Structural and Conformational Properties and Intramolecular Hydrogen Bonding of (Methylenecyclopropyl)methanol, As Studied by Microwave Spectroscopy and Quantum Chemical Calculations

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The microwave spectra of (methylenecyclopropyl)methanol ($H_2C=C_3H_3CH_2OH$) and one deuterated species ($H_2C=C_3H_3CH_2OD$) have been investigated in the 20−80 GHz spectral range. Accurate spectral measurements have been performed in the 40−80 GHz spectral interval. The spectra of two rotameric forms, denoted conformer I and conformer IX, have been assigned. Both these rotamers are stabilized by intramolecular hydrogen bonds formed between the hydrogen atom of the hydroxyl group and the pseudo-π electrons on the outside of the cyclopropyl ring, the so-called "banana bonds". The carbon−carbon bond lengths in the ring are rather different. The bonds adjacent to the methylene group ($H_2C=$) are approximately 7 pm shorter that the carbon−carbon bond opposite to this group. It is found from relative intensity measurements of microwave transitions that conformer IX, in which the hydrogen bond is formed with the banana bonds of the *long* carbon−carbon bond, is 0.4(3) kJ/mol *more* stable than conformer I, where the hydrogen bond is formed with the pseudo-π electrons belonging to the *shortest* carbon−carbon bond of the ring. The microwave study has been augmented by quantum chemical calculations at the MP2/6-311++G**, G3 and B3LYP/6-311++G** levels of theory.

Introduction

The laboratory in Oslo has had a long-standing interest in the way intramolecular hydrogen (H) bonding influences the structural and conformational properties of free molecules. Recent examples of studies undertaken in this laboratory are 2-chloroacetamide ($CH_2ClCONH_2$),[1] cyclopropylmethylselenol ($C_3H_5CH_2SeH$),[2] cyclopentadienylphosphine ($C_5H_5PH_2$),[3] 1,1,1-trifluoro-2-propanol $CF_3CH(OH)CH_3$,[4] cyclopropylmethylphosphine ($C_3H_5CH_2PH_2$),[5] 1-fluorocyclopropanecarboxylic acid (C_3H_4FCOOH),[6] 3-buteneselenol ($H_2C=CHCH_2CH_2SeH$),[7] (1-fluorocyclopropyl)methanol ($C_3H_4FCH_2OH$)[8] and 2-bicyclopropylidenylmethanol ($C_3H_4=C_3H_3CH_2OH$).[9] Further studies of intramolecular H bonding have been summarized in a number of reviews.[10−15]

Infrared (IR) spectroscopic studies starting in the sixties[16,17] showed that the Walsh pseudo-π electrons[18] along the outside of the edges of the cyclopropyl ring (the banana bonds) can act as proton acceptors for intramolecular H bonds in alcohols. Subsequent microwave (MW) spectroscopic studies of a series of cyclopropylmethanols, for example, cyclopropylmethanol ($C_3H_5CH_2OH$),[19−21] 1-cyclopropylethanol ($C_3H_5CH(OH)CH_3$),[22] *trans*-2-methylcyclopropylmethanol ($CH_3C_3H_4CH_2OH$),[23] dicyclopropyl carbinol ($C_3H_5CH(OH)C_3H_5$),[24] 2-cyclopropylethanol ($C_3H_5CH_2CH_2OH$)[25] and 2-bicyclopropylidenylmethanol ($C_3H_4=C_3H_3CH_2OH$),[9] confirmed the classical IR findings.[16,17] The preferred conformers in all these compounds are stabilized

by intramolecular H bonds formed between the H atom of the hydroxyl group and the banana bonds.

The H bonding interaction between the hydroxyl group and the pseudo-π electrons in cyclopropylmethanols is definitely not strong. For example, in the case of (1-fluorocyclopropyl)-methanol ($C_3H_4FCH_2OH$),[8] where it is possible for the hydroxyl group to form an internal H bond with either the pseudo-π electrons or alternatively with the fluorine atom; the molecule prefers the latter option. In fact, the F···H−O internal H bond turned out to be several kJ/mol stronger than the alternative H bond formed between the hydroxyl group and one of the banana bonds, as shown in a combined microwave and quantum chemical study.[8]

