# Molecular Structure of 1,1,8,8-Tetramethyl-1,8-digermacyclotetradecane: the First 14-membered Germacycles

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An X-ray crystallographic analysis indicated that 1,1,8,8-tetramethyl-1,8-digermacyclotetradecane exists exclusively as the [3434] conformer with germanium atoms at corner sites in the crystalline state. Molecular mechanics calculations (MM2) of 1,8-digermacyclotetradecane and germacyclohexanes showed that small C–Ge–C bond angle and C–Ge–C–C dihedral angle are characteristic of germacycles ranging from 14-membered to 6-membered rings. This tendency is also expected for the acyclic system when the C–Ge–C–C moiety is in the *gauche* conformation.

In previous communications we have shown both by experiment and by calculation[1] that the germacyclohexane (**4G**) and 1,1-dimethylgermacyclohexane (**3G**) have unique structures in that the ring adopts a flattened chair form around the germanium atom and C–Ge–C bond angle is sharper than that of the corresponding carbocycle.

Thus, the gas-phase electron diffraction study of **4G** and **3G**[2] has shown that for **4G**, the C–Ge–C bond angle (102.5°) is considerably sharpened as compared with the C–C–C angle (111.4°) of cyclohexane (**4C**),[3] and the dihedral angle (42.0°) through C–Ge–C–C is substantially smaller than that of **4C** (56.3°).[3]

An X-ray crystallographic study of a simple derivative of **4G**, tetraspiro[1,3,5,7-tetraoxa-2,4,6,8-tetragermacyclooctane-2,1′:4,1″:6,1‴:8,1⁗-tetrakisgerminane] (**5G**)[4] revealed that the germacyclohexane moiety possesses in the solid state the characteristics as shown by MM2 calculations or estimated by electron diffraction methods. It must be added that the observed structure of a simple solid derivative of cyclohexane, *trans*-cyclohexane-1,4-dicarboxylic acid (**5C**) has a structure as predicted by calculations.[5]

Recently we reported the synthesis of a variety of hitherto unreported macrocyclic germanium-containing large rings (germamacrocycles) ranging from 10- to 44-membered species.[6] The elucidation of the structure of these germamacrocycles will be intriguing as to whether the unique structural features of **4G** exist in germamacrocycles. In this paper, we report such a study determined by a combination of X-ray crystallographic analysis and molecular mechanics calculations for a 14-membered germacycle, 1,1,8,8-tetramethyl-1,8-digermacyclotetradecane (**1G**).

## Experimental

The preparation of **1G** was reported previously.[6] Single crystals of **1G** for the X-ray diffraction were obtained by slow evaporation of a solution of the compound dissolved in light petroleum.

*X-Ray Crystallographic Analysis.—Crystal data.* $C_{16}H_{36}Ge_2$, $M = 373.7$. Monoclinic, $a = 7.280(2)$, $b = 10.394(2)$, $c = 13.159(1)$ Å, $\beta = 100.12(1)°$, $V = 980.2(3)$ Å$^3$ (by least-squares refinement on diffractometer angles for 25 reflections in the range of $39 < \theta < 40°$, $\lambda = 1.541\ 84$ Å), space group $P2_1/c$ (No. 14), $Z = 2$, $D_x = 1.266$ g cm$^{-3}$. Colourless prism. Crystal dimensions 0.25 × 0.25 × 0.25 mm, $\mu$(Cu-K$\alpha$) = 3.25 mm$^{-1}$.

*Data Collection and Processing.*—Diffraction measurements were made on a Rigaku AFC6A diffractometer with graphite-monochromated Cu-K$\alpha$ radiation at 296 K. The integrated intensities were collected in the $2\theta - \omega$ scan mode with an $\omega$ rate of 4.0° min$^{-1}$. Collection range $h = 0$ to 8, $k = 0$ to 11, $l = -14$ to 14. Three reference reflections $02\bar{4}$, $\bar{1}2\bar{1}$, and $01\bar{5}$ were measured every 150 reflections, intensity variation < 1.8%. The data were corrected for Lorentz and polarisation effects but not for absorption. 1624 reflections measured, 1451 reflections unique, and 1373 reflections observed with $I \geqslant 2\sigma(I)$.

