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Preliminary communication

1,1,2,2,9,9,10,10-Octamethyl-1,2,9,10-tetragerma[2.2]paracyclophane: the first [2.2]paracyclophane bridged by two Ge–Ge bonds

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Abstract

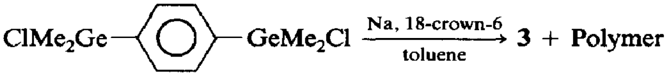
Tetragerma[2.2]paracyclophane, the first [2.2]paracyclophane bridged by two Ge–Ge bonds, has been prepared by the reductive coupling reaction of 1,4-bis(chlorodimethylgermyl)benzene with sodium. The molecular structure, determined by X-ray crystallography, and spectroscopic properties of the new cyclophane are described. Interesting comparisons of the structural features with those of tetrasila[2.2]paracyclophane and [2.2]paracyclophane are made.

Syntheses, structures, and properties of cyclophanes have been extensively studied [1]. [2.2]Paracyclophanes are of particular interest, in order to study the physical and chemical properties based on through-space and through-bond interactions between the two separated benzene rings.

Recently we have reported tetrasila[2.2]paracyclophane (**1**) and hexasila[2.2.2]-(1,3,5)cyclophane (**2**), unique cyclophanes bridged by two and three Si–Si bonds [2,3]. The UV and PE spectra of these compounds revealed interesting electronic properties resulting from the through-bond interaction between the high lying Si–Si σ bond and the benzene π-system owing to their highly rigid structures [4]. Thus electronic structures of **1** and **2** are very much perturbed from the carbon analog. Consequently, preparation and elucidation of the properties of 1,1,2,2,9,9,10,10-octamethyl-1,2,9,10-tetragerma[2.2]paracyclophane (**3**), a higher member of the series, are extremely interesting. Preparation of **3** is also a synthetic challenge in germanium chemistry.

As a part of studies on the chemistry of cyclophanes bridged by Group IVb elements, we here report the first successful synthesis of the cyclophane **3** bridged by two Ge_2Me_4 units as well as its molecular structure determined by X-ray crystallography.

The cyclophane **3** was prepared in 2.6% yield as colorless crystals by the direct condensation of 1,4-bis(chlorodimethylgermyl)benzene with molten sodium in refluxing toluene in the presence of 18-crown-6. Thus a solution of 1,4-bis(chlorodimethylgermyl)benzene (1.44 g, 4.09 mmol) in toluene (50 ml) was added dropwise to molten sodium (0.25 g, 10.9 mmol) in boiling toluene (50 ml) in the presence of 18-crown-6 (1.11 g, 4.20 mmol). After refluxing for 2 h, the resulting salt was filtered. Silica gel chromatography with hexane/benzene followed by recrystallization from benzene gave 30 mg (2.6%) of **3** as colorless crystals *.



The presence of 18-crown-6 is essential; otherwise the reaction resulted in the formation of intractable polymers. Optimization of the yield may be possible and is currently under investigation.

The cyclophane **3** is quite stable and does not change upon heating to 300 °C. Furthermore, the Ge–Ge bonds are inert to trimethylamine *N*-oxide and sulfur in refluxing benzene, contrary to the case of **1** and **2**. The molecular structure of **3**, determined by X-ray crystallography, is shown in Fig. 1 **.

The molecule is highly symmetric with a center of symmetry. The length of the bridging Ge–Ge bonds (2.438 Å) is almost the same as that of normal Ge–Ge bonds [5 ***]. The Ge–Car bond lengths (av. 1.944 Å) are also normal. The bridged aromatic carbons bend inward from the planes of the other aromatic four carbons by 3.1° (C(1), C(1′)) and 5.9° (C(4), C(4′)). In addition, the germanium atoms at the bridges deviate from benzene rings by 10.4° (Ge(1), Ge(1′)) and 8.8° (Ge(2), Ge(2′)). As a result, these two benzene rings are distorted into boat conformations. The two aromatic rings completely eclipse each other, with interplanar space distances of 3.382 Å (C(1)–C(4′)) and 3.496 Å (av. of C(2)–C(5′) and C(3)–C(6′)). The bridging bond lengths, interplanar space distances, and geometrical parameters (α, β, and γ) of **1**, **3**, and [2.2]paracyclophane (**4**) [6] are summarized in Table 1.

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* Compound 3: M.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.55 (s, 24H), 6.74 (s, 8H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ −4.78, 133.07, 140.12; UV (hexane): λ_{max}/nm (ϵ) 223 (25000), 254 (23500); MS (70 eV, rel. int.): 562 (M^+: ^{70}Ge, ^{72}Ge, $^{74}Ge_2$, 69), 547 (100), 475 (56), 297 (86), 267 (98), 252 (72), 119 (68); high-resolution mass: calcd for $C_{20}H_{32}{}^{70}Ge^{72}Ge^{74}Ge_2$: 561, 9391; found: 561, 9410.