This last example shows that atoms or groups attached to the cyclopropyl ring may have a decisive effect on the conformational composition of cyclopropylmethanols. The influence that a methylene ($H_2C=$) group attached to the cyclopropyl ring can have on the conformational preferences of a methanol substituent has not been investigated previously. The substitution (r_s) structure[26] of methylenecyclopropane ($H_2C=C_3H_4$)[27] shows that attachment of a methylene group to the cyclopropyl ring leads to a considerable distortion of the ring. The CC bond adjacent to the methylene group is 145.70-(14) pm, almost 8.5 pm shorter than the CC bond opposite to the methylene group, which is 154.15(3) pm.[27] In cyclopropane, the equilibrium (r_e) CC bond length is 150.1(4) pm.[28] A central point of this investigation has therefore been to determine the extent to which this remarkable distortion might influence the relative populations of the various conformers of (methylenecyclopropyl)methanol ($H_2C=C_3H_3CH_2OH$), which will be called MCPM for brevity.

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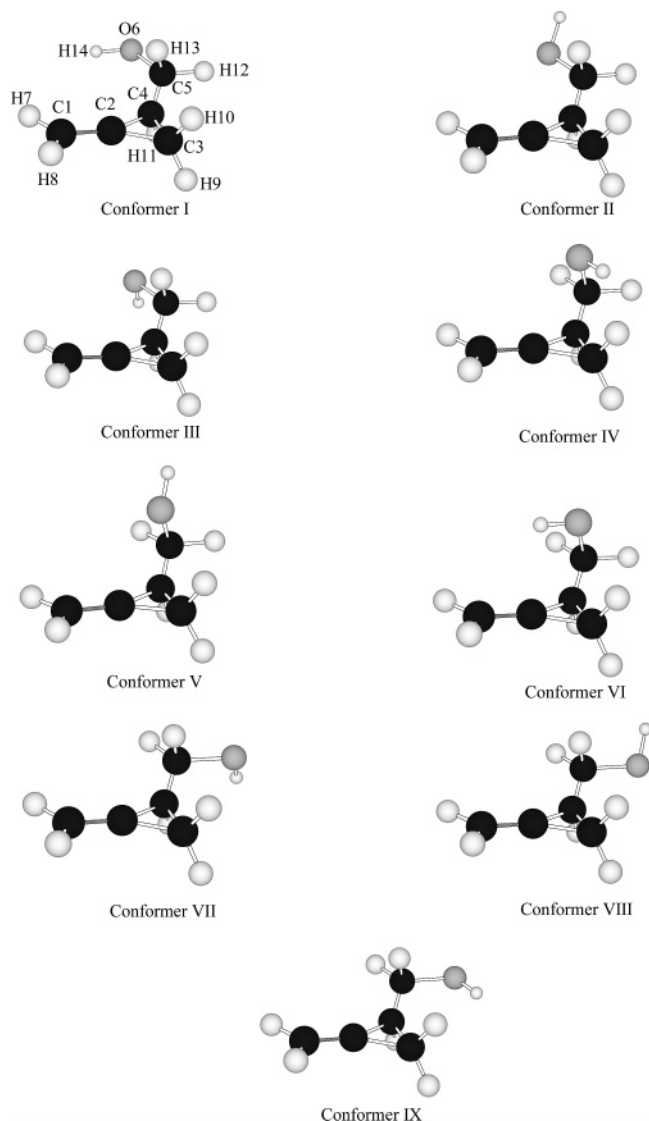‡ Institut für Organische und Biomolekulare Chemie der Georg-August-Universität Göttingen.

Figure 1. Nine rotameric forms of (methylenecyclopropyl)methanol. The atom numbering is shown for conformer I. This rotamer, as well as conformer IX, were assigned in this work and IX was found experimentally to be 0.4(3) kJ/mol more stable than conformer I.

A model of MCPM with atom numbering is shown in Figure 1. Rotation about its C4C5 and C5O6 bonds leads to nine possible rotameric forms denoted conformers I–IX. These conformers are sketched in the same figure. The two dihedral angles formed by the C2C4C5O6 and C4C5O6H14 chains of atoms may be used to characterize the conformations of the rotamers. In conformers I–III, the C2C4C5O6 dihedral angle is about −80° from the *synperiplanar* (0°) position. This dihedral angle is +30° in IV–VI and +80° in VII–IX, respectively. The C4C5O6H14 dihedral angle is roughly 60° from the *synperiplanar* position in I, IV and VII. Rotation about the C5O6 bond by 120 or 240° produces the remaining six conformers. The H14 atom, which may be involved in intramolecular H bonding, is closest to the pseudo-π electrons of the ring in conformers I, VI and IX. In rotamers I and IX, the H14 atom approaches the banana bonds from the outside of the ring, whereas an approach from the inside occurs in VI.