*Structure Analysis and Refinement.*—Structure was solved by heavy-atom method and refined by full-matrix least-squares. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in calculated positions and refined independently. In the final least-squares refinement, the weighting scheme $w = 1/[\sigma^2(F_o) + 0.0001\ F_o^2]$, with $\sigma(F_o)$ from counting statics was used; $R = 0.038$, $R_w = 0.052$, and $(\Delta/\sigma)_{max} = 0.346$. The maximum and the minimum height in the final difference Fourier synthesis were +0.34 and −0.56 e Å$^{-3}$, respectively. All of the crystallographic calculations were performed using XTAL3.0 and XTAL3.2 programs.[7] Full lists of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.†

*Molecular Mechanics Calculations.*—To estimate the structure of germamacrocycles molecular mechanics calculations (MM2) of **1G** and related compounds were carried out. The parameters for germanium, proposed by Allinger *et al.*[8] were incorporated into MM2.

## Results and Discussion

The ORTEP drawing of **1G** is given in Fig. 1. The observed molecular structure is centrosymmetric.

For X-ray crystallographic analysis it is desirable to analyse the parent compound 1,8-digermacyclotetradecane (**2G**), with the advantage that substantial research has been done on the parent carbocycle cyclotetradecane (**2C**). Thus, Dale[9] established, with the aid of early force-field calculations that the most stable conformation of **2C** is the nearly unstrained diamond lattice [3434] conformation. An X-ray crystallographic analysis of **2C** has been carried out by Groth[10] which confirmed the structure predicted by Dale.[9] Furthermore, $^{13}$C DNMR study

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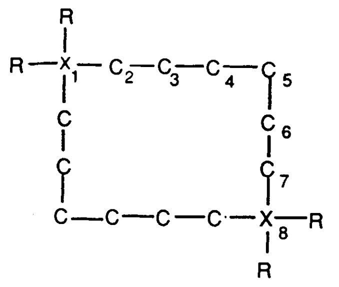
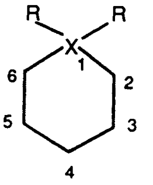
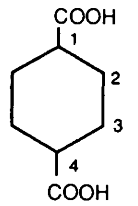
† Details of the deposition scheme are available in 'Instructions for Authors (1993),' *J. Chem. Soc., Perkin Trans 2*, 1993, issue. 1.



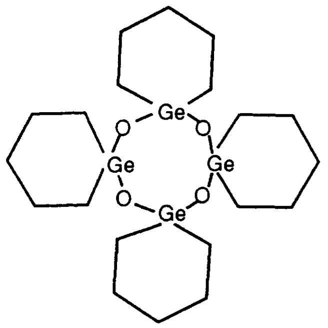
| | X | R |
|---|---|---|
| **1C** | C | Me |
| **1G** | Ge | Me |
| **2C** | C | H |
| **2G** | Ge | H |



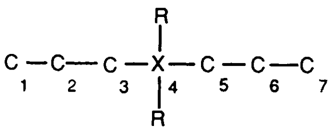
| | X | R |
|---|---|---|
| **3C** | C | Me |
| **3G** | Ge | Me |
| **4C** | C | H |
| **4G** | Ge | H |



**5C**



**5G**



| | X | R |
|---|---|---|
| **6C** | C | Me |
| **6G** | Ge | Me |
| **7C** | C | H |
| **7G** | Ge | H |

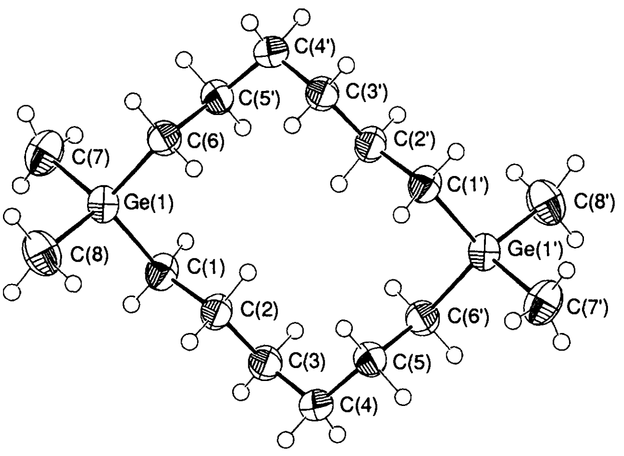


**Fig. 1** ORTEP drawing of **1G**

of **2C** in solution was in agreement with a homogeneous, [3434] conformation.[11]

As the preparation of **2G** was rather difficult, partly because of its instability and partly because of the scarcity of the starting materials, we undertook the study of **1G** rather than **2G**. To our advantage was the fact that **1G** was the most readily crystallised among the germamacrocycles prepared.

