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The higher hydridospherosiloxanes: synthesis and structures of $H_nSi_nO_{1.5n}$ ($n=12, 14, 16, 18$) ☆

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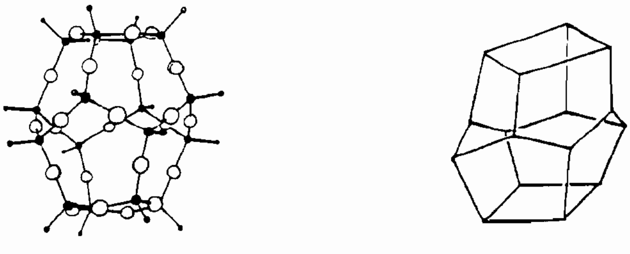
Abstract

The preparation of the four pure compounds O_h-$H_8Si_8O_{12}$, D_{5h}-$H_{10}Si_{10}O_{15}$, D_{2d}-$H_{12}Si_{12}O_{18}$ and D_{3h}-$H_{14}Si_{14}O_{21}$ is described in detail. These compounds were prepared in 0.5, 3.6, 3.5 and 1.1% yields, respectively, based on the starting material $HSiCl_3$. The synthesis was also scaled up to make gram quantities of these compounds. In addition, preparative gas chromatography was used to isolate mixtures of isomers of $H_{14}Si_{14}O_{21}$ and $H_{16}Si_{16}O_{24}$, from which the ^1H and ^{29}Si NMR chemical shift values of particular isomers, and in one case the X-ray crystal structure, were determined. The structure of the major isomer of $H_{16}Si_{16}O_{24}$ is proposed, based on a complete enumeration of all possible isomers of this composition that have chemically reasonable structures and the strong correlation observed between topological features of the polyhedral structures of these compounds and $^{29}Si\{^1H\}$ NMR chemical shift values. This isomer has idealized D_{4d} symmetry, with two 4-rings and eight 5-rings arranged such that there are two sets of eight symmetry-equivalent silicon atoms.

Keywords: Crystal structures; Silicon compounds; Siloxane compounds; Hydridospherosiloxane compounds

1. Introduction

Several years ago we reported a new synthetic route to trimethylsilylated spherosilicates from hydridospherosiloxane precursors [1]. These precursor compounds, which have the general composition $H_nSi_nO_{1.5n}$, were isolated from a complex mixture obtained through the controlled hydrolysis of trichlorosilane in a biphasic reaction medium, as described in 1970 by Frye and Collins [2,3]. We have previously published only partial descriptions [1,4] of the long and involved purification protocol we developed to obtain the pure hydridospherosiloxanes. In recent years, however, interest in the use of these compounds as precursors of ceramics and macromolecular materials with unique architectures and as model compounds for spectroscopic studies has been growing, as evidenced by the fact that the number of publications dealing with these compounds grew from only 8 in the years up to 1989 to about 42 by September 1994 [1–42].



Scheme 1. D_{4d}-$H_{16}Si_{16}O_{24}$.

In view of this, we think it necessary now to publish the full experimental details of the synthesis and comment on the possible structures of these compounds, in particular one that has the composition $H_{16}Si_{16}O_{24}$ (Scheme 1). Our comments are based on the extensive set of ^1H and $^{29}Si\{^1H\}$ NMR data that we have collected on the four pure compounds that we isolated and the various fractions we obtained during the course of their purification.

2. Experimental

The procedure followed to prepare the pure compounds O_h-$H_8Si_8O_{12}$, D_{5h}-$H_{10}Si_{10}O_{15}$, D_{2d}-$H_{12}Si_{12}O_{18}$

☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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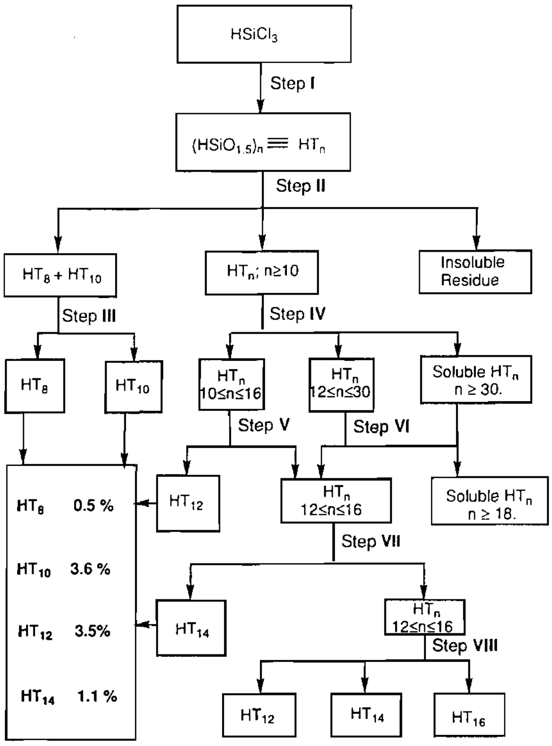

Fig. 1. Flow chart outlining the procedure followed to prepare the pure compounds O_h-$H_8Si_8O_{12}$, D_{5h}-$H_{10}Si_{10}O_{15}$, D_{2d}-$H_{12}Si_{12}O_{18}$ and D_{3h}-$H_{14}Si_{14}O_{21}$ and the mixtures of isomers of HT_{14} and HT_{16}. The molecular formula $(HSiO_{1.5})_n$ is abbreviated HT_n.

and D_{3h}-$H_{14}Si_{14}O_{21}$ is outlined in the flow chart in Fig. 1. The molecular formula, $(HSiO_{1.5})_n$, is abbreviated to HT_n in the figure and in all subsequent occurrences in this paper. The individual steps (I–VIII) shown in Fig. 1 are described in detail below. All steps were repeated to check reproducibility, and the quantities of reagents or products in the second preparation are given in parentheses. The impure products in steps III, V and VII from both preparations were pooled and purified by careful washing with hexane. The yields reported of the HT_n compounds correspond to the total yield from the two preparations. The relative amounts of the HT_n species in the various fractions shown in Fig. 1 were determined from relative peak areas on gas chromatograms obtained on a Varian 3700A instrument equipped with a TCD detector and an Alltech RSL-150 wide-bore column (0.53 mm×15 m).