In this contribution, the conformational problem presented by MCPM is investigated by microwave (MW) spectroscopy and quantum chemical calculations. The reason for applying these two methods of study is that MW spectroscopy is an ideal experimental method to investigate conformational equilibria,

because of its superior accuracy and resolution, whereas quantum chemical calculations have been performed because they are a useful aid in the assignment procedure of complex MW spectra. These computations also predict fairly reliable molecular properties that are not available from the experiments.

Experimental Procedures

(Methylenecylopropyl)methanol was prepared by acid-catalyzed cleavage of its tetrahydropyranyl ether[29−31] and purified by distillation. The deuterated species, $H_2C=C_3H_3CH_2-OD$, was produced in the MW cell by admitting small quantities of heavy water together with the parent species. A rapid exchange of the hydrogen atom of the hydroxyl group with deuterium was observed. An estimated 50% deuteration was achieved in this way.

The spectra of the parent and deuterated species were studied using the Oslo Stark-modulated spectrometer, which has been described elsewhere.[3,6] Measurements were made in the 20−80 GHz spectral region. Measurements of individual MW transitions were made in the 40−80 GHz interval. Radio frequency microwave double resonance (RFMWDR) experiments were carried out as described by Wodarzcyk and Wilson[32] using the equipment mentioned previously.[6,33] The MW cell was cooled to about −15 °C during the experiments and the pressure was about 10 Pa. The spectrum was comparatively weak and the accuracy of the frequency measurements is estimated to be of the order of ±0.15 MHz or better. A study of the spectrum at lower temperatures would have increased its intensity, but such experiments could not be performed, owing to the low vapor pressure of the compound.

Results and Discussion

Quantum Chemical Calculations. The Gaussian 03 program package[34] running on the HP Superdome in Oslo was employed in the quantum chemical calculations. Ab initio and density functional theory (DFT) calculations were performed.

Møller−Plesset second-order perturbation calculations (MP2)[35] using a comparatively large basis set (6-311++G**) were made for two reasons: First, useful approximations of equilibrium distances are predicted this way.[36] Second, there are generally relatively small differences between the approximate equilibrium constants obtained this way and the effective ground-state rotational constants obtained from the MW spectra. The MP2 rotational constants are therefore helpful starting points in the assignment procedure of a complicated MW spectrum, such as that expected for the title compound.

The structures of the nine conformers shown in Figure 1 were fully optimized and the vibrational frequencies were also calculated for each of them in the MP2/6-311++G** calculations. Only positive values were found for the vibrational frequencies, indicating that the nine rotamers are indeed minima on the potential energy hypersurface,[37] and they are therefore "stable conformers".

It is shown below that the spectra of conformers I and IX were assigned. The MP2/6-311++G** structures of these two rotamers are listed in Table 1. The structures of all nine conformers are given in Table 1S in the Supporting Information. The rotational constants of all nine forms, the components of the dipole moment along the principal inertial axes, and the relative energies are listed in Table 2.

The G3 method is renowned for accurate predictions of energy differences.[38] This method was employed to predict the energy differences between rotamers I, VI and IX, because these three rotamers have the lowest energies according to the MP2

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TABLE 1: MP2/6-311++G Structures of Conformer I and Conformer IX of (Methylenecyclopropyl)methanol**

