

Molecular Structures and Conformational Composition of Trisilane and Tetrasilane by Gas-Phase Electron Diffraction

Arne Haaland,*^a Kristin Rypdal,^a Harald Stüger^b and Hans V. Volden^a

^aDepartment of Chemistry, University of Oslo, Box 1033 Blindern, N-0315 Oslo 3, Norway and ^bInstitute for Inorganic Chemistry, Technical University of Graz, Stremayrgasse 16, A-8010 Graz, Austria

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The gas-phase electron diffraction patterns of trisilane and normal tetrasilane have been recorded with an all-glass inlet system and a nozzle temperature of $23 \pm 2^\circ\text{C}$. The molecular structure of trisilane was optimized and the valence force field calculated by *ab initio* MO calculations at the 6-31G**/MP2 level, and the structures and valence force fields of *anti* and *gauche* conformers of tetrasilane were calculated at the 6-31G*/SCF level. The force fields were scaled and used to calculate root mean-square vibrational amplitudes and correction terms for molecular vibrations. Refinement of a geometrically consistent r_g -structure of Si_3H_8 yielded a Si–Si bond distance of $r_a = 233.2(2)$ pm and a valence angle of $\angle_a\text{SiSiSi} = 110.2(4)^\circ$. Refinements of a mixture of geometrically consistent r_g -models of *gauche* and *anti* conformers of Si_4H_{10} yielded the bond distances (r_a) Si(1)–Si(2) = 233.5(3) and Si(2)–Si(3) = 234.0(3) pm and the valence angle $\angle_a\text{SiSiSi} = 109.6^\circ$. The mole fraction of the *gauche* conformer was $\chi = 68(9)\%$ corresponding to a free energy difference of $0.2(1.1)$ kJ mol⁻¹ in favor of *gauche*. Introduction of the thermal vibration correction terms of tetrasilane calculated from the scaled quantum-mechanical force field led to significantly poorer agreement between experimental and calculated intensities.

Trisilane and normal tetrasilane have been known for more than 60 years,¹ but their molecular structures have not been determined, perhaps because of their volatility, flammability and thermal instability. The molecular structures of a handful of completely substituted derivatives have been determined by diffraction techniques; the solid-state structures of four trisilanes carrying large organic substituents have been determined by X-ray crystallography,² and the molecular structures of octamethyltrisilane³ and octachlorotrisilane⁴ have been determined by gas electron diffraction (GED).

Like normal butane, normal tetrasilane presumably consists of a mixture of conformers in the gas phase, and the photoelectron (PE) spectrum of *n*- Si_4H_{10} has been simulated on the basis of an assumed 1:1 mixture of *anti* and *gauche* conformers, CNDO orbital energies and Koopmans' theorem.⁵ Two substituted tetrasilanes have been studied by X-ray diffraction; the 1,5-dichloride $\text{ClSiPh}_2(\text{SiPh}_2)_2\text{SiPh}_2\text{Cl}$ crystallizes in an all planar *anti* conformation,⁶ while the 1,5-diol $\text{HOSiPh}_2(\text{SiPh}_2)_2\text{SiPh}_2\text{OH}$ crystallizes in a *gauche* conformation stabilized by an intramolecular hydrogen bond between the ter-

minal OH groups.⁷ No gas-phase structure of a normal tetrasilane appears to have been determined until now.

The bonding and structures of trisilane and tetrasilane have been studied by *ab initio* MO calculations. Grev and Schaefer have optimized the structure and calculated the vibrational frequencies of Si_3H_8 at the SCF level with a DZ plus polarization basis.⁸ Ortiz and Mintmire have optimized the structure of trisilane and the structure of tetrasilane with the dihedral angle $\phi(\text{SiSiSiSi})$ fixed at 0° (*syn*), 60° (*gauche*), 120° (*anti clinal*) and 180° (*anti*) at the SCF level with a 3-21G* basis.⁹ Separate conformational energy minima were found at 60° and 180° . The energies of the optimized geometries were then calculated by single-point calculations at the 6-31G*/MP2 level. At this level the *gauche* form was found to be the more stable by 0.17 kJ mol⁻¹.⁹

Experimental

Synthesis. Owing to the pyrophoric nature of silanes in the presence of oxygen, all manipulations must be carried out using inert gas or vacuum line techniques.

Si_3H_8 was synthesized by reducing Si_3Cl_8 with LiAlH_4 in di-*n*-butylether, and purified by fractional recondensation as described in the literature.¹⁰ *n*-Tetrasilane was

* To whom correspondence should be addressed.

