1,12-Digermacyclodocosanes. Synthesis, Structure and Anion Transport Capability

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An X-ray crystallographic analysis indicated that 1,1,12,12-tetramethyl-1,12-digermacyclodocosane exists exclusively as the [3838] conformer with germanium atoms at corner sites in the crystalline state. The geometric parameters of this compound are nicely reproduced by MM3 calculations and are found to be comparable with those of relevant carbocycles. The anion transport capability of 1,12-dichloro-1,12-dimethyl-1,12-digermacyclodocosane is much the same with that of the 14-membered-ring analogue.

New anion binding ligands are being sought actively. Use of higher row group 14 elements as the binding sites has opened a novel route to such ligands. Indeed, silicon-[1] and tin-[2] containing large rings have shown anion transport capability. We expected that a germanium atom could equally be a binding site for anions and have shown that although the 14-membered 1,1,8,8-tetramethyl-1,8-digermacyclotetradedane (3G) failed to

	M	R¹	R²
1G	Ge	Me	Me
1Ga	Ge	Me	Cl
1C	C	Me	Me
2G	Ge	H	H
2C	C	H	H

	M	R¹	R²
3G	Ge	Me	Me
3Ga	Ge	Me	Cl
4C	C	Me	Me
4G	Ge	H	H

transport anions,[3] the 1,8-dichloro-1,8-dimethyl derivative (3Ga) effectively transports chloride and bromide anions, with appreciable selectivity in favour of the chloride.[4]

Attempts to isolate or observe the anion–3Ga complex were unsuccessful. One of the possible reasons for this failure may be the fact that the cavity size is not large enough. We have shown by an X-ray crystallographic study that 3G has a [3434] conformation with two dimethylgermyl moieties at corner positions.[5] Hence, the distance between the inner hydrogen of C2 and that of C10 is about 2.3 Å,[5] which is not enough to hold an anion. Thus, the success of anion transport with 3Ga is certainly due to the enhanced Lewis-acidic character of the germanium moiety which will make either a nesting complexion or an apolar surface interaction possible.[4]

In this connection it would be interesting to examine the anion transport capability of larger germamacrocycles which might have a cavity large enough to encapsulate anions. In this paper we describe the synthesis, structure and anion transport behaviour of 22-membered 1,12-digermacyclodocosane derivatives.

Experimental

Spectra.—¹H and ¹³C NMR spectra were determined as solutions in CDCl₃ or C₆D₆ (*ca.* 1% v/v) on a JEOL α-500 spectrometer operating at 500.00 and 125.65 MHz, respectively, at 30 °C in 5 mm tubes. Typical measurement conditions were

as follows: (¹H) pulse width, 5.65 μs (45°); spectral width, 4500 Hz; number of scans, 8; pulse delay, 2.72 s; data points, 32 768: (¹³C) pulse width, 4.70 μs (45°); spectral width, 19 000 Hz; number of scans, 100; pulse delay, 1.48 s; data points, 32 768.

Ion Chromatography.—Ion chromatography was carried out with a Waters system at 35 °C (510 HLPV pump and 430 conductivity detector). The column used was a Waters IC-PAK A with borate buffer as the eluent.
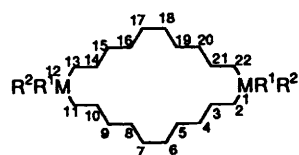
Synthesis.—The preparation of 1,1,12,12-tetramethyl-1,12-digermacyclodocosane (1G) was described previously.[3] 1,12-dichloro-1,12-dimethyl-1,12-digermacyclodocosane (1Ga) was prepared by a procedure essentially similar to that used for the preparation of 1,8-dichloro-1,8-dimethyl-1,8-digerma-cyclotetradecane (3Ga).