	conformer	
	I	IX
Bond Distance (pm)		
C1−C2	133.1	133.0
C1−H7	108.7	108.6
C1−H8	108.6	108.6
C2−C3	147.I	147.1
C2−C4	147.0	146.8
C3−C4	154.6	155.2
C3−H9	108.6	108.6
C3−H10	108.8	108.9
C4−C5	151.0	150.8
C4−H11	108.8	108.9
C5−O6	142.4	142.5
C5−H12	109.3	110.0
C5−H13	109.9	109.3
O6−H14	96.3	96.2
Angle (deg)		
C2−C1−H7	121.1	120.9
C2−C1−H8	121.0	120.9
H7−C1−H8	117.9	118.2
C1−C2−C3	148.3	148.1
C1−C2−C4	148.3	148.1
C2−C3−H9	118.4	118.7
C2−C3−H10	118.6	118.1
C4−C3−H9	117.4	117.5
C4−C3−H10	117.0	117.1
H9−C3−H10	115.3	115.4
C2−C4−C5	118.4	119.8
C2−C4−H11	117.6	117.9
C3−C4−C5	118.3	117.9
C3−C4−H11	116.6	115.8
C5−C4−H11	115.6	115.3
C4−C5−O6	112.2	112.1
C4−C5−H12	110.6	108.9
C4−C5−H13	108.8	110.6
O6−C5−H12	105.8	111.2
O6−C5−H13	110.9	105.7
H12−C5−H13	108.4	108.2
C5−O6−H14	106.2	106.3
Dihedral Angle (deg)		
H7−C1−C2−C3	−178.8	178.9
H7−C1−C2−C4	2.5	2.3
H8−C1−C2−C3	0.4	−1.5
H8−C1−C2−C4	−178.3	−178.1
C1−C2−C3−H9	74.5	75.8
C1−C2−C3−H10	−73.5	−72.06
C1−C2−C4−C5	71.8	71.8
C1−C2−C4−H11	−75.1	−77.5
H9−C3−C4−C5	−144.4	−142.2
H9−C3−C4−H11	0.5	0.1
H10−C3−C4−C5	−0.9	1.8
H10−C3−C4−H11	144.0	144.1
C2−C4−C5−O6	−80.8	150.7
C2−C4−C5−H12	161.3	27.2
C2−C4−C5−H13	42.3	−91.5
C3−C4−C5−O6	−148.1	83.3
C3−C4−C5−H12	94.1	−40.2
C3−C4−C5−H13	−24.9	−159.0
H11−C4−C5−O6	66.7	−59.2
H11−C4−C5−H12	−51.1	177.3
H11−C4−C5−H13	−170.2	58.5
C4−C5−O6−H14	57.5	−52.3
H12−C5−C6−H14	178.2	69.8
H13−C5−O6−H14	−64.4	−173.0

TABLE 2: MP2/6-311++G Rotational Constants (MHz), Dipole Moments (Debye) and Energy Differences (kJ/mol)[a] for (Methylenecyclopropyl)methanol**

	rotational constants			dipole moments			energies
conformer	A	B	C	μ_a	μ_b	μ_c	ΔE
I	5878.7	2692.5	2006.1	1.78	0.70	0.47	+0.2
II	5936.0	2678.0	2008.9	0.83	1.52	1.14	+4.1
III	5930.5	2627.7	1988.4	0.38	1.68	1.20	+4.9
IV	5942.7	2607.5	2330.0	0.17	1.97	0.52	+10.8
V	5992.9	2666.7	2383.4	1.68	0.05	1.27	+8.8
VI	5745.6	2791.3	2395.0	1.06	0.32	1.32	+1.6
VII	8967.4	2079.2	1832.2	0.83	0.26	1.52	+3.4
VIII	9089.7	2094.2	1838.0	0.13	1.40	0.69	+2.9
IX	9018.5	2084.6	1827.3	1.54	0.96	0.39	0.0

[a] Energies have been corrected for zero-point vibrational effect and are relative to conformer IX, whose absolute MP2 energy corrected for ZPE is −707977.47 kJ/mol.

basis set in a B3LYP calculation,[39,40] because this DFT procedure is much faster than the MP2 method. The results obtained in the B3LYP computations are compared with the experimental findings in the text below.

The MP2 structures in Table 1 and Table 1S reveal several interesting features, some of which warrant further discussion. As expected, the structure of the methylenecyclopropyl moiety of the nine conformers is calculated to be close the substitution (r_s) structure[26] of methylenecylopropane ($H_2C=C_3H_4$).[27] The C1C2 bond length is about 133 pm in all nine forms, close the to r_s bond length of 133.17(14) pm determined for the CC distance in the methylene group in methylenecyclopropane.[27] The C2C3 and C2C4 bond lengths of MCPM are both about 147 pm, whereas 145.70(14) pm was found for the corresponding bond length in methylenecyclopropane.[27] The C3C4 bond lengths of MCPM conformers are approximately 154 pm compared to 154.15(3) in methylenecyclopropane.[27]

It was mentioned above that the MP2 and G3 calculations both predict that rotamers I and IX have practically the same energy, with IX being the slightly more stable. Interestingly, the H14 atom in these rotamers approaches the banana bonds from the *outside* of the ring, where the maximum electron density is presumed to reside.[18] The two forms may therefore be stabilized by a weak internal H bond. Support for this assumption is found in the nonbonded distances between H14 and C4 (256 pm) and C2 (289 pm), respectively, in conformer I, as calculated from the structure in Table 1. The corresponding values in IX are similar, being 252 pm between H14 and C4, and 292 pm between H14 and C3. The nonbonded interatomic distances should be compared to the sum of the van der Waals radii[41] of hydrogen (120 pm) and aromatic carbon (170 pm), which is therefore 290 pm.

