

## DEVELOPMENT OF A MOLECULAR MECHANICS (MM2) FORCE FIELD FOR $\alpha$ -CHLOROSILANES

Soo Gyeong Cho and Frank K. Cartledge\*

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803 USA  
and

Raymond J. Unwalla and Salvatore Profeta, Jr.\*

Department of Scientific Computing, Glaxo Inc., Research Triangle Park, NC 27709 USA

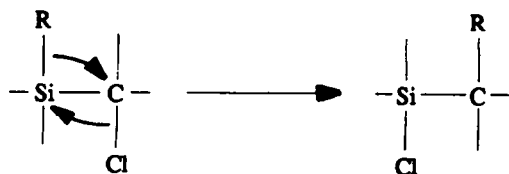
(Received in USA 15 August 1990)

**Abstract:** Molecular mechanics (MM2) parameters for silanes which have a Si-C-Cl fragment have been developed based on available experimental data and *ab initio* molecular orbital (MO) calculations. Molecular properties, mainly rotational barriers and geometries, of  $\alpha$ -chlorosilanes have been studied using our new MM2 parameter set. Changes in the Si-C bond lengths and several bond angles of  $\alpha$ -chlorosilanes due to the additional attachment of polar atom(s) have been investigated utilizing *ab initio* calculations. An electronegativity correction to both bond lengths and angles helps MM2 to reproduce results from *ab initio* calculations. The new force field has been applied to the conformational analysis of 1-(chloromethyl)-1,2-dimethylsilacyclopentane, a model used in our studies of rearrangements of  $\alpha$ -halosilanes.

### 1. INTRODUCTION

Rearrangement reactions of  $\alpha$ -chlorosilanes to chlorosilanes, which include the double migration of a Cl atom from C $_{\alpha}$  to Si, and an R group from Si to C $_{\alpha}$  (see Scheme I), have substantial synthetic potential. However, this reaction could be exploited further if we had a detailed understanding of the reaction mechanism.

Scheme I



Investigators have suggested that this rearrangement involves (1) simultaneous double migrations<sup>1</sup> or (2) stepwise migrations involving either cations alone<sup>2</sup> or a penta-coordinated "inverse ylide" (R<sup>1</sup>R<sup>2</sup>R<sup>3</sup>ClSi<sup>-</sup>-C<sup>+</sup>R<sup>4</sup>R<sup>5</sup>).<sup>3</sup> Each suggested mechanism has been supported by experimental evidence. Furthermore,

using different substrates and reaction conditions makes it difficult to generalize the rearrangement mechanism. Thus, substantial debate remains regarding a generally accepted mechanism of this reaction.

We have been interested in applying theoretical tools to investigate these rearrangement

reactions. Our preliminary semi-empirical (MNDO<sup>4</sup> and AM1<sup>5</sup>) calculations on a model compound, (chloromethyl)methylsilane, have shown that steric hindrance in the transition state may play an important role in determining the activation energy.<sup>6</sup> Recent success in force field modelling of transition states<sup>7</sup> has led toward an enhanced understanding of preferential paths and stereoelectronic effects in reaction mechanisms. Thus, we have developed new MM2<sup>8</sup> parameters for  $\alpha$ -chlorosilanes and chlorosilanes<sup>9</sup> so that we can study reactions in these systems, including the rearrangement mentioned above.

## 2. RESULTS AND DISCUSSION

### 2-1. Computational Details

Ab initio calculations have been carried out using the GAUSSIAN-82 and -86 programs.<sup>10</sup> Geometry optimizations were performed at the Hartree-Fock level using the 3-21G(\*) basis set<sup>11</sup> on each conformer. To examine the change of Si-C bond lengths due to the attachment of Cl atom(s) to C<sub>w</sub>, the geometries of some model compounds have been fully optimized with the basis sets, namely 6-31G(\*),<sup>12</sup> 6-31G(\*\*)<sup>12</sup> and MP2/6-31G(\*).<sup>13a</sup> Relative energies have been evaluated using single-point calculations with the 6-31G(\*) basis set, including correlation energy corrections via 2nd- and 3rd-order Møller-Plesset perturbation theory.<sup>13</sup>

Molecular mechanics calculations have been carried out using the MM2 program.<sup>8</sup> Parameters for alkylsilanes are taken from the MM2-85 parameter set distributed by Dr. Allinger,<sup>14</sup> except the C-C-C-Si torsional parameter,<sup>15</sup> and those for chlorosilanes are from our previous work.<sup>9</sup> The force field developed for  $\alpha$ -chlorosilanes is summarized in Table I.

Table I. Force-Field Parameters<sup>a</sup> Developed for  $\alpha$ -Chlorosilanes.

Bending				
Angle	Type <sup>b</sup>	K <sub>b</sub> <sup>c</sup>	K <sub>b</sub> <sup>c</sup> (lit.values)	$\theta_0$
Si-C-Cl	All	0.15	0.03-0.10 <sup>d</sup>	106.00
Torsional Parameters				
Dihedral angle	V <sub>1</sub>	V <sub>2</sub>	V <sub>3</sub>	
C-Si-C-Cl	-0.980	0.350	0.340	
H-Si-C-Cl	0.000	0.000	0.420	
Cl-Si-C-Cl	0.833	0.070	0.150	
Cl-Si-C-H	0.000	0.000	0.140	

<sup>a</sup> For "electronegativity correction" parameters, see Table IV. <sup>b</sup> Type refers to the substitution at the central C atom: 1, X-CR<sub>2</sub>-Y; 2, X-CHR-Y; 3, X-CH<sub>2</sub>-Y. <sup>c</sup> Values in mdyne Å/rad<sup>2</sup>. <sup>d</sup> References, (a) M. Hayaishi, K. Ohno, and H. Murata, *Bull. Chem. Soc. Jpn.* **46**, 797 (1973). (b) K. Ohno, K. Suehiro, H. Murata, *J. Mol. Struct.* **98**, 251 (1983).

Table II. Relative Conformational Energies<sup>a</sup> and Rotational Barriers<sup>a</sup> of  $\alpha$ -Chlorosilanes.

