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Molecular structure and conformational composition of decamethyl-*n*-tetrasilane, Si_4Me_{10}, by gas electron diffraction and density functional theory calculations

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Dedicated to Professor Stanisław Pasynkiewicz who — during the years when Europe was divided — did so much to promote communication between scientists from the two parts.

Abstract

Density functional theory calculations on n-Si_4Me_{10} at the B3PW91/6-311G* level indicate six minima on the potential-energy surface corresponding to two *anti* conformers with ϕ(SiSiSiSi) dihedral angles of $\pm 160°$, two *gauche* conformers with $\phi = \pm 57°$, and two *orthogonal* conformers with $\phi = \pm 92°$. The relative energies of the three conformers were calculated to be 0.0 (*anti*), 2.9 (*gauche*) and 3.0 kJ mol^{-1} (*orthogonal*). Least-squares refinements on gas electron diffraction data recorded at room temperature yielded the mole fractions χ(*anti*) = 0.51(6), χ(*gauche*) = 0.32(8) and χ(*ortho*) = 0.17(14). The data thus confirm the presence of the *anti* and *gauche* conformers, while the presence of the *ortho* is probable but not certain. The main bond distances and valence angles of the most prevalent (*anti*) conformer are (calc./exp.): Si(1)–Si(2) = 237.1/235.0(6) ppm; Si(2)–Si(3) = 237.4/235.4(6) ppm; Si(1)–C = 189.5/189.3(2) ppm; Si(2)–C = 190.3/190.1(2) ppm; Si(1)Si(2)Si(3) = 112.5/112.4(5)°. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Several studies of normal butane, the simplest molecule with a linear C_4 chain, have demonstrated the existence of three conformers in the gas phase; an *anti* conformer with a CCCC dihedral angle of $\phi = 180°$ and two *gauche* conformers, *gauche*$_+$ and *gauche*$_-$, with dihedral angles of about $\phi = +60°$ and $\phi = -60°$, respectively. The two *gauche* conformers are separated by a barrier with maximum at $\phi = 0°$, corresponding to a *syn* geometry, while the *gauche* and *anti* conformers are separated by barriers with maxima near $\phi = \pm 120°$, corresponding to *anti-clinal* geometries. Experimental evidence has been reviewed briefly in Ref. [1]. Recent quantum chemical calculations with very

large basis sets and electron correlation included up to the CCSD(T) level indicate that the energy of the *gauche* conformers is 2.6 kJ mol^{-1} above that of the *anti* [1,2]. The *anti-clinal* barriers are about 14 kJ mol^{-1}, i.e. about 2 kJ mol^{-1} larger than the barrier to the internal rotation in ethane, while the *syn* barrier is about 23 kJ mol^{-1} [1,2]. Both the destabilisation of the *gauche* conformers relative to the *anti* and the high *syn* barrier may be interpreted as being due to repulsion between the terminal methyl groups.

A study of normal tetrasilane, n-Si_4H_{10}, by gas electron diffraction (GED) indicates that the gas at room temperature consists of a 1:2 mixture of *anti* and *gauche* conformers [3], and ab initio calculations at the 6-31G*/MP2 level indicate an energy difference of only 0.2 kJ mol^{-1} in favour of *gauche* [4]. The *anti-clinal* barrier calculated at the same level is 2.4 kJ mol^{-1}, the *syn* barrier is 5.2 kJ mol^{-1} [4]; the inherent barrier to

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internal rotation about the central Si–Si bond appears to be significantly smaller than the barrier to rotation about C–C bonds, and there is little interaction between the terminal silyl groups, but in other respects the conformational properties of n-Si$_4$H$_{10}$ mirror those of the prototype n-C$_4$H$_{10}$.

Decamethyl-n-tetrasilane, however, may be quite different; Michl and co-workers have published the results of ab initio calculations at the 6-31G*/MP2 level, which indicate the existence of three distinct conformers, all of C_2 symmetry: two *anti* (*anti-periplanar*) conformers with dihedral angles $\phi(\text{SiSiSiSi}) = \pm 162°$, two *orthogonal* conformers with $\phi = \pm 91°$, and two *gauche* conformers with $\phi = \pm 53°$ [5]. Matrix isolation IR spectra were recorded and provided convincing evidence for the presence of two conformers. The calculated mid-IR spectra of the *gauche* and *ortho* (*orthogonal*) conformers were, however, indistinguishable, and the presence of both these conformers could not be demonstrated [5].

