

Conformational Analyses of n-Tetrasilane, 1, 2-Dimethyldisilane, 1, 2-Disilylethane, n-Butane, and Related Molecules : Molecular Mechanics Study

Toshio TANAKA*¹ and Kaz-yuki TATSUMI*²

Abstract: Molecular mechanics parameters are presented for obtaining not only reasonable values of the heats of formation but also appropriate molecular structures for the following a series of ten molecules; $\text{SiH}_3\text{-SiH}_2\text{-SiH}_2\text{-SiH}_3$, $\text{CH}_3\text{-SiH}_2\text{-SiH}_2\text{-SiH}_3$, $\text{SiH}_3\text{-CH}_2\text{-SiH}_2\text{-SiH}_3$, $\text{CH}_3\text{-SiH}_2\text{-SiH}_2\text{-CH}_3$, $\text{CH}_3\text{-CH}_2\text{-SiH}_2\text{-SiH}_3$, $\text{CH}_3\text{-SiH}_2\text{-CH}_2\text{-SiH}_3$, $\text{SiH}_3\text{-CH}_2\text{-CH}_2\text{-SiH}_3$, $\text{CH}_3\text{-CH}_2\text{-SiH}_2\text{-CH}_3$, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-SiH}_3$, and $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$. In addition, the rotational potential functions around the Si-Si and the C-C bonds have been determined for $\text{SiH}_3\text{-SiH}_2\text{-SiH}_2\text{-SiH}_3$, $\text{CH}_3\text{-SiH}_2\text{-SiH}_2\text{-CH}_3$, $\text{SiH}_3\text{-CH}_2\text{-CH}_2\text{-SiH}_3$, and $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$.

INTRODUCTION

Molecular mechanics (MM) force fields¹⁾ have been extended to include silanes and organosilicon compounds. There are, however, limited numbers of MM calculations for such compounds in the literatures.²⁻⁴⁾ MM parameters have been determined not only experimentally but also by MM and *ab initio*^{3,5)} calculations. The parameters reported so far, however, are not necessarily fruitful to achieve the MM computation for a series of linear $\text{XH}_3\text{-XH}_2\text{-XH}_2\text{-XH}_3$ type molecules (X stands for all the combinations of silicon and carbon atoms); the parameters for such molecules are fundamentally of importance in MM technique.¹⁾

The present paper is concerned with the conformational analysis for a series of the following compounds;

n-Tetrasilane	(TTS) : $\text{SiH}_3\text{-SiH}_2\text{-SiH}_2\text{-SiH}_3$
Methyltrisilane	(MTS) : $\text{CH}_3\text{-SiH}_2\text{-SiH}_2\text{-SiH}_3$
Silylmethyldisilane	(SMDS) : $\text{SiH}_3\text{-CH}_2\text{-SiH}_2\text{-SiH}_3$
1,2-dimethyldisilane	(DMDS) : $\text{CH}_3\text{-SiH}_2\text{-SiH}_2\text{-CH}_3$
Ethyldisilane	(EDS) : $\text{CH}_3\text{-CH}_2\text{-SiH}_2\text{-SiH}_3$
Methyldisilmethylene	(MDSM) : $\text{CH}_3\text{-SiH}_2\text{-CH}_2\text{-SiH}_3$

*1 Department of Applied Physics and Chemistry, Faculty of Engineering, Fukui Institute of Technology, Gaku-en 3-6-1, Fukui 910.

*2 Department of Chemistry, Faculty of Engineering Science, Osaka University, Machikaneyama-cho, 1-1, Toyonaka, Osaka 560.

1,2-disilylethane	(DSE) : $\text{SiH}_3\text{-CH}_2\text{-CH}_2\text{-SiH}_3$
Ethylmethylsilane	(EMS) : $\text{CH}_3\text{-CH}_2\text{-SiH}_2\text{-CH}_3$
<u>n</u> -Propylsilane	(PS) : $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-SiH}_3$
<u>n</u> -Butane	(BT) : $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$

as well as a comparison of the rotational potential functions among TTS, DMDS, DSE, and BT.

COMPUTATION

MM computation has been conducted on the MM2PP program kindly supplied from Toray System Center Co. Ltd. The force field parameters adopted in the MM2PP are the same as those reported by Allinger,⁷⁾ except for the following van der Waals (vdw) and torsional constants; 4.000 and 2.852 Å for the sums of vdw radii C|C and H|H, and 0.60, 0.27, and 0.35 kcal/mol for V_3 of the C-C-C-C, C-C-C-H, and H-C-C-H linkages, respectively.