Compound/ conformation <sup>b</sup>	3-21G(*) //3-21G(*)	6-31G(*) //3-21G(*)	MP2/6-31G(*) //3-21G(*)	MP3/6-31G(*) //3-21G(*)	MM2	Experimental values
$\text{ClCH}_2\text{SiH}_3$	2.37	2.08	2.24	2.17	2.56	2.55 <sup>d</sup> , 2.65 <sup>e</sup>
$\text{Cl}_2\text{CHSiH}_3$	3.26	2.74	2.93	2.84	3.40	3.69 <sup>f</sup>
$\text{Cl}_3\text{SiH}_3$	4.63	4.02	4.22	4.13	4.48	
$\text{ClCH}_2\text{SiH}_2\text{Me}$						
g - g	2.48	2.18	2.33	2.19	2.47	
g - a	2.70	2.35	2.63	2.55	2.88	
gauche	0.0	0.0	0.0	0.0	0.0	0.0
anti	0.49	0.36	0.48	0.48	0.32	0.27 <sup>g</sup>
$\text{ClCH}_2\text{SiHMe}_2$						
g - a	2.92	2.43	2.61	2.56	2.80	
a - a	3.00	2.50	2.94	2.85	3.20	
gauche	0.56	0.31	0.43	0.42	0.32	0.34 <sup>f</sup>
anti	0.0	0.0	0.0	0.0	0.0	0.0
$\text{ClCH}_2\text{SiMe}_3$	2.78	2.35	2.61	2.55	2.81	
$\text{ClCH}_2\text{SiH}_2\text{Cl}$						
g - g	4.96	4.76	4.40	4.38	4.29	
g - a	2.68	2.52	2.63	2.54	2.59	
gauche	1.30	1.39	1.16	1.15	1.07	
anti	0.0	0.0	0.0	0.0	0.0	
$\text{Cl}_2\text{CHSiH}_2\text{Cl}$						
g - g	2.56	2.18	2.59	2.47	2.48	
g - a	4.67	4.23	4.15	4.12	4.05	
gauche	0.0	0.0	0.0	0.0	0.0	
anti	1.29	1.36	1.23	1.23	1.03	
$\text{Cl}_3\text{SiH}_2\text{Cl}$	5.21	4.69	4.82	4.78	4.21	
$\text{ClCH}_2\text{SiCl}_3$	3.09	2.84	3.04	2.96	2.28	2.46 <sup>h</sup>
$\text{Cl}_2\text{CHSiCl}_3$	4.82	4.26	4.40	4.34	3.06	
$\text{Cl}_3\text{SiCl}_3$	8.24	7.61	7.66	7.64	4.81	4.3 <sup>i</sup>

<sup>a</sup> Values are relative to the lowest conformational energy (in kcal/mol). <sup>b</sup> The gauche/anti conformations are defined by the following dihedral angles in each compound; Cl-C-Si-C in  $\text{ClCH}_2\text{SiH}_2\text{Me}$ , Cl-C-Si-H in  $\text{ClCH}_2\text{SiHMe}_2$ , Cl-C-Si-Cl in  $\text{ClCH}_2\text{SiH}_2\text{Cl}$ , and H-C-Si-Cl in  $\text{Cl}_2\text{CHSiH}_2\text{Cl}$ . <sup>c</sup> From microwave (MW) in solid, reference V.N. Kostryukov and D.O. Gumbatov, *Zh. Fiz. Khim.* 39, 2099 (1965). <sup>d</sup> From MW, reference 20. <sup>e</sup> From IR-gas, reference J.R. Durig and C.W. Hawley, *J. Chem. Phys.* 59, 1 (1973). <sup>f</sup> From IR-solid, *ibid.* <sup>g</sup> From NMR, reference R. Carleer and M.J.O. Anteunis, *Org. Magn. Reson.* 13, 253 (1980). <sup>h</sup> From electron diffraction (ED), reference 21. <sup>i</sup> From ED, reference 16.

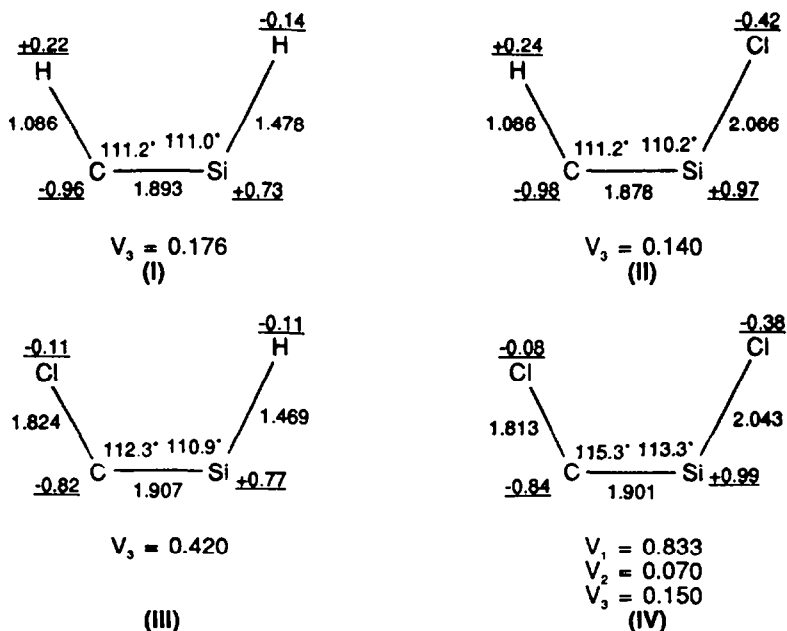
## 2-2. Rotational Barriers and Relative Conformational Energies

Rotational barriers and relative conformational energies of  $\alpha$ -chlorosilanes are summarized in Table II. For the development of the Cl-C-Si-H torsional parameter, the 3-21G(\*)-calculated rotational barriers of  $\text{ClCH}_2\text{SiH}_3$  and  $\text{Cl}_2\text{CHSiH}_3$  are in excellent agreement with those from experiment. Hence, the MM2 torsional parameter was fit easily to both experimental and 3-21G(\*) calculational results. The barriers obtained by MP3 single point calculations using the 6-31G(\*) basis set (uncorrected for zero-point energies) are lower than the experimental ones by 0.4-0.8 kcal/mol. Except for the gauche-anti relative energy in  $\text{ClCH}_2\text{SiH}_2\text{Me}$  and  $\text{ClCH}_2\text{SiHMe}_2$ , experimental values of rotational barriers for

$\alpha$ -chlorosilanes having a Cl-C-Si-C moiety have not been reported. Therefore, the  $V_3$  value of the Cl-C-Si-C parameter was adjusted to reproduce ab initio calculated barriers. The Cl-C-Si-Cl parameter also was developed by using ab initio and experimental values. However, the calculated rotational barriers in  $\text{Cl}_2\text{CSiCl}_2$  diverge substantially from that from experiment.<sup>16</sup> A more detailed analysis of this molecule and related systems is forthcoming.<sup>17</sup>

The change in the rotational barrier heights due to various Cl substitutions at Si and/or C $_{\alpha}$  positions can be derived from the data in Table II. We have explored the origins of the rotational barriers and relative conformational energies in simple butane-like building blocks of chlorosilanes and  $\alpha$ -chlorosilanes by evaluating the steric energies obtained from the MM2 method.<sup>18</sup> Although this technique does not provide an exact physical interpretation,<sup>19</sup> it is meaningful in the context of the MM2 calculations and, moreover, is simple. We have found that torsional energy terms in silicon compounds can account for ca. 80-90% of the rotational barriers. Hence, we need to fit the  $V_n$  terms accurately in torsional potentials. At the same time, it is relatively easy to explain the conformational preferences of butane-like chlorosilanes and  $\alpha$ -chlorosilanes from the components of the derived torsional potentials. Successive Cl substitution for H at Si in methylsilane doesn't change the height of the rotational barriers (1.68 kcal/mol in  $\text{MeSiH}_3$  to 1.73 kcal/mol in  $\text{MeSiCl}_2$ ).<sup>9</sup>

Figure 1. Geometric parameters and partial charges of torsional frames in  $\text{ClCH}_2\text{SiH}_3$ ,  $\text{H}_3\text{CSiH}_2\text{Cl}$ ,  $\text{H}_2\text{CSiH}_2\text{Cl}$ , and  $\text{ClH}_2\text{CSiH}_2\text{Cl}$  (All values are taken from the eclipsed conformations calculated by ab initio 3-21G(\*); the values underlined are partial charges from Mulliken population analysis).



