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Conformational stability, ab initio calculations, and r_0 structural parameters of 3-methyl-1-butene and dimethylvinylsilane

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Abstract

The infrared spectra ($3500\text{--}400\text{ cm}^{-1}$) of 3-methyl-1-butene, $\text{CH}_2=\text{CHCH}(\text{CH}_3)_2$, and dimethylvinylsilane, $\text{CH}_2=\text{CHSiH}(\text{CH}_3)_2$, dissolved in liquid xenon and krypton, respectively, have been recorded. From temperature (-55 to -110°C) dependent FT–IR spectra of xenon solutions, it is shown that the *cis* conformer (hydrogen atom eclipsing the double bond) of 3-methyl-1-butene is the more stable form with an enthalpy difference of $65 \pm 8\text{ cm}^{-1}$ ($0.78 \pm 0.10\text{ kJ/mol}$) which agrees with all of the theoretical predictions. Similar studies for dimethylvinylsilane in krypton solutions (-105 to -150°C) give an enthalpy difference of $55 \pm 5\text{ cm}^{-1}$ ($0.66 \pm 0.06\text{ kJ/mol}$) with the *gauche* conformer (methyl group eclipsing the double bond) the more stable rotamer which is consistent with the ab initio calculations except with the largest basis set MP2/6-311 + G(2d,2p) utilized. Both ab initio calculations with full electron correlation by the perturbation method to the second order (MP2) and density functional theory (DFT) calculations by the B3LYP method have been carried out with a variety of basis sets up to 6-311G(2d,2p) with and without diffuse functions for both molecules to predict the optimized geometries and conformational stabilities. Utilizing previously reported microwave rotational constants for both conformers of 3-methyl-1-butene along with ab initio predictions, adjusted r_0 parameters have been obtained. The r_0 Si–H bond distances of 1.489 and 1.490 Å have been obtained for the *cis* and *gauche* conformers, respectively, from the silicon-hydrogen stretching frequencies and the remaining parameters are estimated from the MP2/6-311 + G(d,p) ab initio calculations.

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1. Introduction

We have carried out a significant number of conformational studies of 3,3-disubstituted allyl compounds to evaluate the effect of the substituent on

the relative stabilities of the conformers. For example the conformational stability of 3,3-difluoropropene has the *cis* conformer (H atom of the difluoromethyl group *cis* to the double bond) the more stable form with an enthalpy difference of $82 \pm 10\text{ cm}^{-1}$ ($0.98 \pm 0.12\text{ kJ/mol}$) which was obtained from variable temperature FT–IR studies of liquid xenon solutions [1]. This is in contrast to the conformer stability of 3-fluoropropene where the fluorine atom is eclipsing

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the double bond [2] although many of the ab initio predicted stabilities give the *gauche* conformer as the more stable form if diffuse functions are used. When the two substituents are methyl groups, i.e. 3-methyl-1-butene, $\text{CH}_2=\text{CHCH}(\text{CH}_3)_2$, the *cis* conformer is again the more stable conformer with an enthalpy difference of $155 \pm 31 \text{ cm}^{-1}$ ($1.85 \pm 0.37 \text{ kJ/mol}$) obtained from variable temperature studies of the Raman spectrum of the gas [2] utilizing one conformer pair. This value was considerably smaller than the value predicted from ab initio MP2/6-31G(d) calculations (266 cm^{-1}) but agreed with the value [3] of 145 cm^{-1} obtained from the asymmetric potential function as well as the value of $130 \pm 20 \text{ cm}^{-1}$ ($1.56 \pm 0.24 \text{ kJ/mol}$) obtained from the microwave study [4]. We also carried out similar studies with one methyl group and one fluorine atom on the three carbon, i.e. 3-fluoro-1-butene, $\text{CH}_2=\text{CHCHF}(\text{CH}_3)$ where three conformers are present at ambient temperature [5]. For this molecule the conformer with the hydrogen atom eclipsing the double bond is the most stable form with an enthalpy difference of $87 \pm 6 \text{ cm}^{-1}$ ($1.04 \pm 0.07 \text{ kJ/mol}$) with the second most stable form which has the fluorine atom eclipsing the double bond. The enthalpy difference to the least stable form with the methyl group eclipsing the double bond has an enthalpy difference of $292 \pm 5 \text{ cm}^{-1}$ ($3.49 \pm 0.06 \text{ kJ/mol}$). All of these values were obtained from variable temperature infrared studies of xenon solutions [5].

As a continuation of these studies we have investigated the corresponding compounds where the 3-carbon has been replaced with a silicon atom. For the difluoride, i.e. vinyl difluorosilane, $\text{CH}_2=\text{CHSiF}_2\text{H}$, the *cis* conformer was determined [6] to be more stable by $119 \pm 12 \text{ cm}^{-1}$ ($1.42 \pm 0.14 \text{ kJ/mol}$) which was in reasonable agreement with the ab initio MP2/6-311 + G(2d,2p) predicted energy difference of 92 cm^{-1} . Continuing these studies we have investigated the conformational stability of dimethylvinylsilane, $\text{CH}_2=\text{CHSiH}(\text{CH}_3)_2$, utilizing variable temperature studies of krypton solutions. We have also carried out ab initio calculations employing the 6-31G(d) basis set at a level of restricted Hartree–Fock (RHF) and Møller–Plesset to second order (MP2) to obtain equilibrium geometries and conformational stabilities. Structural parameters and conformational stabilities have also

been obtained from larger basis sets, i.e. MP2/6-311G(d,p) and MP2/6-311G(2d,2p) as well as these basis sets with diffuse functions. Density functional theory (DFT) calculations by the B3LYP method with the same basis sets have also been carried out. For comparison purposes we have also carried out similar ab initio and DFT calculations as well as the determination of the enthalpy difference for the conformers of 3-methyl-1-butene. The results of these vibrational spectroscopic and theoretical studies are reported herein.

