Methylvinyldifluorosilane and Methylvinyldichlorosilane ($H_2C{=}CHSiX_2CH_3$, X = F, Cl): Structure, Conformation, and Torsional Potential As Determined by Gas-Phase Electron Diffraction and ab Initio Calculations

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The molecular structures and conformations of methylvinyldifluorosilane (VFS), $H_2C{=}CHSiF_2CH_3$, and methylvinyldichlorosilane (VCS), $H_2C{=}CHSiCl_2CH_3$, have been studied by using gas-phase electron diffraction (GED) data at 25 °C. Ab initio molecular orbital (MO) calculations were used to establish constraints in the theoretical model used to analyze the GED data. These molecules exist in the gas phase as a mixture of two conformers, syn (S, torsional angle $\phi(CCSiC) = 0°$) and gauche (G, torsional angle $\phi(CCSiC)$ close to 120°). Relevant structural parameters for VFS (syn) are as follows: bond lengths (r_g), $r(Si{-}C_{vinyl}) = 1.846(3)$ Å, $r(Si{-}CH_3) = 1.851(3)$ Å, $r(C{=}C) = 1.344(5)$ Å, $r(Si{-}F) = 1.592(2)$ Å; bond angles ($\angle_\alpha$), $\angle CSiC = 113.4(11)°$, $\angle CCSi = 123.3(8)°$; torsional angle, $\phi(G) = 117(14)°$. For VFS the experimental gas-phase composition (%) was (syn/gauche) 35/65 (±41)%. An estimated conformational energy difference $\Delta E°_{G-S} = 0.0(\pm1.2)$ kcal/mol was obtained for VFS. Relevant structural parameters for VCS (syn) are as follows: bond lengths (r_g), $r(Si{-}C_{vinyl}) = 1.843(4)$ Å, $r(Si{-}CH_3) = 1.855(4)$ Å, $r(Si{-}Cl) = 2.051(2)$ Å, $r(C{=}C) = 1.341(6)$ Å; bond angles ($\angle_\alpha$), $\angle CSiC = 111.6(17)°$, $\angle CCSi = 123.3(17)°$; torsional angle, $\phi(G) = 121(16)°$. For VCS the experimental composition was (syn/gauche) 45/55 (±64)%. An estimated conformational energy difference $\Delta E°_{G-S} = 0.3(\pm1.8)$ kcal/mol was obtained from this composition. Error estimates are given as 2σ (σ includes estimates of uncertainties in voltage/height measurements and correlation in the experimental data).

Introduction

Considerable interest has been given to the investigation of organosilicon compounds having a vinyl group linked to a silicon atom. Two of the earlier studies are the gas electron diffraction investigation (GED) of vinyltrichlorosilane[1] and a microwave (MW) study of vinylsilane itself.[2] In both of these studies only one type of conformer was found, having a syn-chloro or a syn-hydrogen conformation relative to the planar vinyl group. The observation of a lengthening of the Si−Cl bond in vinyltrichlorosilane ($CH_2{=}CHSiCl_3$) compared to other non-vinyl chlorosilane compounds (i.e., $SiHCl_3$, $SiCl_4$, CH_3SiCl_3) was discussed.[1]

Partial halogenation of the moiety (for example, in a methyl group) attached to the silicon atom, or of the silicon atom itself, has been found to lead to several conformers in the gas phase.[3−10] A molecule like vinylsilylchloride ($CH_2{=}CHSiH_2Cl$) has been the subject of several investigations,[3−5] and both a syn (syn-chloro) and a gauche ("skew"; syn-hydrogen) conformation have been observed. It is seen that the vinyl group is eclipsed in all conformers of these molecules.

Some more recent papers are dealing with the possible effects of (p−d) π-interaction between the planar vinyl group and the silicon atom in the methylated vinylsilanes,[6,7,11] such as vinyldimethylchlorosilane ($(CH_3)_2SiClCH{=}CH_2$; GED),[6] methylvinyldichlorosilane (VCS, early spectroscopic work),[7] and a recent GED study of the molecule trimethylvinylsilane ($(CH_3)_3SiCH{=}CH_2$).[11]

Both in the spectroscopic work on VCS[7] and in the structure determination of vinyldimethylchlorosilane,[6] evidence was found that supported the assumption of (p−d) π-interaction, while in trimethylvinylsilane[11] the authors concluded that nothing in their findings supported such an hypothesis. It seems more difficult to observe this π-electronic effect when no halogens are present functioning as an indicator through bond shortening or bond lengthening, even though Rustad et al. found significant lengthening of the C═C bond on the r_g basis in the tetravinylsilane molecule.[12] Apparently, such interactions will affect both the $Si{-}C_{methyl}$, the C═C, and the Si−X bonds (X = F, Cl), making them longer than when no vinyl group is present.[6,12]

Chlorination of the silicon atom will evidently have two simultaneously competing effects: Inductive effects will increase the Coloumbic attractions when increasing the number of chlorine atoms, making the $Si{-}C_{vinyl}$ and the Si−Cl bonds shorter. At the same time evidence[13] indicates that because of a more positively charged silicon atom due to chlorination, this inductive effect will enhance the (p−d) π-interaction. Because this interaction will weaken the Coloumbic attractions between the silicon and the chlorine atom, due to π-electron density now occupying in part the empty silicon d-orbitals (making it slightly more negative), the Si−Cl bond tends to lengthen.[1,6]

Methylvinyldichlorosilane (VCS) has been studied by IR/Raman spectroscopy,[7] and it was found to exist in both syn (S) and the gauche (G) conformations in the liquid phase, while only the S-conformer persisted in the solid state, based on studies of the 365 cm^{-1} (G) and 338 cm^{-1} (S) Raman lines at various temperatures.[7] From a van't Hoff plot the energy difference was found to be 0.090 ± 0.030 kcal/mol with the syn conformer lower in energy in the liquid phase.[7] The structural parameters of VCS have been previously determined by GED in 1994 by Naumov et al.[8] with vibrational parameters based on the force field presented in the former work by Taga et al.[7] Again the S/G relationship was confirmed with a composition of 33% S

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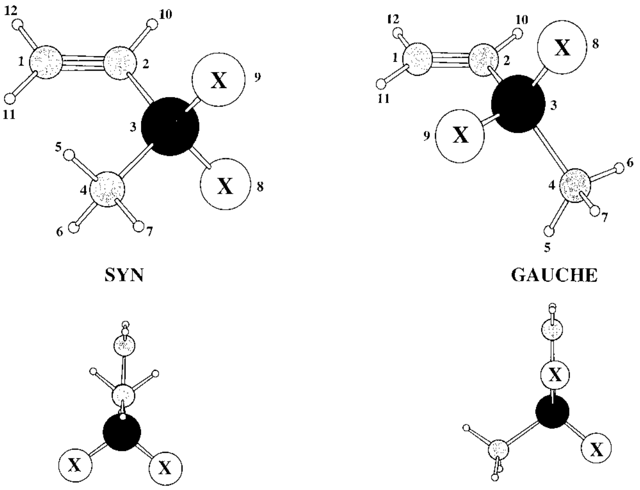

Figure 1. Molecular models of syn and gauche conformers of methylvinyldihalosilane type molecules showing the atom numbering (X = F, Cl).

and 67% G (with error limits ±19%), making the energy difference not significantly different from zero.[8] We have used their error limits and calculated the energy difference as 0.0 ± 1.0 kcal/mol, assuming a simple Boltzmann distribution.[14]

However, contrary to all the evidence of a preference for the eclipsing of the vinyl group, in either conformer, in such vinylsilane molecules[1,6,11,15] (and in the 3-halopropenes and 1-butene as well[16-19]), Naumov et al. found that the Si−Cl bond deviated about 18° from the vinyl plane in the gauche conformer. They found an experimental torsional angle ϕ(CCSiC) of about 104°.[8] This result is in our view quite unexpected.