An examination of the structural and charge features of the two torsional fragments, H-C-Si-H and H-C-Si-Cl, in Figure 1 may provide clues about the similarity of the barriers:

(1) In I and II, charge distributions are roughly the same; attractive interactions dominate.

(2) In butane-like chlorosilanes (II), the low  $V_3$  (0.14) value, which suggests a minimal steric crowding, can be understood primarily in terms of the longer Si-Cl bond length.

In contrast to Cl substitution at Si, Cl substitution at  $C_\alpha$  (III, IV) raises the rotational barriers by ca. 1.0 kcal/mol for each Cl. Perhaps this can be explained by comparing the electrostatic interactions of Cl-C-Si-H (III) and Cl-C-Si-Cl (IV; repulsive dominant) to H-C-Si-H (I; attractive dominant), which will raise the conformational energies in the eclipsed forms of  $\alpha$ -chlorosilanes. Also note the longer C-Si bond lengths in III and IV and that the rotational barrier of  $ClH_2CSiCl_3$  is nearly the same as those of  $ClH_2CSiH_3$ .

### 2-3. Geometries: General

In this section we have summarized the relevant experimental data and given an analysis of the ab initio data used to evaluate which MM2 parameters best reproduce the available structural data. Geometric parameters of only three  $\alpha$ -chlorosilanes, e.g.  $ClCH_2SiH_3$ ,<sup>20</sup>  $Cl_2SiCH_2Cl$ ,<sup>21</sup> and  $(ClCH_2)_2SiMe_2$ ,<sup>22</sup> have been examined by experiment. Thus, it was necessary to supplement the data by ab initio calculations to derive a reliable force field. The 3-21G(\*) basis set gave reliable results in our previous work with chlorosilanes.<sup>9</sup> Furthermore, to use larger basis sets than 3-21G(\*) is unpractical due to the number of basis functions in  $\alpha$ -chlorosilanes which contain multiple 3rd row elements. Thus, it is necessary to compromise between accuracy and computational resources. However, we did perform higher level calculations using larger basis sets and including electron correlations on simple key compounds. When using experimental data one often deals with a paucity of values in the desired series, and substantial variations of the values from different experimental methods. To handle properly the "electronegativity corrections"<sup>23</sup> to the MM2 force field one needs values from an appropriate series of compounds, and such data are rarely available experimentally. We feel that it is reasonable to utilize ab initio calculated data to derive trends in relative values, although there may be intrinsic systematic errors in some geometric parameters.

The structures of simple systems such as  $CH_3SiH_3$ ,<sup>24</sup>  $CH_3SiH_2Cl$ ,<sup>25</sup> and  $CHCl_2SiH_3$ <sup>20</sup> (experimental geometries reported from MW) are shown in Table III. The ab initio calculated geometries on these three model compounds at various calculational levels, e.g. HF/3-21G(\*), HF/6-31G(\*), MP2/6-31G(\*), and HF/6-31G(\*\*) levels, are very similar. The calculated geometries are in good agreement with the observed values. We<sup>9,15,18,26</sup> and others<sup>27</sup> have found that the 3-21G(\*) basis set yields results which are useful as reference values for MM2 parameter development. MM2 geometries for seventeen  $\alpha$ -chlorosilanes are summarized in Appendix I,<sup>32</sup> along with the available experimental data and 3-21G(\*) results.

It is worthwhile to note the following points from the ab initio 3-21G(\*) geometries.

(1) Ab initio calculations usually give bond lengths in good agreement with experiment, the overestimation of Si-Cl bonds by ca. 0.03 Å notwithstanding.

(2) The 3-21G(\*) geometries are similar to those at MP2/6-31G(\*). The coincidence of the 3-21G(\*) and MP2/6-31G(\*) geometries and rotational barriers may arise from a cancellation of errors implicit in the methods.

Table III. Geometries<sup>a</sup> of CH<sub>3</sub>SiH<sub>3</sub>, CH<sub>3</sub>SiHCl<sub>2</sub>, and ClCH<sub>2</sub>SiH<sub>3</sub>, Calculated at the 3-21G(\*), 6-31(\*), 6-31G(\*\*), and MP2/6-31G(\*) Levels (Comparison with the Experimental Data).

Compounds	Experimental data	3-21G(*)//3-21G(*)	6-31G(*)//6-31G(*)	MP2/6-31G(*)//MP2/6-31G(*)	6-31G(**)//6-31G(**)
CH <sub>3</sub> SiH <sub>3</sub> <sup>b</sup>					
Si-C	1.8686(2)	1.884	1.888	1.881	1.887
Si-H	1.4832(4)	1.478	1.478	1.487	1.479
C-H	1.0957(5)	1.087	1.086	1.093	1.086
∠Si-C-H	110.88(3)	111.04	111.04	111.02	111.00
∠C-Si-H	110.50(3)	110.65	110.60	110.61	110.56
∠H-Si-H	108.26	108.32	108.31	108.36	108.36
∠H-C-H	107.86	107.79	107.88	107.90	107.90
CH <sub>3</sub> SiHCl <sub>2</sub>					
Si-Cl	2.040 <sup>c</sup>	2.048	2.059	2.052	2.060
Si-C	1.850 <sup>d</sup>	1.857	1.864	1.856	1.863
Si-H	1.467 <sup>d</sup>	1.461	1.462	1.477	1.463
C-H	1.093 <sup>d</sup>	1.087	1.086	1.093	1.086
∠C-Si-Cl	109.8 <sup>c</sup>	109.06	109.76	109.54	109.73
∠C-Si-H	110.0 <sup>d</sup>	113.53	113.66	113.50	113.80
∠Si-C-H	109.5 <sup>d</sup>	110.82	110.68	110.56	110.56
∠Cl-Si-Cl	108.8 <sup>c</sup>	109.06	108.92	109.21	108.87
∠Cl-Si-H	107.41	107.31	107.48	107.30	107.29
∠H-C-H	108.09	108.24	108.36	108.36	108.36
ClCH <sub>2</sub> SiH <sub>3</sub> <sup>e</sup>					
Si-C	1.889(10)	1.894	1.902	1.894	1.901
Si-H	1.477(5)	1.473	1.474	1.483	1.475
C-Cl	1.788(10)	1.827	1.801	1.791	1.801
C-H	1.096(10)	1.081	1.081	1.092	1.081
∠Si-C-Cl	109.3(3)	109.82	111.03	110.94	111.19
∠Si-C-H	109.3(5)	112.53	111.95	111.49	111.83
∠C-Si-H	109.09	109.09	109.08	109.06	108.74
∠H-Si-H	110.6(5)	109.85	109.85	109.85	109.70
∠Cl-C-H	106.48	106.79	107.48	106.81	106.80
∠H-C-H	107.5(5)	108.66	108.05	107.76	108.11

<sup>a</sup> Units: lengths in Å, angles in degrees. <sup>b</sup> From MW (*r<sub>g</sub>* structure), reference 24.

