J. Phys. Chem. A **1997,** *101,* 9641−9649 **9641**

Perchlorovinylsilane ($Cl_2C{=}CCl{-}SiCl_3$): Conformational Structure, Vibrational Analysis, and Torsional Potential Determined by Gas-Phase Electron Diffraction, ab Initio Calculations, and Variable Temperature Raman Spectroscopy

Tore H. Johansen,*,† Kolbjørn Hagen,† Karl Hassler,‡ Alan Richardson,§ Uwe Pätzold,‡ and Reidar Stølevik†

Department of Chemistry, Norwegian University of Science and Technology, NTNU, N-7034 Trondheim, Norway, Institut für Anorganische Chemie, Technische Universität Graz, Stremayrgasse 16, A-8010 Graz, Austria, and Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

Received: May 21, 1997; In Final Form: October 1, 1997⊗

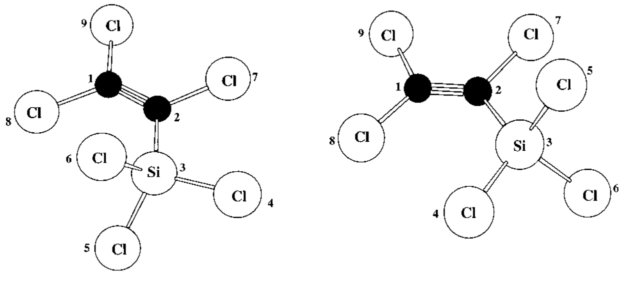
The molecular structure, conformation, vibrational spectra, and torsional potential of perchlorovinylsilane (PCV), $Cl_2C{=}CCl{-}SiCl_3$, have been studied by using gas-phase electron diffraction (GED) data at 100 °C and variable temperature Raman spectroscopy, together with ab initio molecular orbital calculations. The GED data were treated by using a dynamic theoretical model. This involves fitting a chosen two-term potential function to the experimental data, thereby obtaining values for both a 3-fold and a 6-fold potential constant (V_3 and V_6) in the series $V(\phi) = {}^1/_2\Sigma_i V_i[1 - \cos i(180-\phi)]$, where ϕ is the value of the torsional angle CCSiCl. According to the GED refinements, this molecule exists in the gas phase at 100 °C as a mixture of two minimum-energy conformers, syn (torsional angle ϕ(CCSiCl) = 0° or 120°) and anti (torsional angle ϕ(CCSiCl) = 180°), where the anti form predominates, occupying approximately 80% of the gas composition. Relevant structural parameters are as follows (anti): Bond lengths (r_g): r(Si−C) = 1.863(13) Å, $r\langle$(Si−Cl)$\rangle$ = 2.020(3) Å (average value), r(C=C) = 1.349(12) Å. Bond angles ($\angle_\alpha$): $\angle\langle$CSiCl$\rangle$ = 111.1(15)°, $\angle$CCSi = 124.0(12)°. Error limits are given as 2σ (σ includes estimates of uncertainties in voltage/height measurements and correlation in the experimental data). The estimated experimental conformational energy difference obtained from GED is $\Delta E°_{A-S} = -1.04(\pm 0.58)$ kcal/mol, based on the refined value of the V_3 potential constant. From the variable temperature Raman study, two corresponding energy differences obtained from two separate pairs of doublets in the liquid phase are $\Delta E°_{A-S} = -0.30(1)$ and $\Delta E°_{A-S} = -0.43(5)$ kcal/mol. The ab initio value (HF/6-31G(d)) was $\Delta E°_{A-S} = -1.43$ kcal/mol. All results suggest that anti is the low-energy form. Full geometry optimizations were performed for seven pseudoconformers (including 120° and 180° forms), which were employed in the dynamic GED model, by using the ab initio MO HF/6-31G(d) level of theory. Scaled HF zero-point vibrational energy corrections were estimated from frequency calculations. The theoretical results are compared with experimental observations.

Introduction

We have recently studied the structures and conformational properties of the methylvinyldifluorosilane and methylvinyldichlorosilane molecules, $H_2C{=}CH{-}SiX_2{-}CH_3$ (X = F, Cl), by gas-phase electron diffraction (GED).[1] It was established that these molecules exist as a two-conformer mixture in the gas phase, one where the methyl-group eclipses the planar vinyl group (syn), and one where the halogen atom eclipses the vinyl group (gauche). This seems to be the usual behavior when there is no halogen substitution on the planar vinyl group.[1]

In a more fully halogenated molecule, the conformational properties may change substantially. Our continuing interest in the structure and conformation of vinylsilanes has therefore led us to investigate a molecule that should exhibit quite different conformational behavior, the perchlorovinylsilane molecule; $Cl_2C{=}CCl{-}SiCl_3$ (PCV, Figure 1).

The understanding of the conformational behavior of a vinylsilane of this type may be improved by studying the properties of the alkene analogues, since there are very few halogenated vinylsilanes studied in the past. However, a large number of halogensubstituted propenes have been investigated by GED, and their structure and conformational compositions have been determined.[2] Also, a complete ab initio investigation of the chlorosubstituted propenes at the HF/6-31G(d) level of theory has been carried out by our group.[3]



Anti **Syn**

Figure 1. Molecular models of anti and syn conformers of perchlorovinylsilane showing the atom numbering.

The main conclusion in the ab initio study[3] is that the low-energy conformer may be syn, gauche, or anti depending on the substitution of chlorine atoms. It was found, in particular, that anti (meaning C−X is anti to the C=C bond) is a conformational possibility in molecules with $-CX_3$-groups combined with a $X_2C{=}$ or a $HXC{=}$ group, when X is cis to the $-CX_3$ group (X = Cl). Therefore, in molecules such as $X_3C{-}HC{=}CHX$, $X_3C{-}HC{=}CX_2$ and $X_3C{-}XC{=}CHX$, the

---

† Norwegian University of Science and Technology.

‡ Technische Universität Graz.

§ Oregon State University.

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1997.

S1089-5639(97)01686-1 CCC: $14.00

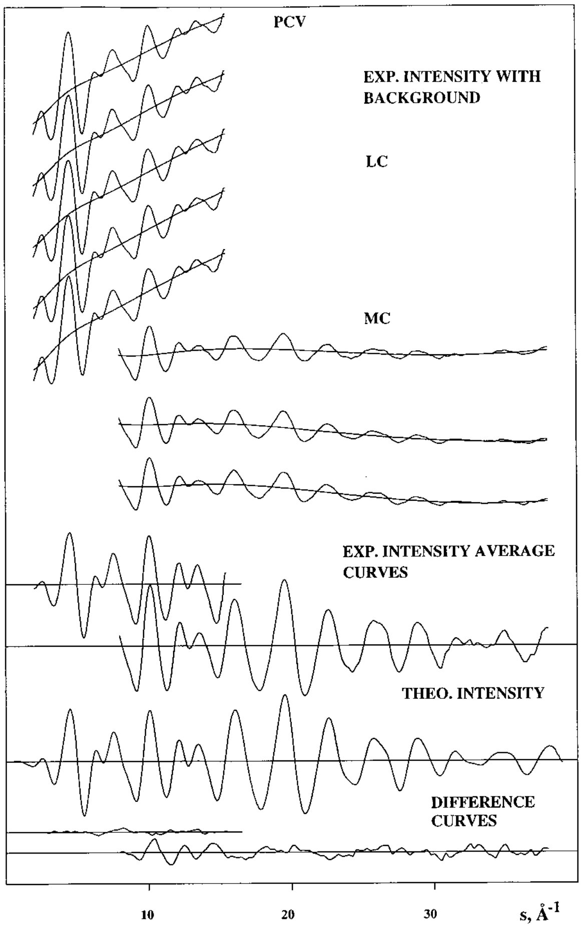


Figure 2. Intensity curves ($sI_m(s)$) for perchlorovinylsilane. The experimental curves are averages of all eight data sets (six plates) shown for the two camera distances. The theoretical curve was calculated from the structural parameters given in Table 1. The difference curves result from subtracting the relevant part of the theoretical curve from the experimental curves.

