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Raman Spectrum and Torsional Potential Function for Vinylcyclopropane

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Abstract: A series of six lines in the low-frequency Raman spectrum of vinylcyclopropane has been observed and assigned to the ($\Delta v = 2$) overtones of the vinyl torsional oscillation. The temperature dependence of the intensities of two pairs of Raman bands indicated the presence of two conformers with an enthalpy difference, $\Delta H = 500 \pm 50 \text{ cm}^{-1}$. The observed torsional transitions, the ΔH , and the relative intensities of the pairs of bands used in the temperature dependence study are all fitted to a potential function of the form $V(\phi) = \sum_{i=1}^4 (V_i/2) (1 - \cos i\phi)$ having minima for the trans conformer ($\phi = 0^\circ$) and two equal energy gauche conformers; the gauche species are found to be the less stable. The potential constants are found to be (in cm^{-1}) $V_1 = 279 \pm 60$; $V_2 = 699 \pm 60$; $V_3 = 782 \pm 32$; and $V_4 = -199 \pm 35$.

Introduction

The solution to the conformational behavior of vinylcyclopropane has remained an elusive one, despite many empirical and theoretical examinations of both the parent molecule and some of its derivatives. Both types of investigation have confirmed that an s-trans structure best represents the ground state or most abundant form of this molecule. Furthermore, both types of investigation have indicated the presence of an appreciable amount of a less stable conformer existing in thermal equilibrium with the s-trans species. However, the only common ground among the published reports is concurrence on the lower energy s-trans conformer; the nature of the other less stable species has been a matter of much confusion.

Nuclear magnetic resonance studies on vinylcyclopropane and many of its cyclopropyl-substituted derivatives have been interpreted in terms of both twofold and threefold torsional potential functions (the former having energy minima for trans and cis conformers, the latter having minima for trans and/or cis and two symmetry related gauche conformers). Lüttke and de Meijere¹ have concluded that their data for the parent molecule are best interpreted in terms of a twofold potential function (trans/cis) with the trans conformer more stable by $385 \pm 70 \text{ cm}^{-1}$ ($4.60 \pm 0.84 \text{ kJ mol}^{-1}$). On the other hand, several independent studies²⁻⁴ have decided upon a threefold potential function (trans/gauche) with the trans species more stable by $278 \pm 48 \text{ cm}^{-1}$ ($3.32 \pm 0.57 \text{ kJ mol}^{-1}$).

De Meijere and Lüttke⁵ have examined gaseous vinylcyclopropane by the electron diffraction method and deduced a

trans/gauche equilibrium, the trans species more stable by $385 \pm 70 \text{ cm}^{-1}$ ($4.60 \pm 0.84 \text{ kJ mol}^{-1}$) and a gauche dihedral angle $110^\circ < \phi < 120^\circ$.

Hehre⁶ has performed an ab initio investigation of vinylcyclopropane using both the STO-3G and the 4-31G minimal basis sets. Both basis sets confirm the trans geometry as representing the molecular ground state. The STO-3G basis predicts the additional presence of both a cis and a gauche conformation, the gauche having the lower energy of the two. On the other hand, use of the 4-31G basis predicts greater definition of the gauche conformer at the expense of the cis conformer. Both basis sets predict a gauche dihedral angle of $\sim 114^\circ$, in good agreement with the electron diffraction work of de Meijere and Lüttke.⁵

Codding and Schwendeman⁷ examined the microwave spectrum of vinylcyclopropane and were able to extract definitive information about the ground state trans geometry; they were not, however, able to extract any information on the nature of the less stable conformational isomer. By examining the relative intensities of torsional satellites, these authors were able to deduce a fundamental torsional frequency of $\sim 125 \text{ cm}^{-1}$ with the suggestion that the barrier hindering interconversion to another rotamer should be at least 625 cm^{-1} (7.48 kJ mol^{-1}).

In order to determine the nature of the conformational equilibrium in vinylcyclopropane we have undertaken the observation and analysis of the low-frequency torsional mode in this molecule.

