8)	0.3399(10)	15.0(6)
C(10)	0.6542(8)	0.5737(8)	0.1230(6)	8.8(3)
C(11)	0.5188(12)	0.6236(12)	0.0932(8)	14.0(6)
C(13)	0.4784(8)	0.9540(7)	0.3585(5)	8.5(3)
C(14)	0.4622(11)	1.0993(8)	0.3608(7)	12.2(4)
C(16)	0.5205(6)	0.9790(5)	0.1392(4)	6.7(2)
C(17)	0.5563(10)	1.1068(7)	0.1173(6)	9.8(4)
C(18)	0.3661(8)	1.0040(9)	0.1509(7)	11.1(4)
C(19)	0.9496(5)	0.8723(5)	0.1137(4)	6.1(2)
C(20)	0.9188(7)	0.8199(7)	0.0382(4)	7.5(2)
C(21)	1.1067(7)	0.8275(9)	0.1062(6)	9.3(3)
C(22)	0.8730(6)	0.9295(5)	0.3257(4)	6.4(2)
C(23)	1.0087(8)	0.8567(7)	0.3566(6)	8.7(3)
C(24)	0.8690(9)	1.0687(6)	0.2890(7)	9.9(4)
C(12A)	0.713(3)	0.426(3)	0.107(2)	13.9(7)[a] 0.5[b]
C(12B)	0.752(3)	0.604(3)	0.053(2)	11.9(8)[a] 0.5[b]
C(15A)	0.342(2)	0.934(2)	0.393(1)	11.6(4)[a] 0.7[b]
C(15B)	0.471(7)	0.877(7)	0.431(5)	16.8(21)[a] 0.3[b]

$$B_{\text{eq}} = 4\left(a^2B_{11} + b^2B_{22} + c^2B_{33} + 2abB_{12}\cos\gamma + 2bcB_{23}\cos\alpha + 2caB_{13}\cos\beta\right)/3.$$

a) Isotropic thermal parameter. b) Site occupancy factor.

The structure was solved by direct methods using the program system MULTAN 78.[13] In the course of refinement, 10 hydrogen atom positions were derived from the D-Fourier synthesis; the remainder were placed at ideal positions. Full matrix least squares refinement of F was done with anisotropic temperature factors for non-H atoms except for the C_{12} and C_{15} atoms. These atoms were refined with isotropic factors, which were disordered and the site occupancy factors for the two carbon atoms were chosen from peak heights on a Fourier map and these factors were not refined. Hydrogen atoms were included in the least-

Table 2. Bond Lengths (Å) and Angles (°)

Bond lengths			
Ge(1)–Ge(2)	2.4786(9)	Ge(1)–Ge(4)	2.4739(8)
Ge(2)–Ge(3)	2.4781(8)	Ge(3)–Ge(4)	2.4675(9)
Ge(1)–C(1)	2.005(5)	Ge(1)–C(4)	1.990(4)
Ge(2)–C(7)	2.001(6)	Ge(2)–C(10)	1.988(10)
Ge(3)–C(13)	1.994(7)	Ge(3)–C(16)	2.009(6)
Ge(4)–C(19)	1.996(6)	Ge(4)–C(22)	2.019(9)
Bond angles			
Ge(2)–Ge(1)–Ge(4)	89.28(2)	Ge(1)–Ge(2)–Ge(3)	89.22(3)
Ge(2)–Ge(3)–Ge(4)	89.44(2)	Ge(1)–Ge(4)–Ge(3)	89.57(3)
Ge(2)–Ge(1)–C(1)	115.3(2)	Ge(2)–Ge(1)–C(4)	118.2(2)
Ge(4)–Ge(1)–C(1)	111.0(2)	Ge(4)–Ge(1)–C(4)	114.4(2)
Ge(1)–Ge(2)–C(7)	115.7(2)	Ge(1)–Ge(2)–C(10)	112.8(3)
Ge(3)–Ge(2)–C(7)	116.0(2)	Ge(3)–Ge(2)–C(10)	112.1(3)
Ge(2)–Ge(3)–C(13)	113.6(2)	Ge(2)–Ge(3)–C(16)	114.8(2)
Ge(4)–Ge(3)–C(13)	110.1(3)	Ge(4)–Ge(3)–C(16)	115.8(2)
Ge(1)–Ge(4)–C(19)	114.7(2)	Ge(1)–Ge(4)–C(22)	112.5(2)
Ge(3)–Ge(4)–C(19)	113.5(2)	Ge(3)–Ge(4)–C(22)	112.5(2)
C(1)–Ge(1)–C(4)	107.8(2)	C(7)–Ge(2)–C(10)	109.8(4)
C(13)–Ge(3)–C(16)	111.4(3)	C(19)–Ge(4)–C(22)	108.8(3)

squares calculation but were not refined. The final result gave R=0.049 (R_w=0.072, w=1/(0.01161$|F_o|^2$−0.3658$|F_o|$+3.2898)); S=2.2243; $((\Delta/\sigma)_{\max}$=1.525 (y of C_{12B}). The final difference Fourier map showed a positive peak of 0.8 e Å^{-3} near the C_{12} atoms and 0.5 e Å^{-3} near the Ge atoms. Calculations were carried out on a FACOM M-780 with UNICS III.[14)]

