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CONFORMATIONAL ANALYSIS OF POLYSILANES BY THE EMPIRICAL FORCE FIELD METHOD

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Abstract—Empirical force field (EFF) parameters have been developed for molecules containing Si–Si bonds. These parameters have been adjoined to those of a standard EFF and the extended force field has been used to calculate structures and relative conformational energies for a variety of acyclic and cyclic catenated polysilanes.

A striking similarity in the chemistry of carbon and silicon is the ability of both elements to form homocatenated structures.[1] In the case of carbon, this has been the root source of the astronomical diversity of structural types which form the subject of organic chemistry. In contradistinction, although silicon atoms are also capable of forming chain-linked arrays, including branched and annular structures, these compounds suffer from comparatively greater susceptibility to a variety of reagents. Historically, this instability of polysilanes to their chemical environment has limited interest in this class of compounds, as compared to the relatively inert carbon congeners. However, recent reports in the literature concerning the syntheses of polysilanes Si_nH_{2n+2} (n = 2–7),[2] their permethylated analogues (n = 2–12),[3] substituted cyclopolysilanes Si_nL_{2n}, where L = Ph (n = 4–6)[4] and L = Me (n = 4–8),[5] permethylated polycyclic polysilanes,[6] and the cyclopolysilane cyclopentasilane[7] have stimulated renewed interest in the structure and bonding of these compounds.

In continuation of our interest in the conformational properties of organosilanes,[8-10] we have initiated an effort to study the conformational properties of polysilanes, employing the full relaxation empirical force field (EFF) approach. The present paper reports the salient results of this study.

The basic force field is one which we have previously employed in the conformational analysis of organosilanes.[9,10] It is based on Allinger's force field with aromatic parameters taken from Boyd's and scaled to match Allinger's. This EFF has been fully described elsewhere.[9,12] In addition to the parameters employed in earlier studies,[9-12] polysilane force constants and "strain free" bond parameters (Table 1) were introduced. Values for these quantities were derived from reported structures determined by a variety of techniques (X-ray,[13-15] electron diffraction,[16-18] ESCA,[19] and IR[20,21]). The pattern search method was used throughout to effect computational strain energy minimization.[22]

The derivation of the polysilane bond parameters in Table 1 is described in greater detail below.

Stretching force constants. Values for the force constant k_r and the ideal (strain free) bond length r^0 were derived from IR stretching force constants and the known bond lengths of disilane **1**, hexamethyldisilane **2**, tetrakis(trimethylsilyl)silane **3**, and dodecamethylcyclohexasilane **4**. Although the structures of **1–3** had been determined by electron diffraction[16-18] and that of **4** by X-ray analysis,[15] the agreement between calculated and experimental structures is close enough so that the differences inherent in the two procedures appear to be unimportant.

The reported force constants for the Si–Si stretch in organosilanes range from 1.4 to 2.15 mydnes/Å.[23-25] The stretching force constant for disilane is reported by several groups to have values of 1.73,[21] 1.78[26] and 1.81[27] mdynes/Å. Our values of 1.85 mdynes/Å and 2.345 Å for k_r and r^0, respectively, were chosen to provide the best fit between calculated and experimental structures (Table 2).

Bending force constants. The H–Si–Si bending force constant (k_θ) was derived by calculating the ratio of the H–Si–H spectroscopic force constant (0.229 mdynes/Å)[26] to Allinger's reported H–Si–H force constant (0.38 mdynes/rad²)[11] and scaling the spectroscopic H–Si–Si force constant (0.183 mdynes/Å)[26] by this value to obtain a value for k_θ of 0.30 mdynes/rad². The remaining force constants were obtained by estimation. The values (Table 1) appear to be reasonable in that they are "softer" than those of the carbon analogues,[9,11] and serve adequately in the computation of known polysilane structures (Table 2). The strain free values of the angles (θ^0) were empirically determined so that the above force constants would give the best fit with the structures in Table 2.