Experimental Section

The sample was purchased from Aldrich Chemical Co. (stated: 99% purity) and used without further purification. After a thorough de-

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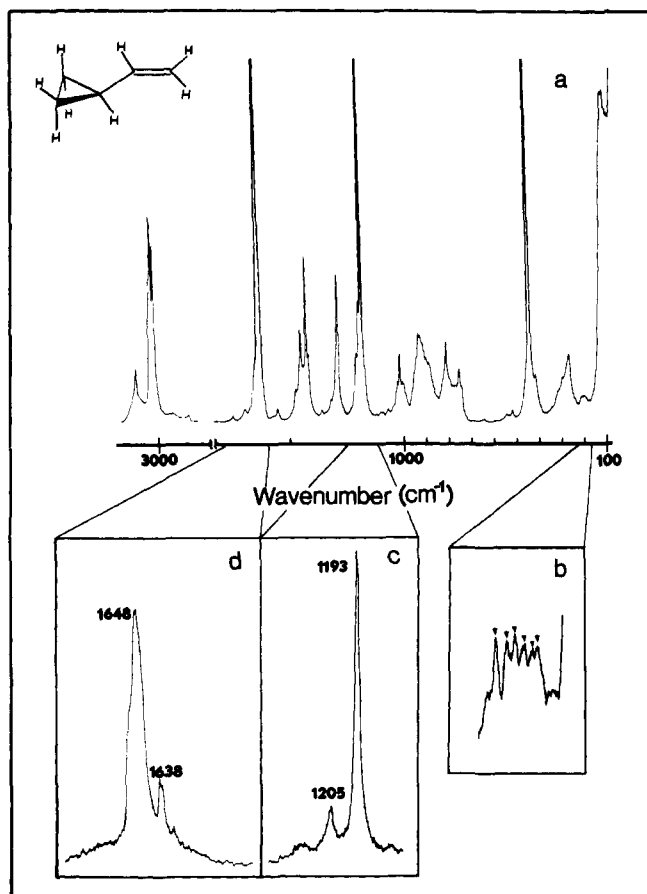


Figure 1. Vapor phase Raman spectra of vinylcyclopropane (see text for details).

gassing, an aliquot was distilled, under low pressure and low temperature, into the side-arm reservoir of a standard Raman gas cell, which was constructed of Spectrosil and had windows mounted at the Brewster angle.

All spectra were recorded at room temperature ($\sim 23^\circ\text{C}$) on a Spex Ramalog Model 1401 (photon-counting) spectrophotometer equipped with a Spectra-Physics Model 164-03 argon ion laser, which delivered 1500 mW at 488.0 nm. Figure 1a shows the survey spectrum of the vapor sample, taken with a spectral slit width, $\Delta\bar{\nu} = 5.0\text{ cm}^{-1}$; Figures 1b (taken with $\Delta\bar{\nu} = 2.0\text{ cm}^{-1}$) and 1c and 1d (taken with $\Delta\bar{\nu} = 1\text{ cm}^{-1}$) show respectively the ($\Delta\nu = 2$) torsional overtone band and the two pairs of bands used in the evaluation of the conformer enthalpy difference.

Results and Discussion

The periodic potential function governing the internal rotation of the vinyl group is assumed to be of the conventional form

$$V(\phi) = \sum_{i=1}^n \frac{V_i}{2} (1 - \cos i\phi) \quad (1)$$

where ϕ is the dihedral angle between the rotor and the frame (as shown in Figure 3). Experience has shown that the summation limit, $n = 6$, is sufficient for the analysis of most problems, and indeed, $n < 6$ often will suffice. (In some cases, e.g., styrene and nitrobenzene, molecular symmetry may permit only even values of the index, "i", but for the case at hand, there is no such restriction.)

