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Raman and infrared vibrational spectra, ab initio calculations and normal coordinate analyses for 1,2-dimethyltetrachlorodisilane and 1,2-dimethyltetrachlorodisilane- d_6

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Abstract

The Raman spectra of CH₃Cl₂SiSiCl₂CH₃ and CD₃Cl₂SiSiCl₂CD₃ between 3000 and 30 cm⁻¹ have been recorded at various temperatures. The infrared spectra at ambient temperature were recorded from 3000 to 50 cm⁻¹. Both isotopomers exist as a mixture of gauche and anti rotamers at room temperature. The energy difference $E_{anti} - E_{gauche}$ was determined from the Raman spectra as being -0.9 ± 0.2 kJ mol⁻¹ for CH₃Cl₂SiSiCl₂CH₃ and -1.2 ± 0.2 kJ mol⁻¹ for CD₃Cl₂SiSiCl₂CD₃. Assisted by ab initio calculations, the vibrational spectra have been assigned using C_{2h} symmetry for the anti rotamers and C_2 symmetry for the gauche rotamers. Scaled and unscaled harmonic frequencies and harmonic symmetry force constants have been reported for both rotamers, and normal coordinate analyses have been carried out. Potential energy distributions have been reported. © 1997 Elsevier Science B.V.

Keywords: Conformational isomerism; Vibrational spectroscopy; Ab initio calculation; Normal cordinate analysis; Silane

1. Introduction

By analogy with 1,2-disubstituted ethanes it is reasonable to assume that 1,2-disubstituted disilanes will also exist as mixtures of two conformers, gauche and anti. ED studies of HBr₂SiSiBr₂H [1], HI₂SiSiI₂H and H₂ISiSiH₂ [2], Me₂ClSiSiClMe₂ [3] and H₃SiSiH₂SiH₂SiH₃ [4] confirm this expectation. The vibrational spectra of MeH₂SiSiH₂Me have also been interpreted as a superposition of the spectra of both rotamers [5]. Other disilanes that have been studied by vibrational spectroscopy are HBr₂SiSiBr₂H and HI_2SiSiI_2H [6] as well as $Me_3SiSiMe_2SiMe_2SiMe_3$ [7]. In all these cases, two conformers were observed. The variations of the dipole moments of disilanes of the type $Me_2SiXSiXMe_2$ with temperature (X is H, F, Cl, Br, I, OMe, SMe [8]) also supply strong evidence for the existence of two rotamers. Molecular mechanics calculations for the tetramethyldihalodisilanes predict that the anti conformers will be more stable by roughly 1 kcal mol⁻¹ [9].

This work is the first of a series of forthcoming papers dealing with the infrared and Raman vibrational spectra of 1,2-dimethyldisilanes MeX₂Si-SiX₂Me and 1,1,2,2 – tetramethyldisilanes Me₂XSiSiXMe₂ (X is H, F, Cl, Br, I). Conformational

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compositions as well as energy differences between the rotamers will be measured by variable temperature Raman spectroscopy, and ab initio calculations of the vibrational spectra and of the harmonic force fields for anti and gauche rotamers will be reported. The harmonic force fields will be used in normal coordinate analyses for these molecules, including the CD₃ isotopomers.

2. Experimental

2.1. Syntheses

Both $CH_3Cl_2SiSiCl_2CH_3$ and $CD_3Cl_2SiSiCl_2CD_3$ were prepared from the tetraphenyldisilanes $(Ph_2CH_3Si)_2$ and $(Ph_2CD_3Si)_2$, cleaving off the phenyl groups with hydrogen chloride. The tetraphenyldimethyldisilanes were prepared from Ph_2ClSi- SiClPh₂ with CH_3MgBr or CD_3MgBr , respectively.

Chlorosilanes are easily hydrolysed by water. All manipulations were therefore carried out under an atmosphere of dry nitrogen. Solvents were dried over potassium and distilled in an N_2 atmosphere prior to use.

Ph₂CH₃SiSiCH₃Ph₂: To a solution of 5.0 g (11.4 mmol) of (Ph₂ClSi)₂ (prepared according to Ref. [10]) in 50 ml of dry diethyl ether (Et₂O), a solution of 22.8 mmol of CH₃MgBr in 50 ml of dry Et₂O was added dropwise. After completion, the reaction mixture was refluxed for three hours. Toluene (300 ml) was added and all diethyl ether was removed by distillation. The salts were filtered off by suction (Ph₂MeSiSiMePh₂ is not sensitive to air or moisture). After removal of the solvent on a rotavapor, the solid residue of Ph2MeSi-SiMePh₂ was recrystallized twice from a mixture of toluene/n-heptane (1:1). The yield was 3.37 g (75%). The purity of the samples was checked by infrared as well as ²⁹Si NMR spectroscopy (δ (²⁹Si) = -21.6 ppm relative to TMS). Infrared spectra are given in the range $< 1200 \text{ cm}^{-1}$ as nujol mulls.

2.2. Infrared spectra

Ph₂CH₃SiSiCH₃Ph₂: 1188m, 1155m, 1105vs, 1100sh, 1068ms, 1027s, 997s, 977w, 917w, 854w, 787vs, 761vs, 734vs, 715vs, 700s, 662s, 618mw, 475 vs, 464vs, 419vs, 368vs, 291vs.