Torsional force constants. The torsional function for polysilanes, as with saturated carbon systems, is approximated by assuming 3-fold periodicity. The torsional parameter (V_0) for H–Si–Si–H was derived from the known rotational barrier of disilane (1.22 kcal/mol).[26] This parameter, the intrinsic torsional strain, was adjusted so that the difference in energy between the eclipsed† and staggered forms of ethane would equal the rotational barrier. The value of V_0 was thus calculated to be 0.40 kcal. An additional parameter, needed to calculate the structure of 1,3,5,7-tetramethyltetrasilaadamantane **5**, is the C_{sp^3}–Si–C_{sp^3}–Si torsional constant. The estimated value, 0.50 kcal/mol, was selected empirically since it yielded a good overall structural fit for this molecule.

The torsional parametrization does not take into ac-

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†In the eclipsed form, one H–Si–Si–H dihedral angle was constrained to be 0.0°. All other degrees of freedom in the molecule were relaxed.

count any possibility of electronic effects, i.e. delocalization through the polysilane sigma bond framework. Delocalization of this type has been observed in polysilane radical anions,[1] and has been postulated to exist in polysilanes.[1,2a] This effect, which would be at a maximum for torsional potentials involving three or four silicon atoms, would tend to lower the barrier to rotation and to stabilize planar conformations of the polysilane frame-

Table 1. Empirical force field parameters for polysilanes[a,b]

Stretch

	$\underline{k}_r$	$\underline{r}^0$
Si-Si	1.85	2.345

Bend ($\underline{k}_3' = -0.401$)

	$\underline{k}_\theta$	θ^0
H-Si-Si	0.30	110.3
C_{sp^3}-Si-Si	0.32	108.6
C_{ar}-Si-Si	0.32	109.0
Si-Si-Si	0.70	111.7

Torsion

	$\underline{V}_0$	$\underline{\beta}$	$\underline{n}$	ϕ_{max}
H-Si-Si-H	0.40	1.0	3	60
C_{sp^3}-Si-Si-Si	0.40	1.0	3	60
C_{sp^3}-Si-Si-C_{sp^3}	0.40	1.0	3	60
H-C_{sp^3}-Si-Si	0.50	1.0	3	60
C_{sp^3}-Si-C_{sp^3}-Si	0.50	1.0	3	60

[a] The potential functions are given in reference 12. [b] The following units apply: Å ($\underline{r}^0$); degrees (θ^0, ϕ_{max}); mdynes/Å ($\underline{k}_r$); mdynes/rad^2 ($\underline{k}_\theta$); radians^{-1} ($\underline{k}_3'$); kcal/mol ($\underline{V}_0$).

Table 2. Bonding parameters of various polysilanes[a]

Disilane 1

Parameter	Experimental[18]	Calculated
Si-Si	2.331 ± 0.003 Å	2.34_3 Å
H-Si	1.492 ± 0.003 Å	1.48_4 Å
H-Si-Si	110.3 ± 0.4°	110.2°
H-Si-H	108.6 ± 0.4°	108.7°
H-Si-Si-H	ca. 60°	60°
Rotational Barrier	1.2 kcal/mol	1.2 kcal/mol

Hexamethyldisilane 2

Parameter	Experimental[17]	Calculated
Si-Si	2.340 ± 0.009 Å	2.33_4 Å
C-Si	1.877 ± 0.003 Å	1.86_8 Å
C-Si-Si	108.4 ± 0.4°	108.7°
C-Si-C	110.5 ± 0.4°	110.2°
H-C-Si	108.7 ± 0.8°	107.4°
H-C-H	110.3 ± 0.8°	111.4°
C-Si-Si-C	ca. 60°	60°
Rotational Barrier	----	1.05 kcal/mol

Table 2. (*Contd.*)

Tetrakis(trimethylsilyl)silane 3

Parameter	Experimental[16]	Calculated
Si-Si	2.361 ± 0.003 Å	2.34_6 Å
C-Si	1.889 ± 0.003 Å	1.86_9 Å
Si-Si-Si	109.5°	109.5°
C-Si-Si	110.9 ± 0.6°	109.9°
H-C-Si	109.3 ± 1.7°	107.7°
C-Si-C	107.9 ± 0.5	109.0°
C-Si-Si-Si	11 ± 3.6°	15.2°

