CRYSTAL STRUCTURE OF 2,2,4,4,6,6-HEXAPHENYL-1,3,5-TRITHIA-2,4,6-TRIGERMACYCLOHEXANE $(Ph_2GeS)_3$

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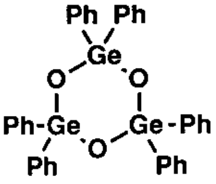
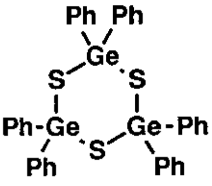
Abstract---The X-ray crystallographic analysis of 2,2,4,4,6,6-hexaphenyl-1,3,5-trithia-2,4,6-trigermacyclohexane(**2**) indicates that the six membered ring $(Ph_2GeS)_3$ is a twist boat which contrasts to a nearly flat structure observed for the $(Ph_2GeO)_3$ ring.

As a part of our extensive investigation on the synthesis and structure of germanium-containing large rings(germamacrocycles)[1] as the key compounds to a new type of host-guest chemistry where germamacrocycles are the host, we attempted to prepare germamacrocycles containing oxygen and sulfur as the ring components. The reaction between $Ph_2Ge(SNa)_2$ and $(ClCH_2CH_2)_2O$ in benzene failed to afford the desired macrocycles and gave only a small amount of colorless prisms which was identified as 2,2,4,4,6,6-hexaphenyl-1,3,5-trithia-2,4,6-trigermacyclohexane $(Ph_2GeS)_3$(**2**). The compound (**2**) was previously prepared by the reaction of $Ph_2Ge(SNa)_2$ and Ph_2GeBr_2.[2]



1



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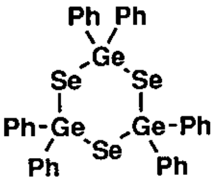

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The conformation of six-membered ring of **2** is interesting in relation to those for the related compounds with the general structure $(R_2XY)_3$ where R = Me or Ph, X = Ge or Sn and Y = O or S. Thus, the six-membered ring of 2,2,4,4,6,6-hexaphenyl-1,3,5-triselena-2,4,6-trigermacyclohexane $(Ph_2GeSe)_3$ (**3**) was reported to have a twist boat.[3] On the other hand, Dräger *et al.*[4] reported that the oxygen analogue, 2,2,4,4,6,6-hexaphenyl-1,3,5-trioxa-2,4,6-trigermacyclohexane(**1**) assumes a nearly planar structure as was revealed by X-ray crystallographic study. The authors state that the observed structure is regarded as a possible intermediate for the racemization of twist-boat enantiomers as well as for the chair-chair interconversion.

We expected that the determination of the conformation of six-membered ring of **2** will make it possible to draw a general feature for the structure of type $(R_2XY)_3$ compounds and attempted an X-ray crystallographic analysis of **2**. The ORTEP drawing of **2** is given in Figure 1, which confirms the twist-boat structure. For the sake of reference a part of ORTEP drawing of **1** is also shown.