Ph₂CD₃SiSiCD₃Ph₂: 1189m, 1155m, 1105sh, 1098vs, 1068ms, 1027s, 996 s, 985vs, 975sh, 917w, 858w, 781ms, 760w, 740vs, 726w, 700vs,b, 680 sh, 653w, 639vs, 612vs, 594vs, 546m, 511m, 472vs, 459vs, 408vs, 362vs, 317 w, 279vs

Cl₂CH₃SiSiCH₃Cl₂: Approx. 0.1 g of AlCl₃ was added to a solution of 5.0 g of Ph₂CH₃SiSiCH₃Ph₂ in 20 ml of dry benzene and a constant stream of dry, gaseous HCl was passed through it. The temperature of the reaction mixture rose immediately, and the process was continued until the solution had cooled to room temperature. CH₃Cl₂SiSiCl₂CH₃ was separated by distillation (b.p. 97°C/94 mbar [11]). For CD₃Cl₂SiSiCl₂CD₃, the procedure was identical.

2.3. Spectra

Infrared spectra in the range between 3000 and 250 cm⁻¹ have been measured with a Perkin Elmer 883 spectrometer as films of the pure liquids between CsBr plates. Far-FTIR spectra of the pure liquids have been recorded with a Bruker IFS 66 spectrometer equipped with a $6-\mu m$ mylar beamsplitter between polyethylene plates. The Raman module of the IFS 66 spectrometer was used for recording the Raman spectra ($\lambda_{\text{Nd:YAG}} = 1064 \text{ nm}$, 350 mW). The samples of CH₃Cl₂SiSiCl₂CH₃ and CD₃Cl₂SiSiCl₂CD₃ have been condensed into 1 mm capillary tubes that were sealed under N₂ atmosphere. Low-temperature Raman spectra have been obtained using a variable temperature assembly constructed by Bruker. Cooling is effected by the flow of cold nitrogen gas across the sample. The rate of flow of cold gas is controlled by the amount of current supplied to a heater immersed in liquid nitrogen. The temperature at the 1 mm Raman tube was monitored with a K-type thermocouple.

3. Vibrational spectra

The infrared and Raman spectra of the liquids and the Raman spectra of the solids (173 K) are summarized in Table 1 and selected portions of the Raman spectra are given in Fig. 1 and Fig. 2. Spectra of $CD_3Cl_2SiSiCl_2CD_3$ have not been previously reported in the literature. Infrared spectra of liquid $CH_3Cl_2Si SiCl_2CH_3$ in the range between 3000 and 300 cm⁻¹ have been reported by Höfler [12], as well as Raman

85	
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Table 1
Infrared and Raman spectra (cm ⁻¹)] of CH ₃ Cl ₂ SiSiCl ₂ CH ₃ and CD ₃ Cl ₂ SiSiCl ₂ CD

CH ₃ Cl ₂ SiSiCl ₂ C	H ₃		CD ₃ Cl ₂ SiSiCl ₂ CD ₃			
Ir (l)	Ra (l)	Ra (s)	Ir (l)	Ra (l)	Ra (s)	
2976 mw	2978 vs	2978 m	2230 vw	2229 s	2229 vs	
2906 mw	2903 s,p 2784 vw	2901 s 2784 w	2120 w	2121 vs	2119 vs	
1986 m	270111	2701 11		1974 w	1973 mw 1603 w	
					1584 mw	
				1174 vvw	1174 mw	
			1035 mw			
1400 vs	1403 m	1406 m 1399 m	1019 ms	1021 w 978 s	1021 m 978 s	
1256 vs	1255 w	1254 mw	997 s	990 s	990 s	
			980 w,sh	985 vw	982 vw	
					852 vvw	
949			775 w			
646 W		701	705 1	700	711	
789 VS		/81 VW	705 sn	708 m	/11 8	
/65 VS		750 1				
701	540 1	750 sh	<i>(</i> 7 <i>(</i>)	<i></i>	<i>cco</i>	
731 vs	743 m,b	745 m	6/6 vs	665 w,b	668 ms	
			642 vs		628 w	
		700	610 s			
	680 vvw	680 vvw	602 s		605 w	
	565 m	561 m	550 sh	552 vw	552 w	
550 vvs,b	545 m		532 vs	536 m		
	535 m	535 m	100.1	520 ms	520 vs	
477vs			480 sh			
466 vs			462 vs			
200	388 vs,p	390 vs		3/3 vs,p	375 vs	
380 ms	382 vs,p	2.42	366 mw	366 vs,p	2.50	
2.42	363 vw	363 vw	355w	357 m	359 m	
243vs	245 vvw		234s	236 vw	236 vw	
22 01	00 / 1	231 vs	224s	225 m	225 vs	
228sh	226 m,b	225 s	215sh	216 m	216 w	
195sh	190 mw,b			203 m	206 vs	
181s	165 s	170 s 165 sh	177s	178 m		
145w	141 s	144 s		150 vs	151 vs	
	133 s	133 s		135 vs	138 vs	
			128 mw		133 vs	
94w					120 m	
	85 w	85 vw		84 w,b	90 w	

spectra from 3000 to 70 cm⁻¹, but no hint of the existence of rotational isomerism has been mentioned. The wavenumbers reported by Höfler agree with ours within ± 3 cm⁻¹ in most cases.