According to both the MP2 and in the G3 methods, conformer VI is calculated to be about 1.5 kJ/mol less stable than both I and IX. The H14 atom is about 254 pm away from C2 and 258 pm away from C4 in this form. However, the H14 atom approaches the pseudo-π electrons from the *inside* of the ring in VI where the electron density is comparatively low,[18] and this unfavorable approach presumably makes the interaction weaker than in the case of I and IX, where this approach takes place from the electron-rich outside.

The remaining conformers are all predicted to have higher energies than I, VI or IX and will consequently have a low population in the MW spectrum. No MW spectra attributable to these species were observed, therefore they are not considered further.

Microwave Spectrum and Assignment of Conformer I. The MP2 calculations above indicate that all nine rotamers have

calculations (Table 2). The G3 method predicts that I and IX have the same energy, whereas conformer VI was predicted to be 1.3 kJ/mol less stable than both I and IX. These results are almost the same as those predicted in the MP2 calculations.

Accurate estimates of the centrifugal distortion constants and the vibration−rotation constants are also useful for the assignment of MW spectra. Calculations of the centrifugal distortion and the vibration−rotation constants are rather computationally expensive and were therefore performed using the 6-311++G**

Microwave Spectrum of (Methylenecyclopropyl)methanol

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TABLE 3: Spectroscopic Constants[a] of the Ground and Vibrationally Excited States of Conformer I of CH$_2$=C$_3$H$_3$CH$_2$OH and of the Ground Vibrational State of CH$_2$=C$_3$H$_3$CH$_2$OD

	species			
	CH$_2$=C$_3$H$_3$CH$_2$OH			CH$_2$=C$_3$H$_3$CH$_2$OD
	ground vib state	torsion[b] vib state	bending[c] vib.= state	ground vib state
A (MHz)	5900.585(18)	5896.4[d]	5893.9[d]	5759.85(27)
B (MHz)	2693.7322(77)	2693.640(44)	2692.415(67)	2662.896(17)
C (MHz)	2008.1999(80)	2009.626(59)	2010.575(94)	1975.202(18)
Δ_J (kHz)	2.377(11)	2.246(17)	2.201(24)	2.4534(57)
Δ_{JK} (kHz)	−9.765(57)	−9.394(55)	−9.15(10)	−9.602(13)
Δ_K (kHz)	16.350(98)	16.350[d]	16.350[d]	16.350[d]
δ_J (kHz)	0.8764(92)	0.8764[d]	0.8764[d]	0.8764[d]
δ_K (kHz)	2.64(20)	2.64[d]	2.64[d]	2.64[d]
rms[e] (MHz)	0.171	0.154	0.186	0.131
no. of transitions	104	45	37	100

[a] A-reduction I[r]-representation.[42] Uncertainties represent one standard deviation. [b] Lowest torsional mode. [c] Lowest bending mode. [d] Fixed. [e] Root-mean-square deviation.

5 normal modes with frequencies lower than 550 cm^{-1} (not given in Tables 1 or 2). Moreover, the predicted rotational constants vary from about 1.8 to 9.1 GHz (Table 2). This indicates that each rotamer of MCPM must have both a comparatively large vibrational and a large rotational partition functions at −15 °C and consequently a low population of each quantum state, which should result in a relatively weak MW spectrum. This was indeed observed. The spectrum is also rich, with absorption lines occurring every few megahertz throughout the MW region.

Conformer I was searched for first because the MP2 and G3 calculations described above indicate that this form should have the lowest energy of all conformers. This rotamer is predicted to have its major component of the dipole moment of approximately 1.8 D along the a-inertial axis (Table 2). This means that the R-branch a-type high-K_{-1} transitions are modulated at low voltages. The approximate frequencies of these transitions were predicted using the rotational constants shown in Table 2. A search for them using a Stark modulation voltage of about 45 V/cm readily resulted in their assignments. Further [a]R lines were then gradually included in the least-squares fit. The assignments of several of these lines were also confirmed using the RFMWDR technique.[32]

Unfortunately, it was not possible to determine the dipole moment of this conformer, as the low-J transitions normally used for this purpose were too weak to allow quantitative measurements to be made. However, the b-type lines should be much weaker than the a-type lines, because μ_b is ≈0.7 D (Table 2). This was found experimentally and only a few b-type Q-branch lines were assigned, owing to their comparatively low intensities. The value predicted for μ_c is ≈0.4 D. Searches for c-type lines were made, but these transitions were not found presumably because they are too weak.

