

A simple route to novel D spherosilicones; the first crystallographic structures of D₆ and D₈ cages†

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The synthesis, characterisation and crystal structure of D₈ and D₆ cages from the corresponding bis(dialkoxy)methane is reported.

Spherosilicate silsesquioxane cages have been used extensively as scaffolds for the development of liquid crystals,^{1,2} biocompatible materials,³ catalysts^{4,5} and dendrimers.⁶ There are now numerous routes to T₆ and T₈ cages and their structures and properties have been reported in detail.^{7,8} In recent years several reviews have appeared on cage silsesquioxanes.^{9,10}

We are interested in preparing, using rational syntheses, the corresponding silicone (D) cages in which each of the RSiO₃ vertices is replaced by RSi(CH₂)O₂. In these D cages one edge Si–O–Si unit is replaced by a Si–CH₂–Si unit as in molecules **1–4**. Both the D₆ and the D₈ cages can exist in two isomeric forms depending upon whether all Si–CH₂–Si edges are aligned parallel to each other or whether two are parallel and the other one or two Si–CH₂–Si edges are orthogonal (Scheme 1).

Wang reported the synthesis of the D₆ cage **1** in 1958, where the R group is methyl¹¹ following on from work by Clarke.¹² Subsequently in 1970, Cooke *et al.* repeated Wang's work and based on ¹H NMR spectroscopy confirmed that Wang had in fact prepared the other isomer of the D₆ cage,¹³ **2**. Cooke also reported the preparation of D₆ cages where R is phenyl.¹³ No detailed structural information was provided on either compound.

Shimajima and Kuroda have reported the preparation of the corresponding T₆ cages **5**, **6** and **7** (Scheme 2).¹⁴ Hydrolysis and polycondensation of bis(triethoxysilyl)methane in the presence of tetramethylammonium hydroxide (TMAOH) in ethanol gave **5** which could be treated with trimethylchlorosilane to give **7**. The isomeric T₆ cage **6** was formed in very small amounts, although the proportion of this cage could be increased by performing the reaction in water. However, the amount of this isomer was such that it could not be isolated. No evidence was reported of the corresponding T₈ cages.

To our knowledge the corresponding D₈ cages, **3** and **4**, have not appeared in the literature although Cooke suggested

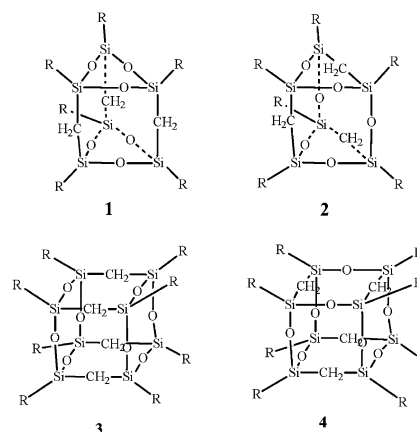
that, based on mass spectroscopy, a D₈ cage was present in their product as an impurity.¹³

Usually T₆ and T₈ cages are prepared by the careful hydrolysis of compounds of the type RSiX₃. Unno and Matsumoto have prepared T₆ cages from 1,1,3,3-tetrahydroxydisiloxane units using dicyclohexylcarbodiimide.¹⁵ This route gives T₆ cages when bulky substituents are employed such as *tert*-butyl or 1,1,2-trimethylpropyl, however, we have obtained T₈ cages with less bulky groups such as cyclohexyl.⁷ We have selectively prepared T₆ cages in reasonable yield by the “non-aqueous” hydrolysis of trichlorosilanes.¹⁶

Based on Unno's strategy we decided to prepare compounds of the type **8**, which we could link together to form cages using our tetrabutylammonium fluoride methodology.^{7,8} In this reaction a solution of tetrabutylammonium fluoride in THF containing 5% water leads to hydrolysis and preferential silsesquioxane cage formation (Scheme 3).