The suggestion that gaseous Si$_4$Me$_{10}$ may adopt three distinct stable conformations receives strong, if indirect support, from the solid-state structures of four permethylated polysilanes: analysis of the conformations adopted by 126 Si$_4$Me$_8$ segments show that 51 may be classified as *gauche* with dihedral angles ranging from 30 to 64°, 32 as *ortho* with dihedral angles ranging from 80 to 106°, and 43 as *anti* with dihedral angles ranging from 131 to 177° [6].

In this article, we publish the results of an investigation of Si$_4$Me$_{10}$ by GED supported by quantum chemical density functional theory (DFT) calculations. Our calculations, like those previously published by Michl and co-workers [5], predict the existence of three distinct conformers. The GED investigation confirms the presence of *anti* and *gauche* conformers, but provides only weak evidence for the presence of the *orthogonal*.

2. Quantum chemical calculations

All calculations were carried out with the program system GAUSSIAN94 [7]. Hartree–Fock (HF) calculations were carried out with the standard 6-31G* basis set for all atoms. DFT calculations were carried out at the B3PW91 level with the 6-311G* basis set [7]. Bond distances, valence angles and dihedral angles in the potential energy minima corresponding to *anti*, *gauche* and *ortho* conformers are listed in Table 1. The molecular force field was obtained by HF/6-31G* calculations and scaled as described by Pulay et al. [8]. Root-mean-square amplitudes and vibrational correction terms at the temperature of the GED experiment calculated by the ASYM program [9] are listed in Table 2.

Table 1
Bond distances (pm), valence angles (°) and dihedral angles (°) for *anti*, *gauche* and *ortho* conformers of n-Si$_4$Me$_{10}$ obtained by density functional theory (DFT) calculations at the B3PW91/6-311G* level and by gas electron diffraction (GED) [a]

	DFT			GED		
	anti	*gauche*	*ortho*	*anti*	*gauche*	*ortho*
	r_e	r_e	r_e	r_a	r_a	r_a
Bond distances						
Si(1)–Si(2)	237.1	237.0	237.1	235.0(6)	235.1(6)	234.5(6)
Si(2)–Si(3)	237.4	237.4	237.9	235.4(6)	235.4(6)	235.9(6)
Si(1)–C	189.5	189.5	189.5	189.3(2)	189.3(2)	189.3(2)
Si(2)–C	190.3	190.5	190.5	190.1(2)	190.3(2)	190.3(2)
C–H(mean)	109.5	109.5	109.6	109.4(2)	109.4(2)	109.5(2)
Valence angles						
Si(1)Si(2)Si(3)	112.5	117.1	115.2	112.4(5)	117.0(5)	115.1(5)
Si(2)Si(1)C(11)	111.7	112.1	108.6	112.5(15)	112.9(15)	109.4(15)
Si(2)Si(1)C(12)	109.4	108.4	108.6	110.2(15)	109.3(15)	109.4(15)
Si(2)Si(1)C(13)	110.7	111.2	112.5	111.5(15)	112.0(15)	113.3(15)
Si(1)Si(2)C(21)	108.8	107.8	108.7	108.4(14)	110.3(14)	108.2(14)
Si(1)Si(2)C(22)	108.2	108.4	110.3	107.9(14)	108.1(14)	109.9(14)
Si(3)Si(2)C(21)	108.2	106.4	107.5	107.8(14)	106.0(14)	107.1(14)
Si(3)Si(2)C(22)	111.1	109.4	110.8	110.7(14)	109.0(14)	110.3(14)
Dihedral angles						
Si(1)Si(2)Si(3)Si(4)	160	55	92	163(8)	[55]	[92]
Si(3)Si(2)Si(1)C(11)	48	44	64	44(7)	[44]	[64]
Relative energies (in kJ mol^{-1})	0.00	2.85	2.97			
Mole fractions				0.51(6)	0.32(8)	0.17(14)
$R = [\Sigma w(I_{\text{obs.}} - I_{\text{calc.}})^2 / \Sigma(w(I_{\text{obs.}})^2]^{1/2}$				0.017(50 cm);	0.042(25 cm);	0.029 (total)

[a] Estimated standard deviations in parentheses in units of the last digit.

Table 2

n-Si$_4$Me$_{10}$: selected root-mean-square vibrational amplitudes, l (in ppm) calculated from a scaled HF/6-31G* force field or determined by gas electron diffraction

Conformer	HF/6-31G*		GED [a]	
	anti	gauche	ortho	anti
Atom pair				
Si(1)–Si(2)	6.0	6.0	6.0	6.4(2) [b]
Si(2)–Si(3)	6.0	6.0	6.1	6.4(2) [b]
Si–C	5.5	5.5	5.5	5.6(1)
C–H	7.8	7.8	7.8	8.0(2)
Si(1)···Si(3)	12.3	12.1	12.4	12.8(3) [b]
Si(1)···Si(4)	13.5	22.1	19.5	14.1(3) [b]

[a] Estimated standard deviations in parentheses in units of the last digit.