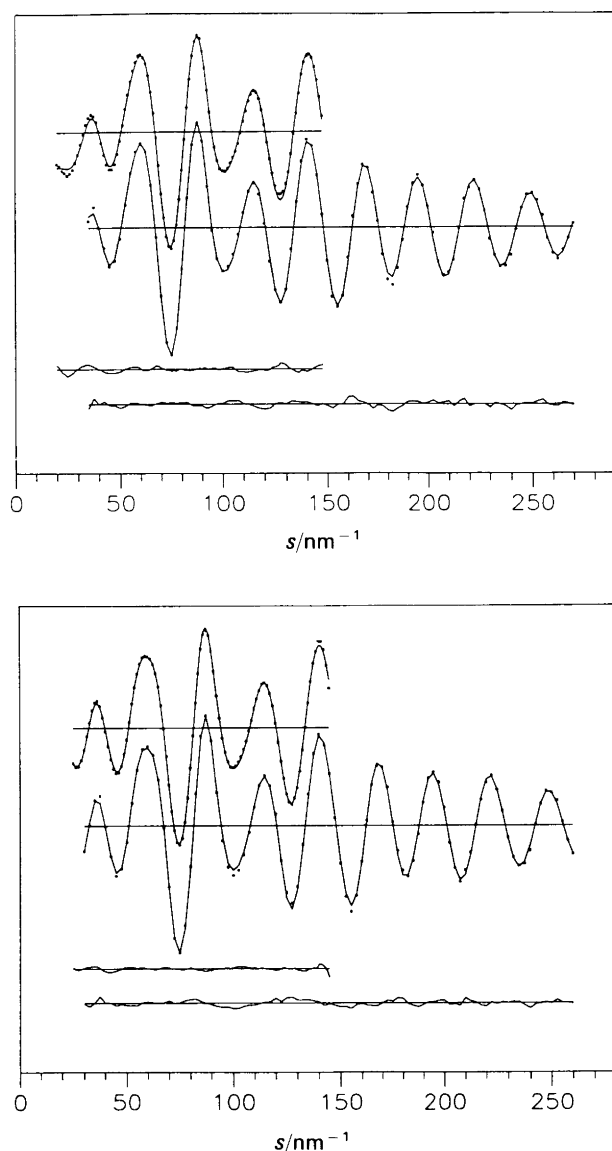


Fig. 1. Experimental (dots) and calculated (lines) modified molecular intensity curves of trisilane (above) and tetrasilane (below).

prepared by a similar procedure. Since $n\text{-Si}_4\text{Cl}_{10}$ usually contains traces of the iso-isomer, 1,4-dibromo- n -tetrasilane¹¹ was used as a starting material in order to prevent contamination of the product by branched isomers. Final purification of $n\text{-Si}_4\text{H}_{10}$ was achieved by fractional distillation at 100 mbar using a 10 cm Vigreux column: b.p. (100 mbar) = 50°C; yield = 45%.

The authenticity and purity of the products were checked by comparing ^1H and ^{29}Si NMR spectra with previously reported spectra.¹²

Gas-phase electron diffraction. Data were recorded on a Balzers KDG-2 instrument¹³ with an all-glass inlet system and a nozzle temperature of $23 \pm 2^\circ\text{C}$. Exposures were made with nozzle-to-plate distances of about 50 and 25 cm. Five or six photographic plates from each of

the four sets were microphotometered, and the data processed by standard procedures.¹⁴ Atomic scattering factors were taken from standard sources.¹⁵ Backgrounds were drawn as polynomials (seventh degree for 50 cm and ninth degree for 25 cm plates) to the difference between total experimental and calculated molecular intensity curves. For Si_3H_8 the final modified molecular intensity curves extended from $s = 20.00$ to 147.50 nm^{-1} with increment $ds = 1.25 \text{ nm}^{-1}$ (50 cm; 5 plates) and from 35.00 to 270.0 nm^{-1} with increment 2.50 nm^{-1} (25 cm; 5 plates). For Si_4H_{10} the final modified intensity curves extended from 25.00 to 145.00 nm^{-1} with $ds = 1.25 \text{ nm}^{-1}$ (50 cm; 6 plates) and from 30.00 to 260.00 nm^{-1} with $ds = 2.50 \text{ nm}^{-1}$ (25 cm; 5 plates) (Fig. 1).

