J. Phys. Chem. A **1999,** *103,* 3629−3635

Conformers of β-Vinylethanol: Internal Hydrogen Bonding to π-Bonded System

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Received: January 7, 1999; In Final Form: March 12, 1999

In a combined experimental spectroscopic and theoretical ab initio MP2/6-311++G(d,p) study of β-vinylethanol a new (second known) conformer (y) has been detected via heated preexpansion free jet microwave spectroscopy. The new species was found to have rotational constants $A = 19928.6325(24)$, $B = 2172.37374(91)$, $C = 2144.28416(76)$ MHz and electric dipole moment components $\mu_a = 0.01284(37)$, $\mu_b = 1.262(11)$, and $\mu_c = 0.486(43)$ D. Species y has been identified with the theoretically predicted extended conformer CAA, having dihedral angles of ∠CCCC = −113.9°, ∠CCCO = 183.1°, ∠CCOH = 181.5° by comparison of experimental data with the ab initio predicted rotational constants and electric dipole moment components for the seven stable conformers of β-vinylethanol. A similar analysis for the first known conformer (x) originally detected by Marstokk and Møllendal in a previous conventional microwave spectroscopy study identifies this species with the theoretically predicted gauche conformer CMG, having dihedral angles of ∠CCCC = −107.4°, ∠CCCO = 64.3°, ∠CCOH = −49.7°. From an ab initio exploration of the energy barriers of the conformational potential hypersurface it has been shown that the two energetically comparable but undetected gauche conformers CMA and CMM would relax in the jet expansion to the lower energy detected species CMG and that similarly the two undetected extended conformers CAG and CAM of slightly higher energy than CAA would relax to the detected species CAA. Relaxation of the extended conformers to the lower energy gauche CGM is precluded by high intervening energy barriers. The observed energy difference between CAA and CGM is consistent with the stabilizing effect of an internal hydrogen bond in CGM linking the hydroxyl hydrogen to the π-electron cloud of the vinyl group. Bonding appears to be directed approximately along an axis perpendicular to the vinyl plane and passing through the nonterminal sp^2-carbon atom.

Introduction

The study of the shapes of XY-disubstituted ethanes has a long history, dating back at least to the Raman spectral studies of Kohlrausch and co-workers.[1] In some instances, notably when X is OH and Y is aromatic or alkenyl, the observation of distinct infrared bands, attributable to free and bound hydroxyl, led to suggestions of hydrogen bonding of the OH to the aromatic or alkenyl substituent.[2] In the case of 3-buten-1-ol (β-vinylethanol) a subsequent more detailed study by means of gaseous electron diffraction[3] inferred the presence of two gas-phase conformers in a concentration ratio of ca. 2:1 at the experiment temperature of 45 °C. The more abundant species displayed interatomic distances consistent with the presence of an intramolecular hydrogen bond between the OH hydrogen and the alkenyl π-system. In a later study via microwave spectroscopy by Marstokk and Møllendal[4] a single conformer was identified accounting for at least 80% of the gas at the experiment temperature of −20 °C. The rotational constants of this species and its O-deutero isotopomer also were consistent with a molecular structure containing the intramolecular hydrogen bond.

More recently, as part of a wider study of conformational structures and energetics, we have investigated several disubstituted ethanes with both π-bonded and NH_2 or OH substituents. In this work we have employed both ab initio molecular orbital calculations and free expansion jet microwave spectroscopy with the aims of identifying the most stable conformers and of assessing the reliability of ab initio molecular orbital calculations at various levels of approximation in predicting the relative stabilities of such ethane conformers.[5] Unlike conventional microwave spectroscopy such as that used in the earlier study of vinylethanol, free expansion jet spectroscopy provides conditions in the microwave absorption zone in which chemical reactions that are reversible at ambient temperature (such as the interconversion of conformers) are not equilibrated to the same temperature as the rotational energy. In free expansion jet spectroscopy chemical equilibrium is established prior to the expansion, where the conditions may involve significantly elevated temperatures that would be impracticable in conventional microwave spectrometers because of the concomitant equally elevated rotational temperature. The subsequent adiabatic cooling in free expansion jet spectrometers reduces the rotational temperature to a few degrees kelvin but in suitable cases leaves the chemical composition of the vapor unaltered from the conditions prior to expansion. Thus, it provides the opportunity to investigate higher energy conformers,[6] such as the second conformer of vinylethanol detected via the earlier electron diffraction study.