Dodecamethylcyclohexasilane 4

Parameter	Experimental[13]	Calculated
Si-Si	2.338 ± 0.004 Å	2.33_5 Å
Si-C_{eq}	1.897 ± 0.005 Å	1.86_8 Å
Si-C_{ax}	1.881 ± 0.003 Å	1.86_9 Å
Si-Si-Si	111.9 ± 0.4°	112.2°
C-Si-C	108.1 ± 0.5°	109.1°
Si-Si-C_{eq}	109.2 ± 1.2°	108.2°
Si-Si-C_{ax}	109.2 ± 1.2°	109.5°
Si-Si-Si-Si	53.5 ± 0.3°	52.5°
Si-Si-Si-C_{eq}	173.5 ± 0.3°	171.9°
Si-Si-Si-C_{ax}	68.2 ± 1.2°	69.2°
C_{eq}-Si-Si-C_{eq}	66.7 ± 0.8°	68.7°
C_{eq}-Si-Si-C_{ax}	51.3 ± 1.3°	50.1°
C_{ax}-Si-Si-C_{ax}	169.3 ± 1.5°	169.0°

1,3,5,7-Tetramethyltetrasilaadamantane 5

Parameter	Experimental[15]	Calculated
Si-CH_2	1.866 ± 0.007 Å	1.86_8 Å
Si-CH_3	1.889 ± 0.010 Å	1.86_8 Å
H-CH_2	1.05 ± 0.04 Å	1.09_3 Å
H-CH	1.07 ± 0.03 Å	1.09_3 Å
CH_3-Si-CH_2	111.1 ± 0.3°	110.6°
CH_2-Si-CH_2	107.8 ± 0.4°	108.3°
Si-CH_2-Si	112.7 ± 0.4°	111.7°

[a] eq = equatorial, ax = axial.

work. Although our torsional potential does not include any explicit consideration of such effects, the success of our calculations in the determination of the structures in Table 2 indicates that sigma delocalization is a negligible factor.

Non-bonded force constants. Although non-bonded potential functions for organosilanes have been used extensively in the past,[9-11] there is a distinct risk in transferring functions found suitable for the shorter non-bonded distances in monosilanes to the longer non-bonded distances in polysilanes. In our calculations, very few non-bonded distances (for example, H · · · H) are less than 2.7 Å, which is approximately the region where repulsive and attractive forces mutually cancel each other. Nevertheless we believe that these functions are at least reasonably satisfactory, since the attractive region of the non-bonded potential (beyond *ca.* 2.7 Å for H · · · H interactions) is very flat and therefore relatively independent of distance. As a test of this hypothesis, we calculated the structures of two polysilanes 3 and 4 without the use of a non-bonded potential (i.e. with all non-bonded parameters set equal to zero). As seen in Table 3, with one exception there is little change in the structure of these molecules as compared to the corresponding structures calculated with inclusion of non-bonded potentials (Table 2). The single exception is the dihedral C–Si–Si–Si angle in 3, a result which we shall comment on in further detail below.

Stretch-bend parameters. There are few structures with which to parametrize the polysilane force field and none in which there are significant deviations from strain-free values of bond angles. This paucity of the data base precludes introduction of stretch-bend terms.

Table 3. Comparison of calculated structures with and without inclusion of nonbonded potentials

Bonding Parameter	Calculated Value[a]	
Tetrakis(trimethylsilyl)silane 3		
	A	B
Si-Si	2.346 Å	2.345 Å
C-Si	1.869 Å	1.872 Å
Si-Si-Si	109.5°	109.5°
C-Si-Si	109.9°	109.3°
C-Si-C	109.0°	109.7°
C-Si-Si-Si	15.2°	0.0°
Dodecamethylcyclohexasilane 4		
	A	B
Si-Si	2.335 Å	2.345 Å
Si-C[b]	1.868 Å	1.872 Å
Si-Si-Si	112.2°	111.5°
C-Si-C	109.1°	109.7°
C-Si-Si[b]	108.8°	108.9°
Si-Si-Si-Si	52.5°	54.6°

[a] A = value calcd. including nonbonded potential; B = value calcd. not including nonbonded potential. [b] Average values for C_{ax} and C_{eq}.

