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CONFORMATIONAL STUDIES AND CRYSTAL STRUCTURES OF *cis*- AND *trans*-1,4-BIS(TRIMETHYLSILYL)HEXAMETHYL-1,4-DISILACYCLOHEXA-2,5-DIENE *

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Summary

The geometries of *cis*- and *trans*-bis(1,4-trimethylsilyl)-1,2,3,4,5,6-hexamethyl-1,4-disilacyclohexa-2,5-diene have been studied by ^{13}C NMR and X-ray single crystal analysis. The *trans* isomer adopts a nearly planar conformation with a slight deformation toward a chair form which is most likely caused by steric interactions between the vinyl-methyl substituents and the groups on the ring silicon atoms. Unlike the *trans* isomer and the other previously reported disilacyclohexadienes, the *cis* isomer resides in a slightly twisted boat conformation. The two bulky trimethylsilyl substituents are located in pseudo-axial positions. This finding is in accord with recent calculations which predict the bulky 1,4 substituents should occupy axial positions in the cyclohexa-2,5-dienyl ring system.

Introduction

The 1,4-disilacyclohexa-2,5-diene ring system was first prepared by Vol'pin and coworkers in 1962 from the reaction of dimethyldichlorosilane, diphenylacetylene and lithium. The products from this reaction were originally proposed to be a silacyclopropene, however a year later the correct structure assignment was established [1,2]. Later studies showed that this ring system is the general product from the thermal reaction of silylenes, the silicon analogs of carbenes, and acetylenes [3]. There has been considerable interest in the mechanism of the formation of these 1,4-disilacyclohexane-2,5-dienes [4], but relatively little has been reported about their conformational geometry [5,6].

The geometry of the analogous carbon compounds, 1,4-cyclohexadienes, has been the subject of a lengthy controversy. It is now generally accepted that 1,4-cyclohexadiene itself prefers a planar orientation rather than ring flipping between boat

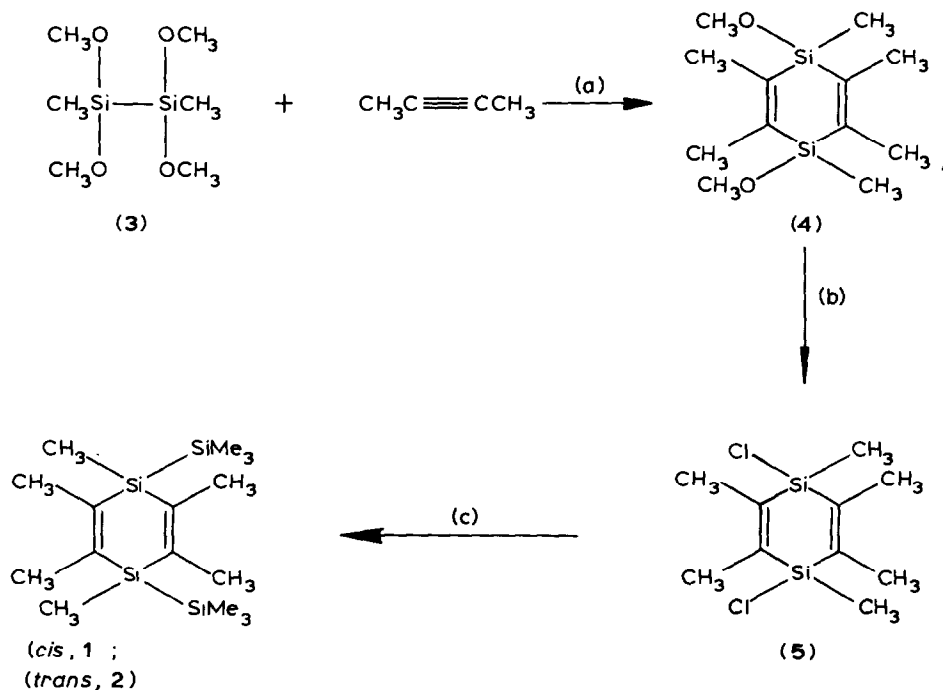
* Dedicated to Professor Raymond Calas for more than 30 years of outstanding research in the field of organometallic chemistry and on the occasion of his 70th birthday, April 8, 1984.

conformations. From analysis of homoallylic ring coupling constants, several substituted 1,4-cyclohexadienes are now known to have either planar or greatly flattened boat conformations [7,8]. In contrast, substitution of a heteroatom in the 1,4-positions leads to substantial distortion of the ring structure from planarity. X-Ray analysis of dithiadene [9] and 1,4-di-*p*-chlorophenyl-2,6-diphenyl-1,4-dihydropyrazine [10] have shown these compounds to be in a boat conformation with the latter example having the nitrogen atoms bent out of the plane of the sp^2 carbon atoms by 37.3°C .

Previous X-ray analysis of 1,4-digermacyclohexa-2,5-dienes by Vol'pin et al. showed the ring structures to be planar [5]. There have been only two reports of 1,4-disilacyclohexadiene structures, by Vol'pin et al. [5] and recently by Ishikawa and coworkers [6]. Both examples showed the ring structures to be nearly planar with slight distortion toward a chair-like structure. In both cases the olefinic carbons were substituted by bulky phenyl substituents which may affect the ring geometry. In this paper we report a study of the conformational properties of *cis*- and *trans*-1,4-bis(trimethylsilyl)hexamethyl-1,4-disilacyclohexa-2,5-diene by temperature dependent ^{13}C NMR and determination of solid state structures of both compounds by X-ray crystallography.

^{13}C NMR

Cis- and *trans*-1,4-dimethoxyhexamethyl-1,4-disilacyclohexadiene (**4**) were synthesized by the static pyrolysis of *sym*-tetramethoxydimethyldisilane (**3**) and dimethylacetylene according to the procedure of Atwell and Weyenberg [3b] (Scheme 1).



SCHEME 1. a. Thermolysis, 240°C , sealed tube, b. Refluxing acetyl chloride, 3 days. c. Lithium, trimethylchlorosilane, 0°C .

Reaction of **4** in refluxing acetyl chloride for 3 d gave a 1/1 mixture of the *cis*- and *trans*-dichlorides (**5**) in 60% yield. Lithium cocondensation of **5** with trimethylchlorosilane afforded the bis(trimethylsilyl) compounds **1** and **2** as a 4/1 ratio of isomers in 71% overall yield. Unlike most sets of isomers of 1,4-disilacyclohexadienes, which cannot be conveniently separated, **1** and **2** were easily separated by preparative gas chromatography.