*The Position of Germanium in Compounds* **1G** *and* **2G**.—It is not unexpected that the germanium atoms with *gem*-dimethyl groups occupy the corner position, since it is already established that atoms and groups much larger than hydrogen strongly prefer to occupy corner sites to reduce hindrance.[12] In order to see whether germanium atoms without *gem*-dimethyl groups will also occupy the corner sites, molecular mechanics calculations were performed for four possible positional isomers, **A**, **B**, **C** and **D**, of **1G** and **2G** (Fig. 2). For comparison the same calculation was performed for 1,1,8,8-tetramethylcyclotetradecane (**1C**). The relative steric energies of these compounds are summarised in Table 1.

**Table 1** Relative steric energy of 1,1,8,8-tetramethylcyclotetradecane (**1C**), 1,8-digermacyclotetradecane (**2G**) and 1,1,8,8-tetramethyl-1,8-digermatetracyclodecane (**1G**) (in kcal mol$^{-1}$)

| Position[a] | 1C | 2G | 1G |
|---|---|---|---|
| **A**[b] | 0 | 0 | 0 |
| **B**[b] | 13.33 | 1.60 | 4.02 |
| **C**[b] | 7.66 | 1.60 | 1.83 |
| **D**[b] | 20.43 | 4.83 | 8.83 |
| **E**[c] | | 1.20 | |
| **F**[c] | | 2.20 | |

[a] For definition of position of germanium atom, see the text. [b] [3434] conformation (Fig. 2). [c] [3344] Conformation (Fig. 3).

For both **1G** and **2G** the isomer with germanium atoms at the corner sites (**A** isomer) is by far the most stable. The energy difference between **A** and the other positional isomers (**B**, **C** and **D** isomers) are smaller for **2G**, which reflects the absence of *gem*-dimethyl group. Thus, the molecular mechanics calculations indicate that **2G** has a [3434] conformation with germanium atoms at the corner sites.

For a 14-membered ring, however, there are in principle other possible conformations the energy of which are not so much different from that of the [3434] conformation. In the case of **2C**, the [3434] structure has indeed the lowest steric energy, but the difference from the next to lowest, the [3344] conformation, is not very large (2.6 kcal mol$^{-1}$).[9,*] This

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* 1 cal. = 4.184 J.

**Table 2** Experimental and calculated bond length ($r$), bond angle ($\theta$), and dihedral angle ($\varphi$) of **1G** and related compounds