The internal rotation constant, F , for the torsional vibration is not truly a constant, but may vary with the dihedral angle, ϕ , and thus, it is better represented in the form

$$F(\phi) = \sum_i F_i \cos i\phi \quad (2)$$

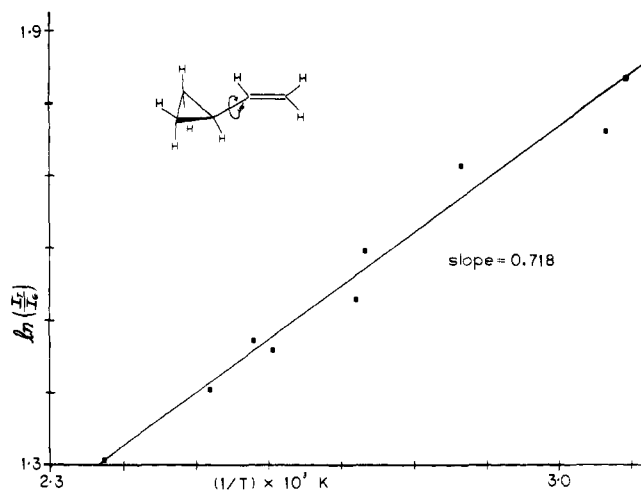


Figure 2. $\bar{\nu}(I_t) = 1193\text{ cm}^{-1}$, $\bar{\nu}(I_g) = 1205\text{ cm}^{-1}$ (see text for explanation; cf. Figure 1c).

Table I. Internal Rotation Constants for Vinylcyclopropane

ϕ	$F(\phi), \text{cm}^{-1}$	ϕ	$F(\phi), \text{cm}^{-1}$
0	1.852	100	1.751
10	1.851	110	1.761
20	1.848	120	1.774
30	1.842	135	1.798
45	1.833	180	1.845
90	1.826		

The structure used in calculating $F(\phi)$ for the trans ($\phi = 0^\circ$) conformer reproduced within $< 2.0\%$ the rotational constants deduced from the microwave work.⁷ The structures used for other dihedral angles between 0° and 180° (cis) assumed a rigid-frame/rigid-top model. The $F(\phi)$'s generated in this fashion were then fitted to the series expansion of eq 2. This series converged rapidly, to yield (in cm^{-1}) $F_0 = 1.8260$, $F_1 = 1.7795 \text{ E-}02$, $F_2 = 2.1968 \text{ E-}02$, $F_3 = 3.0602 \text{ E-}02$, $F_4 = 3.4804 \text{ E-}03$, and $F_5 = 1.9261 \text{ E-}02$; terms greater than F_5 were deemed negligible and were set to zero. Values for $F(\phi)$ for a variety of torsional angles are listed in Table I.

The Hamiltonian for the torsional vibration then becomes

$$\mathcal{H} = - \left\{ \frac{d}{d\phi} F(\phi) \frac{d}{d\phi} \right\} + V(\phi) \quad (3)$$

where the first term represents the kinetic energy contribution while the second term the potential energy contribution. A computer program modeled after that of Lewis et al.⁸ was written to provide the eigenvalues associated with the above Hamiltonian; the program will accommodate kinetic and potential terms through F_6 and V_6 , respectively.

Both the torsional fundamental and the overtone bands are distinctly visible in the vapor phase Raman spectrum of vinylcyclopropane (see Figure 1a). Due to the band types associated with the ($\Delta\nu = 1$) transitions comprising the fundamental band, no resolvable structure was observed. Though the overtone band is considerably weaker than the fundamental, the former is much easier to analyze since it exhibits relatively sharp Q branches corresponding to the individual ($\Delta\nu = 2$) transitions (see Figure 1b). The leftmost in the observed series of transitions is assigned to the ($2 \leftarrow 0$) transition in the trans well; successive double-jumps progress toward lower frequency as marked.