In principle it is possible to distinguish the *cis* and *trans* isomers, **1** and **2**, by temperature dependent NMR if the preferred low energy form of the 1,4-disilacyclohexadienes is the boat form. In this case, the observed chemical shifts for the trimethylsilyl and methylsilyl resonances of each geometric isomer will be represented by the equation.

$$\delta_{\text{obs}} = X_1\delta_1 + X_2\delta_2$$

where X_1 and X_2 are the mole fractions of both conformational forms and δ_1 and δ_2 are the chemical shifts for each of the pure conformers. As shown in Fig. 1, the *trans* isomer **2** undergoes ring exchange between two conformational forms of equal energy ($X_1 = X_2$) so the observed trimethylsilyl and methylsilyl resonances should be temperature independent [11]. The *cis* isomer exchanges between one conformer containing two axial trimethylsilyl groups and one having two equatorial trimethylsilyl groups. Assuming that the chemical shifts for an axial and equatorial SiMe_3 are not accidentally equivalent, the *cis* isomer should exhibit a temperature dependent NMR spectrum if the molecule is oscillating between boat forms in solution.

An NMR sample containing a 4/1 mixture of *cis*-**1** and *trans*-**2** was prepared in deuteriochloroform and analyzed by temperature dependent ^{13}C NMR (200 MHz) over the range -50 to $+50^\circ\text{C}$. Table 1 lists the proton and ^{13}C chemical shifts for **1** and **2**. (Absolute assignment of *cis* and *trans* was based on X-ray structure information, *vide infra*.) Plots of the temperature dependent ^{13}C spectra for the vinyl and allylic methyl carbon atoms are shown in Fig. 2. The ^{13}C chemical shifts of the methylsilyl and trimethylsilyl carbon atoms versus temperature are shown in Fig. 3.

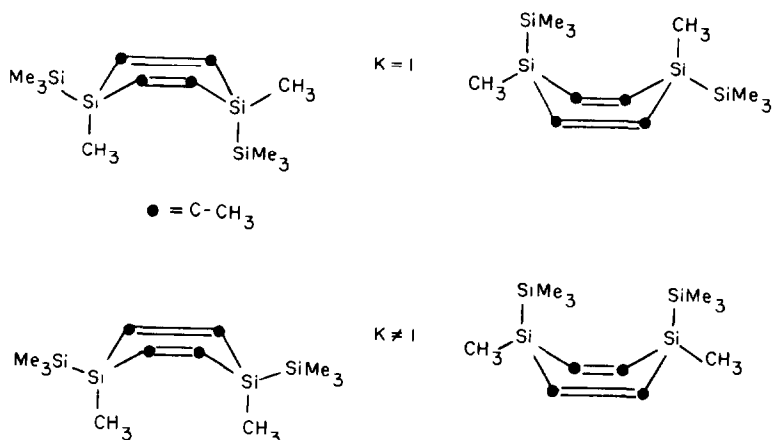
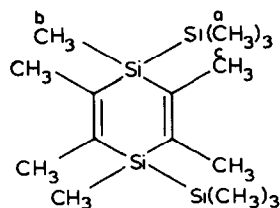


Fig. 1. Possible ring flipping equilibria between boat conformers of *cis*- and *trans*-bis(1,4-trimethylsilyl)hexamethyl-1,4-disilacyclohexa-2,5-diene.

TABLE 1
 PROTON AND ^{13}C SOLUTION CHEMICAL SHIFTS OF



	$\text{CH}_3^{(a)}$	$\text{CH}_3^{(b)}$	$\text{CH}_3^{(c)}$	Ring C
Proton ^a				
<i>cis</i> 1	0.033	0.205	1.736	—
<i>trans</i> 2	0.020	0.187	1.722	—
Carbon ^b				
<i>cis</i> 1	-0.610	-5.186	18.066	146.205
<i>trans</i> 2	-0.939	-6.193	17.957	146.380

^a 270 MHz (24°C) C_6D_6 δ values (ppm) reference $\text{C}_6\text{D}_5\text{H}$ chemical shift ± 0.002 ppm. ^b 200 MHz (15°C) C_6D_6 , δ values (ppm) reference C_6D_6 .

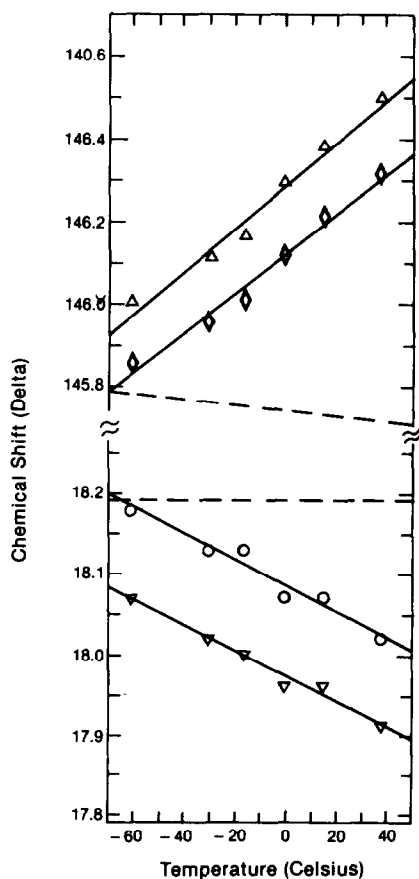


Fig. 2. Top: Temperature dependent ^{13}C chemical shifts for the vinyl carbon resonances. *Cis* isomer 1, (\diamond); *trans* isomer 2 (Δ); *cis* isomer after viscosity shifting correction (-----). Bottom: Temperature dependence of the allylic methyl carbon atom ^{13}C chemical shifts. *Cis* isomer 1 (\circ); *trans* isomer (∇); *cis* isomer after viscosity shifting corrections (-----).

The NMR results indicate that if the isomers are in fact ring flipping between boat conformers, the energy of activation for this process must be small. Over the temperature range examined no broadening of the NMR lines was observed as would be expected if the individual conformers were being frozen out.

Solution viscosity effects are known to cause slight, temperature dependent changes in the observed chemical shifts [13]. Since the *trans* isomer is predicted to show little change in chemical shift due to conformational effects, the temperature dependent shifts for **2** can be explained by viscosity effects. Assuming that viscosity effects for the *trans* isomer are nearly equal to those for the *cis* conformer, the net chemical shift change of the *cis* isomer due to conformational differences can be determined by subtracting the change in slope of the temperature dependent plots for the *trans* isomer from those of the *cis* isomer. The viscosity corrected temperature dependent chemical shifts for the *cis* isomer are shown by the dashed lines in Fig. 2 and 3.