2. Experimental

The sample of dimethylvinylsilane, $\text{CH}_2=\text{CHSiH}(\text{CH}_3)_2$, has been prepared from the reduction of the corresponding silyl chloride derivative (Aldrich Chemical Co.) by lithium aluminum hydride in dry dibutyl ether at 0°C for one hour and then at room temperature for another one hour. The sample was initially purified by trap-to-trap distillation. Further purification was obtained using a low-temperature, low-pressure fractionation column. The purity of the sample was verified by mass and infrared spectroscopy. The sample of 3-methyl-1-butene was obtained from Aldrich Chemical Co. and purified with a low-temperature, low-pressure fractionation column.

The mid-infrared spectra of the samples dissolved in liquefied krypton (Fig. 1) or liquefied xenon as a function of temperature were recorded on a Bruker model IFS-66 Fourier transform spectrometer equipped with a Globar source, a Ge/KBr beam splitter, and a DTGS detector. The temperature studies ranged from -105 to -150°C for krypton and -55 to -100°C for xenon and were performed in a specially designed cryostat cell consisting of a 4 cm path length copper cell with wedged silicon windows sealed to the cell with indium gaskets. The complete system is attached to a pressure manifold to allow for the filling and evacuation of the cell. The cell is cooled by boiling liquid nitrogen, and the temperature is monitored by two platinum thermoresistors. Once the cell is cooled to the designated temperature, a small amount of sample is condensed into the cell. The system is then pressurized with krypton gas, which immediately starts to condense,

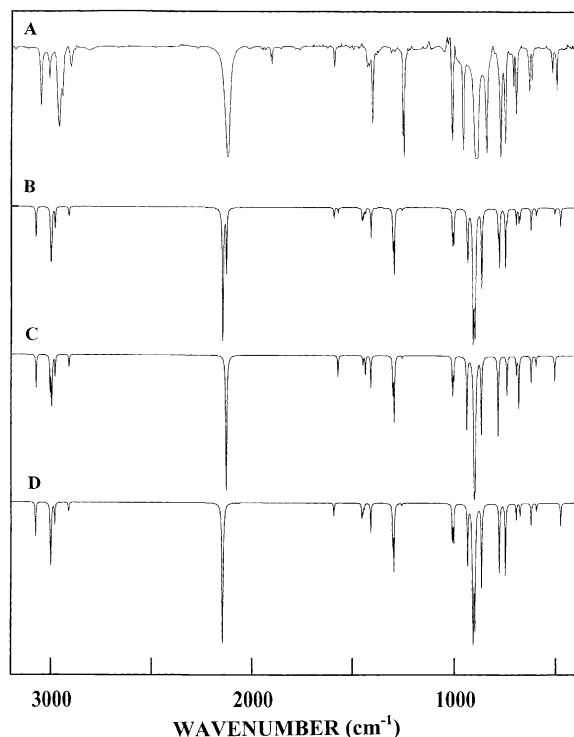


Fig. 1. Mid-infrared spectra of dimethylvinylsilane: (A) experimental spectrum of the sample dissolved in liquid Kr at $-120\text{ }^{\circ}\text{C}$; (B) MP2/6-31G(d) ab initio calculated spectrum of *gauche* and *cis* conformers with $\Delta H = 55\text{ cm}^{-1}$ with the *gauche* form more stable; (C) calculated spectrum of the pure *cis* conformer; (D) calculated spectrum of the pure *gauche* conformer.

allowing the compound to dissolve. For each temperature investigated, 100 interferograms were recorded at 1.0 cm^{-1} resolution, averaged, and transformed with a boxcar truncation function.

3. Ab initio calculations

In order to provide optimized geometries, conformational stabilities and total energies ab initio calculations by using the GAUSSIAN-98 program [7] were carried out at both the restricted Hartree–Fock level (RHF) and with full electron correlation by the perturbation method to second order (MP2). Several basis sets up to 6-311 + G(2d,2p) have been utilized and the predicted conformational stabilities are given in Table 1 for 3-methyl-1-butene. It should be noted that all the ab initio calculations predict the *cis*

Table 1

Calculated energies (Hartree) and energy difference for the two conformations of 3-methyl-1-butene

Method/basis set	<i>cis</i>	<i>gauche</i>	Δ (cm^{-1})
RHF/6-31G(d)	−195.141164	−195.139658	331
MP2/6-31 + G(d)	−195.813710	−195.812517	262
MP2/6-311G(d,p)	−196.031671	−196.030492	259
MP2/6-311 + G(d,p)	−196.035672	−196.034544	248
MP2/6-311G(2d,2p)	−196.091491	−196.090810	130
MP2/6-311 + G(2d,2p)	−196.094467	−196.093922	120
B3LYP/6-31G(d)	−196.535467	−196.534377	239
B3LYP/6-311G(d,p)	−196.593019	−196.591915	242
B3LYP/6-311 + G(d,p)	−196.594647	−196.593569	237
B3LYP/6-311 + G(2d,2p)	−196.603798	−196.602766	139

conformer to be the more stable rotamer with values for the energy differences varying from 120 to 262 cm^{-1} . The predicted structural parameters from three of the ab initio calculations are listed in Table 2 as well as those from the RHF/6-31G(d) calculations.