The relative intensity of the pairs of bands shown in Figures 1c and 1d were recorded as a function of temperature in order to evaluate the enthalpy difference, ΔH , between the trans and

Table II. Observed and Calculated Torsional Transitions (cm^{-1}) for Vinylcyclopropane (Vapor)

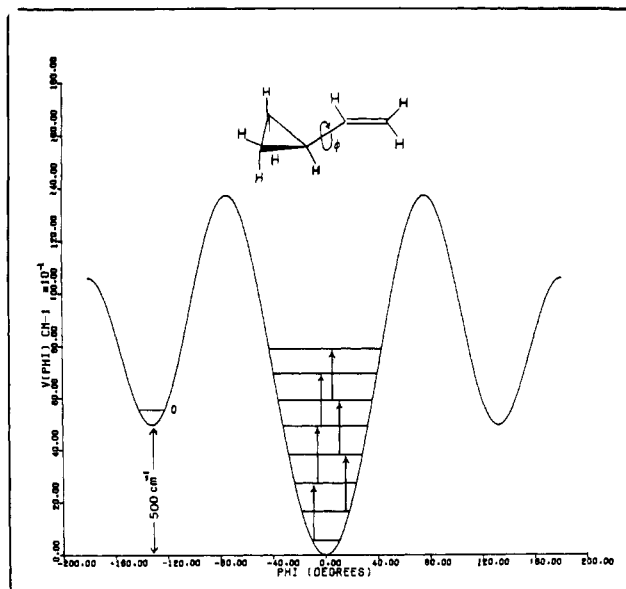
Transition ^a	$\tilde{\nu}$ obsd	$\tilde{\nu}$ calcd ^b	$\Delta\tilde{\nu}$ (obsd - calcd)
$0_G \leftarrow 0_T$	500.0 ^c	500.2	-0.2
$2 \leftarrow 0$	223.0	221.3	1.7
$3 \leftarrow 1$	216.5	217.3	-0.8
$4 \leftarrow 2$	212.0	213.0	-1.0
$5 \leftarrow 3$	207.5	208.4	-1.0
$6 \leftarrow 4$	203.0	203.6	-0.6
$7 \leftarrow 5$	200.0	198.4	1.7

^a All transitions originate in the trans potential well. ^b Calculated using the potential function $V(\phi) = (279.0/2)(1 - \cos \phi) + (699.1/2)(1 - \cos 2\phi) + (781.6/2)(1 - \cos 3\phi) - (199.1/2)(1 - \cos 4\phi)$. ^c Not a transition; deduced from the data presented in Figure 2.

the less stable conformers. Both temperature studies yielded essentially the same result; however, owing to the higher degree of resolution in the 1193-cm^{-1} system (Figure 1c) only these latter results are reported in Figure 2. It should be noted that this band is in good agreement with Van Volkenburgh et al.,⁹ who observed in the infrared spectrum of vinylcyclopropane a strong band at 1191 cm^{-1} which is believed to result from the cyclopropyl ring-breathing vibration. Figure 2 shows a plot of the natural logarithm of the peak intensity ratio vs. the reciprocal of the absolute temperature. As can be seen, the linear least-squares fit is reasonable and has a slope, $m = 0.718$, which indicates $\Delta H = 500 \pm 50\text{ cm}^{-1}$ ($5.98 \pm 0.60\text{ kJ mol}^{-1}$). The intercept, albeit ill determined, is negative and of the order of $\ln(2)$ which would be expected for a gauche rotamer if the polarizability derivatives are the same for the two rotamers.

We found that it was necessary to use narrow slit widths to obtain reliable intensity data for the pair of lines used to determine ΔH . With slit widths of 2 cm^{-1} or greater the resulting overlap of the lines is significant. Since they broaden with temperature, it is rather difficult to correct consistently for the overlap and we found generally that smaller values of ΔH were derived when the experiments were carried out at lower resolution. Our experiments were done with a spectral slit width of 1 cm^{-1} . The error limit on ΔH was derived by performing temperature studies at several different times, obtaining for each, not less than five measurements over the temperature range 23 to $131\text{ }^\circ\text{C}$. The temperature studies also revealed that the weak line at $\sim 1218\text{ cm}^{-1}$ (Figure 1c) is not part of a series of vibrational satellites or due to another rotamer but originates from the ground vibrational state. A reliable temperature dependence study of the torsional overtones was not permitted, owing to the experimental conditions necessary for obtaining the high-resolution spectrum (Figure 1b).