The IR/Raman spectra for methylvinyldifluorosilane ($CH_2{=}CHSiF_2CH_3$) were recently recorded by Durig et al.[9] for the purpose of making a complete reassignment of the spectra in all phases, after an initial assignment had been made in 1974.[20] No experimental structural information existed for the VFS molecule at that time. In agreement with earlier experience, ab initio calculations at several levels of theory[9] and the vibrational spectra of VFS show evidence of two conformers in the fluid phases, while only the syn conformer exists in the crystalline solid, as was the case also for both methylvinylsilane[15,21] and VCS.[7,10] Durig et al. stated in their paper[9] that it would be very interesting to make a structure determination of VFS by GED to see whether the ab initio calculated parameters are reliable and how its structure compare to the VCS molecule.[7,8,10] We agree with this statement.

The ab initio calculations of Durig et al.[9] of the VFS asymmetric torsional angle show that this angle is somewhat dependent on the choice of basis set, and the largest calculated deviation from the syn-fluoro conformation in the G-conformer is 6.7° using HF/3-21G(d) level of theory.[9] However, this deviation is only 1.3° at the HF/3-21G level of theory (i.e., without the polarization functions).[14] At higher levels of calculation the value of the G torsional angle in VFS gets even closer to 120° (HF/6-31G(d) and MP2/6-31G(d)).[9]

With this background in mind, this paper presents a combined GED and ab initio study of the VFS and the VCS molecule (Figure 1). The VCS molecule is reinvestigated by using a different set of experimental data than used by Naumov et al.[8] Calculated parameters from ab initio have been used as constraints in the refinements. Theoretical vibrational parameters were estimated from normal coordinate calculations by using harmonic force fields.[8,9,22-25] Estimates of the conformational compositions are given and comparisons of structural results with related molecules have also been made.

Experimental Section

The sample of VFS was prepared at the Technische Universität in Graz, while the sample of VCS was obtained commercially (Aldrich Chemical Co.; 98%). Electron diffraction patterns of VFS were recorded with the Oregon State University apparatus on Kodak projector slide plates (accelerating voltage of 60 keV), and patterns of VCS were recorded with Balzers Eldigraph KD-G2 (40 keV) at the University of Oslo[26,27] on Kodak electron image plates with nozzle-tip temperatures of 297−298 K for both molecules.

The nozzle-to-plate distances for VFS were 746.96 and 298.96 mm for the long (LC) and the middle (MC) camera distance experiments, respectively. The electron wavelength was $\lambda = 0.048\,71$ Å. A voltage/distance calibration was made with CS_2 as reference. One diffraction photograph from the LC distance and two diffraction photographs from the MC distance were used in the analysis. These photographs were scanned twice for optical densities, making a total of 6 data sets. Optical densities were measured by using a double-beam (Joyce-Loebl) microdensitometer at Oregon State University. The data were reduced as described elsewhere.[28-30]

The nozzle-to-plate distances for VCS were 498.72 and 248.53 mm. The electron wavelength for VCS was $\lambda = 0.058\,69$ Å. Seven diffraction photographs from the LC and six from the MC distance experiments were used in the analysis. A voltage/distance calibration was made with benzene as reference, as described in a paper from the Oslo diffraction unit.[31] Optical densities were measured by using a Joyce-Loebl microdensitometer at the University of Oslo, and the data were reduced in the usual way.[28-30]

The ranges of data for VFS were $2.00 \leq s/\text{Å}^{-1} \leq 16.00$ and $8.50 \leq s/\text{Å}^{-1} \leq 39.00$. The ranges of data for VCS were $2.00 \leq s/\text{Å}^{-1} \leq 15.50$ and $4.00 \leq s/\text{Å}^{-1} \leq 30.25$. The data interval was $\Delta s = 0.25$ Å^{-1}. A calculated background[32] was subtracted from the data for each plate to yield experimental intensity curves in the form $sI_m(s)$. The average experimental intensity curves for VFS are shown in Figure 2 while the curves for VCS are shown in Figure 3. Figure 4 shows the final experimental radial distribution (RD) curve for VFS, and Figure 5 shows the corresponding curves for VCS calculated in the usual way from the modified molecular intensity curves $I'(s) = sI_m(s)Z_{Si}Z_X(A_{Si}A_X)^{-1}\exp(-0.002s^2)$, where X = F or Cl; $A = s^2F$ and F is the absolute value of the complex electron scattering amplitudes. The scattering amplitudes and phases were taken from tables.[33]

Structure Analysis

From the experimental RD curves and results obtained for related molecules, as well as results obtained from theoretical calculations, trial values for bond distances and bond angles were obtained for both VFS and VCS. The geometries were fully optimized at the HF/6-311G(d) and the MP2/6-311G(d) level for VFS while the levels chosen for VCS were HF/6-31G(d) and MP2/6-311G(d) using GAUSSIAN 94.[34]

To calculate energy estimates by using higher basis sets the geometry optimizations were followed by MP2(fc)/6-311+G(d,p) single-point energy calculations (SP-MP2). This method uses the frozen core (fc) approximation and includes correction for electron correlation via perturbation theory through the second order. The basis set is triple-ζ with diffuse functions on non-hydrogen atoms and includes polarization functions on all atoms.

In addition zero-point energies (ZPE) and the vibrational and rotational entropy contributions (S*) were estimated at the HF level by using the 6-311G(d) basis set for VFS and the 6-31G-

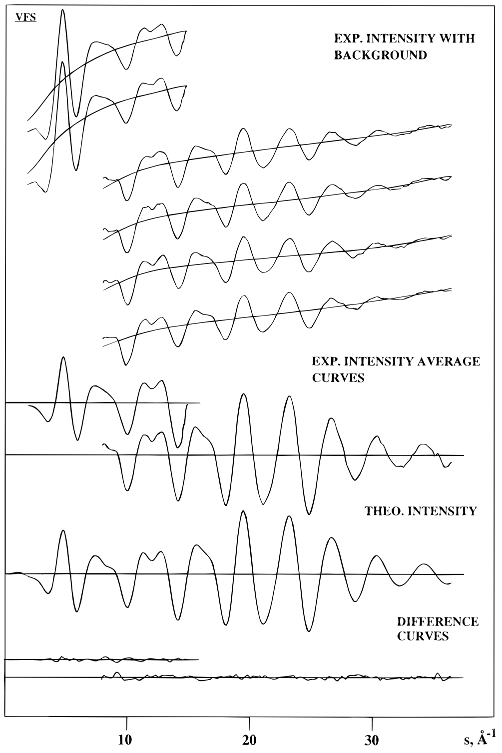

Figure 2. Intensity curves ($sI_m(s)$) for methylvinyldifluorosilane (VFS). The experimental curves are averages of all six data sets (three plates) shown for the two camera distances. The theoretical curve was calculated from the structural parameters given in Table 1. The difference curves result from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

(d) basis set for VCS corresponding to the conformational stationary points found at these levels of theory for the molecules. The ZPE's were scaled before correction of the electronic energies by a factor of 0.893[35] to compensate for neglect of electron correlation at the HF level. This calculating procedure is similar to the one suggested by Wiberg et al.[36]

For both molecules the energy as a function of the asymmetric torsional angle ϕ(CCSiC) was obtained, again using HF level of theory with the 6-311G(d) basis for VFS and the 6-31G(d) basis for VCS with a 30° step size for the asymmetric torsion. ZPE-corrected energies at the conformational minima were also calculated. These data have been assembled in Table 7.

Refinements of the molecular structures based on the GED data were made by the least-squares method,[37] adjusting a theoretical $sI_m(s)$ curve for each molecule simultaneously to the two average experimental intensity curves, one from each of the two camera distances using a unit weight matrix.

