The Vibrational Spectra and Rotational Isomerism of Chloro(chloromethyl)silanes

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The infrared spectra of chloro(chloromethyl)methylsilanes $ClCH_2SiCl_{3-n}(CH_3)_n$ (n=0—2) in the liquid and crystalline states and a part of the Raman spectra in the liquid state have been measured. It has become apparent that, for $ClCH_2SiCl_2CH_3$ and $ClCH_2SiCl(CH_3)_2$, two rotational isomers coexist in the liquid state, while only one isomer persists in the crystalline state. The fundamental vibrations for these molecules have been assigned, and the normal vibrations have been calculated on the basis of a modified Urey-Bradley force field. The solvent effects and the calculation of the normal vibrations have indicated that the *gauche* form for $ClCH_2SiCl_2CH_3$ and the *trans* form for $ClCH_2SiCl(CH_3)_2$ persist in the crystalline state. For $ClCH_2SiCl_3$, the barrier height, $V_3(SiCl_3)$, has been estimated to be 4.6 kcal/mol from the torsional force constant.

In our previous papers,1) we have reported the existence of rotational isomers in the XCH_2SiH_2Y-type (X,Y=Cl or CH_3) molecules. However, with regard to chloro(chloromethyl)dimethylsilane (CCDS) and chloro(ethyl)dimethylsilane, one of the present authors (M. H.) published a paper about fifteen years ago which mentioned that rotational isomers may not exist in these molecules, juaging from the Raman spectra in the liquid and solid states, while the dipole moments of CCDS at various temperatures do indicate the possibility of the existence of the rotational isomers.2) The Raman spectra of the $ClCH_2SiCl_{3-n}(CH_3)_n$ molecules (n=0—2)3) and the infrared spectrum of dichloro(chloromethyl)methylsilane (DCMS)4) have been reported, but no detailed vibrational analyses have been made. The vibrational spectra and assignments of CCDS have been reported by one of the present authors (M. H.),2) by Goubeau *et al.*,5) and by Kriegmann *et al.*,6) but the assignments of the C–Si and C–Cl stretching vibrations have not been consistent with each other.

In the present paper, we will deal anew with the molecular vibrations of the $ClCH_2SiCl_{3-n}(CH_3)_n$ series of molecules (n=0—2) in order to show the existence of the rotational isomers, information about the barrier height around a C–Si bond, and reasonable vibrational assignments for this series of molecules.

Experimental

Trichlorochloromethylsilane (TCS) was prepared by the reaction of tetrachlorosilane with diazomethane.7) The samples of DCMS and CCDS were commercial products purified by redistillation.

The infrared spectra in the 200—4000 cm^{-1} region were recorded on a Perkin-Elmer instrument (Model 621). For the measurements in the crystalline state, the vapor of the sample was directly condensed on a CsI window cooled with liquid nitrogen in a vacuum and was annealed several times near the melting point. The solution spectra were measured using a sealed KRS-5 cell (0.5 mm thick), with carbon disulfide and acetonitrile as solvents. The Raman spectra in the liquid state were recorded on a JEOL Raman spectrometer (Model JRS-02AS), using an argon-ion laser (488.0 nm) for excitation.

Results and Discussion

Rotational Isomerism and Vibrational Assignments. Figure 1 shows the infrared spectra of TCS, DCMS, and CCDS in the liquid and crystalline states. It has been reported, on the basis of microwave study, that staggered configurations are more stable around a C–Si bond in such molecules as chloromethylsilane8) and dimethylsilane.9) For DCMS and CCDS, the two rotational isomers in Fig. 2 are expected. Actually, not for TCS, but for DCMS and CCDS, a few bands observed in the liquid state vanish in the crystalline