Then with the aid of the results of the perturbation theory treatment given by Carreira,¹⁰ the ($2 \leftarrow 0$) torsional frequency and the first second-difference were used to obtain an initial estimate of the potential constants. These constants were then adjusted in a least-squares manner to fit all of the observed overtone frequencies and the ΔH deduced from the temperature dependence study. The constants thus determined are (in cm^{-1}) $V_1 = 279 \pm 60$, $V_2 = 699 \pm 60$, $V_3 = 782 \pm 32$, and $V_4 = -199 \pm 35$, where the error limits ($=2\sigma$) have been estimated from the variance-covariance matrix. The resulting potential function, including the observed transitions, is shown in Figure 3. A comparison of observed and calculated torsional frequencies is given in Table II. During the least-squares fitting of the potential constants, $\Delta H = 500.0$ was weighted 0.025, while each observed frequency was weighed 1.0. The theoretical work of Hehre⁶ using the 4-31G basis set is in qualitative agreement with the spectroscopic results: both indicate a trans/gauche conformational equilibrium; $\Delta H = 475\text{ cm}^{-1}$ (5.68 kJ mol^{-1}), theoretical vs. $\Delta H = 500\text{ cm}^{-1}$ (5.98 kJ mol^{-1}), spectroscopic.

**Figure 3.** Torsional potential function for vinylcyclopropane.

The conformational analysis of vinylcyclopropane, with respect to the torsional potential function, has another interesting feature. While pursuing our initial intuitive notion of a trans/cis equilibrium, we discovered that the frequency data and the conformational energy difference could also be fitted to a twofold potential function ($V_1 = 558\text{ cm}^{-1}$ and $V_2 = 1576\text{ cm}^{-1}$) with nearly the same errors in the calculated transition frequencies. However, if a twofold (trans/cis) torsional potential is assumed, then the relative intensity at room temperature ($\sim 23\text{ }^\circ\text{C}$) of the bands shown in Figures 1c and 1d should be on the order of 14:1 assuming that the polarizability derivatives are the same for the two lines. Whereas, if the potential function is assumed to be threefold (trans/gauche) the relative intensity of these bands should be on the order of 7:1. This latter ratio is obviously much closer to that observed (viz. 6.9:1) the point being that consideration of observed frequencies alone may be grossly misleading in the interpretation of spectroscopic data.

We have recently been informed of a temperature dependence study carried out by Murphy et al.¹¹ The difference between their $\Delta H = 385\text{ cm}^{-1}$ and our value of $\Delta H = 500\text{ cm}^{-1}$ appears to be due both to the choice of baseline (for determining the relative intensities) and to the spectral resolution used. If the conformational enthalpy difference is indeed 385 cm^{-1} , this affects primarily the value of V_1 and leads to a potential function having the following constants: $V_1 = 111$, $V_2 = 752$, $V_3 = 784$, $V_4 = -203\text{ cm}^{-1}$.

Conclusions

The conformational isomerism of vinylcyclopropane is characterized by a threefold torsional potential function having minima for the s-trans and two equal-energy gauche conformers. The gauche conformations are found to be the less stable by 500 cm^{-1} and the barrier to interconversion, trans \rightarrow gauche, is 1372 cm^{-1} (16.41 kJ mol^{-1}).

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The Potential Surfaces for the Lowest Singlet and Triplet States of Cyclobutadiene

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Abstract: The potential surfaces for the lowest singlet and triplet states of cyclobutadiene have been explored by ab initio MO calculations with full π -space, CI, using a basis set of STO-3G orbitals. The calculated force constants for distortion from D_{4h} symmetry are in excellent agreement with qualitative expectations, derived from an analysis in terms of second-order Jahn-Teller effects. A square geometry is found to represent a minimum for the triplet and a transition state between two rectangular geometries for the singlet. The rectangular minimum for the singlet has been located, and the energy difference between square and rectangular singlets is found to be 4.2 kcal/mol. Using a basis set of double ζ quality, the calculated energy difference remains almost unchanged; but additional CI, involving the σ space, increases the difference to 8.3 kcal/mol. It is concluded from these calculations that the parent [4]annulene is not square or effectively square in its ground state, thus casting serious doubt on the interpretation of the IR spectrum of matrix isolated cyclobutadiene as belonging to a square molecule.

