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SPECTROSCOPIC STUDIES OF THE CONFORMATIONS OF n-DECAMETHYLTETRASILANE *

CHARIYA A. ERNST, A. LOUIS ALLRED, and MARK A. RATNER

Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois 60201 (U.S.A.)

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Summary

The conformational properties of n-decamethyltetrasilane, n-$Si_4(CH_3)_{10}$, have been studied by variable temperature NMR (^1H and ^{13}C) and vibrational (IR and Raman) spectroscopy. As in related alkane systems, the *anti* conformer is more stable than the gauche conformer. Values of ΔH^0 and ΔS^0 for the *anti* → *gauche* reaction are 2.26 ± 0.15 kJ mol^{-1} and $\Delta S^0 = 7.82 \pm 0.86$ J $K^{-1} mol^{-1}$, respectively. Thus, the two conformers are present in comparable quantities at room temperature. At very low temperatures, broadening of the two proton resonances ($SiMe_2$, $SiMe_3$) occurs, but phase changes precluded the observation of decoalescence. By approximate lineshape analysis, the free energy of activation, $\Delta G^\ddagger$, for rotation about the central Si—Si bond is estimated to be ~25 kJ mol^{-1}.

Introduction

Many studies have established that the electronic properties of permethylated polysilanes differ greatly from those of their saturated hydrocarbon analogs [1,2]. The transmission of electronic effects through silicon chains has been demonstrated by proton nmr studies [3] of α,ω-disubstituted permethylpolysilanes and by the markedly nonstatistical attack by Grignard reagents [4] on halogen atoms in the α,ω-dihalopermethylpolysilanes. A possible explanation for this phenomenon is that lone-pair electrons in the substituent orbitals of π-symmetry (e.g. chlorine *p*-orbitals) are partially transferred into 3*d* and 4*p* silicon orbitals or perhaps simply σ^*(Si—Si) molecular orbitals on the polysilane chain. In consideration of these effects, conformational populations of the permethylated polysilanes have generally been neglected. It is conceivable that the

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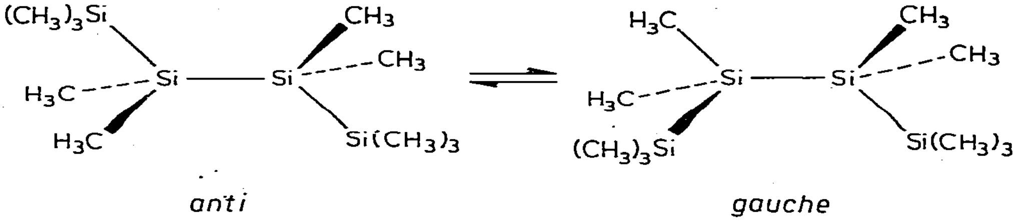
* Dedicated to Professor Eugene G. Rochow on the occasion of his 70th birthday.

occurrence of *gauche* conformations could bring about through-space chlorine—chlorine interactions in the α,ω-dichloro compounds strong enough to be responsible for the apparent transmission of electronic effects. The photoelectron spectra of $Si_n(CH_3)_{2n+2}$ are not adequately accounted for in terms of a simple Si—Si bond-bond interaction model [2] as shown by similar studies of the Si_nH_{2n+2} series [5] in which rotational conformations are taken into consideration.

The permethylpolysilanes may be expected to function as close structural analogs to the C_nH_{2n+2} hydrocarbons since the solid state structure of dodecamethylcyclohexasilane [6], $Si_6(CH_3)_{12}$, is comparable to the chair conformation of cyclohexane. However, the torsional barrier of an Si—Si bond in this class of compounds has been shown to be very small by previous ^1H NMR studies of $Si_6(CH_3)_{12}$ [1d] for which only a single sharp resonance was observed down to —95°C. Vibrational studies [7] of $Si_2(CH_3)_6$ did not lead to an unequivocal assignment of the structure as eclipsed, staggered, or essentially freely rotating. The infrared and Raman spectra of liquid $Si_n(CH_3)_{2n+2}$ (n = 3, 4, 5) have been reported by Stolberg and Fritz [8] who interpreted the vibrational spectrum of $Si_4(CH_3)_{10}$ in terms of a single *anti* isomer. Later reviewers [9] noted a discrepancy but suggested that the sample was a mixture of n and iso forms rather than a pure species.

Since both anti and gauche conformations, with respect to the central bond in n-$Si_4(CH_3)_{10}$ should exist, absorptions due to both conformations can be anticipated in the liquid on the vibrational timescale [10]. This paper will first report the assignment of certain vibrational bands of the *anti* and *gauche* conformations of $Si_4(CH_3)_{10}$ and then the determination of pertinent thermodynamic and kinetic data related to the *anti* ⇌ *gauche* interconversion for n-decamethyltetrasilane. An important goal is the comparison of these data with those for various compounds of carbon.