In the present study we further contribute via both experiment and theory to a more complete picture of the potential energy surface relating to interconversion of such conformers of disubstituted ethanes and of the energetics of hydrogen bonds involving π-systems exemplified by the specific case of vinylethanol. Such increased understanding has broader implications in fields such as supramolecular chemistry and crystal engineering where extended hydrogen-bonded networks to π-systems are involved in shape-specific complexation[7] and in

10.1021/jp990106k CCC: $18.00

TABLE 1: Experimentally Derived Rotational and Centrifugal Distortion Constants[a] for the Previously Identified Conformer x of $CH_2OHCH_2CH{=}CH_2$ and for the Newly Found Conformer y with Its Corresponding O-Deutero Isotopomer

	conformer x	conformer y	
	$CH_2OHCH_2CH{=}CH_2$	$CH_2OHCH_2CH{=}CH_2$	$CH_2ODCH_2CH{=}CH_2$
A/MHz	9185.7309(22)	19928.6325(24)	19713.970(36)
B/MHz	3330.05915(98)	2172.37374(91)	2092.9607(19)
C/MHz	2742.36661(99)	2144.28416(76)	2067.0775(15)
D_j/kHz	5.2002(49)	0.6845(53)	0.690(44)
D_{jk}/kHz	−30.202(44)	−22.961(39)	−22.868(60)
D_k/kHz	72.049(99)	484.82(33)	504.4(70)
d_1/kHz	−1.7419(14)	0.1221(17)	0.088(13)
d_2/kHz	−0.09671(52)	−0.0064(12)	−0.017(11)
H_{jk}/kHz	0.00029(17)		
no. of lines in fit	91[b,c]	37[c]	27[c]
rms residual/MHz	0.050	0.010	0.011

[a] The numbers in parentheses are one standard deviation in units of the least significant quoted digit. [b] Includes the 23 noncoalesced lines in the range 18−32 GHz reported by Marstokk and Møllendal.[4] [c] Observed frequencies, assigned quantum numbers, and residuals from the fitting calculations are listed in Tables 1S, 2S, and 3S in Supporting Information.

relation to the long-standing problem of protein folding. In the latter case it is noteworthy that interest in the issue of the role of hydrogen bonds to π-systems such as tyrosine and phenylalanine in determining the ultimate structure of proteins has undergone a resurgence.[8] Additionally, a study of such hydrogen bonds in an intramolecular context helps illuminate the related small molecule studies of intermolecular bonds in the bimolecular complexes linking small polar hydrides such as water and ammonia with the π-systems of ethylene and benzene.[9]

Methodology

Experimental. The Stark modulated, free expansion jet spectrometer operating in the 48−72 GHz band is based on a design that has been described previously.[10] The liquid sample was purchased from Aldrich and used without further purification. It was utilized as a 10% solution in CCl_4, and this solution was entrained at 3 μL min^{-1} into the 300 std mL min^{-1} argon stream entering the spectrometer. The preexpansion chamber was maintained at a pressure of 65 kPa and a temperature of 80 °C**.** Postexpansion rotational temperatures were found to be ca. 3−5 K under the conditions employed. The O-deuterated isotopomer was prepared by simple direct exchange in the CCl_4 solution with D_2O followed by separation of the nonaqueous layer.

It was a straightforward matter, using narrow spectral scans over a few megahertz, to detect, digitally acquire, and measure by least-squares fitting of a Lorentzian line shape function the newly predicted transitions of the previously identified conformer originally assigned in the 18−32 GHz frequency band by Marstokk and Møllendal.[4] However, it was necessary to undertake extended spectral scans over much wider frequency ranges to search for new conformers (48.1−69.6 GHz). In these strip-chart-recorded wide searches, the sensitivity limit was ca. 1% of the strongest line detected. Once located via the wide search scan, each detected line was measured via the narrow scan method.

The Stark modulation system employed parallel-plate electrodes with a separation of ca. 3.5 cm. The square wave modulation field was established by opposed polarity equal amplitude ground-clamped voltage waveforms applied to the opposing electrodes. For dipole moment measurements the various M_J lobes for selected transitions were scanned, digitally acquired, and the Stark frequency shift measured by least-squares fitting a Lorentzian line shape profile. The preset Stark voltages were measured via a precision a/d converter. The effective electrode spacing, which includes allowance for any scale factor error in the voltage measurement, was calibrated from a series of Stark shift measurements on SO_2 for which a precise dipole moment has been determined via molecular beam electric resonance.[11]

Theoretical. We employed the Gaussian 94 suite of programs[12] calculations being run at the MP2/6-311G++(d,p) level. From our previous combined microwave spectroscopy and quantum chemistry studies on a variety of small molecules,[5,6,13] we have found that at lower levels of approximation the results of calculated structures and conformer energies can be significantly inconsistent with experimental measurements. Frequency computations utilized for the calculation of ab initio vibrational zero-point and Gibbs energy corrections were performed at the MP2/6-31G(d,p) level. Conformer interconversion energy barrier calculations were performed as a series of geometry optimizations at the MP2/6-311G++(d,p) level, performed at chosen fixed values of a single dihedral angle, but otherwise unconstrained.

