# Conformational Stability and Structural Determination of Vinyldichlorosilane by *ab initio* Calculations

Mohammad A. Qtaitat

Chemistry Department, Mu'tah University, Karak – Jordan

Reprint requests to Dr. M. A. Q.; Fax: 962-6-654 061.

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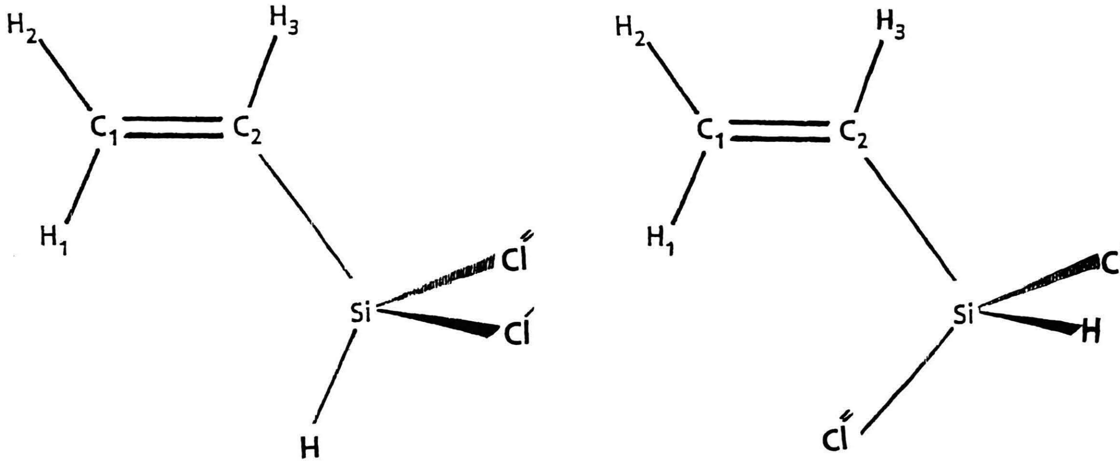
The Conformational stability and barriers of interconversion between the cis and gauche conformers of vinyldichlorosilane, $CH_2CHSiHCl_2$, have been studied using *ab initio* calculations employing the RHF/3-21G* and RHF/6-31G* basis sets. The cis conformer was found to be more stable than the gauche one by 45 $cm^{-1}$ (539 J/mol) and 140 $cm^{-1}$ (1.68 kJ/mol) from the RHF/3-21G* and RHF/6-31G* basis sets, respectively. Additionally, the structural parameters of both rotamers have been calculated. These results are compared with results of related molecules.

*Key words:* Conformational Stability; *ab initio* Calculations; Vinyldichlorosilane.

## Introduction

The structural geometry and conformational stability of vinyl substituted silanes with the general formula: $CH_2CHSiH_2X$ (X: Cl, F, $CH_3$) have been the subject of several studies [1–4]. From these studies, which include *ab initio* calculations and vibrational spectra, we confirmed the existance of the cis and gauche forms of these molecules. A further compound of this family is vinyldichlorosilane: $CH_2CHSiHCl_2$. From previous studies [1–4] and an initial vibrational study [5] of this molecule one expects the existance of two conformations, Fig. 1, the cis form, where the H atom in the $SiHCl_2$ moiety is eclipsing the double bond, and the gauche rotamer, where the H atom is by about 120° away from the double bond. The structural parameters and the potential function governing the barriers of internal rotation of the asymmetric $SiHCl_2$ rotor of this molecule have not yet been investigated. Therefore we have carried out *ab initio* calculations on this molecule, so that the effect of the substituent Cl atoms on the conformational stability and structural geometry of vinyldichlorosilane could be evaluated. Additionally, a comparison of the stability of this molecule with that of its carbon analogue and substituted vinyl silanes was performed.



(a) cis

(b) gauche

Fig. 1. Structural model of vinyldichlorosilane

## *Ab initio* Calculations

The LCAO-MO-SCF calculations were performed with the Gaussian-90 program [6] with Gaussian type functions. The energy minima with respect to the nuclear coordinates were obtained by simultaneous relaxation of all geometric parameters using the gradient method of Pulay [7]. Structural parameters were determined from the RHF/3-21G* and RHF/6-31G* basis sets. Optimized structural parameters were obtained, where the initial parameters were taken from the previously reported microwave study [8] and *ab initio* calculations for vinyl silyl chloride [1] and methylvinyldichlorosilane [9].

The potential surface was obtained by allowing the CCSiH dihedral angle to vary by 10° increments while all other structural parameters were held fixed at the optimized values obtained for the cis conformer. Calculations at the gauche minimum, cis to gauche and gauche to gauche barriers were carried out by simultaneous relaxation of all the geometric parameters.