1,2-Dimethyltetrachlorodisilane and its d_6 isotopomer have 14 atoms with 36 fundamental vibrations. The molecular symmetry will be C_{2h} or C_2 if the two SiC bonds are in the anti or in gauche position, respectively (Fig. 3).

The distribution of the normal modes between the symmetry species as well as the IR and Raman activities will be

$$C_{2h}$$
: $\Gamma = 11A_g(Ra; p) + 7B_g(Ra) + 8A_u(IR) + 10B_u(IR)$



800 775 750 725 700 675 650 625 600 575 550 525 500 475 450 425 400 375 350 325 300 275 250 225 200 175 150 125 100 Fig. 1. Raman spectrum of solid (173 K) and liquid (298 K) CH₃Cl₂SiSiCl₂CH₃.

C_2 : $\Gamma = 19A(IR, Ra, p) + 17B(IR, Ra)$

The spectra of the anti rotamer will follow the rule of mutual exclusion, as the molecule has an inversion centre. For the gauche rotamer, all fundamentals are allowed to be infrared- and Raman-active. The numbering of the fundamentals is included in Table 3, Table 4, Table 5 and Table 6.

Because of the small mass of the H atom, ν_{as} , ν_s , δ_{as} and $\delta_s CH_3/CD_3$ constitute genuine group vibrations that are easily recognised and assigned. They will not be discussed further, as our interest focuses on the vibrations and force constants of the CSiCl₂Cl₂-SiC skeleton. As can be seen from the potential energy distributions (see Section 6), ρCH_3 vibrations are also group vibrations, but ρCD_3 vibrations are not. The rocking fundamentals are therefore regarded as being partially skeleton vibrations. SiCH₃ rocking vibrations usually fall into the range between 850 and 760 cm⁻¹ and are shifted by approx. 150–170 cm⁻¹ upon isotopic substitution [13]. SiCD₃ rocking vibrations are thus expected to be between 600 and 700 cm⁻¹.

For CH₃Cl₂SiSiCl₂CH₃, the ρ CH₃ vibrations lie well above the SiC stretching modes. The strong IR absorptions at 765 and 789 cm⁻¹ (Ra: 781 cm⁻¹) are thus assigned as the rocking fundamentals, and the strong bands at 731 cm⁻¹ (IR) and 745 cm⁻¹ (Ra) as the SiC stretching modes. For the d₆ isotopomer, ν SiC is at 665 cm⁻¹ (Raman) and 676 cm⁻¹ (IR). The ρ CD₃ fundamentals, which are kinetically coupled with SiC stretching modes if they belong to the same irreducible representation (see Section 6), are lower in energy. They gain Raman intensity because of the vibrational coupling. Four strong IR absorptions at 676, 642, 610 and 602 cm⁻¹ as well as three Raman



Wavenumber cm⁻¹

Fig. 2. Raman spectrum of solid (173 K) and liquid (298 K) CD₃Cl₂SiSiCl₂CD₃.

lines at 711, 628 and 605 cm⁻¹, are assigned as ρ CD₃ modes. Even with the help of the ab initio calculations, no unambigous assignment of the ρ CD₃ modes is possible.

The SiCl and SiSi stretching modes of chlorinated disilanes usually lie between 350 and 600 cm⁻¹. A striking feature of these molecules is the strong kinetic coupling between ν SiSi and ν SiCl_n modes, as observed for instance for Si₂Cl₆ [14]. ν SiSi is shifted to higher, ν SiCl_n to lower wavenumbers. A simplified normal coordinate analysis for CH₃Cl₂SiSiCl₂CH₃ [12] yielded the result that the Raman lines at 388 cm⁻¹ and 565 cm⁻¹ have to be described as a 50:50 mixture of ν SiSi (A_g) and ν _sSiCl₂ (A_g). Three Raman-active stretching modes (ν SiSi (A_g), ν _sSiCl₂ (A_g), and ν _{as}SiCl₂ (B_g)) are expected for the anti

rotamer and five for the gauche conformer. In the liquid, five Raman bands are observed, and two of them disappear completely in the solid state. Assisted by ab initio calculations, the three persisting bands at 561, 535 and 390 cm⁻¹ are assigned as belonging to the anti rotamer. The two disappearing bands at 545 and 382 cm⁻¹ then clearly belong to the gauche conformer (see Section 4).

For the anti conformer, five Raman-active and five IR-active deformation modes involving the heavy atoms are predicted. For the gauche rotamer, all ten deformations are allowed to be Raman- and IR-active. As can be seen from Fig. 1 and Fig. 2, five strong Raman bands are observed in the solid state for $CH_3Cl_2SiSiCl_2CH_3$ and also for its d_6 isotopomer (h_6 : 231, 225, 170, 144 and 133 cm⁻¹; d_6 : 225, 206,

87



Fig. 3. Newman projection of anti and gauche 1,2-dimethyltetrachlorodisilane.

151, 138 and 133 cm⁻¹). They are assigned as belonging to the anti rotamers.

Methyl torsional modes are expected to give bands with rather small intensities around 150 cm^{-1} . They have not been observed because of their small intensities, as was also the case with the SiSi torsion.

