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MOLECULAR MECHANICS CALCULATIONS (MM3) ON SILANES

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Molecular structures, conformational energies, heats of formation and vibrational spectra have all been fit using the MM3 force field for a group of 48 silanes and polysilanes for which experimental data are available. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

The MM3 force field[1] was applied originally to saturated hydrocarbons[2], and subsequently extended to cover many other classes of compounds.[3] This paper deals with the silanes.[3e] This class of compounds was originally fit reasonably well with the MM2 force field insofar as structures and energies. However, vibrational spectra could not be adequately dealt with using the MM2 force field, because it simply did not contain a sufficient number of parameters. It has been found that MM3 does a better job with structures and energies in general than MM2 did, although not by much, as MM2 was already fairly accurate. However, vibrational spectra and attendant thermodynamic properties can now be calculated in addition using MM3. This paper discusses the extension of these force field calculations to the MM3 force field.

The usual fitting procedures were followed. Having the MM2 force field available, it was used as a starting parameter set to calculate initial geometries and energies for a number of compounds. The structures calculated using the MM2 parameters in the MM3 force field were not very good, and so the various parameters (particularly θ_0, l_0, and the torsional potentials) were adjusted so as to improve the geometries and the conformational energies. The force parameters for stretching and bending were then adjusted in such a way as to improve the vibrational spectra. The remaining compounds were added to the trial set, and these properties were all optimized with respect to the available parameters, and heats of formation were simultaneously examined also. When further improvements did not seem possible, the optimization was stopped, and the MM3 force field for silanes was generated. The necessary parameters are summarized in Table 1. The silicon atom is type 19, saturated carbon is type 1, unsaturated carbon is type 2 and hydrogen is type 5. If the carbon is contained in a cyclopropane ring, it is type 22, and if it is in a cyclobutane ring, it is type 56. A total of 27 molecules with known vibrational spectra were examined in this work. In general, the calculated frequencies agree with experiment to within about the accuracy that was obtained with hydrocarbons ($\pm 35\ \mathrm{cm}^{-1}$).[2]

To fit the structures of silanes, 27 compounds were examined. The more significant of these are discussed individually below, and the results on the remainder are summarized in tables.

RESULTS AND DISCUSSION

Vibrational spectra

In the following, we discuss some basic vibrational modes involving silicon. First, the Si–H stretching modes are not strongly coupled with other vibrations, and are usually observed in the region 2121–2170 cm^{-1}. The average of the Si–H frequencies over 45 experimental data is 2160 cm^{-1}, compared with the MM3 calculated value of 2154 cm^{-1}. The Si–C stretching modes are often coupled with the CSiH, SiCH or other bending modes, and are more complicated. The MM3 calculation gave an average value of 683 cm^{-1} over 25 Si–C vibrations, while the average experimental value is 712 cm^{-1}. Most of the disagreement here appears from the limited number of types of coupling that are taken into account in the MM3 force field, but there are additionally some experimental difficulties. The average of eight Si–Si stretchings in four polysilanes, which were mostly determined in liquid or solid phases, is 377 cm^{-1}, compared with 388 cm^{-1} calculated by MM3. The skeletal bending modes in silanes and polysilanes, including CCSi,

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Table 1. Force field for silanes and polysilanes[a]

A. Van der Waals[b]

Atom type	r_o	ε
19	2·29	0·140

B. Bond moments[c]

Bond	Bond moment	
5–19	0·00	
1–19	− 0·70	
2–19	− 1·20	
19–56	0·85	
19–22	0·89	
19–56	0·30	4
1–19	–0·55	5

C. Bond stretching parameters[d]

Bond	K_s	l_0	
1–19	3·05	1·876	
2–19	3·00	1·854	
5–19	2·65	1·483	
19–22	3·50	1·837	
19–19	1·65	2·322	
19–56	1·30	1·881	
19–56	3·00	1·884	4
1–19	2·85	1·884	5
19–19	1·65	2·336	5

D. Angle bending parameters

Angle	k_b	$\theta_0(°)$			
		Type 1	Type 2	Type 3	
1– 1–19	0·400	109·00	112·70	111·50	
5– 1–19	0·540	109·50	110·00	108·90	
1–19– 1	0·480	109·50	110·40	109·20	
19– 1–19	0·350	109·50	119·50	117·00	
2– 1–19	0·500	109·50	105·00	109·50	
2– 2–19	0·320	122·00	122·00	–	
1–19– 2	0·400	110·20	110·20	108·50	
1–19– 5	0·400	109·30	107·00	110·00	
5–19– 5	0·460	106·50	108·70	109·50	
5– 2–19	0·525	119·50	–	–	
2–19– 5	0·550	109·50	109·50	109·50	
2–19– 2	0·600	104·50	104·50	104·50	
1–19–19	0·450	109·00	109·00	109·00	
5–19–19	0·350	109·40	109·40	109·40	
19–19–19	0·250	118·00	110·80	111·20	
1–19–22	0·530	110·20	110·20	110·20	
5–19–22	0·460	110·20	110·20	110·20	
5–22–19	0·240	124·50	124·50	–	
19–22–22	0·530	118·00	118·00	–	
1–19–56	0·530	109·50	109·50	109·50	
56–19–56	0·480	124·50	124·50	124·50	
19–56–56	0·480	111·00	111·00	–	
5–56–19	0·680	110·00	110·00	–	
5–19–56	0·450	109·30	107·00	111·00	
19–56–56	0·105	109·00	111·50	112·80	4
56–19–56	0·175	109·50	109·50	109·50	4
1–19– 1	0·650	102·80	103·80	99·50	5
1– 1–19	0·550	107·20	107·20	107·20	5
2– 1–19	0·500	109·00	109·00	109·00	5
19–19–19	0·320	106·00	106·00	106·00	5

E. Torsional parameters[f]

Dihedral angle	V_1	V_2	V_3
1– 1– 1–19	0·000	0·050	0·240
2– 1– 1–19	0·000	0·000	0·167
5– 1– 1–19	0·000	0·000	0·220
19– 1– 1–19	0·000	0·000	0·167
19– 1– 2– 2	− 0·750	0·000	0·505
19– 1– 2– 5	0·000	0·000	0·717
1– 1–19– 2	0·000	0·000	0·167
1– 1–19– 1	0·000	0·000	0·167
1– 1–19– 5	0·000	0·000	0·295
2– 1–19– 2	0·000	0·000	0·400
2– 1–19– 1	0·000	0·000	0·167
2– 1–19– 5	0·000	0·000	0·320
5– 1–19– 1	0·000	0·000	0·195
5– 1–19– 5	0·000	0·000	0·177
19– 1–19– 1	0·000	0·000	0·100
19– 1–19– 5	0·000	0·000	0·167
5– 1–19– 2	0·000	0·000	0·117
1– 1–19–19	0·000	0·000	0·300
5– 1–19–19	0·000	0·000	0·270
1– 2– 2–19	0·000	6·450	0·000
5– 2– 2–19	0·000	6·450	0·000
19– 2– 2–19	0·000	6·450	0·000
2– 2– 2–19	0·000	6·450	0·000
2– 2–19– 1	− 0·300	0·300	0·000
2– 2–19– 5	0·300	0·000	0·000
5– 2–19– 1	0·000	0·000	0·717
5– 2–19– 5	0·000	0·000	0·520
5– 2–19– 2	0·000	0·000	0·600
2– 2–19– 2	0·000	0·000	0·232
1– 2–19– 1	0·000	0·000	0·350
1– 2–19– 2	− 0·440	− 0·240	0·060
2– 2–19–19	− 0·440	− 0·240	0·060
2–19–19– 5	0·000	0·000	0·450
2–19–19– 2	0·000	0·000	0·400
1–19–19– 2	0·007	0·270	0·093
5–19–22–22	0·000	0·000	0·805
5– 1–19–22	0·000	0·000	0·300
19–22–22–22	0·220	0·270	0·093
5–22–22–19	0·000	0·000	0·120
5–19–22– 5	0·000	0·000	0·260
1–19–22–22	0·000	0·000	0·500
1–19–22– 5	0·000	0·000	0·400
5– 1–19–56	0·000	0·000	0·330
1–19–56–56	0·000	0·000	0·300
1–19–56– 5	0·000	0·000	0·300
19–56–56–56	0·000	0·050	0·650
56–19–56–56	0·100	0·000	0·150

Table 1*E*. Continued.

5–19–56– 5	0·000	0·000	0·270	
5–19–56–56	0·000	0·000	0·210	
5–56–56–19	0·000	0·000	0·600	
56–19–56– 5	0·000	0·000	0·195	
1–19–19– 5	0·000	0·000	0·127	
1–19–19– 1	0·100	0·000	0·107	
1–19–19–19	0·000	0·000	0·350	
5–19–19– 5	0·000	0·000	0·132	
5–19–19–19	0·000	0·000	0·070	
19–19–19–19	0·000	0·000	0·125	
19–56–56–56	0·000	0·000	1·300	4
56–19–56–56	0·100	0·000	0·950	4
1– 1– 1–19	0·000	0·000	0·850	5
1– 1–19– 1	0·000	0·800	0·000	5
1– 1–19– 1	0·000	0·000	0·250	5
19– 1– 2– 2	0·000	0·000	0·350	5
19–19–19–19	0·000	0·000	0·175	5

F. Stretch–bend parameters[g]

—	k_{sb}
X—Si—Y	0·10
X—Si—H	0·06

G. Electronegativity correction to l_0[h]

Bond	End of bond	Atom type	Correction
1– 1	1	19	0·009
1– 2	1	19	0·013
2– 2	2	19	0·011
22–22	22	19	0·008
5–19	19	19	0·003
19–19	19	19	− 0·002
19–19	19	5	0·004
1–19	19	19	0·009
56–56	56	19	0·014
1–19	1	19	− 0·004

H. Out-of-plane bending parameters[i]

Angle	k_{opb}
2–19	0·10

I. Torsion–stretch parameters[j]

	k_{ts}
1–19	0·036
2–19	0·087
19–22	0·036
19–56	0·012
19–19	0·012

J. Bend–bend parameters[k]

	k_{bb}
X—Si—Y	0·24
X—Si—H	0·30
H—Si—H	0·00

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[a] Type 1, sp^3 carbon; type 2, sp^2 carbon; type 5, hydrogen; type 19, silicon; type 22, three-membered-ring sp^3 carbon; type 56, four-membered ring sp^3 carbon; for parameters other than type 19, see Ref. 1.