Experimental

Materials. Decamethyltetrasilane, n-Si_4Me_{10}, was prepared by two general routes with the second being more convenient: (1) By cleavage of $(SiMe_2)_6$ with PCl_5 to yield a mixture of $Cl(SiMe_2)_nCl$ species [11] (n = 3, 4, 6) followed by methylation and separation by fractional distillation; (2) By chlorination of Si_2Me_{10} [12], followed by coupling of the resulting Si_2Me_5Cl with Na/K alloy [13] to yield n-Si_4Me_{10}. For careful spectroscopic studies, the n-Si_4Me_{10} was purified by both fractional distillation and by preparative gas-chromatography, using a 3/8″ by 8′ column packed with 10% Apiezon L on Chromosorb W (60—80 mesh).

Analyses. Found (Galbraith Laboratories): C, 45.48; H, 11.34. $C_{10}H_{30}Si_4$ calcd.: C, 45.72; H, 11.51%. Solvents were dried and distilled under a nitrogen atmosphere.

Spectroscopic studies. The integrated ^{1}H NMR spectrum of pure liquid n-Si_4Me_{10} at room temperature was obtained. ^{1}H NMR spectra were also recorded for 1% solutions in various solvents using TMS as reference. Routine room temperature spectra were recorded on a Hitachi Perkin—Elmer R20B 60 MHz spectrometer. Both a Bruker HX-270 spectrometer and a Bruker HFX-10 model 90 MHz spectrometer in conjunction with a Fabritek 1074 time-averaging computer were used for low temperature spectra. For the low temperature studies, a sample consisting of 1% (vol.) n-Si_4Me_{10} and les than 1% TMS in $CHFCl_2/CF_2Cl_2$ (1/9) was prepared in a sealed tube under vacuum. This solution freezes between 125 K and 110 K. The ^{13}C NMR spectra of n-Si_4Me_{10} were obtained on a Varian CFT-20 spectrometer. A room temperature spectrum of n-Si_4Me_{10} in CCl_4/DMSO-d_6 (9/1) with TMS was recorded, whereas a 1% solution of n-Si_4Me_{10} in CF_2Cl_2/d_8-toluene (4/1) and a solution of $(SiMe_2)_6$ in CF_2Cl_2/acetone-d_6 (9/1) with TMS as the reference were used for low temperature ^{13}C NMR studies.

Infrared spectra of the neat liquids were recorded on a Beckman IR-12 and Perkin—Elmer IR-283 spectrometers. Room temperature spectra for the 300—4000 cm^{-1} region were obtained for a liquid sample of 0.05 mm thickness in a KBr cell. For the 200—600 cm^{-1} region, an evacuateable cell constructed by Professor D.F. Shriver and having polyethylene windows, was used to obtain IR spectra of both liquid (35°C) and solid (—138°C) n-Si_4Me_{10}. Frequencies were calibrated with indene absorptions at 2770.9, 1553.2, 1018.5, 590.8, and 381.4 cm^{-1}.

Raman spectra of solid and of pure liquid n-Si_4Me_{10} in sealed Kimax capillaries were observed with a Spex 1401 double monochromator and Spectra Physics 165 lasers by previously described techniques [14]. The Raman spectra were excited by the 4880 Å line or the 5145 Å line of Ar$^+$, employing a 1—2 cm^{-1} bandpass and either a 90° or a back-scattering geometry. Polarization measurements were accomplished using a polaroid analyzer in the scattered beam and a 90° collection geometry. Depolarization ratios were obtained only for the neat liquid. Intensity measurements were made over the —23.5 to +120.5°C temperature range. The experimental data were digitally recorded on magnetic tapes, which were subsequently processed by program Raman [14]. Deconvolution of overlapping bands for the 300—420 and 585—735 cm^{-1} regions was accomplished using a modification of the band-fitting program developed by Pitha and Jones [15]; relative intensities were obtained by numerical integration of the band areas. The variable temperature Raman spectra of solutions of n-Si_4Me_{10} (10% by volume) in acetone, benzene, CCl_4 and CF_2Cl_2 and of the pure solvents were also recorded. The scaled solvent spectra were subtracted from the corresponding solution spectra, and deconvolution of the resulting rotamer Raman bands permitted the evaluation of relative intensities. Sample temperatures, with the maximum error of ± 1°C, were measured with a copper-constantan thermocouple. Estimated errors in thermodynamic quantities are three times the standard deviation.