[b] Sets of amplitudes refined with constant differences.

Table 3

Independent structure parameters of the *anti* conformer of n-Si$_4$Me$_{10}$ and differences between similar, but symmetry-inequivalent parameters constrained to the values obtained by DFT (B3PW91/6-311G*) structure optimisation [a]

Independent parameters	Constrained differences
Bond distances (r_a)	
Si(1)–Si(2)	[Si(2)–Si(3)]–[Si(1)–Si(2)]
Si(1)–C	[Si(2)–C]–[Si(1)–C]
C–H(mean)	
Valence angles ($\angle_\alpha$)	
Si(1)Si(2)Si(3)	
Si(2)Si(1)C(11)	[Si(2)Si(1)C(12)]–[Si(2)Si(1)C(11)]
	[Si(2)Si(1)C(13)]–[Si(2)Si(1)C(11)]
Si(1)Si(2)C(21)	[Si(1)Si(2)C(22)]–[Si(1)Si(2)C(21)]
	[Si(3)Si(2)C(21)]–[Si(1)Si(2)C(21)]
	[Si(3)Si(2)C(22)]–[Si(1)Si(2)C(21)]
SiCH (mean)	
Dihedral angles (ϕ_α)	
Si(1)Si(2)Si(3)Si(4)	
Si(3)Si(2)Si(1)C(11)	[Si(3)Si(2)Si(1)C(12)]–[Si(3)Si(2)Si(1)C(11)]
	[Si(3)Si(2)Si(1)C(13)]–[Si(3)Si(2)Si(1)C(11)]
Mole fractions	
χ(*anti*)	
χ(*gauche*)	χ(*ortho*) = 1 − χ(*anti*) − χ(*gauche*)

[a] The difference between structure parameters in the *gauche* or *orthogonal* conformers and the corresponding parameters in the *anti* conformer were likewise constrained to the calculated values.

3. Gas electron diffraction

The sample of n-Si$_4$Me$_{10}$ was prepared by the coupling of Me$_3$SiSiMe$_2$Cl with a sodium–potassium alloy in toluene [10]. The boiling point and NMR spectra matched those reported in the literature. GED data were recorded on the Balzers KDG2 unit at the University of Oslo [11], with a metal (brass and steel) inlet

system at 67 ± 3°C. Exposures were made with nozzle-to-plate distances of about 50 and 25 cm. Structure refinements were based on data from six plates for each distance. The plates were scanned on an Agfa Arcus II scanner and the data processed as described elsewhere [12]. Atomic scattering factors were taken from Ref. [13]. Backgrounds were drawn as cubic approximation splines to the difference between the total experimental and the calculated molecular intensities using a computer program developed by one of us using the algorithm described by Reinsch [14]. Least-squares structure refinements were carried out with a modified version of the program KCED25 written by G. Gundersen, S. Samdal, T.G. Strand and H.M. Seip. Weight matrices were diagonal, the long nozzle-to-plate distance data were assigned unit, the short distance data half weight. The estimated standard deviations calculated by the program were multiplied by a factor of 2.0 to include added uncertainty due to data correlation and non-refined amplitudes, and expanded to include an estimated scale uncertainty of 0.1%.

Structure refinements were based on a mixture of *anti*, *gauche* and *ortho* conformers of unknown concentrations. Each conformer was assumed to have C_2 symmetry [5]. The nine independent structure parameters of the *anti* conformer are listed in Table 3. The differences between chemically similar, but symmetry inequivalent bond distances, valence angles or dihedral angles were restrained to the values obtained by the DFT calculations as indicated in the table. The differences between bond distances or valence angles in the *gauche* or *ortho* conformers and the corresponding parameters in the *anti* conformer were likewise constrained to calculated values. The dihedral angles of the *gauche* and *ortho* conformers were fixed at calculated values. In addition to the nine structure parameters listed in Table 1, the two independent mole fractions and two scale factors, we also refined the mean vibrational amplitudes of the Si–Si, Si–C and C–H bond distances. The vibrational amplitudes of nonbonded distances were divided into two groups. One consisted of the amplitudes that are affected by internal rotation about Si–Si or Si–C bonds, the other consisted of those that are unaffected. Both groups were refined with constant differences. The best values obtained for the structure parameters and mole fractions are listed in Table 1, the best values obtained for some vibrational amplitudes in Table 2.