Terminology

In labeling the various possible conformers of vinylethanol, we have adopted the notation of Fernández et al. In a related theoretical study[14] of vinylethylamine and vinylethanthiol these authors used the letter code dihedral angle designators $A \equiv$ ca. 180°, $C \equiv$ ca. −120°, $G \equiv$ ca. −60°, and $M \equiv$ ca. 60° to create three-letter acronyms for each possible conformer that in our case implicitly specify the C−C−C−C, O−C−C−C, and H−O−C−C dihedral angles. Further, following the terminology of Marstokk and Møllendal in their study of vinylethylamine,[15] it is instructive to note that the conformers can be subdivided into those that are either gauche or extended (i.e., trans) about the C−C−C−C bond system. The shapes of the various conformers of vinylethanol found from our investigations to be the stable forms are illustrated in Figure 1 together with our adopted acronyms.

Results and Discussion

We observed a total of 67 lines in the range 48−68 GHz that we were able to assign to the same species that was identified by Marstokk and Møllendal as a gauche, internally hydrogen-bonded conformer. We will designate it initially as conformer x. Table 1 lists the spectroscopic constants (I^R representation, S reduction[16]) derived by a least-squares fit to our lines, plus the 23 noncoalesced lines in the range 18−32 GHz reported by Marstokk and Møllendal.[4] A full listing of the observed transitions and the least-squares fit residuals is

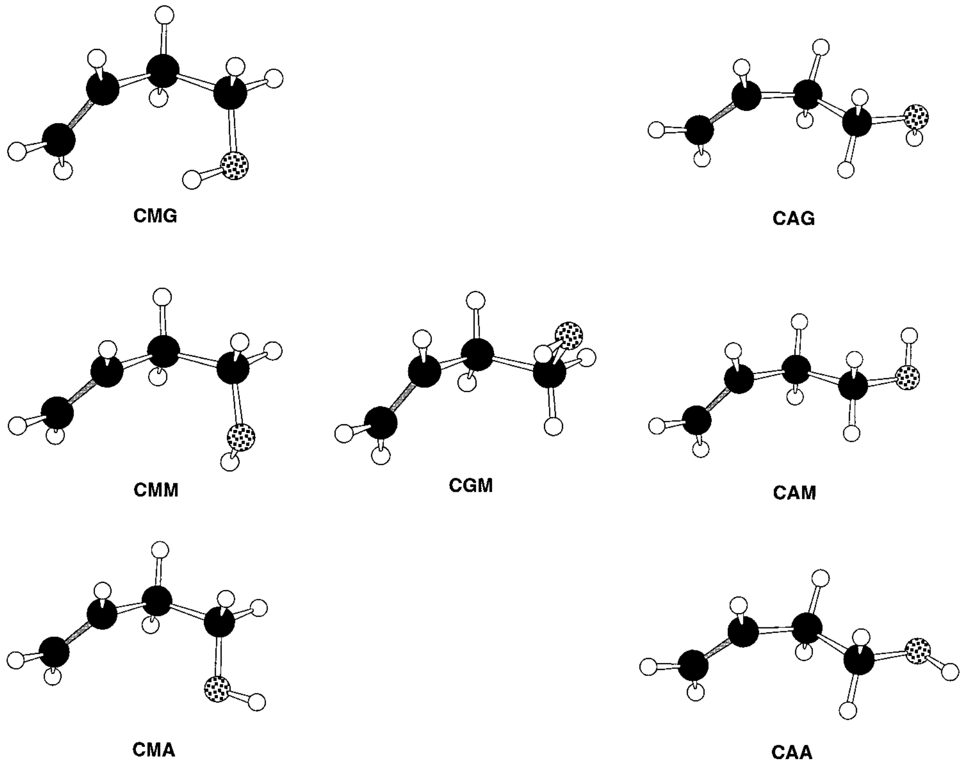

Figure 1. Theoretically predicted structures from ab initio MP2/6-311++G(d,p) calculations of the stable conformers of β-vinylethanol.

given in Table 1S in Supporting Information. We also detected an additional 37 lines that could be assigned to a second species of vinylethanol, which we initially designate as y. The spectroscopic parameters derived in a least-squares fit are also given in Table 1, and the full listing of observed transitions is given in Table 2S in Supporting Information. Similarly listed in Table 1 are the spectroscopic parameters derived from the measurement of 27 lines assigned to the O-deutero isotopomer of y for which the full listing of observed transitions is given in Table 3S in Supporting Information.