A total of 104 transitions (88 a-type and 16 b-type) were used to determine the spectroscopic constants (A-reduction I[r]-representation[42]), which are listed in Table 3. The full spectrum is shown in Table 2S in the Supporting Information.

Comparison of the MP2 rotational constants in Table 2 with the experimental rotational constants shows that they agree to within better than 0.4% in each case. This is another indication that the MP2 structure of conformer I is close to the equilibrium structure, as expected.[36]

The B3LYP centrifugal distortion constants were calculated to be Δ_J = 1.99, Δ_{JK} = −9.22, Δ_K = 17.3, δ_J = 0.690 and

δ_K = 2.09 kHz. The differences between the experimental (Table 3) and the B3LYP values of the centrifugal distortion constants are +16.3, −5.9, −5.8, +21.3 and +20.8%, respectively, for this sequence.

Vibrationally Excited States of Conformer I. Several series of lines with the same Stark patterns as the ground-state transitions, but with lower intensities, were seen to accompany the ground-state lines. The two most intense of these series were assigned as the first excited states of the lowest torsional mode (about the C4C5 bond) and the lowest bending vibration, respectively, as shown in Table 3. Their spectra are listed in Tables 3S and 4S in the Supporting Information. Only a-type lines were assigned for these excited states and accurate values cannot therefore be determined for Δ_K, δ_j and δ_K, which were therefore held fixed in the least-squares fit at the values obtained for the ground state. The A rotational constant was also kept fixed in the fit. Its value was estimated from $\alpha_A = A_0 - A_X$, where α_A is the vibration−rotation constant,[43] A_0 refers to the rotational constant in the ground vibrational state and A_X to its value in an excited state. The B3LYP values for the vibration−rotation constant (α_A) are 4.25 MHz for the torsional mode and 6.67 MHz for the bending vibration.

The vibration−rotation constants referring to the B and C rotational constants, α_B and α_C, are defined in a manner analogous to α_A. The values obtained from the entries in Table 3 for the torsional vibration are α_B = 0.0922(45) MHz and α_C = −1.606(60) MHz, compared to −1.29 and −0.32 MHz, respectively, obtained in the B3LYP calculations. The experimental counterparts for the bending vibration are 1.317(68) and −2.376(95) MHz, respectively, compared to the B3LYP results, which are −1.64 and −0.35 MHz, respectively. The agreement between experiment and theory is therefore poor in this case.

Relative intensity measurements, performed as described by Esbitt and Wilson,[44] yielded 95(20) cm^{-1} for the torsional vibration and 138(25) cm^{-1} for the bending fundamental frequency. The uncorrected MP2 values for these vibrations are 88 and 154 cm^{-1}. The B3LYP calculations yielded uncorrected frequencies of 87 and 150 cm^{-1}, respectively.

Deuterated Species of Conformer I. It is seen in Table 2 that the rotational constants alone cannot be used to discriminate among conformers I−III, because they are so similar. The fact that conformer I is the only rotamer of these three that has a major μ_a is one indication that the rotational constants in Table 3 can be attributed to this form, because this conformer has its major dipole moment along the a-axis. The deuterated species, H$_2$C=C$_3$H$_3$CH$_2$OD, was investigated because it is possible to calculate the substitution coordinates of the hydrogen atom of the hydroxyl group (H14) using the principal moments of inertia of this species together with those of the parent species in Kraitchman's equations.[45] This is a direct way of showing which conformer that has been assigned.

The assignment of the deuterated species was straightforward. Only a-type transitions were assigned in this case; the spectroscopic constants are listed in Table 3 and the spectrum (100 transitions) is shown in Table 5S in the Supporting Information. The Δ_K, δ_J and δ_K centrifugal distortion constants were held constant at the values found for the parent species in the least-squares fit, because only a-type lines were assigned.