A range of disubstituted 1,1-bis(dichlorosilyl)methanes, **10**, could be prepared by simple hydrosilylation of the commercially available 1,1-bis(dichlorosilyl)methane, **9**. This was converted into the dialkoxysilane, **8**, by reaction with an alcohol in the presence of base.

We thus prepared the bis(*n*-heptyldiethoxysilyl)methane **8** (R = C₅H₁₁) by reacting **9** with heptene in the presence of chloroplatinic acid followed by treatment with ethanol-triethylamine.¹⁷ Reaction of **8** with tetra-*n*-butylammonium fluoride in a 1 : 1 molar ratio in dichloromethane at room temperature for 16 h followed by removal of the solvent and washing with acetone gave a gel that displayed four peaks in the ²⁹Si NMR spectrum.¹⁸ Column chromatography gave two



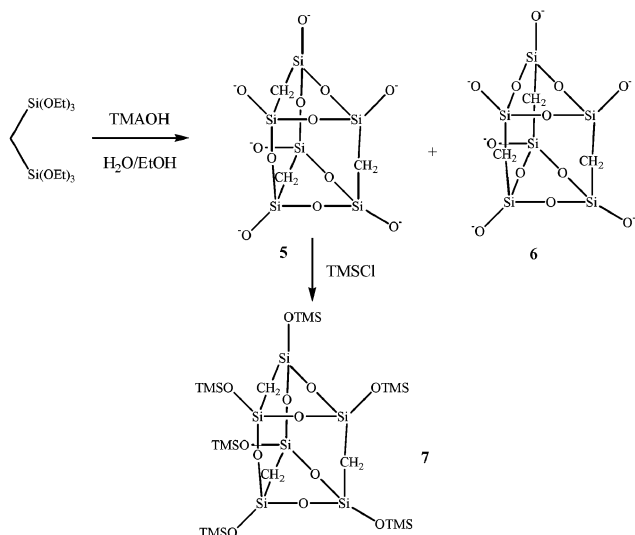
Scheme 1 The possible isomers of D₆ and D₈ spherosilicone cages.

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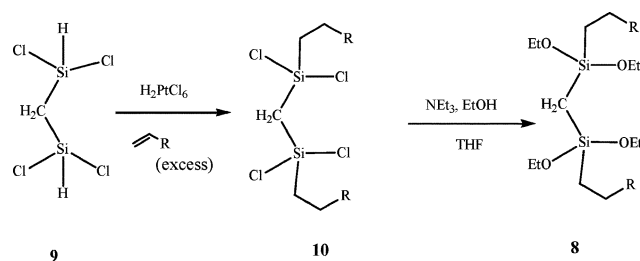
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† Electronic supplementary information (ESI) available: Details of syntheses, characterisation, crystallographic data and selected bond angles and lengths. CCDC 670401 and 670402. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b808456d



Scheme 2 Synthesis of siloxane-based hybrid cages with methylene groups in the frameworks.¹⁴



Scheme 3 Synthetic route to disubstituted 1,1-bis(dialkoxysilyl)-methanes.

fractions. The first fraction (17% yield) had two peaks in the ^{29}Si NMR spectrum at -26.27 and -26.86 ppm and gave a MALDI-TOF spectrum that matched compounds **3** and **4** ($R = \text{heptyl}$). Fractional recrystallisation using a dichloromethane–acetone mixed solvent gave crystals of one isomer with a single peak at -26.27 ppm in the ^{29}Si NMR spectrum. The single-crystal X-ray structure is shown in Fig. 1 confirming it has the structure **4**.[‡] We assume the two isomeric forms **3** and **4** co-eluted from the column chromatography and although we were not able to purify compound **3**, we suggest that it exhibits the peak at -26.86 ppm in the ^{29}Si NMR spectrum of the first fraction. Based on the integration of the ^{29}Si peaks **3** and **4** are obtained in a ratio of 1 : 3.