Principal axis dipole moment component values for y were determined from the analysis of Stark effect measurements on the $M_J = 1$ and 2 lobes of the transitions $2_{20}-1_{11}$, $2_{21}-1_{11}$, and $2_{21}-1_{10}$. The Stark shifts were significantly nonquadratic (to the extent that two lobes actually crossed through each other as the voltage was varied). This was due to rotational near-degeneracies, and so it was necessary to directly least-squares-fit the dipole moment components via our own Stark effect computer program STARKFIT that treated the near-degeneracies explicitly. However, although numerically more complicated than the standard quadratic Stark shift analysis, it was in this case a relatively straightforward matter to derive adequately precise values with uncorrelated errors for all three dipole moment components. The resulting best-fit dipole moment component values are listed in Table 2. The details of the 23 individual Stark shift measurements and the fit residuals are listed in Table 4S.

The seven conformers that are the most stable according to MP2/6-311G++(d,p) level calculations on vinylethanol are shown in Figure 1. The relative energies are listed in Table 3, which also gives relative energies including vibrational zero-point energy (i.e., Gibbs free energies at 0 K) and the Gibbs energies at 353 K, the preexpansion temperature used for the experimental study of rotational spectra. The most stable species is predicted to be the gauche conformer CMG. Then there is a group of three extended conformers, CAA, CAG, and CAM, with relative energies predicted to be in the range 3.8−4.7 kJ mol^{-1} followed by the gauche species CGM, CMM, and CMA with energies upward of 5.2 kJ mol^{-1}. Geometry optimizations started at structures approximating the anticipated gauche conformers CGA, and CGG reverted to CGM during the calculations.

TABLE 2: Experimentally Derived Principal Axis Dipole Moment Components for the Newly Identified Conformer *y* of $CH_2OHCH_2CH{=}CH_2$[a]

μ_a/D	0.01284(37)
μ_b/D	1.262(11)
μ_c/D	0.486(43)
μ_{total}/D	1.352
no. of transitions used	3
no. of Stark shift measurements	23
rms residual/MHz	0.046

[a] The numbers in parentheses are one standard deviation in units of the least significant quoted digit. Stark shifts at a series of voltages were measured for the transitions 2(2,0)−1(1,1), 2(2,1)−1(1,1), and 2(2,1)−1(1,0). Voltages, observed Stark shifts, M_J quantum numbers, and residuals from the dipole moment fitting calculation and from the Stark electrode spacing calibration are detailed in Tables 4S and 5S in Supporting Information, respectively.

TABLE 3: Predicted Relative ab Initio Energies for the Conformers of $CH_2OHCH_2CH{=}CH_2$ Optimized at the MP2/6-311++G(d,p) Level

species	ΔE_{MP2} kJ mol^{-1}	ΔE_{MP2} + ZPE[a] kJ mol^{-1}	ΔG_{353K}[a] kJ mol^{-1}	relative abundance[b] 353 K	relative abundance[b] 313 K
CMG	0.000	0.000	0.000	0.46	0.52
CMM	8.107	6.857	5.361	0.07	0.07
CMA	9.215	7.802	6.198	0.06	0.05
CAM	6.997	6.063	4.650	0.10	0.09
CAG	6.700	5.760	4.345	0.11	0.10
CAA	6.724	5.448	3.817	0.13	0.12

[a] The vibrational zero-point and thermal Gibbs energy contributions are predicted from Gaussian 94 harmonic force field calculations performed at the MP2/6-31G(d,p) level. [b] Calculated from the theoretical relative Gibbs energies.