The substitution coordinates[26] of the hydrogen atom of the hydroxyl group were calculated to be |a| = 145.2(8), |b| = 145.4(8) and |c| = 18.6(65) pm. The uncertainties of these coordinates have been calculated as recommended by Costain.[46] The corresponding coordinates obtained from the structure of conformer I in Table 1 are 147.5, 143.6 and 0.133 pm,
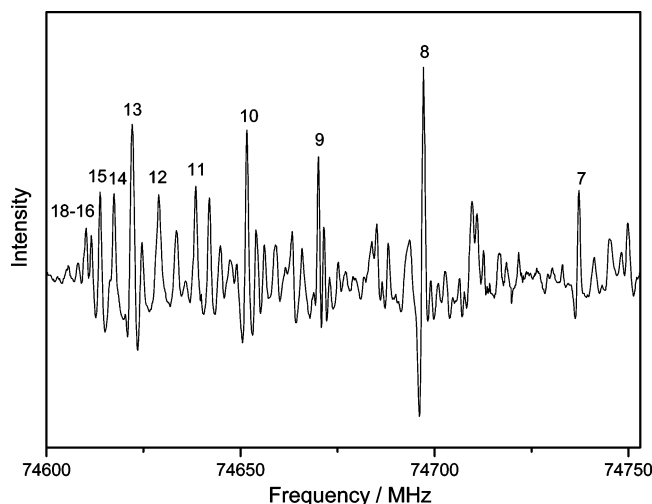
Figure 2. High-K_{-1} a-type $J = 19 \leftarrow 18$ transitions. The values of the pseudo quantum number K_{-1} are indicated above each coalescing line pair. This spectrum was taken using a Stark-modulation voltage of about 45 V/cm.

TABLE 4: Spectroscopic Constants^a of the Ground Vibrational State of Conformer IX of $CH_2=C_3H_3CH_2OH$ and $CH_2=C_3H_3CH_2OD$

	species	
	$CH_2=C_3H_3CH_2OH$	$CH_2=C_3H_3CH_2OD$
A (MHz)	8937.3(35)	8850.0(19)
B (MHz)	2091.567(37)	2044.343(19)
C (MHz)	1832.067(39)	1791.464(20)
Δ_J (kHz)	0.4088(28)	0.3947(27)
Δ_{JK} (kHz)	−1.9185(89)	−1.9128(91)
Δ_K (kHz)	27.0^b	27.0^b
δ_J (kHz)	0.0540^b	0.0540^b
δ_K (kHz)	1.01^b	1.01^b
rms^c (MHz)	0.157	0.128
no. of transitions	143	114

^{a} A-reduction I^r-representation.[42] Uncertainties represent one standard deviation. ^{b} Fixed. ^{c} Root-mean-square deviation.

respectively, whereas those obtained for rotamers II and III differ greatly from these values, which is taken as evidence that the spectra in Tables 2S−5S do indeed belong to conformer I and have not been confused with any other rotameric form.

Assignment of Conformer IX. This rotamer is predicted to have the major component of its dipole moment along the a-axis (Table 2). At low Stark-modulation voltages, its MW spectrum is dominated by series of a-type $J + 1 \leftarrow J$ transitions for the highest values of the K_{-1} pseudo quantum number. The $J = 19 \leftarrow 18$ series of lines shown in Figure 2 is typical. The assignment of its a-type spectrum was made in the same manner as described above for conformer I. Transitions with $K_{-1} < 3$ were difficult to modulate, and their assignments were uncertain. These transitions were therefore omitted in the final fit shown in Table 6S in the Supporting Information, which contains transitions with $K_{-1} \geq 3$ only. Searches were also made for b- or c-type lines, but no definite assignments could be made, presumably because of the low intensity of the spectrum. A total of about 150 transitions were assigned; 143 of these were used to determine the spectroscopic constants appearing in Table 4.

The differences between the experimental ground-state rotational constants (Table 4) and the MP2 rotational constants (Table 2) are less than 1% in each case, which is an indication that the MP2 structure is close to the equilibrium structure, as pointed out by Helgaker et al.[36]

The centrifugal distortion constants Δ_J and Δ_{JK} were adjusted in the least-squares fit, whereas Δ_K, δ_J and δ_K were kept at the B3LYP values. The B3LYP values of Δ_J and Δ_{JK} are +0.356 and −1.45 kHz, respectively, which represents a fair agreement with the experimental values shown in Table 4.

No vibrationally excited states could be assigned in this case, presumably because of frequent overlaps with the ground-state transitions.