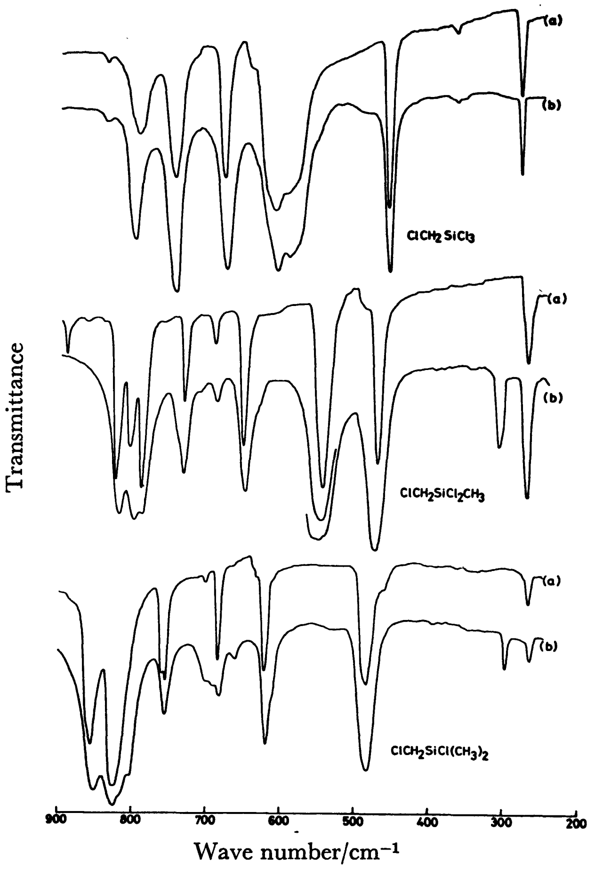
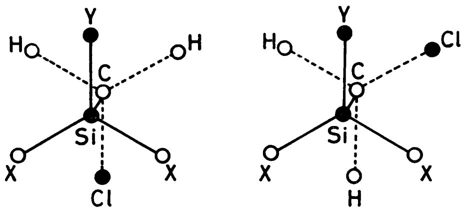


Fig. 1. Infrared spectra of the $ClCH_2SiCl_{3-n}(CH_3)_n$ molecules (n=0—2).
(a): In the crystalline state, (b): in the liquid state.



Trans form(T) *Gauche* form(G)

Fig. 2. Possible molecular forms for $ClCH_2SiCl_2CH_3$ and $ClCH_2SiCl(CH_3)_2$.

state. For CCDS, the Raman spectrum in the solid state has previously been reported by one of the present authors (M. H). Unfortunately, the Raman lines which correspond to the disappeared infrared bands in the crystalline state have not vanished completely, though the relative intensities of these lines have remarkably decreased in the solid state.[2] From the above results and the relative intensity changes in the infrared bands in the solution spectra, it may be concluded that, for DCMS and CCDS, two rotational isomers coexist in the liquid state, while only one isomer persists in the crystalline state.

On the other hand, the fundamental vibrations are assigned on the basis of the spectra in the $ClCH_2SiCl_{3-n}(CH_3)_n$ series of molecules (n=0—3) and on the basis of the relative intensities between the infrared bands and Raman lines. Figure 3 shows the correlation of the vibrational assignments of TCS, DCMS, and CCDS, together with that of chloromethyltrimethylsilane.[10] The assignment for CCDS is consistent with that by Goubeua *et al.*[5]

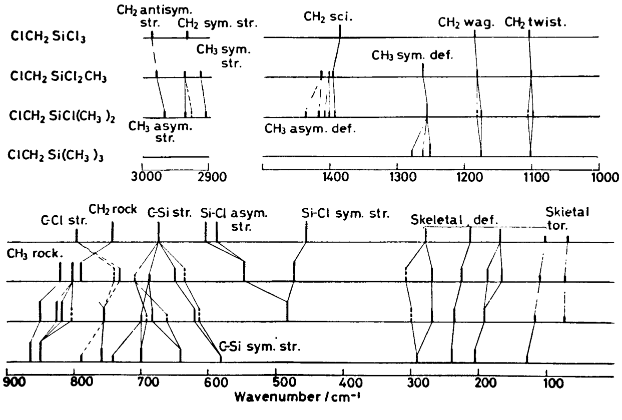


Fig. 3. Correlation of the vibrational assignments of the $ClCH_2SiCl_{3-n}(CH_3)_n$ series of molecules (n=0—3), where the lines in the region below 400 cm^{-1} and above 400 cm^{-1} are the observed Raman lines and the infrared bands respectively.

Solvent Effects. The solvent effects can be used for the determination of the molecular forms for DCMS and CCDS, because the dipole moments are expected to change considerably with an azimuthal angle of internal rotation. The dipole moment calculation based on the bond moments indicates that, for DCMS, the *trans* form is more polar than the *gauche* form, while for CCDS the *gauche* form is more polar than the *trans* form.