Similar calculations have also been carried out for dimethylvinylsilane. All of the ab initio calculations predict the *cis* conformer as the more stable form except the MP2/6-311 + G(2d,2p) calculations which predicts the *gauche* to be more stable by 26 cm^{-1} (0.3 kJ/mol). These calculations along with those from the DFT calculations by the B3LYP method using the same basis sets as those for the ab initio calculations are listed in Table 3. The structural parameters from three of the basis sets as well as those from the RHF/6-31G(d) calculation are listed in Table 4.

To aid in making the vibrational assignments to the individual conformers of dimethylvinylsilane we calculated the theoretical infrared spectra. The infrared intensities were calculated based on the dipole moment derivatives with respect to the Cartesian coordinates. The derivatives were taken from the ab initio calculation transformation to the normal coordinates by:

$$(\partial \mu_u / \partial Q_i) = \left[\sum_j (\partial \mu_u / \partial X_j) \right] L_{ij}$$

where Q_i is the i th Cartesian displacement coordinate, L_{ij} is the transformation matrix between the Cartesian displacement coordinates and normal coordinates.

Table 2

Structural parameters (Å and degree), rotational constants (MHz) and dipole moments (Debye) for *cis* and *gauche* rotamers of 3-methyl-1-butene

	RHF/6-31G(d)		MP2/6-31G(d)		MP2/6-311 + G(d,p)		MP2/6-311 + G(2d,2p)		Adjusted r_0	
	<i>cis</i>	<i>gauche</i>	<i>cis</i>	<i>gauche</i>	<i>cis</i>	<i>gauche</i>	<i>cis</i>	<i>gauche</i>	<i>cis</i>	<i>gauche</i>
$r(\text{C}_1\text{C}_2)$	1.319	1.320	1.337	1.338	1.341	1.342	1.335	1.335	1.340	1.341
$r(\text{C}_2\text{C}_3)$	1.508	1.512	1.500	1.504	1.501	1.505	1.497	1.501	1.500	1.505
$r(\text{C}_3\text{C}_8)$	1.534	1.529	1.530	1.523	1.532	1.525	1.528	1.521	1.533	1.526
$r(\text{C}_3\text{C}_9)$	1.534	1.536	1.530	1.532	1.532	1.534	1.528	1.530	1.533	1.535
$r(\text{C}_1\text{H}_5)$	1.076	1.076	1.085	1.085	1.085	1.085	1.078	1.078	1.085	1.085
$r(\text{C}_1\text{H}_6)$	1.077	1.075	1.087	1.084	1.087	1.085	1.080	1.078	1.087	1.085
$r(\text{C}_2\text{H}_7)$	1.081	1.080	1.092	1.091	1.092	1.091	1.086	1.084	1.092	1.091
$r(\text{C}_3\text{H}_4)$	1.087	1.090	1.098	1.100	1.098	1.100	1.090	1.092	1.098	1.100
$r(\text{C}_8\text{H}_{13})$	1.087	1.086	1.095	1.094	1.096	1.095	1.089	1.088	1.096	1.095
$r(\text{C}_8\text{H}_{14})$	1.085	1.085	1.093	1.093	1.094	1.094	1.086	1.087	1.094	1.094
$r(\text{C}_8\text{H}_{15})$	1.086	1.085	1.095	1.094	1.095	1.094	1.087	1.087	1.095	1.094
$r(\text{C}_9\text{H}_{10})$	1.087	1.086	1.095	1.094	1.096	1.095	1.089	1.088	1.096	1.095
$r(\text{C}_9\text{H}_{11})$	1.085	1.086	1.093	1.094	1.094	1.094	1.086	1.087	1.094	1.094
$r(\text{C}_9\text{H}_{12})$	1.086	1.086	1.095	1.094	1.095	1.094	1.087	1.087	1.095	1.094
$\angle \text{C}_1\text{C}_2\text{C}_3$	125.5	127.9	125.0	126.7	124.8	126.5	125.0	126.4	125.4	126.5
$\angle \text{C}_2\text{C}_3\text{H}_4$	108.0	106.7	108.0	107.1	108.0	107.0	108.0	107.2	108.0	107.0
$\angle \text{C}_1\text{C}_2\text{H}_5$	121.7	121.0	121.9	121.1	121.6	120.7	121.5	120.8	121.6	120.7
$\angle \text{C}_1\text{C}_2\text{H}_6$	121.9	122.9	121.4	122.5	121.0	122.2	120.9	122.0	121.0	122.2
$\angle \text{C}_1\text{C}_2\text{H}_7$	119.0	118.1	119.3	118.3	119.3	118.2	119.0	118.2	119.3	118.2
$\angle \text{C}_3\text{C}_8\text{H}_{10}$	111.0	111.3	110.4	110.7	110.3	110.7	110.3	110.6	110.3	110.7
$\angle \text{C}_3\text{C}_8\text{H}_{11}$	111.1	111.5	111.0	111.5	111.1	111.5	111.2	111.7	111.1	111.5
$\angle \text{C}_3\text{C}_8\text{H}_{12}$	110.9	110.3	110.9	110.3	110.8	110.1	110.9	110.3	110.8	110.1
$\angle \text{C}_3\text{C}_9\text{H}_{13}$	111.0	110.7	110.4	110.1	110.3	110.0	110.3	110.0	110.3	110.0
$\angle \text{C}_3\text{C}_9\text{H}_{14}$	111.1	111.4	111.0	111.3	111.1	111.3	111.2	111.4	111.1	111.3
$\angle \text{C}_3\text{C}_9\text{H}_{15}$	110.9	110.9	110.9	110.9	110.8	110.8	110.9	110.9	110.8	110.8
$\tau \text{H}_4\text{C}_3\text{C}_2\text{C}_1$	0.0	121.7	0.0	122.5	0.0	122.8	0.0	122.4	0.0	121.2
$\tau \text{H}_5\text{C}_1\text{C}_2\text{C}_3$	180.0	179.6	180.0	179.9	180.0	178.9	180.0	178.8	180.0	178.9
$\tau \text{H}_6\text{C}_1\text{C}_2\text{H}_5$	180.0	179.9	180.0	179.9	180.0	179.8	180.0	179.9	180.0	179.8
$\tau \text{H}_7\text{C}_2\text{C}_1\text{C}_3$	180.0	−179.5	180.0	−178.7	180.0	−178.7	180.0	−178.7	180.0	−178.7
$\tau \text{C}_8\text{C}_3\text{H}_4\text{C}_2$	119.9	122.9	119.8	122.8	119.8	122.9	119.8	122.8	118.3	122.9
$\tau \text{C}_9\text{C}_3\text{H}_4\text{C}_2$	−119.9	−117.6	−119.8	−117.6	−119.8	−117.5	−119.8	−117.5	−118.3	−117.5
$\tau \text{H}_{10}\text{C}_9\text{C}_3\text{H}_4$	−179.5	178.8	−179.2	178.6	−179.2	178.5	−178.8	178.7	−179.2	178.5
$\tau \text{H}_{13}\text{C}_8\text{C}_3\text{H}_4$	179.5	−179.5	179.2	−179.7	179.2	−179.9	178.8	−179.2	179.2	−179.9
<i>A</i>	7554	7307	7564	7311	7563	7291	7625	7350	7535	7296
<i>B</i>	3561	3916	3562	3943	3554	3941	3575	3973	3549	3918
<i>C</i>	2747	2880	2756	2908	2753	2906	2769	2928	2742	2880
$ \mu_a $	0.252	0.181	0.255	0.294	0.379	0.425	0.319	0.433	0.379	0.425
$ \mu_b $	0.000	0.068	0.000	0.049	0.000	0.012	0.000	0.014	0.000	0.012
$ \mu_c $	0.021	0.567	0.019	0.126	0.064	0.157	0.034	0.159	0.064	0.157
$ \mu_t $	0.253	0.599	0.255	0.324	0.384	0.536	0.402	0.461	0.384	0.536