[b] Van der Waals distance is in Å and ε in kcal/mol.

[c] Bond moments are in debye.

[d] Stretching force constants are in mdyn/Åmol; natural bond lengths are in Å.

[e] Bending force constants are in mdyn Å/rad^2; natural bond angles are in degrees; type 1, the other two attached groups are both heavy atoms; type 2, the other attached groups are hydrogen and heavy atom; type 3, the other attached groups are both hydrogens.

[f] V_1, V_2 and V_3 are in kcal mol^{-1}.

[g] Stretch-bond force constants are in mdyn rad^{-1} mol^{-1}.

[h] Electronegativity corrections are in Å; secondary electronegativity factor, 0·4.

[i] Out-of-plane bending constants are in mdyn Å rad^{-2}.

[j] Torsion–stretch constants are in kcal Å^{-1} mol^{-2}.

[k] Bend–bend constants are in mdyn^2 rad^{-2}; X, Y are heavy atoms.

CSiC, SiSiC and SiSiSi bendings, are predicted in the lower frequency region, 300 cm^{-1}, but were not measured by most experiments. MM3 calculations of these modes agree well with the few experimental data available. The bending modes involving the hydrogens are more complicated than the others. These modes not only couple with each other, but also couple with other vibrations, such as Si–C stretching, SiCC bending and Si–C torsion. The SiH$_3$ deformation and SiH$_2$ scissoring modes, about 950 cm^{-1} experimentally, are usually well reproduced, but the SiH$_3$ and SiH$_2$ wagging, rocking and SiH$_2$ twist modes are calculated less well. The addition of more cross-term interactions would give better fits for these vibrations. However, this could complicate the program and require additional parameters. It was decided earlier not to include such terms in MM3 as the structures, thermodynamics and, as far as we can determine, everything else, can be acceptably calculated with these errors in the vibrational frequencies. The rms error over seven simple acyclic compounds (Table 2) is 29 cm^{-1} over 160 vibrations, slightly better than found with the saturated hydrocarbons,[2] 35 cm^{-1}. For unsaturated, cyclic and polysilanes, the rms errors are 35, 68 and 41 cm^{-1}, respectively. The error is somewhat large for cyclic silanes. This result mainly comes from the way we parameterized for the four-membered ring. It was assumed that the natural CCC bond angle for cyclobutane was tetrahedral, and then the bending parameter was reduced to fit the molecular structure. This is a first approximation and works well for the structure, but it gave a poor fit to the spectrum. However, to be consistent internally with the earlier work with MM3, we applied the

Table 2 Experimental and calculated vibrational frequencies of acyclic silanes

Silane

	Exp.^{4}	MM3	Δ	sym.	Assignment
1	2189	2162	− 27	*T*	Asym. Si–H stretching
2	2185	2111	− 74	A_1	Sym. Si–H stretching
3	972	1028	56	*E*	H–Si–H bending
4	913	877	− 36	*T*	H–Si–H bending

Methysilane

	Exp.^{5}	MM3	Δ	Sym.	Assignment
1	2982	2984	2	E	Asym. CH_3 stretching
2	2929	2881	− 51	A	Sym. CH_3 stretching
3	2166	2158	− 8	E	Asym. SiH_3 stretching
4	2169	2126	− 43	A_1	Sym. SiH_3 stretching
5	1403	1417	14	E	CH_3 deformation
6	1264	1271	7	A_1	CH_3 deformation
7	946	983	37	E	SiH_3 deformation
8	871	892	21	E	CH_3 rocking
9	(946)	841	–	A	SH_3 deformation
10	701	702	1	A_1	Si–C stretching
11	545	590	45	E	SiH_3 rocking
12	183	208	25	A_2	Si–C torsion

Dimethysilane

	Exp.^{6}	MM3	Δ	Sym.	Assignment
1	2970	2984	14	A_1	Asym. C–H stretching
2	2970	2984	14	B_2	Asym. C–H stretching
3	–	2984	–	A_1	Asym. C–H stretching
4	2970	2984	14	B_2	Asym. C–H stretching
5	2920	2881	− 39	B_2	Sym. C–H stretching
6	2920	2881	− 39	A_1	Sym. C–H stretching
7	2142	2171	29	B_2	Sym. Si–H stretching
8	2145	2153	8	A_1	Sym. Si–H stretching
9	1430	1417	− 13	B_2	Asym. CH_3 deformation
10	1410	1417	7	A_1	Asym. CH_3 deformation
11	1410	1417	7	B_2	Asym. CH_3 deformation
12	–	1417	–	A_2	Asym. CH_3 deformation
13	1260	1274	14	B_2	Sym. CH_3 deformation
14	1260	1272	12	A_1	Sym. CH_3 deformation
15	963	904	− 59	A_1	CH_3 rock, SiH_2 bending
16	919	899	− 20	B_2	CH_3 rock, SiH_2 wagging
17	867	897	30	B_2	CH_3 rock, SiH_2 rock
18	838	890	52	A_1	CH_3 rock, SiH_2 bending
19	–	883	–	A_2	CH_3 rock, SiH_2 twist
20	728	783	55	B_1	Asym. Si–C stretching
21	–	713	–	A_2	CH_3 rock, SiH_2 twist
22	643	698	55	B_1	CH_3 rock, SiH_2 wagging
23	659	671	12	A_1	Sym. Si–C stretching
24	467	465	− 2	B_2	CH_3 rock, SiH_2 rock
25	223	224	1	A_1	C–Si–C bending
26	–	180	–	B_2	Si–C torsion
27	–	170	–	A_2	Si–C torsion

Table 2 Continued

Trimethylsilane

	Exp.^{6}	MM3	Δ	Sym.	Assignment
1		2985	16	*E*	Asym. C–H stretching
2	2969	2984	15	A_1	Asym. C–H stretching
3		2984	15	*E*	Asym. C–H stretching
4	–	2984	–	A_2	Asym. C–H stretching
5	2912	2882	− 30	*E*	Sym. C–H stretching
6		2881	− 31	A_1	Sym. C–H stretching
7	2125	2139	14	A_1	Si–H stretching
8		1419	− 27	A_1	Asym. CH_3 deformation
9	1446	1418	− 28	*E*	Sym. CH_3 deformation
10		1417	− 29	*E*	Sym. CH_3 deformation
11	–	1416	–	A_2	Asym. CH_3 deformation
12	1257	1272	15	*E*	Asym. CH_3 deformation
13	1263	1270	7	*A*	Sym. CH_3 deformation
14	907	915	8	*E*	CH_3 rock, C–Si–H bending
15	835(s)	909	–	A_1	CH_3 rock
16	849	884	35	*E*	CH_3 rock, C–Si–H bending
17	–	878	–	A_2	CH_3 rock
18	616(1)	779	–	*E*	CH_3 rock, C–Si–H bending
19	714	721	7	*E*	Asym. Si–C stretching
20	625	624	− 1	A_1	Sym. Si–C stretching
21	216(1)	250	–	A_1	C–Si–C bending
22	252(1)	229	–	*E*	C–Si–C bending
23	–	177	–	*E*	Si–C torsion
24	–	171	–	A_1	Si–C torsion

same scheme to silacyclobutane. This leads to a very large rms frequency error, 118 cm^{-1}. The overall rms error for the silane frequencies is 47 cm^{-1} over 583 vibrations. The spectra we studied are discussed briefly below.

Acylic silanes

Silane. This simplest silane has nine vibrational modes which are distributed over T_d symmetry species as $2T+A_1+E$. There are only two fundamental kinds of vibrations, the Si–H stretching and HSiH bending. The Si–H stretching modes are calculated too small on average by 46 cm^{-1}, but the HSiH bending modes agree well with the observed.[2] (It was decided to let more error appear in the parent silane so the alkylsilane results would be better.) The rms error of silane, 45 cm^{-1}, is thus slightly larger than the average error for hydrocarbons,[2] 35 cm^{-1}. The problem here is similar to that encountered earlier in hydrocarbons, namely, that the Si–H force constant varies slightly from primary to secondary, to tertiary, to quarternary (1–4°). It was decided earlier to use different stretching constants for 1–4° C–H bonds as a special case, but not to introduce this complexity into MM3 generally.

Methylsilane. Methylsilane belongs to the point group C_3, and the representation of the 18 vibrational modes is formed by $5A_1+A_2+6E$. Two large errors are in the SiH_3 deformation and SiH_3 rock frequencies. From the spectrum,[4] only one absorption was recorded, at 946 cm^{-1}, and it was assigned for both symmetric and asymmetric SiH_3 deformations. We believe that one of the absorptions may have been missed or misassigned.

Dimethylsilane. The infrared spectrum of the gas and the Raman spectrum[6] of the liquid have been obtained for dimethylsilane. This molecule belongs to the point group C_2, and the 27 vibrational modes are formed by $9A_1+5A_2+7B_1+6B_2$. The SiH_2 bending modes are coupled with other motions in the molecule to a considerable extent. The asymmetric Si–C stretching is calculated too large by 55 cm^{-1}, whereas the symmetric stretching is fit fairly well. The rms error is 31 cm^{-1}.

Trimethylsilane. Trimethylsilane has C_3 symmetry, and the 24 symmetry species of the vibrations are distributed as $8A_1+4A_2+12E$. In general, the vibrational frequencies of this molecule are fit pretty well with an rms error of 22 cm^{-1}.

Ethylsilane. Ethylsilane has a plane of symmetry and belongs to the C_s point group in the rotational ground state. A gas-phase infrared spectrum[7] has been measured for ethysilane. Of the 27 normal modes of vibration, 16 are A' modes and eleven are A'' modes. A very large error, 104 cm^{-1} too small, was found for the calculated SiH_3 deformation. This is similar to what was observed in methylsilane; we think this could also be misassigned (see Supplementary Material).

Diethylsilane. The infrared spectrum[8] of the gaseous diethylsilane molecule was measured over the range 4000–600 cm^{-1}, but the vibrational mode assignments were carried out for the bands above 800 cm^{-1} only. Diethylsilane has several different stable conformers, but no information regarding them is available from experiment. The MM3 calculation indicates that the most stable form is the *gauche–gauche* conformation with respect to the two ethyl groups. A strong, sharp absorption was observed at 720 cm^{-1}. We believe this band is the symmetric Si–C stretching mode, which may be compared with the MM3 value, 676 cm^{-1} (see Supplementary Material).