The vinyl and allylic methyl resonances should be insensitive to ring flipping

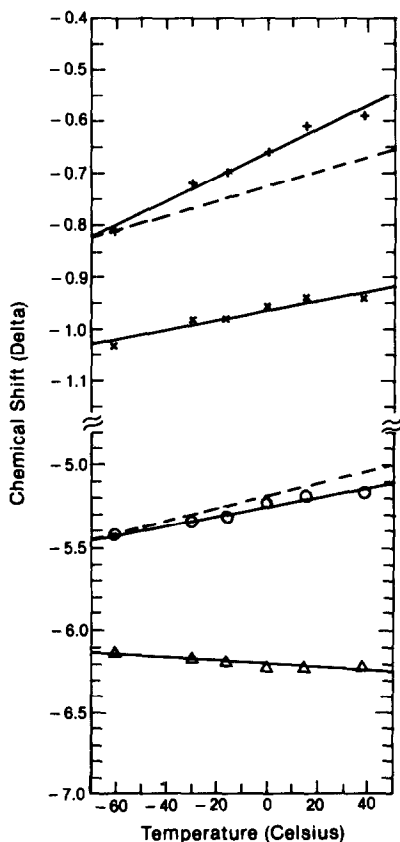


Fig. 3. Top: Temperature dependent ^{13}C chemical shifts for the trimethylsilyl carbon resonances. *Cis* isomer (+); *trans* isomer (x); *cis* isomer after viscosity shifting correction (-----). Bottom: Temperature dependence of the methylsilyl carbon atom ^{13}C chemical shifts. *Cis* isomer (O); *trans* isomer (Δ); *cis* isomer after viscosity shifting correction.

effects and this is indicated by the nearly parallel lines for these carbons in both *cis*-1 and *trans*-2. The corrected chemical shifts for *cis*-1 are nearly temperature independent in both examples (see Fig. 2). The trimethylsilyl and methylsilyl resonances are not parallel, with the most dramatic difference seen for the methylsilyl peaks. The corrected *cis* value for the methylsilyl peak shows a temperature dependent shift of 0.5 ppm over a 100° range (see Fig. 2) [14].

There are several possible ways in which the results could be explained, but a very likely possibility is that 1 exists in solution in nonequivalent boat forms which undergo rapid interconversion by ring flipping. Because of the symmetry properties of the *trans* isomer, the NMR experiment does not provide any information about the solution geometry of 2. In order to obtain more conclusive evidence about the structures of 1 and 2, these compounds were investigated by X-ray crystallography.

X-Ray results

X-Ray analysis showed that the major product from the reaction of 1,4-dichlorohexamethyl-1,4-disilacyclohexa-2,5-diene and trimethylchlorosilane with lithium was the *cis* isomer, 1, with the minor product being *trans*-2. Selected interatomic distances (Å) and bond angles (degree) for 1 and 2 are given in Tables 2 and 3, respectively. Table 4 presents the least-squares planes and distances (Å) of the individual atoms from the planes for 1 and 2, respectively. The Si-C bond lengths range from 1.868(2) to 1.884(2) Å in 1 with an average of 1.874(3) Å and in 2 they range from 1.870(2) to 1.878(2) Å with an average of 1.873(3) Å. The Si-Si bond distances are 2.360(1) and 2.362(1) Å in 1 and 2, respectively. The Si-Si, Si-C and C-C bond distances are all within the normally observed ranges, and there are no unusual bond angles. The hydrogen atoms were refined for both 1 and 2 and the C-H distances, ranging from 0.88–1.02 Å, are given in Table 8.

The 1,4-disilacyclohexadiene ring structure of the *trans* isomer, 2, exhibits remarkable planarity as can be seen in Fig. 5b, the view parallel to the four olefinic carbon atoms (Plane A in Table 4; in fact, the four olefinic carbon atoms are required to be planar by the crystallographic inversion center in the molecule). Si(1) and its centrosymmetric counterpart deviate from the olefinic carbon atom plane (Plane A) by only 0.072 Å in *trans*-2. This 0.072 Å deviation of Si(1) from the olefinic carbon atom plane is slightly larger than in *trans*-1,4-dimethyl-1,2,4,5-tetra-phenyl-3,6-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (6) reported by Ishikawa et al. [6] (0.054 Å) and smaller than in 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexa-2,5-diene, (7) reported by Vol'pin et al. [5] (0.146 Å). In accord with previously studied 1,4-disilacyclohexa-2,5-dienes, the small distortion which is observed orients the molecule slightly in the chair conformation rather than the boat form; the larger SiMe₃ groups orient in the axial directions. The plane passing through Si(1) and its attached olefinic carbon atoms (Plane B) forms an angle of four degrees with the plane of the four olefinic carbon atoms (Plane A), a value which is intermediate between those observed previously for similar planes in 6 and 7 of 3 and 7.8 degrees, respectively. Similar to the previous examples [5,6], *trans*-2 forms a perfect chair (required by the inversion center). As in the case of the tetraphenyl derivatives, the allylic methyl groups in 2 distort above and below the plane of the cyclic vinyl carbons (C(4), 0.050; C(5), -0.035 Å).

Unlike all previously studied 1,4-disilacyclohexa-2,5-dienes, the *cis* molecule

TABLE 2
 SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (degree) FOR *cis*-Si₄C₁₆H₃₆ (1)

<i>Distances</i>					
Si(1)-Si(3)	2.361(1)	Si(2)-C(13)	1.882(3)	C(1)-C(2)	1.519(3)
Si(2)-Si(4)	2.360(1)	Si(3)-C(10)	1.872(3)	C(3)-C(4)	1.524(3)
Si(1)-C(1)	1.871(2)	Si(3)-C(11)	1.875(3)	C(5)-C(6)	1.515(3)
Si(1)-C(3)	1.868(2)	Si(3)-C(12)	1.870(3)	C(7)-C(8)	1.525(3)
Si(1)-C(9)	1.884(2)	Si(4)-C(14)	1.877(3)	C(1)-C(7)	1.350(3)
Si(2)-C(5)	1.875(2)	Si(4)-C(15)	1.872(3)	C(3)-C(5)	1.348(3)
Si(2)-C(7)	1.873(2)	Si(4)-C(16)	1.873(3)		
<i>Angles</i>					
Si(3)-Si(1)-C(1)	106.30(7)	Si(4)-Si(2)-C(7)	111.54(7)	Si(1)-Si(3)-C(12)	111.15(10)
Si(3)-Si(1)-C(3)	111.48(7)	Si(4)-Si(2)-C(13)	109.99(9)	Si(2)-Si(4)-C(14)	112.23(10)
Si(3)-Si(1)-C(9)	109.33(10)	Si(1)-Si(3)-C(10)	109.91(10)	Si(2)-Si(4)-C(15)	108.52(10)
Si(4)-Si(2)-C(5)	104.64(7)	Si(1)-Si(3)-C(11)	109.77(10)	Si(2)-Si(4)-C(16)	110.48(9)
Si(1)-C(1)-C(2)	114.87(17)	Si(2)-C(5)-C(3)	122.90(16)	C(2)-C(1)-C(7)	121.60(20)
Si(1)-C(1)-C(7)	123.38(16)	Si(2)-C(5)-C(6)	115.25(17)	C(4)-C(3)-C(5)	121.16(21)
Si(1)-C(3)-C(4)	115.29(17)	Si(2)-C(7)-C(1)	123.12(16)	C(3)-C(5)-C(6)	121.62(21)
Si(1)-C(3)-C(5)	123.52(16)	Si(2)-C(7)-C(8)	115.30(18)	C(1)-C(7)-C(8)	121.58(21)
C(1)-Si(1)-C(3)	112.23(10)	C(5)-Si(2)-C(13)	109.94(12)	C(11)-Si(3)-C(12)	108.70(15)
C(1)-Si(1)-C(9)	109.89(11)	C(7)-Si(2)-C(13)	108.57(12)	C(14)-Si(4)-C(15)	107.83(14)
C(3)-Si(1)-C(9)	107.59(11)	C(10)-Si(3)-C(11)	108.34(14)	C(14)-Si(4)-C(16)	108.40(14)
C(5)-Si(2)-C(7)	112.11(10)	C(10)-Si(3)-C(12)	108.91(15)	C(15)-Si(4)-C(16)	109.30(15)
Plane C-Plane D	8.4	Plane C-Plane E	11.1	Plane D-Plane E	19.5