4. Rotational isomerism

The variations in the intensity ratios of the Raman bands at 388/382 cm⁻¹ (CH₃Cl₂SiSiCl₂CH₃) and at $373/366 \text{ cm}^{-1}$ (CD₃Cl₂SiSiCl₂CD₃) with temperature have been used to determine the energy differences between the anti and gauche conformers using the van't Hoff's equation. The bands at 388 and 373 cm⁻¹ belong to the anti conformers, those at 382 and 366 cm⁻¹ to the gauche conformers. As can be clearly seen from Fig. 1 and Fig. 2, the anti conformer is more stable.

In Fig. 4 and Fig. 5, the logarithms of the intensity ratios (as determined from deconvolutions of the bands) are plotted against the reciprocal temperature, giving energy differences $E_{anti} - E_{gauche}$ of -0.9 ± 0.2 kJ mol⁻¹ and -1.2 ± 0.2 kJ mol⁻¹ for the h₆ and d₆ isotopomers, respectively. The two values agree satisfactorily within the error limits of ± 0.2 kJ mol⁻¹. They are considerably smaller than the ΔE values calculated with empirical force field methods (-1.23 kcal $\text{mol}^{-1} = -5.15 \text{ kJ mol}^{-1}$ [9])

5. Ab initio calculations

The ab initio calculations that have been performed during this work are part of a series of studies of methylated disilanes MeX₂SiSiX₂Me and Me₂XSi-SiXMe₂ (X is H, F, Cl, Br and I). To make the entire series feasible from the viewpoint of computational cost, a fairly simple computational scheme was used throughout. The core electrons of all heavy atoms





Fig. 5. Logarithm of the intensity ratio of the Raman bands at 373 and 366 cm⁻¹ of CD₃Cl₂SiSiCl₂CD₃ as a function of reciprocal temperature.

were represented by an effective core potential (ECP); the ECPs for Br and I are relativistic ECPs. The ECPs and basis sets use the parameters fitted by Stevens et al. [15]. A valence double-zeta basis with polarisation functions on all atoms was used. Geometries were optimised on the level of RHF calculations; the harmonic frequencies at the equilibrium positions were also obtained at the RHF level.

The calculated ab initio structural parameters of anti and gauche CH₃Cl₂SiSiCl₂CH₃ are summarised in Table 2. As was pointed out in [16] for ClSi₂H₅, a chlorine substitution into Si2H6 influences the frequency of the SiH bonds gauche to the chlorine atom, but has no effect on the SiH bond in the trans position. The same gauche effect is observed with 1,2dimethyltetrachlorodisilane. For the gauche rotamer, the SiCl bonds that have two Cl atoms in the gauche position (see Fig. 3) are shorter by 1.09 pm than the SiCl bonds that have one Cl atom in the anti and one in the gauche position. In the anti conformer, the SiCl bond length is in between the two values for the gauche conformation. A small effect is also calculated for the SiC bond lengths. Anti CH₃Cl₂Si-SiCl₂CH₃, with two chlorine atoms gauche to the SiC bond, possesses the smaller silicon carbon bond distance.

Table 3, Table 4, Table 5, Table 6 give the calculated and observed fundamental vibrations of anti and gauche CH₃Cl₂SiSiCl₂CH₃ and CD₃Cl₂SiSiCl₂CD₃. A single scale factor of 0.92 was used for all compounds and all vibrations. Potential energy distributions (see Section 6) were calculated by transforming the ab initio force field defined in cartesian coordinates into a force field defined with symmetry coordinates. As the calculated CSiSiC torsion angle of the anti conformer is 179.23°, the point group C_{2h} was used for the construction of the symmetry coordinates. According to the correlation tables, A_g and A_u vibrations of point group C_{2h} combine into A type vibrations of point group C_2 .

$$C_{2h}$$
 C_2
 $A_{v} \rightarrow A$

$$B_{\rho} \rightarrow B$$

- $A_u \rightarrow A$
- $B_u \rightarrow B$

Table 2

Parameter	anti CH ₃ Cl ₂ SiSiCl ₂ CH ₃	gauche CH ₃ Cl ₂ SiSiCl ₂ CH ₃
r(SiSi)	237.05	237.38
r(SiC)	187.05	187.29
r(SiCl)	207.53	206.62 ^a ; 207.71 ^b
r(CH)	109.88	109.93; 109.88; 109.87
∠SiSiC	115.50	114.08
∠SiSiCl	107.38	109.50 ^a ; 106.94 ^b
∠ClSiCl	107.53	108.25
∠CSiCl	109.44	109.16 ^a ; 108.75 ^b
∠CSiSiC	179.23	69.34
∠ClSiSiCl	64.01; 179.34	45.35; -71.72
∠ClSiSiCl		- 71.72; 171.21
∠HCSi	110.27; 109.93	110.57; 109.92; 110.27
∠HCH	108.90; 108.73	108.48; 108.85; 108.69

Structural parameters (pm, deg.) for anti and gauche CH₃Cl₂SiSiCl₂CH₃

^aBond distance and bond angle with two Cl atoms in the gauche position.

^bBond distance and bond angle with one Cl atom in the gauche and one in the trans position.

Identical symmetry coordinates were therefore used for the gauche conformer.

by them can be obtained from the authors upon request.

