

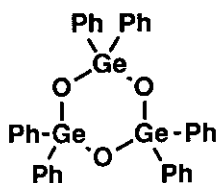
CRYSTAL STRUCTURE OF 2,2,4,4,6,6-HEXAPHENYL-1,3,5-TRITHIA-2,4,6-TRIGERMACYCLOHEXANE (Ph_2GeS)₃

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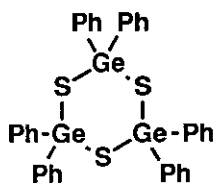
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Abstract---The X-ray crystallographic analysis of 2,2,4,4,6,6-hexaphenyl-1,3,5-trithia-2,4,6-trigermacyclohexane(**2**) indicates that the six membered ring (Ph_2GeS)₃ is a twist boat which contrasts to a nearly flat structure observed for the (Ph_2GeO)₃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

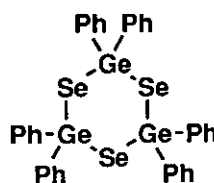
As a part of our extensive investigation on the synthesis and structure of germanium-containing large rings(germamacrocycles)¹ as the key compounds to a new type of host-guest chemistry where germamacrocycles are the host, we attempted to prepare germamacrocycles containing oxygen and sulfur as the ring components. The reaction between $\text{Ph}_2\text{Ge}(\text{SNa})_2$ and $(\text{ClCH}_2\text{CH}_2)_2\text{O}$ 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 $\text{Ph}_2\text{Ge}(\text{SNa})_2$ and Ph_2GeBr_2 .²



1



2



3

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 $R = \text{Me}$ or Ph , $X = \text{Ge}$ or Sn and $Y = \text{O}$ or S . Thus, the six-membered ring of 2,2,4,4,6,6-hexaphenyl-1,3,5-triseleno-2,4,6-trigermacyclohexane $(\text{Ph}_2\text{GeSe})_3$ (**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.

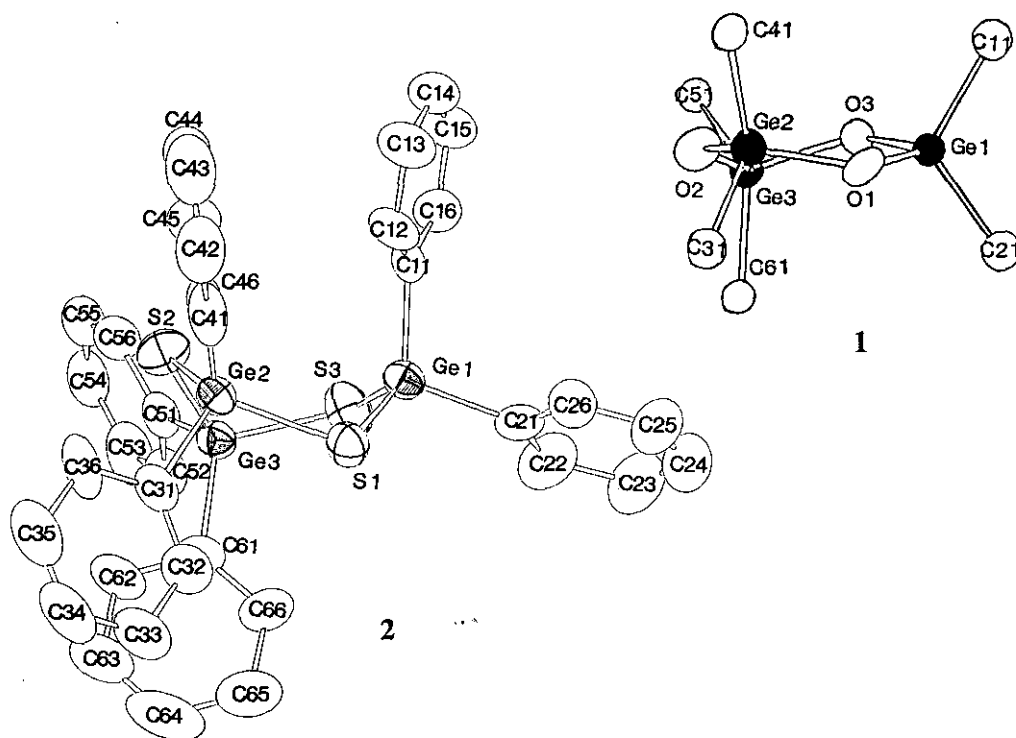


Figure1 ORTEP Drawings of **2** and **1**.