TABLE 3
 SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (degree) FOR *trans*-Si₄Cl₁₆H₃₆ (2)

<i>Distances</i>					
Si(1)-Si(2)	2.362(1)	Si(2)-C(6)	1.870(2)	C(1)-C(2)	1.347(2)
Si(1)-C(1)	1.871(1)	Si(2)-C(7)	1.875(2)	C(1)-C(4)	1.523(2)
Si(1)-C(2)	1.871(1)	Si(2)-C(8)	1.876(2)	C(2)-C(5)	1.524(2)
Si(1)-C(3)	1.878(2)				
<i>Angles</i>					
Si(2)-Si(1)-C(1)	109.99(4)	Si(1)-C(1)-C(2)	123.46(10)	C(2)-Si(1)-C(3)	109.11(9)
Si(2)-Si(1)-C(2)	106.21(4)	Si(1)-C(1)-C(4)	115.25(11)	C(6)-Si(2)-C(7)	109.22(9)
Si(2)-Si(1)-C(3)	110.33(7)	Si(1)-C(2)-C(5)	114.69(11)	C(6)-Si(2)-C(8)	108.34(9)
Si(1)-Si(2)-C(6)	108.26(7)	Si(1)-C(2)-C(1')	123.84(10)	C(7)-Si(2)-C(8)	107.07(10)
Si(1)-Si(2)-C(7)	112.94(6)	C(1)-Si(1)-C(2)	112.52(6)	C(4)-C(1)-C(2)	121.30(13)
Si(1)-Si(2)-C(8)	110.90(7)	C(1)-Si(1)-C(3)	108.67(9)	C(5)-C(2)-C(1')	121.35(13)
Plane A - Plane B	4.0				

distorts from planarity to form a slightly twisted boat conformer. The four olefinic carbon atoms are slightly skewed as shown in Fig. 4b. The distance of each carbon atom from the least-squares plane (C) through the olefinic carbons is given in Table 4. Si(1) and Si(2) deviate from plane C by 0.150 and 0.200 Å. The least-squares planes D, Si(1)–C(1)–C(3), and E, Si(2)–C(5)–C(7) (see Fig. 4b), make angles of 8.4 and 11.1° with least-squares plane C, respectively. The two large trimethylsilyl groups occupy pseudoaxial positions while the smaller methyl groups are in pseudo-equatorial orientations.

Current knowledge of the effects of substituents on the preferred conformations of 1,4-dihydrobenzenes is incomplete, but suggests that *cis*-1,4-disubstituted 1,4-dihydrobenzenes with large substituents prefer boat conformers in which the larger groups are thought to occupy equatorial positions. In contrast, the planar structure is preferred for the corresponding *trans* isomers [15]. These results have been rationalized as follows: In a planar ring, 1,4-interactions may be expected across the ring between large substituents in the *cis* compounds. Distortion of the molecule to a

TABLE 4
EQUATIONS OF THE LEAST SQUARES PLANES AND DISTANCES (Å) TO THE INDIVIDUAL ATOMS FROM THE PLANES FOR Si₄C₁₆H₃₆.

trans-Isomer (2)

Plane A: C(1), C(2), C(1'), C(2')

$$0.7870x + 0.3246y - 0.5246z - 3.3001 = 0$$

C(1)	0.0	C(4)	0.050	Si(1)	-0.072
C(2)	0.0	C(5)	-0.035	Si(1')	0.072
C(1')	0.0	C(4')	-0.050		
C(2')	0.0	C(5')	0.035		

Plane B: Si(1), C(1), C(2)

$$0.7620x + 0.2895y - 0.5794z - 3.1480 = 0$$

Si(1)	0.0	Si(1')	-0.094	C(4)	0.105
C(1)	0.0	C(1')	-0.094	C(5)	0.021
C(2)	0.0	C(2')	-0.094	C(4')	-0.198
				C(5')	-0.115

cis-Isomer (1)

Plane C: C(1), C(3), C(5), C(7)

$$0.7009x + 0.2031x - 0.6838z + 1.9669 = 0$$

C(1)	0.037	C(2)	0.174	Si(1)	-0.150
C(3)	-0.037	C(4)	0.013	Si(2)	-0.200
C(5)	0.037	C(6)	0.193		
C(7)	-0.037	C(8)	0.002		

Plane D: Si(1), C(1), C(3)

$$0.7588x + 0.0734x - 0.6472z + 1.6632 = 0$$

Si(1)	0.0	Si(2)	-0.541	C(2)	0.220
C(1)	0.0	C(5)	-0.121	C(4)	0.194
C(3)	0.0	C(7)	-0.268	C(6)	-0.051
				C(8)	-0.375

Plane E: Si(2), C(5), C(7)

$$0.5973x + 0.3635y - 0.7149z + 2.6184 = 0$$

Si(2)	0.0	Si(1)	-0.603	C(2)	-0.174
C(5)	0.0	C(1)	-0.186	C(4)	-0.462
C(7)	0.0	C(3)	-0.330	C(6)	0.275
				C(8)	0.220

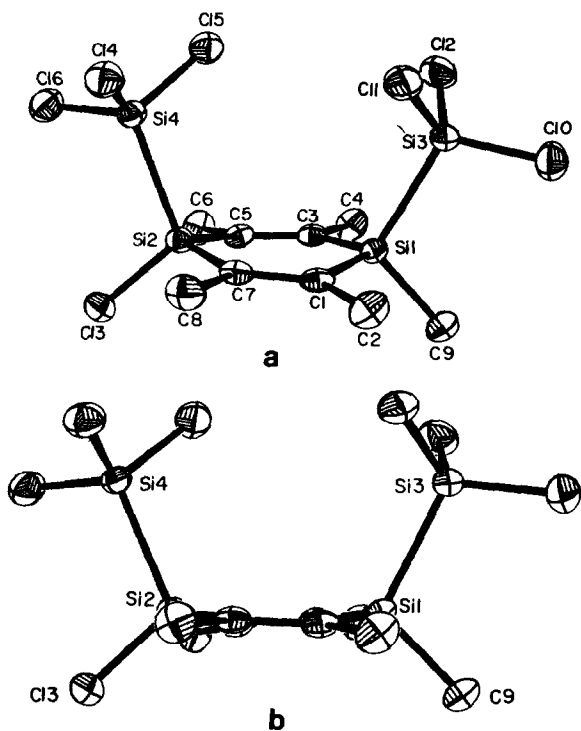


Fig. 4. ORTEP drawings of *cis*-Si₄C₁₆H₃₆ (1). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