6. Normal coordinate analysis

Normal coordinate analyses (NCA) were performed for both anti and gauche MeCl₂SiSiCl₂Me using the FG-formalism [17]. The cartesian coordinates obtained for the optimized geometries were input into the G-matrix program, together with a set of 37 internal coordinates (bond lengths and bond angles). Torsional coordinates were omitted from the calculations. The 37 internal coordinates were used to form symmetry coordinates. With the symmetry force constants obtained from ab initio calculations, the pure ab initio frequencies were reproduced to within ± 1 cm⁻¹, the small deviations being attributed to rounding errors and to the neglect of the torsional vibrations.

The calculated potential energy distributions are presented in Tables 3–6. As was expected from a previous simplified NCA [12], strong vibrational coupling occurs between SiSi and SiCl stretching modes, but also within the skeletal deformational modes. Upon isotopic substitution, ρ CD₃ modes become involved in the coupling patterns.

Detailed tables of the symmetry coordinates that have been used and of the force fields defined

7. Discussion

For disilanes, energy differences between conformers are of the order $\approx 0-10 \text{ kJ mol}^{-1}$, with the set of available experimental data being very small. Table 7 summarises experimental ΔE values that have been reported so far. Obviously, ED experiments do not allow ΔE values to be obtained with any accuracy, and no estimated error limits are given for the dipole moment measurements. Therefore, the only reliable ΔE values are derived from vibrational spectroscopy. For both molecules that have been investigated by temperature-dependent Raman spectroscopy, the anti conformers are more stable. This contradicts the "gauche effect" [18] stating that the more stable structure is the one which has the maximum number of gauche interactions between adjacent electron pairs and/or polar bonds. As SiCl bonds are more polar than SiC bonds, and SiC bonds are more polar than SiSi bonds, the gauche structures are predicted to be more stable because they possess three gauche interactions between the most polar bonds (Fig. 6).

However, the results of the dipole moment measurements (Table 7) are in accordance with the

Species	Vibr. no.	Description	Ab initio		Obs.	PED
			Unscaled	Scaled		
A _g (Ra)	ν_1	$\nu_{\rm as} CH_3$	3281.8	3019	2978	100(1)
5	ν_2	$\nu_{\rm s} \rm CH_3$	3185.6	2931	2903	100(2)
	ν_3	$\delta_{as}CH_3$	1543.2	1420	1403	94(3)
	ν_4	$\delta_{s}CH_{3}$	1399.6	1288	1255	100(4)
	ν_5	$ ho CH_3$	891.9	821	-	75(5)
	ν_6	νSiC	778.7	716	745	85(6)
	ν_7	νSiSi	404.9	372	388	32(7),38(8),21(9)
	ν_8	$\nu_{s}SiCl_{2}$	596.1	548	565	56(8),11(5),35(7)
	ν_9	δSiSiC	165.7	152	170	36(9),16(5),11(7),55(11)
	ν_{10}	δSiCl ₂	134.4	124	133	51(10),13(7),22(9),20(11)
	ν_{11}	$\gamma SiCl_2$	246.3	227	231	31(11),17(9),37(10)
$B_{g}(Ra)$	ν_{12}	$\nu_{\rm as} CH_3$	3282.5	3020	2978	100(12)
U	ν_{13}	$\delta_{as}CH_3$	1543.5	1420	1403	94(13)
	ν_{14}	ρCH_3	863.7	795	781	85(14)
	ν_{15}	$\nu_{\rm as} {\rm SiCl}_2$	574.8	529	535	105(15)
	ν_{16}	$\rho SiCl_2$	229.4	211	225	92(16),17(14)
	ν_{17}	$\tau SiCl_2$	146.1	134	144	99(17)
	ν_{18}	CH ₃ torsion	167.7	154	-	_
$A_u(IR)$	ν_{19}	$\nu_{\rm as} CH_3$	3281.8	3019	2976	100(19)
	ν20	$\delta_{as}CH_3$	1542.5	1419	1400	94(20)
	ν21	ρCH_3	864.7	796	789	84(21)
	ν_{22}	$\nu_{\rm as} {\rm SiCl}_2$	587.2	540	550	100(22)
	ν_{23}	$\rho SiCl_2$	203.1	187	195	45(23),21(21),38(24)
	ν_{24}	$\tau SiCl_2$	70.1	64	-	72(24),67(23)
	ν_{25}	CH ₃ torsion	166,8	153	-	_
	ν_{26}	SiSi torsion	23.9	22	-	_
B _u (IR)	ν_{27}	$\nu_{\rm as} CH_3$	3282.5	3020	2978	100(27)
	ν_{28}	$\nu_{\rm as} CH_3$	3185.3	2930	2903	100(28)
	ν_{29}	$\delta_{as}CH_3$	1543.0	1420	1403	94(29)
	ν_{30}	δCH_3	1398.3	1286	1255	100(30)
	ν_{31}	ρCH_3	841.5	774	765	85(31)
	ν_{32}	νSiC	766.5	705	731	87(32)
	ν_{33}	$\nu_s SiCl_2$	501.0	461	466	94(33)
	ν_{34}	δSiSiC	257.8	237	243	66(34),14(31),11(35)
	ν_{35}	δSiCl ₂	193.8	178	181	85(35),11(34)
	ν_{36}	$\gamma SiCl_2$	87.9	81	-	99(36),30(34)

Table 3 Observed and calculated wave numbers and potential energy distributions (> 10%) for anti CH₃Cl₂SiSiCl₂CH₃

concept of the "gauche effect", as the anti conformation seems to be successively stabilised with increasing mass of the halogen atom (and decreasing polarity of the SiX bond). Unfortunately, the number of accurate experimental data is far too small to deduce any systematic trends.