anti conformer is found to be the low-energy form.[3] However, it is worth noting that in the isomer $X_3C-XC=CHX$, when the X in $=CHX$ is trans to the CX_3-group, the syn conformer remains the low-energy form. This strongly implies that steric strain due to crowding of chlorine atoms, and the need to minimize bonding electron repulsions, seem to be the main factors in determining conformational stability.[3]

One halogenated propene of particular interest is the hexachloropropene molecule, $Cl_2C=CCl-CCl_3$, which was found by GED to exist almost solely in the anti form.[2] Ab initio calculations gave, however, a slight potential minimum for the syn conformer, but with 2.1 kcal/mol higher energy. The refinement on the GED data gave a structure fully consistent with the calculated anti form, where there is no eclipsing of the carbon−carbon double bond, and no significant contribution from the assumed stable syn form could be found experimentally.[2]

Based on the behavior of the propene analogues, it was expected that the perchlorovinylsilane molecule would have similar conformational properties, but it should be easier to detect experimentally a possible syn form, where one Si−Cl bond eclipses the C=C bond. The reason for this basic assumption is that both the =C−Si and the Si−Cl bond distances are longer than the corresponding =C−C and C−Cl bonds in the propenes. This will relieve some of the steric strain due to heavy chlorination, and the presence of a syn form should be more abundant in the vinylsilane case.

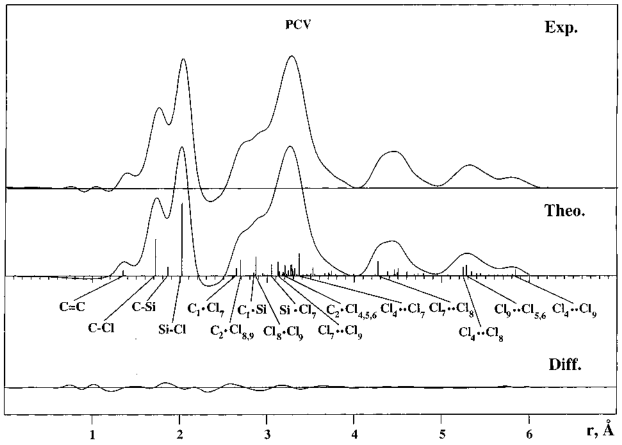


Figure 3. Radial distribution curves for perchlorovinylsilane. The experimental curve was calculated from the composite of the two average experimental curves shown in Figure 2 with the use of theoretical data for the region $0 \leq s/\text{Å}^{-1} \leq 1.75$ and $B/\text{Å}^2 = 0.0020$. The difference curve is experimental minus theoretical. The vertical lines indicate the anti interatomic distances; they have lengths proportional to the distance weights.

To study these properties in detail, we report in this paper an investigation of the perchlorovinylsilane molecule, by using dynamically modeled GED-data, ab initio calculations, and variable temperature Raman spectroscopy.

Experimental Section

Synthesis. Ethyltrichlorosilane dissolved in CCl_4 was chlorinated with Cl_2 under UV irradiation to give pentachloroethyltrichlorosilane which was subsequently treated with copper powder forming trichlorovinyltrichlorosilane (PCV).[4] The purity of the sample was checked with ^{29}Si NMR spectroscopy, elemental analysis, gas chromatography as well as infrared and Raman vibrational spectroscopy.

Variable Temperature Raman Spectroscopy. Samples of PCV were distilled into 1 mm capillary tubes that were sealed under an inert (N_2) atmosphere. The variable temperature cell consisted of a copper block that was cooled with liquid nitrogen and heated resistively. The capillary was mounted on the copper block which was placed in a vacuum chamber equipped with Spectrosil windows. The temperature of the sample was monitored by a thermocouple.

Raman spectra were recorded with the help of a T 64000 triple monochromator spectrometer of Jobin-Yvon equipped with an argon laser operating on the 514.5 nm line. Typically, laser powers as low as 100 mW at the sample were chosen to avoid heating or decomposition. A CCD camera was used to detect the scattered radiation. The reported lines are expected to be accurate to ±2 cm^{-1}.

Gas Electron Diffraction. The sample of PCV was used without further purification. Electron diffraction patterns were recorded with the Oregon State University apparatus on Kodak projector slide plates (nominal accelerating voltage of 60 kV) with a nozzle-tip temperature of 373 K and with a sample temperature of about 338 K.

The nozzle-to-plate distances were 748.25 and 299.78 mm for the long (LC) and the middle (MC) camera distance experiments, respectively. The electron wavelength was $\lambda = 0.04887$ Å. A voltage/distance calibration was made with CS_2 as reference ($r_a(C=S) = 1.557$ Å and $r_a(S\cdots S) = 3.109$ Å). Three diffraction photographs from the LC distance and three diffraction photographs from the MC distance were used in the analysis. The LC distance photographs were scanned twice for optical densities, making a total of nine data sets. During

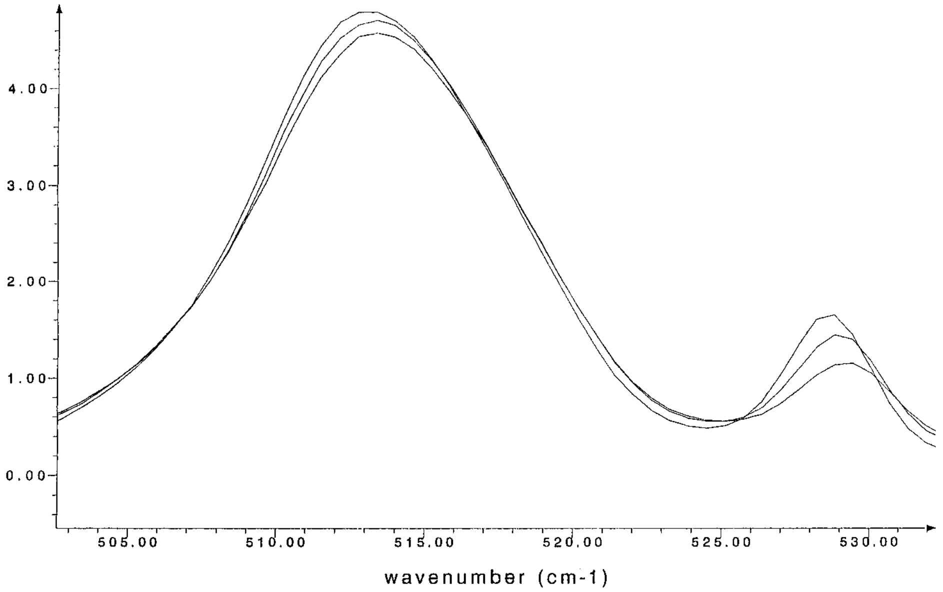


Figure 4. Variation of the intensities of the Raman lines at 511 and 527 cm^{-1} for PCV.

refinement one of the LC sets were excluded, making a total of eight data sets being used for structure analysis. Optical densities were measured by using a double-beam (Joyce-Loebl) microdensitometer at Oregon State University. The data were reduced in the usual way as described elsewhere.[5−7]

The ranges of data were $2.00 \le s/\text{Å}^{-1} \le 15.50$ and $8.00 \le s/\text{Å}^{-1} \le 38.00$ for the LC and the MC distance experiments, respectively. The data interval was $\Delta s = 0.25$ Å^{-1}. A calculated background[8] was subtracted from the data for each plate to yield experimental intensity curves in the form $sI_m(s)$. The average experimental intensity curves are shown in Figure 2. Figure 3 shows the final experimental radial distribution (RD) curve calculated in the usual way from the modified molecular intensity curve $I'(s) = sI_m(s)Z_{Si}Z_{Cl}(A_{Si}A_{Cl})^{-1}\exp(-0.002s^2)$, where $A = s^2F$ and F is the absolute value of the complex electron scattering amplitudes. Theoretical intensity data were used for $s \le 1.75$ Å^{-1} in the experimental curve before the RD curve was calculated. The scattering amplitudes and phases were taken from tables.[9]

Structure Analysis

Vibrational Analysis by Raman Spectroscopy. *Conformational Analysis.* A close examination of the Raman spectra recorded at various temperatures revealed that the intensity ratios of the Raman line pairs observed at 511/527 and 871/887 cm^{-1} are temperature dependent as shown in Figure 4 for the 511/527 cm^{-1} pair. By application of the van't Hoff isochore $-\ln K = (\Delta H/RT) - (\Delta S/R)$, where ΔS is the entropy change, ΔH ($= H_{anti} - H_{syn}$) has been determined from a plot of $\ln K$ versus $1/T$. The intensity ratio K has been established by deconvolution of the doublets. Figure 5 illustrates the van't Hoff plots that were obtained for the two line pairs, giving values of -0.30 ± 0.01 and -0.43 ± 0.05 kcal/mol for ΔH, respectively.