2.1. Preparation of HT_n mixture

Step I: A mixture of cyclohexane and toluene (400 ml, 2:1 vol./vol.) was added to a 2 l round-bottom flask containing H_2SO_4 (200 ml, ca. 93% wt./wt.). This mixture was stirred vigorously with a mechanical stirrer for 30 min so that a milky dispersion was obtained. A solution of $HSiCl_3$ (20 ml, ca. 0.2 mol) in a mixture of cyclohexane and toluene (200 ml, 2:1 vol./vol.) was added dropwise over a period of 6 h to the two-phase mixture in the flask. The final mixture was stirred until the formation of HCl had ceased. The almost clear organic layer (ca. 500 ml) was separated from the acid layer and washed gently with four portions of H_2SO_4 (50 ml each, 50% wt./wt.), followed by six portions of distilled water (60 ml each). The solvents were then stripped off on a rotary evaporator to give 9.49 g (9.29 g) of a white powder. The infrared spectrum (Nujol null, KBr plates) showed no signs of residual hydroxyl groups.

The ^1H NMR spectrum (Fig. 2) showed a broad asymmetric peak between $\delta = 4.2$ and $\delta = 4.9$ with a maximum at around $\delta = 4.35$, on which were superimposed several sharp lines that can be assigned to individual hydridospherosiloxane species as described below.

Gas chromatographic analysis (HP5890A, self-referencing TCD, Alltech RSL-200, 0.2 μm, 0.25 mm i.d., length 30 m, temperature program: 50 °C/1 min//15 °C min^{-1}//250 °C/15 min) showed several volatile components (Fig. 3). These were unambiguously assigned using GC–MS analysis with high-resolution single-ion detection (Fig. 4) to compounds of composition HT_n, $n = 8,10,12,14,16,18,20$. The relative amounts of these components based on peak areas in the GC trace shown in Fig. 3 were HT_8 (5.7%), HT_{10} (16.7%), HT_{12} (36.6%), HT_{14} (23.9%), HT_{16} (10.5%), HT_{18} (3.7%) and HT_{20} (2.9%).

Gel permeation chromatographic analysis (refractive index detector) of a 200 μL aliquot of a solution of the HT_n mixture in toluene (5 mg ml^{-1}) on two coupled GPC columns (PLgel 10 μm, 500 Å, 30 cm and PLgel 10 μm, 100 Å, 30 cm) showed a multimodal molecular weight distribution (Fig. 5) extending beyond the exclusion limit of the columns used (>40 000 daltons).

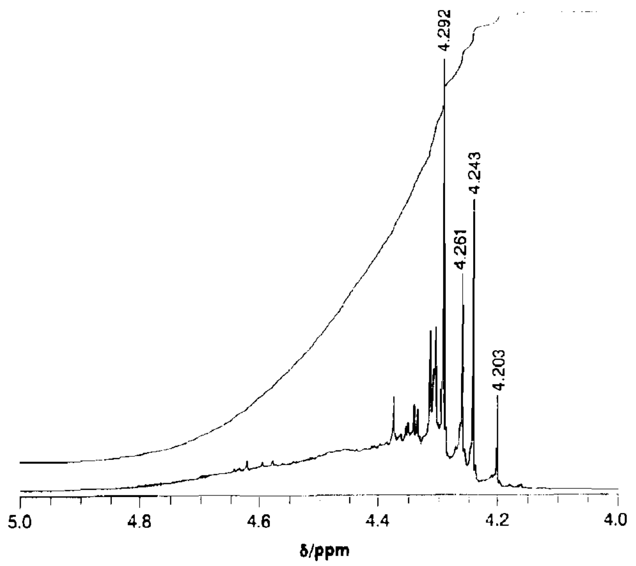

Fig. 2. ^1H NMR (C_6D_6, $(CH_3)_4Si = 0$, 500 MHz) spectrum of the mixture of HT_n compounds obtained in Step I of the synthetic procedure outlined in Fig. 1.

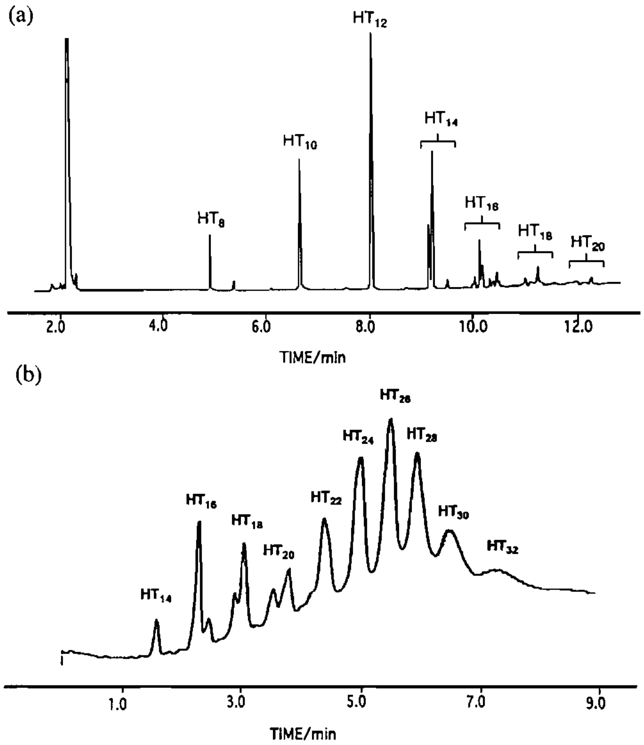

Fig. 3. (a) Gas chromatographic analysis on a narrow-bore column, of the mixture of HT_n compounds obtained in Step I of the synthetic procedure outlined in Fig. 1. (b) Gas chromatographic analysis on a wide-bore column, of Fraction 1 in Step VI, showing the second set of volatile HT_n compounds with 90% of the compounds having $n \geq 18$ (cf. Footnote 6).