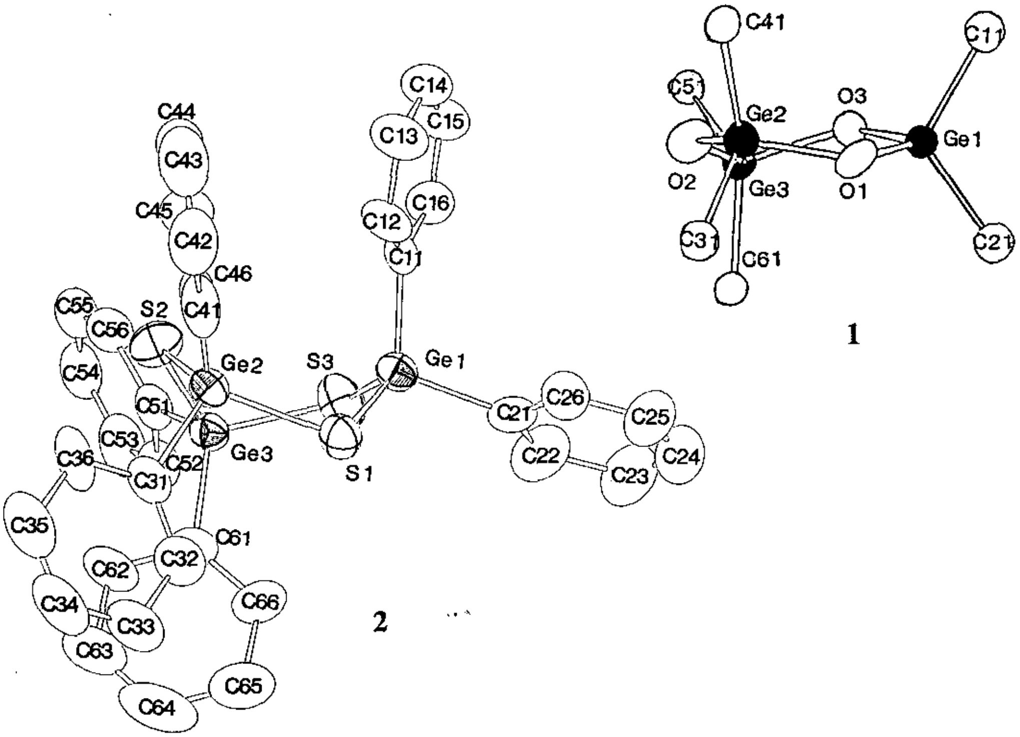

Figure1 ORTEP Drawings of 2 and 1.

Table 1 Selected Atomic Parameters for $(Ph_2GeS)_3$ (2)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ge(1)	0.11195(9)	0.11656(5)	0.31971(8)	C(34)	0.366(1)	0.1205(7)	-0.1906(9)
Ge(2)	0.32029(9)	0.15398(5)	0.15245(7)	C(35)	0.449(1)	0.1500(7)	-0.131(1)
Ge(3)	0.30949(9)	0.00521(5)	0.25767(7)	C(36)	0.435(1)	0.1609(6)	-0.0281(9)
S(1)	0.1351(2)	0.1479(1)	0.1645(1)	C(41)	0.3854(8)	0.2360(5)	0.1857(8)
S(2)	0.4177(2)	0.0982(1)	0.2542(2)	C(42)	0.3676(10)	0.2842(5)	0.1151(10)
S(3)	0.1688(2)	0.0203(1)	0.3535(2)	C(43)	0.410(1)	0.3446(6)	0.132(1)
C(11)	0.1748(7)	0.1768(4)	0.4168(7)	C(44)	0.470(1)	0.3563(7)	0.223(2)
C(12)	0.1737(9)	0.1616(5)	0.5205(8)	C(45)	0.491(1)	0.3108(8)	0.296(1)
C(13)	0.206(1)	0.2076(6)	0.5917(8)	C(46)	0.447(1)	0.2478(6)	0.2766(10)
C(14)	0.2382(10)	0.2666(6)	0.5626(9)	C(51)	0.3978(8)	0.3978(8)	0.3318(6)
C(15)	0.237(1)	0.2823(5)	0.4594(9)	C(52)	0.3628(9)	-0;1216(5)	0.3236(8)
C(16)	0.2059(9)	0.2365(5)	0.3874(8)	C(53)	0.423(1)	-0;.1680(5)	0.3826(9)
C(21)	-0.0506(9)	0.1136(6)	0.3296(7)	C(54)	0.5164(10)	-0.1520(6)	0.4440(8)
C(22)	-0.103(1)	0.0579(7)	0.3534(10)	C(55)	0.5511(10)	-0.0894(6)	0.4503(8)
C(23)	-0.223(1)	0.0612(10)	0.369(1)	C(56)	0.4958(9)	-0.0421(5)	0.3929(8)
C(24)	-0.277(1)	0.118(1)	0.362(1)	C(61)	0.2577(8)	-0.0229(4)	0.1234(6)
C(25)	-0.224(1)	0.1711(9)	0.336(1)	C(62)	0.3438(10)	-0.0330(5)	0.0567(7)
C(26)	-0.109(1)	0.1709(7)	0.3203(9)	C(63)	0.316(1)	-0.0538(5)	-0.0411(9)
C(31)	0.3360(g)	0.1384(5)	0.0102(7)	C(64)	0.205(2)	-0.0647(6)	-0.0707(10)
C(32)	0.2518(10)	0.1080(5)	-0.0498(8)	C(65)	0.118(1)	-0.0544(5)	-0.0050(10)
C(33)	0.266(1)	0.0979(6)	-0.1528(8)	C(66)	0.1470(9)	-0.0324(5)	0.0952(8)

Table 2 Selected Bond Distances and Angles for $(Ph_2GeS)_3$ (2)