The force constants of the gauche conformer do not differ very much from those of the anti conformer. The SiSi stretching force constants (2.00 N cm⁻¹ for anti, 1.99 for gauche 1,2-dimethyltetrachlorodisilane, unscaled) are identical, but considerably smaller than

the values predicted by normal coordinate analyses. For Si_2Cl_6 and for Si_2Me_6 , 2.40 N cm⁻¹ [14] and 1.65 N cm⁻¹ [19] are reported in the literature. A linear interpolation between these two values gives an estimated SiSi force constant of 2.15 N cm⁻¹ for MeCl₂SiSiCl₂Me, which compares with a scaled (0.92) ab initio force constant of 1.69 N cm⁻¹. In a recent RHF/6-31G* calculation for Si_2Me_6 [20], a SiSi stretching force constant of 1.303 was reported, which is also considerably smaller than the value obtained from the NCA. For disilane, Si_2H_6 , however,

Species	Vib. no.	Description	Ab initio			PED
			Unscaled	Scaled	Obs.	
Ag	ν_1	$\nu_{\rm as} \rm CD_3$	2431.9	2237	2229	100(1)
0	ν_2	$\nu_{\rm s} \rm CD_3$	2287.4	2104	2121	100(2)
	ν_3	$\delta_{as}CD_3$	1114.8	1026	1021	85(3)
	ν_4	$\delta_s CD_3$	1108.1	1019	1021	78(4),20(6)
	ν_5	ρCD_3	750.6	691	708	33(5),17(6),20(7)
	ν_6	νSiC	708.7	652	665	50(6),10(4),17(5),18(8)
	ν_7	νSiSi	389.4	358	366	33(7),11(6),34(8),17(11)
	ν_8	$\nu_s SiCl_2$	556.9	512	520	48(8),33(5),22(7)
	ν_9	δSiSiC	148.5	137	150	56(9),22(5),35(11)
	ν_{10}	δSiCl ₂	134.3	124	135	52(10),12(7),24(9),19(11)
	ν_{11}	$\gamma SiCl_2$	239.7	221	225	22(11),24(9),41(10)
Bg	ν_{12}	$\nu_{\rm as} CD_3$	2431.9	2237	2229	100(12)
5	ν_{13}	$\delta_{as}CD_3$	1113.6	1024	1021	96(13)
	ν_{14}	ρCD_3	692.9	638	628	67(14),18(15),12(16)
	ν_{15}	$\nu_{\rm as} {\rm SiCl}_2$	556.7	512	520	90(15),15(14)
	ν_{16}	$\rho SiCl_2$	212.8	196	203	94(16),20(14)
	ν_{17}	$\tau SiCl_2$	142.1	131	120	102(17)
	ν_{18}	CD ₃ torsion	119.9	110	_	_
A _u	ν_{19}	$\nu_{\rm as} CD_3$	2432.1	2238	2230	100(19)
	ν20	$\delta_{as}CD_3$	1113.4	1024	1035	96(20)
	ν21	ρCD_3	695.5	640	642	64(21),21(22)
	ν_{22}	$\nu_{as}SiCl_2$	566.8	521	532	82(22),19(21)
	ν_{23}	$\rho SiCl_2$	181.2	167	177	44(23),28(21),40(24)
	ν_{24}	$\tau SiCl_2$	69.4	64	-	72(24),68(23)
	ν_{25}	CD ₃ torsion	117.3	108	_	_
	ν_{26}	SiSi torsion	23.2	21	-	_
B _u	ν_{27}	$\nu_{\rm as} CD_3$	2432.4	2238	2230	100(27)
	ν_{28}	$\nu_{\rm s} \rm CD_3$	2287.6	2105	2120	100(28)
	ν_{29}	$\delta_{as}CD_3$	1114.1	1025	1035	92(29)
	ν_{30}	$\delta_s CD_3$	1106.2	1018	1019	85(30)
	ν_{31}	δCD_3	656.8	604	602	79(31)
	ν_{32}	νSiC	709.1	652	676	68(32),12(30)
	ν_{33}	$\nu_{s}SiCl_{2}$	490.8	452	462	87(33),10(32)
	ν_{34}	δSiSiC	80.6	74	_	101(34),25(36)
	ν_{35}	δSiCl ₂	191.2	176	177	79(35),17(36)
	ν_{36}	$\gamma SiCl_2$	240.0	221	224	62(36),16(35)

Table 4 Observed and calculated wave numbers and potential energy distributions (> 10%) for anti CD₃Cl₂SiSiCl₂CD₃

values for the SiSi stretch obtained by normal coordinate analyses agree very well with those calculated at the MP2/6-31G** level. The differences are of the order of 0.07–0.14 N cm⁻¹ [20], which is a much better correlation and must be attributed to the inclusion of configuration interactions. The ab initio calculations do, however, predict an increase in the SiSi stretching force constants in the series Si₂Me₆ < Si₂H₆ < Si₂Me₆ < Si₂H₆ < Si₂Me₂Cl₄, paralleling the results of normal coordinate analyses [21].