As the 871/887 cm^{-1} line pair possesses only small Raman intensity, the ΔH value derived from it has considerably larger error limits. Consistent with the results of the ab initio calculations and of the GED experiments (Table 1), the anti conformer is thermodynamically preferred, although the ΔH values in the liquid state differ somewhat from the results for the gaseous phase. The energy differences obtained correspond to an amount of the anti conformer in the liquid phase of approximately 60−70% at room temperature.

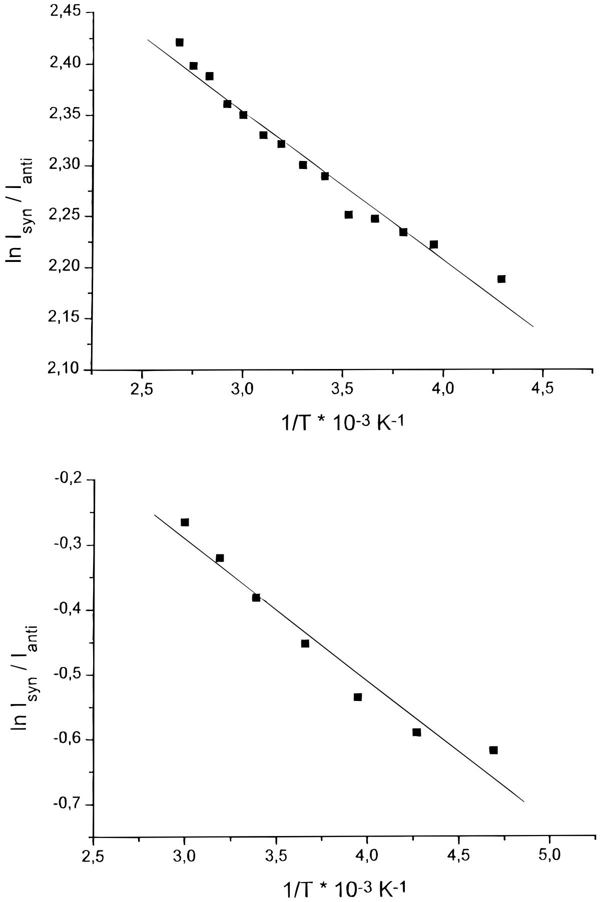


Figure 5. Van't Hoff plots for the line pairs at 511/527 cm^{-1} (top) and 871/887 cm^{-1} (bottom).

Vibrational Assignment. Table 2 lists all of the observed Raman wavenumbers for liquid and solid (crystalline) PCV as well as the infrared wavenumbers for the liquid along with their assignments. Selected portions of the Raman spectra are given in Figure 6. For the syn conformer there are a significant number of the fundamentals which cannot be distinguished from the corresponding modes of the anti conformer.

The assignments given in Table 2, which are based on the results of the ab initio calculations, are therefore given for the anti form. Modes assigned explicitly to the syn conformer are

TABLE 1: Structural Parameters for *anti*-Perchlorovinylsilane[a]

	GED				ab initio values HF/6-31G(d)
	$r_\alpha/\angle_\alpha$	r_g	l_{calc}	l_{exp}	$r/\angle$
$r(\mathrm{C{=}C})$	1.344(12)	1.349	0.043	0.038(20)	1.327
$r(\mathrm{C{-}Si})$	1.859(13)	1.863	0.056	0.074(34)	1.895
$r(\langle\mathrm{C{-}Cl}\rangle)$	1.706(5)				1.725
$r(\langle\mathrm{Si{-}Cl}\rangle)$	2.012(3)				2.035
$\angle\mathrm{CCSi}$	124.0(12)				124.5
$\angle\langle\mathrm{CCCl}\rangle$	121.6(4)				122.0
$P(\mathrm{ClSiCl})$	116.9(71)				
$\angle\langle\mathrm{CSiCl}\rangle$	111.1(15)				110.3
V_3 (kcal/mol)[i]	1.04(58)				
V_6 (kcal/mol)[i]	0.96(86)				
Dependent Parameters					
$r(\mathrm{C_2{-}Cl})$	1.719(5)	1.725	0.051	0.056(6)[b]	1.738
$r(\mathrm{C{-}Cl_{8)}})$	1.703(5)	1.714	0.050	0.055(6)[b]	1.722
$r(\mathrm{C{-}Cl_9})$	1.696(5)	1.711	0.050	0.055(6)[b]	1.715
$r(\mathrm{Si{-}Cl_4})$	2.008(3)	2.015	0.051	0.056(4)[c]	2.032
$r(\mathrm{Si{-}Cl_{5,6}})$	2.013(3)	2.022	0.051	0.056(4)[c]	2.037
$\angle\mathrm{CSiCl_4}$	110.7(15)				109.9
$\angle\mathrm{CSiCl_{5,6}}$	111.3(15)				110.5
$\angle\mathrm{CCCl_7}$	119.0(4)				119.3
$\angle\mathrm{CCCl_8}$	121.8(4)				122.2
$\angle\mathrm{CCCl_9}$	124.1(4)				124.5
$\angle\mathrm{SiCCl_7}$	117.1(14)				116.2
$\angle\mathrm{ClC_1Cl}$	114.0(7)				113.3
$r(\mathrm{C_1\cdots Si})$	2.838(22)	2.841	0.072		2.863
$r(\mathrm{C_1\cdots Cl_7})$	2.646(8)	2.648	0.063	0.058(9)[d]	2.653
$r(\mathrm{C_2\cdots Cl_8})$	2.669(8)	2.676	0.064	0.059(9)[d]	2.676
$r(\mathrm{C_2\cdots Cl_9})$	2.691(8)	2.704	0.062	0.057(9)[d]	2.698
$r(\mathrm{C_2\cdots Cl_4})$	3.183(24)	3.188	0.096	0.122(88)[e]	3.216
$r(\mathrm{C_2\cdots Cl_5})$	3.199(24)	3.206	0.106	0.132(88)[e]	3.233
$r(\mathrm{C_2\cdots Cl_6})$	3.199(24)	3.206	0.106	0.132(88)[e]	3.233
$r(\mathrm{Si\cdots Cl_{7)}}$	3.053(24)	3.056	0.080	0.086(39)[f]	3.085
$r(\mathrm{Si\cdots Cl_{8)}}$	3.283(36)	3.289	0.120	0.126(39)[f]	3.319
$r(\mathrm{Si\cdots Cl_{9)}}$	4.449(19)	4.455	0.074	0.073(19)	4.496
$r(\mathrm{Cl_4\cdots Cl_5})$	3.275(49)	3.283	0.100	0.086(59)[g]	3.291
$r(\mathrm{Cl_4\cdots Cl_6})$	3.275(49)	3.283	0.100	0.086(59)[g]	3.291
$r(\mathrm{Cl_5\cdots Cl_6})$	3.197(141)	3.207	0.104	0.090(59)[g]	3.334
$r(\mathrm{Cl_8\cdots Cl_9})$	2.851(13)	2.871	0.070		2.871
$r(\mathrm{Cl_7\cdots Cl_8})$	4.262(10)	4.266	0.067		4.291
$r(\mathrm{Cl_7\cdots Cl_9})$	3.129(15)	3.138	0.108		3.150
$r(\mathrm{C_1\cdots Cl_4})$	4.470(19)	4.474	0.093		4.491
$r(\mathrm{C_1\cdots Cl_5})$	3.707(33)	3.712	0.141		3.755
$r(\mathrm{C_1\cdots Cl_6})$	3.707(33)	3.712	0.141		3.755
$r(\mathrm{Cl_4\cdots Cl_7})$	3.371(64)	3.374	0.146	0.080(55)	3.374
$r(\mathrm{Cl_5\cdots Cl_7})$	4.500(53)	4.504	0.126		4.513
$r(\mathrm{Cl_6\cdots Cl_7})$	4.500(53)	4.504	0.126		4.513
$r(\mathrm{Cl_4\cdots Cl_8})$	5.249(29)	5.253	0.119	0.110(49)	5.300
$r(\mathrm{Cl_5\cdots Cl_8})$	3.520(79)	3.530	0.173		3.608
$r(\mathrm{Cl_6\cdots Cl_8})$	3.520(79)	3.530	0.173		3.608
$r(\mathrm{Cl_4\cdots Cl_9})$	5.844(29)	5.849	0.113	0.093(27)[h]	5.879
$r(\mathrm{Cl_5\cdots Cl_9})$	5.288(31)	5.292	0.184	0.164(28)[h]	5.345
$r(\mathrm{Cl_6\cdots Cl_9})$	5.288(31)	5.292	0.184	0.164(28)[h]	5.345

