Microwave Spectrum, Conformation and Intramolecular Hydrogen Bonding of 1-Cyclopropylethanol

K.-M. MARSTOKK and HARALD MØLLENDAL

Department of Chemistry, The University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo 3, Norway

The microwave spectrum of 1-cyclopropylethanol, $CH_2CH_2CHCH(OH)CH_3$, and one deuterated species, $CH_2CH_2CHCH(OD)CH_3$, has been investigated in the 26.5—38.0 GHz spectral region at about −20 °C. Only one conformation was assigned and shown to be at least 4 kJ/mol more stable than any other possible rotamer. The identified conformation has a weak intramolecular hydrogen bond formed between the hydroxyl group hydrogen atom and the pseudo-π electrons of the cyclopropane ring. Four vibrationally excited states belonging to three different normal modes were assigned and their vibrational frequencies determined by relative intensity measurements.

Infrared spectroscopic studies from the late sixties [1,2] have shown that the cyclopropane ring can function as a weak proton acceptor in intramolecular hydrogen bonds where the hydroxyl group acts as proton donor. The simplest example for which this interaction is possible, is (hydroxymethyl)cyclopropane. This molecule has been studied by microwave spectroscopy.[3] Only one conformation, the predominating one, was assigned. This rotamer is the *gauche* conformation which possesses an intramolecular hydrogen bond formed between the hydroxyl group hydrogen atom and the pseudo π-electrons which have maximum electron density along the edges of the cyclopropyl ring. The existence of further rotameric forms of (hydroxymethyl)cyclopropane has not been ruled out.[3,4] Wurrey and coworkers [5] are now making new attempts to elucidate its complete conformational makeup and determine enthalpy differences between the various forms.

It is also noted that (aminomethyl)cyclopropane behaves very similar to (hydroxymethyl)-cyclopropane, as shown recently in a microwave study.[6]

1-Cyclopropylethanol was chosen for investigation in order to extend the study of intramolecular hydrogen bonding involving the cyclopropane ring. Infrared studies [1,2,4] have shown that an internal hydrogen bond exists in this molecule, but its conformational properties were not established.

Three heavy-atom orientations are possible for the title compound, as shown in Fig. 1. In addition, three different, staggered orientations of the hydroxyl group are conceivable for each of the three conformations of this figure, so that a total of nine rotameric forms are possible for 1-cyclopropylethanol.

Intramolecular hydrogen bonding between the hydroxyl group hydrogen atom and the pseudo-π electrons of the ring is presumed to be best for one of the conformations of each of
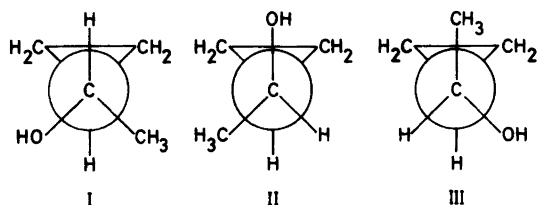
Fig. 1. Possible rotameric forms of 1-cyclopropylethanol produced by rotation about the $C_{ring}-CH(OH)CH_3$ bond. Three staggered conformations about the $C-O$ bond is possible for each of *I, II* and *III*. Conformation *I* with an intramolecular hydrogen bond was found to be at least 4 kJ/mol more stable than any further conformation.

I and *III*, because the $O-H$ bond is closer to the edge in these two cases than it would have been for the two possible hydrogen-bonded forms of *II*. Investigation of 1-cyclopropylethanol may thus provide information about which forces decide the conformational behaviour of this and related molecules.

It is found in this work that a conformation similar to *I* possessing an intramolecular hydrogen bond predominates, and is at least 4 kJ/mol more stable than any further form of the molecule.

EXPERIMENTAL

1-Cyclopropylethanol was purchased from Fluka AG, Buchs, Switzerland and purified by gas chromatography before use. Studies were made in the 26.5–38.0 GHz spectral region with cell cooled to about −20 °C. Lower temperatures could not be used because of insufficient vapour pressure of the compound. The spectrum was measured with pressures in the 1.5–4.0 Pa range.

RESULTS

Assignment. Preliminary rotational constants of conformation *I* were computed by combining structural parameters taken from related compounds. Bond moment calculations of the dipole moment[7] of *I* with the hydroxyl group oriented such that an intramolecular hydrogen bond might be formed, yielded μ_a=1.5 D, μ_b=0.3 D, and μ_c=0.7 D, respectively. A simple, *a*-type *R*-branch spectrum was thus predicted to predominate for this conformation, and this was indeed immediately found. The ground-state spectrum* is shown in Table 1 and the spectroscopic constants (I^r representation, *A*-reduction) are listed in Table 2. The two *J*=9←8 transitions shown in Table 1 were the strongest ones observed having peak absorption coefficients of roughly 3×10^{-7} cm^{-1} at −20 °C.