Propylsilane. Propylsilane has two possible conformers, *trans* and *gauche*, with respect to the C—C—C—Si dihedral angle. The infrared and Raman spectra[9] of these two forms were measured in the gas, liquid and solid states. This molecule was used to optimize the force parameter for CCSi bending. Experment gives 198 and 258 cm^{-1} for the bending frequencies of the *trans* and *gauche* conformers, respectively. The MM3 calculations gave the values of 213 and 212 cm^{-1}, and show the desirability of a torsion–bend cross term (see Supplementary Material).

Unsaturated silanes

Vinylsilane. The gas-phase infrared and Raman spectra of vinylsilane have been reported.[10] Vinylsilane belongs to the C_s point group, and the 21 normal vibrations can be categorized as $14A'$ and $7A''$. The three sp^2-type C–H stretching modes are calculated too high by 45 cm^{-1}. This is due to the electropositivity of the silicon, which was not taken into account. MM3 takes into account the effect of electronegativity on the stretching constant of the saturated C—H bond (type 1–5) only. In summary, the calculated frequencies are fit adequately with an rms error of 34 cm^{-1} (Table 3).

Methyvinylsilane. The infrared and Raman spectra have been measured for methylvinylsilane.[11] For this molecule, the *cis* and skew forms (with respect to the C=C—Si—C torsional angle) were found to coexist in the gaseous and liquid states. Except for the SiH_2 twist mode, MM3 reproduces the experimental results fairly well. The experimental data and calculated results are summarized in the Supplementary Material.

Allylsilane. Gas-phase infrared and liquid-phase Raman spectroscopy have been applied to a study of this molecule.[11] The molecules exist predominantly in the skew form in the gaseous state. As expected, the bending motions involving hydrogens are still a problem. The overall rms error is 32 cm^{-1} (Table 3).

Tetravinylsilane. The gas-phase infrared and Raman spectra have been recorded, and vibrational assignments were presented for tetravinylsilane.[12] From the spectroscopic analysis, this molecule was assigned D_{2d} symmetry, which is different from the S_4 symmetry found in the MM3 calculation. The electron diffraction method[13] was also used to study this molecule, and S_4 symmetry was found (see Supplementary Material).

Cyclic silanes

Cyclobutylsilane. The infrared and Raman spectra of gaseous cyclobutylsilane have been obtained.[14] It was found that two stable conformers exist in the gas phase, which are the equatorial and axial forms. For both conformers, the molecular vibrations are expected to span the irreducible representations $23A'+16A''$. The observed and calculated vibrational frequencies are summarized in the Supplementary Material. The most interesting aspect of cyclobutylsilane is the ring-puckering libration. From the analysis of the low-frequency Raman spectrum, it was suggested that the energetics of the ring-puckering motion in this molecule should be characterized by an asymmetric double minimum potential. The observed frequencies were 125 and 112 cm^{-1} for equatorial and axial conformers, respectively. The MM3 calculated frequencies are higher, 169 and 173 cm^{-1}. This may be due to the use of the harmonic approximation in MM3 and anharmonicity in the

Table 3. Experimental and calculated vibrational frequencies of unsaturated silanes[a]

Vinylsilane

	Exp.[10]	MM3	Δ	Sym.	Assignment
1	3067	3105	38	A'	Asym. CH_2 stretching
2	2994	3045	51	A'	Sym. CH_2 stretching
3	2962	3008	46	A'	C–H stretching
4	2163	2161	−2	A''	Asym. Si–H stretching
5	2170	2161	−9	A'	Asym. Si–H stretching
6	2168	2128	−40	A'	Sym. Si–H stretching
7	1599	1601	2	A'	C=C stretching
8	1406	1429	23	A'	CH_2 deformation
9	1269	1227	−42	A'	C=C–H in-plane bending
10	1018	1080	62	A''	CH_2 twist, C=C–H out-plane bending
11	1008	1044	36	A'	CH_2 rock
12	961	984	23	A''	Asym. SiH_3 deformation
13	955	983	28	A'	Sym. SiH_2 deformation
14	937	902	−35	A''	CH_2 wagging
15	932	882	−50	A'	Asym. SiH_3 deformation
16	716	689	−27	A''	SiH_3 rock
17	707	678	−29	A'	SiH_3 rock
18	624	631	7	A'	Si–C stretching
19	428	470	42	A''	C=C–H out-plane bending
20	284	325	41	A'	C=C–Si bending
21	132	131	−1	A''	Si–C torsion

Allylsilane

	Exp.[11]	MM3	Δ	Sym.	Assignment
1	3093	3107	14	*S*	C–H stretching (=CH_2)
2	3001	3037	36	*A*	C–H stretching (CH)
3	2987	3008	21	*A*	C–H stretching (=CH_2)
4	2939	2943	4	*A*	CH_2 stretching
5	2902	2890	−12	*A*	CH_2 stretching
6	2167	2158	−1	*A*	Asym. Si–H stretching
7		2157	−10	*A*	Asym. Si–H stretching
8		2126	−41	*A*	Sym. Si–H stretching
9	1636	1668	28	*A*	C=C stretching
10	1426	1478	52	*A*	CH_2 scissoring
11	1397	1414	17	*A*	=CH_2 scissoring
12	1300	1318	18	*A*	–CH in-plane bending
13	1195	1232	37	*A*	CH_2 twisting
14	1163	1159	−4	*A*	CH_2 wagging, scissoring
15	1039	1101	62	*A*	CH_2 rocking, C–C stretching
16	995	1081	86	*A*	=CH_2 twist
17	979	986	7	*A*	=CH_2 wagging
18	–	985	–	*A*	Asym. SiH_3 def.
19	931	970	39	*A*	Asym. SiH_3 def.
20	923	950	27	*A*	Sym. SiH_3 def.
21	834	842	8	*A*	C–C stretching
22	–	818	–	*A*	CH_2 rocking, twist
23	767	733	−34	*A*	C–Si stretching
24	589	589	0	*A*	Sym. SiH_3 rocking
25		587	−2	*A*	Asym. SiH_3 rocking
26	527	579	52	*A*	C–H out-plane bending
27	407	403	−4	*A*	C–C–C bending
28	227(1)	255	–	*A*	C–C–Si bending
29	–	148	–	*A*	C–C–Si–H torsion
30	112(1)	72	–	*A*	C=C–C–Si torsion

[a] The spectra of four additional compounds are available in the Supplementary Material.

Table 4. Experimental and calculated vibrational frequencies of disilane[a]

	Exp.[18] IR(g)	Ra(1)	MM3	Δ	Sym.	Assignment
1	2178	–	2163	− 15	E_u	Asym. Si–H stretching
2	–	2155	2162	7	E_g	Sym. Si–H stretching
3	2154	–	2129	− 25	A_{1g}	Sym. Si–H stretching
4	–	2152	2128	− 24	A_{2u}	Asym. Si–H stretching
5	940	–	968	28	E_u	Asym. SiH_3 deformation
6	–	929	962	33	E_g	Sym. SiH_3 deformation
7	–	909	771	− 128	A_{2u}	Asym. SiH_3 deformation
8	844	–	765	− 79	A_{1g}	Sym. SiH_3 deformation
9	–	625	555	− 70	E_g	Sym. SiH_3 wagging
10	379	–	509	130	E_u	Asym. SiH_3 rocking
11	–	434	428	− 6	A_{lg}	Si–Si stretching
12	–	–	147	–	A_{lu}	Si–Si torsion

[a] The spectra of four additional compounds are available in the Supplementary Material.

real molecule. Another error is in the Si–C stretching mode. The experimental frequencies are 495 and 545 cm^{-1} from IR spectra for the equatorial and axial forms, respectively. The MM3 calculated Si–C stretching frequencies are 544 and 485 cm^{-1}, which are opposite to the experimental values. There are some large errors in four-membered ring compounds in the range around 1200 cm^{-1}, which are the CH_2's in-phase and out-of-phase rocks (or wags). These errors could be reduced by employing the bend–torsion–bend interaction.[19] The overall rms errors for four-membered ring compounds are fairly large (see Table 5), but they are largely inherent in MM3.

Silacyclobutane. The infrared and Raman spectra[15] of silacyclobutane and three derivatives have been recorded. Normal coordinate calculations were also carried out. All the evidence showed that this four-membered ring compound is non-planar and has C_s symmetry, and the MM3 calculation agrees with this. The 30 vibrations are distributed as $18A'$ species and $12A''$ species. The experimental and calculated values are listed in the Supplementary Material.

Silacyclopentane. The infrared spectra[16] of silacyclopentane in both the gaseous and liquid states were recorded. The 39 fundamental modes of vibration of silacyclopentane can be described by $20A + 19B$. The experimental data ruled out the planar configuration for silacyclopentane, and were shown to be consistent with a C_2 structure.

1-Silacyclopent-3-ene. The infrared and Raman spectra have been recorded in the gaseous phase and the vibrations have been asigned.[17] A series of far-infrared absorption bands which result from the transitions between different energy levels of the ring-puckering vibration have also been observed. This evidence suggests that this molecule is planar with C_{2v} symmetry. The MM3 calculation agrees with these data. These 33 vibrations were distributed as $11A_1+6A_2+9B_1+7B_2$. The spectra of the five-membered ring compounds are fit with 31 and 46 cm^{-1} rms errors for silacyclopentane and 1-silacyclopent-3-ene, respectively.

Polysilanes

Disilane. The Raman spectrum in the liquid and the infrared gas-phase spectrum have been examined for disilane.[18] Similarly to its carbon analog, ethane, this molecule has the staggered (D_{3d} symmetry) conformation in the rotational ground state. The ethane spectrum had an MM3 calculated error of 127 cm^{-1} for a methyl rocking mode. There is an even larger corresponding error in the symmetric SiH_3 rocking mode, which is calculated to be 130 cm^{-1} too large (Table 4). Subsequent studies with ethane showed the problem with ethane could be taken care of by a bend–torsion–bend interaction term,[19] and while the error here could be similarly taken care of, such terms are not included in MM3.

Hexamethyldisilane. The gaseous infrared and liquid Raman spectra[20] of the hexamethyldisilane molecule have been measured. The molecule has a staggered configuration with D_{3d} symmetry. The observed and calculated frequencies are listed in the Supplementary Material.