The infrared intensities were then calculated by:

$$I_i = [(N\pi)/(3c^2)][(\partial\mu_x/\partial Q_i)^2 + (\partial\mu_y/\partial Q_i)^2 + (\partial\mu_z/\partial Q_i)^2]$$

In Fig. 1D and C are the predicted spectra of pure *cis* and *gauche* conformers and in Fig. 1B is the predicted spectrum of the mixture utilizing the ΔH value of 55 cm^{-1} . The predicted infrared spectrum is in good agreement with the experimental spectrum of

Table 3

Calculated energies (Hartree) and energy difference for the two conformations of dimethylvinyl silane

Method/basis set	<i>cis</i>	<i>gauche</i>	Δ (cm ⁻¹)
RHF/6-31G(d)	-446.207470	-446.207024	98
MP2/6-31G(d)	-446.833359	-446.833205	34
MP2/6-311G	-447.087054	-447.086955	3
MP2/6-311G(d,p)	-447.167559	-447.167520	9
MP2/6-311 + G(d,p)	-447.171946	-447.171931	22
MP2/6-311 + G(2d,2p)	-447.242457	-447.242574	-26
B3LYP/6-31G(d)	-447.939498	-447.939097	88
B3LYP/6-311G(d,p)	-448.015241	-448.014960	62
B3LYP/6-311 + G(d,p)	-448.016885	-448.016525	79
B3LYP/6-311 + G(2d,2p)	-448.027973	-448.027623	77

the samples dissolved in liquid krypton solution (Fig. 1A) at the temperature of -120 °C. This agreement between the predicted spectrum and the observed one shows that the ab initio predictions can be very helpful for making the correct vibrational assignments for the two conformers.