Although for several substituted cyclobutadienes a singlet ground state with a nonsquare equilibrium geometry has been indicated¹ or established,² the IR spectrum of the matrix isolated parent [4]annulene has been interpreted as belonging to a square molecule.³ Not only have all attempts to detect an EPR signal from the matrix isolated species failed,⁴ but also, one of us recently showed theoretically that the lowest singlet state of cyclobutadiene most certainly lies below the triplet, even at square geometries.⁵ Kollmar and Staemmler have subsequently verified this theoretical result and have termed the interorbital electron correlation effect responsible for it "dynamic spin polarization",⁶ a designation we find most appropriate in view of the previously demonstrated relationship between this effect in cyclobutadiene and the static spin polarization in radicals like allyl.⁵

Since dynamic spin polarization results in a singlet ground state for cyclobutadiene, even at square geometries, the IR of the matrix isolated molecule could reasonably be assigned to this state, *if* the lowest singlet state were expected to have a square equilibrium geometry, or if the potential surface for distortion away from a D_{4h} geometry were very flat. Although it has been argued that electron repulsion results in a rather flat potential curve for rectangular distortion in the singlet,^{5,7} the ab initio calculations published at the time that we began the present theoretical study found the lowest energy square geometry to lie $8^{3d}-11^8$ kcal/mol above the equilibrium rectangular one. One goal of this study was to examine the basis set dependence of the calculated energy difference between the rectangular and the square singlet and to see whether inclusion of correlation between the σ and π electrons would reduce the computed difference. In addition, we wanted to test the merit of suggestions in the literature that a rhomboidal geometry might be lower in energy than a square one⁹ and that a trapezoidal carbon skeleton might have a smaller energy content than a rectangular one.⁷ Thus, we did not confine ourselves to studying only the rectangle-square potential curve for the

singlet but set out instead to establish by ab initio MO calculations some of the important features of the complete potential surfaces for both the lowest singlet and triplet states of cyclobutadiene.

Results and Discussion

Square Cyclobutadiene. As in our previous studies of the potential surfaces for other open-shell molecules,^{10,11} we began by finding the optimum cyclobutadiene geometry of highest (D_{4h}) symmetry and then considered distortions away from this square array of carbons. Unlike the case in trimethylenemethane¹⁰ and the cyclopropenyl anion,¹¹ the lowest singlet state of square cyclobutadiene is nondegenerate ($^1B_{1g}$). Square cyclobutadiene may be considered a diradical,¹² since in the lowest singlet state each of the degenerate (e_g) nonbonding π MOs

$$\psi_2 = \phi_1 - \phi_3 \quad (1)$$

$$\psi_3 = \phi_2 - \phi_4 \quad (2)$$

contains one electron. Thus, the SCF wave functions for $^1B_{1g}$ and the $m_s = 0$ component of the lowest triplet ($^3A_{2g}$) can be written

$$^1B_{1g}, ^3A_{2g} = (| \dots \psi_1^2 \psi_2^\alpha \psi_3^\beta \rangle \mp | \dots \psi_1^2 \psi_2^\beta \psi_3^\alpha \rangle) / \sqrt{2} \quad (3)$$

where the upper sign gives the singlet wave function, the lower the triplet, and

$$\psi_1 = \phi_1 + \phi_2 + \phi_3 + \phi_4 \quad (4)$$

is the lowest energy (a_{2u}) π MO. Since ψ_2 and ψ_3 are confined to different sets of atoms, the exchange integral between them is expected to be small (zero when differential overlap is neglected).⁵ Therefore, this set of nonbonding MOs is useful for understanding why $^1B_{1g}$ and $^3A_{2g}$ are nearly degenerate at the SCF level. Nevertheless, for considering all but rhomboidal