1,12-*Dichloro-1,12-dimethyl-1,12-digermacyclodocosane* (1Ga). A mixture of 1G (0.5 g, 1.3 mmol) and anhydrous SnCl₄ (1.0 g, 3.8 mmol) in nitromethane (320 cm³) was heated to reflux for 5 h. After cooling, the solvent and Sn compounds (mostly MeSnCl₃) were evaporated under reduced pressure and the residue was dried (0.1 mmHg/room temp.) to afford white crystals of 1Ga (0.48 g, 87%), m.p. 134–135 °C (Found: C, 40.9; H, 7.12. Calc. for C₁₄H₃₀Cl₂Ge₂: C, 40.57; H, 7.30%); δH(500 MHz, CDCl₃) 0.66 (6 H, s, Me), 1.09–1.16 (4 H, m, CH₂), 1.24–1.30 (4 H, m, CH₂) and 1.40–1.53 (16 H, m, CH₂); δC(125 MHz, CDCl₃) 0.66 (6 H, s, Me), 1.09–1.16 (4 H, m, CH₂), 1.24–1.30 (4 H, m, CH₂) and 1.40–1.53 (16 H, m, CH₂).
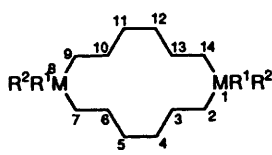
X-Ray Crystallographic Analysis.—*Crystal data.* C₂₄H₅₂-Ge₂, M = 485.86, monoclinic, a = 6.849(1), b = 14.303(2), c = 14.864(1) Å, β = 102.91(1)°, V = 1419.3(3) Å³ (by least-squares refinement on diffractometer angles for 25 reflections in the range of 35.11 < θ < 38.05°, λ = 1.541 84 Å), space group P2₁/c (no. 14), Z = 2, Dₑ = 1.137 g cm⁻³. Colourless prism. Crystal dimensions 0.25 × 0.25 × 0.25 mm, μ(Cu-Kα) = 2.34 mm⁻¹.

Data collection and processing. Diffraction measurements were made on a Rigaku AFC6A diffractometer with graphite-monochromated Cu-Kα radiation at 296 K. The integrated intensities were collected in the 2θ-ω scan mode with an ω rate of 4° min⁻¹. Collection range h = 0–7, k = 0–16, l = −15 to 15. Three reflections 141, 121 and 211 were measured every 150 reflections, intensity variation <2%. The data were corrected for Lorentz and polarization effects but not for absorption. 2154 reflections, 1923 unique and 1613 reflections observed with I ≥ 2σ(I).

Structure analysis and refinement. The structure was solved

by a direct method with SIR92[6] and refined by full-matrix least-square methods. 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 $w = 1/[\sigma^2(F_o) + 0.0002F_o^2]$, with $\sigma(F_o)$ from counting statistics was used; $R = 0.037$, $R_w = 0.046$ and $(\Delta/\sigma)_{max} = 0.55$. The maximum and minimum height in the final difference Fourier synthesis were $+0.32$ and -0.36 e Å^{-3}, respectively. All of the crystallographic calculations except the direct method were performed using XTAL3.2 program.[7] Full lists of atomic coordinates, bond lengths and angles and thermal parameters have been deposited under the Cambridge Crystallographic Deposition Scheme.†

Molecular Mechanics Calculations.—To estimate the structures of 1G, 2G, 1C and 2C, we carried out molecular mechanics calculations (MM3).[8] For parameters for germanium, those proposed by Allinger et al.[9] were incorporated into the MM3 program.

During our preliminary calculations we found that we had to start with a good, diamond-like structure to obtain a global minimum. If we started the calculations from an arbitrary structure, they tended to end up with a local minimum which had a considerably different structure from that of global minimum (e.g., larger dihedral angle). This was also the case with carbocycles. Thus, for MM3 calculation of 1C and 2C, the X-ray structure of 1G was also used after modification.‡

Anion Migration Experiment.—To estimate the anion transport capability of organogermanium compounds, the so-called U-tube test[10] was attempted. Thus, in the bottom part of the U-tube§, a methylene chloride solution of 1,8-digermacyclotetradecane (0.05 mol dm^{-3}; 0.7 cm^3, 3.5 mmol) was added and in the right arm of the U-tube, aqueous tetrabutylammonium chloride or bromide (1.5 mol dm^{-3}; 0.2 cm^3, 0.3 mmol) was added. Pure water was in the left arm of the U-tube. A small magnetic bar stirrer was placed in the bottom of each arm. A 0.25 mm^3 (1 mm^3 = 1 µl) portion of water was taken from the left arm by means of a syringe at intervals and the amount of anions transported was determined by means of ion chromatography. The estimation was attempted for 40 h. By this time, the amount of halogens from the decomposed germanium compounds began to obscure the anion transport estimation. The blank test was also performed where no germamacrocycle was dissolved in the organic layer: no anion was detected in the water in the left arm.