## Results and Discussion

### *Conformational Stability*

The potential energy surface obtained without relaxation of the structural parameters is shown by the dashed line in Figure 2. It predicts two minima at the cis and gauche positions, and the cis conformer is the stable form. This rough estimate is consistent with the results obtained by relaxation of all geometrical parameters, the resulting potential function being shown by the solid line in Figure 2. From this potential function, the cis conformer was found to be more stable than the gauche rotamer by 45 $\mathrm{cm}^{-1}$ (539 J/mol) and 140 $\mathrm{cm}^{-1}$ (1.68 kJ/mol) obtained with RHF/3-21G* and RHF/6-31G* basis sets, respectively.

In the previous study [5] of vinyldichlorosilane, the gauche conformer was found to be more stable than the cis form by $772 \pm 286\ \mathrm{cm}^{-1}$ in the liquid phase. This stability was not confirmed by a variable temperature study of another conformer doublet. Additionally, the uncertainty in the energy difference between the two conformers is relatively high, and no conclusion was drawn about which is the stable form in the gas and solid states. From the present study the cis form, having a larger dipole moment than the gauche conformer was found to be the stable rotamer. Therefore it is not expected that the conformational stability will change from the gaseous to the liquid phase. This is consistent and supported by both an experimental study and *ab initio* calculations on methylvinyldichlorosilane: $CH_2CHSiCl_2CH_3$[9], where the cis rotamer was found to be the one with larger dipole moment and is the stable form in all phases. Similar were obtained for the carbon analogue of vinyldichlorosilane: 3,3-dichloropropene [10]. It would be interesting to investigate the conformational stability of vinyldichlorosilane from the far infrared spectra of the gas with appropriate analysis of asymmetric torsional data, and variable temperature studies with a relatively high resolution instrument for the gaseous and liquid phases. Then it would be possible to draw a definite conclusion about the stability of the conformers of vinyldichlorosilane.

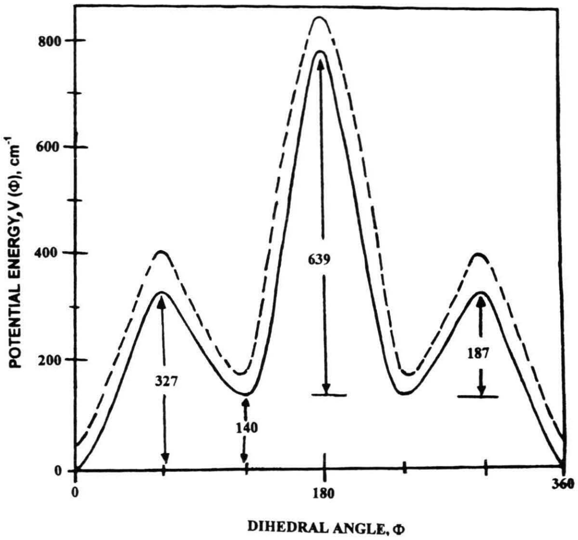


Fig. 2. Potential function governing the internal rotation of vinyldichlorosilane as determined by *ab initio* calculations with the RHF/6-31G* basis set. The potential surface (dashed line) obtained by allowing the dihedral angle to vary by 10° increment, while all other structural parameters were held fixed at the optimized values for the cis conformer. The potential surface (solid line) was obtained by optimization of the gauche minimum and the transition states by relaxation of all geometrical parameters.

The conformational stability of vinyldichlorosilane in the present study is consistent with previous studies of vinyl substituted silanes [1–4] in that the energy difference between the cis and gauche conformer does not exceed about 250 $\mathrm{cm}^{-1}$ compared to their carbon analogues: 3-halopropenes [11–12] and 3,3-dihalopropene [10], where the energy difference is larger. It may be that the steric effect plays a greater role in the conformational stability for substituted halopropenes. This effect is

Table 1. Structural parameters[a], rotational constants, and dipole moments for vinyldichlorosilane