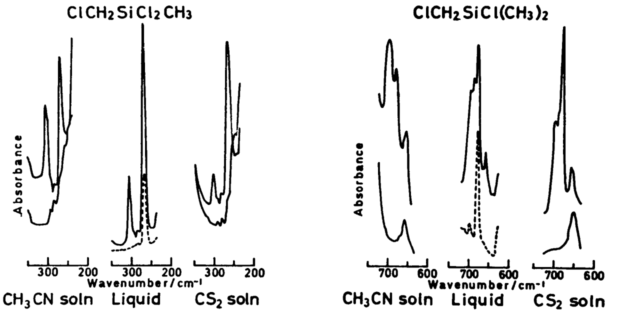


Fig. 4. The solvent effects of the infrared bands for $ClCH_2SiCl_2CH_3$ and $ClCH_2SiCl(CH_3)_2$.
……: The spectra in the crystalline state.

For DCMS, the solvent effects of the infrared spectra are measured, using the bands at 308 and 269 cm^{-1} assigned to the skeletal deformation vibrations. The band at 308 cm^{-1} vanishes in the crystalline state. Figure 4 shows the solvent effects of the infrared bands. The A_{308}/A_{269} ratio increases when it is mixed with a polar solvent such as acetonitrile, while the reverse is true in a mixture with a non-polar solvent such as carbon disulfide. Therefore, the isomer disappearing in the crystalline state (the *trans* form) is more polar than the other (the *gauche* form).

For CCDS, the solvent effects of the bands at 692 and 683 cm^{-1} assigned to the C–Si stretching vibrations indicate that the isomer disappearing in the crystalline state (the *gauche* form) is more polar than the other

TABLE 1. OBSERVED AND CALCULATED FREQUENCIES OF TRICHLORO(CHLOROMETHYL)SILANE[a] (cm^{-1})

Infrared Liquid Int.	Raman Liquid Int.	Calcd C_s	P. E. D.
2987 w	2987 w	2993 A″	$\nu_a(CH_2)$
2934 m	2936 ms	2948 A′	$\nu_s(CH_2)$
1386 ms	1387 w	1421 A′	$s(CH_2)$
1185 w	1186 vw	1167 A′	$w(CH)_2$
1103 w	1104 vw	1115 A″	$t(CH_2)$
838 vw			
798 ms	799 w	745 A′	ν(C–Cl), ν(C–Si)
743 vs		748 A″	$r(CH_2)$
674 s	676 m	676 A′	ν(C–Si), ν(C–Cl)
604 s	597 sh w	606 A′	$\nu_a(SiCl_3)$
588 s	586	594 A″	$\nu_a(SiCl_3)$
454 s	456 vvs	456 A′	$\nu_s(SiCl_3)$
361 vw			
276 m	277 s	263 A′	$\delta(ClCSi)$, $\delta_s(SiCl_3)$
	212 s	230 A″	$r(SiCl_3)$, $\delta_a(SiCl_3)$
		208 A′	$\delta_s(SiCl_3)$, $\delta_a(SiCl_3)$
	167 s	167 A″	$\delta_a(SiCl_3)$, $r(SiCl_3)$
		156 A′	$\delta_a(SiCl_3)$
	101 m	101 A′	$r(SiCl_3)$, $\delta(ClCSi)$
	68 m	67 A″	$\tau(SiCl_3)$

a) Int.=intensity; s, m, w=strong, medium, weak; v=very; sh=shoulder; A′, A″=A′ symmetry species, A″ symmetry species; P.E.D.=potential energy distributions; ν, s, w, t, r, δ, τ=stretching, scissoring, wagging, twisting, rocking, deformation, torsion; potential energy distributions greater than 20% are included.

(the *trans* form), as is shown in Fig. 4.

Normal Vibration Calculation. In order to confirm the results of the molecular forms and the vibrational assignments, the normal vibrations of the ClCH$_2$SiCl$_{3-n}$(CH$_3$)$_n$ molecules (n=0—2) were calculated, using Wilson's **GF**-matrix method. The bond lengths used were C–Cl=1.788 Å, CH$_2$–Si=1.889 Å, CH$_3$–Si=1.868 Å, Si–Cl=2.021 Å, and C–H=1.095 Å.[8,9,11] All the valence angles were assumed to be tetrahedral, and the internal rotation angles were 180° (*trans*) and 60° (*gauche*). The force constants in the modified Urey-Bradley force field were transferred from those of trichloromethylsilane,[11] chloromethylsilane,[12] and dichloroethylmethylsilane;[13] only the force constants of the skeletal torsions were adjusted to reproduce well the observed torsional frequencies.