Results and Discussion

A larger germamacrocycle may have a larger cavity for anion encapsulation. On the other hand, it is reported that a large cycloalkane has a [3n3n], rather than a square, structure. Thus, Groth reported that cyclotetracosane is essentially in a 'rectangular' diamond-lattice [3939] conformation at -160 °C.[11] A similar [3,14,3,14] conformation was reported for a 34-membered cyclotetratriacontane.[12] Since both cyclotetradecane (4C)[13] and its germanium analogue 3G[5] have a [3434] conformation, it is most likely that 1,12-digermadocosane derivatives have a [3838] conformation. With this in mind, we attempted an X-ray crystallographic analysis and molecular mechanics calculations (MM3) of 1G.
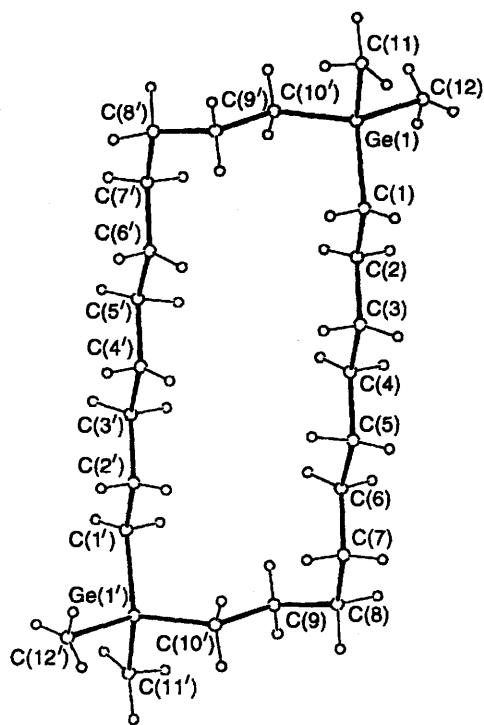

Fig. 1 ORTEP drawing of 1,1,12,12-tetramethyl-1,12-digermacyclodocosane (1G)

X-Ray Structure.—The ORTEP drawing of 1G is given in Fig. 1. The geometric parameters are listed in Table 1 together with the data obtained from molecular mechanics calculations.

The most characteristic structural feature observed for 1G is its [3838] conformation as expected. The bond lengths remain in the normal range for each type of bond. The smaller bond angle at germanium is characteristic of germacycles, as previously pointed out.

The longer chain has a zigzag structure with the dihedral angles (excluding those of the corner sites) cloe to 180°. The two dihedral angles at the germanium corners of 1G are a little smaller than 60°, while those at the carbon corners are larger than 60°. This is also the case with 3G and again proves the general tendency of flattening around germanium.

Molecular Mechanics Calculations.—The steric energy and its component energies in the [3838] conformation are calculated by MM3 for 1G, 1,12-digermacyclodocosane (2G) and their carbon analogues, 1,1,12,12-tetramethylcyclodocosane (1C) and cyclodocosane (2C). The data are listed in Table 2. The steric energy and its component energies of 3C, 4C, 3G and 4G in the [3434] conformation were calculated by MM2[14] in the previous paper.[4] Since the details were not given there, the data are also included in Table 2. In Table 2, the corresponding values for 1G, as determined by X-ray crystallographic analysis, are included.

In MM2 calculations, total steric energies (E_s) are the sum of compression energy (E_c), bending energy (E_b), stretch–bend energy (E_{sb}), van der Waals energy [which is subdivided into the energy associated with 1,4-interaction ($E_{1,4}$) and that with other interactions (E_{others})] and torsion energy (E_t). In MM3 calculations energies due to bending–bending energy (E_{bb}), torsion–stretch energy (E_{ts}) and dipole–dipole interaction energy (E_{dipole}) are also included. For such non-polar compounds discussed in this paper, these additional terms are essentially negligible to allow qualitative comparison among MM2 and MM3 values.

It is interesting to notice that the steric energy relation among

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‡ This is due to the extreme flexibility of the ring involved. The authors wish to thank the referee who pointed out this possibility to us.
§ The original U-tube was modified to an H-tube so that a small magnetic bar could be used to effect the mixing.