RESULTS AND DISCUSSION

Inspection of Table 2 reveals that previously employed EFF parameters,[9-12] in conjunction with the polysilane parameters developed in the present work (Table 1), yield satisfactory agreement between calculated and experimentally determined structures for compounds **1**-**5**. In the following, we shall briefly discuss features of special interest associated with these molecules and several others whose structures were calculated using the same EFF.

Disilane **1**. All bonding parameters in the staggered (D_{3d}) form are very close to the strain free values. The eclipsed (D_{3h}) conformation is less stable by 1.2 kcal/mol, and the entire magnitude of the barrier is found to reside in the torsional term. A comparison with ethane is instructive: whereas V_0 for H-Si-Si-H (0.40 kcal/mol) is 80% of the value for H-C-C-H (0.50 kcal/mol[12]), the rotation barrier for **1** (1.2 kcal/mol) is only *ca.* 40% of that for ethane (2.8 kcal/mol). Evidently, in the case of ethane the non-bonded and other potentials account for nearly half the barrier, whereas in **1** these terms do not contribute significantly to the barrier. We hasten to add that in thus partitioning strain among the component EFF potential terms we merely hope to provide what is at best a *qualitative* insight into the origin of the strain in the eclipsed form of **1** (as compared to ethane), for we are well aware that a *quantitative* analysis of strain based on partitioning procedures is of doubtful physical significance.[29]

Hexamethyldisilane **2**. Taking the torsional constant for C-Si-Si-C to be roughly equal to that of H-Si-Si-H (by analogy to V_0 for C-C-C-C, which is taken to be roughly equal to that of H-C-C-H[12]), we find that the calculated and experimental structures are in good agreement (Table 2). Somewhat unexpectedly, however, we have also found that the rotation barrier in this molecule, which intuitively seems to be more crowded than disilane, is lower than the barrier in disilane, 1.05 vs 1.20 kcal/mol. The cause of this apparent anomaly is the increase in *attractive* non-bonded Me ··· Me interaction in the eclipsed conformation, as compared to the staggered conformation, since the methyl groups are closer together in the eclipsed form. This result obviously depends on the particular non-bonded potential function used, and ability of this function to reproduce strain energies accurately in the region beyond 3 Å will have to await experimental verification in cases such as this. Still, it is interesting to note in this connection that a recent study utilizing our hydrocarbon force field[12] has provided strong evidence that *attractive* steric effects are also the determining factor in conformational equilibria of 1,3,5-trineopentylbenzene.[30]

Hexaphenyldisilane. Interest in this compound derives from its relationship to the fascinating and still unknown congener, hexaphenylethane.[31] Our calculated structure of hexaphenyldisilane, based on the parameters developed in the present study (Table 1), has been described elsewhere in connection with the hexaphenylethane problem.[32]

Trisilane. The Si-Si bond lengths in the calculated structure (2.343 Å) are close to the strain free value. The closest non-geminal H ··· H non-bonded distance is 3.51 Å. The Si-Si-Si bond angle (109.9°) is significantly compressed from the strain free value of 111.7°.

Tetrasilane. Like its congener *n*-butane, tetrasilane exists in conformationally isomeric (gauche and anti) forms. An ESCA study[19] indicates that the two conformers are approximately equally populated. According to our calculations, the gauche form is slightly (but not significantly) more stable than the anti (ΔE, 0.09 kcal/mol), in qualitative agreement with the experimental findings; the Si-Si-Si angles are *ca.* 110.5°. The contrasting behavior of the carbon analog (the anti form of *n*-butane is more stable than the gauche by

0.8 kcal/mol[11]) is conventionally ascribed to the dominant effect of non-bonded repulsive Me ⋯ Me interactions[14] in the relatively more crowded butane.