boat form alleviates the steric congestion by placing the large substituents in pseudoequatorial environments. For the *trans* isomers, puckering to a boat form forces one substituent to an unfavorable axial position, whereas planar geometry can accommodate both substituents with no 1,4-interactions whatsoever.

However, recent theoretical work has placed doubts on this argument [8a]. Calculations indicate that bulky *cis* substituents in 1,4-cyclohexadienes actually prefer the *axial* positions. In the series of dihydroaromatic compounds, 1,4-dihydrobenzene, 1,4-dihydronaphthalene and 9,10-dihydroanthracene, nonbonded interactions are minimized in the axial position and maximized in the equatorial position where the substituent is eclipsed with the adjacent vinyl hydrogen atoms.

Our results are in accord with these calculations. The *cis* isomer has a slightly twisted boat shape with the large groups pseudoaxial [16]. If the major steric interaction is indeed between the 1,4-substituents and the adjacent vinyl carbon substituent, then for *cis*-1 these repulsions should be large due to the presence of the allylic methyl groups. On this basis, more pronounced distortion to the boat form might be expected than that actually observed. The *trans* form is nearly planar (very slightly chair distorted), similar to *trans*-1,4-dihydrobenzenes. The more severe distortions found in the 1,4-disilacyclohexadienes studied earlier probably are due to the presence of phenyl substituents on the carbons.

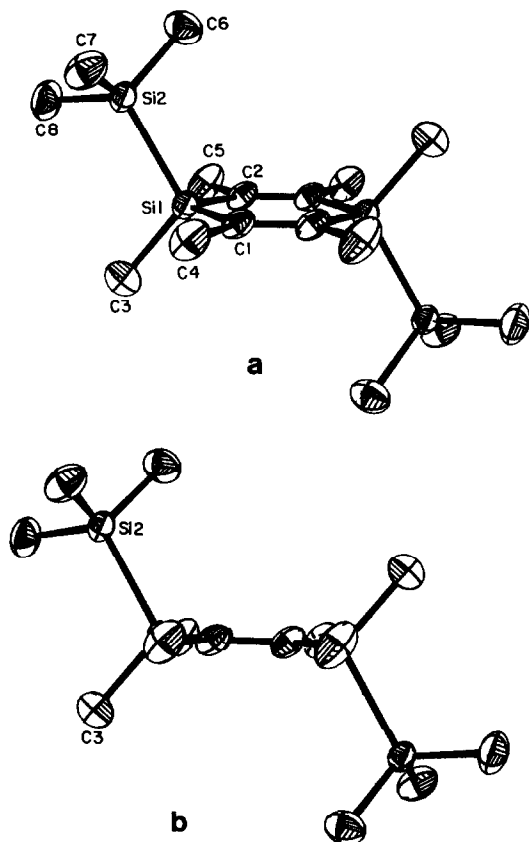


Fig. 5. ORTEP drawings of *trans*-Si₄C₁₆H₃₆ (**2**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Experimental

General. Proton NMR was recorded on a Bruker WH270 MHz spectrometer equipped with a variable temperature probe which was precalibrated before use. Carbon-13 spectra were obtained on a JEOL FX-200 NMR spectrometer. Both proton and carbon samples were prepared in CDCl₃ with the CHCl₃ spectrum used as an internal standard. Proton spectra were recorded at -50, 0, +25 and +50°C, and carbon spectra were recorded at -61, -30, 0, +15 and +35°C.

All chemical reactions were carried out under an atmosphere of dry nitrogen. Analytical GLC were performed on a Hewlett-Packard Model 5720A gas chromatograph. Preparative GLC was carried out on a Varian Aerograph Model 90-P. All reagents not referenced were commercially available.

Synthesis of 1,4-dimethoxyhexamethyl-1,4-disilacyclohexa-2,5-diene. The procedure used was a modification of the synthesis described by Atwell and Weyenberg [3]. *sym*-Tetramethoxydimethyldisilane, 6.36 g (3.0×10^{-2} mol) and 2.9 g (5.4×10^{-2} mol) of 2-butyne were placed neat into a 25 ml thick walled sealed tube (3 mm glass) and after several freeze-thaw degassing cycles the tube was sealed under a high

vacuum (5×10^{-5} Torr). The reaction vessel was placed in a Lindberg furnace (Fischer Model No. 55035) and pyrolyzed for 18 h at 250–260°C. CAUTION: during two of the experiments the tube exploded violently. Therefore appropriate high pressure safety procedure should be taken. The tube was removed and cooled to -196°C before opening. The volatile reaction products, mostly $(\text{MeO})_2\text{SiMe}_2$ were removed in vacuo leaving 3.5 g (90%) of crude 1,4-dimethoxyhexamethyl-1,4-disilacyclohexa-2,5-diene as an oily solid. This material was generally used without further purification, but could be recrystallized from CCl_4 if higher purity was required. NMR analysis showed a $\sim 4/1$ ratio of isomers.

NMR (major isomer, CDCl_3): δ 3.20 (s, 6H), 1.80(s, 12H), 0.0(s, 6H) ppm; minor isomer: δ 3.17 (s, 6H), 1.80(s, 12H), 0.02(s, 6H) ppm. Careful recrystallization of the material from CCl_4 afforded only one of the isomers as determined by NMR.

Synthesis of 1,4-dichlorohexamethyl-1,4-disilacyclohexa-2,5-diene. A solution of 8.5 g (3.3×10^{-2} mol) of a mixture of isomers of 1,4-dimethoxyhexamethyl-1,4-disilacyclohexa-2,5-diene and 30 ml of acetyl chloride was heated to reflux for three days. The excess acetyl chloride and the methyl acetate formed were distilled under nitrogen with the final amounts being removed under high vacuum. 1,4-Dichlorohexamethyl-1,4-disilacyclohexa-2,5-diene was isolated by sublimation (70°C , 1 Torr) from the distillation residue material (5.2 g, 60%). GLC analysis showed the product to be a nearly 1/1 mixture of isomers. NMR (CCl_4 , CHCl_3 ref): isomer 1: δ 1.85(s, 12H), 0.42 (s, 6H) ppm; isomer 2: δ 1.85(s, 12H), 0.39(s, 6H) ppm; mass spec. calcd. 264.0324; obs. 264.0325; dev. 0.4 ppm.