[a] Distances (r_α, r_g) and amplitudes (l_{ij}) are in angstroms (Å), angles ($\angle_\alpha$) in degrees. Parenthesized values are 2σ and include estimates of uncertainty in voltage/nozzle heights and of correlation in the experimental data. Quality of fit factor for final refinement was $R = 0.096$. [b−h] These amplitudes (l_{ij}) were refined as groups. [i] The potential constants; see text.

TABLE 2: Observed Infrared and Raman Wavenumbers ($\mathrm{cm^{-1}}$) for Perchorovinylsilane (PCV)

Ir(l)	int.[a]	Ra(l)	int.[a]	Ra(s)	int.[a]	ν_i[b]	assignment
1537	vs	1536	s	1541	ms	ν_1	CC stretch
				1534	ms		
1508	w	1508	w	1508	w		
1052	vw	1054	vw	1051	w		
				1003	w		
997	vs	994	vw	990	vw	ν_4	CCl stretch
980	sh	982	vw			$\nu_{4'}$	CCl stretch
887	vs	887	vw	884	w	ν_5	CCl stretch
870	sh	871	w	873	w	$\nu_{5'}$	CCl stretch
798	vw			798	vw		
				787	vw		
760	sh					$\nu_{3'?}$	CCl stretch
753	s	753	vw	749	w	ν_3	CCl stretch
715	mw						
605	vvs	604	w	607	ms	ν_7	$\mathrm{SiCl_3}$ antisym. stretch
						ν_{15}	
				592	w,sh	ν_{18}	$\mathrm{CCl_2}$ out of plane def.
		527	w	526	ms	ν_6	$\mathrm{SiCl_3}$ sym. stretch
512	vs	511	m	513	s	$\nu_{6'}$	$\mathrm{SiCl_3}$ sym. stretch
				458	vw		
450	vvw	450	vw	447	vw		
400	vvw	406	vs	407	vs	ν_2	SiC stretch
		366	vw	368	w		
330	s	330	m	329	s	ν_9	$\mathrm{CCl_2}$ rock
						ν_{19}	CSiCl out of plane def.
320	sh			321	sh		
301	s	302	m	306	s	ν_8	$\mathrm{CCl_2}$ in plane def.
				224	sh		
		222	m	219	m	ν_{10}	CSiCl in plane def.
		198	m	196	sh	ν_{11}	CSiCl rock
		191	sh	194	m	ν_{16}	$\mathrm{SiCl_3}$ antisym. def.
				186	sh		
		176	m	175	m	ν_{12}	$\mathrm{SiCl_3}$ sym. deformation
				157	m		
		147	mw	145	m	ν_{13}	$\mathrm{SiCl_3}$ antisym. def.
		128	w	138	m	ν_{17}	$\mathrm{SiCl_3}$ rock
		111	w	114	w	ν_{14}	$\mathrm{SiCl_3}$ rock
				84	s		lattice mode
		71	mw			ν_{20}	CC torsion
				62	m		lattice mode
				44	vs		lattice mode
				35	vs		lattice mode

[a] s, strong; m, medium; w, weak; v, very; sh, shoulder. [b] Modes indicated by a prime are assigned to the syn conformer.

indicated by a prime. Even repeated annealing of the amorphous solid did not give crystals of a single rotamer. In the crystalline solid, both conformers were still present.

Ab Initio Calculations and Normal Coordinate Analysis. Ab initio calculations (RHF−SCF) with the program GAUSSIAN 94[10] by using Gaussian-type basis functions were carried out for both syn and anti PCV. The force fields in Cartesian coordinates were calculated with the 6-31G(d) basis set, and 24 internal coordinates (Figure 7) were used to calculate the **G**-matrix by using the ab initio structural parameters (Table 1). The force field for each conformer was then converted to a force field defined in symmetry coordinates by using the program ASYM40.[11]

Table 3 lists the symmetry coordinates that were used in the normal coordinate analysis. A single factor kept fixed at 0.92 was used to obtain the scaled frequencies for the fundamental vibrations. The observed and calculated frequencies (unscaled and scaled) for both conformers as well as the potential energy distributions are summarized in Table 4. The observed frequencies of the anti conformer are reproduced to about 2.3%.

As can be expected from the masses of the atoms that compose the molecule strong vibrational couplings between the modes are the rule. The calculated potential energy distributions point out that up to six coordinates may contribute significantly to a single normal vibration. As the ab initio calculations obviously overestimate interaction force constants of CC and SiC torsions with angle bending deformations, the contributions of $F_{17,20}$, $F_{19,20}$, $F_{17,21}$, $F_{18,20}$, and $F_{19,21}$ to the potential energies can be exceedingly large. For instance, the contribution of $F_{17,21}$ to ν_{21} of syn PCV is −0.55, with the contributions of the diagonal force constants ($\Sigma V_k(F_{ii})$) summing up to a value >4.00 accordingly. The remedy for achieving more reasonable PED's ($\Sigma V_k(F_{ii}) \leq 1.30$[12]) would be to give this interaction constants