The deuterated species, $H_2C=C_3H_3CH_2OD$, was assigned in a straightforward manner. Its MW spectrum is displayed in Table 7S, whereas the spectroscopic constants are listed in Table 4. The substitution coordinates[26] with Costain uncertainties[46] are $|a| = 237.7(5)$, $|b| = 79.8(15)$ and $|c| = 24.3(49)$ pm for the hydrogen atom of the hydroxyl group (H14). The structure in Table 1 yields 231.5, 81.5 and 30.4 pm, respectively, for these coordinates, which are therefore in good agreement with the substitution coordinates.

Searches for Further Conformers. Searches were carried out for additional rotamers using the rotational constants and dipole moment predictions in Table 2 as the starting points. These searches were first concentrated on conformer VI, which was predicted above to be approximately 1.5 kJ/mol less stable than I, or IX. Both ordinary Stark spectroscopy and the RFMWDR technique were employed, but no assignments could be made for this, or any of the other high-energy rotamers. Interestingly, conformers similar to IX have not been found experimentally for any of the cyclopropylmethanols studied previously.[9,19−24] It is concluded that most of the gas is composed of conformers I and IX, but the presence of additional forms in relatively small concentrations cannot be ruled out.

Energy Difference. The internal energy difference between conformers I and IX has been derived using a variant of eq 3 of Esbitt and Wilson.[44] According to Wilson,[47] the internal energy difference is given by

$$E_v - E'_{v'} = E'_{J'} - E_J + RT \ln L \qquad (1)$$

where E_v and $E'_{v'}$ are the internal energies of the two conformers in the v and v' vibrational states, respectively, $E'_{J'}$ and E_J are the lowest energy levels of the two rotational transitions under investigation, R is the universal gas constant and T is the absolute temperature. L is given by

$$L = \frac{S'}{S''} \frac{g''}{g'} \left(\frac{v''\mu''}{v'\mu'}\right)^2 \frac{l''}{l'} \frac{\Delta v'}{\Delta v''} \frac{\lambda''}{\lambda'} \frac{(2J'+1)}{(2J''+1)} \qquad (2)$$

where S is the peak signal amplitude of the radiation-unsaturated line, g is the degeneracy other than the rotational degeneracy, which is $2J + l$. v is the frequency of the transition, μ is the principal-axis dipole moment component, l is the radiation wavelength in the Stark cell,[48] Δv is the line breadth at half-height, λ is the line strength, and J is the principal rotational quantum number.

The internal energy difference between the ground vibrational states of conformers I and IX were determined by comparing the intensities of four selected ground-state transitions. The lines employed in this comparison procedure were relatively strong a-type transitions and not detectably overlapped by other lines. The statistical weights (g) were assumed to be 1 for both rotamers. The dipole moment components of the two forms were those predicted in the MP2 calculations (Table 2).

The internal energy difference, $E_I - E_{IX}$, obtained this in way varied between 0.6 and 0.3 kJ/mol (conformer IX *more* stable than I). The average value was found to be $E_I - E_{IX} = 0.4$ kJ/mol. There are several sources of errors in this procedure.

One standard deviation has been conservatively estimated to be ±0.3 kJ/mol by evaluating the uncertainties associated with the many parameters of eq 2.

Conclusions

The MW spectra of two rotameric forms, denoted conformers I and IX, of (methylenecyclopropyl)methanol have been assigned. Both these forms are stabilized by intramolecular H bonds formed with the banana bonds of the cyclopropyl group. Relative intensity measurements suggest that conformer IX is more stable than conformer I by 0.4(3) kJ/mol.

There are relatively large differences in the CC bond lengths of the cyclopropyl ring. The bond lengths of the two CC bonds adjacent to methylene ($H_2C=$) is about 147 pm, whereas the $C-C$ bond opposite to the methylene group is approximately 7 pm longer. However, the geometries of the two H bonds characterized by the nonbonded distances between H14 and the carbon atoms of the ring are similar, as remarked above.

Perhaps the most interesting finding in this work is that conformer IX, in which the H bond is formed with the pseudo-π electrons residing on the outside of the long (154 pm) C3C4 bond, tends to be slightly more *stable* (by 0.4(3) kJ/mol) than conformer I, in which the H bond is formed with the short (147 pm) C2C4 banana bond. The bonding conditions in the methylenecyclopropyl moiety are obviously strained and this unusual situation seems to result in a proton affinity of the pseudo-π electrons that is slightly higher for the long C2C4 bond than for the short C2C3 bond.

Supporting Information Available: Tables showing the MP2 geometries of the nine conformers shown in Figure 1 and the MW spectra of conformer I and conformer IX are available free of charge via the Internet at http://pubs.acs.org.

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