From the experimental compositions, an energy difference between the two conformers for each molecule was estimated. If α is the composition from the GED data, the energy difference, ΔE^0, was found by the formula

$$\Delta E^0_{G-S} \approx \Delta H^0_{G-S} = \Delta G^0_{G-S} + T\Delta S^0_{G-S} = -RT\ln\left(\frac{\alpha_G}{\alpha_S}\right) + RT\ln 2 + T\Delta S^*_{G-S}$$

where $\Delta S^*_{G-S} = S^*_G - S^*_S$ is the entropy difference from vibration and rotation calculated from the respective ab initio results.

The structures were converted from the geometrically consistent r_α to the r_a-type required by the formula for the scattered intensities 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 a temperature of 298 K from harmonic force fields ($r_a = r_g - l^2/r = r_\alpha - l^2/r + K + \delta r$).[38,39]

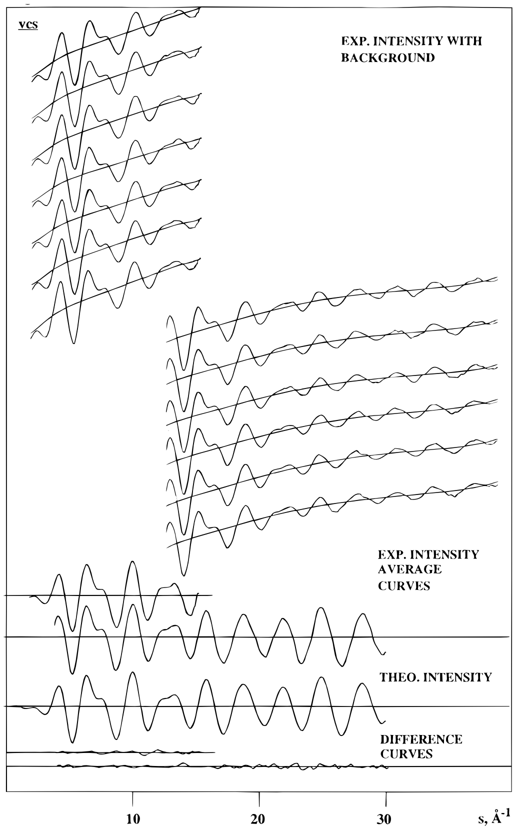

Figure 3. Intensity curves ($sI_m(s)$) for methylvinyldichlorosilane (VCS). The experimental curves are averages of all 13 plates shown for the two camera distances. The theoretical curve was calculated from the structural parameters given in Table 4. The difference curves result from subtracting the relevant part of the theoretical curve from the average experimental curves.

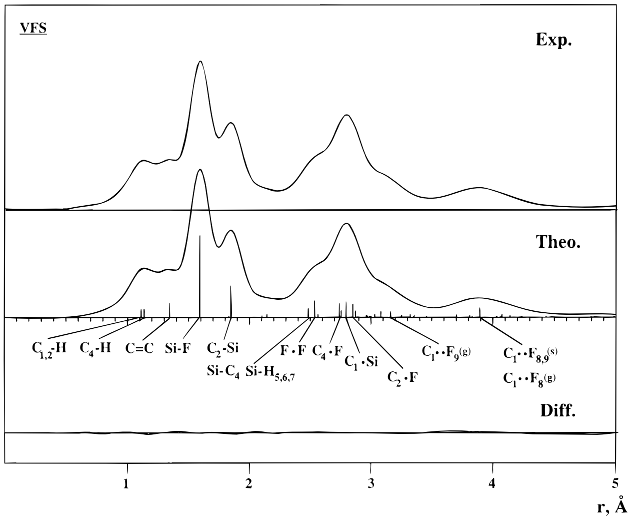

Figure 4. Radial distribution curves for methylvinyldifluorosilane (VFS). The experimental curve was calculated from the composite of the two average experimental curves shown in Figure 2 with the use of theoretical data for the region $0 \leq s/\text{Å}^{-1} \leq 1.75$ and $B/\text{Å}^2 = 0.0020$. The difference curve is experimental minus theoretical. The vertical lines indicate the interatomic distances; they have lengths proportional to the distance weights.

The internal coordinate force constants for VFS were taken from the results of the normal coordinate analysis carried out by Durig et al.[9] based on their Cartesian MP2 force field

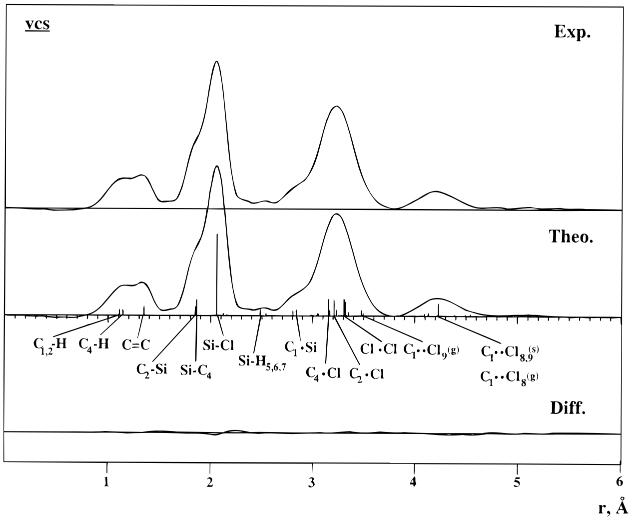

Figure 5. Radial distribution curves for methylvinyldichlorosilane (VCS). The experimental curve was calculated from the composite of the two average experimental curves shown in Figure 3 with the use of theoretical data for the region $0 \leq s/\text{Å}^{-1} \leq 1.75$ and $B/\text{Å}^2 = 0.0020$. The difference curve is experimental minus theoretical. The vertical lines indicate the interatomic distances, they have lengths proportional to the distance weights.

obtained with the 6-31G(d) basis set. The magnitudes of our calculated K_T values became reasonable first after introducing torsional and out-of-plane force constants from the work of Naumov et al.[8] For VCS a more general force field was used,[22-25] incorporating some values from the work of Naumov et al.[8]

The results from the HF/6-311G(d) and HF/6-31G(d) ab initio geometry calculations are incorporated in the GED analysis as constraints for VFS and VCS, respectively. This procedure of using ab initio results as constraints in the GED analysis has been shown to be very useful.[19,40,41]

For the remainder of the structure analysis, we will discuss each molecule separately.

Analysis of Methylvinyldifluorosilane. The geometry of the conformers was described by a set of independent parameters, in our refinements chosen as r(C=C), r(C_{vinyl}—Si), r(⟨C—H⟩) (average distance), r($Si—F_9$), ∠(⟨CCH⟩) (average angle), ∠(CCSi), ∠(C_2SiF_9), P(FSiF) (projection angle; the angle between the two Si—F bonds projected on a plane perpendicular to Si—C), P(HC_4H) (projection angle; the angle between the two C—H bonds projected on a plane perpendicular to Si—C), ∠(SiC_4H), ∠(CSiC), $\phi 1 = \phi(\text{CCSiC})_{\text{Syn}}$, $\phi 2 = \phi(\text{H}_5\text{CSiC}_{\text{vinyl}})_{\text{Syn}}$, $\phi 1_{\text{Gauche}}$, and $\phi 2_{\text{Gauche}}$ (torsional angles, only the torsional $\phi 1_{\text{Gauche}}$ parameter is refined). In addition several constant values of differences between parameters were incorporated as constraints; for instance the parameter r(Si—C_{methyl}) is not listed above because its value is dependent on the value of r(C_{vinyl}—Si), and the difference between these two bonds is set equal to 0.0043 Å in the syn conformer. Differences between corresponding bond distances and bond angles between syn and the gauche conformers were also kept constant at calculated values.

The vibrational properties of the molecule were specified by 66 amplitude parameters for each conformer, corresponding to the number of interatomic distances in the molecule. 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 force field.