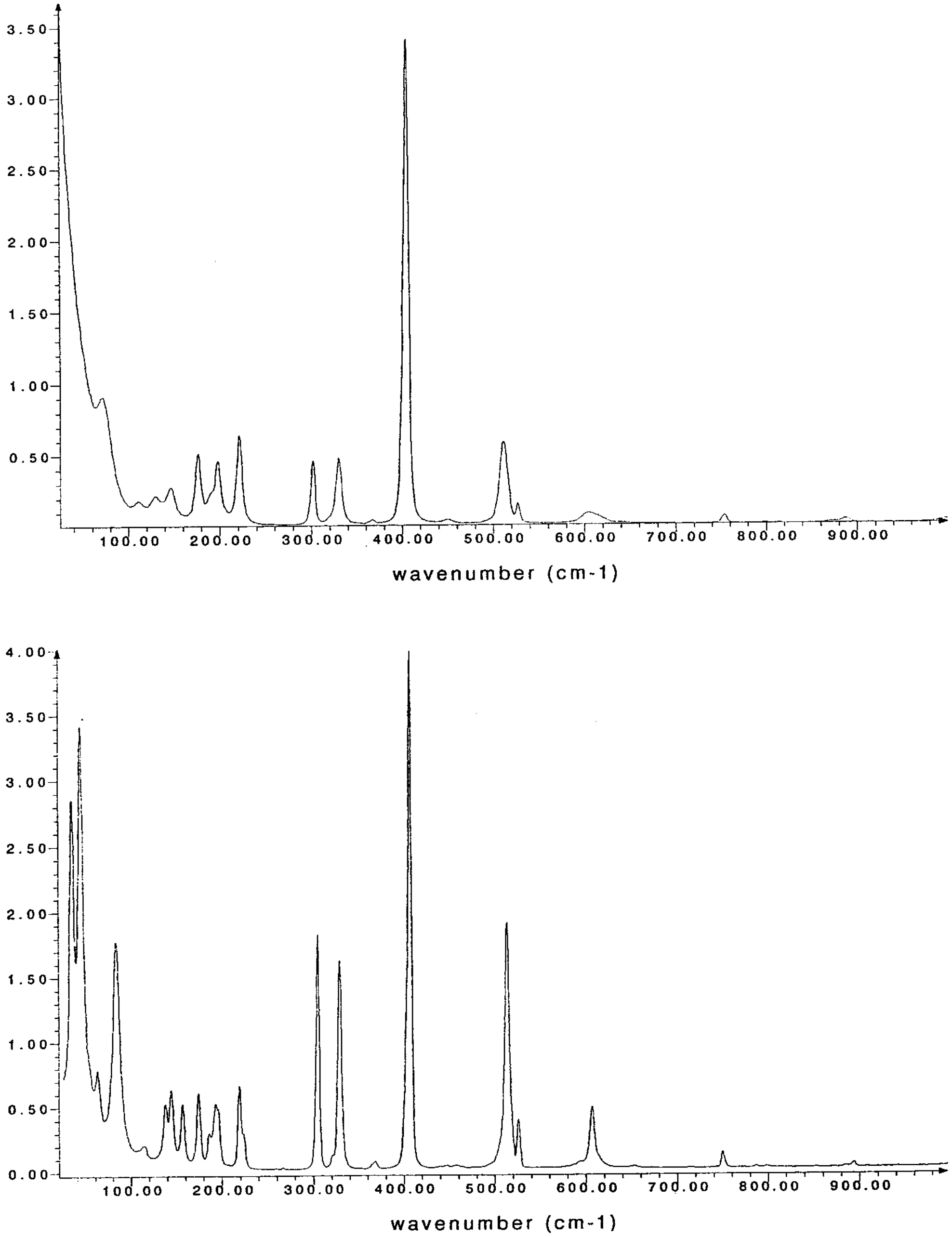


Figure 6. Raman spectra of liquid PCV (top) and solid (crystalline) PCV (bottom).

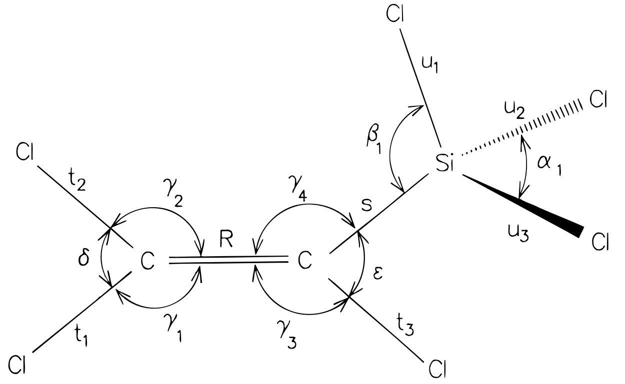


Figure 7. Internal coordinates of PCV used for the construction of symmetry coordinates.

independent (small) scale factors, a procedure which has not been chosen in this work.

For ν_1, ν_3, ν_4, ν_5, ν_{13}, ν_{14}, ν_{19}, and ν_{21} (which could not be resolved from the Rayleigh line), the ab initio calculations predict differences of the wavenumbers between the two conformers larger than 5 cm^{-1}, but not all of them could be observed as for ν_1 and ν_3. For ν_6, on the other hand, a difference of 16 cm^{-1} was observed while 1 cm^{-1} was predicted. The line pair at 994/982 cm^{-1} (ν_4) was too weak to be used for the conformational analysis. Although the spectra of the crystalline solid below 250 cm^{-1} differed quite clearly from the spectra of the liquid, no unambiguous assignments for the anti conformer could be deduced as appreciable amounts of syn PCV were still present. Because of many overlapping bands, this spectral region could not be used for determining ΔH values.

The force constants of the stretching vibrations for the two conformers have very similar values, the relative differences being smaller than 4%. The individual SiCl stretching force constants can be calculated from $F_{6,6}$, $F_{7,7}$, $F_{6,7}$, and $F_{15,15}$, with the result that the chlorine atom which is in anti or syn position to the carbon double bond possesses the larger stretching force constant (3.51 N cm^{-1} for anti, 3.48 N cm^{-1} for syn PCV). The bonds in gauche position are weaker by 0.09 N cm^{-1} (anti) and 0.02 N cm^{-1} (syn), all values unscaled. The silicon−

TABLE 3: Symmetry Coordinates (Not Normalized) Used in the Normal Coordinate Analysis for *anti*- and *syn*-Perchlorovinylsilane (PCV)

species (C_s)	approximate description	symmetry coordinate
A′	C═C stretch	$S_1 = R$
	Si−C stretch	$S_2 = s$
	CCl stretch	$S_3 = t_1$
	CCl stretch	$S_4 = t_2$
	CCl stretch	$S_5 = t_3$
	$SiCl_3$ symmetric stretch	$S_6 = u_1 + u_2 + u_3$
	$SiCl_3$ antisymmetric stretch	$S_7 = 2u_1 - u_2 - u_3$
	CCl_2 in plane deformation	$S_8 = 2\delta - \gamma_1 - \gamma_2$
	CCl_2 rock	$S_9 = \gamma_2 - \gamma_1$
	CSiCl in plane deformation	$S_{10} = 2\epsilon - \gamma_3 - \gamma_4$
	CSiCl rock	$S_{11} = \gamma_4 - \gamma_3$
	$SiCl_3$ symmetric deformation	$S_{12} = \alpha_1 + \alpha_2 + \alpha_3 - \beta_1 - \beta_2 - \beta_3$
	$SiCl_3$ antisymmetric deformation	$S_{13} = 2\alpha_1 - \alpha_2 - \alpha_3$
	$SiCl_3$ rock	$S_{14} = 2\beta_1 - \beta_2 - \beta_3$
A″	$SiCl_3$ antisymmetric stretch	$S_{15} = u_2 - u_3$
	$SiCl_3$ antisymmetric deformation	$S_{16} = \alpha_2 - \alpha_3$
	$SiCl_3$ rock	$S_{17} = \beta_2 - \beta_3$
	CCl_2 out of plane deformation	$S_{18} = \pi_1$
	CSiCl out of plane deformation	$S_{19} = \pi_2$
	CC torsion	$S_{20} = \theta$
	SiCl torsion	$S_{21} = \tau$

chlorine bond which is in anti or syn position is also shorter (Table 1, ab initio geometry values).

Force constants relating to deformations of CCSi angles ($F_{11,11}$ and $F_{19,19}$) show quite large differences, as do also the torsional force constants. All deformation force constants of the syn conformer are either larger or only marginally smaller than the corresponding values for anti PCV, indicating that syn PCV is a more strained ("stiffer") molecule.

Gas Electron Diffraction Analysis. *Details of the Dynamic Model.* From the experimental RD curves and from results obtained for related molecules, as well as results obtained from theoretical calculations, trial values for bond distances and bond angles were obtained for PCV. The GED data were treated by using a dynamic theoretical model. This involves fitting a chosen two-term potential function to the experimental data by using a predefined set of nonstable forms called *pseudo-conformers*. This makes it possible to obtain experimentally refined values for both a 3-fold and a 6-fold potential constant (V_3 and V_6) in the series $V(\phi) = {}^1\!/_2\Sigma_i V_i[1 - \cos i(180-\phi)]$, with $i = 3$ and 6, where ϕ is the value of the torsional angle CCSiCl. The potential function $V(\phi)$ has the property that $V(0) = V_3$, which corresponds to the anti − syn conformational energy difference. By using pseudo-conformers at 10° intervals, refined values for V_3 and V_6 were obtained, and from these values the experimental torsional potential curve for the rotation around the C−Si bond could be calculated.

Ab initio molecular orbital (MO) calculations were used to establish constraints in this dynamic model, by incorporating geometrical differences between the seven pseudo-conformers comprised by the dynamic model, spaced at 10° interval between the syn ($\phi = 0°$ or 120°) and the anti ($\phi = 180°$) form. The geometries for all seven forms were fully optimized at the HF/6-31G(d) level using GAUSSIAN 94.[10] This procedure of using ab initio results as constraints in the GED analysis has been shown to be very useful.[13−15]

In addition zero-point energies (ZPE) were also estimated ab initio. The ZPE's were scaled before correction of the electronic energies for the two stable forms by a factor of 0.893[16] to compensate for neglect of electron correlation at the HF level. Energy estimates obtained for the pseudo-conformers at the HF/6-31G(d) level were used to calculate a theoretical conformational distribution by using the simple Boltzmann model. These values along with the corresponding experimental data from the dynamic GED model are shown in Table 5.