The second fraction from the column chromatography (42% yield) again exhibited two peaks in the ^{29}Si NMR spectrum at -12.06 ppm and -18.75 ppm in a ratio of about 1 : 2. MALDI-TOF analysis gave a peak corresponding to the corresponding D_6 cage. Again we obtained a crystalline solid after recrystallisation using a dichloromethane–acetone mixed solvent and the single-crystal X-ray structure[‡] is shown in Fig. 2 confirming it has the structure **2**, as suggested by Cooke *et al.*¹³ In this compound the silicon atoms in the cage are in two different environments and so, based on the ^{29}Si NMR evidence, we infer that only one D_6 compound was formed. Compound **2** corresponds to the same isomer that Shimojima and Kuroda obtained when forming the corresponding

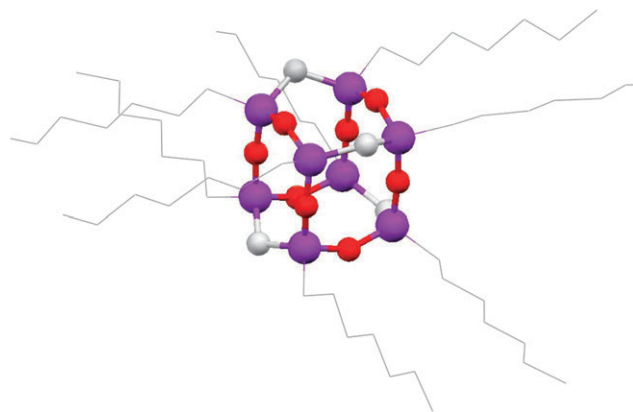


Fig. 1 X-Ray crystal structure of the octaheptyl D_8 cage **4**. Silicon atoms are shown in purple, oxygen atoms in red and carbon atoms in grey. The arms are represented as a wire frame to emphasise the cage structure. Selected distances (\AA): Si–C (cage) = $1.842(6)$, Si–O (top face) = $1.642(2)$, Si–O (side face) = $1.616(2)$; selected bond angles ($^\circ$): Si–C–Si = $116.8(3)$, O–Si–O = $109.1(2)$, C–Si–O (top face) = $108.9(3)$, C–Si–O (side face) = $110.0(3)$.

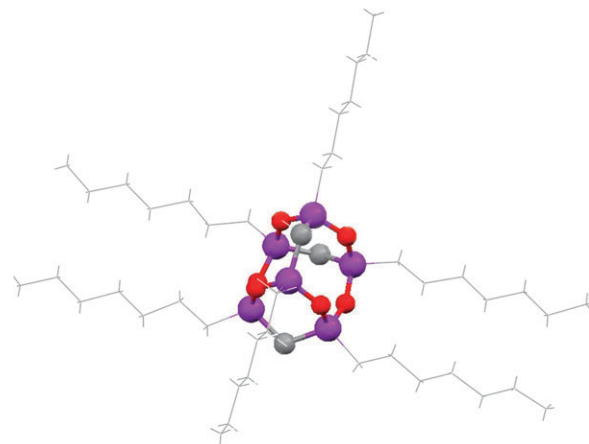


Fig. 2 X-Ray crystal structure of the hexaheptyl D_6 cage **2**, using the same representation as in Fig. 1. Selected distances (\AA): Si–C (cage top face) = $1.860(10)$, Si–C (cage bottom edge) = $1.833(11)$, Si–O (top face) = $1.632(7)$, Si–O (side face upper) = $1.651(7)$, Si–O (side face lower) = $1.660(8)$; selected bond angles ($^\circ$): Si–C–Si (top face) = $112.6(5)$, Si–C–Si (bottom edge) = $119.9(6)$, Si–O–Si (top face) = $144.7(5)$, Si–O–Si (side face) = $135.6(4)$, O–Si–O (Si4 ring) = $110.0(4)$, O–Si–O (Si3 ring) = $106.8(4)$, C–Si–O (top face) = $108.7(5)$, C–Si–O (side face) = $110.2(5)$, C–Si–O (bottom edge) = $109.6(4)$.