Method for calculating ΔH^0 and ΔS^0. The equilibrium constant (K) for the interconversion *anti* (a) $\rightleftharpoons$ *gauche* (g) can be written in accordance with Beer's Law: $K = C_g/C_a = S_g\alpha_a/S_a\alpha_g$, where C_i, S_i and α_i are the rotamer concentrations, vibrational band intensities and the scattering coefficients, respectively. Therefore, from the definition of $\Delta G°$:

$$\ln(S_g/S_a) = -\frac{\Delta H°}{R}\left(\frac{1}{T}\right) + \frac{\Delta S°}{R} - \ln\frac{\alpha_a}{\alpha_g} \tag{1}$$

Correct values of $\Delta H°$ and $\Delta S°$ from a plot of $\ln K$ versus $1/T$ are assured only if the α_a/α_g ratio is temperature invariant as shown, for example, by a linear plot of observed A_a versus A_g for a series of temperatures (l = length of cell) [16]:

$$C_{\text{total}} \equiv C_t = C_g + C_a = \frac{S_g}{\alpha_g l} + \frac{S_a}{\alpha_a l}$$

or

$$S_a = C_t l \alpha_a - \frac{\alpha_a}{\alpha_g} S_g \tag{2}$$

This approach is limited by experimental difficulties in keeping other external conditions constant over a temperature range as well as by the usual uncertainties in measurement of absolute intensities. In the present Raman studies, problems arose in keeping the instrumental power constant during a long run, and the sample set-ups for low and high temperature are unavoidably different (resulting in the variation of l). Thus a non-linear plot of S_a versus S_g resulted. However, the α_a/α_g ratio was shown to be independent of temperature by a variation of a previously suggested [17] method involving a third Raman band common to both isomers and having intensity: $S_{\text{co}}/l = \alpha_{\text{co}}C_t = \alpha_{\text{co}}C_g + \alpha_{\text{co}}C_a$, where α_{co} is assumed equal for both conformers scattering at the same frequency. After division of equation 2 by S_{co} and substitution for C_t, an analogous equation is obtained, in which environmental dependence (except for temperature) has now dropped out. If the plot of S_a/S_{co} versus S_g/S_{co} is linear,

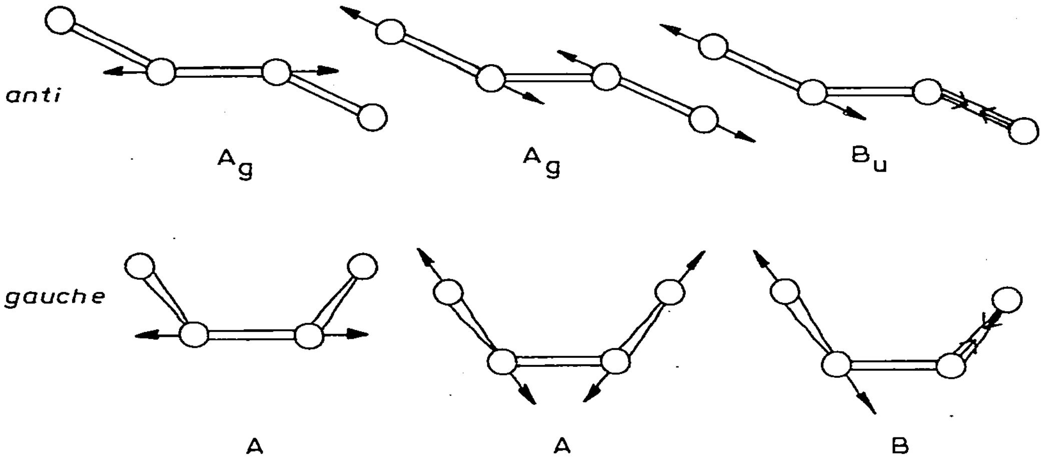
$$\frac{S_a}{S_{\text{co}}} = \frac{\alpha_a}{\alpha_{\text{co}}} - \frac{\alpha_a S_g}{\alpha_g S_{\text{co}}} \tag{3}$$

the calculation of ΔH^0 from eq. 1 is valid, and, in addition, ΔS^0 is obtainable by using the value of the slope ($= -\alpha_a/\alpha_g$) in the expression for the intercept of the Van 't Hoff plot.

Results

Vibrational spectra and assignments. Application of the selection rules for the two rotamers of n-Si_4Me_{10} show that they should be distinguishable since the *anti* (C_{2h}) conformer contains an inversion center and the gauche (C_2) conformer does not. The infrared (IR) and Raman (R) activities of the *anti* skeletal vibrations (the methyl groups are treated as single particles) must be mutually exclusive. Symmetry coordinates for the *gauche* rotamer are either A or B

modes, both being active in IR and Raman. The Si—Si stretches are of primary interest here: $2A_g(\mathrm{R}) + B_u(\mathrm{IR})$ modes for the *anti* and $2A + B(\mathrm{IR, R})$ modes for the *gauche*:



The Raman spectra of liquid (47.2° C) and solid (—67.8° C) n-Si_4Me_{10} below 1500 cm^{-1} are presented for comparison in Fig. 1. The liquid supercooled while the temperature was being slowly decreased and solidified at —67.8° C (lit. [27] m.p. —14.5° C). The disappearance of many Raman bands in the spectrum of the solid strongly indicates that only one conformer persists [28]. In particular, in the region 350—450 cm^{-1} characteristic of Si—Si stretches [29] the relative intensities of the two strongly polarized and intense bands at 355 and 366 cm^{-1} are temperature dependent, with the former disappearing completely in the solid phase. Earlier workers [8] assigned these two Raman bands to two symmetric (A_g) Si—Si stretches, and also assigned the IR bands at 407 and 413 cm^{-1} to *anti*-symmetric stretches, based on the *anti* conformer only. A new