The observed and calculated frequencies are summarized in Tables 1—3, together with the predominant potential energy distributions in the internal symmetry coordinates. The force constants are listed in Table 4. The vibrational assignments in Fig. 3 are consistent with the results of the calculations, though the potential energy distributions indicate large mixings between the C–Si and C–Cl stretching vibrations and between the

TABLE 2. OBSERVED AND CALCULATED FREQUENCIES OF DICHLORO(CHLOROMETHYL)METHYLSILANE[a] (cm^{-1})

Infrared		Raman[b]	Calcd[c]		P. E. D.
Liq. Int.	Cryst. Int.	Liq. Int.	T form	G form	
2979 vw	2974 vw		2992 A″	2992	ν_a(CH$_2$)
			2964 A′	2964	ν_a(CH$_3$)
			2964 A″	2964	ν_a(CH$_3$)
2938 w	2938 w		2944 A′	2944	ν_s(CH$_2$)
2914 vw	2914 vw		2900 A′	2900	ν_s(CH$_3$)
1402 m	1407 sh 1403 m		1416 A″	1416	δ_a(CH$_3$)
			1416 A′	1416	δ_a(CH$_3$)
1396 m	1396 m		1421 A′	1421	s(CH$_2$)
1384 sh w	—				
1375 sh w	1373 w				
1262 s	1261 s		1283 A′	1283	δ_s(CH$_3$)
1181 w	1182 1179 w		1165 A′	1166	w(CH$_2$)
1101 w	1101 1097 w		1115 A″	1115	t(CH$_2$)
	941 vw				
	897 w				
821 vs	825 vs	823 w	836 A′	837	r(CH$_3$)
802 vs	807 vs	804 w	832 A″	831	r(CH$_3$)
790 vs	792 vs	791 vw		763	r(CH$_2$), ν_a(C–Si)
741sh m	—		746 A′		ν(C–Cl), ν_a(C–Si)
			741 A″		r(CH$_2$)
734 s	735 s	735 ms		736	ν(C–Cl), ν_a(C–Si)
710 vw	—		704 A′		ν_s(C–Si)
689 w	693 w	690 w		700	ν_s(C–Si), ν(C–Cl), r(CH$_2$)
650 s	654 s	651 vs		648	ν_s(C–Si), ν(C–Cl)
635 sh w	—	635 sh w	644 A′		ν_a(C–Si), ν(C–Cl)
547 vs	547 vs	552 w	531 A″	542	ν_a(SiCl$_2$)
473 vs	473 vs	472 vvs	461 A′	471	ν_s(SiCl$_2$)
308 m	—	307 w	281 A′		δ(ClCSi), w(SiCl$_2$)
269 m	271 m	268 s		265	δ(ClCSi), w(SiCl$_2$), δ(CSiC)
		225 s	231 A″		r(SiCl$_2$)
				239	δ(CSiC), w(SiCl$_2$), r(SiCl$_2$)
			220 A′		δ(CSiC), s(SiCl$_2$)
				218	w(SiCl$_2$), r(SiCl$_2$)
		186 ms	183 A″		t(SiCl$_2$)
				179	t(SiCl$_2$), s(SiCl$_2$)
		165 ms	169 A′		s(SiCl$_2$), δ(CSiC)
				162	s(SiCl$_2$)
			165 A″	165	τ(SiCH$_3$)
		109 mw	107 A′		w(SiCl$_2$), δ(ClCSi), δ(CSiC)
				111	t(SiCl$_2$), δ(ClCSi)
		73 w	70 A″	75	τ(skel)

a) See footnote a) of Table 1. b) The Raman spectrum is measured in the region below 900 cm^{-1}.
c) T, G=*trans*, *gauche*.

skeletal deformation vibrations. For the molecular forms of DCMS and CCDS, the conclusion regarding the solvent effects is consistent with that obtained from the comparison of the observed frequencies with the calculated frequencies of the highest-frequency skeletal deformation for each molecular form.