Distances(Å)		S(1)-Ge(1)-C(11)	111.2(3)
Ge(1)-S(1)	2.214(3)	S(3)-Ge(1)-C(11)	112.1(3)
Ge(2)-S(2)	2.206(3)	C(11)-Ge(1)-C(21)	108.4(5)
Ge(3)-S(3)	2.212(4)	S(1)-Ge(2)-C(31)	103.1(3)
Ge(1)-C(11)	1.93(1)	S(2)-Ge(2)-C(31)	114.3(3)
Ge(2)-C(31)	1.93(1)	C(31)-Ge(2)-C(41)	108.0(5)
Ge(3)-C(51)	1.95(1)	S(2)-Ge(3)-C(51)	105.9(3)
Ge(2)-S(1)	2.238(3)	S(3)-Ge(3)-C(51)	102.4(3)
Ge(3)-S(2)	2.203(3)	C(51)-Ge(3)-C(61)	112.4(4)
Ge(1)-S(3)	2.187(3)	S(1)-Ge(2)-S(2)	113.7(1)
Ge(1)-C(21)	1.96(1)	S(2)-Ge(3)-S(3)	111.7(1)
Ge(2)-C(41)	1.94(1)	S(3)-Ge(1)-S(1)	114.5(1)
Ge(3)-C(61)	1.95(1)	S(1)-Ge(1-C(21)	105.4(3)
		S(3)-Ge(1)-C(21)	104.6(4)
Bond Angles(°)		S(1)-Ge(2)-C(41)	114.8(3)
Ge(1)-S(1)-Ge(2)	106.1(1)	S(2)-Ge(2)-C(41)	103.3(3)
Ge(2)-S(2)-Ge(3)	103.3(1)	S(2)-Ge(3)-C(61)	112.1(3)
Ge(3)-S(3)-Ge(1)	104.7(2)	S(3)-Ge(3)-C(61)	111.9(3)

Torsion Angles(°)[a]		
S(3)Ge(1)-S(1)Ge(2)	-67.1(2)	(-28.5)
Ge(1)S(1)-Ge(2)S(2)	27.7(2)	(3.3)
S(1)Ge(2)-S(2)Ge(3)	35.3(2)	(22.8)
Ge(2)S(2)-Ge(3)S(3)	-76.7(2)	(-16.3)
S(2)Ge(3)-S(3)Ge(1)	41.2(2)	(-18.4)
Ge(3)S(3)-Ge(1)S(1)	30.7(2)	(37.4)

a) Values for the oxygen analogue **1** are given in the parenthesis

Selected atomic coordinates and geometrical parameters are given in Tables 1 and 2. All the Ge-S bond lengths(2.187-2.214Å) and Ge-C bond lengths(1.93-1.96Å) are normal in that the values are within the range of previously reported values for relevant compounds. The S-Ge-S angles (111.7-114.5°) for **2** are slightly larger than those of **1**(107.0-108.1°) while the Ge-S-Ge angles are 103.3-106.1° for **2**, which is in a sharp contrast with the Ge-O-Ge angles (127.7-130.3°) for **1**. Since compounds of the type $(Me_2SnX)_3$ and $(Ph_2SnX)_3$ where X = S or Se has a twist-boat, the nearly flat six-membered ring for **1** is most likely an exceptional case. We are continuing study to elucidate the principle which governs the shape of six-membered rings $(R_2XY)_3$.

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EXPERIMENTAL

Compound (**2**) for X-ray crystallographic analysis was prepared according to the literature[2] and was twice recrystallized from acetonitirle, m p 172°C. Infrared and C-13 nmr spectra were determined by JASCO-A-202 and JEOL α500 spectrometer, respectively. Ir(KBr; cm^{-1}: (s) strong, (m) medium, (w) weak)1082(s), 990(m), 800(m), 725(s), 690(s), 450(s); C-13 nmr(δ from TMS); 136.75(C_{11}), 133.83($C_{12,16}$), 127.81($C_{13,15}$), 129.75(C_{14}). *Crystal Data*: $C_{36}H_{30}S_3Ge_3$, colorless crystals, monoclinic, space group $P2_1/n$ (No. 14), $a = 11.974(2)$, $b = 21.181(2)$, $c = 13.395(2)$ Å, $V = 3381(1)Å^3$, $Z = 4$, $D_x = 1.526$ g cm^{-3}, $D_m = 1.55$ g cm^{-3}, $F(000) = 1560$, $T = 293K$, crystal dimensions 0.20 x 0.20 x 0.35 mm^3, 4259 reflections measured, range ($4 < 2\theta < 55°$), 1628 observed with $I > 3\sigma(I)$, $\mu = 2.81$ mm^{-1}. Final $R = 0.077$ and $R_W = 0.085$, $w = [\sigma(F_o)^2 + 8.15x10^{-4}F_o^2]^{-1}$. X-Ray experimental procedures: Mo-Kα radiation (λ= 0.71073Å). A Rigaku AFC5 diffractometer equipped with a graphite monochrometer was used to collect the data. The structure was solved by direct methods(SHELXS-86) and refined by full-matrix least squares. The non-H atoms were refined with anisotropic displacement parameters. All of the H atoms were initially calculated in idealized positions but were refined under C-H bond length constraint during the final refinement cycles.

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