TABLE 4: Theoretical Rotational Constants and Dipole Moment Components for the Conformers of $CH_2OHCH_2CH{=}CH_2$ Predicted at the MP2/6-311++G(d,p) Level Shown in Comparison with the Corresponding Values Obtained from Experiment

species	A MHz	B MHz	C MHz	μ_a D	μ_b D	μ_c D
CMG	9148. 8	3348.4	2756.3	1.44	1.30	0.63
CAG	19119.4	2170.5	2150.5	1.42	0.92	0.42
CAM	19121.1	2164.5	2152.9	1.03	0.67	1.43
CAA	19500.5	2183.1	2161.4	0.03	1.49	0.93
CMA	9769.6	3137.4	2670.9	1.60	1.14	0.75
CMM	9815.8	3059.5	2634.4	0.37	1.37	1.29
CGM	11544.5	2780.3	2533.8	1.59	0.34	0.73
x[a]	9185.73	3330.06	2742.37	1.23(2)	1.02(2)	0.44(7)
y[b]	19928.63	2172.37	2144.28	0.0128(4)	1.26(1)	0.49(4)

[a] Rotational constant values are as listed in Table 1. Dipole moment values are taken from the published work of Marstokk and Møllendal.[4] [b] Rotational constant values are as listed in Table 1. Dipole moment values are as listed in Table 2.

TABLE 5: Principal Axis Coordinates of the Hydroxyl H Atom for the Conformers of $CH_2OHCH_2CH{=}CH_2$ Predicted at the MP2/6311++G(d,p) Level Shown in Comparison with the Corresponding Values Obtained from the Application of Kraitchman's Equations to the Experimental Moments of Inertia Found for the Normal and OD Isotopomers of Species y

species	$\|a\|$ Å	$\|b\|$ Å	$\|c\|$ Å
CMG	0.683864	1.367820	0.274960
CAG	2.297645	1.029012	0.410785
CAM	2.516720	0.404379	0.724338
CAA	2.956277	0.370697	0.442278
CMA	2.328576	1.189348	0.275943
CMM	1.352741	1.163415	0.896535
CGM	1.313762	1.420901	0.180601
x[a]	0.4148	1.4228	0.2555
y[b]	2.955	0.355	0.405

[a] Taken from the published work of Marstokk and Møllendal.[4] [b] Calculated via Kraitchman's equations from the rotational constant values for species y and its O-deutero isotopomer as listed in Table 1.

The spectroscopic constants predicted from the ab intio optimized structures for these conformers are listed in Table 4. It is evident that only for CMG are the predicted rotational constants in agreement with those observed for vinylethanol species x. The rotational constants for CMG are within 0.5% of those observed for x, while the constants predicted for other conformers are distinctly different from those of x. [The nearest are the constants for CMA, and these diverge by 2.6−6.4% from those of x.]

For species y, not previously detected spectroscopically, CAA has rotational constants closest to those observed. CAG and CAM have A rotational constants twice as discrepant but might possibly be considered. However, the measured dipole moment components also listed for comparison in Table 4 clearly point to CAA as the species, the very small value for μ_a being decisive, although all three components are substantially different for the two competing identifications.

As further confirmation of the identity of the second observed conformer, we considered the assigned O-deutero species. The substitution coordinates for the hydroxyl hydrogen were calculated via Kraitchman's equations[17] and are listed in Table 5. Again, it is clear that the species y is CAA.

Thus, the conformer x is identified with the gauche conformer CMG, which from the detailed ab initio structural data in Table 6S in Supporting Information, is predicted to have dihedral angles of $\angle CCCC = -107.4^\circ$, $\angle CCCO = 64.3^\circ$, $\angle CCOH = -49.7^\circ$. Similarly, the newly detected conformer y is identified with the extended conformer CAA, having dihedral angles of $\angle CCCC = -113.9^\circ$, $\angle CCCO = 183.1^\circ$, $\angle CCOH = 181.5^\circ$. These dihedral angles bear little resemblance to those deduced for the second conformer in the electron diffraction study of Trætteberg, and Østensen,[3] but in light of the theoretical relative abundances of the conformers for their experiment temperature of 40 °C (313 K) shown in the last column of Table 3, it seems that their analysis of the diffraction data as arising from just two conformers was inappropriate. However, it should be noted that their derived structure for the major species present $\angle CCCC = 118.4(43)^\circ$, $\angle CCCO = -70.7(25)^\circ$, $\angle CCOH = 26.0^\circ$ is broadly consistent with the enantiomeric form of the gauche conformer CMG.

Next we tried to estimate the relative abundances of the two species, x and y (i.e., CMG and CAA) in the spectrometer. We measured the signal strengths of lines and divided by the predicted fractional absorption coefficients. Such quotients for y lines compared with quotients for x lines should represent molar ratios within the spectrometer, but there are appreciable uncertainties. Of most importance in this respect, the degree of rotational cooling in the jet expansion of the two species under comparison may differ, since there is a large difference in the size of the rotational constant A. This strongly influences the density of the rotational states and, as a consequence, the kinetics of collisional cooling. We determined, by trial and error, the effective rotational temperature that gave the smallest scatter of the quotients. The approximate rotational temperatures thus determined were 5 K for x and 3 K for y. The resultant estimated molar ratio was 92% for x, 8% for y. The estimated probable error in this ratio based on the uncertainties mentioned earlier is ca. ±30%.