In the final refinement eight geometrical parameters, eight amplitude parameters, and the conformational composition (α) were refined simultaneously. The results of this refinement are given in Table 1 where also the corresponding geometrical values from the ab initio calculations are given (HF/6-311G(d)). Selected bonding and nonbonding distances together with refined and calculated vibrational amplitudes from the scaled MP2 force field[9] are given in Table 2, where also the ab initio MP2/6-311G(d) values are shown. The correlation matrix for the refined parameters is given in Table 3.

TABLE 1: Structural Parameters Obtained for Methylvinyldifluorosilane (VFS), Syn Conformer, from the GED Data Together with HF ab Initio Values

	electron diffraction,[a] syn			ab initio calculations, HF/6-311G(d)	
	r_g	l_{ij}(exptl)	l_{ij}(calcd)	syn	gauche
bond lengths					
C=C	1.344(5)	0.051(5)	0.041	1.324	1.325
C_2—Si	1.846(3)	0.054(3)[b]	0.049	1.848	1.847
Si—C_4	1.851(3)	0.055(3)[b]	0.050	1.852	1.852
C_2—H	[1.114]	0.058(8)[c]	0.075	1.080	1.080
C—H_{11}	[1.119]	0.057(8)[c]	0.075	1.078	1.077
C—H_{12}	[1.109]	0.057(8)[c]	0.075	1.077	1.077
Si—F_8	1.592(2)	0.046(2)[d]	0.040	1.592	1.592
Si—F_9	1.592(2)	0.046(2)[d]	0.040	1.592	1.592
C_4—H_7	[1.140]		0.075	1.085	1.086
C_4—$H_{5,6}$	[1.140]		0.075	1.085	1.086
valence angles					
CCH_{10}		[117.9]		117.9	118.1
CCH_{11}		[122.5]		122.5	122.1
CCH_{12}		[122.1]		122.1	122.1
CCSi		123.3(8)		123.8	122.8
CSiC		113.4(11)		115.9	115.7
C_2SiF_8		112.8(5)		108.8	109.6
C_2SiF_9		112.8(5)		108.8	107.8
SiC_4H		111.6(34)		111.1	111.1
HC_1H		[115.4]		115.4	115.9
FSiF		106.0(6)		104.5	105.8
$FSiC_4$		105.6(8)		109.1	108.8
SiC_2H		118.8(8)		118.3	119.1
HC_4H		107.2(37)		107.7	107.8
torsion angles	syn	gauche		syn	gauche
$\phi 1$(CCSiC)	[0.0]	117.4 (±14.3)		0.0	120.2
$\phi 2$(HC_4Si_2)	[60.0]	[60.0]		60.6	59.8
α(×100)[e]	35(41)	65(41)		20.7	79.3
ΔE_{G-S}[f]		0.0(±1.2)		−0.39	

[a] Distances (r_g) and amplitudes (l_{ij}) are in ångstrøms (Å), angles (∠α) in degrees. Parenthesized values are 2σ are include estimates of uncertainties in voltage/nozzle heights and of correlation in the experimental data. Values in square brackets were kept constant in the final refinement. $R = 0.062 = [\sum w_i \Delta_i^2 / \sum w_i (s_i I_m^{\text{exp}}(s_i))^2]^{1/2}$ and $\Delta_i = s_i I_m^{\text{exp}}(s_i) - s_i I_m^{calc}(s_i)$. [b-d] These amplitudes (l_{ij}) were refined as groups. [e] Conformational composition (α-values in percent) from the GED refinements and as calculated from the HF/6-311G(d) energy difference by using a Boltzmann distribution and scaled zero-point energy corrections. [f] Energy differences in kcal/mol. The ab initio value is corrected with the scaled ZPE difference. The GED value is estimated from the experimental α-values including vibrational and rotational entropy differences ($\Delta S^*_{\text{G-S}} = -2.8\times 10^{-4}$ kcal/mol·K).

The theoretical intensity curve for the final model is shown in Figure 2 together with experimental and difference curves. Figure 4 shows the corresponding RD curves. In Figure 6 the experimental RD curve is shown together with theoretical curves calculated for the 100% syn conformer, the 100% gauche conformer, and a mixture of 35% syn and 65% gauche conformers. This is done to give a visual impression of the sensitivity of the experimental data to the conformational composition. In all models the methyl group on the silicon had an exact staggered position.

Analysis of Methylvinyldichlorosilane. The geometries of the conformers of VCS were described similarly to VFS by a set of independent parameters: r(C=C), r(C_{vinyl}—Si), r(⟨C—H⟩),

TABLE 2: Selected Interatomic Distances for Methylvinyldifluorosilane (VFS) from the GED Data Together with MP2 ab Initio Values

	electron diffraction[a]				ab initio calculations
	r_g	l_{ij}(exptl)	l_{ij}(calcd)	r_α	MP2/6-311G(d)
		Syn			
$r(C{=}C)$	1.344(5)	0.051(5)[b]	0.041	1.323	1.346
$r(C_2{-}Si)$	1.846(3)	0.054(3)[c]	0.049	1.842	1.844
$r(Si{-}C_4)$	1.851(3)	0.055(3)[c]	0.050	1.846	1.847
$r(Si{-}F_8)$	1.592(2)	0.046(2)[d]	0.040	1.586	1.613
$r(Si{-}F_9)$	1.592(2)	0.046(2)[d]	0.040	1.586	1.613
$r(C_1{\cdot}Si)$	2.804(9)	0.055(11)[e]	0.081	2.796	2.807
$r(C_2{\cdot}C_4)$	3.087(20)	0.085(23)[f]	0.095	3.083	3.113
$r(C_2{\cdot}F_8)$	2.863(9)	0.065(7)[g]	0.087	2.859	2.817
$r(C_2{\cdot}F_9)$	2.863(9)	0.065(7)[g]	0.087	2.859	2.817
$r(C_4{\cdot}F_8)$	2.744(14)	0.069(7)[g]	0.091	2.739	2.823
$r(C_4{\cdot}CF_9)$	2.744(14)	0.069(7)[g]	0.091	2.739	2.823
$r(C_1{\cdots}C_4)$	3.362(39)	0.157(23)[f]	0.166	3.353	3.390
$r(C_1{\cdots}F_8)$	3.891(12)	0.154(42)[h]	0.128	3.887	3.880
$r(C_1{\cdots}F_9)$	3.891(12)	0.154(42)[h]	0.128	3.887	3.880
		Gauche			
$r(C_1{\cdots}C_4)_G$	4.079(108)		0.143	4.076	4.150
$r(C_1{\cdots}F_8)_G$	3.908(86)	0.155(42)[h]	0.129	3.904	3.837
$r(C_1{\cdots}F_9)_G$	3.166(21)	0.135(9)[g]	0.157	3.156	3.065

[a] Distances (r_g,r_α) and amplitudes (l_{ij}) are in ångstrøms (Å), angles ($\angle_\alpha$) in degrees. Parenthesized values are 2σ and include estimates of uncertainties in voltage/nozzle heights and of correlation in the experimental data. [b−h] These amplitudes were refined as groups as noted in the text.