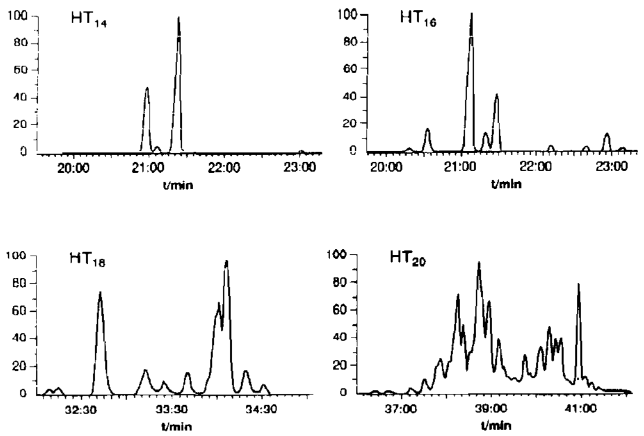

Fig. 4. Gas chromatographic analysis with high-resolution single-ion detection, confirming the assignment of the peaks observed in the GC trace shown in Fig. 3. Only one isomer each was observed of the three compounds HT_8, HT_{10} and HT_{12}. The traces show four well-resolved isomers of HT_{14}, at least nine isomers of HT_{16}, ten to twelve isomers of HT_{18} and many unresolved isomers of HT_{20}.

The low-molecular-weight peaks ($t > 14.4$ min) can be assigned to the hydridospherosiloxanes [12] and account for about 28% of the total area under the trace.

2.2. Preparation of HT_8 and HT_{10}

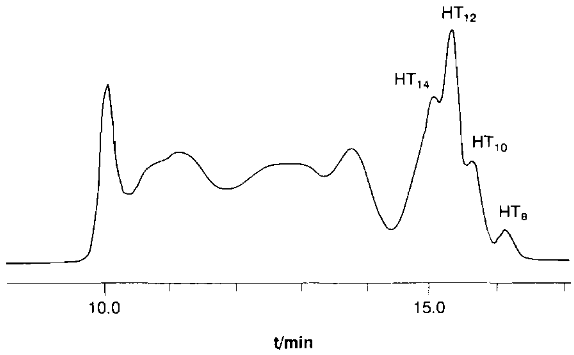

Fig. 5. Analysis by gel permeation chromatography showing that the low-molecular-weight fraction ($t > 14.4$ min) consisting of hydridospherosiloxanes accounts for about 28% of the total mixture. The second hump in this trace corresponds to the volatile compounds seen in the GC trace in Fig. 3(b).

Step II: The HT_n mixture (9.0 g (9.0 g)) obtained in Step I was dissolved in 120 ml benzene and the solution was clarified by centrifugation. The insoluble residue (0.3 g (0.4 g)) was discarded. The volume of the solution was slowly reduced to ca. 10 ml. Fine white crystals were obtained, which after recrystallization from benzene weighed 0.66 g (0.65 g). GC analysis showed that this crop of crystals was a mixture with the approximate composition HT_8 (17%), HT_{10} (76%) and HT_{12} (6%).

Step III: The crystals obtained in both preparations were mixed, washed with pentane (3 ml total) to remove residual HT_{12} and placed in a sublimator. A fraction (0.23 g) volatile at 0.01 torr, 30–35 °C, was collected for 2 days. It consisted of HT_8 (70%) and HT_{10} (30%). The residue was mostly HT_{10} (96%).

The volatile fraction was washed with small portions (1 ml) of pentane until the washings were free of HT_{10}. The residue, which weighed 0.1 g, was pure HT_8. The yield, based on $HSiCl_3$, was 0.5%.

Anal. Calc. for $H_8Si_8O_{12}$: C, 0.0; H, 1.90. Found: C, 0.25; H, 1.85%. MS: $(M-H)^+$; $m/z = 423$ d. IR (Nujol mull, KBr plates): 2290 (s), 1140 (vs), 918 (w), 885 (sh), 870 (s), 500 (sh), 470 (w), 395 (m) cm^{-1}. ^1H NMR (C_6D_6, $(CH_3)_4Si = 0$, 500 MHz): $\delta = 4.203$ (s). $^{29}Si\{^1H\}$ NMR (C_6D_6, $(CH_3)_4Si = 0$, $Cr(acac)_3$ 0.026 M, 59.6 MHz): $\delta = -84.452$ (s).

The residue from the sublimator was washed with small portions of pentane (1 ml) until the washings were free of HT_8. The weight of pure HT_{10} obtained was 0.76 g. The yield, based on $HSiCl_3$, was 3.6%.

Anal. Calc. for $H_{10}Si_{10}O_{15}$: C, 0.0; H, 1.90. Found: C, 0.26; H, 1.95%. MS: $(M-H)^+$; $m/z = 529$ d. IR (Nujol mull, KBr plates): 2280 (s), 1145 (vs), 925 (w), 880 (s), 865 (sh), 565 (m), 390 (w) cm^{-1}. ^1H NMR (C_6D_6, $(CH_3)_4Si = 0$, 500 MHz): $\delta = 4.244$ (s). $^{29}Si\{^1H\}$ NMR (C_6D_6, $(CH_3)_4Si = 0$, $Cr(acac)_3$ 0.026 M, 59.6 MHz): $\delta = -86.255$ (s).

2.3. Preparation of HT_{12}

Step IV: The volume of the mother liquor from Step II was adjusted to about 10 ml and applied to the top of a 25 mm×100 cm column that was packed (bed height = 90 cm) with a mixture of BioBeads SX-1 and SX-2 (1:2 wt./wt.) fully swollen in benzene. The column was eluted with benzene at a head pressure of 2 psig at a flow rate of around 3.5 ml min^{-1}. The first 150 ml of eluent was the void volume and was discarded. The next 100 ml contained 4.66 g (4.19 g) of residue (Fraction 1) after the solvent was removed. This fraction had no volatile component detectable by GC. The next 50 ml contained 1.68 g (1.67 g) of residue (Fraction 2), which consisted of volatile HT_n, $n = 12,14,16...30$. The first three constituted about 50% of the total. The last 100 ml contained 1.36 g (1.29 g) of residue (Fraction 3), which consisted of HT_{10} (10%), HT_{12} (52%), HT_{14} (23%), HT_{16} (9%) and some higher oligomers.

Step V: Fraction 3 was dissolved in about 10 ml of pentane and the volume was reduced by slow evaporation to less than 1 ml. The white crystals that formed were separated from the mother liquor and washed with 0.25 ml of pentane. The composition of the crystalline residue, which weighed 0.66 g (0.68 g), was approximately HT_8 (4%), HT_{10} (17%), HT_{12} (72%) and HT_{14} (7%). The solvent was removed from the mother liquor to yield 0.7 g (0.6 g) of residue whose composition was HT_{12} (36%), HT_{14} (47%), HT_{16} (11%), and a mixture of higher oligomers (6%).