From the difference [3.82 kJ mol^{-1}] in predicted Gibbs free energies at the preexpansion chamber temperature (353 K), we would predict the vapor to contain 46% CMG and 13% CAA. The remainder consists of the other conformers (see mole fractions listed in Table 3). In fact the differences in predicted mole fractions are small enough that several more conformers (particularly CAM and CAG) should have also been detected, and they were not.

Previous studies of somewhat similar compounds[5c,6,18] have shown that during a free jet expansion such as that occurring in our spectrometer, it is possible for certain conformers to interconvert into others with lower zero-point energy levels. The efficiency of this process has been found to be strongly dependent on the height of the energy barrier to interconversion. As described by Ruoff et al.,[18b] with jet expansion in argon carrier gas from room temperature efficient conformational relaxation is observed to occur whenever the barrier to interconversion is lower than a critical value. Of the 13 compounds studied by these authors 9 compounds were found not to relax. Where the barrier heights were known for these species, they ranged from 800 cm^{-1} upward, with one exception, deuterioacetaldehyde (CH_2DCHO), which has a barrier of 400 cm^{-1}. From these results a critical value of 400 cm^{-1} was deduced. However, deuterioacetaldehyde is unique among the 13 compounds in having almost identical energies for the two possible conformers. Thus, unlike the other 12 compounds, the observation of both conformers in the expanded jet is not inconsistent with rapid relaxation between the two conformers of deuterioacetaldehyde, since even if quasi-equilibrated at the low temperatures that develop during the expansion, both species would be expected to be present in comparable concentrations. Thus, the appropriate value of the critical barrier height may be somewhat greater than 400 cm^{-1}. As implied by Felder and Günthard,[18a] the critical barrier height parameter relates to a truncated rate process and is anticipated to be dependent on both the temperature and pressure prior to expansion. From our own past studies[5c,6] under similar preexpansion conditions to those used in the present study, we have observed that the critical barrier height necessary to prevent efficient conformational relaxation is ca. 1000 cm^{-1}.

We investigated the possibility of conformational relaxation theoretically by computing total energies of the vinylethanol species with stepped constrained values of the H−O−C−C angle, embracing the interconversion between CMM, CMG, and CMA. The results, shown in Figure 2a, indicate that the barriers are particularly low, no more than 200 cm^{-1}, so that we expect rapid relaxation during the expansion from CMM and CMA to the species of lowest energy, namely, CMG.

The possibility of interconversion between CAM, CAA, and CAG was likewise investigated via calculations involving stepped constrained values of the HOCC angle, the results being shown in Figure 2b. Again in this case, the barriers are predicted to be quite low, less than 400 cm^{-1}, and so we expect rapid interconversion among these three conformers to persist during the expansion. Our theoretical predictions of vibrational ground-state relative energies shown in Table 3 point to CAA as the lowest energy species of the triad, and hence, CAM and CAG would be predicted to relax to this conformer. It should be noted that the predicted energy differences between these species is of the order of the anticipated systematic uncertainties (based on our experience with somewhat larger molecules)[5c] in ab initio relative energy calculations, and so it would not be too surprising if CAG or CAM were found experimentally to be the favored conformer. However, the fact that the experimentally observed conformer was indeed CAA lends strength to the view that for molecules as small as vinylethanol, the systematic uncertainties in ab initio relative energies, at least among this closely related triad of conformers, may be significantly smaller.

As is shown in Figure 2c, a substantial energy barrier in excess of 2000 cm^{-1}, corresponding to passing through an eclipsed substituted ethane structure, precludes relaxation between the extended [CAM, CAA, CAG] triad and the gauche [CMM, CMA, CMG] set of conformers. A similar barrier isolates the alternative gauche conformer CGM from the other six.

The consequence of these predicted relaxations of conformers would be to produce an expanded plume of vinylethanol containing 59% CMG and 34% of CAA and a quite small amount of CGM. This would account for our ability to detect only two conformers in the jet spectrometer. The predicted CMG/CAA ratio differs appreciably from our experimental estimate of the relative abundances of x/y, but on one hand there is a substantial experimental error bar and on the other we do not expect the ab initio calculations to yield conformational relative energies more reliably than to ±1−2 kJ mol^{-1}. It thus appears that, as in our previous studies, ab initio theoretical calculations at the level of MP2/6-311G++(d,p) and vibrational corrections at a slightly lower level (MP2/6-31G(d,p)) give a satisfactory basis for interpreting jet spectroscopy observations of multiconformational molecules such as vinylethanol.