Cyclopentasilane. The infrared and Raman spectra[21] of cyclopentasilane have been recorded and assigned. Analogously to cyclopentane, cyclopentasilane is non-planar and undergoes rapid pseudorotation. The 39 vibrations are distributed over C_2 symmetry species as $20A+19B$. Even though the experimental spectrum was not determined in the gas phase, the MM3 calculated results are considered to be in good agreement (see Supplementary Material).

Cyclohexasilane. The liquid-phase Raman and solid-phase infrared spectra of cyclohexasilane have been measured.[22] The experimental results indicate that this molecule exists in a chair conformation with D_{3d} symmetry (see Supplementary Material).

Table 5. Root-mean-square errors of Silanes and Polysilanes

Compound		RMS
Silane		45
Methylsilane		28
Dimethylsilane		31
Trimethylsilane		22
Ethylsilane		38
Diethylsilane(*gauche-gauche*)		24
Propylsilane	*Trans*	25
	Gauche	24
Vinylsilane		34
Methylvinylsilane	*Cis*	27
	Skew	26
Trimethylvinylsilane		38
Allylsilane	*Skew*	33
Tetravinylsilane		38
Cyclobutylsilane	Equatorial	62
	Axial	54
Silacyclobutane		118
1,1-Dimethyl-1-silacyclobutane		61
Silacyclopentane		31
1-Silacyclopent-3-ene		46
Disilane		65
Hexamethyldisilane		26
Overall		47

Molecular structures and relative energies

Acylic silanes

Silane. Numerous experimental methods[23–25] have been applied to study this molecule. The structural parameters of silane determined by a combination of infrared and microwave spectroscopy are believed to be the best. The experimental and MM3 structures are given in Table 7. The MM3 calculated Si—H bond length is longer than the observed value by about 0·002 Å. The calculated moments of inertia, I_x, I_y and I_z, are each 0·41% larger than the experimental values.[25] These differences correspond to the difference between the r_g structure (MM3) and the r_z structure (experimental).

Methylsilane. The molecular structure of methylsilane has been reported by a combined infrared/microwave method[26] and by the microwave method.[27] A torsion–stretch interaction has been added for silanes in order to take the bond length elongation for eclipsed conformations into account, analogous to the treatment of hydrocarbons.[2] *Ab initio* calculations with the 6–31G** basis, at the MP2 level to include the electron correlation, have been applied in the present work. It was found that the Si—C bond length for methylsilane stretched by 0·010 Å on going to the eclipsed form. The K_{ts} value was chosen to reproduce this effect. It is also used for vinylsilane where the bond stretches a little less, only 0·007 Å. The MM3 calculation fits the experimental data well. The errors in the calculated moments of inertia are 1·39, 0·63 and 0·63% for I_x, I_y and I_z, respectively, and the differences in bond lengths are about as expected for r_s and r_g structures (Table 6).

Dimethylsilane. Dimethysilane and six of its isotopically substituted derivatives have been studied by microwave spectroscopy.[28] The molecular structure (r_s) was then determined by fitting the observed moments of inertia. The CSiC angle is open a little from tetrahedral, 111·0(2)°. The internal rotation barrier was 1·647(3) kcal mol^{-1}. The calculated structures, barrier and dipole moment all fit closely to the experimental values.

Trimethylsilane. This molecule has C_3 symmetry, with a staggered conformation in the ground state. The MM3 structure is fit well to the experimental data. The errors in the moments of inertia are 0·49 and 0·40% for I_x and I_z, respectively. The internal rotational barrier of a methyl group calculated from the microwave spectrum[29] is 1·83 kcal mol^{-1}, and the MM3 calculation gives 1·81 kcal mol^{-1}.

Tetramethylsilane. This compound was studied by the electron diffraction method.[30] The MM3 structure agrees well with that observed, and both are summarized in Table 7. The methyl rotational barrier is 1·90 kcal/mol calculated by MM3, compared with the value 2·00 kcal/mol experimentally.[31]

Ethylsilane. The MM3 calculation for this molecule gives the Si—C bond longer by 0·016 Å than the microwave value.[32] The conformational energies fit fairly well. The MM3 values of the SiH_3 and methyl barriers are 2·01 and 2·64 kcal mol^{-1}, while the experimental values[33] are 1·98 and 2·62 kcal mol^{-1}, respectively. The moments of inertia are calculated 1·02, 1·63 and 1·43% larger than experiment, which seem slightly higher than expected, but the geometry has to be compromised with those of other structures.

Triethylsilane. The most stable conformation has C_3 symmetry from both electron diffraction[34] and MM3 calculation. The MM3 structure is fit to the experimental structure to within the experimental errors (see Supplementary Material).

Propysilane. From the IR and Raman spectra, two stable conformations were found, the *trans* and *gauche* forms with respect to the C—C—C—Si torsion angle. The experimental energy difference between the two forms is 0·60–0·65 kcal mol^{-1}, with the *trans* form more stable, and the value is 0·60 kcal mol^{-1} by MM3 calculation. Only the microwave structural data[35] of the *trans* conformer are available for this molecule, because the spectra of the *gauche* form were too weak to be assigned.

Ethylmethylsilane. It was found by microwave spectroscopy[36] that the *trans* conformation with respect to the C—Si—C—C dihedral angle is the most stable form.

Table 6. Experimental and calculated structures of acyclic silanes[a]

Silane

	Exp. (IR + MW)[23]	MM3	Δ
Si–H(r_0)	1·481185(3)	1·483	0·0018
∠HSiH	—	109·5	—

	Exp.[25]	MM3	Δ(%)
I_x	0·978	0·982	0·41
I_y	0·978	0·982	0·41
I_z	0·978	0·982	0·41

Methylsilane

	Exp. (IR + MW)[26]	MW[27]	MM3	Δ
Si—C	1·8686(2)(r_s)	1·8668(30)(r_0)	1·876(stg)	0·007
Si—H	1·4832(4)	1·485(5)	1·483(stg)	0·000
C—H	1·0957(5)	1·093(5)	1·112(stg)	0·016
∠HSiH	—	108·3(5)(θ_0)	108·3(stg)	—
∠HCH	—	107·7(5)	108·7(stg)	—
∠CSiH	110·50(3)(θ_0)	—	110·6(stg)	0·1
∠SiCH	110·88(3)	—	110·2(stg)	− 0·7

	Exp.[26]	MM3	Δ(%)
I_x	8·996(12)	9·121	1·39
I_y	46·002	46·294	0·63
I_z	46·002	46·294	0·63

Dimethylsilane

	Expt. (MW)[28]	MM3	Δ
Si—C(r_s)	1·867(3)	1·873(stg)	0·006
Si—H	1·483(5)	1·482(stg)	− 0·001
C–H	1·095(5)	1·112(stg)	0·017
∠HSiH(θ_0)	107·8(5)	107·5(stg)	− 0·3
∠CSiC	111·0(2)	111·3(stg)	− 0·3
∠CSiH	—	109·5(stg)	—
∠SiCH	—	110·2(stg)	—

	Exp.[28]	MM3	Δ(%)
I_x[b]	30·094	30·254	0·53
I_y	84·842	85·554	0·84
I_z	102·771	103·470	0·68

Trimethylsilane

	Expt.(MW)[29]	MM3	Δ
Si–C(r_s)	1·868(3)	1·876(stg)	0·008
Si–H	1·489(3)	1·484(stg)	− 0·006
C–H	1·095(3)	1·112(stg)	0·017
∠CSiC	110·2(2)	110·1(stg)	− 0·1
∠HCH	107·9(3)	108·7(stg)	− 0·8
∠CSiH	—	108·8(stg)	—
∠SiCH	—	110·2(stg)	—

	Exp.[29]	MM3	Δ(%)
I_x[b]	15·715	15·792	0·49
I_y	15·715	15·792	0·49
I_z	26·532	26·638	0·40

Tetramethylsilane

	Expt.(ED)[30]	MM3	Δ
Si–C(r_g)	1·877(2)	1·876(stg)	− 0·001
C–H	1·117(7)	1·112(stg)	− 0·005
∠CSiC	—	109·5(stg)	—
∠HCH	109·8(8)	108·7(stg)	− 1·1
∠SiCH	109·2(8)	110·2(stg)	1·0

Ethylsilane

	Expt.(MW)[32]	MM3	Δ
Si–C(r_s)	1·866(3)	1·882(stg)	0·016
Si–H_s	1·483(5)	1·483(stg)	0·000
Si–H_a	1·480(5)	1·483(stg)	0·003
C–C	1·540(3)	1·542(stg)	0·002
C_1–H	1·093(3)	1·114(stg)	0·021
C_2–H	1·097(3)	1·113(stg)	0·016
∠SiCC(θ_0)	113·2(2)	113·3(stg)	− 0·10
∠SiCH	—	109·0(stg)	—
∠CSiH	—	110·6(stg)	—
∠H_aSiH_a	108·3(5)	108·3(stg)	0·0
∠H_aSiH_s	108·2(5)	108·3(stg)	0·1
∠$H_aC_1H_a$	107·0(5)	106·8(stg)	− 0·2
∠$H_aC_1H_s$	107·3(5)	107·3(stg)	0·0
∠C_2C_1H	110·5(5)	109·3(stg)	− 1·2
∠C_1C_2H	112·0(5)	111·6(stg)	− 0·4

	Exp.[32]	MM3	Δ (%)
I_x	3·598	3·635	1·02
I_y	16·999	17·277	1·63
I_z	18·603	18·869	1·43

Ethylmethylsilane

	Expt.(MW)[36]	MM3	Δ
Si—C(r_0)	1·867	1·873(Me)	0·006
		1·879(Et)	—
Si–H	1·483	1·482	− 0·001
C–C	1·540	1·542	0·002
∠SiCC(θ_0)	114·2(20)	113·4	− 0·8
∠CSiC	111(assumed)	111·2	—
∠SiC_2H	109·2(30)	109·0	− 0·2
∠CCH	109·2(20)	110·6	1·4
∠HC_2H	105·8(assumed)	106·7	—
ωCSiCC	trans	180·0	—

Table 6. Continued

	Exp.[36]	MM3	Δ(%)
I_x[c]	33·4381	33·8186	1·14
I_y	186·8454	187·8513	0·54
I_z	205·1668	206·1484	0·48

Tri-tert-*Butylslane*

	Expt.(ED)[38]	MM3	Δ
Si–C(r_g)	1·934(6)	1·931	− 0·003
Si–H	1·49(fixed)	1·490	—
C–C	1·548(3)	1·552	0·004
C–H	1·121(9)	1·112	− 0·009
∠SiCC(θ_α)	111·5(5)	111·2	− 0·30
∠CSiC	—	114·1	—
∠CSiH	105·3(13)	104·3	− 0·98
∠CCH	110·0(15)	112·0	2·03
∠HCH	—	106·8	—
ωCCSiH	—	15·5[d]	—

Disilylmethane

	Exp. (ED)[39]	MM3	Δ
Si–C(r_g)	1·875(2)	1·877	0·002
Si–H	1·514(6)	1·485	− 0·029
C–H	1·11(2)	1·113	0·003
∠SiCSi(θ_0)	114·4(2)	115·5	1·1
∠HSiH	108·1(11)	108·3	0·2
∠HCH	110·0(fixed)	106·8	—
ωHSiCSi	—	180·0	—
ωHSiCH	—	177·8	—

[a] Throughout the paper the dimensions used are: Å: bond length; °: bond angle and dihedral angle; kcal/mol: energy; Debye: dipole moment; $gm*^2cm*10^{-39}$: moments of inertia. Structural data for three additional compounds are available in the Supplementary Material.