There has been no report on the torsional parameters of C-Si-Si-H and Si-C-Si-Si bonds required to perform MM calculations for a part of the present molecules. Thus, the former parameter has been taken as 0.385 kcal/mol, which is an average of the torsional constants of C-Si-Si-C (0.633 kcal/mol) and H-Si-Si-H (0.136 kcal/mol) bonds,⁴⁾ while the latter has been assumed as 0.167 kcal/mol, which is the same value as those of Si-C-C-Si, C-C-Si-C, Si-C-Si-C, and Si-C-Si-H bonds.⁴⁾ Other force field parameters associated with silicon atom were taken from the paper reported by Frierson et al.,⁴⁾ except for the H-Si-H angle of type 1 (-SiR₂-, R≠H), which has been assumed to be the same as that of type 2 (-SiHR-, 108.7°), because the conformational analysis by adopting the angle of type 1 (104.5°) or close values such as 106.6° (average of types 1 and 2), without any change of other parameters, afforded unusual structures as well as abnormal values of the heat of formation for MTS and DMDS.⁶⁾

By using such force field parameters involving newly proposed and revised those were performed the analyses for gauche and trans conformers of a series of ten compounds from TTS to BT for determining their optimized structures and heats of formation. The validity of the parameters used in the present work was examined, though a part of those, by conducting the conformational analyses for some silanes and alkanes, whose heats of formation are well known. The comparison of the heats of formation obtained by conformational analyses for these molecules with their observed values is shown in Table 1, which indicates that there is excellent agreement between the calculated and observed values, except for ethane. Thus, the force field parameters used here may be pertinent.

Table 1. Calculated and observed heats of formation.

Molecule	$\Delta H_f(\text{calcd})^{\text{a)}}$	$\Delta H_f(\text{obsd, gas})^{\text{a)}}$	$\Delta \Delta^{\text{b)}}$
SiH_4	8.92	8.2 ^{c)}	+0.7
Si_2H_6	18.57	19.2 ^{c)}	-0.6
Si_3H_8	27.93	28.9 ^{c)}	-1.0
C_2H_6	-18.52	-20.24 ^{d)}	+1.72
C_3H_8	-24.30	-24.82 ^{d)}	+0.52

a) Unit in kcal/mol. b) $\Delta \Delta = \Delta H_f(\text{calcd}) - \Delta H_f(\text{obsd})$.

c) J. A. Dean ed., "Lange's Handbook of Chemistry," 13th ed., McGraw Hill (1985). d) Ref. 8.

Results and Discussion

Conformational Analysis.

Table 2 shows the heats of formation and the relevant structural features obtained by analyses for gauche and trans conformers of the present molecules. Unfortunately, there is no reliable datum on the heat of formation determined experimentally for comparing with the calculated values, except for BT, whose calculated value agrees well with the experimental value, -30.15 kcal/mol.⁸⁾

Of the present molecules, TTS, MTS, and DMDS are very sensitive to structure parameters to be input in conformational analysis; somewhat inappropriate input data result in abnormal structures and unacceptable heats of formation, as discussed in the Computation part. Thus, the optimized structures and the heats of formation for the gauche and trans conformers of remaining compounds (Table 2) may also be considered as reasonable ones.

It should be noted that the gauche conformers are more stable than the corresponding trans conformers in the seven molecules other than DSE, PS, and BT (Table 2). This may be due to strongly attractive vdw interaction in the gauche conformers of those molecules involving a rather long central Si-Si or Si-C bond; in particular strongly attractive 1,4-vdw energy between Si/Si, Si/C, or C/C may be responsible for the gauche conformer stabilized more than the trans conformer in each molecule, as displayed in Fig. 1a, which shows the Newman projection for TTS as a representative. On the other hand, DSE, PS, and BT with rather short central C-C bonds exhibit strong 1,4-vdw repulsion between Si/Si, Si/C, or C/C, leading to stable trans conformers more than the corresponding gauche ones; the Newman projection for DSE as such an instance is illustrated in Fig. 1b.