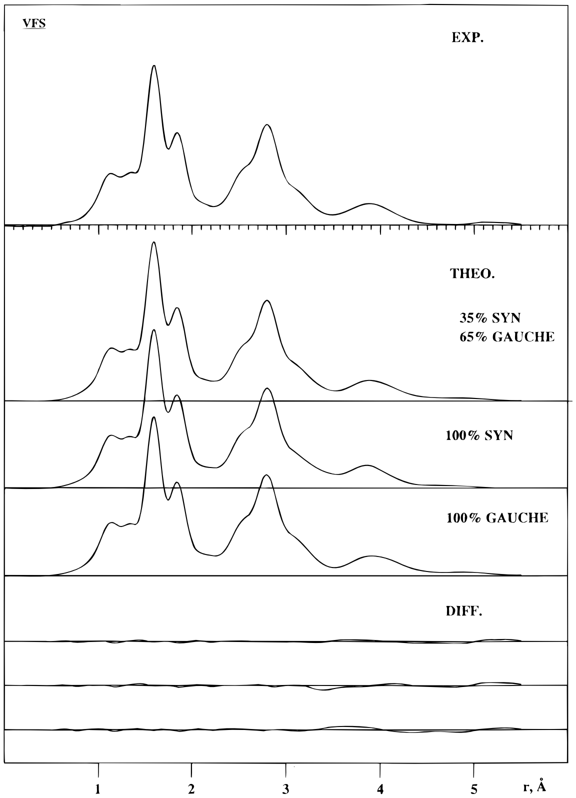

Figure 6. Theoretical radial distribution curves for methylvinyldifluorosilane (VFS), showing a mixture of 35% syn and 65% gauche conformers and curves for 100% of the syn and gauche conformers, together with the experimental curve (EXP.) and difference curves (DIFF.).

$r(Si{-}Cl_9)$, $\angle(\langle CCH\rangle)$, $\angle(CCSi)$, $\angle(C_2SiCl_9)$, $P(ClSiCl)$ (projection angle), $P(HC_4H)$ (projection angle), $\angle(SiC_4H)$, $\angle(CSiC)$, $\phi 1 = \phi(CCSiC)_{Syn}$, $\phi 2 = \phi(H_5CSiC_{vinyl})_{Syn}$, $\phi 1_{Gauche}$, $\phi 2_{Gauche}$ (torsional angles, only the torsional $\phi 1_{Gauche}$ parameter is refined). Like in the analysis of the VFS molecule, several constant values of differences between parameters were incorporated as constraints. Again, none of the difference parameters included were refined but were held constant at the ab initio values.

The vibrational amplitudes were treated as described for VFS. In the final refinement seven geometrical parameters, seven amplitude parameters, and the conformational composition (α) were refined simultaneously.

The results of this refinement are given in Table 4 where also the corresponding geometrical values from the ab initio calculations are given (HF/6-31G(d)). Selected bonding and nonbonding distances together with calculated and refined vibrational amplitudes are given in Table 5, where also the ab initio MP2/6-311G(d) values are shown. The correlation matrix for the refined parameters is given in Table 6.

The theoretical intensity curve for the final model is shown in Figure 3 together with experimental and difference curves. Figure 5 shows the corresponding RD curves. In Figure 7 the experimental RD curve is shown together with different theoretical curves for reasons described in the VFS section.

Discussion

1. General Points. In this work we have used results from the ab initio calculations as constraints in the least-squares refinements. The differences in structural parameters between the syn and gauche conformers of VFS and VCS are not large (see Table 9).

TABLE 3: Correlation Matrix (×100) for the Refined Parameters of Methylvinyldifluorosilane (VFS)

	σ_{LS}[a]	r_1	r_2	r_3	$\angle_4$	$\angle_5$	$\angle_6$	$\angle_7$	$\angle_8$	l_9	l_{10}	l_{11}	l_{12}	l_{13}	l_{14}	l_{15}	l_{16}	α_{17}
$C{=}C$	0.18	100																
$C_2{-}Si$	0.06	−11	100															
$Si{-}F$	0.03	1	3	100														
CCSi	27	−43	−22	12	100													
C_2SiF	18	13	−8	5	8	100												
$SiCH_{5,6,7}$	120	6	5	−11	−16	37	100											
CSiC	39	8	−1	8	39	34	−39	100										
$\phi 1(G)$	504	1	2	−8	−16	−8	7	−8	100									
$l(C{=}C)$	0.14	−4	−2	−6	−3	0	13	0	1	100								
$l(C_2{-}Si)$	0.06	15	−18	10	3	1	−19	13	−4	−4	100							
$l(C_2{-}H)$	0.28	16	−8	5	−4	3	−9	8	−2	−13	24	100						
$l(Si{-}F_9)$	0.05	25	−25	8	−1	7	−14	12	−3	−1	50	30	100					
$l(C{\cdot}Si)$	0.38	−11	0	−3	−19	−78	−10	−67	7	0	2	−1	1	100				
$l(C{\cdot}C)$	0.80	−3	−4	0	2	−18	−5	−1	0	1	−6	−5	−7	9	100			
$l(C_2{\cdot}F)$	0.24	−1	−5	−3	−2	−58	−45	−14	4	3	18	9	23	36	17	100		
$l(C_1{\cdots}F)$	1.5	8	1	−17	−39	−5	24	−22	46	2	−4	−1	1	9	−10	−1	100	
α	15	17	7	−27	−55	4	5	12	21	1	−3	1	−1	−16	−21	−9	47	100

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

TABLE 4: Structural Parameters Obtained for Methylvinyldichlorosilane (VCS), Syn Conformer, from the GED Data Together with HF ab Initio Values

	electron diffraction,[a] syn			ab initio calculations, HF/6-31G(d)	
	r_g	l_{ij}(exptl)	l_{ij}(calcd)	syn	gauche
bond lengths					
C═C	1.341(6)	0.032(7)	0.042	1.325	1.325
C_2—Si	1.843(4)	0.054(4)[b]	0.051	1.856	1.857
Si—C_4	1.855(4)	0.055(4)[b]	0.052	1.867	1.867
C_2—H	[1.112]	0.105(23)[c]	0.077	1.079	1.081
C—H_{11}	[1.113]	0.105(23)[c]	0.077	1.076	1.075
C—H_{12}	[1.104]	0.105(23)[c]	0.077	1.077	1.077
Si—Cl_8	2.051(2)	0.052(3)[d]	0.047	2.068	2.069
Si—Cl_9	2.051(2)	0.052(3)[d]	0.047	2.068	2.066
C_4—H_7	[1.140]		0.078	1.085	1.085
C_4—$H_{5,6}$	[1.140]		0.078	1.086	1.086
valence angles:					
CCH_{10}		[118.7]		118.7	118.3
CCH_{11}		[122.6]		122.6	122.4
CCH_{12}		[121.9]		121.9	121.7
CCSi		123.3(17)		123.0	125.5
CSiC		111.6(17)		114.7	113.8
C_2SiCl_8		110.8(7)		108.7	108.4
C_2SiCl_9		110.8(7)		108.7	109.8
SiC_4H		[110.7]		110.7	110.7
HC_1H		[115.5]		115.5	115.9
ClSiCl		108.1(7)		107.0	107.9
$ClSiC_4$		107.7(11)		108.8	108.3
SiC_2H		118.0(17)		118.3	116.2
HC_4H		[108.2]		108.2	108.2
torsion angles	syn	gauche		syn	gauche
$\phi 1$(CCSiC)	[0.0]	121.2(±15.7)		0.0	118.9
$\phi 2$(HC_4SiC_2)	[60.0]	[60.0]		60.4	61.9
α (×100)[e]	45(64)	55(64)		36.3	63.7
ΔE_{G-S}[f]		0.3(±1.8)		0.08	

[a] Distances (r_g) and amplitudes (l_{ij}) are in ångstrøms (Å), angles ($\angle_\alpha$) in degrees. Parenthesized values are 2σ and include estimates of uncertainties in voltage/nozzle heights and of correlation in the experimental data. Values in square brackets were kept constant in the final refinement. $R = 0.064 = [\sum w_i\Delta_i^2/\sum w_i(s_iI_m^{\exp}(s_i))^2]^{1/2}$ and $\Delta_i = s_iI_m^{\exp}(s_i) - s_iI_m^{calc}(s_i)$. [b–d] These amplitudes (l_{ij}) were refined as groups. [e] Conformational composition (α-value in percent) from the GED refinements and as calculated from the HF/6-31G(d) energy difference using a Boltzmann distribution and scaled zero-point energy corrections. [f] Energy differences in kcal/mol. The ab initio value is corrected with the scaled ZPE difference. The GED value is estimated from the experimental α-values including vibrational and rotational entropy differences ($\Delta S^*_{G-S} = -3.6 \times 10^{-5}$ kcal/mol·K).