Table 1 Total steric energies and their component energies of cyclodocosanes and digermacyclodocosanes (in kcal mol^{-1})[a,b]

Compd.	Total steric	Compression	Bending	Bend–bend	Stretch–bend	1,4-Energy	Other	Torsional	Torsion–stretch	Dipole–dipole
1C[a]	38.34	2.59	4.14	0.08	0.61	24.50	2.26	4.20	−0.04	0.00
2C[a]	29.29	1.48	3.06	0.07	0.49	20.90	0.53	2.79	−0.02	0.00
3C[b]	22.50	1.33	4.93	—	0.62	9.48	−2.33	3.44	0.00	—
4C[b]	17.47	2.53	5.87	—	0.76	11.93	−3.84	5.24	0.00	—
1G[a]	19.66	1.35	2.46	0.06	0.18	18.72	−4.60	1.50	−0.02	0.00
2G[a]	22.38	1.28	2.34	0.07	0.27	19.65	−2.75	1.52	−0.02	0.00
3G[b]	4.22	0.93	3.27	—	0.35	7.14	−9.14	1.68	0.00	—
4G[b]	9.21	0.96	3.16	—	0.35	8.75	−5.68	1.66	0.00	—

[a] MM3 calculations. [b] MM2 calculations. Steric energies were reported in ref. 5. [b] For definition of each component energy, see the text.

Table 2 Molecular parameters of cyclodocosanes and digermacyclodocosanes as determined by molecular mechanics calculations and X-ray crystallographic analysis[a]

Bond length[b]

		r_1	r_2	r_3	r_4	r_5	r_6	r_7	r_8	r_9	r_{10}	r_{11}
1C	MM3	1.542	1.541	1.541	1.541	1.538	1.538	1.537	1.537	1.538	1.539	1.552
2C	MM3	1.541	1.539	1.540	1.541	1.538	1.538	1.537	1.538	1.537	1.538	1.541
3C	MM2	1.551	1.539	1.541	1.541	1.539	1.539	1.552				
4C	MM2	1.541	1.538	1.541	1.542	1.538	1.538	1.542				
1G	X-Ray[c]	1.949	1.526	1.517	1.536	1.523	1.523	1.496	1.534	1.510	1.533	1.948
1G	MM3	1.968	1.539	1.540	1.540	1.538	1.538	1.537	1.537	1.537	1.538	1.965
2G	MM3	1.965	1.538	1.540	1.540	1.538	1.538	1.539	1.537	1.537	1.538	1.965
3G	X-Ray	1.956	1.541	1.536	1.536	1.516	1.535	1.953				
3G	MM2	1.961	1.538	1.540	1.540	1.538	1.539	1.961				
4G	MM2	1.962	1.538	1.541	1.540	1.538	1.539	1.962				

Bond angle[d]

		θ_1	θ_2	θ_3	θ_4	θ_5	θ_6	θ_7	θ_8	θ_9	θ_{10}	θ_{11}
1C	MM3	112.3	115.5	113.1	111.4	113.3	112.9	113.8	115.5	113.8	116.0	112.3
2C	MM3	115.2	113.7	113.1	111.6	113.1	114.0	110.5	115.3	114.0	114.0	115.1
3C	MM2	113.4	116.2	114.0	116.0	114.0	112.6	116.1				
4C	MM2	116.0	114.2	114.2	116.0	113.9	113.0	113.9				
1G	X-Ray[e]	109.5	112.7	113.3	112.7	113.3	114.7	111.6	113.4	115.5	115.7	114.6
1G	MM3	108.9	112.9	112.5	112.1	112.6	112.2	114.0	115.5	113.7	113.2	108.9
2G	MM3	108.3	112.7	112.1	112.0	112.7	112.5	114.0	115.5	113.7	113.0	108.8
3G	X-Ray	108.8	113.2	114.0	115.1	113.1	112.6	113.0				
3G	MM2	109.4	113.3	113.4	115.9	113.8	112.0	113.0				
4G	MM2	109.5	113.2	113.4	115.9	113.7	112.1	112.8				

Dihedral angle[f]

		φ_{12}	φ_{23}	φ_{34}	φ_{45}	φ_{56}	φ_{67}	φ_{78}	φ_{89}	φ_{910}	φ_{1011}	φ_{1112}
1C	MM3	−58.1	175.0	−66.8	−62.8	−178.5	−179.4	178.3	−178.4	173.3	−174.6	56.0
2C	MM3	−61.1	175.7	−64.1	−60.5	−179.8	−178.3	177.1	−177.6	175.6	−177.7	56.9
3C	MM3	−58.5	169.6	−67.6	−61.0	−179.8	−171.9	55.1				
4C	MM3	−63.3	170.7	−62.3	−56.8	−184.6	−175.5	57.7				
1G	X-Ray[g]	−56.5	172.8	−66.1	−64.0	−175.1	−178.9	178.0	−179.7	178.2	−177.4	55.6
1G	MM3	−58.1	172.8	−64.8	−62.8	−177.6	−181.0	179.0	−180.3	178.4	−176.1	54.1
2G	MM3	−58.1	175.2	−63.9	−62.6	−177.6	−180.2	179.0	−180.5	177.7	−176.2	53.3
3G	X-Ray	−57.6	173.8	−64.7	−63.5	−178.4	−176.8	53.8				
3G	MM2	−60.9	174.6	−63.9	−60.1	−178.5	−177.3	52.4				
4G	MM2	−61.3	175.0	−63.6	−59.7	−178.7	−177.4	52.2				