<sup>c</sup> From MW; Assumed C<sub>3v</sub> symmetry for the CH<sub>3</sub> group and with assumed structural parameters (See <sup>d</sup>), reference 25. <sup>d</sup> From MW; assumed parameters, *ibid.* <sup>e</sup> From MW, reference 20.

The deviations between MM2 and ab initio 3-21G(\*) geometries listed in Appendix I<sup>2</sup> are given in Appendix II.<sup>32</sup>

While we are aware of the possible systematic errors in data from ab initio 3-21G(\*) calculations, three approaches were used to fit the MM2 parameters to give results consistent with those from 3-21G(\*). Our first MM2 calculations were performed without inclusion of any "electronegativity correction" terms (Method I), and the results show an average deviation of 0.022 Å in bond lengths, and 1.67° in bond angles from 3-21G(\*) geometries. These relatively large deviations may provide the rationale for use of "electronegativity correction" terms to minimize the deviations. The next set of calculations performed (Method II) included the "electronegativity correction" terms developed by Allinger's group<sup>14,23</sup> and by us<sup>9</sup> (for chlorosilanes). The average difference between the 3-21G(\*) and MM2 (Method II) bond angles remain above 1° (Appendix II<sup>32</sup>). We found that bond angles centered

at the Si atom require different equilibrium angles when electronegative atoms are attached.<sup>9</sup> Sources of bond angle deviations are probably (1) the systematic errors in ab initio 3-21G(\*) bond angles or (2) changes in hybridization at Si and C <sub>$\alpha$</sub>  due to the attachment of polar atom(s). Explanation (2) prompted us to try a third alternative, which is presented as Method III. We utilized new "electronegativity correction" terms for bond angles derived to minimize the systematic deviations in the bond angle data. Our rationale for using this method is discussed in detail in the next section. With our new "electronegativity correction" parameters (see Table IV), MM2 geometries can reproduce the ab initio 3-21G(\*) values within 0.02 Å in lengths and 0.1° in angles.

Table IV. "Electronegativity Correction" Scheme Used in This Work.

Correction Terms to $l_0^a$				
Bond	Atoms Attached to	End of Bond	$\delta l_0$	Ref.
Si-C	Cl	Si	-0.013	9
Si-C	Cl	C	+0.011	This work
C-Cl	Cl	C	-0.020 <sup>b</sup>	23
Si-Cl	Cl	Si	-0.008	9
Si-H	Cl	Si	-0.005	9
C-C	Si	C	+0.015	14

Correction Terms to $\theta_0^c$			
Angle	Atom Attached to Center of Angle	$\delta\theta_0$	Ref.
$\angle$ Cl-Si-Cl	C* <sup>d</sup>	+2.0	This work
$\angle$ C-Si-C	C*	+2.0	This work
$\angle$ C-Si-H	C*	+2.0	This work
$\angle$ H-Si-H	C*	+2.0	This work
$\angle$ Si-C*-H	Cl	+2.0	This work
$\angle$ Cl-C*-Cl	Si	-2.0	This work
$\angle$ H-C*-H	Si and Cl	-1.5	This work
$\angle$ H-C*-H	Si	-4.0	This work

<sup>a</sup> Values in Å. <sup>b</sup> Effect of the correction term is reduced by the factor of 0.67 factor, when second or third atoms are attached. <sup>c</sup> Values in deg. <sup>d</sup> C\* means a C atom which is connected to both Si and Cl atoms.

#### 2-4. Geometries: "Electronegativity Corrections"

Allinger et al. have introduced recently the "electronegativity effect"<sup>14,23</sup> in the MM2 program to reproduce the changes in bond lengths due to the attachment of electronegative or electropositive atoms. We also have confirmed that the "electronegativity correction" of bond lengths is essential not only to reduce the average errors of bond lengths in chlorosilanes by 30-40% but also to reproduce the correct trend of bond lengths.<sup>9</sup>

In Table V, ab initio results using various larger basis sets and including electron correlation clearly show that Si-C bonds undergo elongation when additional Cl atoms are attached at the  $\alpha$ -carbon. This result is sharply in contrast with the trend of shortening in Si-C bond lengths due to the additional attachment of Cl atom(s) at Si. The recent observation<sup>28</sup> that Si-CF<sub>3</sub> bonds are much

longer than Si-CH<sub>3</sub> adds support to our results. Beckers *et al.*<sup>28</sup> suggested that the difference in bond lengths is due to the greater repulsive polar contribution in the Si-CF<sub>3</sub> bond (Si<sup>+</sup>-C<sup>-</sup>F<sub>3</sub>) relative to the more attractive polarization of the Si-CH<sub>3</sub> bond (Si<sup>+</sup>-C<sup>-</sup>H<sub>3</sub>).

**Table V.** Ab Initio-Calculated Si-C Bond Lengths,<sup>a</sup> Bond Orders, and Partial Charges of Methylsilane and Ethane-like  $\alpha$ -Chlorosilanes.

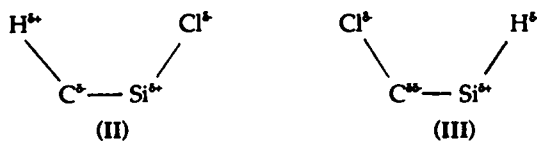
Compounds	HF/ 3-21G(*)	HF/ 6-31G(*)	MP2/ 6-31G(*)	HF/ 6-31G(**)	Experimental value
CH <sub>3</sub> SiH <sub>3</sub>	1.884 (0.68) <sup>b</sup> [C:-0.95] <sup>c</sup> [Si:+0.73]	1.888 (0.75) [C:-0.78] [Si:+0.68]	1.881 (0.75) [C:-0.78] [Si:+0.68]	1.887 (0.75) [C:-0.63] [Si:+0.78]	1.867 <sup>d</sup>
ClCH <sub>2</sub> SiH <sub>3</sub>	1.894 (0.60) [C:-0.81] [Si:+0.76]	1.901 (0.69) [C:-0.66] [Si:+0.71]	1.894 (0.69) [C:-0.66] [Si:+0.71]	1.901 (0.68) [C:-0.56] [Si:+0.80]	1.889 <sup>e</sup>
Cl <sub>2</sub> CHSiH <sub>3</sub>	1.905 (0.52) [C:-0.70] [Si:+0.79]	1.917 (0.63) [C:-0.56] [Si:+0.73]	1.908 (0.63) [C:-0.56] [Si:+0.73]	1.917 (0.63) [C:-0.52] [Si:+0.83]	
Cl <sub>3</sub> CSiH <sub>3</sub>	1.943 (0.47) [C:-0.62] [Si:+0.81]	1.932 (0.59) [C:-0.49] [Si:+0.75]		1.931 (0.59) [C:-0.49] [Si:+0.85]	

<sup>a</sup> Values in Å. <sup>b</sup> The values in parentheses are bond order. <sup>c</sup> The values in brackets are partial charge of Si and C atoms calculated from Mulliken population analysis.<sup>f</sup> <sup>d</sup> From MW, reference R.W. Kilb and L. Pierce *J. Chem. Phys.* **27**, 108 (1957). <sup>e</sup> From MW, reference 20. <sup>f</sup> References R.B. Mulliken, *J. Chem. Phys.* **23**, 1833, 1841, 2338, 2343 (1955).