The crystals obtained from both preparations were pooled and recrystallized from pentane by slow evaporation of the solvent. The mother liquor (0.2 ml) was removed and the crystals were transferred to a sublimator, where the fraction volatile at 0.01 torr and 40–45 °C was collected over a period of 2 days. The residue was pure HT_{12} and weighed 0.74 g. The yield, based on $HSiCl_3$, was 3.5%.

Anal. Calc. for $H_{12}Si_{12}O_{18}$: C, 0.0; H, 1.90. Found: C, 0.22; H, 1.90%. MS: $(M-H)^+$; $m/z = 635$. IR (Nujol mull, KBr plates): 2260 (s), 1140 (vs), 875 (vs), 565 (m), 390 (w) cm^{-1}. ^1H NMR (C_6D_6, $(CH_3)_4Si = 0.0$, 500 MHz): $\delta = 4.294$ (s,2); 4.263 (s,1). $^{29}Si\{^1H\}$ NMR (C_6D_6, $(CH_3)_4Si = 0.0$, $Cr(acac)_3$ 0.026 M, 59.6 MHz): $\delta = 85.784$ (s,1); -87.760 (s,2).

2.4. Preparation of HT_{14}

Step VI: Fraction 2 from Step IV was dissolved in benzene (5 ml) and applied to the top of a 25 mm (i.d.)×100 cm column packed with BioBeads SX-4 fully swollen in benzene. The column was eluted with benzene at a head pressure of 2 psig and a flow rate of around 3.5 ml min^{-1}. The first 180 ml was the void volume and was discarded. The next 90 ml contained 1.08 g (1.18 g) of a residue (Fraction 1) that consisted mainly of HT_n, $n = 18, 20...30$ (ca. 90%). The last 50 ml contained 0.48 g (0.37 g) of residue (Fraction 2) that consisted of HT_{12} (35%), HT_{14} (42%) and HT_{16} (23%).

Step VII: Fraction 2 from Step VI and the residue from the mother liquor of Step V were mixed to give 1.18 g (0.97 g) of a mixture whose composition was approximately HT_{12} (33%), HT_{14} (39%) and HT_{16} (13%). This was taken into a drybox and dissolved in 1.2 ml (1.0 ml) of hot tetrahydrofuran, to which was added hot acetonitrile (3.0 ml (2.5 ml)) until a slightly turbid solution was obtained. This was allowed to cool slowly to room temperature and then cooled further to ca. 10 °C. The crystals that had formed were separated from the mother liquor and washed with a cold mixture of tetrahydrofuran and acetonitrile (1:9 vol./vol.). The solvents were stripped off under vacuum in the drybox. The crystals weighed 0.177 g (0.186 g). The composition was approximately HT_{12} (11%) and HT_{14} (88%). The residue from the mother liquor weighed 0.95 g (0.76 g), and its approximate composition was HT_{12} (50%), HT_{14} (28%) and HT_{16} (17%).

The crystals of impure HT_{14} obtained from both preparations were pooled and transferred to a sublimator. The fraction volatile at 0.01 torr, 50–55 °C, was collected over a period of 2 days. The residue was HT_{14} and weighed 0.24 g. The yield, based on $HSiCl_3$, was 1.1%.

Anal. Calc. for $H_{14}Si_{14}O_{21}$: C, 0.0; H, 1.90. Found: C, 3.28; H, 2.12% [2]. MS: $(M-H)^+$; $m/z = 741$. IR (Nujol mull, KBr plates): 2260 (s), 1150 (vs), 880 (vs), 575 (m) cm^{-1}. ^1H NMR (C_6D_6, $(CH_3)_4Si = 0.0$, 500 MHz): $\delta = 4.306$ (s,3); 4.316 (s,3); 4.343 (s,1). $^{29}Si\{^1H\}$ NMR (C_6D_6, $(CH_3)_4Si = 0.0$, $Cr(acac)_3$ 0.026 M, 59.6 MHz): $\delta = -87.890$ (s,3); -88.034 (s,3); -89.711 (s,1).

2.5. Separation of HT_{12}, HT_{14} and HT_{16}

Step VIII: The residues from the mother liquor in Step VII from both preparations were combined and then separated into three fractions using preparative gas chromatography. A GOW-MAC 550 instrument modified for preparative work was used with a copper column (9.5 mm i.d. and 300 cm length) that was packed with 13.5% OV-17 on Chromosorb-W.

The first fraction, which weighed 0.31 g, was predominantly HT_{12} (>92%). The second fraction was mostly HT_{14} (85%) and weighed 0.22 g. The third fraction was mostly HT_{16} (80%) and weighed 0.11 g.

GC–MS analysis of the second fraction showed that the HT_{14} was a mixture of two major isomers (in approximately equal amounts) and a minor isomer (ca. 6%). One of these major isomers was the isomer isolated in Step VII. The ^1H and $^{29}Si\{^1H\}$ NMR resonances arising from the second major isomer were identified in the NMR spectra of the mixture, as described in the next section.

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[2] The crystals submitted for analysis contained benzene. *Anal.* Calc. for $H_{14}Si_{14}O_{21} \cdot (1/3)C_6H_6$: C, 3.12; H, 2.08. Found: C, 3.28; H, 2.12%. A strong peak at m/z 78 (M^+) confirmed this.

Table 1
^{1}H NMR and ^{29}Si{^{1}H} NMR chemical shifts of the hydridospherosiloxanes O_h-HT$_8$, D_{5h}-HT$_{10}$, D_{2d}-HT$_{12}$, D_{3h}-HT$_{14}$, C_{2v}-HT$_{14}$ and D_{4d}-HT$_{16}$

Sym.-HT$_n$	δ (ppm) [a]		
	(Benzene-d_6, ^{1}H 500 MHz)	(Cyclohexane-d_{12}, ^{1}H 500 MHz)	(Benzene-d_6, ^{29}Si{^{1}H} 59.6 MHz)
O_h-HT$_8$	4.203 (s,1)	4.131 (s,1)	−84.452 (s,1)
D_{5h}-HT$_{10}$	4.244 (s,1)	4.175 (s,1)	−86.255 (s,1)
D_{2d}-HT$_{12}$	4.263 (s,1)	4.159 (s,1)	−85.784 (s,1)
	4.294 (s,2)	4.210 (s,2)	−87.760 (s,2)
D_{3h}-HT$_{14}$	4.316 (s,3)	4.226 (s,3)	−87.890 (s,3)
	4.306 (s,3)	4.228 (s,3)	−88.034 (s,3)
	4.343 (s,1)	4.272 (s,1)	−89.711 (s,1)
C_{2v}-HT$_{14}$	4.264 (s,1)	4.280 (s,1)	−85.354 (s,1)
	4.307 (s,2)	4.278 (s,2)	−85.762 (s,1)
	4.308 (s,1)	4.218 (s,2)	−87.676 (s,2)
	4.355 (s,2)	4.204 (s,1)	−87.947 (s,2)
	4.352 (s,1)	4.149 (s,1)	−88.720 (s,1)
D_{4d}-HT$_{16}$	4.310 (s,1)	4.275 (s,1)	−88.095 (s,1)
	4.375 (s,1)	4.211 (s,1)	−89.272 (s,1)

[a] $Me_4Si = 0.0$.