Calculations

Ab initio MO and molecular force-field calculations. *Ab initio* molecular-orbital calculations were carried out with Gaussian 90, Revision F.¹⁶ The structure of trisilane was optimized and the valence force field calculated at the 6-31G**/MP2 level. The structures of *anti* and *gauche* conformers of tetrasilane were optimized, and the molecular force fields were calculated at the 6-31G*/SCF level with the dihedral angle $\phi(\text{SiSiSiSi})$ fixed at 180 and 60° , respectively. The force fields were scaled as described in Ref. 17, and root-mean-square amplitudes, l , and vibrational correction terms, $D = r_a - r_s$, at the temperature of our experiments were calculated by the program ASYM

Table 1. Trisilane; interatomic distances (r_a), root-mean-square vibrational amplitudes (l) determined from gas electron diffraction (GED) and vibrational amplitudes and vibrational correction terms $D = r_a - r_s$ calculated from a scaled *ab initio* force field (FF).^a

	$r_a(\text{GED})$	$l(\text{GED})$	$l(\text{FF})$	$D(\text{FF})$
Bond distances				
Si-Si	233.2(2)	6.2(2)	5.8	-0.26
Si(1)-H	148.3(3) ^b	10.5(2) ^c	9.0	-2.98
Si(2)-H	148.6(3) ^b	10.5(2) ^c	9.0	-1.52
Nonbonded distances				
Si...Si	381.5(4)	15.4(6)	15.8	0.61
Si(1)...H(2)	314.9(4)	16.0(6) ^d	15.5	-0.25
Si(2)...H(1)	320.1(12)	15.5(6) ^d	15.0	-1.24
Si...H(3)	415.2(10)	[28.5]	28.5	1.04
Si(1)...H(3')	511.4(20)	[15.7]	15.7	-0.46
Valence angles				
$\angle_a \text{SiSiSi}$	110.2(4)			
$\angle_a \text{Si(2)Si(1)H}$	112.9(7)			
$\angle_a \text{HSi(2)H}$	[107.8]			
R-factors^e	0.049 (50 cm)	0.059 (25 cm)	0.053 (total)	

^aDistances, amplitudes and D -values in pm, angles in degrees. Estimated standard deviations in parentheses in units of the last digit. Parameter values in square brackets have not been refined. ^{b-d}Denote pairs of parameters which were refined with constant difference, see text. ^e $R = [\sum w(l_{\text{obs}} - l_{\text{calc}})^2 / \sum w l_{\text{obs}}^2]^{1/2}$.

written by Hedberg.¹⁸ The vibrational amplitudes and correction terms obtained for trisilane are listed in Table 1. Some of the vibrational amplitudes obtained for tetrasilane are listed in Table 2. As described in the next section, inclusion of the vibrational correction terms for tetrasilane led to a significantly poorer fit between experimental and calculated GED intensities, and we do not believe it is worthwhile to list them.

Molecular structure refinement. The molecular symmetry of trisilane was assumed to be C_{2v} , and SiSiH_3 fragments

were assumed to have local C_{3v} symmetry. The valence angle $\angle \text{H}(2)\text{Si}(2)\text{H}(2)$ was fixed at the value obtained by the *ab initio* calculation (107.75°); so was the difference between the $\text{Si}(2)\text{--H}(2)$ and $\text{Si}(1)\text{--H}(1)$ bond distances (0.35 pm). The molecular structure is then determined by four independent parameters, *viz.* the bond distances Si--Si and $\text{Si}(1)\text{--H}$ and the valence angles $\angle \text{SiSiSi}$ and $\angle \text{Si}(2)\text{Si}(1)\text{H}$. These were first refined under the constraints of a geometrically consistent r_a model along with four root-mean-square vibrational amplitudes.¹⁹ Non-refined amplitudes were fixed at the values calcul-

Table 2. *n*-Tetrasilane; interatomic distances (r_a), root-mean-square vibrational amplitudes (l), valence angles and dihedral angles, mole fractions of *anti* and *gauche* conformers and restricting potential obtained by least-squares refinement on the GED data.^a