[b] In atomic units.

[c] The observed rotational constants: $A = 15114·85(20)$, $B = 2703·36(10)$ and $C = 2463·25(10)$ MHz. The conversion factor is 505377 MHz/amu*A^2.

[d] The average distorted angle from the staggered form.

[e] ω_1: torsional angle of SiC_1SiC_2.

According to Ouelette *et al.*,[37] the *gauche* form is more stable than the *trans* form by 0·2 kcal mol^{-1} (ΔE) experimentally, but no reference was given. The MM3 calculations agree with the microwave result, and the *trans* form is more stable by 0·01 kcal mol^{-1}. The moments of inertia were measured for the *trans* form to be 33·4381, 186·8454 and 205·1668 amuÅ^2 for I_x, I_y and I_z, respectively.[36] The MM3 calculated values are 1·14, 0·48 and 0·48% larger, respectively. The experimental methyl (on silicon) barrier was 1·54 ± 0.03 kcal mol^{-1}. The MM3 calculations give the values of 1·74 and 2·14 kcal mol^{-1} for methyl (on silicon) and ethyl (*anti*→*gauche*) barriers.

Table 7. The Rotational Barriers of Acyclic Silanes

Compound		Exp.	MM3	Δ
Methylsilane	Methyl barrier	1·67[26]	1·65	− 0·02
Dimethylsilane	Methyl barrier	1·65[28]	1·74	0·09
Trimethylsilane	Methyl barrier	1·83[29]	1·81	− 0·02
Tetramethylsilane	Methyl barrier	2·00[31]	1·90	− 0·10
Ethylsilane	Methyl barrier	2·62[33]	2·64	0·02
	SiH_3 barrier	1·98[33]	2·01	0·03
Propylsilane	ΔE[a]	0·60–0·65[9]	0·60	—
Ethylmethylsilane	Methyl barrier[b]	1·54(3)[36]	1·74	0·20
	Ethyl barrier[c]	—	2·14	—

[a] Energy difference between gauche and trans conformations.

[b] Methyl on silicon.

[c] Barrier for *anti* form to *gauche* form.

Tri-*tert*-butylsilane. Gas-phase electron diffraction data[38] have been reported for this compound (Table 7). The most stable conformer has C_3 symmetry. The Si—C and C—C bonds stretch out to 1·933 and 1·552 Å by MM3 and 1·934(6) and 1·548(3) by ED. The CSiC angles open wide to 114·1° by MM3, and the dihedral angles are distorted away from the staggered form by 15·5° so as to reduce the van der Waals interactions between the three bulky *tert*-butyl groups (experimental values not given). This effect is similar to that observed in the highly strained tri-*tert*-butylmethane, but is somewhat less serious here because the Si—C bond is much longer than the C—C bond. In general, the structure was fit to within experimental error.

Disilylmethane. The molecular structure of disilylmethane has been determined by gas electron diffraction.[39] The SiCSi angle, 114·4(2)°, is considerably larger than the tetrahedral angle. The MM3 calculation gives the SiCSi angle of 115·5° which is larger than the experimental value, 114·4°.

Bis(trimethylsilyl)methane. Structural studies[40] have been reported for this molecule. The SiCSi angle is opened wide, to 123·2(9)°, because of the steric interaction between the two trimethylsilyl groups. The MM3 calculated value is 120·8°, which does not open wide enough compared with the observed data. This is also true for the other bond angles. The individual Si—C bonds lengths were calculated slightly off from experiment. In fact, the actual bond lengths of the two different types of Si—C bond cannot be well determined from the radial distribution curve. A better comparison is the average of Si—C bond lengths, which is well determined. Here the calculations agree well with the experiment. The torsional displacement of the methyl groups is 25(5)° from the staggered form, and MM3 gives only 14·4° (see Supplementary Material).

Tris(trimethylsilyl)methane. The molecular structure of this sterically crowded molecule has been studied using electron diffraction.[41] To overcome the steric interactions among three bulky tertiary groups, the inner Si—C bonds have to stretch out. The average MM3 Si—C length is 0·013 Å longer than the experimental value. However, the calculated SiCSi angles are 1·4° smaller than experiment (see Supplementary Material), so the 1,3 distances are about right.

Rotational barriers. The MM3 values of the rotational barriers for this class of compound generally agree well with experiment, and they are summarized in Table 7. The SiH_3 barrier for axial cyclobutylsilane is calculated to be 1·97 kcal mol^{-1} by MM3, compared with the experimental value of 2·18 kcal mol^{-1}.

Table 8. Experimental and calculated structures of unsaturated silanes[a]

Vinylsilane

	Exp.(MW)[42]	MM3	Δ
Si–C(r_s)	1·853(2)	1·860	0·007
Si–H	1·475(5)	1·483	0·008
C=C	1·347(3)	1·350	0·003
C_1–H	1·095(5)	1·102	0·007
C_2–H	1·097(5)	1·103	0·006
∠SiCC(θ_0)	122·9(3)	123·4	0·5
∠SiCH	—	117·7	—
∠CSiH	—	110·0	—
∠HSiH	108·7(3)	109·0	0·3
ωHCCSi	—	eclipsed	—

	Exp.[42]	MM3	Δ(%)
I_x[b]	2·460	2·477	0·69
I_y	15·928	16·023	0·60
I_z	17·430	17·525	0·55

Allylsilane

	Exp.(ED)[45]	Exp.(MW)[46]	MM3	Δ
Si–C	1·877(4)(r_g)	1·875(4)(r_s)	1·880	0·003
Si–H	1·481(fixed)	1·4854(ave)	1·483	—
$C_1=C_2$	1·327(4)	1·328(7)	1·344	0·017
C_2–C_3	1·502(fixed)	1·492(8)	1·519	—
C—H	1·092(fixed)	1·111(ave)	1·113(C_3)	—
		1·084(ave)	1·102(C_1)	—
		1·102	1·104(C_2)	—
∠SiCC	113·1(4)(θ_a)	111·6(5)	110·5	−2·6
∠CSiH	—	110·61	110·6	—
∠C=C–C	125·6(fixed)	126·7(8)	124·2	—
∠C=C–H	117(2)	121·4[c]	120·9	3·9
∠HC_1H	—	117·1(3)	118·2	—
∠HSiH	108·7(3)	108·7	108·3	−0·4
ωC=C–C–Si	102(1)	106·8(11)	109·5	7·5

	Exp.[46]	MM3	Δ(%)
I_x[d]	32·098	32·286	0·59
I_y	182·261	184·162	1·04
I_z	190·267	191·564	0·68

[a] Structural data for three additional compounds are available in Supplementary Material.

[b] In atomic units. The rotational constants: $A=9599{\cdot}30(45)$, $B=3984{\cdot}78(6)$ and $C=2962{\cdot}59(5)$ MHz for *cis* form; $A=13728{\cdot}17(12)$, $B=3048{\cdot}64(1)$, $C=2825{\cdot}24(1)$ MHz for *skew* form.

[c] Average value of C_2–C_1–H.

[d] In atomic units. The rotational constants: $A=15744{\cdot}615(14)$, $B=2772{\cdot}823(3)$ and $C=2655{\cdot}728(3)$ MHz.

Unsaturated silanes

Vinylsilane. Only microwave data[42] have been reported for vinylsilane. They indicate that the eclipsed (C=C—Si—H) form is the most stable conformation, and the MM3 calculation reproduces this. The observed and calculated structures and moments of inertia are listed in Table 9. The MM3 calculated SiH_3 internal rotational barrier is 1·50 kcal mol^{-1} and 1·51 kcal mol^{-1} from microwave data.[42]

Methylvinylsilane. It was shown by experiment that two conformers coexisted, *cis* and *skew* with respect to C=C—Si—C torsion angle, in the gaseous and liquid states, while only the former persisted in the solid state.[43] In the liquid state, the *cis* form is more stable by 0·66 ± 0·05 kcal mol^{-1} (ΔH).[43] The MM3 calculated energy difference is 0·51 kcal mol^{-1}, with the *cis* conformation being lower. The molecular structure of methylvinylsilane has been determined by microwave spectroscopy.[44] The moments of inertia for the *cis* and skew forms could not be well fit at the same time by MM3. This problem can probably be overcome by including a torsion–bend interaction. The observed data and calculated results are summarized in the Supplementary Material.

Allylsilane. This molecule has been studied by the electron diffraction method.[45] It was found that the conformer in which the hydrogen (not silicon) eclipsed the C=C bond was the most stable one. The MM3 calculation agrees with the experimental results. The SiCC angle was determined to be 113·1(4)° and 111·6(5)° by electron diffraction and microwave spectroscopy,[46] respectively. Our MM3 value appears too small by 2·5°, compared with the electron diffraction data. A similar bond angle in cyclopentadienylsilane was measured to be small, only 106·6(6)°.[47] A still smaller SiCC angle for the MM3 structure would give a better fit to the experimental moments of inertia. Therefore, we decide to accept this discrepancy for allylsilane.