Refinements, Vibrational Corrections, and Normal Coordinate Calculations. Refinements of the molecular structures based

TABLE 4: Observed and Calculated Wavenumbers (cm^{-1}) for *anti* and *syn*-Perchlorovinylsilane (PCV)

	vib. no.	description	anti				syn			
			a	*b*	obsvd	PED	*a*	*b*	obsvd	PED
A′	ν_1	C═C stretch	1767	1625	1536	99(1)	1775	1633	1536	98(1)
	ν_2	SiC stretch	436	401	406	24(4), 17(5), 15(6)	435	400	406	24(4), 15(5), 15(6)
	ν_3	CCl stretch	817	752	753	29(3), 16(2), 16(4), 20(5), 15(8), 14(10)	824	758	753	29(3), 15(2), 16(4), 26(5), 15(8), 12(10)
	ν_4	CCl stretch	1106	1018	994	27(4), 16(2), 21(3), 18(5)	1091	1004	982	38(4), 13(2), 23(3), 13(5), 57(9), 57(11)
	ν_5	CCl stretch	961	885	887	35(5), 24(2), 26(3), 28(4)	938	863	871	38(5), 21(4), 26(3), 27(2)
	ν_6	$SiCl_3$ sym.stretch	551	507	527	66(6), 12(2), 16(12)	550	506	511	68(6), 11(2), 11(3), 16(12)
	ν_7	$SiCl_3$ antisym.stretch	653	601	604	97(7)	654	602	604	96(7)
	ν_8	CCl_2 in plane deformation	332	305	302	49(8), 16(10), 16(12)	328	302	302	50(8), 12(10), 20(12)
	ν_9	CCl_2 rock	354	326	330	24(9), 12(2), 11(6), 18(11), 12(12)	357	329	330	27(9), 11(2), 10(6), 24(11), 11(12)
	ν_{10}	CSiCl in plane deformation	246	227	222	40(10), 21(8), 12(13)	248	228	222	41(10), 17(8), 12(13)
	ν_{11}	CSiCl rock	220	202	198	49(11), 16(2), 21(3), 27(4), 18(5), 51(9)	224	206	198	10(11), 29(9), 32(13), 15(14)
	ν_{12}	$SiCl_3$ sym. deformation	189	173	176	48(12)	188	173	176	49(12), 12(2), 11(10)
	ν_{13}	$SiCl_3$ antisym. deformation	158	146	147	51(13), 44(14), 11(11), 15(10)	147	135	147	34(13), 12(9), 19(10), 33(11), 17(14)
	ν_{14}	$SiCl_3$ rock	114	105	111	38(14), 26(11), 10(10)	129	119	111	74(14), 17(13)
A″	ν_{15}	$SiCl_3$ antisym. stretch	669	616	604	56(15), 13(17), 25(18), 25(19)	667	614	604	57(15), 13(17), 22(18), 30(19)
	ν_{16}	$SiCl_3$ antisym. deformation	207	190	191	81(16)	208	191	191	79(16)
	ν_{17}	$SiCl_3$ rock	138	127	128	39(17), 16(16), 23(20)	140	129	128	45(17), 19(16), 14(20)
	ν_{18}	CCl_2 out of plane deformation	623	573	592?	49(18), 43(16), 20(19)	622	573	592?	48(18), 42(15), 26(19)
	ν_{19}	CSiCl out of plane deformation	363	334	330	27(19), 33(18), 24(17)	374	344	330	27(19), 30(18), 23(17)
	ν_{20}	CC torsion	70	64	71	102(20), 24(19), 27(17)	68	62	71	99(20), 25(17), 32(19)
	ν_{21}	SiC torsion	35	33		167(21), 13(19), 29(17)	12	11		273(21), 87(19), 42(16), 13(17)

[a] Ab initio HF/6-31G(d) calculations. [b] Scaled by 0.92.

TABLE 5: Distribution and Potential Energies of Pseudoconformers of Perchlorovinylsilane According to Experimental and Theoretical Results

form	GED energy (kcal/mol)[a]	exp. distribution (%)[b]	ab initio energy (kcal/mol)[c]	ab initio distribution (%)[b]
180 (anti)	0.0	24.8	0.0	24.5
170	0.31	32.7	0.25	35.0
160	0.98	13.3	0.83	16.0
150	1.48	6.8	1.35	7.9
140	1.50	6.6	1.51	6.4
130	1.21	9.7	1.49	6.6
120 (syn)	1.04	6.1	1.43	3.6
sum:		100		100

[a] Potential energies calculated using the refined potential constants $V_3 = 1.04$ kcal/mol and $V_6 = 0.96$ kcal/mol in the two-term function: $V(\phi) = {}^1/_2V_3[1 - \cos 3(180-\phi)] + {}^1/_2V_6[1 - \cos 6(180-\phi)]$, where ϕ is the torsional angle CCSiCl. [b] Conformational distributions calculated from the respective experimental and theoretical energy values, with multiplicities of 2 for the pseudo-conformers (130−170) and a multiplicity of 1 for the 180 and 120 (C_s) forms. [c] Ab initio HF/6-31G(d) calculations.

on the GED data were made by the least-squares method,[17] adjusting a theoretical $sI_m(s)$ curve simultaneously to the two average experimental intensity curves, one from each of the two camera distances. Due to heavy chlorination in the PCV molecule, calculated intensity curves showed that there were relatively large contributions from the nonbonded internuclear distances streching over two angles or more. These data are important in the determination of the conformation of the molecule, and the LC-data were therefore weighted more than the MC-data (relative weights 3.0 and 1.0, respectively).

The structures were converted from the geometrically consistent r_α to the r_a −type required by the formula for the scattered intensities ($r_a(T) = r_g(T) - l^2(T)/r = r_\alpha(T) - l^2/r + K_T + \delta r(T)$),[18,19] by using values of the centrifugal distortion constants ($\delta r(T)$), perpendicular amplitude corrections (K_T), and root-mean-square amplitudes of vibration ($l(T)$) calculated at the temperature of the experiment, 373 K.

These vibrational frame values were estimated from the ab initio Cartesian force fields by using normal coordinate calculations (NCA) performed in the program ASYM40.[11] The Cartesian force fields were used as input in the program along with the appropriate **U**-matrix, and then transformed into force fields based on the symmetry coordinates (Table 3), including 21 internal diagonal force constants, corresponding to the 21 vibrational normal modes. Further, the force constants for the first 20 of these 21 diagonal values, were scaled with a factor of 0.8 before NCA was performed.

The 21st normal mode, mainly corresponding to the torsional motion of the $-SiCl_3$ group (Table 4), was treated differently. The use of a dynamic model in the GED refinements made it necessary to practically remove the contribution from the large-amplitude motion of the $-SiCl_3$ group, and the corresponding internal force constant was therefore set to an intentionally high value. This procedure made it possible to obtain reasonable values for the frame amplitudes and perpendicular corrections used in the GED refinements. The obtained symmetrized force fields for the anti and syn forms were used in the calculation of similar frame values for all pseudo-conformers comprised by the dynamic model.

The Molecular Parameters. The geometry of the conformers was described by a set of independent parameters, along with the potential constants in the two-term potential function that were to be fitted to the experimental data. In our refinements these parameters were chosen as: $r(C{=}C)$, $r(C_{vinyl}{-}Si)$, $r(\langle C{-}Cl\rangle)$ (average value), $r(\langle Si{-}Cl\rangle)$, (average value), $\angle(CCSi)$, $\angle(\langle CCCl\rangle)$ (average value), $P(ClSiCl)$ (projection angle; the angle between the two Si−Cl bonds projected on a plane perpendicular to the =C−Si -bond), $\angle(\langle CSiCl\rangle)$ (average value) and the two potential constants V_3 and V_6. In addition, ab initio differences between each particular geometrical parameter in the molecule and the average were incorporated as constraints. Differences between corresponding bond distances and bond angles between all forms were kept constant at calculated ab initio values.