Table 2. Calculated heats of formation (ΔH_f , kcal/mol)^{a)} and relevant bond lengths (R in Å)^{b,c)} and valence angles (A in degree).^{c)}

Compound	ΔH_f	RSiSi	RSiC	RCC	ASiSiSi (ASiCC)	ASiSiC (ACSiC)	ASiCSi (ACCC)	ASiSiH	ASiCH	ACSiH	ACCH
TTS gauche	36.92	2.291			112.7			109.0			
trans	37.13	2.283			114.2			108.7			
MTS gauche	9.89	2.307	1.880		111.7	110.8		109.7	108.4	107.6	
trans	10.08	2.303	1.880		111.7	110.8		109.5	108.4	107.7	
SMDS gauche	14.33	2.303	1.884			110.3	114.0	109.4	108.6	110.0	
trans	14.49	2.303	1.884			110.8	114.6	109.5	108.7	110.1	
DMDS gauche	-17.06	2.350	1.878			109.5		112.1	108.4	107.0	
trans	-16.95	2.344	1.878			109.8		111.8	108.4	107.6	
EDS gauche	-0.12	2.316	1.890	1.533	(114.1)	110.6		110.2	108.5	107.9	110.0
trans	-0.02	2.318	1.890	1.533	(113.7)	110.3		110.3	108.6	107.9	110.0
MDSM gauche	-12.78		1.887			(110.2)	114.5		108.5	109.6	
trans	-12.64		1.887			(109.4)	113.9		108.6	109.7	
DSE gauche	0.23		1.889	1.536	(115.5)				108.1	110.5	108.9
trans	-0.08		1.888	1.536	(113.7)				108.1	110.4	109.4
EMS gauche	-27.32		1.892	1.533	(114.0)	(109.6)			109.5	109.2	110.1
trans	-27.25		1.893	1.533	(113.6)	(109.1)			109.6	109.2	110.1
PS gauche	-14.77		1.888	1.535	(115.7)		(113.5)		108.0	110.4	109.5
trans	-15.19		1.887	1.535	(113.8)		(111.8)		108.3	110.4	109.7
BT gauche	-29.26			1.535			(113.6)				109.7
trans	-30.10			1.535			(111.8)				109.9

a) Strainless ΔH_f : TTS, 37.33; MTS, 10.93; SMDS, 15.27; DMDS, -15.47; EDS, 0.19; MDSM, -11.13; DSE, 0.03; EMS, -26.21; PS, -15.04; BT, -30.12 kcal/mol. b) RSiH=1.489 Å for all the compounds except for BT, and RCH=1.113 or 1.114 Å for all the compounds except for TTS. c) The mean of the lengths or the angles when plural the same types of bonds or linkages are involved.

Some time ago, Profeta and his co-workers³⁾ examined the rotational potential functions and structures of DSE, EMS, and PS using ab initio (3-21G*) and MM2 techniques. Both methods yielded virtually identical relative energies and barrier heights for the DSE and EMS, as well as structures in good agreement. In addition, they have pointed out that the C-C bond length of 1.523 Å may be elongated by 0.04 Å (1.563 Å) when it is adjacent to two Si-C bonds.³⁾ The present work, however, yielded the optimized structure involving normal C-C (1.536 Å) and Si-C (1.888-1.889 Å) bond lengths for DSE (Table 2).

The calculated structural feature of EMS, including dipole moments, are in good agreement with the results obtained not only from microwave spectra⁹⁾ but also from ab initio and MM2 calculations reported previously.³⁾ Moreover, our optimized structure for trans PS is in excellent agreement with the structure