4. Results and discussion

4.1. Quantum chemical calculations

Structure optimisation of an *anti-periplanar* model of C_2 symmetry by DFT calculations at the B3PW91/6-

311G* level yielded the structure parameters listed in the first column of Table 1. A sketch of the molecule in this conformation is presented in Fig. 1. Calculations of the molecular force field and vibrational frequencies confirmed that this model represents a minimum on the potential energy surface. Similar optimisation of a *gauche* model of C_2 symmetry yielded the structure parameters listed in the second column. The energy of this *gauche* conformer was calculated to be only 2.85 kJ mol^{-1} above the *anti*. As calculation of the molecular force field yielded one imaginary frequency, the optimisation of the *gauche* model was continued under C_1 symmetry. This led to an energy decrease by only 0.13
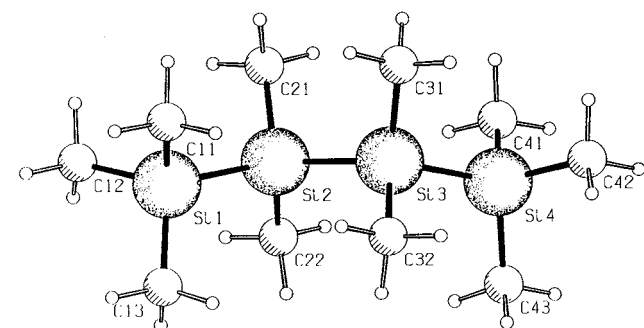

Fig. 1. Molecular model of *n*-Si$_4$Me$_{10}$ in an *anti* conformation. The molecular symmetry is C_2 with the symmetry axis in the plane of the paper and perpendicular to the Si(2)–Si(3) bond.

Table 4
Relative energies (in kJ mol^{-1}) and dihedral angles (°) of *anti*, *gauche* and *ortho* conformers of *n*-Si$_4$Me$_{10}$ obtained by quantum chemical calculations at various levels

	anti	gauche	ortho	Reference
HF/3-21G*				[5]
Relative energy	0.00	2.9	3.7	
ϕ(SiSiSiSi)	164	54	92	
MP2/3-21G*				[5]
Relative energy	0.00	0.5	3.3	
ϕ(SiSiSiSi)	162	53	93	
HF/6-31G*				This work
Relative energy	0.00	2.5	2.6	
ϕ(SiSiSiSi)	163	55	90	
MP2/6-31G*				[5]
Relative energy	0.00	0.4	2.7	
ϕ(SiSiSiSi)	162	53	91	
MP2/6-311G*				[5]
Relative energy [a]	0.00	0.7	2.1	
ϕ(SiSiSiSi)	[162]	[55]	[91]	
B3PW91/6-311G*				This work
Relative energy	0.00	2.9	3.0	
ϕ(SiSiSiSi)	160	57	92	

[a] Fixed geometry calculations with the MP2/6-31G* optimised structure.

kJ mol^{-1}, no bond distance changed by more than 0.2 ppm, no valence angle by more than 0.5°, and no torsional angle by more than 2.0°. We believe, therefore, that the apparent deviation from C_2 symmetry is an artifact due to numerical noise.

Repeated attempts to carry out optimisation of an orthogonal conformer failed to give convergence. The optimum dihedral angle ϕ(SiSiSiSi) was therefore determined by optimising models in which this angle was fixed at 80, 90 and 100° respectively. Parabolic interpolation indicated an energy minimum at $\phi = 91.7$°. Optimisation with the dihedral angle fixed at this value yielded the structure parameters listed in the third column of Table 1 and an energy 2.97 kJ mol^{-1} above the *anti* conformer.

Thus our calculations, like those of Michl and co-workers [5], indicate the existence of three distinct conformers with dihedral angles near ± 160, ± 60 and ± 90°, respectively. In Table 4 we compare the dihedral angles and relative energies of the three conformers obtained at different computational levels. The *anti* conformer is indicated consistently to be the most stable, followed by the *gauche* and *ortho* conformers. The energy of the latter is predicted to be 2.0–4.0 kJ mol^{-1} higher than the *anti*.