** The crystals for X-ray analysis were obtained from toluene solution. A crystal with sizes of 0.2×0.2×0.2 mm was used for the data collection on a Rigaku-Denki AFC 5R four circle diffractometer with graphite monchromatized Mo-K_α radiation (λ = 0.71069 Å). A total of 3414 reflections within $2\theta = 60°$ were collected by the $2\theta-\omega$ scan method with a scan rate of 4°/min. Crystal data for $C_{20}H_{32}Ge_4$, M.W. 562.8, monoclinic, a 12.938(1), b 13.536(1), c 6.801(1) Å, β 98.13(1)°, V 1178.14(20) Å^3, space group $P2_1/n$, $Z = 2$, D_c 1.587 g/cm^3. The final R factor was 0.065 for 1989 reflections of $F_o > 3\sigma(F_o)$. Further details of the crystal structure are available as supplementary material.

*** Reference number with asterisk indicates a note in the list of references.

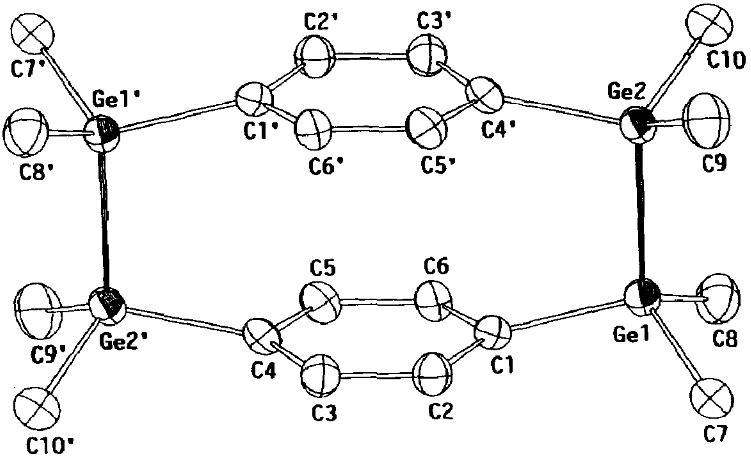
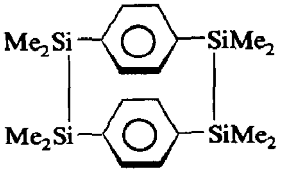
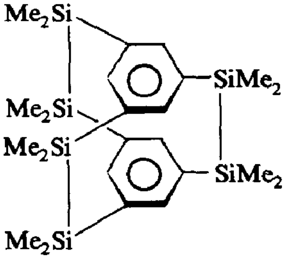


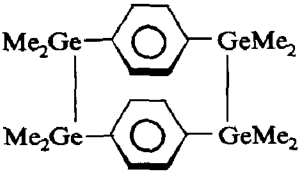
Fig. 1. ORTEP drawing of 3. Selected bond lengths (Å): Ge(1)–Ge(2) 2.438(2), Ge(1)–C(1) 1.941(10), Ge(2)–C(4′) 1.946(10). Selected bond angles (°): Ge(2)–Ge(1)–C(1) 103.9(3), Ge(1)–Ge(2)–C(4′) 104.2(3). Interplanar space distances (Å): C(1)–C(4′) 3.382, C(2)–C(5′) 3.493, C(3)–C(6′) 3.499.



(1)



(2)



(3)

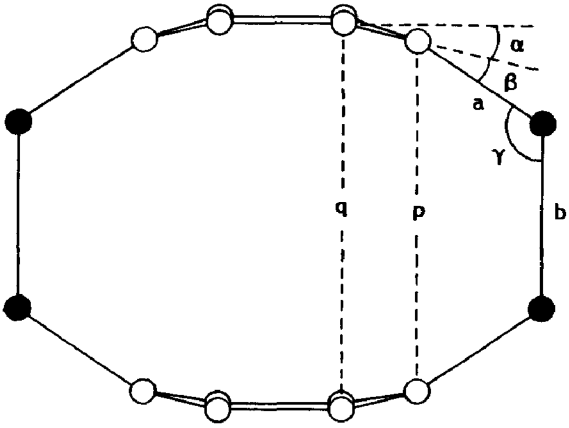
The β angles of both **1** and **3** are larger than the corresponding α angles. In the cyclophane **4**, however, the situation is opposite. The distortions in the cyclophanes **1** and **3** are accumulated upon the Si–Car and Ge–Car bonds to a larger extent than the benzene ring. Distortions of the benzene rings of both **1** and **3** are very small. In contrast, the distortion in **4** is concentrated on the benzene rings, resulting in the relatively larger deformation of the benzene rings. This can evidently be ascribed to the marked differences in the bond lengths at the bridge.