Results and Discussion

The positional parameters for non-H atoms, and interatomic distances and angles are given in Tables 1 and 2, respectively. An ORTEP[15)] view is shown in Fig. 1. The Ge–Ge distance of $[(i\text{-Pr})_2Ge]_4$ is in the range 2.47—2.48 Å. It is of interest to compare the Ge–Ge bond lengths in $[(i\text{-Pr})_2Ge]_4$ with those of other linear and cyclic polygermanes that have been reported. The Ge–Ge bond lengths of $[(i\text{-Pr})_2Ge]_4$ are slightly longer than those of Ph_6Ge_2 (2.437 Å)[16)] and H_6Ge_2 (2.41 Å)[17)] due to the steric hindrance of the isopropyl groups. The Ge–Ge bond lengths of $[(i\text{-Pr})_2Ge]_4$ are the longest among the reported cyclotetragermanes, $[PhClGe]_4$ (2.455—2.471 Å)[8)] and $[Ph_2Ge]_4$ (2.465 Å).[3)] To compare some pertinent structural data for a series of cyclopolygermanes, data from $[R_2Ge]_n$, where R are alkyls and/or aryls; n=3—6, have been accumulated. The Ge–Ge bond length increases in the order: $Ge_6 < Ge_5 < Ge_4 < Ge_3$ probably due to the increasing repulsion between the substituents on the germanium atoms and ring strain.[1—9)]

The most intriguing structural feature of $[(i\text{-Pr})_2Ge]_4$ is the puckered configuration of the Ge_4 ring. The dihedral angle between the wings of the folded ring is 17.5°, which lies between $[PhClGe]_4$ (dihedral angle of 21°) and $[Ph_2Ge]_4$ (angle of pucker 3.9°). It is also of interest to compare the Si_4 ring of $[(i\text{-Pr})_2Si]_4$ with quite large dihedral angles of 37.1°[18)] with the present results. The Ge–Ge–Ge bond angles comprising the Ge_4 ring are in the range of 89.2—89.6°, which is nearly 90°; rather unexpected in view of the large puckering. These bond angles can be rationalized by the long Ge–Ge bond length. The Ge–Ge–C bond angles (112—118°) in the ring system of $[(i\text{-Pr})_2Ge]_4$ are expanded due to the steric repulsion. The axial and equatorial carbon atoms attached to the ring Ge atoms also appear to bend away from the normal configuration. The planes of the Ge–C bond pair at each Ge atom in the tops of the wings are nearly perpendicular to the corresponding planes.

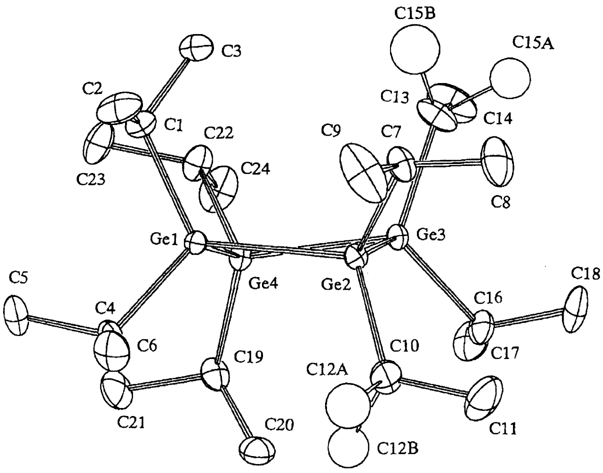

Fig. 1. A perspective view of the title compound. (The atoms are drawn with ellipsoids of thermal vibration of 20% probability. C_{12A}, C_{12B}, C_{15A}, and C_{15B} are represented with isotropic ellipsoids (spheres).)

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19) Tables of anisotropic thermal parameters, positional parameters of the hydrogen atoms, and observed and calculated structure factors are deposited as Document No. 66032 at the Office of the Editor of Bull. Chem. Soc. Jpn.