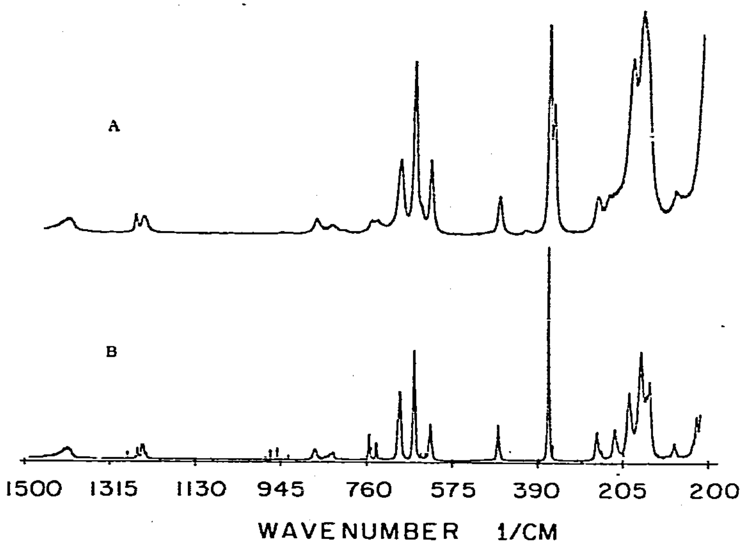


Fig. 1. Raman spectra of n-$Si_4(CH_3)_{10}$ in (a) liquid at 47.2° C, (b) crystalline form at —67.8° C.

assignment of vibrational bands n-Si_4Me_{10}, especially Si—Si stretches, is made herein on the basis of two conformers being present in the liquid phase with only the more stable anti conformer in the solid phase [28]. Thus, the two polarized Raman bands at 366 and 473 cm^{-1}, which are observed in both solid and liquid spectra, can be assigned to the two A_g anti Si—Si stretches, while the band at 355 cm^{-1}, which disappears in the solid Raman spectrum, belongs to one of the two symmetric (A) Si—Si stretches for the *gauche* isomer. The assignment of the second *gauche* A mode is not obvious, and it is probably close to the other anti A_g mode at 473 cm^{-1} and too weak to be observed. The vibrations of silicon skeletons are in general weak and are sometimes not observed in the IR [29], as is the case here. The depolarized Raman band at 415 cm^{-1} which is observed also in the IR and dissappears in the solid spectrum, and the IR band at 407 cm^{-1}, which is not observed in the Raman and persists in the solid IR spectrum, can be assigned consistently to the *gauche* B and the *anti* B_u Si—Si stretching modes, respectively. The assignments of the Raman and IR spectra are summarized in Tables 1 and 2. The broad bands at 89 and

TABLE 1

OBSERVED RAMAN FREQUENCIES IN LIQUID AND SOLID n-Si_4Me_{10}

Liquid (21°C)			Solid (—67.8°C)		Approximate assignment
cm^{-1}	I^a	ρ^b	cm^{-1}	I^a	
			45	w	Si—CH_3 torsions
89	w	0.39	93	w	C_3Si—SiC_2 torsions
150	s	?	147	m	Si—Si—Si bend
180	(br)		153	m	Si—Si—C bend and C—Si—C bend
164	s	0.56	165	s	
184	s	0.49	191	m	
210	w	0.70			
219	w	0.70	222	w	
234	w	0.68			
254	vw	0.70	255	vw	
260	w	0.73	260	w	
355	m	0.00			Si—Si stretch, (A, *gauche*)
366	s	0.00	365	vs	Si—Si stretch, (A_g, *anti*)
415	vw	0.80			Si—Si stretch, (B, *gauche*)
473	w	0.32	474	w	Si—Si stretch, (A_g, *anti*)
622	m	0.02	621	w	Si—C stretch
641	w	0.46			
656	s	0.11	656	s	
687	m	0.77	687	m	
730	w	0.7	738	w	SiC_3 rock SiC_2 rock
750	(br)		754	w	
807	vw	0.77	810	vw	
834	w(br)	0.77	831	w	
870	vw	0.50	869	w	
943	vw	0.14	951	vw	
1242	vw	0.68	1242	vw	CH_3 rock
1260	vw	0.06	1254	w	
1406	w(br)	0.70	1406	w	CH_3 bend
2899	vs	0.04	2899	vs	C—H stretch
2958	vs	0.73	2958	vs	

[a] The following abbreviations are used to compare relative intensities: s, strong; m, medium; w, weak; v, very; (br), broad. [b] ρ denotes the depolarization ratio.