The distances p and q between the two aromatic rings increase to some extent with increases of the bridging bond lengths. However, distances between two benzene rings (q) for **1** and **3** are almost the same. The angles α are also in the same range of magnitude for **1** and **3**. Moreover, it is interesting to note that the lengths q for **1** (3.458 Å) and **3** (3.496 Å) are very close to that of graphite (3.40 Å) and longer than the mean intramolecular aromatic ring separation of **4**, which is around 3.00 Å, as we have pointed out before [2]. Apparently longer bond lengths of Ge–Ge and Si–Si than that of C–C functions to decrease the angle strain α. In this respect, it is very interesting and highly desirable to examine the structure of the unknown corresponding tin analog.

In the proton NMR spectra, the aromatic protons of **3**, **1**, and **4** appear at 6.74, 6.79, 6.48 ppm, respectively. These aromatic protons appreciably shift upfield ($\Delta\delta = 0.59$–0.63 ppm) relative to 1,4-bis(pentamethyldigermanyl)benzene (**5**, 7.35

Table 1

Bridging bond lengths, interplanar distances, and strain angles of paracyclophanes bridged by M–M (M = C, Si, and Ge) bonds



	C	Si	Ge
a (Å)	1.551	1.883	1.944
b (Å)	1.593	2.376	2.438
p (Å)	2.778	3.347	3.382
q (Å)	3.093	3.458	3.496
α (°)	12.6	4.3	4.5
β (°)	11.2	10.6	9.6
γ (°)	113.7	105.0	104.1

ppm), 1,4-bis(pentamethyldisilanyl)benzene (**6**, 7.38 ppm), and 1,4-diethylbenzene (**7**, 7.11 ppm).

The electronic spectra of the cyclophanes are of particular interest. Absorption bands with maxima at 254 (ϵ 23,500), 263 (ϵ 22,400), and 223 nm (ϵ 18,200) are observed for **3**, **1**, and **4** (Table 2).

In [2,2]paracyclophanes, the bridging M–M (M = C, Si, Ge) bonds are parallel to the $p\pi$-orbitals of the benzene rings and therefore available for σ–π interaction, if

Table 2

UV spectra of cyclophanes **3**, **1**, and **4** and related *para*-substituted benzenes

Compounds	UV (^1L_a)		$\Delta\tilde{\nu}$
	λ_{max} (nm)	$\tilde{\nu}$ (cm^{-1})	
3	254	39300	
1,4-bis(pentamethyldigermanyl)benzene (**5**)	242	41300	2000
1	263	38100	
1,4-bis(pentamethyldisilanyl)benzene (**6**)	246	40600	2500
4	223	44800	
1,4-diethylbenzene (**7**)	217	46200	1400

orbital energies match each other. The $b_{3u}(\sigma)$ orbital energy levels of M–M (Si and Ge) bonds are appreciably higher than those of C–C bonds, therefore effective σ–π interactions can be achieved in **1** and **3** [7*].

The large bathochromic shifts in **3** and **1** from the corresponding acyclic compounds, **5** and **6**, (**3**: $\Delta\tilde{\nu} = 2{,}000$ cm^{-1}; **1**: $\Delta\tilde{\nu} = 2{,}500$ cm^{-1}) result from the strong through-bond interaction due to σ–π mixing between M–M bonds and the aromatic π-systems in the ground state. Such orbital interaction causes appreciable destabilization of the $b_{3u}(\pi)$ orbital.

References and notes

1 P.M. Keehn and S.M. Rosenfeld, Cyclophanes, Academic Press, New York, 1983.

2 H. Sakurai, S. Hoshi, A. Kamiya, A. Hosomi and C. Kabuto, Chem. Lett., (1986) 1781.

3 A. Sekiguchi, T. Yatabe, C. Kabuto and H. Sakurai, Angew. Chem. Int. Ed. Engl., 28 (1989) 757.

4 R. Gleiter, W. Schäfer, G. Krennrich and H. Sakurai, J. Am. Chem. Soc., 110 (1988) 4117.

5 In $(Ph_2Ge)_6$, the Ge–Ge bond lengths are 2.463–2.457 Å and the Ge–Car bond lengths are 1.959–1.981 Å M. Dräger and L.Z. Ross, Anorg. Allg. Chem., 95 (1981) 476.

6 H. Hope, J. Bernstein and K.N. Trueblood, Acta Cryst., B28 (1972) 1733.

7 (a) R. Gleiter, Pure Appl. Chem., 59 (1987) 1585; (b) H. Sakurai, Pure Appl. Chem., 59 (1987) 1637. It is reported from the PE spectra of cyclophanes **1** and **4**, that the first ionization occurs from the $b_{3u}(\pi)$ orbital of **1** and the $b_{2g}(\pi)$ orbital of **4**.