The nature of bonding in Si compounds has attracted considerable interest for many years,<sup>29</sup> particularly focused on the contribution of (p-d) $\pi$  bonding. We have examined charge distributions, overlap populations, and bond lengths from ab initio calculations on methylsilane and a series of  $\alpha$ -chlorosilanes, e.g. H<sub>3</sub>Si-CH<sub>2</sub>-Cl<sub>n</sub> (n = 0-3) and the results are summarized in Table V. The electrostatic nature of Si-C bonds has been investigated by using charge distribution contour maps. Figure 2 illustrates the charge distribution in the plane including the Si-C bond for MeSiH<sub>3</sub> and ClCH<sub>2</sub>SiH<sub>3</sub>. The bonds to Si generally have low electron density at the critical point compared with the corresponding bonds to C, which is consistent with the recent result of Streitwieser and coworkers.<sup>28c</sup> Mulliken population analysis of ethane-like  $\alpha$ -chlorosilanes shows that the net charge transfer from Si to C <sub>$\alpha$</sub>  becomes larger as Cl is substituted at the C <sub>$\alpha$</sub>  atom, but the direction of the polarization of all Si-C bonds remains the same; a positive end at Si and a negative end at C <sub>$\alpha$</sub> . Furthermore, the electron density maps show that, qualitatively, the electron density in the region of Si-C bonds remains nearly the same (see Figure 2). Thus, the explanation for the lengthening of the Si-C bond in H<sub>3</sub>Si-CF<sub>3</sub> by Beckers *et al.* is not consistent with our electron density maps and charge distributions. If electrostatic interactions are the main factors which govern the Si-C bond length, then changes in the interaction between the 1,4-atoms would be critical. The substitution of Cl at Si (II) increases the attractive electrostatic interactions between 1,4-Cl...H atoms.<sup>18</sup> In contrast, the substitu-

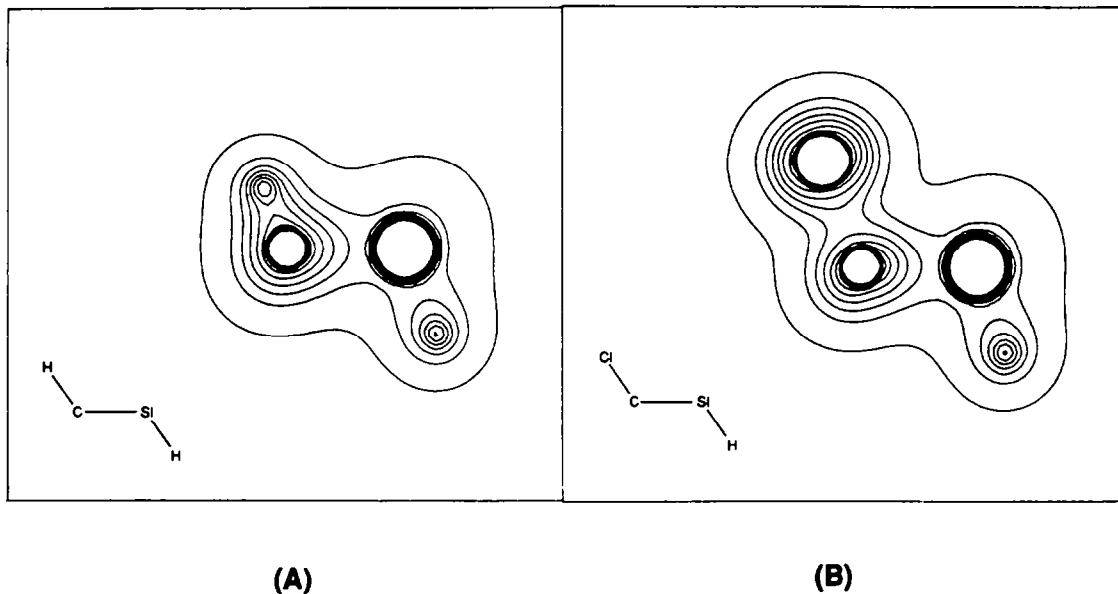


tion of Cl at  $C_\alpha$  (III) increases repulsive 1,4-Cl $\cdots$ H electrostatic interactions which may contribute to elongation of the central C-Si bond to relieve these nonbonded interactions.



Although we have examined the HOMOs and LUMOs of several model systems, we have not found any substantial evidence to explain the trends in the bond lengths as a function of the Cl substitution pattern.

Figure 2. Contour map of total electron density in the plane including the Si-C bond of Me-SiH<sub>3</sub> (A) and ClH<sub>2</sub>CSiH<sub>3</sub> (B) (Contours from 0.01 e/au<sup>3</sup> to 0.51 e/au<sup>3</sup> with a gradient of 0.05 e/au<sup>3</sup>).



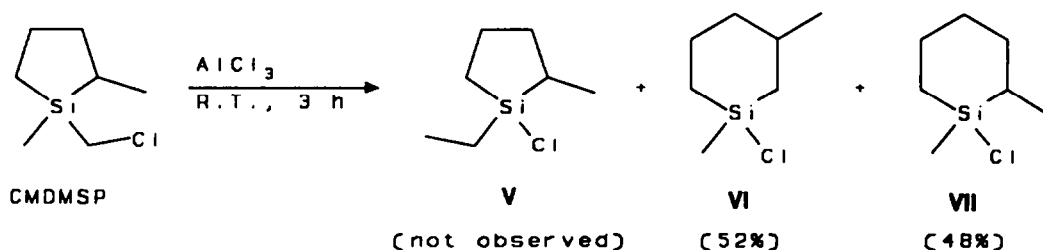
As stated earlier, one of the difficulties encountered in fitting MM2 geometries centered at adjusting bond angles (see bond angles without inclusion of "electronegativity corrections" in Appendix II<sup>32</sup>). This trend is quite ubiquitous in silicon systems,<sup>9,14</sup> but has not surfaced generally as a serious problem in carbon systems. In silicon compounds, Si and the adjacent atom have large partial charges as indicated by Mulliken population analysis (see Table V). The large variation in bond angles may be due to induced 1,3-dipolar interactions between polar atoms. Currently one may adjust bond angles in the MM2 program to reproduce this variation by using: (1) TYPE selection by counting H's attached to the center atom, and (2) by adjusting the equilibrium bond angle ( $\theta_0$ ) of the