^{1}H NMR (C_6D_6, $(CH_3)_4Si = 0.0$, 500 MHz): $\delta = 4.264$ (s,1); 4.307 (s,2); 4.308 (s,1)[3]; 4.335 (s,2); 4.352 (s,1). ^{29}Si{^{1}H} NMR (C_6D_6, $(CH_3)_4Si = 0.0$, $Cr(acac)_3$ 0.026 M, 59.6 MHz): $\delta = -85.354$ (s,1); −85.762 (s,1); −87.676 (s,2); −87.947 (s,2); −88.720 (s,1).

GC–MS analysis of the HT$_{16}$ isolated in this step showed that it too was a mixture of isomers, with one major isomer (ca. 50%). The ^{1}H and ^{29}Si{^{1}H} NMR spectra both showed a large number of resonances. Of these, two resonances with equal intensities accounted for ca. 50% of the total intensity and were assigned to the major isomer.

^{1}H NMR (C_6D_6, $(CH_3)_4Si = 0.0$, 500 MHz): $\delta = 4.375$ (s,1); 4.310 (s,1). ^{29}Si{^{1}H} NMR (C_6D_6, $Me_4Si = 0.0$, $Cr(acac)_3$ 0.026 M, 59.6 MHz): $\delta = -88.095$ (s,1); −89.272 (s,1).

3. Results

The first step of the long and involved synthetic procedure described in the previous section was based on a method of synthesizing a soluble silanol-free mixture of oligomers of composition $H_nSi_nO_{1.5n}$, which had been described by Frye and Collins in 1970 [2,3]. The purification protocol that we developed to prepare pure hydridospherosiloxanes from this mixture is reproducible, as shown by our results from two separate parallel preparations.

The ^{1}H and ^{29}Si{^{1}H} NMR data given in Table 1 were consistent with the known structures of the three pure compounds O_h-HT$_8$, D_{5h}-HT$_{10}$ and D_{2d}-HT$_{12}$, which had been isolated in small quantities using preparative gas chromatography by Frye and Collins [2], and with the structure of D_{3h}-HT$_{14}$, determined by X-ray diffraction methods [1]. The ^{1}H NMR spectrum of a solution made by dissolving approximately equal amounts of these four compounds in benzene-d_6 is shown in Fig. 6, and the structures of these compounds are shown schematically in Fig. 7.

A single crystal of a second isomer of HT$_{14}$ was picked out of the mixture of HT$_{14}$ isomers prepared in Step VIII of the purification protocol described earlier and its structure, also shown in Fig. 7, was determined by X-ray diffraction methods [1]. The idealized symmetry of this isomer was C_{2v}, with an expected intensity pattern of 2:2:1:1:1 in its NMR spectra. The peaks in the NMR spectra arising from this isomer

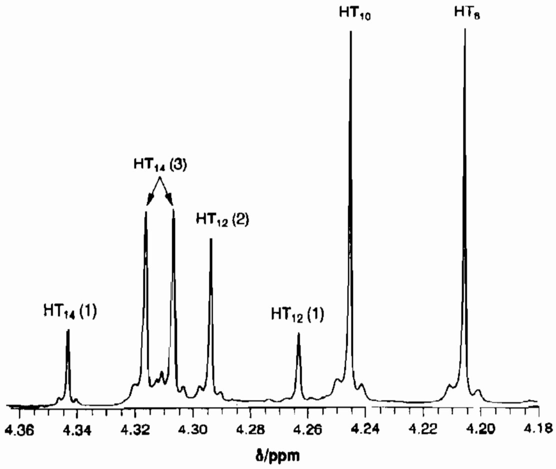

Fig. 6. ^{1}H NMR (C_6D_6, $(CH_3)_4Si = 0$, 500 MHz) spectrum of a mixture consisting of approximately equal quantities of the pure compounds O_h-HT$_8$, D_{5h}-HT$_{10}$, D_{2d}-HT$_{12}$ and D_{3h}-HT$_{14}$ in benzene-d_6.

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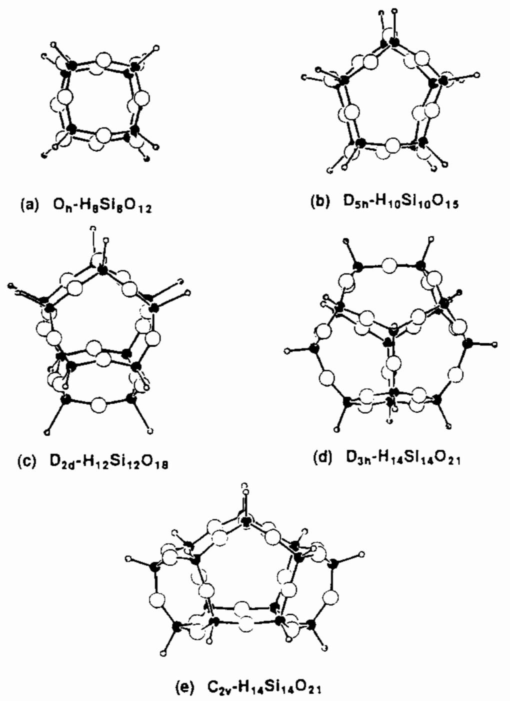
[3] The position of this resonance was calculated from the positions of its ^{29}Si satellites.