4. Conformational stability

The predicted frequencies for the fundamentals of 3-methyl-1-butene were used [2] to assign the fundamentals of the *cis* and *gauche* conformers and there are only a limited number of bands for the *gauche* conformer that can be used for an enthalpy determination. Some of the more pronounced ones are found at 1094, 1138 and 1174 cm⁻¹. Three bands at 1109, 1166, and 1190 cm⁻¹ which were assigned to the *cis* conformer in the same spectral region were chosen for the intensity measurements. To obtain the enthalpy difference between the two conformers similar to what is expected for the gas, variable temperature studies in liquefied xenon were carried out. For most of these bands only small frequency shift were observed when passing from the gas phase to the xenon solution. The areas of the conformer peaks are more accurately determined than those from the spectrum of the gas. Spectral data were collected at ten different temperatures over the range from -55 to -100 °C (Table 5) for three pairs of bands. The band areas were utilized for relative intensity data. The enthalpy difference was calculated by the van't Hoff equation, $-\ln K =$

$(\Delta H/RT) - \Delta S/R$, with the assumption that the value of ΔH is constant within the temperature range utilized and I_g/I_c is substituted for K . The values of ΔH ranged from a low value of 61 ± 15 cm⁻¹ to a high value of 72 ± 16 cm⁻¹ with an average value of 65 ± 8 cm⁻¹ with the *cis* conformer the more stable rotamer. The uncertainty is the statistical uncertainty and does not take into account possible overtones or combination bands affecting the intensities but appears to be a reasonable value. This ΔH value should be near that of the gas [8–12] since both conformers have similar size and polarity.

Since no assignments for the fundamentals of dimethylvinylsilane have previously been reported for the two potential conformers, the fundamental frequencies were predicted from ab initio MP2/6-31G(d) calculations utilizing only two scaling factors of the force constants. For the carbon-hydrogen and silicon-hydrogen stretches a scaling factor of 0.88 was used whereas for the heavy atom stretches and light atom bending modes a scaling factor of 0.90 was used. The heavy atom bends were not scaled. It is expected that these predictions should give frequencies with an average error of 10 cm⁻¹ which is less than 1% for both conformers. With these predicted frequencies it should be possible to assign individual bands to many of the fundamentals for each conformer [13–18]. However, most of the fundamentals of the *cis* and *gauche* conformers are near degenerate (Fig. 1) and therefore only a very limited number of conformer bands are available for an enthalpy determination. Nevertheless, there is still a clear indication for the presence of two conformers in the fluid phases. The best example is for the two pronounced bands at 488 cm⁻¹ (strong Q-branch) and the apparent minimum of B-type band at 510 cm⁻¹ in the spectrum of the gas. The corresponding bands are observed at 489 and 511 cm⁻¹ in the infrared spectrum of the krypton solution. Each conformer has only one fundamental predicted in this region with the band for the *gauche* conformer estimated at 473 cm⁻¹ and the corresponding band for the *cis* conformer at 502 cm⁻¹. The predicted separation of 29 cm⁻¹ with the *cis* conformer having the higher frequency is consistent with these observed bands separated by 23 cm⁻¹ with the higher frequency weaker one due to the *cis* form.

To obtain the enthalpy difference between the two conformers, variable temperature studies in liquefied

Table 4

Structural parameters (Å and degree), rotational constants (MHz) and dipole moments (Debye) for *cis* and *gauche* rotamers of dimethylvinyl silane