Barriers to Internal Rotation. The barrier height, V_3, assuming the harmonic oscillation ($V=(1/2)V_3(1-\cos 3\alpha)$, $V_3>2.5$ kcal/mol) can be calculated by the use of the torsional frequency or its force constants as

Table 3. Observed and calculated frequencies of chloro(chloromethyl)dimethylsilane[a] (cm^{-1})

Infrared		Raman[b] Liq. Int.	Calcd[c]		P. E. D.
Liq. Int.	Cryst. Int.		T form	G form	
	2981 vw				
2967 m	2969 w	2976 7b	2992 A″	2993	$\nu_a(\mathrm{CH_2})$
			2964 A′	2964	$\nu_a(\mathrm{CH_3})$
			2964 A′	2964	$\nu_a(\mathrm{CH_3})$
			2963 A″	2963	$\nu_a(\mathrm{CH_3})$
			2963 A″	2963	$\nu_a(\mathrm{CH_3})$
2936 m	2943 w	2932 5	2948 A′		$\nu_s(\mathrm{CH_2})$
2927 m	—			2949	$\nu_s(\mathrm{CH_2})$
2905 vw	2902 vw	2908 7b	2900 A″	2900	$\nu_s(\mathrm{CH_3})$
			2900 A′	2900	$\nu_s(\mathrm{CH_3})$
1437 vw	1438 w		1416 A′	1417	$\delta_a(\mathrm{CH_3})$
1417 vw	1414 w		1416 A′	1416	$\delta_a(\mathrm{CH_3})$
1408sh m			1416 A″	1416	$\delta_a(\mathrm{CH_3})$
1401sh m	1399 m		1415 A″	1415	$\delta_a(\mathrm{CH_3})$
1393 m	1389 m	1397 5b	1421 A′	1421	$s(\mathrm{CH_2})$
		1361 1			
1256 vs	1260 vs	1258 3	1282 A′	1282	$\delta_s(\mathrm{CH_3})$
	1255		1282 A″	1282	$\delta_s(\mathrm{CH_3})$
1181sh m	—			1166	$w(\mathrm{CH_2})$
1175	1178 s	1174 3	1166 A′		$w(\mathrm{CH_2})$
1104 w	—			1115	$t(\mathrm{CH_2})$
1096 m	1097 m	1101 1	1115 A″		$t(\mathrm{CH_2})$
851 vs	855 vs	853 1	851 A′	859	$r(\mathrm{CH_3})$
			843 A′	844	$r(\mathrm{CH_3})$
826 vs	827 vs	822 1	833 A″	832	$r(\mathrm{CH_3})$
818 sh			816 A″		$r(\mathrm{CH_3})$
804 sh	—	806 1		816	$r(\mathrm{CH_3})$
756 s	759 s	756 4	761 A″	751	$r(\mathrm{CH_2})$, $\nu_a(\mathrm{C{-}Si})$
	755		733 A′	732	$\nu(\mathrm{C{-}Cl})$, $\nu_s(\mathrm{C{-}Si})$
700	700 vw	709 2	695 A″		$\nu_a(\mathrm{C{-}Si})$, $r(\mathrm{CH_2})$
692 m	—			718	$\nu_a(\mathrm{C{-}Si})$, $r(\mathrm{CH_2})$
683 s	684 s	686 1	690 A′		$\nu_a(\mathrm{C{-}Si})$, $\nu(\mathrm{C{-}Cl})$
661 w	—	663 1		667	$\nu_a(\mathrm{C{-}Si})$, $\nu(\mathrm{C{-}Cl})$
620 s	619 s	620 10b	612 A′		$\nu_s(\mathrm{C{-}Si})$, $\nu_a(\mathrm{C{-}Si})$, $\nu(\mathrm{C{-}Cl})$
613sh s	—			634	$\nu_s(\mathrm{C{-}Si})$ $\nu_a(\mathrm{C{-}Si})$
483 vs	481 s	482 9b	493 A′	473	$\nu(\mathrm{Si{-}Cl})$
298 m	—	299 4		278	$\delta(\mathrm{ClCSi})$, $\delta_a(\mathrm{CSiC})$
266 m	265 w	268 4	262 A′		$\delta(\mathrm{ClCSi})$, $\delta_s(\mathrm{CSiC})$, $\delta_a(\mathrm{CSiC})$
		235 5b	242 A″		$\delta_a(\mathrm{CSiC})$
				235	$\delta_s(\mathrm{CSiC})$
			228 A′		$\delta_a(\mathrm{CSiC})$, $\delta_s(\mathrm{CSiC})$
				221	$\delta_s(\mathrm{CSiC})$, $\delta(\mathrm{CSiCl})$
		191 5b	190 A″	198	$\delta(\mathrm{CSiCl})$, $\delta_a(\mathrm{CSiC})$
				182	$\delta(\mathrm{CSiCl})$, $\delta_a(\mathrm{CSiC})$
			172 A′		$\delta(\mathrm{CSiCl})$, $\delta(\mathrm{ClCSi})$
			166 A″	165	$\tau(\mathrm{SiCH_3})$
			165 A′	164	$\tau(\mathrm{SiCH_3})$
		117 1	119 A′		$\delta_s(\mathrm{CSiC})$, $\delta(\mathrm{ClCSi})$, $\delta(\mathrm{CSiCl})$
				116	$\delta_a(\mathrm{CSiC})$, $\delta(\mathrm{ClCSi})$
		73 1	77 A″	70	$\tau(\mathrm{skel})$