| Parameter | 3-21 G* | | 6-31 G* | |
|---|---|---|---|---|
| | cis | gauche | cis | gauche |
| C=C | 1.325 | 1.324 | 1.236 | 1.325 |
| Si–C | 1.841 | 1.845 | 1.850 | 1.853 |
| $C–H_1$ | 1.075 | 1.073 | 1.077 | 1.075 |
| $C–H_2$ | 1.074 | 1.074 | 1.077 | 1.077 |
| $C–H_3$ | 1.078 | 1.080 | 1.079 | 1.080 |
| Si–H | 1.461 | 1.460 | 1.461 | 1.461 |
| Si–Cl′ | 2.046 | 2.048 | 2.059 | 2.060 |
| Si–Cl″ | 2.046 | 2.047 | 2.059 | 2.057 |
| <CCSi | 121.7 | 125.0 | 121.2 | 125.1 |
| $<CCH_1$ | 122.4 | 122.4 | 122.3 | 122.5 |
| $<CCH_2$ | 122.1 | 121.7 | 122.0 | 121.6 |
| $<CCH_3$ | 119.2 | 118.6 | 119.2 | 118.5 |
| <CSiH | 111.3 | 113.5 | 111.5 | 113.4 |
| <CSiCl′ | 110.4 | 109.5 | 110.6 | 109.5 |
| <CSiCl″ | 110.4 | 110.2 | 110.6 | 110.7 |
| <Cl′SiCl″ | 108.2 | 109.2 | 107.9 | 109.1 |
| $<H_1CH_2$ | 115.5 | 115.9 | 115.6 | 115.9 |
| $\tau$(CCSiH) | 0.0 | 118.3 | 0.0 | 116.5 |
| $A$ | 2428 | 2735 | 2410 | 2702 |
| $B$ | 2064 | 1997 | 2044 | 1979 |
| $C$ | 1200 | 1275 | 1189 | 1257 |
| $\lvert\mu_a\rvert$ | 3.041 | 1.828 | 3.131 | 1.931 |
| $\lvert\mu_b\rvert$ | 0.0 | 1.980 | 0.0 | 2.009 |
| $\lvert\mu_c\rvert$ | 0.450 | 0.894 | 0.483 | 0.831 |
| $\lvert\mu_t\rvert$ | 3.074 | 2.839 | 3.168 | 2.908 |
| $(E-1280)$ | 0.028621 | 0.028420 | 6.033650 | 6.033018 |

[a] Bond lengths in Å, bond angles in degrees, rotational constants in MHz, dipole moments in Debye and energy in Hartrees.

reduced in vinyl substituted silanes, and may be basically attributed to the longer Si–C bond distance compared to the C–C bond length in their carbon analogues.

### *Geometry Optimization*

The structural parameters calculated by the *ab initio* method using the RHF/3-21G* and RHF/6-31G* basis sets for the cis and gauche conformers are shown in Table 1. A comparison of the geometrical parameters for a given basis set indicates that a small difference is observed for the cis and gauche rotamers. The bond distances agree within 0.003 Å, and the bond angles agree within 1° with a major exception of the CCSi angle. This angle increases for the gauche compared to the cis form by 3.3° and 3.9° at RHF/3-21G* and RHF/6-31G* basis sets, respectively. A similar trend was observed for methylvinyldichlorosilane: $CH_2CHSiCl_2CH_3$ [9]. It is interesting to note that the opening of the CCSi angle for the gauche conformer in the above mentioned molecules is reversed for dimethlyvinylchlorosilane: $CH_2CHSiCl(CH_3)_2$ [13], where this angle is larger for the cis (the chlorine atom is eclipsing the double bond) than for the gauche rotamer. The opening of this angle may minimize the repulsion of the electronegative chlorine atom by the vinylic group. Additionally, the chlorine atom and the methyl group are of comparable size. If the size is the only factor that affects the CCSi angle, then one would expect that the value of this angle would be comparable for both conformers of methylvinyldichlorosilane [9] and dimethylvinylchlorosilane [13], which is not the case and inconsistent with the results obtained. It can be concluded that, for all these molecules, the CCSi angle is larger for the conformer that has the chlorine atom eclipsing or abscuring the double bond of the vinylic group. It should be mentioned that these findings are consistent with the conformational stability for these molecules. The cis conformer is the most stable form in vinyldichlorosilane and methyl vinyldichlorosilane [9], while for dimethylvinylchlorosilane [13] the gauche form is the stable rotamer.

The bond lengths obtained by the RHF/3-21G* and RHF/6-31G* basis sets agreed well, with exception of the Si–C and Si–Cl bond lengths. With the larger basis sets, the distances obtained for these two parameters are longer than those obtained with the smaller sets.

The effect of chlorine atoms on some skeletal structural parameters predicated by *ab initio* calculations for vinyldichlorosilane in the present study, vinyl silyl chloride [1] and vinyltrichlorosilane [14] is rather interesting. For example, the Si–C distance decreases with increasing number of substituted chlorine atoms. A similar trend is observed for the Si–Cl distance. It would be interesting if a structural determination were conducted for vinyldichlorosilane, with appropriate techniques such as microwave spectroscopy or electron diffraction. Then, it would be possible to see if these determinations support the trends obtained by the *ab initio* calculations for vinyldichlorosilane and agree with the above conclusions of the effect of chlorine atoms on the structural parameters for related substituted vinyl silanes compounds.

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