Unfortunately, we were not able to determine the dipole moment, because of insufficient intensities and resolution of the individual Stark lobes.

Outside the lumps of lines belonging to the particular *R*-branch transitions, only quite weak transitions were seen. Attempts to find *b*- and *c*-type *Q*-branch lines among these weak transitions were futile.

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* The complete microwave spectra of the parent and deuterated species are available from the authors upon request or from the Molelcular Spectra Data Center, Bldg. 221, Room B 265, National Bureau of Standards, Washington D.C. 20234, U.S.A., where they have been deposited.

Table 1. Microwave spectrum of the ground vibrational state of $\overline{CH_2CH_2}CHCH(OH)CH_3$.

Transition	Observed frequency[a] (MHz)	Obs.−calc. frequency (MHz)
$6_{1,5} \leftarrow 5_{1,4}$	28952.49	0.04
$6_{2,4} \leftarrow 5_{2,3}$	29378.12	0.05
$6_{2,5} \leftarrow 5_{2,4}$	27549.93	0.10
$6_{3,3} \leftarrow 5_{3,2}$	28414.73	−0.06
$6_{3,4} \leftarrow 5_{3,3}$	28132.47	0.10
$7_{0,7} \leftarrow 6_{0,6}$	30011.85	0.12
$7_{1,6} \leftarrow 6_{1,5}$	33366.90	−0.09
$7_{1,7} \leftarrow 6_{1,6}$	29743.38	−0.02
$7_{2,5} \leftarrow 6_{2,4}$	34433.66	−0.03
$7_{2,6} \leftarrow 6_{2,5}$	31969.29	−0.04
$7_{3,4} \leftarrow 6_{3,3}$	33423.67	0.02
$7_{3,5} \leftarrow 6_{3,4}$	32829.02	−0.03
$7_{4,3} \leftarrow 6_{4,2}$	32896.67	−0.11
$7_{4,4} \leftarrow 6_{4,3}$	32857.86	0.01
$7_{5,2} \leftarrow 6_{5,1}$	32771.95	−0.06
$7_{6,1} \leftarrow 6_{6,0}$	32716.81	−0.07
$7_{6,0} \leftarrow 6_{6,1}$	32716.81	−0.06
$8_{0,8} \leftarrow 7_{0,7}$	34000.30	−0.01
$8_{1,7} \leftarrow 7_{1,6}$	37585.84	0.00
$8_{1,8} \leftarrow 7_{1,7}$	33838.30	−0.09
$8_{2,7} \leftarrow 7_{2,6}$	36320.15	−0.03
$8_{3,6} \leftarrow 7_{3,5}$	37492.84	0.07
$8_{4,4} \leftarrow 7_{4,3}$	37727.17	−0.01
$8_{4,5} \leftarrow 7_{4,4}$	37623.23	0.03
$8_{6,2} \leftarrow 7_{6,1}$	37432.22	0.04
$8_{6,3} \leftarrow 7_{6,2}$	37432.22	0.12
$8_{7,1} \leftarrow 7_{7,0}$	37383.95	0.00
$8_{7,2} \leftarrow 7_{7,1}$	37383.95	0.00
$9_{0,9} \leftarrow 8_{0,8}$	38005.01	−0.01
$9_{1,9} \leftarrow 8_{1,8}$	37912.46	0.02

[a] ±0.10 MHz.

Table 2. Spectroscopic constants of the ground vibrational states of $\overline{CH_2CH_2}CHCH(OH)CH_3$ and $\overline{CH_2CH_2}CHCH(OD)CH_3$[a].

Species	$\overline{CH_2CH_2}CHCH(OH)CH_3$	$\overline{CH_2CH_2}CHCH(OD)CH_3$
N.o.t.[b]	30	28
R.m.s.[c] (MHz)	0.066	0.085
A_0 (MHz)	6096.665(95)	5845.31(10)
B_0 (MHz)	2623.8831(41)	2613.5392(53)
C_0 (MHz)	2021.1376(67)	1986.7781(89)
Δ_J (kHz)	0.082(43)	0.061(57)
Δ_{JK}[d] (kHz)	1.342(66)	1.750(88)

[a] Uncertainties represent one standard deviation. [b] Number of transitions. [c] Root-mean-square deviation. [d] Further quartic centrifugal distortion constants preset at zero.