[a] The numbering of ring atoms is made so that atoms of the shorter chain are numbered first. Selected data for 3C, 4C, 3G and 4G were reported in ref. 5. [b] Bond length in Å: r_1 indicates the bond length Ge1–C2 or C1–C2. [c] Estimated standard deviations (e.s.d.s) for C–Ge and C–C bonds are in the range 0.007–0.009 and 0.005–0.007 Å, respectively. [d] Bond angle θ_1 indicates the angle C22–Ge1–C2 for 1G and 2G and C14–Ge1–C2 for 3G and 4G. [e] E.s.d.s are in the range 0.2–0.4°. [f] φ_{12} Indicates the dihedral angle C22–Ge1–C2–C3 for 1G, 2G and C14–Ge1–C2–C3 for 3G and 4G. [g] E.s.d.s are in the range 0.4–0.5°.

hydro (2) and methyl (1) compounds is quite similar to that observed for 14-membered rings (e.g. between 4 and 3). Thus, 1C (and 3C) has a much larger steric energy than that of 2C (and 4C), while the steric energy of 1G (and 3G) is smaller than that of 2G (and 4G). Though a direct comparison of steric energies of different compounds is meaningless, this tendency clearly

reflects the characteristic relaxation in dimethylgermacycles as compared with dimethylcarbocycles where most of the contributing terms tend to be larger. In germacycles the bending and torsion term reduces the steric energy to a considerable extent, which is again a characteristic of germacycles.

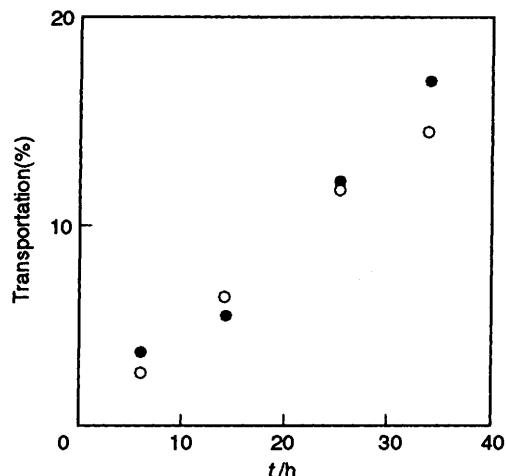For 1G, the agreement between experimental (X-ray) and

Fig. 2 Anion migration experiments with 1,12-dichloro-1,12-dimethyl-1,12-digermacyclodocosane (1Ga); ●, 1Ga; (○, 3Ga, ref. 4)

calculated (MM3) values are excellent. The C–Ge bond length is in the range of standard values though X-ray values are slightly smaller than those calculated. It is intriguing to notice that the small difference between two dihedral angles associated with germanium (e.g. φ_{111} for the short chain and φ_{12} for the longer chain) is clearly reproduced by MM3 calculations. Hence it can be concluded that the structural feature observed for 1G— smaller bond angle at germanium, flattened ring around germanium and finally, smaller dihedral angle associated with the longer chain—should be common to all germacycles of this type.

Anion Migration Experiment.—An anion transfer experiment similar to that for 3Ga was carried out for 1Ga. The result is shown in Fig. 2, which indicates that 1Ga does transport chloride, but with much the same efficiency as with that for 3Ga. This result is expected, in view of the [3838] conformation of 1Ga the cavity width of which is much the same as that for 3Ga. This in return supports the nesting mechanism of anion transport.

It is clear that the ring size (the number of atoms in the ring) is not the critical factor for germacycle encapsulation of anions. If the conformation is always [3n3n], the width of the cavity is not affected by the number of carbons forming the ring. In this connection the structure and anion transport capability of such a compound as 1,8,15,22-tetragermaoctacosane which is likely to be forced to have a [7777] conformation is most intriguing. Study along this line is under progress in this laboratory.

Acknowledgements

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