T cages, however, unlike Shimojima and Kuroda we were unable to observe any of the other isomer.¹⁴

The X-Ray crystal structure of compound **3** (Fig. 1) shows that instead of spreading to occupy all the space the chains take up a linear arrangement in the direction of the Si–CH₂–Si units effectively creating a 17 atom linear chain.

The chains on one face of the D_8 extend in one direction and the chains on the opposite face in an orthogonal direction. The Si–CH₂–Si bond angle in the cage is about 118° whereas the Si–O–Si bond angle is about 160° as opposed to about 150° in conventional T_8 cages. The orthogonal arrangement of the chains means they pack in layers as shown in Fig. 3. The chains on one face of the cage are aligned in either side with the chains

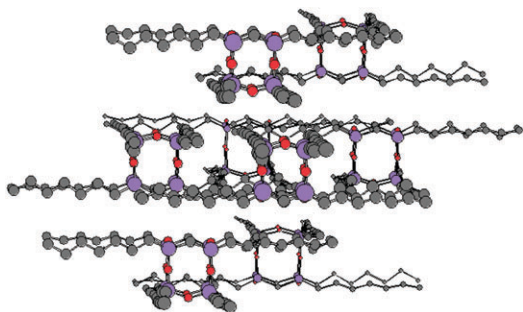


Fig. 3 Packing of the octaheptyl D_8 cages, **3**, in layers.

of two other cages. The cages are offset in order for the chains on the other face to also line up. These linear arrays of cages then line up in the same layer with a linear array of cages where the chains lie in the orthogonal direction. These monolayers then stack to give the three dimensional packed array.

Fig. 2 shows a similar pattern for the D_6 cages. On one D_4 face the chains are linear and point in the same direction.

Opposite this face the two heptyl chains are arranged in an orthogonal direction. The Si-CH₂-Si bond angle in the D_3 face of the cage is about 113° and the Si-CH₂-Si bond angle in the D_4 face of the cage is about 120°. The Si-O-Si bond angle in the D_3 face of the cage is about 134° and the Si-O-Si bond angle in the D_4 face of the cage is about 146°. As Fig. 4 shows again the chains pack in layers but the cages provide a bridge between the layers. Again the chains on the D_4 face align with each other to form linear arrays, but because the opposite face has only one set of chains, two such layers interdigitate their single strands in an orthogonal arrangement.

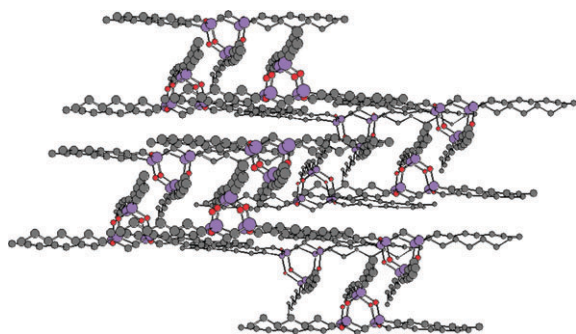


Fig. 4 Packing of the hexaheptyl D_6 cages, **2**, in layers.

In conclusion we have prepared and characterised a D_8 and a D_6 cage and for the first time obtained their X-ray crystal structure. There is also evidence for the formation of the D_8 isomer. We are at present synthesising similar disubstituted 1,1-bis(diethoxysilyl)methanes with the intention of preparing a range of such D cages.

Notes and references

† Crystallographic data: Suitable crystals of **2** and **4** were selected and data collected on a Bruker Nonius KappaCCD Area Detector at the window of a Bruker Nonius FR591 rotating anode ($\lambda_{Mo-K\alpha} = 0.71073 \text{ \AA}$) driven by COLLECT software at 120 K. The structures were determined

in SHELXS-97 and refined using SHELXL-97. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were included in idealized positions with thermal parameters riding on those of the parent atom.