(a) O_h-$H_8Si_8O_{12}$ (b) D_{5h}-$H_{10}Si_{10}O_{15}$

(c) D_{2d}-$H_{12}Si_{12}O_{18}$ (d) D_{3h}-$H_{14}Si_{14}O_{21}$

(e) C_{2v}-$H_{14}Si_{14}O_{21}$

Fig. 7. Ball and stick diagrams illustrating the structures of the five well-characterized hydridospherosiloxanes (a) O_h-HT_8, (b) D_{5h}-HT_{10}, (c) D_{2d}-HT_{12}, (d) D_{3h}-HT_{14} and (e) C_{2v}-HT_{14}.

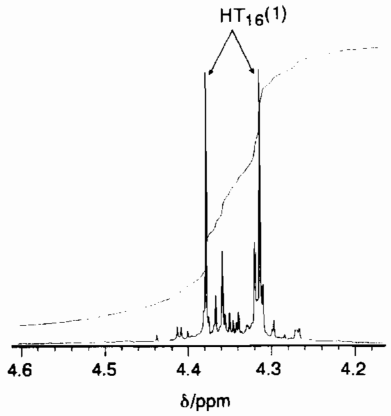


Fig. 8. ^1H NMR (C_6D_6, $(CH_3)_4Si=0$, 500 MHz) spectrum of the mixture of HT_{16} isomers obtained by preparative gas chromatographic methods, showing the two lines of equal intensity that account for about 50% of the integrated intensity.

could then be identified, and their chemical shift values are also given in Table 1. All attempts to prepare pure samples of the major isomer of HT_{16} were unsuccessful, and no single crystals suitable for X-ray analysis could be picked out of the mixture. However, the GC–MS data showed that the mixture of HT_{16} isomers obtained in Step VIII contained one major isomer (≈50%), and the NMR spectrum, shown in Fig. 8, showed two lines of equal intensity that accounted for ≈50% of the total intensity. NMR spectra of partially decomposed samples of HT_{16} mixtures showed no change in the relative intensities of these two lines, which were therefore assigned to the major isomer of HT_{16}.

4. Discussion

The structures of the well-characterized hydridospherosiloxanes can be represented by 3-valent 3-connected convex polyhedra [4], with the vertices representing the Si–H groups in these compounds and each edge representing a Si–O–Si linkage. Another useful way of representing these polyhedra is through the use of straight-line nets drawn by expanding one face and projecting all the remaining edges of the polyhedron onto the plane of this face such that they lie entirely within its boundaries [5]. All possible nets with n nodes can be generated by starting with the complete set of nets with $n-2$ nodes and adding an edge in each of two possible orientations, across all possible symmetry-inequivalent pairs of edges, in each member of this set. Thus starting with the tetrahedron, the simplest polyhedron of this kind, it is possible to generate a complete set of 3-valent 3-connected convex polyhedra with any number of vertices. The mathematical application of this procedure and a complete list of such polyhedra with up to eighteen vertices were described in detail by Grace [43] in 1965 and can be used to interpret the GC–MS analysis data shown in Fig. 4.

The nets representing O_h-HT_8, D_{5h}-HT_{10} and D_{2d}-HT_{12} are shown in Fig. 9(a), (b) and (d), respectively, while Fig. 9(c) represents the hexagonal prismatic structure of D_{6h}-HT_{12}, a compound that was not detected by us in the mixture of hydridospherosiloxanes generated in Step I. The nets shown in Fig. 10(a) and (b) represent the structures of D_{3h}-HT_{14} and C_{2v}-HT_{14}, respectively, which are the first and second most abundant isomers

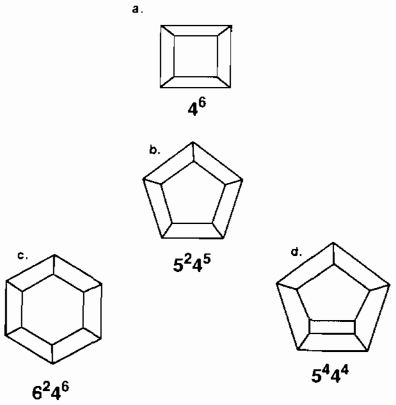


Fig. 9. Straight-line nets representing the structures of the compounds (a) O_h-HT_8, (b) D_{5h}-HT_{10} and (d) D_{2d}-HT_{12}. The net shown in (c) represents the structure of the compound D_{6h}-HT_{12} that does not exist in the mixture. These nets can also be described by a series of numbers $A^aB^bC^c\cdots$, where a, b and c represent the number of faces with A, B and C edges, respectively, as shown in the figure.

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[4] Each vertex of a 3-valent polyhedron is shared by three edges, and a 3-connected polyhedron is one in which a minimum of three edges must be broken to form two separate fragments.

[5] These are often referred to as Schlegel diagrams.

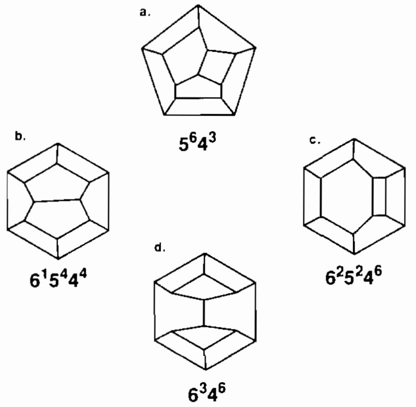

Fig. 10. Straight-line nets representing the structures of the compounds (a) D_{3h}-HT_{14} and (b) C_{2v}-HT_{14}. Nets (c) and (d) represent the possible structures of the other two isomers observed by GC–MS analysis.

of HT_{14}, as shown in Fig. 4, while the nets shown in Fig. 10(c) and (d) represent possible structures for the other two isomers of HT_{14} observed by GC–MS, as described below.

The number of possible 3-connected polyhedral structures[6] of HT_n compounds with 8, 10, 12 and 14 vertices and with no restriction on ring size is sixty-nine, if one does not count separately the enantiomers of compounds with C_1 symmetry such as those represented by the nets shown in Fig. 11(c) and (d). However, if one restricts the ring sizes to the range $4 \leq n \leq 6$, as observed in the five compounds whose structures are known and which account for 82% of the total amount of hydridospherosiloxanes, then this number is reduced to eight, which is close to the number (seven) observed by GC–MS analysis[7]. This indicates that there is a strong preference for the formation of the 3-connected polyhedral hydridospherosiloxanes with ring sizes in the range $4 \leq n \leq 6$ under the conditions of the Frye and Collins procedure.