Tetravinylsilane. The structural parameters of tetravinylsilane have been determined in the vapor phase using the electron diffraction method.[48] The conformation with S_4 symmetry gave the best fit with the experimental radial distribution function, which agrees with the MM3 results. The C=C—Si—C torsional angles are 17·5(6)° from the eclipsed conformation. The MM3 calculation shows that these dihedral angles, similar to the corresponding angle in methylvinylsilane, are only 1·8° away from the eclipsed form (see Supplementary Material).

Table 9. Experimental and calculated rotational barriers of unsaturated silanes

Compound		Exp.	MM3	Δ
Vinylsilane	SiH_3 Barrier	1·51[42]	1·47	− 0·04
Methylvinylsilane	ΔE^a	0·66(5)[43]	0·51	− 0·15
	CH_3 Barrier	1·866(39)[44](*cis*)	1·99	0·12
		1·698(22)[44](*skew*)	1·52	− 0·18
Allylsilane	SiH_3 Barrier	2·117(100)[46]	2·12	0·00

[a] Energy difference of *cis* and *skew* forms.

1-Methyl-1-silabicyclo[2.2.2]octa-2,5,7-triene. This structure was determined by electron diffraction.[49] The molecule was assumed to have C_3 symmetry, and this was found with the MM3 calculations. Several assumptions were made in the experimental work to reduce the number of parameters. The symmetry of the molecule was assumed to be C_3, all C—H bond lengths were assumed to be equal, etc. This molecule was found to exhibit a great deal of angular distortion at the silicon bridgehead. The angles at the silicon bridgehead [C=C—Si 109·9(5)°, C_9SiC_2 118·7(2)°, C_2SiC_6 98·8(3)°] are unusually distorted compared with typical sp^3 and sp^2 angles. The MM3 calculation gives fairly good results (see Supplementary Material).

The rotational barriers of unsaturated silanes from calculations and experiment are summarized in Table 9.

Cyclic silanes

Cyclopropylsilane. The molecular structure of cyclopropylsilane has been determined by the anlaysis of the rotational spectrum in the region 9·0–35·0 GHz.[50] Since only three rotational constants were obtained, the structure determination could not be completed unless some assumptions concerning the structural parameters were made. The observed data and MM3 results are summarized in Table 10. The internal rotation barrier of the silyl group was measured to be equal to or larger than 1·95 kcal mol^{-1}, and the MM3 value is 1·96 kcal mol^{-1}.

Cyclopropyltrimethylsilane. The electron diffraction method[29] was applied to study this molecule. It was impossible to resolve the individual Si—C bonds from the radial distribution curve. However, the average Si—C bond length was fit well to the experimental value. Usually, the length of the C—C bond of a cyclopropane is about 1·510 Å. The observed average C—C bond length in this molecule was determined to be much longer, 1·538(8) Å. MM3 gives a bond length of 1·521 Å, after the electronegativity effect is included.

Cyclobutylsilane. A gas electron diffraction study[51] of cyclobutylsilane shows a mixture of equatorial and axial conformers. In Table 11, the experimental structural parameters for the equatorial form and the MM3 calculated structures of both conformations are listed. The energy difference between the equatorial and axial forms varies with different methods. The values are 0·19 ± 0.1, 0·54 and 0·1 kcal mol^{-1} from electron diffraction,[52] Raman spectroscopy[53] and *ab initio* calculations,[54] respectively, with the equatorial form always being more stable. The MM3 calculated energy difference is 0·51 kcal mol^{-1}. The moments of inertia of the two conformers were also measured,[55] and the MM3 values agree well with experiment.

Silacyclobutane. The structure of silacyclobutane in the vapor phase has been determined by the electron diffraction method[56] and also by microwave spectroscopy.[57] This molecule is puckered with a dihedral angle of about 30°. MM3 calculated structures are in good agreement with the experimental data. The inversion barrier of silacyclobutane is 1·26 and 1·13 kcal mol^{-1} from experiment[58] and MM3, respectively.

4-Silaspiro[3.3]heptane. An electron diffraction[47] investigation of the highly strained 4-silaspiro[3.3]heptane molecule has been reported. Several assumptions were made to reduce the number of parameters to be determined. The molecular structure is calculated in good agreement with experiment (see Supplementary Material).

5-Silycyclopentadiene. The molecular structure of gaseous silylcyclopentadiene has been determined by electron diffraction.[59] It was found that the ring is almost flat, similar to the planar unsubstituted cyclopentadiene ring. The external SiCC angle is calculated too large by 2·7°. The MM3 calculation gives a good structure for cyclopentadiene, but the individual C—C bond lengths from this ED study agree poorly with the MM3 values. The RD curve showed only one peak, so it is impossible to determine accurately the individual bond lengths, while the average bond length should be reliable, 1·445 Å (r_g) compared with the MM3 value of 1·448 Å (r_g). If the bond lengths were determined incorrectly, the SiCC angle would also be wrong. Furthermore, the same angle was calculated close to the experimental value for the trimethylsilyl derivative. We believe that most of the errors come from experiment rather than from MM3 (see Supplementary Material).

Table 10. Experimental and calculated structures of cyclic silanes[a]

Cyclopropylsilane

	Exp.(MW)[50]	MM3	Δ
Si–C(r_0)	1·853(assumed)	1·852	—
Si–H	1·475(assumed)	1·483	—
C_1–C_2	1·520(10)	1·523	0·003
C_2–C_3	1·508(10)	1·519	0·011
∠CSiH	110·2(assumed)	110·3	—
∠CCH	117·5(assumed)	117·4	—
∠SiCH	114·0(assumed)	114·0	—
∠$C_2C_1C_3$	—	59·8	—
∠$C_1C_2C_3$	—	60·2	—
∠C_2C_1Si	—	119·6	—
ϕ^b	124·2(10)	124·4	0·2

	Exp.[50]	MM3	Δ(%)
I_x^c	36·108	36·386	0·77
I_y	140·723	141·174	0·32
I_z	150·375	151·101	0·48

Cyclopropyltrimethylsilane

	Exp.(ED)[51]	MM3	Δ
Si–C(r_g)$_{ave}$	1·874(4)	1·872	− 0·002
C–C_{ave}	1·535(8)	1·521	− 0·014
∠$CSiC^d$	108·7(13)	108·8	0·1
∠CCSi	—	110·1	—
ϕ^e	54·2(20)	55·4	1·2

Cyclobutylsilane

	Exp.(ED)[52]	MM3	Δ
Si–C(r_g)	1·875	1·878(eq)	0·003
		1·900(ax)	—
Si–H	1·498(6)	1·483(eq)	− 0·015
		1·483(ax)	—
C_1–C_2	1·575(4)	1·569(eq)	− 0·006
		1·573(ax)	—
C_2–C_3	1·559(4)	1·564(eq)	0·005
		1·563(ax)	
C–C_{ave}	1·567	1·566(eq)	− 0·001
		1·568(ax)	—
C–H	1·128(8)	1·113(eq)	− 0·015
		1·112(ax)	—
∠HSiH(θ_a)	110·9(20)	108·3(eq)	− 2·6
		108·3(ax)	—
∠CCSi	—	117·8(eq)	—
		115·0(ax)	—
∠CCC_{ave}	88·5(8)	87·2(eq)	− 1·3
		87·6(ax)	—
∠HCH	114·0(22)	112·3(eq)	− 1·7
		111·9(ax)	—
ϕ^f	132·0(31)	130·0(eq)	− 2·0
	123·6(27)	125·6(ax)	2·0
ϕ^g	31·8(30)	35·8(eq)	4·0
	− 23·3(41)	32·9(ax)	9·6

	Exp.[55]	MM3	Δ (%)
I_x	9·350(eq)	9·374	0·27
	11·344(ax)	11·580	2·08
I_y	35·064(eq)	35·234	0·48
	31·312(ax)	31·838	1·68
I_z	39·980(eq)	40·020	0·10
	34·343(ax)	34·415	0·21

Silacyclobutane

	Exp.(ED)[56]	MM3	Δ
Si–C(r_g)	1·899(10)	1·892	− 0·003
Si–H	1·487(30)	1·479	− 0·008
C–C	1·587(10)	1·586	− 0·001
C–H	1·13(2)	1·112	− 0·018
∠CsiC	80 (2)	79·1	− 0·9
∠SiCC	86 (2)	86·4	0·4
∠CCC	100·4(10)	99·2	− 1·2
∠HCH	110 (assumed)	112·0	—
∠HSiH	111·0(assumed)	117·1	—
ωSiCCC	—	24·4	—
ϕ^h	30(5)	32·3	2·3

	Exp.[57]	MM3	Δ(%)
I_x	9·528	9·685	1·65
I_y	13·357	13·529	1·29
I_z	19·800	19·838	0·19

Silacyclopentane

	Exp. (ED + MW)[60]	ED[60]	MM3	Δ
Si–C_2(r_g)	1·892(2)	1·893(2)	1·893(C_2 sym.)	0·001
			1·878(C_s sym.)	—
C_2–C_3	1·535(5)	—	1·549	0·014
C_3–C_4	1·580(5)		1·544	− 0·036
C–C_{ave}	1·550(2)	1·549(3)	1·547	− 0·003
Si–H	1·497(8)	1·496(22)	1·479(C_2 sym.)	− 0·018
			1·478(C_s sym.)	—
C–H_{ave}	1·112(6)	1·118(5)	1·113	0·001
∠CSiH	113·2(3)	115·3(30)	112·5	− 0·7
∠CSiC	96·3(3)	96·0(3)	95·8	− 0·5
∠SiCC	103·6(3)	103·7(3)	103·5	− 0·1
∠CCC	108·4(7)	108·7(6)	108·2	− 0·2
∠HSiH	112·3(29)	100·1(106)	110·2	− 2·0
ωC_3C_4	49·7(14)	48·8(19)	50·7	1·0
ωSiC_2	13·3(4)	12·8(5)	13·3	0·0
ωC_2C_3	36·1(10)	35·7(14)	37·2	1·1

	Exp.[63]	MM3	Δ(%)
I_x	92·334(2)	92·834	0·54
I_y	122·160(1)	123·037	0·72
I_z	189·882(1)	190·791	0·48