SiCl stretching force constants are different for the

two conformers, reflecting the gauche effect. For gauche 1,2-dimethyltetrachlorodisilane, the force constants of the SiCl bonds that have two adjacent gauche SiCl bonds (these will be called "inner" bonds further on, compare Fig. 6) are 2.65 N cm⁻¹ (scaled by 0.92), whereas the value for the "outer" bonds is 2.55 N cm⁻¹. The inner bonds are also shorter by 1.09 pm (Table 2). The interaction force constants f(SiCl/SiCl) (same Si atom) are identical (0.144 and 0.142 for anti and gauche, respectively), as are all interactions separated by the SiSi bond (0.04 N cm⁻¹).

Species	Vib. no.	Description	Ab initio			PED
			Unscaled	Scaled	Obs.	
A	ν_1	$\nu_{\rm as} CH_3$	3281.4	3019	2978	75(1),25(3)
	ν_2	$\nu_{as}CH_3$	3274.3	3012	2978	75(2),25(1)
	ν_3	$\nu_{s}CH_{3}$	3182.7	2928	2903	100(3)
	ν_4	δ _{as} CH ₃	1542.1	1419	1403	88(4)
	ν_5	$\delta_{as}CH_3$	1546.0	1422	1403	88(5)
	ν_6	δ _s CH ₃	1400.8	1289	1255	100(6)
	ν_7	ρCH ₃	881.9	811	789	71(7)
	ν_8	ρCH_3	861.6	793	765	83(8)
	ν ₉	νSiC	768.7	707	743	86(9)
	ν_{10}	ν_{as} SiCl ₂	578.2	532	545	84(10),13(12)
	ν_{11}	νSiSi	397.4	366	382	35(11),38(12),16(15)
	ν_{12}	$\nu_s SiCl_2$	609.8	561	565	42(12),20(10),28(11)
	ν_{13}	δSiSiC	81.5	75	85	83(13)
	ν_{14}	δSiCl ₂	197.7	182	190	44(14),12(15),19(16),27(17)
	ν_{15}	$\gamma SiCl_2$	164.9	152	165	25(15),13(7),14(11),40(13)
	ν_{16}	$\rho SiCl_2$	235.7	217	226	54(16),17(14)
	ν_{17}	$\tau SiCl_2$	139.3	128	133	40(17),32(14),11(15)
	ν_{18}	CH ₃ torsion	171.7	158	_	_
	ν_{19}	SiSi torsion	21.0	19	_	_
В	ν_{20}	$\nu_{\rm as} CH_3$	3281.3	3019	2978	64(20),35(21)
	ν_{21}	$\nu_{as}CH_3$	3275.5	3013	2978	64(21),36(20)
	ν_{22}	$\nu_{\rm s} CH_3$	3182.9	2928	2903	100(22)
	V 23	δ _{as} CH ₃	1544.8	1421	1403	76(23),18(24)
	ν_{24}	$\delta_{as}CH_3$	1542.7	1419	1403	76(24),18(23)
	ν_{25}	δ _s CH ₃	1398.4	1287	1255	100(25)
	ν_{26}	ρCH_3	863.2	794	789	77(26)
	ν_{27}	ρCH_3	849.9	782	789	80(27)
	ν_{28}	νSiC	764.6	703	743	88(28)
	ν_{29}	ν_{as} SiCl ₂	589.2	542	545	100(29)
	ν_{30}	$\nu_{s}SiCl_{2}$	501.4	461	477	94(39)
	ν_{31}	δSiSiC	149.2	137	133	52(31),43(32),13(35)
	ν_{32}	δSiCl ₂	239.4	220	226	34(32),24(31),20(34)
	ν_{33}	$\gamma SiCl_2$	263.5	242	245	88(33)
	ν_{34}	ρ SiCl ₂	202.8	187	190	34(34),17(26),36(35)
	ν_{35}	$\tau SiCl_2$	75.5	69	_	62(35),30(31),53(34)
	ν_{36}	CH ₃ torsion	172.6	159	_	_

Table 5 Observed and calculated wave numbers and potential energy distributions (> 10%) for gauche CH₂Cl₂SiSiCl₂CH



Fig. 6. Newman projection of gauche $MeCl_2SiSiCl_2Me$ (left) and gauche $Me_3SiMe_2SiSiMe_2SiMe_3$ (right) with the gauche interactions indicated by arrows.