TABLE 2

OBSERVED IR FREQUENCIES IN LIQUID AND SOLID n-$Si_4(CH_3)_{10}$

Liquid (35°C)		Solid [a] (−138°C)		Approximate assignment
cm^{-1}	I^b	cm^{-1}	I^b	
205	w(sh)			Si—Si—Si bend, Si—Si—C bend, and C—Si—C bend
211	w(sh)			
217	w(sh)	222.0	w	
236	w(br)			
246	w(br)	247.5	w(br)	
352	vw(br)			Si—Si stretch, (*A*, *gauche*)
407	vw(br)	405.5	vw (sharp)	Si—Si stretch, (B_u, *anti*)
414	vw(br)			Si—Si stretch, (*B*, *gauche*)
614	s			Si—C stretch
637	s			
650	m(sh)			
685	s			
724	s			SiC_3 rock, SiC_2 rock
770	vs			
778	m(sh)			
801	m(sh)			
824	vs(br)			
854	m(sh)			
1246	s			CH_3 rock
1301	w			
1323	vw			
1398	m(br)			CH_3 bend
1429	w(sh)			
2809	w(sh)			C—H stretch
2891	s			
2945	vs			

[a] The solid spectrum was obtained for the region between 200 to 600 cm^{-1}.

[b] The following abbreviations are used to compare relative intensities: s, strong; m, medium; w, weak; v, very; (br), broad; (sh) shoulder.

45 cm^{-1}, which appear in both solid and liquid Raman spectra, are probably due to Si—C torsions and/or C_2Si—SiC_3 torsions. The C_2Si—SiC_2 torsional mode for the *anti* rotamer is Raman inactive and for the *gauche* rotamer probably contributes to these broad bands. Attempts to evaluate from Raman spectra the interconversion equilibrium of n-Si_4Me_{10} in acetone, benzene, CCl_4, and CF_2Cl_2 solutions failed due to the low signal-to-noise ratio of spectra in these dilute (10%) solutions.

Evaluation of ΔH^0 *and* ΔS^0. The two intense Raman bands at 355 cm^{-1} (*gauche*) and 366 cm^{-1} (*anti*) were selected for the determination of the relative populations, and an example of the deconvolution of these overlapping bands is presented in Fig. 2. With the method described in the Experimental section, a value of 2.26 ± 0.15 kJ mol^{-1} was obtained for ΔH^0 of *anti* $\rightleftharpoons$ *gauche* interconversion. The Van 't Hoff plot is displayed in Fig. 3. Similar analyses of the 656 cm^{-1} (*anti* Si—C stretch) and 355 cm^{-1} pair and the 622 cm^{-1} (*anti* Si—C stretch) and 355 cm^{-1} pair gave 2.36 ± 0.65 kJ mol^{-1} and 1.98 ± 0.74 kJ mol^{-1}, respectively, for ΔH^0. Deconvolutions [15] of these bands are shown in Fig. 4. The above 2.26 ± 0.15 kJ mol^{-1} value is selected since the 355 and 366

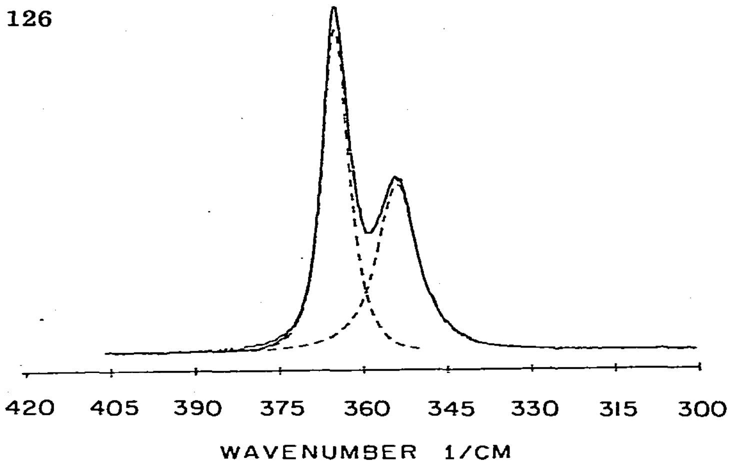


Fig. 2. Raman spectrum of n-$Si_4(CH_3)_{10}$ between 300 and 406 cm^{-1} showing the results of deconvolution of the 366 and 355 cm^{-1} bands at —15.5°C.

peaks were scanned slowly and obtained with relatively high signal-to-noise ratios. The intense Raman band at 687 cm^{-1} belongs to both *anti* and *gauche* rotamers since the relative ratio of this band intensity to either an *anti* or a *gauche* band does not correlate with temperature change, and therefore can be utilized in the evaluation of ΔS^0 according to the procedure described in the Experimental section. A plot of S_{366}/S_{687} versus S_{355}/S_{687} is linear. From the slope of the plot, the ratio of the scattering coefficients, $\alpha_{366}/\alpha_{355}$, is 1.066 (probable error ± 0.10). ΔS^0 (*anti* → *gauche*) can now be calculated from eq. 1 as 7.82 ± 0.86 J K^{-1} mol^{-1}. From S_{355}/S_{366} data and $\alpha_{366}/\alpha_{355}$, K is 0.95 ± 0.10 at 298 K.