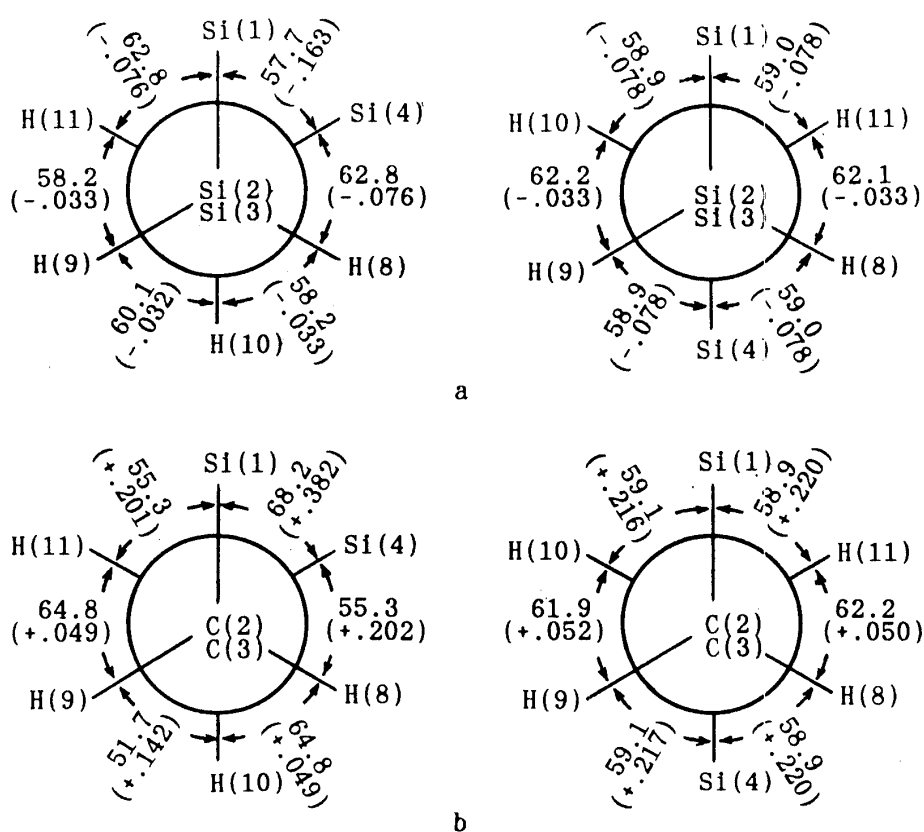


Fig. 1. Newman projections of the gauche and trans conformers of TTS(a) and DSE(b), units: angle in degree and 1,4-vdw energy (in parentheses) in kcal/mol.

Table 3. Structural features of trans PS, units: R in Å, A in degree, and dipole moment in Debye.

Feature	This work	Profeta et al. ³⁾	Microwave ¹⁰⁾
RSiC ₁	1.887	1.875	1.886
RC ₁ C ₂	1.534	1.551	1.528
RC ₂ C ₃	1.536	1.536	1.534
RSiH (mean)	1.489	1.485	1.482
RCH (mean)	1.114	1.115	1.095
ASiC ₁ C ₂	113.8	112.3	113.2
AC ₁ C ₂ C ₃	111.8	111.6	112.2
AHSiH (mean)	108.6	108.5	108.7
AHCH (mean)	108.1	108.1	105.6-108.6
Dipole moment	0.600	0.600	0.811

determined by microwave spectroscopy¹⁰⁾ more than that reported by Profeta et al.,³⁾ as listed in Table 3. The energy difference between gauche and trans conformers of PS (0.42 kcal/mol, Table 2) also agrees with the experimental value (0.60-0.65 kcal/mol).¹¹⁾

Potential Functions of Rotation Around the Si-Si and C-C Bonds.

Variations of the heats of formation attended by the internal rotation around the central Si-Si or C-C bond have been calculated for four representative molecules; TTS, DMDS, DSE, and BT, where as the input data of bond lengths and angles were taken the mean values of those in the optimized gauche and trans conformers. Table 4 and Fig. 2 show the energies for various dihedral angles of the skeletons (15° intervals) relative to the most stable conformers of each molecule; gauche for TTS and DMDS, and trans for DSE and BT.

Table 4. Relative energies of various conformers of TTS, DMDS, DSE, and BT, kcal/mol.

Angle	TTS ^{a)}	DMDS ^{a)}	DSE ^{b)}	BT ^{b)}
0	1.36	2.69	7.50	7.76
15	1.23	2.29	6.59	6.73
30	0.91	1.34	4.52	4.67
45	0.61	0.40	2.33	2.76
60	0.52	0.03	0.87	1.49
75	0.72	0.45	0.69	1.44
90	1.11	1.44	1.61	2.53
105	1.47	2.41	2.73	3.82
120	1.64	2.84	3.23	4.33
135	1.52	2.44	2.78	3.69
150	1.20	1.48	1.67	2.24
165	0.88	0.53	0.56	0.80
180	0.75	0.14	0.11	0.20

a) Relative to the optimized gauche conformer. b) Relative to the optimized trans conformer.