	Refinement 1; <i>anti/gauche</i> mixture		Refinement 2; potential energy curve	
	r_a (GED)	l (GED) or [FF]	r_a (GED)	l (GED) or [FF]
Bond distances				
Si(1)–Si(2)	233.5(3) ^b	6.1(1) ^c	233.6(3) ^b	6.1(1) ^c
Si(2)–Si(3)	234.0(3) ^b	6.2(1) ^c	234.0(3) ^b	6.2(1) ^c
Si(1)–H(1)	147.3(2) ^d	9.6(2) ^e	147.5(2) ^d	9.3(2) ^c
Si(2)–H(2)	147.7(2) ^d	9.6(2) ^e	147.8(2) ^d	9.3(2) ^c
Nonbonded distances:				
Si(1) ⋯ Si(3)	382.0(5)	15.3(4)	382.2	15.2(4)
Si(1) ⋯ H(2)	316	15.9(5) ^f	316	16.1(5) ^f
Si(2) ⋯ H(1)	319	16.0(5) ^f	320	16.2(5) ^f
Si(2) ⋯ H(3)	316	15.9(5) ^f	317	16.1(5) ^f
Si(2) ⋯ H(4)	415	[38.3]	415	[38.3]
Si(2) ⋯ H(4')	512	[15.8]	512	[15.8]
	The <i>anti</i> conformer, $\phi = [180^\circ]$		An <i>anti</i> pseudoconformer, $\phi = 171^\circ$	
Si(1) ⋯ Si(4)	588.4(7)	14.4	587.8	[15.2]
Si(1) ⋯ H(3)	409	[41.8]	401, 419	[27.0, 22.8]
Si(1) ⋯ H(4)	630	[36.2]	624, 636	[29.3, 31.6]
Si(1) ⋯ H(4')	698	[20.1]	698	[20.4]
	The <i>gauche</i> conformer, $\phi = 44(13)^\circ$		A <i>gauche</i> pseudoconformer, $\phi = 45^\circ$	
Si(1) ⋯ Si(4)	424.8(8)	[45]	427	[24]
Si(1) ⋯ H(3)	430	[42]	429	[30]
Si(1) ⋯ H(3')	508	[16]	509	[15]
Si(1) ⋯ H(4)	373	[59]	375	[50]
Si(1) ⋯ H(4')	461	[84]	464	[46]
Si(1) ⋯ H(4'')	564	[40]	566	[31]
Valence angles				
$\angle_\alpha \text{SiSiSi}$	109.6(2)		109.7(2)	
$\angle_\alpha \text{Si}(2)\text{Si}(1)\text{H}(1)$	111.9(9)		112.0(9)	
$\angle_\alpha \text{H}(2)\text{Si}(2)\text{H}(2')$	[107.4]		[107.4]	
	Mole fractions		Restricting potential	
The <i>anti</i> conformer	$\chi = 32(9)\%$		$V_1 = V_2 = 1.5(9) \text{ kJ mol}^{-1}$	
The <i>gauche</i> conformer	$\chi = 68(9)\%$		$V_3 = 2.8(24) \text{ kJ mol}^{-1}$	
R-factors^g (50 cm; 25 cm; total)				
	0.033; 0.054; 0.042		0.037; 0.053; 0.043	

^a Distances and amplitudes in pm, angles in degrees. Estimated standard deviations in parentheses in units of the last digit. Vibrational amplitudes in square brackets have been calculated from a scaled *ab initio* force field and were not varied during the refinement. ^{b–f} Denote pairs of parameters which have been refined with constant difference. See text. ^g $R = [\sum w(I_{\text{obs}} - I_{\text{calc}})^2 / \sum w I_{\text{obs}}^2]^{1/2}$.