It is relevant to compare the case of vinylethanol with a related microwave study of the corresponding thiol by Marstokk and Møllendal.[19] In this work the authors commented that their detection of three different conformers of vinylethanethiol compared with only one of vinylethanol was an indication of the greater strength of the intramolecular hydrogen bond in the alcohol. This was also consistent with their finding of four conformers of vinylethylamine because they considered the hydrogen bonding to be weaker in the amine.[15] To investigate

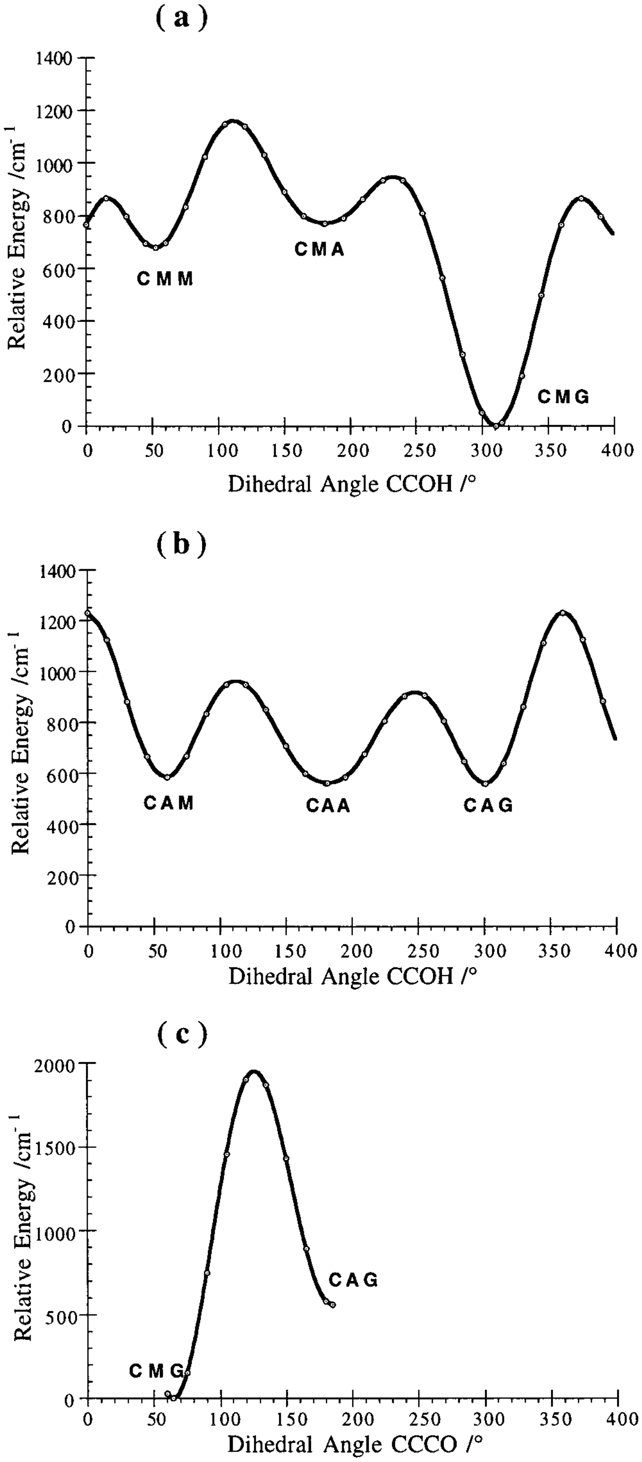

Figure 2. Interconformational energy profiles predicted from ab initio MP2/6-311++G(d,p) calculations on β-vinylethanol constrained in a single geometric parameter. The low barriers shown in (a) will enable efficient relaxation of both CMM and CMA to the lower energy hydrogen-bonded CMG. The low barriers shown in (b) enable rapid relaxation between all three conformers CAM, CAA, and CAG. Both theoretically and experimentally, it appears that CAA has a slightly lower ground-state vibrational energy level and hence will be the favored conformer following jet cooling. The high barrier shown in (c) is typical of the consequence of an eclipsed ethane structure that precludes relaxation of any member of the [CAM, CAA, CAG] triad to CMG.