a) See footnote a) of Table 1. b) The Raman spectrum is remeasured in the region below 100 cm^{-1}.
c) See footnote c) of Table 2.

TABLE 4. FORCE CONSTANTS FOR CHLORO(CHLOROMETHYL) METHYLSILANES[a)]

Force const.		Force const.	
K(C–H), CH_3	4.403	$k(CH_3)$	0.014
K(C–H), CH_2	4.390	$\kappa(CH_2)$	0.027
K(C–Cl)	1.697	$\kappa(CSiCl_3)$	0.170
K(C–Si)	1.991	$\kappa(C_2SiCl_2)$	0.149
K(Si–Cl), SiCl	2.166	$\kappa(C_3SiCl)$	0.090
K(Si–Cl), $SiCl_2$	2.226	$p(SiCl_2)$	0.174
K(Si–Cl), $SiCl_3$	2.590	p(C–H)	−0.084
H(Si–C–Cl)	0.100	F(Si·C·Cl)	0.210
H(Si–C–H), CH_2	0.104	F(Si·C·H), CH_2	0.271
H(Si–C–H), CH_3	0.123	F(Si·C·H), CH_3	0.271
H(Cl–C–H)	0.147	F(Cl·C·H)	0.588
H(H–C–H)	0.349	F(H·C·H)	0.200
H(C–Si–Cl)	0.085	F(C·Si·Cl)	0.162
H(C–Si–C)	0.133	F(C·Si·C)	0.040
H(Cl–Si–Cl)	0.059	F(Cl·Si·Cl)	0.290
$Y(Si\text{–}CH_3)$	0.051	$Y(C\text{–}SiCl_2CH_3)$	0.149
$Y(C\text{–}SiCl_3)$	0.143	$Y(C\text{–}SiCl(CH_3)_2)$	0.130

a) The units of the force constants are in md/Å for stretching, K; bending, H; repulsion, F; bond interaction, p; and in md.Å for intramolecular tension, κ; torsion, Y.

follows: V_3 (kcal/mol) $=2.858\times10^{-3}\,\nu^2/(9F)$ or $k=(\partial^2V/\partial\alpha^2)_{\alpha=0}=9/2V_3$, that is, k (md. Å) $=0.03126\ V_3$ (kcal/mol), where F is the reduced rotational constant for internal rotation ($F(SiCl_3)=0.3859\ cm^{-1}$); ν, the observed torsional frequency in cm^{-1}, and k, the torsional force constant.[14)] For TCS, the barrier heights, V_3, calculated from the torsional frequency (68 cm^{-1}) and its force constant (0.143 md. Å) are 3.8 and 4.6 kcal/mol respectively. For the former, the interactions between the torsional vibration and the other vibrations are neglected, while for the latter the kinetic effect of the other vibrations (the **G**-matrix elements between the torsional vibration and the other vibrations) is taken into account. Actually, the potential energy distributions of the skeletal torsion are skeletal tor (79), $SiCl_3$ rock(14), and CH_2 rock(6). The torsional force constants of DCMS and CCDS are 0.149 and 0.130 md.Å, and the barrier heights of $V_3(SiCl_2CH_3)$ and $V_3(SiCl(CH_3)_2)$, assuming a symmetrical-three fold barrier, are 4.8 and 4.2 kcal/mol respectively.

On the other hand, for 1,1,1,2-tetrachloroethane, $V_3(CCl_3)$, has been reported to be 10.2 kcal/mol.[15)] Therefore, the barrier height of V_3 for $ClCH_2SiCl_3$ is considerably smaller than that for $ClCH_2CCl_3$, but is higher than that of the free rotation (*ca.* 0.6 kcal/mol).

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