The vibrational properties of the molecule were specified by 36 amplitude parameters for each pseudo-conformer, corresponding to the number of interatomic distances in the molecule, making a total of 252 distances included in the dynamic model. Many, but not all, of the amplitudes could successfully be refined. Some of the amplitudes were refined together as groups. The amplitudes which could not be refined were kept constant at the values calculated from the scaled ab initio force fields.

In the final refinement eight geometrical parameters, the two potential constants (V_3 and V_6), along with 12 amplitude parameters were refined simultaneously. The results of this

TABLE 6: Correlation Matrix (×100) for the Refined Parameters of Perchlorovinylsilane (PCV)

parameter:	σ_{LS}[a]	r_1	r_2	r_3	r_4	$\angle_1$	$\angle_2$	$\angle_3$	$\angle_4$	V_3	V_6	l_1	l_2	l_3	l_4	l_5	l_6	l_7	l_8	l_9	l_{10}	l_{11}	l_{12}
C=C	0.42	100																					
C−Si	0.47	−8	100																				
C−Cl	0.16	−41	26	100																			
Si−Cl	0.08	9	12	12	100																		
CCCl	12.9	−65	15	22	−6	100																	
CCSi	42.1	−16	13	0	6	39	100																
CSiCl	51.6	−19	−56	−13	−11	−3	−37	100															
P(ClSiCl)	251	23	39	−1	7	−8	10	−51	100														
V_3	20.4	−9	3	9	−4	−1	−4	−7	8	100													
V_6	30.6	8	−20	−17	−4	−7	11	19	−6	−63	100												
l(C=C)	0.72	−1	7	9	9	−1	2	−6	5	2	−2	100											
l(C−Si)	1.19	−27	2	52	−32	18	−5	3	−7	0	−5	−18	100										
$l(C_2{-}Cl)$	0.21	−27	−19	27	−6	13	1	16	−13	1	1	−18	58	100									
$l(Si{-}Cl_4)$	0.11	−9	6	10	−17	4	2	6	4	−8	3	−5	48	49	100								
$l(C_1{\cdot}Cl)$	0.31	−5	6	10	19	11	−15	5	8	−6	3	−4	4	2	17	100							
$l(C_2{\cdot}Cl_4)$	3.10	−21	−39	−3	−21	−12	−64	79	−42	28	−14	−5	9	15	8	−2	100						
$l(Si{\cdot}Cl_7)$	1.36	−5	2	17	9	−33	5	−22	−25	30	−32	0	5	1	−3	−10	−4	100					
$l(Cl_4{\cdot}Cl_5)$	2.07	17	46	4	12	12	46	−81	85	12	−12	6	−8	−13	0	3	−75	−3	100				
$l(Si{\cdot\cdot}Cl_9)$	0.66	8	1	2	−4	4	12	−10	15	18	17	4	0	2	−1	0	−9	−3	11	100			
$l(Cl_4{\cdot\cdot}Cl_7)$	1.95	−1	43	18	20	24	41	−79	17	36	−46	5	−3	−9	−4	−3	−49	28	12	40	100		
$l(Cl_4{\cdot\cdot}Cl_8)$	1.74	−1	−5	5	−10	−4	−20	−25	−2	55	−49	3	3	4	−7	−7	10	32	7	17	−13	100	
$l(Cl_4{\cdot\cdot}Cl_9)$	0.95	−6	9	3	10	13	35	−1	8	39	−15	0	−5	−2	4	1	−3	3	2	−5	−11	10	100

[a] Standard deviations (×100) from least-squares refinement. Distances (r) and amplitudes (l) are in angstroms; angles (∠) are in degrees.

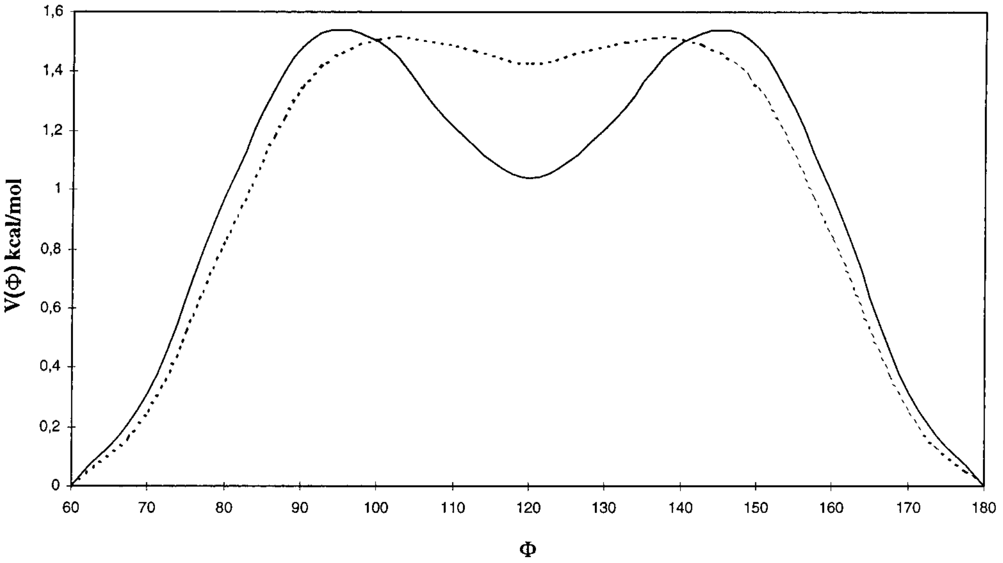


Figure 8. Torsional potential curves (kcal/mol) for perchlorovinylsilane, as obtained from the GED data using a dynamic model and as calculated from ab initio HF/6-31G(d) energy values, showing the potential energy (*V*) as a function of the torsional angle ϕ(CCSiCl). The broken line shows the ab initio potential, while the solid line shows the curve resulting from the two-term potential function outlined in the text.

TABLE 7: Comparison of Several Vinylsilanes and Hexachloropropene[c]

			parameters						
molecule	conf.	method	r(C=C)	r(C−Si) r(C−C)	r(Si−X)/r(C−X) r(Si−H)	∠XSiX ∠XCX	∠C=CSi	∠CSiX ∠CCX	ref
CH_2=$CHSiH_3$	syn	MW	1.347(3)	1.853(3)	1.475		122.9(3)		21
CH_2=$CHSiCl_3$	syn	GED[a]	1.35[b]	1.81(2)	2.060(5)	107(1)	121(3)		22
Cl_2C=$CClCCl_3$	anti	GED	1.350(13)	1.536(17)	1.748(3)	109.9[b]	124.4(11)	114.6(26)	2
Cl_2C=$CClSiCl_3$	anti	GED	1.349(12)	1.863(13)	2.020(3)	105.1(66)	124.0(12)	110.7(15)	this work

[a] Type of bond is not specifically given in this article, probably r_a values. Standard deviation (σ) as given in the original text. [b] Assumed value. [c] Bond distances in angstrom (Å), valence and torsional angles in degrees (°). (X = Cl; MW = microwave spectroscopy, GED = gas electron diffraction).

refinement are given in Table 1 where also the corresponding geometrical values from the ab initio calculations are given. The dependent bonding and nonbonding distances, valence angles, and refined and calculated vibrational amplitudes from the scaled ab initio force fields are also given in Table 1. The correlation matrix for the refined parameters is given in Table 6.

The theoretical intensity curve for the final model is shown in Figure 2 together with average experimental and difference curves. Figure 3 shows the corresponding RD curves along with the difference curve. Figure 8 shows the energy values in Table 5 plotted as a function of the torsional angle ϕ(CCSiCl), obtaining torsional potential curves both from the refined experimental (GED) potential constants and from the theoretical ab initio values. The agreement is quite acceptable.

Discussion

In the study of hexachloropropene,[2] it was concluded from the combined GED/ab initio analysis that this molecule in the gas phase existed mainly as an anti conformer. Small amounts of a syn conformer could not be excluded, but the amount of such a conformer had to be smaller than 10%. From the ab initio-constrained GED analysis, by using a dynamic model, similar conclusions may be drawn for perchlorovinylsilane.