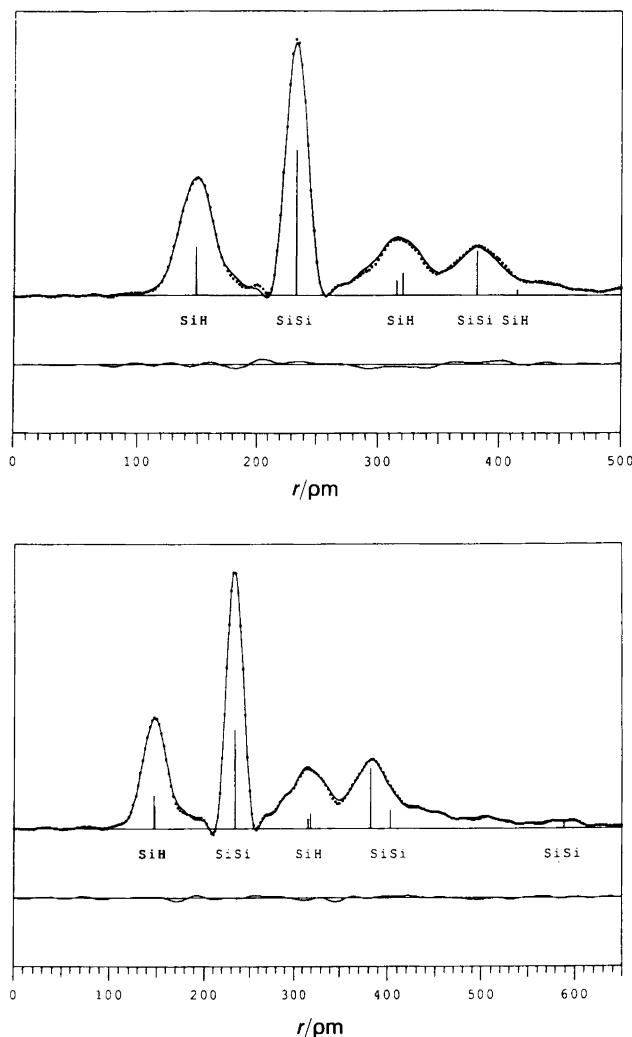


Fig. 2. Experimental (dots) and calculated (lines) radial distribution curves of trisilane (above) and tetrasilane (below). Artificial damping constant $k = 25 \text{ pm}^2$.

ated from the scaled quantum-mechanical force field. Introduction of vibrational correction terms and refinements under the constraints of a geometrically consistent r_α -structure increased the total R -factor slightly, from 0.051 to 0.053, and led to an increase of the valence angles $\angle \text{SiSiSi}$ and $\angle \text{Si(2)Si(1)H}$ by 0.5 and 1.1° , respectively. The best values obtained by this refinement are listed in Table 1. The estimated standard deviations given in the table have been multiplied by a factor of 2.0 to include uncertainty due to data correlation, and expanded to include a scale uncertainty of 0.1%.

Experimental and calculated intensity curves and radial distribution curves are compared in Figs. 1 and 2, respectively.

The molecular symmetry of the *anti* conformer of tetrasilane was assumed to be C_{2h} , the molecular symmetry of the *gauche* conformer C_2 . The SiSiH_3 fragments were assumed to have local C_{3v} symmetry.

The *ab initio* molecular orbital calculations indicate

that the Si-Si bond distances increase by about 0.1 pm when the dihedral angle $\phi(\text{SiSiSiSi})$ changes from 180 to 60° . We therefore assumed the bond distances to be independent of the dihedral angle and fixed the difference between Si(2)-Si(3) and Si(1)-Si(2) bond distances at the *ab initio* value (0.4 pm). Similarly the valence angle $\angle \text{SiSiSi}$ was regarded as independent of the dihedral angle, since the *ab initio* calculations indicate that it increases by only about 0.2° when the dihedral angle changes from 180 to 60° . Finally the Si(2)-H bonds were assumed to be 0.4 pm longer than the Si(1)-H bonds, and the angles $\angle \text{HSi(2)H}$ fixed at the optimal *ab initio* value, 107.75° .

The molecular structure of tetrasilane is then determined by the two bond distances Si(1)-Si(2) and Si(1)-H and the valence angles $\angle \text{SiSiSi}$ and $\angle \text{Si(2)Si(1)H}$; the conformational mixture is described by the mole fraction and the dihedral angle of the *gauche* conformer. These parameters were refined along with five vibrational amplitudes under the constraints of a geometrically consistent r_α -model. The refinements converged to yield the values listed in Table 2.

In a second series of refinements the conformational energy was assumed to be given by eqn. (1). The gas was

$$V(\phi) = (V_1/2)(\cos \phi + 1) + (V_2/2)(\cos 2\phi - 1) + (V_3/2)(\cos 3\phi + 1) \quad (1)$$

modeled by 10 pseudoconformers with dihedral angles ranging from 9 to 171° in steps of 18° . The vibrational amplitudes for each pseudoconformer were calculated by including the contributions from all normal modes except torsion about the central Si-Si bond. The mole fraction of each pseudoconformer was calculated from $V(\phi)$ by Boltzmann statistics. Attempts to refine the three parameters V_1 , V_2 and V_3 were, however, not successful. Refinements made under the assumption that $V_1 = V_2$, which implies that $V(60^\circ) = V(180^\circ) = 0$, converged to the values listed under Refinement 2 in Table 2.