TABLE 5: Selected Interatomic Distances for Methylvinyldichlorosilane (VCS) from the GED Data Together with MP2 ab Initio Values

	electron diffraction[a]				ab initio calculations
	r_g	l_{ij}(exptl)	l_{ij}(calcd)	r_α	MP2/6-311G(d)
Syn					
r(C═C)	1.341(6)	0.032(7)[b]	0.042	1.317	1.346
r(C_2—Si)	1.843(4)	0.054(4)[c]	0.051	1.838	1.845
r(Si—C_4)	1.855(4)	0.055(4)[c]	0.052	1.849	1.851
r(Si—Cl_8)	2.051(2)	0.052(3)[d]	0.047	2.046	2.057
r(Si—Cl_9)	2.051(2)	0.052(3)[d]	0.047	2.046	2.057
r(C_1·Si)	2.799(23)	0.068(10)[e]	0.080	2.787	2.809
r(C_2·C_4)	3.054(32)		0.096	3.049	3.100
r(C_2·Cl_8)	3.204(14)	0.097(6)[f]	0.101	3.200	3.171
r(C_2·Cl_9)	3.204(14)	0.097(6)[f]	0.101	3.200	3.171
r(C_4·Cl_8)	3.152(22)	0.098(6)[f]	0.103	3.147	3.187
r(C_4·Cl_9)	3.152(22)	0.098(6)[f]	0.103	3.147	3.187
r(C_1···C_4)	3.310(39)		0.162	3.299	3.370
r(C_1···Cl_8)	4.223(17)	0.146(46)[g]	0.147	4.218	4.223
r(C_1···Cl_9)	4.223(17)	0.146(46)[g]	0.147	4.218	4.223
Gauche					
r(C_1···C_4)$_G$	4.093(108)		0.143	4.086	4.142
r(C_1···Cl_8)$_G$	4.238(114)	0.149(46)[g]	0.151	4.227	4.231
r(C_1···Cl_9)$_G$	3.479(36)		0.174	3.473	3.397

[a] Distances (r_g, r_α) and amplitudes (l_{ij}) are in ångstrøms (Å), angles ($\angle_\alpha$) in degrees. Parenthesized values are 2σ and include estimates of uncertainties in voltage/nozzle heights and of correlation in the experimental data. [b–g] These amplitudes were refined as groups as noted in the text.

We have also calculated geometries and energies employing the MP2 level with the 6-311G(d) basis set. Table 9 shows that within each molecule, the sign of the differences are the same for all listed parameters in going from HF to MP2 level of theory, and even the values themselves are nearly identical, especially for the bond distances. This is true for both the VFS and the VCS molecule. This suggests that using constraining difference values from the HF level of calculation should be sufficiently accurate in GED investigations of these molecules.

Depending on the basis set in use and the system under consideration, differences between experimental and HF-level ab initio calculations usually lie within 0.02 Å in bond lengths and within 1° in bond angles.[42] For most of the parameters in the molecules treated in this paper, this is almost true. However, the ab initio values for $\angle C_2SiX$ in the conformers of both molecules are not within the experimental error limits of the GED values (111−113°; Tables 1 and 4). Instead, both HF and MP2 calculations seem to give results around the standard tetrahedral value of 109.5° or lower. For X = F this may be seen in all calculations, including the HF-level calculations with the 3-21G(d),[9] 6-31G(d),[9] and 6-311G(d) basis sets and the MP2-level calculations with the 6-31G(d)[9] and 6-311G(d) basis sets. For X = Cl all the HF and MP2 calculations also give $\angle C_2SiX$ values smaller than experimental results, with the

TABLE 6: Correlation Matrix (×100) for the Refined Parameters of Methylvinyldichlorosilane (VCS)

	σ_{LS}[a]	r_1	r_2	r_3	$\angle_4$	$\angle_5$	$\angle_6$	$\angle_7$	l_8	l_9	l_{10}	l_{11}	l_{12}	l_{13}	l_{14}	α_{15}
C═C	0.19	100														
C_2—Si	0.13	−14	100													
Si—Cl	0.05	−9	25	100												
CCSi	60	−8	23	−34	100											
C_2SiCl	24	−9	0	31	−36	100										
CSiC	59	−15	9	50	−61	54	100									
$\phi 1$(G)	556	−6	−7	−5	−14	−7	15	100								
l(C═C)	0.26	0	−26	−17	1	−5	−7	1	100							
l(C_2—Si)	0.10	18	8	38	−3	4	6	−6	−10	100						
l(C_2—H)	0.82	18	−2	−5	1	−2	−5	−3	10	7	100					
l(Si—Cl_9)	0.06	22	−61	−22	−4	−9	−13	−3	24	1	6	100				
l(C—Si)	0.34	−2	1	2	−3	−7	−7	0	−1	2	−4	6	100			
l(C_2·Cl)	0.64	9	−7	−23	6	31	−12	−20	9	−6	2	20	−12	100		
l(C_1···Cl)	1.6	12	25	−26	65	−26	−56	−44	−1	4	6	−1	−3	24	100	
α	23	12	31	−41	85	−41	−71	−11	−2	1	5	−8	−4	21	75	100

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

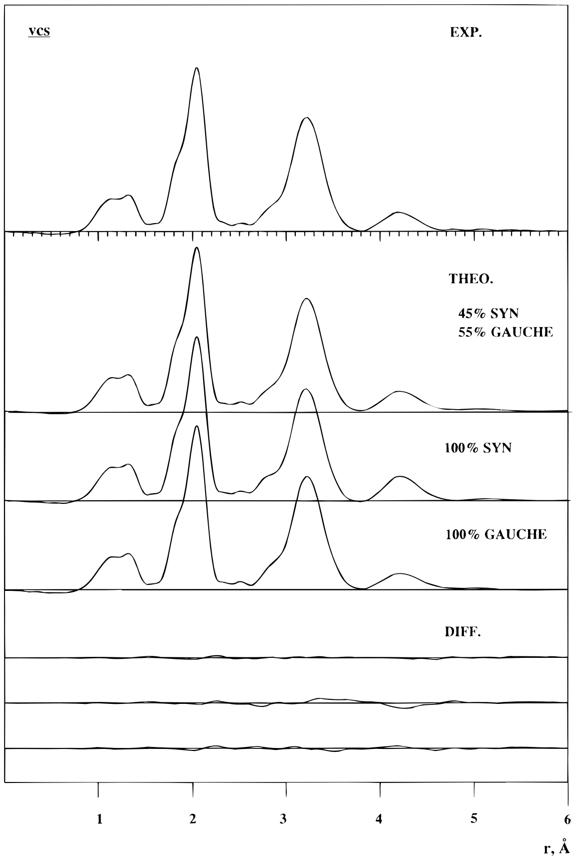

Figure 7. Theoretical radial distribution curves for methylvinyldichlorosilane (VCS), showing a mixture of 45% syn and 55% gauche conformers and curves for 100% of the syn and gauche conformers, together with the experimental curve (EXP.) and difference curves (DIFF.).

TABLE 7: Ab Initio Relative Energies (kcal/mol) for Methylvinyldilfuorosilane (VFS, HF/6-311G(d)) and Methylvinyldichlorosilane (VCS, HF/6-31G(d)) as a Function of the Asymmetric Torsional Angle $\phi 1$[a]

$\phi 1 = \phi$(CCSiC)	$\Delta E(\phi 1)$, VFS	$\Delta E(\phi 1)$, VCS
0 (syn)	0.39	0.0
30	0.93	0.75
60	1.55	1.57
90	0.84	0.82
120.2 (VFS gauche angle)	0.0	
118.9 (VCS gauche angle)		0.08
150	0.78	0.89
180 (anti)	1.73	1.76

[a] For stable conformations the energies shown are corrected with scaled ZPE values for both molecules.