Decamethyltetrasilane. In this molecule, the anti form is less strained than the gauche by 0.13 kcal/mol. The average Si–Si bond lengths in both the gauche and anti conformers (2.339 and 2.338 Å, respectively) are very close to the strain free value. The Si–Si–Si bond angles are expanded to 113.4° and 116.8° in the anti and gauche conformers, respectively; the calculated Si–Si–Si–Si dihedral angles for the anti and gauche forms are 166.0° and 52.5°, respectively.

Tetrakis(trimethylsilyl)silane **3**. The electron diffraction study of this molecule[16] indicates that each trimethylsilyl group is twisted in the same sense and to the same extent (*ca.* 11°) from the reference $\mathbf{T_d}$ structure. As a result, **3** has **T** symmetry in the ground state. An interesting historical point is that this very mode of $\mathbf{T_d} \rightarrow \mathbf{T}$ desymmetrization was discussed some years ago by Herzberg[15] for the hypothetical case of neopentane. Our calculated structure reproduces all bond parameters with considerable accuracy (Table 2), including the angle of twist (*ca.* 15°). It is noteworthy that the structure relaxes to the completely staggered ($\mathbf{T_d}$) form when the non-bonded potential is turned off (Table 3), indicating that desymmetrization to the **T** conformation principally results from the operation of non-bonded interactions. The same conclusions have been reached by Bartell *et al.*[16] on the basis of a simplified force field model.

A search of the hypersurface of **3** has revealed a second minimum, corresponding to the $\mathbf{S_4}$ form of **3**. In this conformer, which 4.08 kcal/mol more strained than the **T** ground state, two of the trimethylsilyl groups are rotated away from the reference $\mathbf{T_d}$ structure by +12.7° and +12.6°, while the other two are rotated in the opposite sense to the same extent (−12.6° and −12.9°).

Cyclopentasilane and Decamethylcyclopentasilane. The data base for the new force field parameters (Table 1) does not include any structures with severely distorted bond angles or lengths; for this reason a study of strained ring structures (such as $(SiH_2)_3$ or $(SiH_2)_4$) does not appear to be justified. The smallest ring system studied in this work is therefore $(SiH_2)_5$.

The conformational analysis of cyclopentasilane is remarkably similar to that of cyclopentane. In the hydrocarbon analog, the $\mathbf{C_2}$ and $\mathbf{C_s}$ conformers are approximately equal in energy, and are interconvertible by virtually free pseudorotation.[16] The planar $\mathbf{D_{5h}}$ form is 3.5–5 kcal/mol less stable. The calculated relative strain energies of the $\mathbf{C_2}$, $\mathbf{C_s}$ and $\mathbf{D_{5h}}$ forms of cyclopentasilane are 0.00, 0.05 and 1.82 kcal/mol, respectively.† The results are in agreement with the experimental finding[21] that the molecule is nonplanar and undergoes rapid pseudorotation between the $\mathbf{C_2}$ and $\mathbf{C_s}$ conformers.

Decamethylcyclopentasilane is similar to the parent cyclosilane except that the $\mathbf{C_s}$ form is now slightly more stable than the $\mathbf{C_2}$ form (by 0.01 kcal/mol), and the $\mathbf{D_{5h}}$ conformation lies 1.88 kcal/mol above the $\mathbf{C_s}$ ground state.†

Cyclohexasilane and dodecamethylcyclohexasilane **4**. Compared to the amount of attention devoted to the conformational properties of cyclohexane, the chemistry of the silicon analogues cyclohexasilane and dodecamethylcyclohexasilane **4** has been relatively unexplored. An X-ray study of **4**[11] shows that in the solid state **4** possesses a chair conformation. Cyclohexasilane is at present still unknown. Information relating to the conformational interconversions of cyclohexasilanes has not been reported.