complementary bond angles. Both of these methods work effectively in nonpolar or moderately polar carbofunctional systems, in which the bond angles are governed primarily by steric effects. However, in polar silicon systems, especially chloro- and fluorosilanes, the angle distortions due to 1,3-electrostatic interactions may dominate steric crowding. Thus, in TYPE selection, it may be necessary to differentiate electronegative atoms from electropositive atoms, rather than counting numbers of H's. This is done ideally by selecting proper equilibrium bond angles ( $\theta_0$ ) and bending force constants ( $k_b$ ). However, it is very difficult to make adjustments greater than 6-7° using the current option in the MM2 program. Hence, we propose using "electronegativity correction" terms for bond angles as well as for bond lengths. However, we are aware of possible systematic errors in the 3-21G(\*) calculations, and accurate reproduction of the 3-21G(\*) geometries is not necessarily our ultimate goal. Our technique should be considered as a "tentative" one which requires a full examination when appropriate experimental data are available. One should be able to vary the TYPE values of bond angles in the MM2 program by checking the atom type as well as counting H atoms. Furthermore, careful systematic investigation of these "electronegativity corrections" in the bond angles may enable us to reproduce accurately the geometries of polar organic and/or biomolecules.

#### 2-5. Application: Conformational Analysis of CMDMSP

The migration of the R and Cl groups in 1-(chloromethyl)-1,2-dimethylsilacyclopentane (CMDMSP; see Figure 3) can yield a new silacyclopentane (V) through Me migration, or two different chlorosilacyclohexane derivatives (VI, VII) by the competitive migrations of the two different ring bonds. Although the regioselectivity is probably governed by stereoelectronic effects in the transition state,<sup>6</sup> it should be informative to examine the stereochemical preferences in the reactant stage. MM2 calculations have been performed on appropriate conformers, including half-chair, envelope, and planar forms, by imposing the appropriate symmetry, and then minimizing to check if the calculated conformer is a local minimum.

Figure 3. The  $\text{AlCl}_3$ -catalyzed rearrangement of CMDMSP (the values in parentheses are the experimental results from proton NMR integration).



Our previous MM2 results<sup>9,30</sup> on the silacyclopentane derivatives showed that (1) silacyclopentane and its derivatives are usually stable in half chair conformations and (2) energy differences between half-chair and envelope forms become larger when the substituents at Si and adjacent endocyclic C atoms are bulky. The MM2 results on CMDMSP are consistent with our previous results on

silacyclopentanes. Relative energies of envelope forms are always higher than those of the corresponding half-chair forms by 3.2-3.5 kcal/mol. Furthermore, all envelope forms converge to the corresponding half-chair forms when symmetry restrictions are removed. The energies of the planar forms are much higher than corresponding half-chair forms by ca. 6.5 kcal/mol. Therefore, the potential energy surface of each isomer has 6 local minima (A, A', A'', B, B', B'' of the (Z)-isomer and C, C', C'', D, D', D'' of the (E)-isomer in Figure 4), which are all in half-chair forms. A summary of the MM2 calculated steric energies of these conformers is presented in Table VI. Energy difference between two different groups of conformers (A and B; C and D) is ca. 1.5 kcal/mol. The MM2 energy differences among conformers involving the C<sub>2</sub>-Si-C<sub>4</sub>-Cl fragment are less than 0.3 kcal/mol in both sets of isomers, and rotational barriers are ca. 3-5 kcal/mol (see Figure 5). Hence, we conclude that the C<sub>2</sub>-Si-C<sub>4</sub>-Cl fragment does not show any conformational preference. Since different conformers can give different products, this rotation is important, if the outcome of the rearrangement reaction is dependent on the conformational preference of the reactant. Our experimental studies using AlCl<sub>3</sub>-catalyzed rearrangements show that the relative order of migratory aptitudes is the ring bonds (less substituted  $\approx$  more substituted)  $\gg$  Si-Me.<sup>31</sup>

Figure 4. MM2-calculated geometries and relative conformational energies of the local minima of (E)- and (Z)-CMDMSP (The values in parentheses are relative conformational energies; units in kcal/mol).

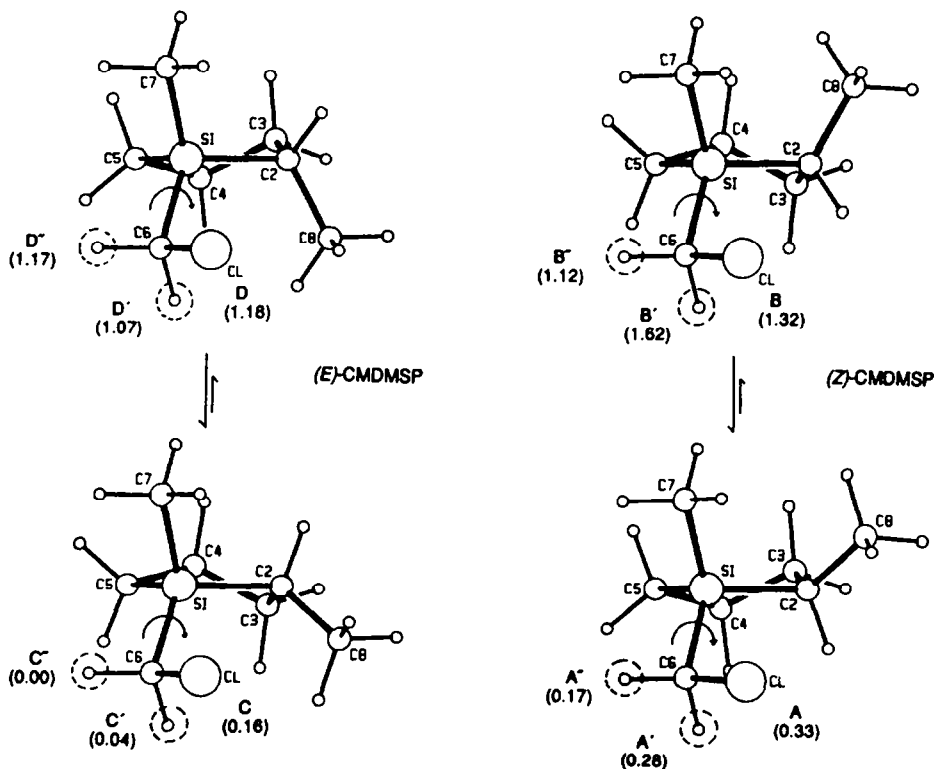
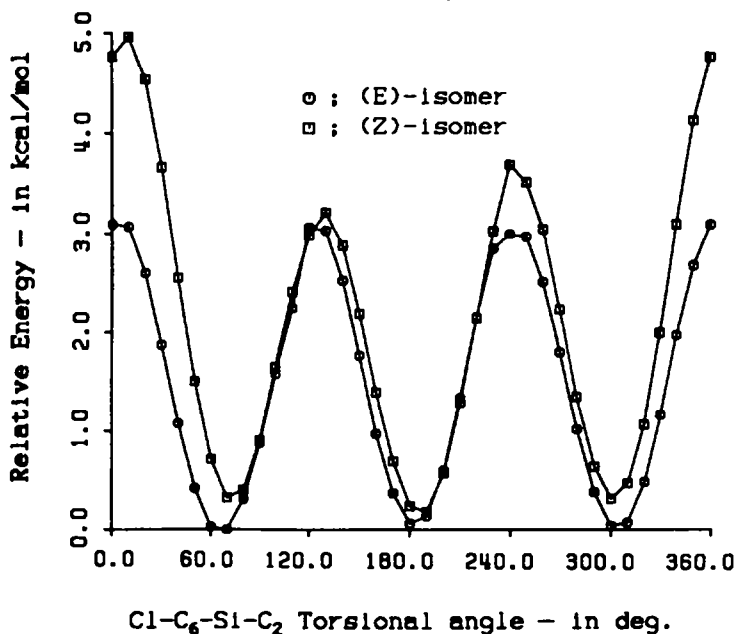