Table 1 Selected Atomic Parameters for (Ph₂GeS)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 (Ph₂GeS)₃ (2)

Distances(Å)			
Ge(1)-S(1)	2.214(3)	S(1)-Ge(1)-C(11)	111.2(3)
Ge(2)-S(2)	2.206(3)	S(3)-Ge(1)-C(11)	112.1(3)
Ge(3)-S(3)	2.212(4)	C(11)-Ge(1)-C(21)	108.4(5)
Ge(1)-C(11)	1.93(1)	S(1)-Ge(2)-C(31)	103.1(3)
Ge(2)-C(31)	1.93(1)	S(2)-Ge(2)-C(31)	114.3(3)
Ge(3)-C(51)	1.95(1)	C(31)-Ge(2)-C(41)	108.0(5)
Ge(2)-S(1)	2.238(3)	S(2)-Ge(3)-C(51)	105.9(3)
Ge(3)-S(2)	2.203(3)	S(3)-Ge(3)-C(51)	102.4(3)
Ge(1)-S(3)	2.187(3)	C(51)-Ge(3)-C(61)	112.4(4)
Ge(1)-C(21)	1.96(1)	S(1)-Ge(2)-S(2)	113.7(1)
Ge(2)-C(41)	1.94(1)	S(2)-Ge(3)-S(3)	111.7(1)
Ge(3)-C(61)	1.95(1)	S(3)-Ge(1)-S(1)	114.5(1)
Bond Angles(°)		S(1)-Ge(1)-C(21)	105.4(3)
Ge(1)-S(1)-Ge(2)	106.1(1)	S(3)-Ge(1)-C(21)	104.6(4)
Ge(2)-S(2)-Ge(3)	103.3(1)	S(1)-Ge(2)-C(41)	114.8(3)
Ge(3)-S(3)-Ge(1)	104.7(2)	S(2)-Ge(2)-C(41)	103.3(3)
Torsion Angles(°) ^{a)}		S(2)-Ge(3)-C(61)	112.1(3)
S(3)Ge(1)-S(1)Ge(2)	-67.1(2)	S(3)-Ge(3)-C(61)	111.9(3)
Ge(1)S(1)-Ge(2)S(2)	27.7(2)		
S(1)Ge(2)-S(2)Ge(3)	35.3(2)		
Ge(2)S(2)-Ge(3)S(3)	-76.7(2)		
S(2)Ge(3)-S(3)Ge(1)	41.2(2)		
Ge(3)S(3)-Ge(1)S(1)	30.7(2)		

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 (2.187-2.214 Å) and Ge-C bond lengths (1.93-1.96 Å) 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 $(\text{Me}_2\text{SnX})_3$ and $(\text{Ph}_2\text{SnX})_3$ where $\text{X} = \text{S}$ 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 $(\text{R}_2\text{XY})_3$.

ACKNOWLEDGMENT

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EXPERIMENTAL

Compound (**2**) for X-ray crystallographic analysis was prepared according to the literature² and was twice recrystallized from acetonitrile, m.p. 172°C. Infrared and C-13 nmr spectra were determined by JASCO-A-202 and JEOL α 500 spectrometer, respectively. $\nu(\text{KBr}; \text{cm}^{-1})$: (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(C₁₁), 133.83(C_{12,16}), 127.81(C_{13,15}), 129.75(C₁₄). *Crystal Data*: $\text{C}_{36}\text{H}_{30}\text{S}_3\text{Ge}_3$, colorless crystals, monoclinic, space group $P2_1/n$ (No. 14), $a = 11.974(2)$, $b = 21.181(2)$, $c = 13.395(2)$ Å, $V = 3381(1)$ Å³, $Z = 4$, $D_x = 1.526 \text{ g cm}^{-3}$, $D_m = 1.55 \text{ g cm}^{-3}$, $F(000) = 1560$, $T = 293\text{K}$, crystal dimensions $0.20 \times 0.20 \times 0.35 \text{ mm}^3$, 4259 reflections measured, range $(4 < 2\theta < 55^\circ)$, 1628 observed with $I > 3\sigma(I)$, $\mu = 2.81 \text{ mm}^{-1}$. Final $R = 0.077$ and $R_w = 0.085$, $w = [\sigma(F_o)^2 + 8.15 \times 10^{-4} F_o^2]^{-1}$. X-Ray experimental procedures: Mo-K α radiation ($\lambda = 0.71073$ Å). A Rigaku AFC5 diffractometer equipped with a graphite monochromator 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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