Synthesis of cis and trans-1,4-bis(trimethylsilyl)-hexamethyl-1,4-disilacyclohexa-2,5-diene (1 and 2). All reactions were carried out in Schlenk glassware under an atmosphere of dry argon. A highly reactive mirror of lithium was prepared by dissolving 0.11 g, (1.51 mmol) of lithium wire in liquid ammonia and then removing the NH_3 under high vacuum. Ten ml of dry THF was added and the mixture stirred at room temperature. A mixture of 1.00 g (3.77 mmol) of *cis*- and *trans*-1,4-dichlorohexamethyl-1,4-disilacyclohexane-2,5-diene and 0.86 g (7.92 mmol) of trimethylchlorosilane was dissolved in 5 ml of THF. This solution was slowly added to the lithium metal and after the addition was complete the mixture was stirred for 2 h at room temperature. The solution was poured onto 10% aqueous HCl and extracted with ether. After aqueous washing and drying over sodium sulfate the solvent was removed in vacuo to leave the crude product as a waxy solid. Preparative gas chromatography ($6' \times 3/8''$ 20% SE30 Chromosorb W 60/80, 205°C) readily separated the isomers giving 81% *cis*-1,4-bis(trimethylsilyl)hexamethyl-1,4-disilacyclohexa-2,5-diene (1) and 19% *trans*-1,4 bis(trimethylsilyl)hexamethyl-1,4-disilacyclohexa-2,5-diene (2).

X-Ray data collection. Crystals of *cis*- and *trans*-1,4-bis(trimethylsilyl)1,2,3,4,5,6-hexamethyl-1,4-disilacyclohexa-2,5-diene (1 and 2) were obtained by vapor diffusion at room temperature using Et_2O as a solvent and MeOH as a non-solvent. Data were collected on a Syntex-Nicolet P $\bar{1}$ four-circle diffractometer equipped with a modified LT-1 low temperature device. Unit cell parameters were obtained from least-squares refinements based on the setting angles of 60 reflections collected at $\pm 2\theta$ ($|\rho| \sim 30^\circ$) at the same temperature as the data collection. The dimensions of the crystals, the unit cell parameters and other crystal data are listed in Table 5. Delaunay cell reductions did not reveal any hidden symmetry.

TABLE 5
SUMMARY OF CRYSTAL DATA AND INTENSITY COLLECTION

Parameters	<i>cis</i> -Si ₄ C ₁₆ H ₃₆ (1)	<i>trans</i> -Si ₄ C ₁₆ H ₃₆ (2)
Crystal dimensions (mm)	0.20 × 0.20 × 0.45	0.55 × 0.55 × 0.20
Temperature (°C)	-65 ± 5	-55 ± 5
Cell parameters		
<i>a</i> (Å)	9.955(2)	8.386(1)
<i>b</i> (Å)	15.568(3)	9.526(2)
<i>c</i> (Å)	7.951(2)	14.143(2)
α (deg)	104.43(2)	
β (deg)	107.80(2)	97.98(1)
γ (deg)	98.95(1)	
<i>V</i> (Å ³)	1100.0	1118.9
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i>	2	2
Density, calculated (g/cm ³)	1.03	1.01
Radiation	graphite, monochromated Mo- <i>K</i> _α ($\bar{\lambda}$ 0.71073 Å)	
Absorption coefficient, μ (cm ⁻¹)	2.24	2.20
Scan range (deg below 2θ(<i>K</i> _{α1}))	0.8	0.8
(deg above 2θ(<i>K</i> _{α2}))	0.8	0.8
Scan rate (deg/min)	2.4–24.0	2.0–24.0
2θ limits (deg)	3.5–54.9	3.5–58.7
Sin θ/λ _{max} (Å ⁻¹)	0.649	0.690
Unique data, theoretical	5029	3074
observed, <i>F</i> ₀ > 3σ(<i>F</i> ₀)	3780	2581

Intensity data were collected with the crystals used for the preliminary examinations. Details of the intensity measurements are given in Table 5. Four standard reflections from diverse regions of reciprocal space were measured every 50 reflections throughout data collection to monitor the long term stability. There were no significant trends for either compound. Structure amplitudes and their standard deviations were calculated from the intensity data by procedures similar to those described previously [17]. Absorption corrections were not applied.

Structure solution and refinement. The structures were solved by direct methods using the MULTAN package [18]. The positions of the silicon atoms and several of the carbon atoms were revealed by the E maps and the rest of the carbon atoms were located by subsequent electron density difference maps. The full-matrix least-squares refinements of the structures were based on *F*₀ and used the reflections with *F*₀ > 3σ(*F*₀). Both structures were initially refined to convergence using isotropic thermal parameters for the non-hydrogen atoms. Difference electron density maps revealed the positions for all the hydrogen atoms. In the final cycles of refinement all non-hydrogen atoms were assumed to vibrate anisotropically and all hydrogen atoms were assumed to vibrate isotropically. Atomic form factors were taken from standard references [19,20].

The hydrogen atom parameters were refined in the final cycles of refinement of both compounds. The final values of the discrepancy indices for *trans*-Si₄C₁₆H₃₆ were $R_1 = \Sigma|F_0| - |F_c|/\Sigma|F_0| = 0.033$ and $R_2 = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w(F_0)^2]^{1/2} =$

TABLE 6
 FRACTIONAL TRICLINIC ATOMIC COORDINATES AND FINAL ANISOTROPIC THERMAL PARAMETERS FOR *cis*-Si₄C₁₆H₃₆ (1)