Table VI. Relative Conformational Energies<sup>a</sup> for Conformers of CMDMSP.

	Total steric energies	Relative to	
		lowest energy rotamer <sup>b</sup>	global minimum
(Z)-isomer			
Half-chair with 2-Me pseudoequatorial			
A	7.68	0.16	0.33
A'	7.63	0.11	0.28
A''	7.52	0.0	0.17
Half-chair with 2-Me pseudoaxial			
B	8.47	0.0	1.32
B'	8.97	0.50	1.62
B''	8.67	0.20	1.12
(E)-isomer			
Half-chair with 2-Me pseudoequatorial			
C	7.51	0.16	0.16
C'	7.39	0.04	0.04
C''	7.35	0.0	0.0
Half-chair with 2-Me pseudoaxial			
D	8.53	0.11	1.18
D'	8.42	0.0	1.07
D''	8.52	0.10	1.17

<sup>a</sup> Values in kcal/mol. <sup>b</sup> Around Si-C<sub>6</sub> bond.

Figure 5. Relative conformational energy changes of (Z)- and (E)-CMDMSP due to the rotation of the Cl atom around the Si-C bond calculated by MM2.



The failure to correlate the regioselectivity of the rearrangement reaction with the conformational preference of CMDMSP suggests that stereoelectronic effects in the transition state in this reaction may be most important. Relevant transition state calculations using semi-empirical methods (AM1 and MNDO) based on our MM2 structures of CMDMSP and additional experiments are currently underway.

### 3. CONCLUSIONS

A new MM2 force field for  $\alpha$ -chlorosilanes has been developed. The MM2 geometries and relative conformational energies of  $\alpha$ -chlorosilanes are in good agreement with both experimental and ab initio results. "Electronegativity corrections" have been applied to both Si-C bonds and several bond angles which are centered at Si or  $C_\alpha$  atoms. These parameters enable us to calculate MM2 geometries which accurately reproduce ab initio 3-21G(\*) geometries. Si-Cl bond lengths also have been examined using ab initio calculations with 3-21G(\*), 6-31G(\*), 6-31G(\*\*) basis sets, and 6-31G(\*) with MP2 theory. The Si-C bond lengths were found to be most sensitive to the number of Cl's on the  $\alpha$ -position and insensitive to the level of the theory used to calculate these values. In  $\alpha$ -chlorosilanes we found that additional Cl atom(s) on the  $C_\alpha$  atom cause the Si-C bond to elongate. This effect is reflected in the Mulliken overlap populations. We also present an alternative method for accurately fitting the geometries, especially bond angles, of polar compounds. The new force field has been applied to the conformational analysis of CMDMSP. CMDMSP, an example of silacyclopentane derivatives which undergo  $AlCl_3$ -catalyzed 1,2-migrations, is stable in half-chair conformers. Energy differences among three different isomers arising due to the rotation of the Cl atom around the exocyclic Si- $C_\alpha$  bond are very small, and rotational barriers are only 3-5 kcal/mol.

### REFERENCES

1. a) Bott, R.W.; Eaborn, C.; Rushton, B.M. *J. Organomet. Chem.* **1965**, *3*, 455. b) Steward, O.W.; Uhl, W.J.; Sands, B.W. *J. Organomet. Chem.* **1968**, *15*, 329. c) Larson, G.L.; Klesse, R.; Cartledge, F.K. *Organometallics* **1987**, *6*, 2250. d) Clarke, M.P.; Damrauer, R.; Davidson, I.M.T.; Simon, R. *Organometallics* **1989**, *8*, 2031.
2. a) Hairston T.J.; O'Brien, D.H. *J. Organomet. Chem.* **1971**, *29*, 79. b) Bassindale, A.R.; Brook, A.G.; Jones, P.F.; Lennon, J.M. *Can. J. Chem.* **1975**, *53*, 332.
3. a) Kumada, M.; Nakajima, J.-I.; Ishikawa, M.; Yamamoto, Y. *J. Org. Chem.* **1958**, *23*, 292. b) Kumada M.; Ishikawa, M. *J. Organomet. Chem.* **1964**, *1*, 411. c) Kumada, M.; Ishikawa, M.; Maeda, S.; Ikura, K. *J. Organomet. Chem.* **1964**, *2*, 411.
4. Dewar M.J.S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.
5. Dewar, M.J.S.; Zoebisch, E.G.; Healy, E.F.; Stewart J.J.P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
6. Cho, S.G.; Cartledge, F.K.; Unwalla, R.J.; Profeta, S. Jr. 197th National Meeting of the American Chemical Society: Dallas, April 7-14, 1989; PHYS 58.
7. For examples, see a) Sherrod M.J.; Menger, F.M. *J. Am. Chem. Soc.* **1989**, *111*, 2611. b) Sauer R.R.; Krogh-Jespersen, K. *Tetrahedron Lett.* **1989**, *30*, 527. c) Loncharich, R.J.; Brown, F.K.; Houk, K.N. *J. Org. Chem.* **1989**, *54*, 1129. d) Li Y.; Houk, K.N. *J. Am. Chem. Soc.* **1989**, *111*, 1236. e) Amici, M.D.; Micheli, C.D.; Ortisi, A.; Gatti, G.; Gandolfi, R.; Toma, L. *J. Org. Chem.* **1989**, *54*, 793. f) Dorigo A.E.; Houk, K.N. *J. Org. Chem.* **1988**, *53*, 1650. g) Hassner, A.; Murthy, K.S.K.; Powda, A.; Bullock, W.H.; Stull, P.D. *J. Org. Chem.* **1980**, *53*, 5063. h) Takahashi, T.; Shimizu, K.; Doi, T.; Tsuji, J. *J. Am. Chem. Soc.* **1988**, *110*, 2674. i) Dorigo A.E.; Houk, K.N. *J. Am. Chem. Soc.* **1987**, *109*, 3698. j) Spellmeyer D.C.; Houk, K.N. *J. Org. Chem.* **1987**, *52*, 959. k) Green, M.M.; Boyle, B.A.; Vairamani, M.; Mukhopadhyay, T.; Saunders, W.H. Jr.; Bowen, P.; Allinger, N.L. *J. Am. Chem. Soc.* **1986**, *108*, 2381. l) Mereland D.W.; Dauben, W.G. *J. Am. Chem. Soc.* **1985**, *107*, 2264. m) Houk, K.N.; Rondan, N.G.; Wu, Y.-D.; Metz, J.T.; Paddon-Row, M.N. *Tetrahedron* **1984**, *40*, 2257. n) DeTar, D.F. *Biochemistry* **1981**, *20*, 1730. o) DeTar D.; Luthra, N.P. *J. Am. Chem. Soc.* **1980**, *102*, 4505. p) DeTar, D.F.; McMullen, D.F.; Luthra, N.P. *J. Am. Chem. Soc.* **1978**, *100*, 2484.