Cyclohexasilane is calculated to have a chair conformation in the ground state. The Si–Si bond lengths (2.343 Å) are close to the strain free values. The Si–Si–Si bond angles (ave. value 109.6°) are compressed by *ca.* 2° from the strain free value, but are in line with the values calculated for trisilane (see above). The Si–Si–Si–Si dihedral angles are calculated to be very close to 60°. Cyclohexasilane is thus seen to have close to "ideal" bond and dihedral angles, in contrast to cyclohexane, whose relatively flattened structure (C–C–C = 111.5°, C–C–C–C = 54.5°)[1] is the result of repulsive gauche $CH_2 \cdots CH_2$ interactions. In cyclohexasilane, considerably longer Si–Si bond distances open up the annular structure, with a concomitant decrease in non-bonded interactions.

Conformations having $\mathbf{D_2}$ (twist), $\mathbf{C_{2v}}$ (boat) and $\mathbf{C_2}$ symmetry lie 1.95, 2.31 and 4.14 kcal/mol, respectively, above the $\mathbf{D_{3d}}$ (chair) ground state.† The relative ordering of strain energies parallels that in cyclohexane; the major distinction lies in the smaller magnitude of the energy differences,[18] which can be attributed to the lessened non-bonded interactions described above. As in the case of cyclohexane, the $\mathbf{C_{2v}}$ conformation may be considered the transition state separating two twist conformers, and the $\mathbf{C_2}$ conformation a transition state separating a chair and a twist form.[18]

Very similar results are obtained for **4**. The calculated structure agrees well with the experimentally determined one[11] (Table 2). A small number of transannular interactions are only weakly repulsive (transannular $CH_3 \cdots CH_3$ = 4.21 Å; closest transannular H ⋯ H = 2.62 Å). The relative ordering of conformational energies is the same as in the parent cyclosilane: conformations having $\mathbf{D_2}$, $\mathbf{C_{2v}}$ and $\mathbf{C_2}$ symmetry lie 2.35, 3.83 and 4.10 kcal/mol above the $\mathbf{D_{3d}}$ ground state.†

Hexadecamethylbicyclo[3.3.1]*nonasilane*. This molecule is of interest because the X-ray structure[14] indicates that one cyclohexasilane ring exists in the chair conformation while the other exists in the half-chair. Our calculations indicate that this molecule possesses a minimum conformation corresponding to the X-ray structure, and that the chair-chair conformation is 1.6 kcal/mol more strained than the chair-half-chair ground state. A half-chair-half-chair minimum could not be located on the hypersurface: all input structures relaxed to the ground state. We conclude that the conformation in the solid state is the true ground state of the molecule and not an artifact of crystal packing.

1,3,5,7-*Tetramethyltetrasilaadamantane* **5**. Among the structures studied in this work, that of **5** is unique in not possessing any Si–Si bonds. It was nevertheless included in the present investigation since it contributed the value of V_0 for C_{sp^3}–Si–C_{sp^3}–Si to the new force field. The molecule possesses perfect $\mathbf{T_d}$ symmetry; all methyl groups are staggered and all Si–C bond distances are calculated to be 1.868 Å. The molecule in the crystal however deviates significantly from tetrahedral symmetry;[15] individual bond lengths which should be symmetry related vary greatly, e.g. from 1.832 to 1.890 Å.

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† The three cyclopentasilane conformations, as well as the C_2 and boat forms of cyclohexasilane, were constrained to remain in each particular conformation by restricting the motion of three or more Si atoms to a plane. Similar constraints were imposed on the permethylated derivatives.

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Note added in proof. After this work had been completed, an electron diffraction study by Z. Smith, H. M. Seip, E. Hengge and G. Bauer (*Acta Chem. Scand.*, **A30**, 697 (1976)) appeared in which it was shown that the ground state conformation of cyclopentasilane is either C_2 or C_s, or a mixture of the two. Empirical force field calculations indicated that these conformers are of equal energy, and between 1.21 to 2.19 kcal/mol more stable than the D_{5h} form. These results are in satisfactory agreement with our findings.

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