Atom	x	y	z	B _{iso} ^b	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Si(1)	0.58059(6) ^a	0.30750(4)	0.91058(8)	1.68	1.648(24) ^a	1.714(23)	1.682(23)	0.365(18)	0.713(19)	0.340(18)
Si(2)	0.80795(7)	0.17630(4)	1.05270(8)	1.79	1.947(25)	1.816(23)	1.715(23)	0.479(19)	0.809(19)	0.474(18)
Si(3)	0.58965(7)	0.35073(4)	0.64912(8)	2.02	2.194(27)	2.309(26)	1.951(25)	0.787(20)	0.966(21)	0.797(20)
Si(4)	0.98050(7)	0.16480(4)	0.90557(8)	1.93	1.998(25)	2.106(25)	1.875(24)	0.611(19)	0.896(20)	0.573(19)
C(1)	0.52518(23)	0.17934(14)	0.8303(3)	1.79	1.71(8)	1.89(8)	1.74(8)	-0.08(7)	0.77(7)	0.23(6)
C(2)	0.37073(28)	0.13695(20)	0.6907(4)	2.67	2.04(10)	2.67(11)	2.78(11)	-0.07(9)	0.47(9)	0.06(9)
C(3)	0.75926(23)	0.35462(14)	1.10873(28)	1.70	2.10(9)	1.59(8)	1.56(8)	0.15(7)	0.93(7)	0.09(6)
C(4)	0.8018(3)	0.45823(17)	1.1993(4)	2.61	2.87(12)	1.91(10)	2.81(11)	0.39(9)	0.85(9)	-0.03(8)
C(5)	0.84467(23)	0.30205(14)	1.17340(28)	1.80	1.75(8)	2.13(9)	1.49(8)	0.21(7)	0.68(7)	0.16(7)
C(6)	0.9854(3)	0.34300(20)	1.3404(4)	2.77	2.46(11)	2.91(12)	2.31(11)	0.35(9)	0.00(9)	0.11(9)
C(7)	0.61698(24)	0.12720(14)	0.8807(3)	1.82	2.20(9)	1.66(8)	1.76(8)	-0.06(7)	1.00(7)	0.24(6)
C(8)	0.5709(3)	0.02297(17)	0.7989(4)	2.68	3.13(12)	1.74(9)	3.25(12)	0.19(9)	1.26(10)	0.30(8)
C(9)	0.4399(3)	0.35454(19)	0.9916(4)	2.55	2.41(11)	2.86(11)	2.92(11)	0.89(9)	1.42(9)	0.61(9)
C(10)	0.4203(3)	0.38615(23)	0.5439(4)	3.15	3.30(13)	4.14(14)	2.81(12)	1.75(11)	1.02(10)	1.42(10)
C(11)	0.6012(4)	0.25109(21)	0.4693(4)	3.05	4.56(15)	3.73(13)	2.71(11)	2.00(12)	2.18(11)	1.10(10)
C(12)	0.7515(3)	0.44806(22)	0.7150(5)	3.24	3.33(13)	3.59(13)	3.87(14)	0.38(11)	1.62(11)	1.96(11)
C(13)	0.8384(3)	0.11304(20)	1.2287(4)	2.79	3.66(13)	3.10(12)	2.94(11)	1.43(10)	1.77(11)	1.56(9)
C(14)	0.9143(3)	0.06225(19)	0.6909(4)	2.89	3.60(13)	3.08(12)	2.30(11)	0.85(10)	1.35(10)	0.39(9)
C(15)	1.0148(3)	0.26952(20)	0.8341(5)	3.06	2.92(12)	3.15(12)	4.32(14)	0.83(10)	1.88(11)	1.76(11)
C(16)	1.1557(3)	0.15675(23)	1.0687(4)	3.11	2.64(11)	4.49(15)	2.93(12)	1.43(11)	1.10(10)	1.27(11)
H(2A)	0.370(4)	0.1104(23)	0.572(5)	5.7(8)						
H(2B)	0.322(4)	0.0935(25)	0.728(5)	6.6(9)						
H(2C)	0.321(4)	0.180(3)	0.674(5)	7.5(11)						
H(4A)	0.744(3)	0.4874(21)	1.142(4)	4.4(7)						
H(4B)	0.897(4)	0.4818(22)	1.212(4)	5.3(8)						
H(4C)	0.798(3)	0.4749(20)	1.324(5)	4.5(7)						
H(6A)	1.034(4)	0.3019(26)	1.372(5)	6.9(10)						

H(6B)	1.052(4)	0.3908(27)	1.334(5)	7.0(10)
H(6C)	0.972(5)	0.368(3)	1.449(6)	9.2(13)
H(8A)	0.650(4)	-0.0033(23)	0.818(5)	6.3(9)
H(8B)	0.504(4)	-0.0038(26)	0.833(6)	7.5(11)
H(8C)	0.522(4)	0.0007(24)	0.664(6)	6.6(9)
H(9A)	0.463(3)	0.4179(21)	1.034(4)	3.8(6)
H(9B)	0.340(4)	0.3402(21)	0.892(4)	5.0(7)
H(9C)	0.431(3)	0.3331(19)	1.085(4)	3.6(6)
H(10A)	0.410(3)	0.4391(20)	0.628(4)	4.2(7)
H(10B)	0.334(4)	0.3408(21)	0.516(4)	4.5(7)
H(10C)	0.417(3)	0.3988(21)	0.432(5)	5.0(7)
H(11A)	0.511(4)	0.2037(23)	0.416(4)	5.0(8)
H(11B)	0.616(4)	0.2723(21)	0.373(5)	5.4(8)
H(11C)	0.673(4)	0.2237(22)	0.524(5)	5.3(8)
H(12A)	0.744(4)	0.5015(24)	0.794(5)	5.9(9)
H(12B)	0.837(4)	0.4342(22)	0.773(5)	5.3(8)
H(12C)	0.758(3)	0.4606(20)	0.609(5)	4.6(7)
H(13A)	0.827(3)	0.0525(23)	1.175(4)	4.7(7)
H(13B)	0.941(3)	0.1351(19)	1.323(4)	4.3(7)
H(13C)	0.777(3)	0.1209(19)	1.287(4)	3.6(6)
H(14A)	0.832(3)	0.0677(18)	0.610(4)	3.5(6)
H(14B)	0.896(3)	0.0067(22)	0.719(4)	4.7(7)
H(14C)	0.985(3)	0.0611(19)	0.634(4)	4.1(7)
H(15A)	1.075(3)	0.2639(20)	0.766(4)	4.6(7)
H(15B)	1.061(3)	0.3213(22)	0.939(5)	5.0(8)
H(15C)	0.933(4)	0.2804(23)	0.766(5)	5.8(9)
H(16A)	1.196(3)	0.2067(23)	1.173(5)	5.1(8)
H(16B)	1.144(3)	0.1044(22)	1.109(4)	4.6(7)
H(16C)	1.230(3)	0.1518(20)	1.011(4)	4.3(7)

^a The numbers given in parentheses are the estimated standard deviations of the least significant digits. ^b Isotropic equivalents are given for the atoms refined anisotropically.