TABLE 6: Ab Initio Internuclear Distances from the Hydroxyl Hydrogen Atoms to the Vinyl Carbon Atoms and the Corresponding H−C−2p$_\pi$ Angles[a]

species	OH···C$_1$ pm	angle deg	OH···C$_2$ pm	angle deg
CMG	279	32.6	251	20.6
CMM	359	46.8	315	38.5
CMA	446		377	16.2
CAM	508		399	
CAG	481		400	
CAA	541		443	
CGM	375	58.6	271	43.8

[a] The terminal vinyl carbon is labeled C$_1$ and the inner vinyl carbon C$_2$.

this interaction further, we have computed the H···C distance for the interaction of OH and NH$_2$ with both the terminal and inner carbon atoms (C$_1$ and C$_2$) of the vinyl group. Because we assume that the interaction of the hydrogen is primarily with one lobe of the 2p$_\pi$ orbital on the carbons of the vinyl group, we also computed the angle between the H···C direction and the symmetry axis of the 2p$_\pi$ orbital. The results are summarized in Table 6.

We see that the shortest interaction distance is predicted to be for CMG, for which the H···C$_2$ distance is 251 pm. This is a "bent" hydrogen bond interaction, the OH vector being at an angle of about 21° with the axis of the 2p$_\pi$ orbital. Such intramolecular nonlinear interactions are common because necessarily the bonding in the remainder of the molecule often restricts the alignment of the internal hydrogen bond. For comparison, the internal hydrogen bond between the carboxyl OH and the amino N is computed to have an H···N distance of 188 pm in glycine and 189 pm in alanine.[6]

When the bonding is not restrained geometrically by intramolecular limitations, much shorter hydrogen bonds are frequently encountered. Cleland and Krevoy for example[20] proposed that short hydrogen bonds with an O···O distance around 250 pm [for comparison, weak unconstrained hydrogen have an O···O distance of 280−300 pm] play a central role in enzymic catalysis. In the present case the corresponding interaction is O···C(π). Because of the bent geometry, this distance is, at 298 pm, shorter than might be anticipated from the H···C(π) distance. We have little data for comparison, but we judge this interaction to be similar to that in phenylethylamine where the N···C distance in the bent intramolecular hydrogen bond is computed to be 295 pm[5b] and the corresponding closest interaction in β-vinylethylamine is computed to have a N···C distance of 299 pm.[21]

For weak intermolecular interactions the hydrogen bond lengths are often found to be longer. For example, in the complex between water and ethylene the R_{cm} is reported[9a] to be about 340 pm. The spectroscopic results were interpreted to imply that one H of the water molecule is bonded to the center of the ethylenic linkage, but it might as well be thought of as being bonded to both 2p$_\pi$ lobes of the two C atoms. In the case of the benzene···ammonia intermolecular hydrogen bond, the distance from the nitrogen atom to the benzene plane also was found to be relatively large at 359 pm.[9c]

It seems that intramolecular hydrogen bonds play an important role in determining which conformer is of greatest stability in those small molecules in which rotations about a disubstituted ethane linkage has to be considered. Presumably a fuller knowledge of these interactions will help in understanding the shapes of larger molecules, including many of biological importance.

Conclusion

We have detected via microwave spectroscopy and rotationally assigned the spectrum of a second conformer of vinylethanol. Through comparison of measured and ab initio predicted theoretical rotational constants, deuterium substitution coordinates, and dipole moment components, we have shown that the new conformer is the extended form CAA. A similar comparison of the measured and ab initio predicted data for the most stable conformer earlier detected and assigned by Marstokk and Møllendal confirms their conclusion that this is a gauche conformer, specifically CMG, which is stabilized by an intramolecular hydrogen bond from the OH hydrogen to the π-bond charge cloud.

The observed absence in the jet-expanded microwave spectrum of the conformers CAM, CAG, CMM, and CMA, despite their being predicted on the basis of ab initio energies to be significantly populated at the preexpansion temperature, is due to their conformational relaxation to the detected forms CAA and CGM. This process is a predictable consequence of the low interconversion energy barriers given by the ab initio calculations.

At a more general level this study supports the view that ab initio calculations at the MP2/6-311++G(d,p) level provide adequately reliable structural and energetic predictions for conformers of organic molecules.

Acknowledgment. The research was supported by a grant from the Australian Research Council.

Supporting Information Available: This collection of Tables 1S − 6S contains all the measured and assigned microwave transition frequencies used to derive the rotational constants reported in this work, all the measured and assigned Stark shifts used to derive the dipole moment components reported in this work, and the complete ab initio optimized geometries for each structural form of vinylethanol. This material is available free of charge via the Internet at http://pubs.acs.org.

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