| Compound | Method[a] | $r_1$[b] | $r_2$[c] | $\theta$[d] | $\varphi_1$[e] | $\varphi_2$[f] | Reference |
|---|---|---|---|---|---|---|---|
| **1G** | X-ray | 0.1956 | 0.1953 | 108.8 | 57.6 | 53.8 | this study |
| | MM2 | 0.1961 | 0.1961 | 109.4 | 61.1 | 52.4 | this study |
| **2G** | MM2 | 0.1962 | 0.1962 | 109.5 | 61.6 | 52.2 | this study |
| **3G** | ED | 0.1957 | 0.1957 | 103.1 | 42.3 | 42.3 | ref. 2 |
| | MM2 | 0.1946 | 0.1946 | 101.9 | 47.5 | 47.5 | ref. 1(*a*) |
| **4G** | Ed[g] | 0.1956 | 0.1956 | 102.5 | 42.0 | 42.0 | ref. 2 |
| | MM2 | 0.1947 | 0.1947 | 101.6 | 47.8 | 47.8 | ref. 1(*a*) |
| **5G** | X-ray | 0.1940 | 0.1940 | 106.9 | 42.4 | 42.4 | ref. 4 |
| **6G** | MM2 | 0.1960 | 0.1960 | 109.9 | 57.0 | 56.8 | this study |
| **7G** | MM2 | 0.1960 | 0.1960 | 109.9 | 56.9 | 56.9 | this study |
| **1C** | MM2 | 0.1552 | 0.1551 | 113.3 | 58.5 | 55.1 | this study |
| **2C** | X-ray | 0.1531 | 0.1536 | 114.6 | 64.4 | 58.0 | ref. 10 |
| | MM2 | 0.1542 | 0.1542 | 115.9 | 62.3 | 56.8 | this study |
| **3C** | ED | 0.1532 | 0.1532 | 109.8 | 50.4 | 50.4 | ref. 3 |
| | MM2 | 0.1545 | 0.1545 | 109.4 | 52.6 | 52.6 | ref. 1(*a*) |
| **4C** | ED | 0.1531 | 0.1531 | 111.4 | 54.9 | 54.9 | ref. 3 |
| | MM2 | 0.1536 | 0.1536 | 110.9 | 56.3 | 56.3 | ref. 1(*a*) |
| **5C** | X-ray | 0.1537 | 0.1537 | 113.3 | 53.5 | 53.5 | ref. 5 |
| **6C** | MM2 | 0.1549 | 0.1549 | 113.2 | 56.0 | 56.0 | this study |
| **7C** | MM2 | 0.1539 | 0.1539 | 115.7 | 59.5 | 59.5 | this study |

[a] MM2, molecular mechanics calculations (by MM2); X-ray, X-ray crystallographic analysis; ED, electron diffraction method. [b] Ge–C bond length in nm. For **1G**, **2G**, **1C** and **2C**, the values are for the shorter side. [c] Ge–C bond length in nm. For **1G**, **2G**, **1C** and **2C**, the values are for the longer side. [d] C–Ge–C Bond angle. [e] C–Ge–C–C Dihedral angle. For **1G**, **2G**, **1C** and **2C**, the values are for the shorter side. [f] C–Ge–C–C Dihedral angle. For **1G**, **2G**, **1C** and **2C**, the values are for the longer side.

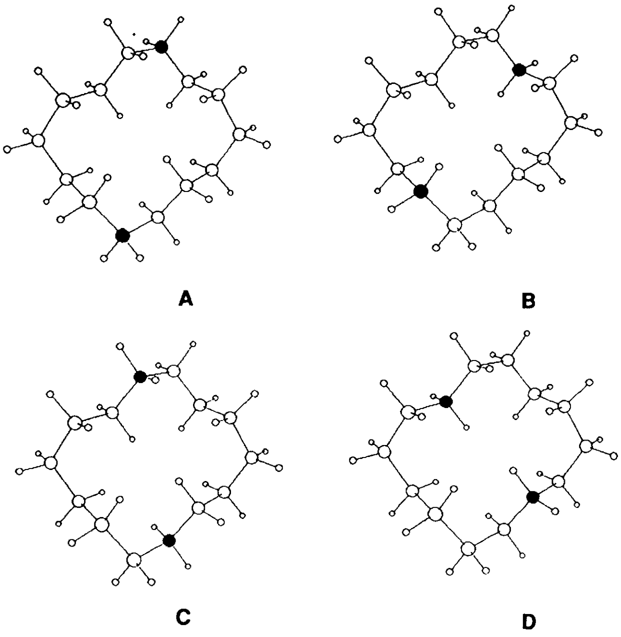

**Fig. 2** Position of $GeH_2$, $GeMe_2$ and $CMe_2$ moieties in the [3434] conformation of **2G**, **1G** and **2C**. ● Indicates the position of $GeH_2$, $GeMe_2$ and $CMe_2$ moieties.

conformation can also be a candidate for **2G** since two germanium atoms can conveniently occupy the corner sites (structure **E**). The steric energy of this form is 1.2 kcal mol$^{-1}$ higher than the **A** conformation. It must be added that other positional isomers for [3344] conformation requires at least one germanium atom at non-corner site (*e.g.*, structure **F**). The structures of **E** and **F** are given in Fig. 3, and the results of calculations for these two compounds are included in Table 1. Indeed, the energy of the **F** form is higher than that of the **E** isomer by *ca.* 1 kcal mol$^{-1}$.