Data for **2**: Colourless needle, size = $0.32 \times 0.08 \times 0.03 \text{ mm}$, $C_{45}H_{96}O_8Si_6$; $M_r = 901.76$, $T = 120(2) \text{ K}$; triclinic, space group $P1$, $a = 11.9106(15)$, $b = 13.264(2)$, $c = 18.823(4) \text{ \AA}$, $\alpha = 101.383(7)^\circ$, $\beta = 93.251(7)^\circ$, $\gamma = 111.848(10)^\circ$; $V = 2678.1(8) \text{ \AA}^3$, $Z = 2$; $D_c = 1.118 \text{ Mg m}^{-3}$, $\mu = 0.197 \text{ mm}^{-1}$, reflections collected = 29934, independent reflections = 9172 ($R_{int} = 0.2482$), final R indices [$I > 2\sigma(I)$], $R_1 = 0.1188$, $wR_2 = 0.2407$; R indices (all data), $R_1 = 0.2799$, $wR_2 = 0.3210$.

Data for **3**: Colourless plate, size = $0.46 \times 0.22 \times 0.03 \text{ mm}$, $C_{60}H_{128}O_8Si_8$; $M_r = 1202.34$, $T = 120(2) \text{ K}$; monoclinic, space group $C2/c$, $a = 17.1468(8)$, $b = 34.4636(15)$, $c = 13.2620(7) \text{ \AA}$, $\beta = 111.651(2)^\circ$; $V = 7284.1(6) \text{ \AA}^3$, $Z = 4$; $D_c = 1.096 \text{ Mg m}^{-3}$, $\mu = 0.193 \text{ mm}^{-1}$, reflections collected = 33358, independent reflections = 8180 ($R_{int} = 0.1003$), final R indices [$I > 2\sigma(I)$], $R_1 = 0.0613$, $wR_2 = 0.1256$; R indices (all data), $R_1 = 0.1620$, $wR_2 = 0.1574$.

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- A. R. Bassindale, I. A. MacKinnon, M. G. Maesano and P. G. Taylor, *Chem. Commun.*, 2003, 1382.
- Synthesis of bis(heptyldiethoxysilyl)methane*: Bis(dichlorosilyl)methane (0.4929 g, $2.303 \times 10^{-3} \text{ mol}$), *n*-heptene (1.04 g, 0.0106 mol) and 0.20 mL of a 0.02 mol L⁻¹ solution of H₂PtCl₆ in isopropyl alcohol were placed in a small vial. The vial was capped and placed in an oil-bath at 60 °C for 24 h. After cooling to room temperature, the product was transferred to a solution of ethanol (1.15 g, 0.025 mol) in 200 mL dry THF. Then dry triethylamine (1.20 g, 0.0117 mol) was added to the solution dropwise, white solid was starting coming out during the dropping. After finishing the dropping, the solution was kept stirring for another 2 h at room temperature. The solution was filtered and the remaining solution was put under vacuum to remove THF and other low boiling point impurities. The oil left was purified by column chromatography (SiO₂/CH₂Cl₂) to give a colourless oil. Yield: 0.8048 g, 78%.
- Synthesis of D₆ and D₈ cages*: (Bis(heptyldiethoxysilyl)methane (0.1275 g, $2.846 \times 10^{-4} \text{ mol}$) and tetrabutylammonium fluoride (5% H₂O) (0.284 mL, 1 M in THF, $2.84 \times 10^{-4} \text{ mol}$) were mixed together in 50 mL CH₂Cl₂ and stirred at room temperature for overnight. Then the solution was put into a separating funnel together with 20 mL H₂O and 200 mL CH₂Cl₂. After the extraction, the organic layer was dried by MgSO₄ before the removal of solvent under vacuum. The product was washed with 20 mL acetone to give a wax-like solid. The solid was purified by column chromatography (SiO₂/hexane) to give two fractions.