3-21G(d) (HF),[10] 6-31G(d) (HF), 6-31G(d) (MP2), and 6-311G-(d) (MP2) basis sets.

2. The Behavior of the C═C Double Bond Distance. We would like to discuss some particular features encountered regarding the correlation between ab initio calculations and GED results for the C═C double bond. For both molecules the HF-level calculations of the r(C═C) distance parameter is about 0.02 Å too short compared to the r_g values of 1.344(5) Å and 1.341(6) Å (syn values of VFS and VCS, respectively). At the MP2 level, the agreement with the r_g experimental values is much better, giving calculated values of about 1.346 Å for both molecules (Tables 2 and 5).

It seems correlated optimizations are required to estimate correctly the thermal average interatomic value (the r_g value) of the C═C double bond. However, the theoretical ab initio values are usually regarded as being derived from equilibrium nuclear positions; i.e., they are regarded as r_e values. The accuracy of these "equilibrium" values, apparently, has to be limited depending on the level of theory used and the type and size of the basis set.

It may be recalled that the formula $r_\alpha = r_e + 3a_3l^2/2$ approximately applies[43] where a_3 is the anharmonicity constant. Because of this the r_α values obtained from the GED experiment should be regarded as the most appropriate set of values to compare with any set of ab initio values. Based on this, it can not unambiguously be said that the MP2 calculations are more "correct" than the HF calculations for the C═C double bond. For instance, it can be seen that the r_α values are more HF-like than MP2-like (Tables 1−4) for both the VFS and the VCS molecule, where r_α(C═C) = 1.323(5) Å and 1.317(6) Å, respectively, compared to the HF values of 1.324 Å and 1.325 Å, respectively. The MP2 values are, however, closer to the r_g values, and any discussion concerning these values should be based on the vibrational theory involved. This is not always explicitly done in the current literature.

3. The Syn−Gauche Energy Differences. Table 8 shows the ΔE_{G-S} values calculated, corrected with scaled ZPE values, for both molecules at all levels of theory employed in this work and as found from the works of Durig et al.[9,10] It may be seen that for VFS all calculations give an energy difference value with a negative sign, suggesting that the gauche form is the low-energy conformer in the gas phase. An average theoretical energy difference value of −0.25 kcal/mol may be calculated from Table 8 for VFS, whereas the experimental value found in our work is $\Delta E^0_{G-S} = 0.0 \pm 1.2$ kcal/mol. The experimental work in ref 9 does not include any variable temperature studies, so their assumption that the gauche form is the more stable is solely based on the relative intensity of the assigned conformer doublets and their theoretical calculations. The authors therefore question this conclusion in their later paper on the VCS molecule.[10]

In the spectroscopic work on VCS by Durig et al.[10] they confirm the presence of both syn and gauche conformers in the

TABLE 8: Ab Initio Values at Different Levels of Theory of the Conformational Energy Difference in Methylvinyldifluorosilane (VFS) and Methylvinyldichlorosilane (VCS)[a]

	VFS[b]						VCS[b]				
	HF/ 3-21G(d)[c]	HF/ 6-31G(d)[c]	HF/ 6-311G(d)	MP2/ 6-31G(d)[c]	MP2/6-311+G(d,p)// HF/6-311G(d)	MP2/ 6-311G(d)	HF/ 6-31G(d)	HF/ 3-21G(d)[c]	MP2/ 6-31G(d)	MP2/6-311+G(d,p)// HF/6-31G(d)	MP2/ 6-311G(d)
ΔE_{G-S}	−0.19	−0.27	−0.39	−0.10	−0.03	−0.32	0.08	−0.02	0.073	0.0	−0.05
α(G)	0.73	0.76	0.79	0.70	0.68	0.77	0.64	0.67	0.64	0.67	0.68

[a] All energy values (ΔE_{G-S}) are in kcal/mol and modified with scaled ZPE corrections. Calculated mole fractions (α(G)) of the gauche conformer corresponding to the energy values shown are also given (undenominated). For VFS: Δ[ZPE(HF/6-311G(d))]$_{G-S}$ = 0.017 71 kcal/mol. For VCS: Δ[ZPE(HF/6-31G(d))]$_{G-S}$ = −0.015 85 kcal/mol. Both values calculated at their corresponding optimized HF structure. [b] The lowest absolute energy values are obtained with the SP-MP2 method. We have for the gauche conformers (Hartrees): E(SP-MP2)$_{VFS}$ = −606.075 190 and E(SP-MP2)$_{VCS}$ = −1325.989 314. [c] These theoretical energy values are calculated from the works of J. R. Durig et al.[9,10] The α-values are calculated from a simple Boltzmann distribution including the multiplicities of 1 (syn) and 2 (gauche). The average α(G)-values from all these methods are 0.74 for VFS (exptl 0.65(41)) and 0.66 for VCS (exptl 0.55(64)).

TABLE 9: Comparison of Differences in Parameters between Syn (S) and Gauche (G) Conformers of Methylvinyldifluorosilane (VFS) and Methylvinyldichlorosilane (VCS) As Calculated at Different Levels of ab Initio Theory (Δ(*G*−*S*))[a]

	Δ(*G*−*S*)			
	VFS (X = F)		VCS (X = Cl)	
	HF/6-311G(d)[b]	MP2/6-311G(d)	HF/6-31G(d)[b]	MP2/6-311G(d)
$C{=}C$	0.001	0.001	0.000	0.000
$C_2{-}Si$	−0.001	0.000	0.001	0.002
$Si{-}C_4$	−0.001	−0.001	0.000	0.000
$C_2{-}H$	0.000	0.000	0.002	0.001
$C{-}H_{11}$	−0.001	−0.001	−0.001	−0.001
$C{-}H_{12}$	0.000	0.000	0.000	0.000
$Si{-}X_8$	0.000	0.000	0.001	0.001
$Si{-}X_9$	0.000	0.000	−0.002	−0.002
$C_4{-}H$	0.000	0.001	0.000	0.000
∠CCSi	−1.0	−0.7	2.5	2.1
∠CSiC	−0.2	0.1	−0.9	−0.4
$\angle C_2SiX_8$	0.8	0.7	−0.3	−0.2
$\angle C_2SiX_9$	−1.0	−1.4	1.1	0.7
$\angle SiC_4H$	0.0	−0.1	0.0	0.0
$\angle HC_1H$	0.5	0.5	0.4	0.5
$\angle CCH_{10}$	0.2	0.2	−0.4	−0.4
$\angle CCH_{11}$	−0.4	−0.5	−0.2	−0.2
$\angle CCH_{12}$	0.0	0.0	−0.2	−0.2
∠XSiX	1.3	1.0	0.9	1.1
$\angle XSiC_4$	−0.3	−0.2	−0.5	−0.6
$\angle SiC_2H$	0.8	0.6	−2.1	−1.7
$\angle HC_4H$	0.1	0.1	0.0	0.0

[a] Units in ångstrøm (Å) and degrees (°). [b] These values were used as constraints in the least-squares analysis of the GED data.

fluid phases, while only the syn conformer remains in the solid. This work[10] includes a variable temperature study where the sample of VCS is dissolved in liquid xenon, which should give results close to the values found in the gas phase. The experimental results gave an enthalpy difference of 220 ± 23 cal/mol, with the syn (termed "cis" by the authors) conformer being the more stable rotamer. The GED experimental value found for VCS in our work is very uncertain with $\Delta E^0_{G-S} = 0.3 \pm 1.8$ kcal/mol, but the two values agree.