The calculations at HF/3-21G* and MP2/3-21G* published by Michl and co-workers [5] indicate that the *ortho* conformer is separated from the *gauche* by a barrier little over 2.0 kJ mol^{-1} and from the *anti* by a barrier of about 4.0 kJ mol^{-1}. We have not studied the barriers in detail, but structure optimisation of a model with the SiSiSiSi dihedral angle fixed at 70° indicates that the barrier separating the *ortho* and *gauche* conformers is equal to, or slightly larger than, 1.2 kJ mol^{-1} at the B3PW91/6-311G* level. The barrier height is thus only half the thermal energy per vibrational degree of freedom at 300 K, $RT = 2.4$ kJ mol^{-1}; at room temperature the thermal energy is sufficiently high to allow a large portion of the molecules to pass freely across the barrier.

We note, however, that since the SiSiSiSi torsional mode is calculated to be below 25 cm^{-1} (i.e. $h\varpi < 0.30$ kJ mol^{-1}) for both *gauche* and *ortho* conformers there are probably several vibrational levels below the barrier and it remains meaningful to describe *gauche* and *ortho* as distinct conformers.

Michl and co-workers have suggested that the splitting of the usual *gauche* minimum into separate *gauche* and *ortho* minima is due to repulsion between the terminal SiMe$_3$ groups [15]. This suggestion is consistent both with the higher energies of these conformers relative to the *anti*, and with the opening of the SiSiSi valence angles on reduction of the dihedral SiSiSiSi angle. Indeed, as indicated below, in a fictive *gauche* conformer with dihedral SiSiSiSi equal to 60° and the terminal SiMe$_3$ groups fixed in staggered orientations,
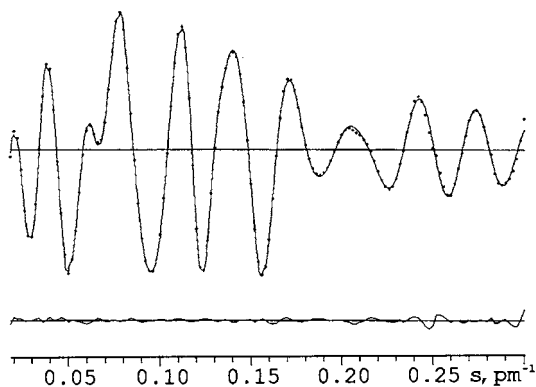
Fig. 2. Experimental (points) and calculated (line) modified molecular intensity curves for *n*-Si$_4$Me$_{10}$. The vertical scale is arbitrary. Below: difference curve.
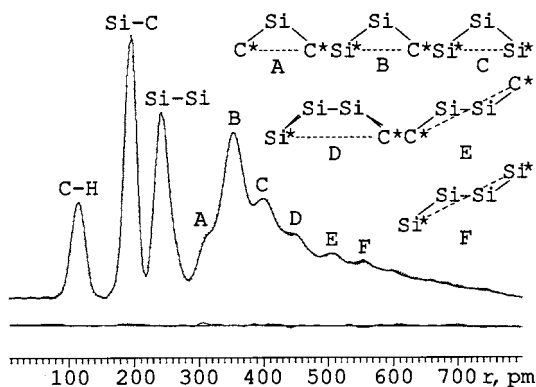
Fig. 3. Experimental (points) and calculated radial distribution functions of *n*-Si$_4$Me$_{10}$. The vertical scale is arbitrary. Below: difference curve. Artificial damping constant $k = 25$ ppm^2.

the closest C⋯C distance between SiMe$_3$ groups would be about 310 ppm as compared to a methyl group van der Waals' diameter of 400 ppm. In the real *gauche* conformer this distance is increased to about 440 ppm, mainly through 17° clockwise rotation of the two SiMe$_3$ groups; in the *ortho* conformer it is increased to about 440 ppm, mainly through an 30° anticlockwise rotation about the central Si–Si bond.

≈ 310 pm

I
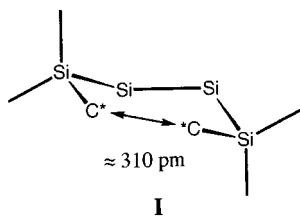
4.2. Gas electron diffraction

Least-squares refinements to the GED data yield the structure parameters listed in Table 1 and the vibrational amplitudes listed in Table 2. Experimental and

calculated intensity curves are compared in Fig. 2, experimental and calculated radial distribution curves in Fig. 3.

The good agreement between calculated and experimental bond distances, valence angles and vibrational amplitudes indicates that the computational level allows an adequate description of the molecule. The mole fractions of the *anti*, *gauche* and *ortho* conformers are found to be 0.51(6), 0.31(8) and 0.17(14) respectively; the GED data thus confirm the presence of the *anti* and *gauche* conformers, while the presence of the *orthogonal* is probable but not certain.

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