The vibrational correction terms $D = r_\alpha - r_a$ calculated for tetrasilane were very large; thus the correction term for the Si(1)-H(1) bond distance was -17 pm and the correction term for the nonbonded distance Si(2)-H(1) was -12 pm. Introduction of these correction terms and refinements under the constraints of a geometrically consistent r_α -structure increased the R -factors to 0.044 (50 cm), 0.062 (25 cm) and 0.051 (total). The vibrational amplitudes in tetrasilane are obviously too large for corrections to be adequately computed under a model based on (relatively) small-amplitude rectilinear notion.

Results and discussion

Bond distances and valence angles. Neither the Si-Si bond distance in trisilane, $233.3(2)$ pm, nor the terminal

Si(1)–Si(2) bond distance in tetrasilane, 233.5(3) pm, is significantly different from the Si–Si bond distance in disilane,²⁰ 233.1(3) pm. The central bond in tetrasilane, Si(2)–Si(3) = 234.0(3) pm, is similar to the Si–S bond distances in *cyclo*-pentasilane,²¹ 234.2(3) pm, or *cyclo*-hexasilane,²² 234.2(3). It appears that silylene–silyl bonds, SiH₂–SiH₃, are slightly shorter than silylylene–silylene bonds, SiH₂–SiH₂.

The valence angle \angle_{α} CCC in propane, 112.4(3)°, is significantly greater than tetrahedral.²³ Since consideration of the relative electronegativities of the two C and two H atoms bonded to the central C atom would lead to the prediction that \angle CCC is smaller than tetrahedral, the angle may be expanded by repulsion between the methyl groups. The valence angle \angle_{α} SiSiSi in trisilane, 110.2(4)°, on the other hand, is very close to tetrahedral; H is a relatively smaller substituent on Si than on C.

The valence angle \angle_{α} SiSiSi for tetrasilane listed in Table 2 has not been corrected for vibrational effects; such correction would presumably increase the value by about 0.5 to 110.1°, a value indistinguishable from that of trisilane. The valence angle in butane is \angle_{α} CCC = 113.8(4)°.²⁴

The Si–Si bond distances and \angle SiSiSi valence angles obtained for Si₃H₈ by *ab initio* calculations at the 6-31G**/MP2 level were 233.7 pm and 112.3° respectively. The Si–Si bond distances and the \angle SiSiSi valence angle obtained for Si₄H₁₀ in the *gauche* conformation were Si(1)–Si(2) = 235.7 and Si(2)–Si(3) = 236.2 pm and 113.0° at the 6-31G*/SCF level.

The conformational composition of tetrasilane. Several experimental studies of *n*-butane have shown that the *anti* conformer is more stable than the *gauche* conformer by 3 or 4 kJ mol⁻¹, and this energy difference is well reproduced by *ab initio* MO calculations at a reasonable level.²⁵ The equilibrium dihedral angle ϕ (CCCC) in the *gauche* conformer is 65° rather than 60°.²⁵ When the dihedral angle is reduced from 180 to 65°, the \angle CCC angle increases by more than 1°; when ϕ is reduced to zero, \angle CCC is increased by another 2 or 3°.²⁵ These results indicate that the *gauche* conformer is destabilized by repulsion between the terminal methyl groups.

Our first refinement on tetrasilane indicates that the ratio of *gauche* to *anti* conformers in the gas phase is about 2:1. Since there are two (enantiomeric) *gauche* forms, and only one *anti*, this in turn suggests that the free energy difference is small, 0.2(1.1) kJ mol⁻¹. *Ab initio* MO calculations at the 6-31G*/MBPT(2) level indicate an energy difference of 0.15 kJ mol⁻¹, also in favor of *gauche*.⁹

Thus both calculations and experiment indicate that *anti* and *gauche* conformers have very nearly the same energy. The calculations also suggest that the angle \angle SiSiSi increases by only 1° when the dihedral angle ϕ is reduced from 180 to 0°. We have already noted that H is a relatively smaller substituent on Si than on C. The steric repulsion between terminal groups which destabilizes the

gauche conformation in butane appears to be absent in tetrasilane.

In the second refinement of tetrasilane we refined a potential-energy curve of the form indicated by eqn. (1) with $V_1 = V_2$, which implies that $V(60^\circ) = V(180^\circ) = 0$. The best values for V_1 and V_3 (Table 2) indicate that the barrier at the *syn* conformation is $V(0^\circ) = 4$ kJ mol⁻¹ and the barrier at 120° is $V(120^\circ) = 2$ kJ mol⁻¹. The corresponding calculated barriers obtained at the 6-31G*/MP(2) level are 5.2 and 2.4 kJ mol⁻¹, respectively.⁹

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