	RHF/6-31G(d)		MP2/6-31G(d)		MP2/6-311 + G(d,p)		MP2/6-311 + G(2d,2p)		Predicted r_0	
	<i>cis</i>	<i>gauche</i>	<i>cis</i>	<i>gauche</i>	<i>cis</i>	<i>gauche</i>	<i>cis</i>	<i>gauche</i>	<i>cis</i>	<i>gauche</i>
$r(\text{C}_1\text{C}_2)$	1.325	1.325	1.344	1.344	1.347	1.347	1.341	1.340	1.347	1.347
$r(\text{C}_2\text{Si}_3)$	1.880	1.881	1.869	1.871	1.868	1.871	1.867	1.867	1.863	1.866
$r(\text{Si}_3\text{C}_8)$	1.891	1.889	1.882	1.880	1.876	1.875	1.874	1.873	1.871	1.870
$r(\text{Si}_3\text{C}_9)$	1.891	1.891	1.882	1.882	1.876	1.877	1.874	1.875	1.871	1.872
$r(\text{C}_1\text{H}_5)$	1.078	1.078	1.088	1.088	1.088	1.088	1.081	1.081	1.088	1.088
$r(\text{C}_1\text{H}_6)$	1.078	1.077	1.087	1.087	1.088	1.088	1.081	1.081	1.088	1.088
$r(\text{C}_2\text{H}_7)$	1.082	1.082	1.092	1.092	1.092	1.092	1.085	1.084	1.092	1.092
$r(\text{Si}_3\text{H}_4)$	1.482	1.483	1.493	1.494	1.484	1.484	1.481	1.481	1.489	1.490
$r(\text{C}_8\text{H}_{10})$	1.087	1.087	1.094	1.094	1.095	1.094	1.087	1.087	1.095	1.094
$r(\text{C}_8\text{H}_{11})$	1.086	1.086	1.093	1.093	1.094	1.094	1.086	1.086	1.094	1.094
$r(\text{C}_8\text{H}_{12})$	1.087	1.087	1.094	1.094	1.094	1.094	1.087	1.087	1.094	1.094
$r(\text{C}_9\text{H}_{13})$	1.087	1.087	1.094	1.094	1.095	1.094	1.087	1.087	1.095	1.094
$r(\text{C}_9\text{H}_{14})$	1.086	1.087	1.093	1.094	1.094	1.094	1.086	1.087	1.094	1.094
$r(\text{C}_9\text{H}_{15})$	1.087	1.087	1.094	1.094	1.094	1.094	1.087	1.087	1.094	1.094
$\angle \text{C}_1\text{C}_2\text{Si}_3$	123.9	125.2	123.3	124.3	122.9	124.0	123.1	123.7	122.9	124.0
$\angle \text{C}_2\text{Si}_3\text{H}_4$	107.1	108.2	106.8	108.5	106.7	108.6	106.8	108.6	106.7	108.6
$\angle \text{C}_1\text{C}_2\text{H}_5$	122.5	122.3	122.7	122.5	122.3	122.1	122.2	122.1	122.3	122.1
$\angle \text{C}_1\text{C}_2\text{H}_6$	122.0	122.3	121.6	121.9	121.3	121.7	121.3	121.5	121.3	121.7
$\angle \text{C}_1\text{C}_2\text{H}_7$	117.3	117.1	117.3	117.1	117.2	116.9	116.9	116.7	117.2	116.9
$\angle \text{Si}_3\text{C}_8\text{H}_{10}$	111.4	111.6	111.0	111.2	110.9	111.1	110.6	110.8	110.9	111.1
$\angle \text{Si}_3\text{C}_8\text{H}_{11}$	111.3	111.8	111.2	111.7	111.1	111.7	111.1	111.6	111.1	111.7
$\angle \text{Si}_3\text{C}_8\text{H}_{12}$	111.2	110.5	111.1	110.5	111.0	110.4	111.0	110.4	111.0	110.4
$\angle \text{Si}_3\text{C}_9\text{H}_{13}$	111.4	111.3	111.0	110.8	110.9	110.5	110.6	110.4	110.9	110.5
$\angle \text{Si}_3\text{C}_9\text{H}_{14}$	111.3	111.4	111.2	111.4	111.1	111.3	111.1	111.2	111.1	111.3
$\angle \text{Si}_3\text{C}_9\text{H}_{15}$	111.2	111.2	111.1	111.2	111.0	111.3	111.0	111.2	111.0	111.3
$\tau \text{H}_4\text{Si}_3\text{C}_2\text{C}_1$	0.0	119.3	0.0	119.3	0.0	120.3	0.0	121.1	0.0	120.3
$\tau \text{C}_8\text{Si}_3\text{H}_4\text{C}_2$	119.9	119.3	119.7	120.3	119.6	120.1	119.6	119.8	119.6	120.1
$\tau \text{C}_9\text{Si}_3\text{H}_4\text{C}_2$	−119.9	−120.8	−119.7	−119.3	−119.6	−119.2	−119.6	−119.3	−119.6	−119.2
$\tau \text{H}_{10}\text{C}_8\text{Si}_3\text{H}_4$	−178.5	179.6	−178.3	179.6	−178.4	179.4	−178.3	179.7	−178.4	179.4
$\tau \text{H}_{13}\text{C}_9\text{Si}_3\text{H}_4$	178.5	−179.1	178.3	−179.1	178.4	179.8	178.3	−179.4	178.4	179.8
<i>A</i>	5199	4983	5229	5018	5253	5029	5280	5048	5277	5025
<i>B</i>	2584	2804	2593	2838	2599	2837	2610	2856	2609	2846
<i>C</i>	1961	2067	1973	2090	1981	2105	1991	2121	1990	2111
$ \mu_a $	0.043	0.196	0.044	0.216	0.085	0.098	0.090	0.079	0.085	0.098
$ \mu_b $	0.000	0.069	0.000	0.070	0.000	0.111	0.000	0.100	0.000	0.111
$ \mu_c $	0.471	0.562	0.485	0.585	0.386	0.515	0.417	0.527	0.386	0.515
$ \mu_t $	0.472	0.599	0.487	0.627	0.391	0.536	0.427	0.542	0.391	0.536

krypton were carried out for this conformer pair. For most of the bands only small frequency shift were observed when passing from the gas phase to the krypton solution. The areas of the conformer peaks are more accurately determined than those from the spectrum of the gas. Spectral data were collected at ten different temperatures (Fig. 2) over the range from −105 to −150 °C (Table 6) for this pair of bands.

The band areas were utilized for relative intensity data and it was necessary to include a small peak on the high frequency wing of the 489 cm^{−1} band for fitting the observed band contours. The enthalpy difference was calculated by the van't Hoff equation, $-\ln K = (\Delta H/RT) - \Delta S/R$, with the assumption that the value of ΔH is constant within the temperature range utilized and I_c/I_g is substituted for K .

Table 5

Temperature and intensity ratios from the study of 3-methyl-1-butene dissolved in liquid xenon

T (°C)	$1000/T$ (K)	$A_{1092g}/1103c$	$A_{1135g}/1161c$	$I_{1181g}/1194c$
–55	4.5872	0.82574	3.1703	1.2107
–60	4.6948	0.77677	2.9848	1.1407
–65	4.8077	0.80726	2.9374	1.1289
–70	4.9261	0.77880	2.8211	1.1404
–75	5.0505	0.77407	2.8140	1.1486
–80	5.1813	0.75750	2.7820	1.1228
–85	5.3191	0.71788	2.7758	1.1050
–90	5.4645	0.76447	2.8333	1.0907
–95	5.6180	0.73968	2.6797	1.0667
–100	5.7803	0.73393	2.7368	1.0622
ΔH^a (cm ^{–1})		61 ± 15	72 ± 16	62 ± 9

^a Average enthalpy difference ΔH between the *gauche* and *cis* conformation is 65 ± 8 cm^{–1} with the *cis* conformer more stable. The *A* stands for peak area and *I* for peak height.