Species	Vib. no.	Description	Ab initio			PED
			Unscaled	Scaled	Obs.	
A	ν_1	$\nu_{\rm as} \rm CD_3$	2432.5	2238	2229	71(1),30(2)
	ν_2	$\nu_{\rm as} \rm CD_3$	2426.2	2232	2229	70(2),30(1)
	ν_3	$\nu_{s}CD_{3}$	2286.0	2103	2121	100(3)
	ν_4	$\delta_{as}CD_3$	1115.4	1026	1021	48(4),28(5),17(6)
	ν_5	$\delta_{as}CD_3$	1116.2	1027	1021	67(5),19(4)
	ν_6	$\delta_s CD_3$	1106.6	1018	1021	62(6),29(4)
	ν_7	ρCD_3	748.9	689	708	30(7),20(9),20(11)
	ν_8	ρCD_3	697.3	642	642	55(8),16(109
	ν_9	νSiC	696.5	641	642	42(9),12(5),19(12)
	ν_{10}	$\nu_{\rm as} {\rm SiCl}_2$	572.3	527	552	52(10),15(8),12(12)
	ν_{11}	νSiSi	381.9	351	373	37(11),33(12)
	ν_{12}	ν_{s} SiCl ₂	550.8	507	520	31(12),25(7),33(10),13(11)
	ν_{13}	δSiSiC	78.3	72	84	73(13),26(15),28(16),25(17)
	ν_{14}	δSiCl ₂	184.9	170	178	37(14),35(16),19(17)
	ν_{15}	$\gamma SiCl_2$	149.3	137	135	31(15),16(7),14(11),30(13)
	ν_{16}	$\rho SiCl_2$	225.4	207	216	48(16),28(14),11(15)
	ν_{17}	$\tau SiCl_2$	136.9	126	135	49(17),28(14),11(15)
	ν_{18}	CD ₃ torsion	121.7	112	-	_
	ν_{19}	SiSi torsion	29.4	27	-	_
В	ν_{20}	$\nu_{\rm as} CD_3$	2432.6	2238	2229	62(20),38(21)
	ν_{21}	$\nu_{\rm as} \rm CD_3$	2426.7	2233	2229	63(21),39(20)
	ν_{22}	$\nu_{s}CD_{3}$	2286.1	2103	2121	100(22)
	ν_{23}	$\delta_{as}CD_3$	1112.8	1024	1021	56(23),38(24)
	ν_{24}	$\delta_{as}CD_3$	1113.4	1024	1021	57(24),35(23)
	ν_{25}	$\delta_s CD_3$	1107.5	1019	1021	83(25),20(28)
	ν_{26}	ρCD_3	668.2	615	610	75(269
	ν_{27}	ρCD_3	694.6	639	642	51(27),10(28),19(29)
	ν_{28}	νSiC	704.4	648	642	59(28),12(25),10(30)
	ν_{29}	$\nu_{\rm as} {\rm SiCl}_2$	567.8	522	536	80(29),21(27)
	ν_{30}	$\nu_s SiCl_2$	490.8	451	462	88(30)
	ν_{31}	δSiSiC	141.0	130	135	52(31),34(32),20(35)
	ν_{32}	δSiCl ₂	229.2	211	203	49(32),20(31),10(34)
	ν_{33}	$\gamma SiCl_2$	250.4	230	236	88(33)
	ν_{34}	$\rho SiCl_2$	184.2	169	178	41(34),24(27),13(32),31(35)
	ν_{35}	$\tau SiCl_2$	73.5	68	_	58(35),35(31),52(34)
	ν_{36}	CD ₃ torsion	121.7	112	_	_

Table 6 Observed and calculated wave numbers and potential energy distributions (> 10%) for gauche CD₃Cl₂SiSiCl₂CD₃

Neither their absolute value nor their sign depends on the dihedral angle between the two SiCl bonds. The SiC stretching force constants are also slightly influenced by the molecular conformations, as the values for the trans rotamer (two adjacent SiCl bonds in the gauche position) and for the gauche rotamer are 2.789 and 2.806 N cm⁻¹, respectively.

The SiCl force constants calculated by the ab initio method used in this work are also considerably smaller than values deduced from normal coordinate analyses (Si₂Cl₆: 2.90 [14], Si₃Cl₈: 2.80 [22]), but this

is not the case for the SiC force constants. For hexamethyldisilane, Höfler [19] gave a value of 2.88 N cm^{-1} , and for octamethyltrisilane, 290 N cm^{-1} was reported [23]. The poor correlation for the SiCl force constants and the much better one for the SiC force constants is again caused by the neglect of configuration interactions, as their inclusion should cause a shortening of the SiCl bond. Atomic distances for single bonds between two second row elements are usually calculated too long when configuration interactions are neglected [24], whereas single bonds

Table 7	
Energy differences $E_{anti} - E_{gaugha}$	(kJ mol ⁻¹) between anti and gauche conformations of disilanes

Molecule	ΔE	Method	
Br ₂ HSiSiHBr ₂	-2.09 ± 2.51	ED [1]	
I2HSiSiHI2	-0.84 ± 2.51	ED [2]	
IH ₂ SiSiH ₂ I	1.25 ± 2.51	ED [2]	
H ₃ SiSiH ₂ SiH ₂ SiH ₃	0.2 ± 1.1	ED [6]	
MeCl ₂ SiSiCl ₂ Me	-1.05 ± 0.2	Ra, this work	
	- 2.50	Dipole moment [8]	
Me ₂ ClSiSiClMe ₂	2.51 ± 2.09	ED [3]	
	- 2.17	Dipole moment [8]	
Me ₂ FSiSiFMe ₂	- 2.09	Dipole moment [8]	
Me ₂ BrSiSiBrMe ₂	- 4.16	Dipole moment [8]	
Me ₂ ISiSiIMe ₂	- 6.54	Dipole moment [8]	
Me ₂ (MeO)SiSi(OMe)Me ₂	- 10.15	Dipole moment [8]	
Me ₂ (MeS)SiSi(SMe)Me ₂	- 2.93	Dipole moment [8]	
$Me_{3}SiSiMe_{2}SiMe_{2}SiMe_{3}$	-2.26 ± 0.15	Ra [7]	

involving first row elements tend to lengthen when these interactions are included.

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