8. a) Burkert U.; Allinger, N.L. *Molecular Mechanics*, American Chemical Society, Washington, D.C., 1982. b) Allinger, N.L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1.
9. Cho, S.G.; Unwalla, R.J.; Cartledge, F.K.; Profeta, S. Jr. *J. Comput. Chem.* **1989**, *10*, 832.
10. a) Binkley, J.S.; Frisch, M.; Raghavachari, K.; DeFrees, D.J.; Schlegel, H.B.; Whiteside, R.A.; Fluder, E.; Seeger, R.; Pople, J.A. GAUSSIAN 82, Release H, Carnegie-Mellon University, Pittsburgh, PA, 1984. b) Frisch, M.J.; Binkley, J.S.; Schlegel, H.B.; Raghavachari, K.; Melius, C.F.; Martin, R.L.; Stewart, J.J.P.; Bobrowicz, F.W.; Rohlfing, C.M.; Kahn, L.R.; DeFrees, D.J.; Seeger, R.; Whiteside, R.A.; Fox, D.J.; Fleuder, E.M.; Pople, J.A. GAUSSIAN 86, Carnegie-Mellon University, Pittsburgh, PA, 1984.
11. Pietro, W.J.; Francl, M.M.; Hehre, W.J.; Defrees, D.J.; Pople, J.A.; Binkley, J.S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.
12. Hariharan P.C.; Pople, J.A. *Theor. Chim. Acta* **1973**, *28*, 213.
13. a) Møller C.; Plesset, M.S. *Phys. Rev.* **1934**, *46*, 618. b) Krishnan, R.; Frisch, M.J.; Pople, J.A. *J. Chem. Phys.* **1980**, *72*, 4244.
14. a) Frierson, M.R.; Imam, M.R.; Zalkow, V.B.; Allinger, N.L. *J. Org. Chem.* **1988**, *53*, 5248. b) Frierson, M., Ph.D. Dissertation, University of Georgia, 1984.
15. For the C-C-C-Si torsional parameter, the following  $V_n$  (kcal/mol) were used:  $V_1=0.0$ ,  $V_2=0.1$ ,  $V_3=0.5$ ; Profeta, S. Jr.; Unwalla, R.J.; Cartledge, F.K. *J. Comput. Chem.* **1989**, *10*, 99.
16. Morino Y.; Hirota, E. *J. Chem. Phys.* **1958**, *28*, 185.
17. Cho, S.G.; Unwalla, R.J.; Profeta, S. Jr.; Cartledge, F.K., in preparation.
18. Cho, S.G.; Cartledge, F.K.; Unwalla, R.J.; Profeta, S. Jr. *J. Mol. Struct. (Theochem)* **1990**, *204*, 79.
19. Wiberg, K.B. *J. Am. Chem. Soc.* **1986**, *108*, 5817.
20. Schwendeman R.H.; Jacobs, G.D. *J. Chem. Phys.* **1962**, *36*, 1251.
21. Vajda, E.; Szekely, T.; Hargittai, I.; Maltsev, A.K.; Baskir, E.G.; Nefedov, O.M.; Brunvoll, J. *J. Organomet. Chem.* **1978**, *188*, 321.
22. Shen, Q. *J. Mol. Struct.* **1978**, *49*, 337.
23. Allinger, N.L.; Imam, M.R.; Frierson, M.R.; Yuh Y.; Schäfer, L., in N. Trinajstić, (Ed.), *Mathematics and Computational Concepts in Chemistry*, John Wiley & Sons, New York, 1986, Chapter 3.
24. Duncan, J.L.; Harvie, J.L.; McKean, D.C.; Cradock, S. *J. Mol. Struct.* **1986**, *145*, 225.
25. Endo, K.; Takeo, H.; Matsumura, C. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 626.
26. a) Profeta, S. Jr.; Unwalla, R.J.; Cartledge, F.K. *J. Org. Chem.* **1986**, *51*, 1884. b) Profeta, S. Jr.; Unwalla, R.J.; Nguyen, B.T.; Cartledge, F.K. *J. Comput. Chem.* **1986**, *5*, 528. c) Unwalla, R.J.; Profeta, S. Jr.; Cartledge, F.K. *J. Org. Chem.* **1988**, *53*, 5658.
27. a) Schmidt M.W.; Gordon, M.S. *Can. J. Chem.* **1985**, *63*, 1609. b) Luke, B.T.; Pople, J.A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Chandrasekhar, J.; Schleyer, P.v.R. *J. Am. Chem. Soc.* **1986**, *108*, 260. c) Karri, M.; Chandrasekhar, J.; Schleyer, P.v.R. *J. Am. Chem. Soc.* **1986**, *108*, 270. d) Dobbs K.D.; Hehre, W.J. *J. Comput. Chem.* **1986**, *7*, 359. e) Spitznagel, G.W.; Clark, T.; Schleyer, P.v.R.; Hehre, W.J. *J. Comput. Chem.* **1987**, *8*, 1109.
28. Beckers, H.; Brauer, D.J.; Bürger, H.; Wilke, C.J. *J. Organomet. Chem.* **1988**, *356*, 31 and references therein.
29. For examples, see a) Howell J.M.; van Wazer J.R. *J. Am. Chem. Soc.* **1974**, *96*, 3064. b) Rempfer, B.; Oberhammer, H.; Auner, N. *J. Am. Chem. Soc.* **1986**, *108*, 3893. c) Gronert, S.; Glaser, R.; Streitwieser, A. *J. Am. Chem. Soc.* **1989**, *111*, 3111.
30. Cartledge, F.K. *J. Organomet. Chem.* **1982**, *225*, 131.
31. a) Shui, L., M.S. Thesis, Louisiana State University, 1987. b) Cho, S.G.; Cartledge, F.K.; Shui, L.; Nguyen, E.T., 197th National Meeting of the American Chemical Society: Dallas, April 7-14, 1989; ORGN 89.
32. Appendix I and II: see *Tetrahedron Comp. Method.*, in press.