Table 3. Spectroscopic constants of vibrationally excited states of $\overline{\text{CH}_2\text{CH}_2}\text{CHCH(OH)CH}_3{}^a$.

Vibrational state	First ex. tors. vib.	Second ex. tors. vib.	First ex. of *Bend. I*[e]	First ex. of *Bend. II*[e]
N.o.t.[b]	28	26	26	28
R.m.s.[c](MHz)	0.065	0.072	0.111	0.074
A_v (MHz)	6098.617(98)	6101.19(14)	6091.43(21)	6096.60(11)
B_v (MHz)	2618.6260(41)	2613.6376(50)	2622.9849(72)	2626.2079(47)
C_v (MHz)	2021.3878(66)	2021.6075(82)	2019.993(13)	2019.8244(77)
Δ_J (kHz)	0.074(42)	0.138(51)	0.131(77)	0.153(49)
Δ_{JK} (kHz)[d]	1.387(68)	1.417(73)	1.45(12)	1.509(75)

^{a,b,c,d} Comments as for Table 2. ^{e} Tentative assignment of vibrational fundamental; see text.

Vibrationally excited states. The ground state transitions were accompanied by a satellite spectrum presumably belonging to vibrationally excited states of the molecule. Four such states were assigned as shown in Table 3. The strongest of these excited states has about 50 % of the ground state intensity. Relative intensity measurements[8] yielded 112(20) cm^{-1} for this vibration which is assumed to be the *ring*-C torsional vibration because of its low frequency. In (aminomethyl)cyclopropane[6] the corresponding vibration of the two conformations *I* and *II* of this molecule, occur at 159(20) cm^{-1} and 148(20) cm^{-1}, respectively.

The second excited state of this torsional vibration was also assigned (Table 3). The fact that the rotational constants change almost linearly through the two first excited states of the *ring*-C torsional vibration (see Tables 2 and 3) indicates that this mode is rather harmonic.

The next excited state assigned is denoted *Bend. I* in Table 3. Its intensity was about 30 % of the ground vibrational state. A vibrational frequency of 200(30) cm^{-1} was determined by relative intensity measurements.[8]

Finally, *Bend. II* of Table 3 was assigned. Relative intensity measurements[8] yielded 195(30) cm^{-1} for this fundamental.

It is likely that *Bend. I* and *Bend. II* are the two lowest heavy-atom bending vibrations of 1-cyclopropylethanol, but one of them could be the C–O torsional vibration.

Further conformations. As noted above, there are many weak and very weak transitions seen between the strong assigned a-type R-branch lines belonging to conformation *I* (with an intramolecular hydrogen bond). These weak, unidentified lines could be unassigned b- or c-type high-J transitions of *I*, they could belong to one or more unidentified forms, or they could belong to impurities. All possible rotameric forms of 1-cyclopropylethanol are likely to have sizable dipole moments. As the strongest unassigned transition is less than 10 % as intense as the ground state transitions appearing in Table 1, it is conservatively estimated that conformation *I* with a hydrogen bond is at least 4 kJ/mol more stable than any further form of the molecule.

Deuterated species. The deuterated species, $\overline{\text{CH}_2\text{CH}_2\text{CHCH(OD)}}\text{CH}_3$, was studied in order to confirm that the hydroxyl group hydrogen atom points towards the pseudo-π electrons of the cyclopropane ring. The assignment of this species was straightforward. Its rotational constants are listed in Table 2, and Kraitchman's coordinates[9] which show that an intramolecular bond is indeed formed in this conformation, are shown in Table 4.

Table 4. Plausible structural parameters [a] (bond lengths in *pm*, angles in *degrees*), observed and calculated rotational constants, and Kraitchman's coordinates for the hydroxyl group hydrogen atom of $\overline{CH_2CH_2C}HCH(OH)CH_3$.