Table 10. Continued

1-Silabicyclo[2.2.1]heptane

	Exp.(MW)[69]	MM3	Δ
Si–C_2(r_0)	1·868(assumed)	1·883	—
Si–C_7	1·9481(50)	1·870	− 0·078
C_2–C_3	1·5527(assumed)	1·569	—
C_3–C_4	1·5362(assumed)	1·564	—
C_4–C_7	1·5579(assumed)	1·551	—
Si–H	1·489(assumed)	1·471	—
∠C_2SiC_6	104·1(5)	102·9	− 1·2
∠SiC_2C_3	102·8(5)	100·0	− 2·8
∠$C_2C_3C_4$	106·5(assumed)	110·2	—
∠$C_3C_4C_5$	110·0(assumed)	111·1	—
∠$HSIC_7$	109·4(assumed)	120·7	—

	Exp.[49]	MM3	Δ(%)
I_x[i]	184·123	183·969	− 0·08
I_y	189·847	191·294	0·76
I_z	235·498	237·135	0·70

Silacyclohexane

	Exp.(ED)[60]	MM3	Δ
Si–C(r_g)	1·885(3)	1·875	− 0·010
C–C_{ave}	1·550(3)	1·545 1·546(next to Si) 1·545(others)	− 0·005
Si–H	1·465(22)	1·480	0·015
C–H	1·115(5)	1·114	− 0·001
∠SiCC(θ_α)	110·6(6)	110·4	− 0·2
∠CSiC	104·2(14)	105·0	0·8
∠CSiH	112·0(37)	110·8	− 1·2
∠CCC	113·7(11)	113·4(next to Si)	− 0·3
	111·4(19)	114·2	− 0·2
∠SiCH	110·5(8)	109·7	− 0·8
∠HSiH	105·0(139)	108·7	3·7
ωSiC	44·0(42)	45·6	1·6
ωC_1C_2	57·3(20)	55·7(next to Si)	1·4
ωC_2C_3	67·5(20)	65·1	− 2·4
ϕ_1[j]	138·7(41)	137·6	− 1·1
ϕ_2[j]	121·3(15)	122·9	1·6

1-Methyl-1-silaadmantane

	Exp.(ED)[71]	MM3	Δ
Si–C(r_g)$_{ave}$	1·879(3)	1·870	− 0·009
C–C_{ave}	1·548(2)	1·550	0·002
C–H	1·112(6)	1·114	0·002
∠SiCC(θ_α)	107·4(4)	107·2	− 0·2
∠C(Me)SiC	115·2(4)	114·8	− 0·4
∠CSiC	—	103·7	—
∠CCC	—	111·3	—
∠$SiCH_{ave}$	107·2(21)	110·4	3·2
∠CCH_{ave}	112·2(4)	109·3	− 2·9

[a] Structural data for seven additional compounds are available in the Supplementary Material.

[b] Dihedral angle between cyclopropyl ring and Si–C bond.

[c] In atomic unit. The rotational constants: A=13996·4091(35); B=3591·2915(10); C=3360·7719(9)MHz and conversion factor is 505377 amu*Å^2/MHz.

[d] Outside three-membered ring.

[e] Dihedral angle between cyclopropyl ring and Si–C_1 bond.

[f] Dihedral angle between line Si–C_1 and plane $C_2C_1C_4$ plane.

[g] Puckering angle.

[h] Angles inside four-membered ring.

[i] The rotational constants are: A=2744·775(2); B=2662·017(2); and C=2145·994(2) MHz. The conversion factor is 505377 amu*Å^2/MHz.

[j] ϕ_1: The obtuse dihedral flap angle between the plane containing C_5, Si and C_1 and the plane C_1, C_2, C_4 and C_5, ϕ_2: the obtuse dihedral flap angle betweeen the plane containing C_2, C_3 and C_4 and the plane C_1, C_2, C_4 and C_5.

Trimethylcyclopentadienylsilane. The molecular structure of trimethylsilycyclopentadiene has been studied by electron diffraction.[60] The angle between the planes $C_1C_4C_5$ and $C_1C_2C_3C_4$ was reported to be 22 ± 4°, which is far from the MM3 calculated value, 1·2°. The authors claimed that the Si···C_2 non-bonded distance was 3·41 Å. Therefore, the model with a planar cyclopentadienyl fragment turned out to be unacceptable. From the MM3 calculation, we find that the distance between Si and C_2 is 3·680 Å, and some of the distances between methyl groups and C_1 are close to 3·4 Å. It seems that the radial distribution curve contains insufficient information to resolve all of those distances. Hence we think the experimentalists could have misassigned the distance of Si···C_2. If this is the case, $\boldsymbol{\phi}_1$ would be calculated too large and $\boldsymbol{\phi}_2$ would be calculated too small. Furthermore, the two SiCC angles are 105·0° and 114·5° from experiment. There is no apparent reason for such very different SiCC angles for this molecule. The MM3 calculation gives them almost the same value, 109·5°. The average experimental value is very close, 109·8°. Based on the above reasons, we think our values are better than the experimental results (see Supplementary Material).

Silacyclopentane. Silacyclopentane has been studied by a variety of methods. Both electron diffraction[61] and a combined analysis of electron diffraction and microwave spectroscopic data[61] showed that this molecule exists in the twist conformation with C_2 symmetry. Lanne[62] investigated the hindered pseudorotation of silacyclopentane by far-IR spectroscopy, and concluded that this molecule had a twofold pseudorotational potential function with a barrier height of 4·04 kcal mol^{-1}. Later, this was further reinforced by the complete vibrational assignment and far IR study of Durig and co-workers. They calculated that the pseudorotational barrier was 3·9 kcal mol^{-1}.[63] The MM3 calculation gives 3·74 kcal mol^{-1}. The moments of inertia of the title compound have been determined[64] and MM3 fits them fairly well.

Silacyclopenta-3-ene. Electron diffraction data[65–67] have been reported for this molecule. All the electron diffraction studies strongly suggested that the most stable conformer of this compound was puckered, with C_2 symmetry. If this molecule is non-planar, analogous to cyclopentane, the puckering potential would have a double minimum with some inversion barrier. The complete infrared and Raman spectra[68] of silacyclopent-3-ene and its dideuterium and dihalo derivatives were also analyzed and showed that the structures were planar and had C_2 symmetry. Also, from a series of far IR absorptions,[69] it was found that the ring puckering potential function can be interpreted using a pure quartic term. The puckering angle determined by electron diffraction is so small (8·9°) that there is little difference between the puckered form and the planar form with a wide amplitude vibration. Both models would be expected to fit the experimental radial distribution curve equally well. Therefore, we believe that the planar form is more stable. MM3 calculation shows that the planar form is the most stable conformer (see Supplementary Material).

1-Silabicyclo[2.2.1]heptane. The molecular structure of this bicyclic compound was determined by microwave spectroscopy.[70] To reproduce the observed rotational constants, several structural parameters were assumed and only three parameters were determined, which were SiC_7, C_2SiC_6, and SiC_2C_3. With these assumptions, it was found that the Si—C_7 bond was longer than the Si—C_2 bond by 0·08 Å. Our MM3 calculated results disagree with the experiment, with the value being 0·002 Å shorter. Our calculated moments of inertia agree with the experimental values, however.

1-Methyl-1-silabicyclo[2.2.1]heptane. The structure of this molecule has been determined by electron diffraction.[71] The MM3 calculated Si—C and C—C average bond lengths are too short by 0·012 and 0·001 Å, respectively (see Supplementary Material).

Silacyclohexane. Electron diffraction data[61] for silacyclohexane are available. From experiment, it was found that the chair form with C_s symmetry is the most stable conformer. The MM3 calculated Si—C bonds are too short. This bond length is only 1·875 Å in MM3, compared with 1·885(3) Å experimental.

1-Methyl-1-silaadamantane. Again, the average calculated bond distance of the Si—C bonds is too short by 0·009 Å compared with experiment.[72] For the bond angles, the SiCH angles are calculated too large by 3·1°. Since the hydrogen has a nuclear charge of only one, it is difficult to determine these bond angles accurately by electron diffraction.

3-Silabicyclo[3.2.1]octane. The gas-phase electron diffraction technique[73] has been applied to study the molecular structure of this compound. The average Si—C bond length, 1·891(4) Å, is fairly large compared with the MM3 value, 1·881 Å (see Supplementary Material).

endo-3-Methyl-3-silabicyclo[3.2.1]octane. This diastereomer has been selectively obtained, and the molecular structure was determined by electron diffraction.[73] The method of synthesis was expected to give the *endo* isomer, and the electron diffraction confirms the correctness of the structural assignment. The MM3 calculated structure and the observed data are given in Table 11 (see Supplementary Material). Regarding the stability of the molecule, four possible isomers/conformations were taken into consideration in the present work. The methyl group is either in the *endo* or in the *exo* position, and the six-membered ring is either in a chair or a boat form. MM3 found the boat form six-membered ring is highly unfavorable because of the high C—C torsional barriers. These two boat conformations (not discussed by previous authors) were found not to be stable, but rather went over to the chair conformation during every minimization. A calculation carried out with the program EMIN indicated that the *endo* form with chair six-membered ring was more stable than the *exo* form by 0·54 kcal mol^{-1}.[73] However, MM3 shows that the *exo* form is more stable by 0·67 kcal mol^{-1}, which agrees with the earlier study by Ouellette (0·60 kcal mol^{-1}), and also is consistent with the ratio of 3:7 for *endo*:*exo* in the CsF catalyzed equilibration in dimethylformamide solvent observed by Cremer and Blankenship.[73b]

If we look only at the silicon-substituted six-membered ring compounds, it is found that the Si—C bond distances are always too short from the MM3 calculation. The other structural parameters are not fit perfectly, but are approximately within the experimental error.

In Table 11 are given data on rotational and inversion barriers for some of these compounds.