The VCS work of Durig et al.[10] also contains several ab initio calculations, including values tabulated as MP2/6-31G(d) results. However, the absolute energy values in Hartrees listed for this calculation cannot be correct, since they are tabulated as higher (less negative) than the HF/6-31G(d) values listed beside it. These apparent erroneous values made us calculate our own values using the MP2(fc)/6-31G(d) method, and we found values in accordance with what was expected when looking at the corresponding values for the SP-MP2 and the MP2/6-311G(d) calculations (Table 8). The listed energy difference[10] not corrected with the ZPE difference was 0.10 kcal/mol (35 cm^{-1}) in favor of the syn form. Using our MP2/6-31G(d) results an energy difference corrected with the scaled ZPE difference is 0.07 kcal/mol (25 cm^{-1}). The uncorrected value in our case was 0.09 kcal/mol (31 cm^{-1}). The energy difference given by Durig et al. is therefore close to but not the same as our results. However, the absolute energies differ by a large amount and the parameter values listed also do not match our results. We therefore conclude that the MP2 results listed in ref 10 cannot be correct.

For both molecules the single-point energy calculations (SP-MP2) give Δ*E* values close to or equal to zero. These values are in somewhat contrast to the other non-SP methods of calculation, even though for VCS all the values are seen to be quite small. It may be important to use correlation-level optimized geometries when calculating correlated energy values if a high level of accuracy is sought, as errors in correlation-level energies from insufficient geometry optimizations do not necessarily cancel, even when differences between the HF and the MP2 geometries are small.[44]

4. Conclusions. Table 10 shows results for several vinylsilane and methylvinylsilane molecules. The value of *r*(Si−F) in VFS suggests no evidence for extended (p−d) π-interaction between the vinyl group and the silicon atom. The study of Si−F bond distances in the work by Stølevik et al.[43] gave an average value of 1.580(5) Å for disubstituted fragments. The value found from the GED data in our work is $r_g = 1.592(2)$ Å. This seems to be a slight significant increase, but the average value in ref 43 is from a mixture of several (physical) types of distances, and therefore it is very hard to know if this increase is real or not. Based on comparison with our r_α value (1.586(2) Å), the increase is no longer significant.

For VCS a slight significant lengthening of the *r*(Si−Cl) parameter may be observed when comparing the experimental values in VCS with the average value obtained for the chlorosilanes in ref 43. We found $r_g(Si{-}Cl) = 2.051(2)$ Å in

TABLE 10: Comparison of Several Vinyl- and Methylvinylsilanes

			Parameters									
Molecule	conf	method[g]	*r*(C=C), Å	*r*(C_2−Si), Å	*r*(C_4−Si), Å	*r*(Si−X), Å	∠XSiX, deg	∠C=CSi, deg	∠CSiC, deg	∠C_2SiX, deg	φ(torsion)	ref
$CH_2{=}CHSiH_2CH_3$	syn	MW	1.353	1.850	1.865	1.483		124.5	111.5	109.0	0°	21
	gauche		1.341	1.847	1.871	1.483		124.5	111.0	108.8	119°	
$CH_2{=}CHSiH_3$	syn	MW	1.347(3)	1.853(3)		1.475		122.9(3)				2
$CH_2{=}CHSi(CH_3)_3$	syn	ED (r_g)	1.359(10)	1.867(3)	1.877(3)			124.6(18)	112.6(8)		0°	11
$CH_2{=}CHSiCl(CH_3)_2$	syn	ED (r_g)	1.347(5)	1.838(3)	1.876(3)	2.078(2)		127.8(12)	110.0[b]	107(1)	17(6)°	6
$CH_2{=}CHSiCl_2CH_3$	syn +	ED (r_α)	1.319(7)	1.837(3)	1.860(3)	2.048(2)	107.5(6)	125.5(13) (s)	115.6(13)	108.4(4)	0°	8
	gauche	(r_g)[f]	1.341	1.840	1.868	2.052		124.3 (13) (g)			103.8° [e]	
$CH_2{=}CHSiCl_2CH_3$	syn	ED (r_g)	1.341(6)	1.843(4)	1.855(4)	2.051(2)	108.1(7)	123.3(17)	111.6(17)	110.8(7)	0°	this work
	gauche		1.342(6)	1.844(4)	1.856(4)	2.049(2)[c]	109.0(7)	125.7(17)	110.7(17)	112.0(7)[d]	121.2° [e]	this work
$CH_2{=}CHSiCl_3$	syn	ED[a]	1.35[b]	1.81(2)		2.060(5)	107(1)	121(3)	111.5(10)			1
$CH_2{=}CHSiF_2CH_3$	syn	ED (r_g)	1.344(5)	1.846(3)	1.851(3)	1.592(2)	106.0(6)	123.3(8)	113.4(11)	112.8(5)	0°	this work
	gauche		1.347(5)	1.845(3)	1.852(3)	1.591(2)	107.3(6)	122.3(8)	113.2(11)	111.7(5)[d]	117.4°[e]	this work
$Si(CH{=}CH_2)_4$	S_4	ED (r_α)	1.324(2)	1.850(2)				124.0(3)	109.5[b]	118.4(10)	17.5(6)°	12
		(r_a)	1.355(2)	1.855(2)						(∠SiCH)		

[a] Type of bond is not specifically given in this article, probably r_a values. Standard deviation (σ) as given in the original text. Some reference books[45] give this error estimate as three times the standard deviation (i.e. 3σ). [b] Assumed value. [c] This value corresponds to the Si−Cl bond lying in the plane of the vinyl group in the gauche conformer. The other bond (by constraining 6-31G(d) value) is 2.052(2) Å. [d] These values correspond to the $\angle C_{(vinyl)}SiX_{(in\text{-}plane)}$ angle in the gauche conformer. The other angles are (by constraining 6-311G(d) and 6-31G(d) values, respectively) 113.5(5)° (X = F) and 110.6(7)° (X = Cl). [e] The error limits for these torsional angles are for VCS, by Naumov et al.,[8] ±5.4° (3σ); for VCS (this work), ±15.7° (2σ); for VFS (this work), ±14.3° (2σ). [f] r_g values from ref 8 calculated by us for comparison with the corresponding data from the present work. [g] MW = microwave spectroscopy; ED = electron diffraction.

VCS, compared to an average value of 2.040(5) Å from ref 43. This average value[43] is based on ethane-type molecules, indicating therefore a slight significant increase, when a vinyl group is attached to the silicon atom. However, as for VFS, it is still difficult to say if this apparent small lengthening is due to any real (p−d) π-interaction in the VCS molecule.

In Table 10, the VCS values found by Naumov et al.[8] are shown both as r_α and r_g types. The r_g values are calculated by us from the data available in ref 10, since the authors did not explicitly tabulate these values.[8] Here we should note that the high $r_g(C_4{-}Si)$ value of 1.868(3) Å[8] is due to a constraining value of +2.3 pm relative to $r_g(C_2{-}Si)$, while our work has a corresponding constraining value of +1.1 pm calculated from the HF/6-31G(d) results for VCS. From the MP2/6-311G(d) results this value is only +0.6 pm. The constraining value used in ref 8 therefore seems too high. Most of the other bond distances and bond angles from the two investigations are in good agreement. This is not, however, the case for the gauche torsional angle.

No significant deviation from a syn-fluoro or a syn-chloro conformation is found in the gauche conformer of either the VFS or the VCS molecule in the present work. We have found $\phi(CCSiC)_{VFS} = 117.4(14.3)°$ and $\phi(CCSiC)_{VCS} = 121.2(15.7)°$, confirming the syn preference in relation to the vinyl group that has previously been found in these types of molecules. All theoretical calculations also give values of ϕ_{Gauche} close to 120°. We therefore believe the earlier reported value[8] of 103.8° most probably is in error.

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