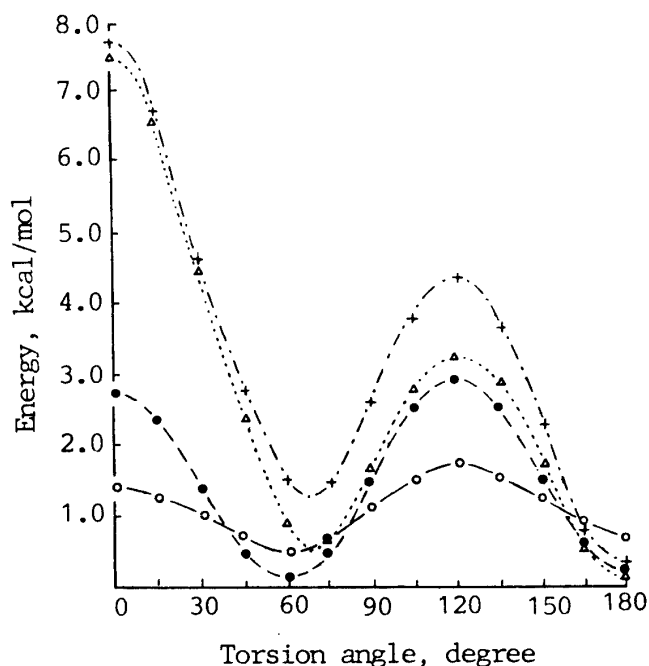


Fig. 2. Torsional Potentials for TTS(—○—), DMDS(---●---), DSE(---▲---), and BT(-·+·-).

As pointed out previously,³⁾ the C-C rotational potential of DSE is very much like BT (see Fig. 2). One may expect, however, the long Si-C bond length of DSE relative to C-C of BT to reduce the repulsive non-bonded interactions in

the eclipsed and gauche conformers. Thus, the rotational potential barrier for DSE is lower than that for BT, particularly in the 60° to 150° region. This is in contrast to the result reported by Profeta et al.,³⁾ who have mentioned that the Si-H bond of DSE longer than the C-H bond of BT may compensate for the reduced repulsion (or increased end-to-end attraction) by interacting with neighboring atoms in the 0-120° region, leading to the rotational barrier of DSE a little higher than that of BT.

Both TTS and DMDS involve the Si-Si bond longer than C-C in the center of their skeletons, resulting in the increased vdw attraction (no repulsion in these molecules), as seen in Table 5, so that the rotational potential barriers around the central Si-Si bond may be lowered more than those around the C-C bond for DSE and BT (Fig. 2). It is to be noted that the barrier of DMDS is higher than that of TTS. This fact arises mainly from large torsional energies in the vicinities of the eclipsed and cis conformers of DMDS, compared with those of the optimized gauche conformer, while the torsional energies in the eclipsed and cis conformers of TTS are not so much in comparison with those in the optimized gauche conformer (see Table 5).

Table 5. Steric energy components for some conformers of DMDS and TTS, kcal/mol.

Component	DMDS			TTS		
	C-Si-Si-C Dihedral angle			Si-Si-Si-Si Dihedral angle		
	0°	57.7° ^{a)}	120°	0°	59.7° ^{a)}	120°
Compression	0.002	0.041	0.002	0.408	0.744	0.408
Bending	0.006	0.225	0.006	0.981	0.636	0.981
Stretch-Bend	-0.003	-0.087	-0.003	-0.986	-1.457	-0.986
1,4-vdw	-1.235	-1.274	-1.289	-1.003	-1.138	-1.090
Other vdw	-0.529	-0.391	-0.278	-0.542	-0.371	-0.181
Torsional	2.717	0.008	2.717	0.925	0.005	0.925
Dipole	0.149	0.110	0.075	0	0	0
Steric (Total)	1.107	-1.368	1.231	-0.216	-1.581	0.058
Dipole moment ^{b)}	1.131	0.981	0.566	0	0	0

a) Angles in the optimized structures. b) Unit in Debye.

CONCLUSION

Torsional constants of the C-Si-Si-H and Si-C-Si-Si bonds as well as a

revised H-Si-H bending constant of the type 1 ($-\text{SiR}_2-$, $\text{R}\neq\text{H}$) have newly been proposed. The MM calculation for a series of ten molecules, thus, indicates that the trans conformers of DSE, PS, and BT are more stable than the corresponding gauche conformers, and *vice versa* in the remaining molecules. This is interpreted as due to strongly attractive vdw energy between Si/Si, Si/C, and C/C in the gauche conformers with rather long central Si-Si or Si-C bonds in the skeletons, in contrast to strong vdw repulsions between Si/Si, Si/C, or C/C in EMS, PS, and BT.

Further, the calculation of rotational potentials of C-C bonds confirms the barrier in DSE being lower than that in BT, which may be due to the long Si-C bond length of DSE relative to C-C of BT to reduce the repulsive non-bonded interactions. On the other hand, the rotational potential barrier around the Si-Si bond of TTS is lower than that of DMDS, owing to large torsional energies of DMDS.

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References and Notes

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