Table 11. Experimental and calculated rotational barrier of Cyclic Silanes

Compound		Exp.	MM3	Δ
Cyclopropylsilane	SiH_3 Barrier	∠1·95[50]	1·96	0·01
Cyclobutylsilane	SiH_3 Barrier	1·87(eq)[53]	2·05	0·18
		2·18(ax)[53]	2·01	− 0·17
	ΔE[a]	0·54[53]	0·51	− 0·03
Silacyclobutane	Inversion Barrier	1·26[58]	1·13	− 0·13
Silacyclopentane	Pseudo-Rotation	3·9[63]	3·84	− 0·06

[a] Energy difference between equatorial and axial forms

Polysilanes

Disilane. This molecule has been studied by various methods,[26,74] including electron diffraction[74] and microwave

Table 12. Experimental and calculated structures of disilane.[a]

	Exp.(ED)[53]	MM3	Δ
Si–Si(r_g)	2·331(3)	2·331(stg)	0·000
Si–H	1·492(3)	1·486(stg)	− 0·006
∠HSiH	108·6(4)	109·0(stg)	0·4
∠SiSiH	110·3(4)	109·9(stg)	− 0·4
	Exp.[54]	MM3	Errors(%)
I_x	1·955	1·959	0·20
I_y	16·224	16·412	1·16
I_z	16·224	16·412	1·16

[a] Structural data for eight additional compounds are available in the Supplementary Material.

specroscopy.[26] The MM3 calculation gives Si—Si and Si—H bond lengths of 2·331 and 1·486 Å, compared with the observed values of 2·331(3) and 1·492(3) Å,[74] respectively. The moments of inertia are also calculated fairly well by MM3 (see Table 12). The SiH_3 internal rotation barrier is 1·22 kcal mol^{-1} experimentally.[74] The MM3 calculated value is 1·19 kcal/mol.

Hexamethyldisilane. The MM3 structure of hexamethyldisilane agrees with the electron diffraction structures.[30] The rotational barrier about the Si—Si bond was 5·7 kcal mol^{-1} according to Yukitoshi *et al.*[75] This valuer was determined by a NMR study of solid hexamethyldisilane. No other direct experimental measurements of the barrier to rotation of the C—Si—Si—C fragment are available. Recently, *ab initio* calculations,[76] using 3–21G(*) geometry optimization and single-point energies derived from MP2/MP3 at the 6–31(*)//3–21G(*) level, were applied to study the conformations of a series of five simple alkyldisilanes: disilane, methyldisilane, 1,2-dimethyldisilane, 1,1,2,2-tetramethyldisilane and hexamethyldisilane. In this study, it was found that the barriers to rotation about the Si—Si bond were about 1 kcal mol^{-1} for all five disilane derivatives. Since the Si—Si and Si—C bond distances are much longer than the corresponding distances in hydrocarbons, the steric effects should be considerably reduced, and typically the barriers are considerably smaller. The NMR study[75] was done in the crystal phase, and the high barrier is probably an artifact resulting from the lattice forces. Therefore, we believe the *ab initio* values should be more reliable. The MM3 calculated rotational barrier is 1·19 kcal mol^{-1} for hexamethyldisilane (see Supplementary Material).

Trisilane. The molecular structure has been reported by electron diffraction[77] in gas the phase. The Si—Si bond lengths were found to be similar to that in disilane. MM3 calculation reproduces the structure fairly well (see Supplementary Material).

Tetrasilane. There are two conformers with respect to the Si—Si—Si—Si torsional angle, *trans* and *gauche*. Electron diffraction and *ab initio* calculations at the MP2/6–31G** level have been applied to study this compound.[77] It was found that the *gauche* form is more stable by 0·05(0·26) kcal mol^{-1} (ΔG). The mole fraction of the *gauche* form is 68(9)%. MM3 gives 58%. The Si—Si bond distances are calculated too short by MM3. In particular, the central bond is 0·010 Å too short (see Supplementary Material).

Octamethyltrisilane. An electron diffraction[78] study was used to determine the molecular structure of octamethyltrisilane. A comparison of the observed and the MM3 calculated structures is given in the Supplementary Material. The MM3 results agree well with experiment. The SiSiSi angle is opened wide, up to 118·0(25)°, to reduce the steric strain caused by the $SiMe_3$ groups. The MM3 calculated value is 1·2° smaller, but within the experimental error (see Supplementary Material).

Tetrakis(trimethylsilyl)silane. The molecular structure of the title molecule was studied by the electron diffraction method.[79] The experimental results indicated that this overcrowded molecule underwent some torsional displacements from T_d symmetry and has unusually long Si—Si bonds, 2·361(3) Å, compared with an average Si—Si bond length of 2·33 Å. The C—C—Si—Si torsional angles are calculated to be distorted by 13·9° from the staggered conformation by MM3. Electron diffraction gave the value of 11 ± 3·6° (see Supplementary Material).

Cyclopentasilane. This molecule has been studied by electron diffraction.[80] The ring was found to be puckered, and both the twist form (C_2 symmetry) and envelope form (C_s symmetry) matched well with the experimental radial distribution curve. MM3 calculations show those two conformations are equally stable. The energy difference between the puckered and planar forms was estimated[80] to be between 1·2 and 2·2 kcal mol^{-1}. The MM3 difference is 1·94 kcal mol^{-1}, smaller than in the case in cyclopentane, which is about 5 kcal mol^{-1}. This result is not surprising because the rather long Si—Si and Si—H bond lengths reduce the non-bonded interactions between hydrogens, and the rotational barriers become smaller. The MM3 structural results are in good agreement with the experimental data (see Supplementary Material).

Cyclohexasilane. For the analogous cyclohexane, the most stable and only conformation at room temperature is the chair form with D_{3d} symmetry. The second stable form is the twist form (D_2) having an energy 5–6 kcal mol^{-1} above the chair form. The boat form (C_{2v}) is 0·6 kcal mol^{-1} above the twist. The molecular structure of cyclohexasilane has been studied by gas-phase electron diffraction at 130 °C.[81] The chair form was found to predominate, but the conformational composition was not determined uniquely. There were three models, all of which fit well to the experimental data (100% chair; 63% chair and 37% twist; 62% chair, 25% twist and 8% boat). The twist and boat forms have energies (ΔE) of 1·80 and 1·99 kcal mol^{-1} higher than the chair form, respectively, according to MM3. Allowing for the extra entropy of the twist form, this corresponds to an equilibrium mixture which is 76% chair and 24% twist. In the entropy calculation, we only take the contributions from symmetry and *d,l* form mixing into account and assume all others are the same for each conformer. For the chair→twist, $\Delta G = 0{\cdot}92$ kcal mol^{-1} ($\Delta H = 1{\cdot}80$ kcal mol^{-1}, $\Delta S = 2{\cdot}18$ eu), and the barrier $\Delta G^{\ddagger}$ is 1·89 kcal mol^{-1} ($\Delta H^{\ddagger}$3·88 kcal mol^{-1}, $\Delta S^{\ddagger}$4.94 eu). The MM3 calculation agrees with the second ED model, except that the Si—Si bond distances are too short by 0·011 Å (see Supplementary Material).

Dodecamethylcyclohexasilane. The x-ray diffraction technique[82] has been used to study this molecule. Table 13 shows the MM3 results and the observed structural parameters. The average Si—C bond lengths at the equatorial and axial positions were measured to be 1·935(6) and 1·913(6) Å, respectively, which are much longer than the normal bond length, 1·88–1·89 Å. The MM3 calculations give much shorter and almost identical bond lengths for both cases. The structures and rotational barriers of polysilanes are given in the Supplementary Material.

Dipole moments

We also examined the dipole moments of a variety of silicon compounds. The MM3 calculations give pretty good results. The MM3 values and the observed data for 14 silanes are given in Table 15. Except for allylsilane and 1-silabicyclo-[2.2.1]heptane, the MM3 calculations agree with experiment to within 0.1 D (see Supplementary Material).

Heats of formation

The heat of formation is a fundamental property of a molecule. MM3 has been fairly successful in calculating the heats of formation of various classes of compounds.[2,3] The standard deviation of a list of 53 hydrocarbons is 0·41 kcal mol^{-1}.[2] The MM3 force field used basically the ‘bond increment’ scheme which has been well described in previous publications.[2,3,92] There are four bond enthalpy parameters, Si—C, Si—Si, Si—H and Si—56 (four-membered ring carbon), and seven structural features, such as SiH_4, ME, TERT, 2-Si, 2CSUB, 3CSUB, 4CSUB and 2Si2C, were chosen for silanes and polysilanes. Because the incomplete combustion and indeterminate nature of the combustion products of silanes and polysilanes, there is some controversy in the literature regarding the heats of formation of these compounds.[85,86] Therefore, the data cited in Pedley’s CATCH table,[87] which appear to have internal consistency, are used here. The values for several compounds have not been included, because we feel there are considerable errors in the observed values. The standard deviation between calculated and experimental heats of formation is 0·47 kcal mol^{-1}, compared with an average experimental error of 3·45 kcal mol^{-1}. We do not believe that the MM3 calculated values are as good as these numbers appear to suggest. The apparently good agreement is due in large part to the large number of adjustable parameters that are required in the calculations. No experimental data were found for the isopropyl group. From our previous experience, the value of this structural feature is between the values for methyl and tertiary groups. Hence values of $-4{\cdot}1766$ and $-3{\cdot}8050$ kcal mol^{-1} were assigned for normal and strainless cases. The input and the results of this calculation and the input and results of strainless calculations are included in the Supplementary Material.

CONCLUSIONS

MM3 calculations on silanes show that these compounds can be treated by MM3 nearly as well as hydrocarbons. Molecular structures can, on the whole, be calculated with an accuracy competitive with experiment. With other than very simple molecules, electron diffraction experiments usually give average bond distances, and not individual values. When the experimental averages are compared with the MM3 averages, usually the results agree well. The individual values do not agree so well, but on the whole this is probably more of an experimental problem than an inaccuracy with MM3.

There is one apparent systematic error in the MM3 calculations of the C—Si bond lengths. The bond lengths are fit to small molecules, and these are usually either in the *anti* conformation, or a mixture of *anti* and *gauche* conformations. In six-membered rings, where the system is constrained to *gauche* conformations, there is a systematic discrepancy of about 0·010 Å in these bond lengths. This suggests that a torsion–stretch interaction may be needed to bring these numbers into agreement, but such was not included in MM3.

Vibrational spectra are reasonably calculated for these compounds by MM3, but not accurately calculated. The major problem stems from the ommission of bend–torsion–bend interactions, which were omitted in the development of the MM3 hydrocarbon force field. The vibrational frequency errors that result here are similar to those found with saturated hydrocarbons. They could presumably be reduced here as they were for hydrocarbons when the MM4 force field was developed.[19, 93]

SUPPLEMENTARY MATERIAL

The package of Supplementary Material referred to in the text (MM3 calculations of 14 spectra, 21 molecular structures, 2 rotational barriers, 16 dipole moments and heats of formation) is available from the authors upon request.

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