Table 5 shows the distribution of pseudo-conformers found by the dynamic model and as calculated from ab initio energy values by use of simple Boltzmann statistics. From the experimental distribution one may obtain an approximative value for the amount of the more stable anti form (in the vibrational average sense) in the gas phase, by summing the given percentage of the 180, 170, 160, and 150 forms. This gives 78% anti conformer from the dynamically modeled GED data. Correspondingly, the ab initio anti value is 83%.

The ab initio calculations predict a shallow minimum at the stationary point corresponding to the 120° form (syn), and this stationary point has an energy of 1.43 kcal/mol relative to the 180° (anti) form. However, the theoretical syn to anti torsional barrier is calculated to be very small, only about 0.08 kcal/mol (see Figure 8). The experimental results give a more distinctive (sharp) minimum for the syn conformer, which is found to be 1.04 ± 0.58 kcal/mol higher in energy. The syn to anti torsional barrier is also higher, about 0.50 kcal/mol according to Figure 8, indicating more clearly the existence of a stable syn conformer.

The preference of the anti form in these perhalogenated molecules seems to arise from the unfavorable steric interactions that occur in the syn form, where the C_3−Cl or Si−Cl bond is in the plane of the C=C bond. However, it should be evident that steric effects are counteracted by the favorable eclipsing usually found in these types of molecules, as established in ref 1. The key to understanding why the syn form is a minimum in the potential curve at all, is to regard the double bond as consisting of a pair of bent single bonds, making the syn form a complete staggered possibility. This particular point is further discussed in a recent paper by Page et al.,[20] dealing with the vinyltrimethylsilane molecule, in which the syn form was the only stable form.

In the PCV case, the Cl_4 atom on silicon is 3.37 Å away from the coplanar Cl_7 atom in the anti form. This is almost the same as the distance between the Cl_4 atom and the cis Cl atom on C_1 in the syn conformer, but this is obtained at the cost of some energetically unfavorable changes in the central bond angles. The ab initio calculations reveal large conformational differences in the CCSi parameter value for PCV. While the anti form has a calculated CCSi bond angle of 124.5° (Table 1), the corresponding syn value is calculated as large as 131.6°. This difference of 7.1° is incorporated as constraint in the GED least-squares refinements. Concequently, the anti CCSi bond angle value represents less molecular strain than the large syn value. Also, the $CSiCl_{\text{in plane}}$ bond angle value shows a large difference, with calculated values of 109.9° in the anti and 116.7° in the syn form. Thus, the anti conformer must be more sterically relaxed than its syn counterpart, making this form the preferred species in PCV.

The preference of the anti form in PCV is supported by the Raman data analysis of the liquid phase. The variable temperature study gives the syn form a higher energy of about 0.30−0.43 kcal/mol from the two separate doublets at 511/527 and 871/887 cm^{-1}. Some of the difference between the GED and the spectroscopy energy values may come from the fact that the experimental values are obtained in different phases.

As shown in Table 7, the structural parameters of anti PCV are not significantly different from the values found in hexachloropropene,[2] vinylsilane,[21] or vinyltrichlorosilane.[22] However, one important exception is observed: The Si−Cl bond distance in vinyltrichlorosilane[22] is reported to be $r_a(Si{-}Cl) = 2.060(5)$ Å, which is unusually large for a $-SiCl_3$ fragment. The corresponding value found for PCV in the present work is $r_g(\langle Si{-}Cl\rangle) = 2.020(3)$ Å, which is close to the normal value found for $-SiCl_3$ fragments in molecules where *no* vinyl-group is present.[23] Based on previous discussions[1] of possible electronic interactions appearing in such vinylsilane molecules (the vinyl−silicon (p−d) π interactions) the observed significant difference in the Si−Cl bond length may be explained from strong (p−d) π interaction possibly occurring in vinyltrichlorosilane,[22] while little or no such interaction is present in PCV, making the observed value of 2.020(3) Å reasonable. In PCV, the π electron density on the vinyl group is expected to be restricted by the electronegative chlorine atoms present, making any extended (p−d) π interaction between the vinyl group and the silicon atom more difficult or impossible.

In conclusion, the main effect of replacing the C_3 atom in hexachloropropene[2] with a Si atom in PCV is to make the energy difference between the syn and anti conformers smaller. In hexachloropropene the GED-data suggested very little syn form present, the amount had to be less than 10%. In PCV the GED-data shows about 20% syn conformer present at 373 K.

Acknowledgment. We are very grateful to Professor Kenneth W. Hedberg for use of the Oregon State University GED-apparatus and to Dr. Lise Hedberg for help with the normal coordinate calculations used in this work. This work has received support from National Science Foundation under Grant CHE95-23581 and from The Research Council of Norway (Program for Supercomputing) and Oregon State University through grants of computing time.

Supporting Information Available: Tables of the harmonic symmetry force constants for anti and syn conformers of PCV calculated at the HF/6-31G(d) level of ab initio theory (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Johansen, T. H.; Hagen, K.; Stølevik, R.; Hassler, K. *J. Phys. Chem. A* **1997**, *101*, 3580.

(2) Hagen, K.; Stølevik, R.; Kaleem, H. *J. Phys. Chem.* **1994**, *98*, 6293.

(3) Hagen, K.; Stølevik, R. *J. Mol. Struct.* **1996**, *376*, 83.

(4) Motsarev, G. V.; Dzhagatspanyan, R. V.; Snegova, A. D. *Zh. Obshch. Khim.* **1968**, *38*, 1186.

(5) Hagen, K.; Hedberg, K. *J. Am. Chem. Soc.* **1973**, *95*, 1003.

(6) Andersen, B.; Seip, H. M.; Strand, T. G.; Stølevik, R. *Acta Chem. Scand.* **1969**, *23*, 3224.

(7) Gundersen, G.; Hedberg, K. *J. Chem. Phys.* **1969**, *51*, 2500.

(8) Hedberg, L. *Abstracts of Papers*, 5th Austin Symposium on Gas-Phase Molecular Structure, Austin, TX, March 1974; p 37.

(9) Ross, A. W.; Fink, M.; Hilderbrandt, R. *International Tables of Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; Vol. 4, p 245.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision B.1 and C.2; Gaussian, Inc.: Pittsburgh PA, 1995.

(11) Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117 (ASYM20). The later ASYM40 version presented in: Hedberg, L. *Abstracts*, 15th Austin Symposium on Molecular Structure, Austin, TX, March 1994.

(12) Becher, H. J.; Ballein, K. *Z. Phys. Chem.* **1967**, *NF54*, 302.

(13) Van Hemelrijk, D.; Van den Enden, L.; Geise, H. J.; Sellers, H. L.; Schäfer, L. *J. Am. Chem. Soc.* **1980**, *102*, 2189.

(14) Schäfer, L.; Ewbank, J. D.; Siam, K.; Chiu, N.; Sellers, H. L. in *Stereochemical Applications of Gas-Phase Electron Diffraction*; Hargittai, I.; Hargittai, M.. Eds.; VCH Publishers Inc.: New York, 1988; p 301.

(15) Klimkowski, V. J.; Ewbank, J. D.; Van Alsenoy, C.; Scardale, J. N.; Schäfer, L. *J. Am. Chem. Soc.* **1982**, *104*, 1476.

(16) Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 5622.

(17) Hedberg, K.; Iwasaki, M. *Acta Crystallogr.* **1964**, *17*, 529.

(18) Bartell, L. S. *J. Chem. Phys.* **1963**, *38*, 1827.

(19) Kuchitsu, K.; Morino, Y. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 841.

(20) Page, E. M.; Rice, D. A.; Walsh, R.; Hagen, K. *J. Mol. Struct.* **1997**, *403*, 199.

(21) O'Reilley, J. M.; Pierce, L. *J. Chem. Phys.* **1961**, *34*, 1176.

(22) Vilkov, L. V.; Mastryukov, V. S.; Akishin, P. A. *Russ. J. Struct. Chem.* **1964**, *5*, 168.

(23) Stølevik, R.; Postmyr, L. *J. Mol. Struct.* **1996**, *375*, 273.