For a 10% solution of n-Si_4Me_{10} in CF_2Cl_2, ΔH^0 is calculated, from S_{355}/S_{366}

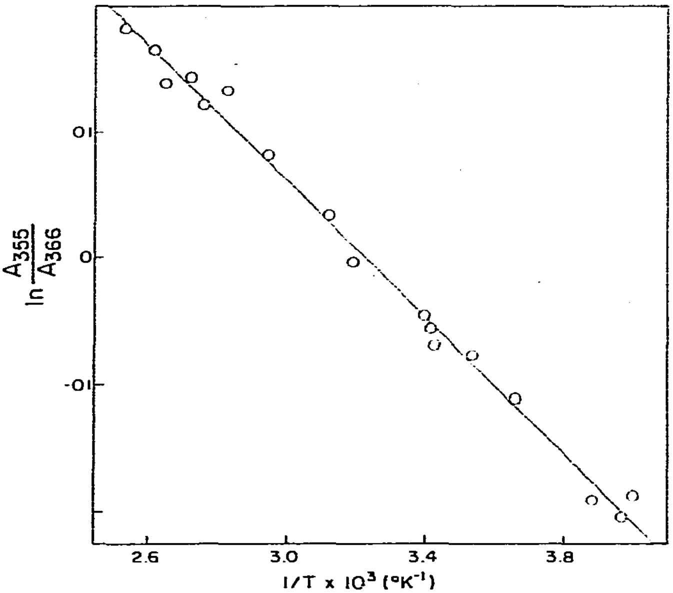


Fig. 3. Van 't Hoff plot for n-Si_4Me_{10}.

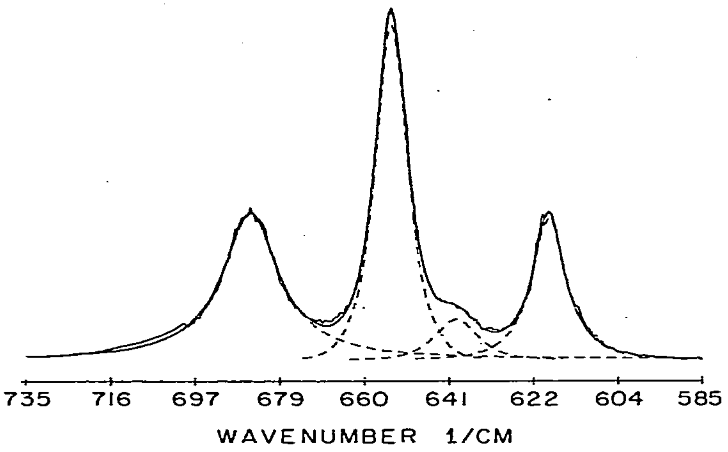
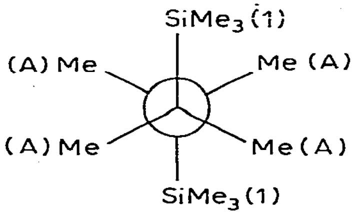


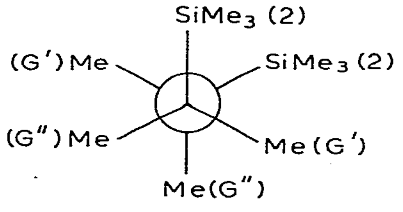
Fig. 4. Raman spectrum of n-$Si_4(CH_3)_{10}$ between 565 and 735 cm^{-1} showing the results of the band fitting procedure at 47.2° C.

data in the —49 to +21° C range, to be +2.2 ± 0.4 kJ mol^{-1}.

NMR studies. Due to rapid internal rotations about all bonds at room temperature, the spectrum of n-Si_4Me_{10} consists of only two proton signals ($SiMe_2$, $SiMe_3$) [30]. As the temperature is lowered, both proton resonances practically simultaneously broaden, the $SiMe_2$ signal becoming somewhat wider than the $SiMe_3$ signal, as shown in NMR spectra recorded at 270 MHz (Fig. 5) and in slightly less broadened spectra at 90 MHz. Apparently, rotation about the central Si—Si bond must be more restricted than about the terminal bonds and occurs most likely by a *gauche* ⇌ *anti* ⇌ *gauche* process because such a process will produce concurrent broadening of both signals, whereas hindered rotations about the end bonds will broaden only the $SiMe_3$ signal and a direct *gauche* ⇌ *gauche* interconversion about the middle bond alone will broaden only the $SiMe_2$ signal [25].



anti



gauche

Below 125 K, some of the tetrasilane probably aggregated as indicated by the appearance of new resonances and a dramatic increase in the TMS intensity relative to n-Si_4Me_{10}. Decoalescence and separate rotamer signals were never observed. At 123 K, the ^{13}C NMR spectra of n-Si_4Me_{10} revealed very little broadening of the two ^{13}C absorptions (at 35° C, $\delta(SiMe_3)$ —1.39 ppm, $\delta(SiMe_2)$ —6.05 ppm relative to TMS in CCl_4/DMSO-d_6 solvent at 35° C).