Assumed structure

$C_{ring}-C_{ring}$	151.2	$\angle\ C_{ring}-C_{ring}-C_{ring}$	60.0	
$C_{ring}-CH(OH)CH_3$	152.0	$\angle\ H-C_{ring}-H$	116.0	
$C-CH_3$	153.0	$\angle\ H-C_{ring}-C$	116.0	
$C-O$	141.5	$\angle\ C-C-H^b$	109.47	
$C_{ring}-H_{ring}$	108.3	$\angle\ C-O-H$	104.0	
$C-H^b$	109.3	$\angle\ H_{ring}-C_{ring}-C-O^c$	+ 60.0	from *syn*
$O-H$	95.0	$\angle\ H_{ring}-C_{ring}-C-C^c$	− 60.0	from *syn*
		$\angle\ H-O-C-CH_3^c$	180.0	from *syn*

Rotational constants (MHz)

	$\overline{CH_2CH_2C}HCH(OH)CH_3$			$\overline{CH_2CH_2C}HCH(OD)CH_3$		
	Obs	Calc.	Diff. (%)	Obs.	Calc.	Diff. (%)
A	6096.665(95)	6105.53	0.15	5845.31(10)	5856.94	0.20
B	2623.8831(41)	2622.56	0.05	2613.5392(53)	2609.71	0.15
C	2021.1376(67)	2026.18	0.25	1986.7781(89)	1991.16	0.22

Kraitchman's coordinates [d]

	$|a|$	$|b|$	$|c|$
From rotational constants	86.04(7)	189.93(3)	3.7(18)
From plausible structure	94.23	187.65	20.17

Hydrogen bond parameters

$H\cdots C_\alpha^e$	255	$H\cdots C_\beta^f$	295	
$O\cdots C_\alpha$	244	$O\cdots C_\beta$	329	
$\angle\ O-H\cdots C_\alpha$	73	$\angle\ O-H\cdots C_\beta$	103	
$\angle\ H\cdots C_\alpha-C_\beta$	90	$\angle\ H\cdots C_\beta-C_\alpha$	60	
$\angle\ O-H,\ C_\alpha-C_\beta$	21[g]			

Sum of van der Waals radii [h]

$H\cdots C^i$	290	$O\cdots C^i$	310

[a] See text. [b] Of −CH(OH)− and −CH₃ groups. [c] Dihedral angle. [d] Ref. 9. [e] C_α is the ring-carbon atom closest to the hydroxyl group hydrogen atom. [f] C_β is the other carbon atom of the edge of the ring closest to the hydroxyl group hydrogen atom. [g] Angle between O−H and $C_\alpha-C_\beta$ bonds. [h] Taken from Ref. 13. [i] van der Waals radius of carbon taken to be 170 *pm* as in aromatic molecules.[13]

Structure. Only two isotopic species were studied for this molecule. The six different rotational constants are insufficient to determine a full geometrical structure. Attempts were first made to fit the H_{ring}–C_{ring}–C–O (and H_{ring}–C_{ring}–C–C) dihedral angle, but it was found that the rotational constants are relatively independent of this parameter, so no accurate dihedral angle could be obtained this way.

The substitution coordinates of the hydroxyl group hydrogen atom (Table 4) undoubtedly shows that an intramolecular hydrogen bond is formed, but due to the low-frequency C_{ring}–C and C–O torsional vibrations, its position is perhaps not so accurately fixed (see Refs. 10 and 11) that it may be used for reliable structural fitting. No attempts to fit structural parameters to the substitution coordinates of this atom were therefore made.

The plausible structural parameters shown in Table 4 were taken from recent, accurate structural studies of related compounds. The atomic arrangements about dihedral angles were all assumed to be staggered. It can be seen from this table that the rotational constants are very well reproduced, and that the substitution coordinates of the hydroxyl group hydrogen atom are satisfactorily reproduced by this choice of structural parameters.

The hydrogen bond of 1-cyclopropylethanol is seen (Table 4) to have the distance between the hydroxyl group hydrogen atom and the nearest ring-carbon atom approximately 35 *pm* shorter than the sum of the van der Waals radii of aromatic carbon and hydrogen.[13] The angle between the O–H bond and the C–C edge of the ring involved in hydrogen bonding is about 21° from being parallel.

DISCUSSION

There are presumably many factors influencing the conformational choices of the title compound. Hydrogen bonding is postulated to be one. The reason why conformation *I* (with a hydrogen bond) (see Fig. 1) is preferred to the hypothetical rotamer *III* (with a hydrogen bond), may be caused largely by steric repulsion in *III* between the methyl group and the cyclopropane ring. This repulsion must be quite important since *I* is more stable than *III* by at least 4 kJ/mol. This parallels the findings made for a similar molecule, ethylcyclopropane.[12] This molecule exists only in the *gauche* conformation as shown by Raman and IR spectroscopy.[12]

The steric conditions in the hypothetical conformation *II* (and its three hydroxyl-group staggered forms) should be rather favourable. The reason why the identified conformation is considerably more stable than any one of the three forms of *II*, could be either repulsion between the hydroxyl group and the ring, or the inability to form a sufficiently strong hydrogen bond when this group takes the *syn* position, as it does in *II*.

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