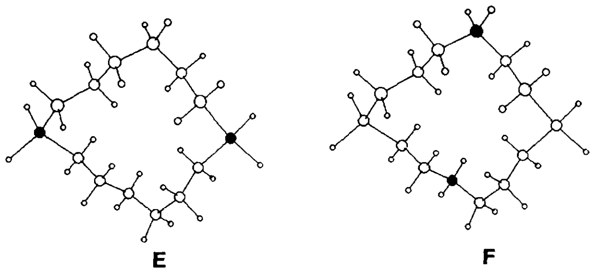

**Fig. 3** Position of $GeMe_2$ moiety in the [3344] conformation of **1G**. ● Indicates the position of $GeMe_2$ moieties.

Thus, the observed structure of **1G**, the [3434] conformation with two germanium atoms at the corner sites, is in a complete agreement with the prediction based on the molecular mechanics calculations.

*Structural Features of* **1G** *and* **2G**.—In Table 2, selected geometrical parameters, *i.e.*, Ge–C bond length ($r$), C–Ge–C bond angle ($\theta$) and C–Ge–C–C dihedral angle ($\varphi$) of **1G** and related compounds as estimated by MM2 together with experimental values are summarised.

Our crucial finding was that, when compared with **4C**, the structure of **4G** is characteristic in that it has sharper C–Ge–C bond angle and flattened ring around germanium as indicated by smaller C–Ge–C–C dihedral angle.[1,2,4]

It will be interesting to see whether the structural features associated with compound **4G** exist in compound **1G**. For a better discussion on the structures of **1** and **2**, it will be necessary to generalise the characteristics of geometrical parameters for **3** and **4** obtained by various methods. Comparison of data for carbocycles indicates that: (i) the agreement among calculated and experimental (both X-ray and electron diffraction) values of $\theta$ and $\varphi$ is fair; (ii) the *gem*-dimethyl group makes the dihedral angle $\varphi$ smaller. For germacycles: (iii) the agreement among calculated and experimental (both X-ray and electron diffraction) values of $\theta$ is fair, but the agreement for values of $\varphi$ is poor. The observed values are smaller than the calculated values; (iv) there is no further ring flattening caused by the *gem*-dimethyl group.

For **1G**, the C–Ge–C bond angle $\theta$ is 108.8°, the C–Ge–C–C dihedral angle $\varphi$ associated with the Ge–C bond along the shorter (*i.e.*, three bonds) side is 57.6°, and that associated with the Ge–C bond along the longer (*i.e.*, four bonds) side is 53.8°, respectively. The corresponding values for **2C** as reported by Groth[9] are 114.6, 64.4 and 58.0°, respectively. In the light of above discussions, it is certain that both $\theta$ and $\varphi$ of **1G** are smaller than these of **2C** (and hence than these of **1C**) to indicate that there still remain the characteristics of **4G** in the 'diamond-like' structure of **1G**.

Another interesting point is whether the smaller bond and dihedal angles associated with germanium are observed for acyclic systems or only for ring structure. Molecular mechanics calculations were carried out for model compounds, 4,4-dimethylheptane (**6C**), heptane (**7C**), 4,4-dimethyl-4-germaheptane (**6G**) and 4-germaheptane (**7G**) in the *t-g-g-t* conformation (Fig. 4).

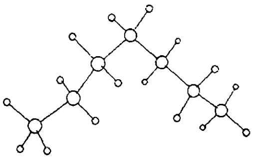

**Fig. 4** The *t-g-g-t* conformation of **6G**, **7G**, **6C** and **7C**

It is evident from the data in Table 2 that both bond angles and dihedral angles around germanium are smaller for **7G** compared with those for **7C**. *gem*-Dimethyl substitution causes flattening around germanium to make the dihedral angle for **6G** and **6C** very similar, as was observed for **1G** and **1C**. Taking all these observations into consideration, the acyclic compound **7G** can be said to be flattened, relative to **7C**, around germanium as is the case with **1G** and **4G**.

In conclusion, the reduced C–Ge–C bond angle and C–Ge–C–C dihedral angles are a characteristic of all organogermanium compounds rather than solely cyclic species.

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