For lineshape analysis, the individual rotamer chemical shifts for the *gem*-dimethyl ($SiMe_2$) protons were approximated by solving for the unknown δ_A

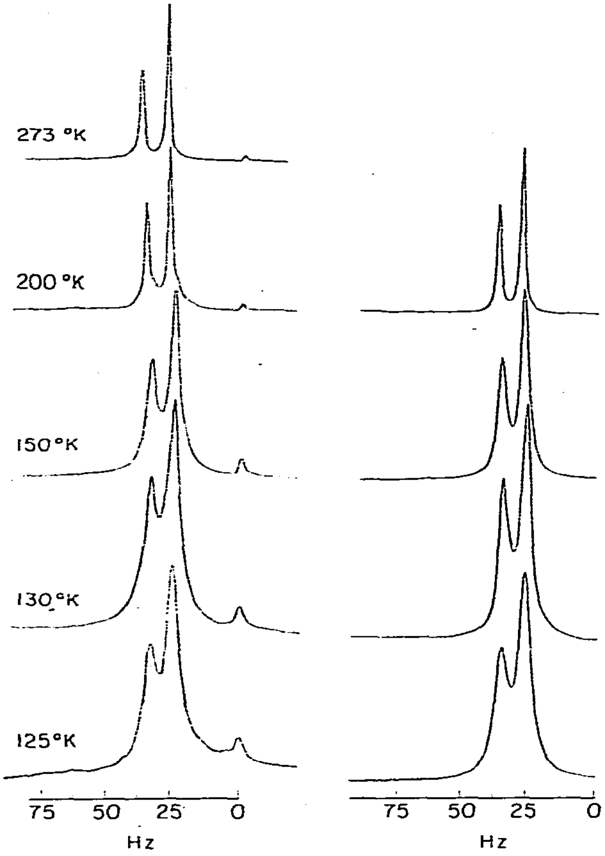


Fig. 5. Temperature dependence of 270 MHz ^{1}H spectra of n-$\mathrm{Si_4(CH_3)_{10}}$ in 10% $\mathrm{CHClF_2}$/90%/$\mathrm{CF_2Cl_2}$. The spectra to the right are computer-simulations.

($\mathrm{SiMe_2}$ shift for anti) and $\delta_{G'} + \delta_{G''}$ (for *gauche*) in the equation for the observed average $\delta(\mathrm{SiMe_2})$ in the fast exchange limit [18]: $\delta(\mathrm{SiMe_2})$ (av.) = $n_A\delta_A + n_G(\delta_{G'} + \delta_{G''})/2$, where the mole fraction of *anti*, $n_A = (1 + \exp(-\Delta H/RT + \Delta S/R))^{-1}$. With $\Delta H = 2.26$ kJ mol^{-1} and $\Delta S = 7.82$ J K^{-1} mol^{-1} for the pure liquid as obtained from vibrational studies and with a least-squares minimization program, the values 0.117 for δ_A and 0.162 ppm for $\delta_G[=\frac{1}{2}\delta_{G'} + \frac{1}{2}\delta_{G''}]$ were calculated [19]. In the lineshape analysis [20] of the broadening of the $\mathrm{SiMe_2}$ resonance, it was assumed that solvent effects [21] and the temperature dependence of rotamer chemical shifts relative to TMS [22] were negligible and that the only important barrier is for the indirect *gauche* ⇌ *anti* ⇌ *gauche* process *. Furthermore, from comparisons with related molecules [23—26] $\delta_{G'}$ and $\delta_{G''}$ were approximated by making $\delta_{G''} > \delta_{G'} > \delta_A$

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* There are two schemes for interconversion of the rotamers: (I) *gauche* ⇌ *anti* ⇌ *gauche*, and (II) *anti* ⇌ *gauche* ⇌ *gauche* (two types of barriers are involved). Since averaging of the *anti* and *gauche* signals is observed, at least the former process occurs and it has a lower barrier. If the barrier for direct *gauche* ⇌ *gauche* is not much larger, then process II is pertinent.

ative to TMS with equal spacing and linewidths at a given temperature. Field inhomogeneity contributions at each temperature were taken into account by comparison of the approximated $SiMe_2$ linewidths with the TMS linewidth. Best agreement of the fitted spectra for all temperatures was achieved when it was assumed that the individual rotamer $SiMe_2$ linewidths were the same as the TMS linewidths at all given temperatures.