TABLE 7
 FRACTIONAL MONOCLINIC ATOMIC COORDINATES AND FINAL ANISOTROPIC THERMAL PARAMETERS FOR *trans*-Si₄C₁₆H₃₆ (2)

Atom	x	y	z	B _{iso} ^b	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Si(1)	0.59714(4) ^a	0.09073(4)	0.095499(24)	2.32	2.283(14) ^a	2.258(15)	2.408(15)	-0.288(10)	0.028(10)	-0.072(10)
Si(2)	0.82778(4)	0.22898(4)	0.084962(25)	2.39	2.428(15)	2.337(15)	2.434(15)	-0.369(10)	-0.186(10)	0.055(11)
C(1)	0.63956(15)	-0.09724(13)	0.06977(10)	2.40	2.08(4)	2.14(5)	3.23(5)	-0.16(5)	-0.08(4)	0.61(4)
C(2)	0.43229(14)	0.16651(13)	0.00764(10)	2.45	2.09(4)	1.87(5)	3.73(6)	-0.06(4)	0.16(4)	0.16(5)
C(3)	0.53834(28)	0.10273(26)	0.21858(13)	4.36	4.99(9)	5.66(10)	3.26(7)	-0.91(8)	1.20(6)	-0.45(7)
C(4)	0.76394(20)	-0.16870(19)	0.14284(14)	3.41	3.14(6)	3.26(7)	4.60(8)	-0.08(5)	-0.98(6)	1.28(6)
C(5)	0.39112(21)	0.31900(17)	0.02617(18)	3.62	3.17(6)	2.21(6)	6.82(11)	0.24(5)	-0.06(7)	-0.52(6)
C(6)	0.82118(23)	0.28837(22)	-0.04153(12)	3.80	3.92(7)	4.75(9)	3.15(7)	0.25(6)	0.52(5)	0.98(6)
C(7)	1.02073(19)	0.13201(21)	0.12243(15)	3.74	2.60(6)	4.12(8)	5.14(9)	-0.11(5)	-0.28(6)	1.14(7)
C(8)	0.83034(25)	0.38839(19)	0.16305(14)	3.85	4.95(8)	3.17(7)	4.23(8)	-1.11(6)	-0.10(6)	-0.99(6)
H(3A)	0.439(3)	0.054(3)	0.2191(18)	7.8(6)						
H(3B)	0.527(3)	0.199(3)	0.2372(18)	7.0(6)						
H(3C)	0.620(3)	0.0645(27)	0.2577(19)	6.9(6)						
H(4A)	0.721(3)	-0.2461(28)	0.1734(17)	7.3(6)						
H(4B)	0.784(3)	-0.113(3)	0.1946(20)	7.8(7)						
H(4C)	0.862(3)	-0.2086(27)	0.1204(18)	7.0(6)						
H(5A)	0.281(3)	0.3449(25)	0.0114(17)	6.7(6)						
H(5B)	0.432(3)	0.352(3)	0.0861(21)	8.4(7)						
H(5C)	0.442(3)	0.381(3)	-0.0111(20)	8.2(7)						
H(6A)	0.7266(26)	0.3478(23)	-0.0638(14)	5.0(4)						
H(6B)	0.8095(28)	0.207(3)	-0.0814(18)	7.2(6)						
H(6C)	0.912(3)	0.341(3)	-0.0473(21)	8.9(7)						
H(7A)	1.0341(26)	0.1012(24)	0.1898(18)	6.1(5)						
H(7B)	1.109(3)	0.192(3)	0.1150(17)	7.4(6)						
H(7C)	1.0253(26)	0.0585(26)	0.0839(16)	5.3(5)						
H(8A)	0.9218(28)	0.4451(26)	0.1542(16)	6.0(5)						
H(8B)	0.7335(28)	0.4488(26)	0.1460(17)	6.2(5)						
H(8C)	0.834(3)	0.3561(26)	0.2324(20)	7.4(6)						

^a The numbers given in parentheses are the estimated standard deviations of the least significant digits. ^b Isotropic equivalents are given for the atoms that were refined anisotropically.

TABLE 8
INTERATOMIC CARBON AND HYDROGEN DISTANCES (Å)

<i>trans</i> -Si ₄ C ₁₆ H ₃₆ (1)					
C(3)–H(3a)	0.96(3)	C(5)–H(5A)	0.95(3)	C(7)–H(7A)	0.99(3)
C(3)–H(3B)	0.96(3)	C(5)–H(5B)	0.93(3)	C(7)–H(7B)	0.96(3)
C(3)–H(3C)	0.89(3)	C(5)–H(5C)	0.93(3)	C(7)–H(7C)	0.89(2)
C(4)–H(4A)	0.95(3)	C(6)–H(6A)	0.99(3)	C(8)–H(8A)	0.96(3)
C(4)–H(4B)	0.90(3)	C(6)–H(6B)	0.96(3)	C(8)–H(8B)	1.00(3)
C(4)–H(4C)	1.00(3)	C(6)–H(6C)	0.92(3)	C(8)–H(8C)	1.02(3)
<i>cis</i> -Si ₄ C ₁₆ H ₃₆ (2)					
C(2)–H(2A)	0.93(4)	C(9)–H(9A)	0.92(3)	C(13)–H(13A)	0.91(3)
C(2)–H(2B)	0.93(4)	C(9)–H(9B)	1.01(3)	C(13)–H(13B)	1.01(3)
C(2)–H(2C)	0.91(4)	C(9)–H(9C)	0.91(3)	C(13)–H(13C)	0.88(3)
C(4)–H(4A)	0.88(3)	C(10)–H(10A)	0.97(3)	C(14)–H(14A)	0.90(3)
C(4)–H(4B)	0.92(3)	C(10)–H(10B)	0.95(3)	C(14)–H(14B)	0.95(3)
C(4)–H(4C)	0.98(3)	C(10)–H(10C)	0.95(3)	C(14)–H(14C)	0.94(3)
C(6)–H(6A)	0.91(4)	C(11)–H(11A)	0.96(3)	C(15)–H(15A)	0.92(3)
C(6)–H(6B)	0.94(4)	C(11)–H(11B)	0.95(3)	C(15)–H(15B)	0.93(3)
C(6)–H(6C)	0.91(5)	C(11)–H(11C)	0.94(3)	C(15)–H(15C)	0.89(4)
C(8)–H(8A)	0.93(4)	C(12)–H(12A)	0.94(4)	C(16)–H(16A)	0.91(3)
C(8)–H(8B)	0.88(4)	C(12)–H(12B)	0.92(3)	C(16)–H(16B)	0.95(3)
C(8)–H(8C)	0.98(4)	C(12)–H(12C)	0.93(3)	C(16)–H(16C)	0.98(3)

0.044. The estimated standard deviation of an observation of unit weight was 1.49, with a final data/variable ratio of 15.9. The final difference electron density map was featureless. Final atomic coordinates and anisotropic thermal parameters are given in Table 7 and selected distances and angles are given in Table 3. A listing of observed and calculated structure factors ($\times 10$) is available as supplementary material (Table 12).

The final values of the discrepancy indices for *cis*-Si₄C₁₆H₃₆ were $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.040$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2} = 0.046$. The estimated standard deviation of an observation of unit weight was 1.30, the final data/variable ratio was 11.7. There were no significant features on the final difference electron density map. Final atomic coordinates and anisotropic thermal parameters are given in Table 6 and selected distances and angles are given in Table 2. A listing of observed and calculated structure factors ($\times 10$) is available as supplementary material (Table 11).

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