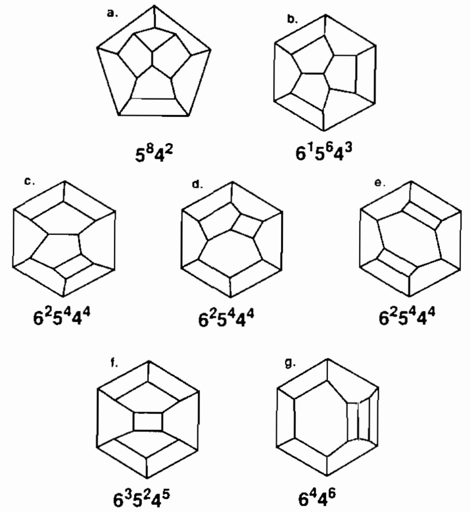

Fig. 11. Straight-line nets representing the structures of the isomers of HT_{16} with ring sizes in the range $4 \leq n \leq 6$. The structure of the major isomer of HT_{16} is represented by either net (a) or net (g), since both represent polyhedra having two sets of eight symmetry-equivalent vertices.

The nets representing all possible isomers of HT_{16} and HT_{18} with ring sizes within this range are shown in Figs. 11 and 12, respectively. It can be seen that there are only seven nets with sixteen vertices having ring sizes in the range $4 \leq n \leq 6$, while Fig. 4 shows that there are at least nine isomers of HT_{16} formed during the synthesis. Thus the restriction on ring sizes is looser in the higher hydridospherosiloxanes; however, the two major isomers, which account for 70% of the total amount of HT_{16}, are still likely to have ring sizes in the range $4 \leq n \leq 6$. The possible structure of the major isomer therefore should be found among the nets shown in Fig. 11.

The ^1H NMR spectrum of the mixture of HT_{16} isomers shown in Fig. 8 shows two major resonances of equal intensity. If these are assigned to the major isomer of HT_{16}, as explained in the previous section, the choice of possible structures is reduced to the two nets shown in Fig. 11(a) and (g), which represent polyhedra with two sets of eight symmetry-equivalent vertices. The polyhedral representations of these two nets and ball-and-stick diagrams of the two possible structures of HT_{16} with D_{4d} and D_{2d} symmetry are shown in Fig. 13(a) and (b), respectively.

The choice between these two structures can be based on the correlation observed between the average of the three Si–O–Si bond angles around each silicon atom and the $^{29}Si\{^1H\}$ NMR chemical shifts. The value of the average Si–O–Si bond angle is also related to a topological feature of the structures of these compounds, viz., the number of 4-rings that include a particular silicon atom. The $^{29}Si\{^1H\}$ shift values listed in Table 1 are retabulated in Table 2 along with the values of the Si–O–Si bond angles and the number of 4-rings. The plot in Fig. 14 shows the linear dependence

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[6] GC analysis of Fraction 1 in Step VI, Fig. 3(b), shows that a second set of volatile compounds HT_n, $n = 22, 24, 26...32$, is present in the HT_n mixture prepared in Step I. This second set of compounds corresponds to the second hump in the GPC analysis trace shown in Fig. 5. These compounds are probably formed from two HT_n precursors with odd values of n which cannot adopt 3-connected structures. The structure of most of these large molecules is thus likely to be a 1-connected polyhedron, which can be derived from two 3-connected polyhedra by opening an edge in each of the two polyhedra and joining them through an additional edge. This would explain the occurrence of a maximum at $n = 26$, since the most abundant 3-connected species is HT_{12}.

[7] The unmarked peaks in Fig. 3(a) were not identified positively; however, they are not spherosiloxanes, since they were not observed by GC–MS analysis using high-resolution single-ion detection.

of the $^{29}Si\{^1H\}$ NMR shift values on the secant of the Si–O–Si angle [8] and also on the number of 4-rings.

The shift values of the resonances assigned to the major isomer of HT_{16} can therefore be used to deduce the number of 4-rings around the two symmetry-inequivalent environments of the silicon atoms in this compound. The plot in Fig. 15 shows that the D_{4d} structure does not violate the observed correlation, while the D_{2d} structure does. We believe this is con-

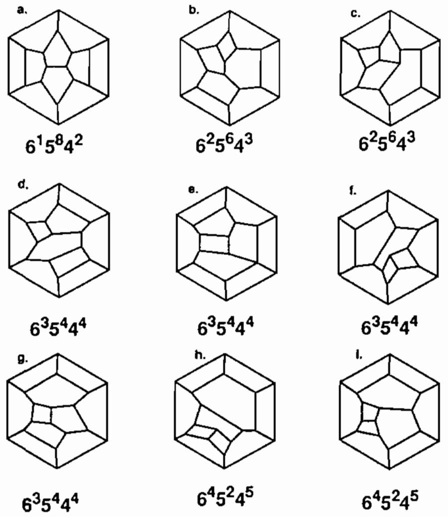

Fig. 12. Straight-line nets representing the structures of the isomers of HT_{18} with ring sizes in the range $4 \leq n \leq 6$.

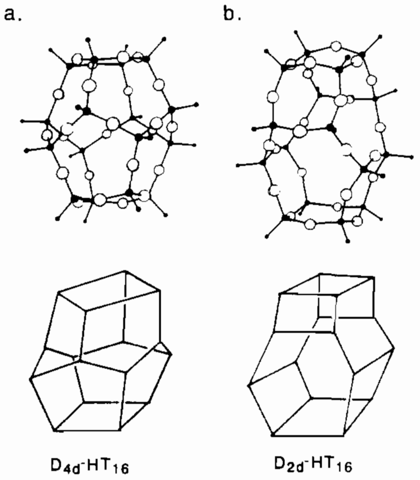

Fig. 13. Polyhedral representations of the nets shown in Fig. 11(a) and (g) and ball-and-stick diagrams of the corresponding structures of the hydridospherosiloxanes D_{4d}-HT_{16} and D_{2d}-HT_{16}.

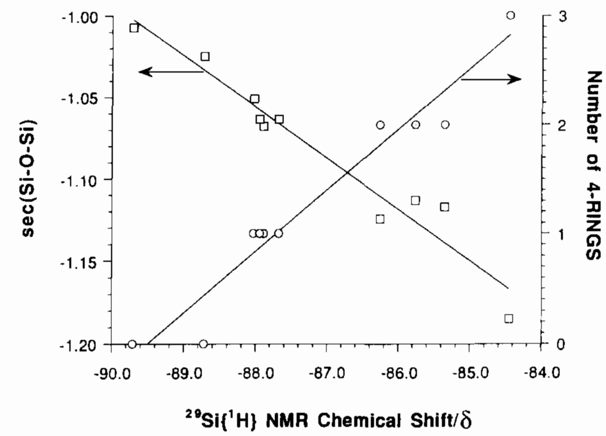

Fig. 14. Plot showing the linear correlation observed between the secant of the average Si–O–Si bond angle of each silicon atom, the number of 4-rings around each silicon atom and the $^{29}Si\{^1H\}$ NMR chemical shift value.