From the analysis [20] of line-shapes at 270 MHz, the rate constants are 102, 170, 200, and 3350 sec^{-1} at 125, 130, 150 and 200 K, respectively. Computer-simulated spectra * are presented with the observed spectra in Fig. 5.

From the rate constants at 125 and 130 K, the $\Delta G^{\ddagger}$ are calculated to be 24.8 and 25.3 kJ $mole^{-1}$, respectively. In view of uncertainties introduced by the above assumptions, these values must be considered quite rough. The rate process is described here in the activated complex theory form $k = k_BT(h^{-1}) \exp(\Delta G^{\ddagger}/RT)$ as recommended by several workers [18]; such calculations are less prone to systematic error than are those involving ordinary Arrhenius factors.

Discussion

The value of $\Delta H^0 = 2.26 \pm 0.15$ kJ mol^{-1} for liquid n-Si_4Me_{10} can be compared with 4.04 ± 0.22 kJ mol^{-1} for gaseous n-butane [31], 2.85 ± 0.15 kJ mol^{-1} for liquid n-butane [32], 3.38 ± 0.21 kJ mol^{-1} for 2-methylbutane [31], 0.22 ± 0.12 kJ mol^{-1} for 2,3-dimethylbutane [31], and $\Delta E = 1.7$ kJ mol^{-1} for gaseous n-Si_4H_{10} [5], in all cases favoring the *anti* rotamer. The value, 7.82 ± 0.86 J K^{-1} mol^{-1}, of ΔS^0 (*anti* → *gauche*) is close to the expected statistical value ($R \ln 2 = 5.76$ J K^{-1} mol^{-1}) indicating a small difference in the moments of inertia of the anti and gauche rotamers [10]. The energy barriers around the Si—Si bonds are usually lower than for C—C bonds, e.g. 5.12 kJ mol^{-1} [33] for Si_2H_6 versus 11—13 kJ mol^{-1} [34] for C_2H_6, and $\leqslant 4.2$ kJ mol^{-1} [35] for Si_2Cl_6 versus 45 kJ mol^{-1} [35b] for C_2Cl_6. Dipole moment studies [36] of $Me_2XSiSiXMe_2$ (X = H, F, Cl, Br, I, OMe and SMe) also showed that the hindrance to rotation about the Si—Si bond in these compounds is weaker than in the corresponding ethane derivatives with the X = SMe derivative being most hindered and the X = H derivative showing no steric effect.

The ΔH^0 difference for internal rotation around Si—Si bonds in n-Si_4Me_{10} is lower than those for the shorter C—C bonds in analogous compounds. In comparing the ΔH^0 values of n-Si_4Me_{10} and n-C_4H_{10}, one can infer that the effect of the increased size of Me relative to H is outweighed by the larger covalent radius of silicon, so that the conformers of n-Si_4Me_{10} are more similar energetically. In comparison with the n-Si_4H_{10} system, the *gauche* conformer of n-Si_4Me_{10} has been slightly destabilized (with respect to the *anti* conformer), and this destabilization can be directly attributed to non-bonding repulsive interactions [37] between the methyl groups. The magnitude of this effect is nearly sufficient to bring the Si_4Me_{10} parameters into the same range as those for n-butane. While the *anti*-Si_4Me_{10} conformer is energetically more stable than

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* The slight difference in appearance between the observed and simulated spectra as seen in Fig. 5 results from the presence of $^{29}Si—^{1}H$ satellite bands which concurrently broaden.

its gauche counterpart, the entropic contribution results in comparable conformer populations at room temperature.

The value of $\Delta G^{\ddagger}$ for the *anti—gauche* interconversion apparently has not been measured for n-butane but is 18.0 ± 0.8 kJ mol^{-1} at 95 K for 2,3-dimethylbutane [23]. The present value of ~25 kJ mol^{-1} for the corresponding $\Delta G^{\ddagger}$ in n-Si_4Me_{10} is thus reasonable. From a comparison of $\Delta G^{\ddagger}$ values for Si_4Me_{10} with those found for analogous substituted hydrocarbons, one can infer that the steric repulsion effect is more marked in the hydrocarbons, due to the shorter C—C distance. For $[(CH_3)_3Si]_2CHCH[Si(CH_3)_3]_2$ at 353 K, a value of $\Delta G^{\ddagger}$ of 79 kJ mol^{-1} was observed [26]. In addition, a large negative $\Delta S^{\ddagger}$ (—109 ± 54 J K^{-1} mol^{-1}) was reported and attributed to the requirement for cooperative movement among many groups to attain the transition state [26]; analysis of the present rate data also shows a large $\Delta S^{\ddagger}$.

As a final comment, it should be noted that the *gauche* conformation in permethylpolysilanes (as exhibited by n-Si_4Me_{10}) is present to a significant extent even at room temperature and should not be overlooked as in some past vibrational spectroscopy studies.

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