The determined value (Fig. 3) of ΔH is 55 ± 5 cm^{–1} (0.66 ± 0.06 kJ/mol) with the *gauche* conformer the more stable rotamer. The uncertainty is the statistical uncertainty but because of the low frequencies of these fundamentals further overtones or combination bands affecting the intensities are not expected. The value should be near the value for the gas [8–12] since both conformers have similar size and polarity.

5. Discussion

The experimentally determined value of 65 ± 8 cm^{–1} (1.42 ± 0.14 kJ/mol) for 3-methyl-1-butene seems a little low compared to the predictions from the *ab initio* and DFT calculations which indicate a value about 120 cm^{–1} with the larger basis sets. Since conformer pairs had to be used in the 1000 cm^{–1} region there is considerable opportunity for interference from a large number of overtone and combination bands. There was considerable difficulty in obtaining well-defined baselines and the separation of the bands was not as well defined as usually obtained with the lower frequency pairs. Nevertheless it is quite clear that the *cis* conformer is the more stable form. Since the *gauche* conformer has two equivalent forms the estimated percent of this rotamer present at room temperature is $59 \pm 2\%$ which makes it the conformer in the larger abundance. With this large abundance it is difficult to obtain bands due to the *cis* conformer in several of the spectral ranges for enthalpy measurements. It might be possible to obtain better conformational data in the far infrared spectral region where there would be much less interference from combination and overtone bands but we currently do not have the equipment to carry out such studies.

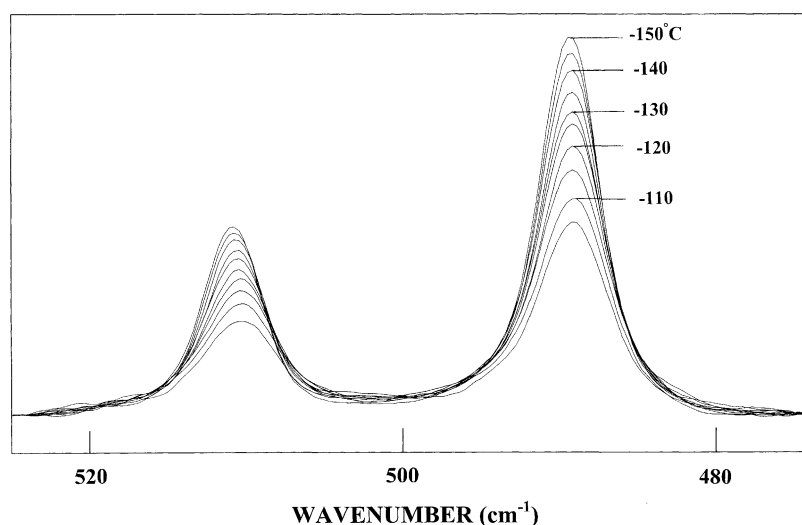


Fig. 2. Temperature (–105 to –150 °C) dependent infrared spectra of dimethylvinylsilane dissolved in liquid Kr in the region from 475 to 525 cm^{–1}.

Table 6

Temperature and intensity ratios from the study of dimethylvinyl silane dissolved in liquid krypton

T (°C)	$1000/T$ (K)	A_{511c}/A_{489g}
–105	5.9471	0.60356
–110	6.1293	0.62270
–115	6.3231	0.60908
–120	6.5295	0.59252
–125	6.7499	0.56955
–130	6.9857	0.57888
–135	7.2385	0.55302
–140	7.5103	0.54949
–145	7.8034	0.53420
–150	8.1202	0.51976
ΔH^a (cm ^{–1})		55 ± 5

^a Enthalpy difference ΔH between the *gauche* and *cis* conformation is 55 ± 5 cm^{–1} with the *gauche* conformer more stable.

For dimethylvinylsilane the experimentally determined enthalpy value of 55 ± 5 cm^{–1} leads to a predicted $72 \pm 2\%$ *gauche* conformer present at ambient temperature. Since the predicted intensities of the two bands are nearly the same for the two fundamentals used to determine the enthalpy difference one can estimate that the *gauche* conformer is the more stable form from the relative intensities of these two fundamentals. There are some other bands in the infrared spectrum of the krypton solution where

similar estimates can be made and for all cases the *gauche* conformer is predicted to be the more stable rotamer.

We have found [19] that we can obtain good structural parameters by adjusting the structural parameters obtained from the ab initio calculations to fit rotational constants (computer program A&M, ab initio and Microwave, developed in our laboratory) obtained from the microwave experimental data. In order to reduce the number of independent variables, the structural parameters are separated into sets according to their type. Bond lengths in the same set keep their relative ratio, and bond angles in the same set keep their differences in degree. This assumption is based on the fact that the errors from ab initio calculations are systematic. Additionally we have found [20] that the ab initio MP2/6-311 + G(d,p) predictions for the carbon-hydrogen bond lengths are predicted within 0.002 Å uncertainty for a large number of organic compounds. Therefore it is possible to obtain good structural parameters for 3-methyl-1-butene from the previously reported [4] microwave rotational constants which are six for the two conformers.