Table 2

$^{29}Si\{^1H\}$ NMR chemical shifts of silicon atoms in hydridospherosiloxanes [a]

Siloxane bond angle (°)	Average siloxane bond angle (°)	Number of 4-rings	δ (ppm) (Benzene-d_6, $Me_4Si = 0.0$, $Cr(acac)_3$ 0.026 M, 59.6 MHz)
147.5 [b]	147.55	3	−84.452 (O_h-HT_8; 1)
152.8 [c]	153.41	2	−86.255 (D_{5h}-HT_{10}; 1)
153.0 [d]			−85.784 (D_{2d}-HT_{12}; 1)
153.9 [e]			−85.762 (C_{2v}-HT_{14}; 1)
153.5 [e]			−85.354 (C_{2v}-HT_{14}; 1)
			−88.095 (D_{2d}-HT_{16}; 1)
149.1 [d]	160.46	1	−87.760 (D_{2d}-HT_{12}; 2)
159.5 [e]			−87.890 (D_{3h}-HT_{14}; 3)
162.1 [e]			−88.034 (D_{3h}-HT_{14}; 3)
160.1 [e]			−87.676 (C_{2v}-HT_{14}; 2)
160.1 [e]			−87.947 (C_{2v}-HT_{14}; 2)
			−88.095 (D_{4d}-HT_{16}; 1)
			−89.272 (D_{2d}-HT_{16}; 1)
173.2 [e]	170.25	0	−89.711 (D_{3h}-HT_{14}; 1)
167.3 [e]			−88.720 (C_{2v}-HT_{14}; 1)
			−89.272 (D_{4d}-HT_{16}; 1)

[a] Ambiguities have been systematically resolved by assigning the most negative chemical shift values first to the silicon atom with the smallest number of 4-rings around it and then to the silicon atom with the larger Si–O–Si bond angle. The values given in italics are the chemical shift values of the HT_{16} compound tabulated assuming the structure has D_{2d} symmetry, while the values given in bold are the chemical shift values of the HT_{16} compound assuming the structure has D_{4d} symmetry.

[b] From Ref. [22]. Structure at 100 K.

[c] From Ref. [43].

[d] From Ref. [48]. The X-ray crystal structure of HT_{12} is not yet reported. These values are from the structure of $(C_6H_5SiO_{1.5})_{12}$. The value of the angle around the silicon with one 4-ring differs considerably from other such angles, possibly owing to packing forces in the crystal arising from the large phenyl substituents, and is not used in the plot shown in Fig. 14 (see Section 6).

[e] From Ref. [1].

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[8] The ^{29}Si NMR chemical shift in compounds containing SiO_4 units, such as zeolites, has been shown to be linearly related to the secant of the mean Si–O–Si bond angle [44] and also to the mean Si–O–Si angle itself [45]. A semi-empirical rationalization [46] of these correlations can be based on the relationship between the electronegativity of the substituents on silicon and the chemical shift values [47], since the degree of hybridization of the oxygen atoms is related both to the Si–O–Si bond angle and to the oxygen electronegativity. These arguments are directly applicable to the HT_n compounds, which have $HSiO_3$ units instead of SiO_4.

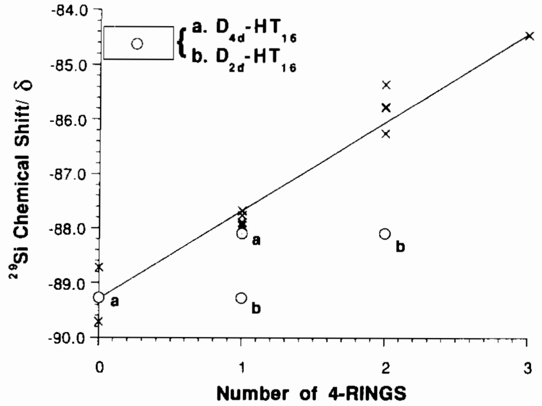

Fig. 15. Plot showing the linear correlation observed between the number of 4-rings around a silicon atom and the ^{29}Si NMR chemical shift values. The shift values of the major isomer of HT_{16} are plotted assuming each of the two possible structures. The structure D_{4d}-HT_{16} clearly gives a better agreement with the observed correlation than the structure D_{2d}-HT_{16}.

vincing evidence that the former is the correct structure of the major isomer of HT_{16}.

5. Conclusions

The total yield of the pure compounds, O_h-$H_8Si_8O_{12}$, D_{5h}-$H_{10}Si_{10}O_{15}$, D_{2d}-$H_{12}Si_{12}O_{18}$ and D_{3h}-$H_{14}Si_{14}O_{21}$, was only 8.7%, which represents a recovery yield of only 30% based on the amounts of these compounds present in the mixture; however, considering the complexity of the mixture obtained in the first step, as shown in Figs. 2–5, these yields are not unreasonably low. The starting materials are simple and the reaction can be scaled up to make gram quantities of the pure compounds, as we have done in our laboratory. In addition, we have used preparative gas chromatography to isolate mixtures of isomers of HT_{14} and HT_{16}, from which we can determine the ^{1}H and ^{29}Si NMR chemical shift values of particular isomers and in one case the X-ray crystal structure. A structure is proposed for the major isomer of HT_{16} based on a complete enumeration of all possible isomers of this composition that have chemically reasonable structures and the strong correlation observed between topological features of the polyhedral structures of these compounds and ^{29}Si chemical shift values. Thus six hydridospherosiloxanes, which account for 87% of the total amount of such compounds generated by the Frye and Collins procedure, now have well-characterized structures, although only four can be prepared as pure compounds.

6. Note added in proof

The crystal structure of HT_{12} has now been determined (K.W. Törnroos et al., *Acta Crystallogr., Sect. B*, in press). The average Si–O–Si bond angles of the silicon atoms with one and two 4-rings around them are 152.0 and 156.5°, respectively.

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