To be determined are the $C_1=C_2$, $=C_2=C_3$, and $C_3-C_{8,9}$ distances along with the two angles $\angle C_1C_2C_3$ and $\angle C_2C_3C_{8,9}$ and dihedral angle for the *gauche* conformer. Utilizing the A&M program gives

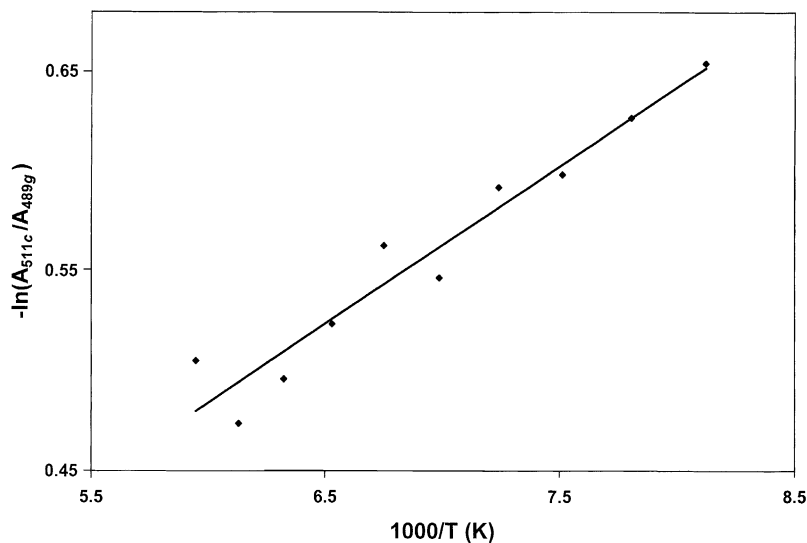


Fig. 3. van't Hoff plot of $-\ln(A_{511c}/A_{489g})$ as a function of $1000/T$.

Table 7

Comparison of rotational constants (MHz) obtained from the microwave spectra of 3-methyl-1-butene with those from the adjusted ab initio structural parameters

Molecule	Rotational constants	Observed	Calculated	Δ
<i>cis</i> $\text{CH}_2=\text{CHCH}(\text{CH}_3)_2$	A	7536.3	7534.5	1.8
	B	3551.0	3548.8	2.2
	C	2741.6	2742.5	0.9
<i>gauche</i> $\text{CH}_2=\text{CHCH}(\text{CH}_3)_2$	A	7294.4	7296.4	2.0
	B	3916.1	3917.5	1.5
	C	2879.3	2880.1	0.8

an excellent fit of the six rotational constants with very little change in the indicated distances and angles. The fit of the rotational constants is shown in Table 7 which is better than 2 MHz for all six of them. The small changes are consistent with the results which we found for many C–C distances of several different organic molecules which were predicted by MP2/6-311 + G(d,p) calculations and compared to the experimentally determined r_0 parameters [20].

Since there is a single hydrogen atom on the silicon-containing moiety of dimethylvinylsilane, it is possible to obtain the two different Si–H bond distances for the two conformers from the SiH stretching frequencies [21]. Using the frequencies of 2134 cm^{-1} for the *cis* conformer and 2130 cm^{-1} for the *gauche* form, Si–H bond distances of 1.489 and 1.490 Å are obtained, respectively, which are 0.005 and 0.006 Å longer than the ab initio MP2/6-311 + G(d,p) predicted values. In an earlier study [22] of ethylsilane-Si- d_2 , the Si–H bond distance was found to be 0.006 Å longer than the value predicted from MP2/6-311 + G(d,p) calculations. However, for ethylchlorosilane, the Si–H distances was determined [23] to be 1.480 Å, whereas the predicted value from MP2/6-311 + G(d,p) calculations is 1.472 Å so the difference is 0.008 Å. Therefore, at present, the ab initio MP2/6-311 + G(d,p) predicted values for the Si–H bond distance appear to be too short from 0.005 to 0.008 Å for the silyl moiety, when the other substituents are hydrocarbons, hydrogen, fluorine and chlorine atoms, but it is not possible with the limited data to evaluate whether the trend is linear.

Since we have found that MP2/6-311 + G(d,p) calculations predict Si–C distances longer by about 0.005 Å than the experimentally determined r_0 values,

it should be possible to predict the rotational constants for both conformers by using the determined Si–H distances of 1.489 and 1.490 Å for the *cis* and *gauche* conformers, respectively, and reduce the Si–C distances by 0.005 Å while keeping the remaining parameters from the MP2/6-311 + G(d,p) calculations the same and predict rotational constants which should be within a few MHz of the actual ones. Such predictions should aid significantly the assignment of the microwave spectrum of both conformers. The rotational constants would provide sufficient data for the determination of the heavy atom bond distances and angle.

Since so many of the fundamentals of the two conformers of dimethylvinylsilane are nearly degenerate, it will be necessary to utilize the Si–D isotopomer to make a vibrational assignment. Additional data from matrix isolation studies should help to distinguish the assignments for the two conformers. Such studies are currently planned and the results will be reported in the future.

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