

# Microwave Spectrum, Intramolecular Hydrogen Bond, Dipole Moment and Centrifugal Distortion of 3-Buten-1-ol

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The microwave spectra of  $\text{CH}_2\text{OHCH}_2\text{CH}=\text{CH}_2$  and  $\text{CH}_2\text{ODCH}_2\text{CH}=\text{CH}_2$  have been investigated in the 18.0–32.0 GHz spectral region. The hydrogen-bonded conformation shown in Fig. 1 was assigned. This conformer make up at least 80% of the gas at  $-20^\circ\text{C}$ .

The C1C2C3C4 dihedral angle is  $75(3)^\circ$ , the C2C3C4O dihedral angle is  $64(3)^\circ$  from *syn*, and the C3C4OH dihedral angle is  $225(10)^\circ$ .

The dipole moment is  $\mu_a=1.23(2)$  D,  $\mu_b=1.02(2)$  D,  $\mu_c=0.44(7)$  D, and  $\mu_{\text{tot}}=1.65(5)$  D.

Three vibrationally excited states were assigned. Two of these belong to the C2–C3 torsional mode and one to the C3–C4 torsional vibration. Relative intensity measurements yielded 84(20) and 172(15)  $\text{cm}^{-1}$ , respectively, for these two frequencies.

The conformational properties and the possibility of forming an internal hydrogen bond between the hydroxyl group hydrogen and the double bond of 3-buten-1-ol have interested chemists for years.<sup>1</sup> It was established by infrared spectroscopy more than twenty years ago that the preferred conformation of this molecule in dilute solutions has an intramolecular hydrogen bond.<sup>2</sup> Another IR study by Luck and Differ<sup>3</sup> showed that this conformation is more stable by about 4 kJ/mol in dilute carbon tetrachloride solution. Very recently, Trætteberg and Østensen studied 3-buten-1-ol in the gas phase using the electron-diffraction method.<sup>1</sup> A mixture of two conformations was identified. The more stable of these clearly possesses a hydrogen bond. At  $45^\circ\text{C}$  they found that 68.6(8)% of the mixture consists of the more stable hydrogen-bonded conformation and 31.4(8)% of the less stable rotamer. Furthermore, it was shown that an additional third conformation is not present in concentrations exceeding 10% of the total.

The motivation for carrying out the present research has been to study gaseous 3-buten-1-ol by a third independent method. The hydrogen-bonded conformation was again identified and it was found that at least 80% of the gas consists of this conformation at  $-20^\circ\text{C}$ . Moreover, the rotational constants are sensitive to the structurally important dihedral angles  $\alpha$ ,  $\beta$ , and  $\gamma$ , (see Fig. 2 for definition) which were not determined with high accuracy by electron diffraction. It was thus hoped that a microwave investigation might, in combination with results from the electron-diffraction study, yield improved dihedral angles.

## EXPERIMENTAL

3-buten-1-ol was purchased from Fluka A.G., Buchs, Switzerland, and used without further purification. Studies were made in the 18–32 GHz spectral region on a conventional spectrometer with the cell cooled to about  $-20^\circ\text{C}$ . Lower temperatures could not be utilized because of insufficient vapour pressure. Vapour pressures in the 5–25 micron range were employed during the spectral measurements.  $\text{CH}_2\text{ODCH}_2\text{CH}=\text{CH}_2$  was produced by direct exchange with heavy water in the wave guide.

## RESULTS

*Microwave spectrum and assignment.* Preliminary rotational constants of the hydrogen-bonded rotamer were computed using structural parameters taken largely from the electron-diffraction investigation<sup>1</sup> of 3-buten-1-ol.

The observed spectrum was dense and of moderate strength. Assignments were first made for the  $J=3\rightarrow 4$  and  $J=4\rightarrow 5$  *a*-type *R*-branch transitions and

Table 1. Selected transitions for the ground vibrational state of  $\text{CH}_2\text{OHCH}_2\text{CH}=\text{CH}_2$ .

Transition	Observed frequency <sup>a</sup> (MHz)	Obs.-calc. frequency (MHz)	Centrifugal distortion	
			Total (MHz)	Sextic (MHz)
<i>a</i> -type				
$2_{0,2} \rightarrow 3_{0,3}$	18049.92	-0.01	-0.49	
$2_{1,1} \rightarrow 3_{1,2}$	19070.89	-0.02	-0.61	
$3_{1,3} \rightarrow 4_{1,4}$	23035.03	0.11	-0.53	
$3_{0,3} \rightarrow 4_{0,4}$	23880.37	-0.05	-1.03	
$3_{2,2} \rightarrow 4_{2,3}$	24256.60	0.03	-0.32	
$3_{2,1} \rightarrow 4_{2,2}$	24664.47	0.13	-0.66	
$3_{1,2} \rightarrow 4_{1,3}$	25373.52	-0.01	-1.54	
$4_{1,4} \rightarrow 5_{1,5}$	28726.41	0.13	-1.19	
$4_{3,2} \rightarrow 5_{3,3}$	30487.89	0.07	0.02	
$4_{2,2} \rightarrow 5_{2,3}$	31049.10	0.16	-2.18	
<i>b</i> -type				
$8_{0,8} \rightarrow 8_{1,7}$	21313.51	0.12	-13.76	
$10_{0,10} \rightarrow 10_{1,9}$	29909.50	0.02	-28.21	-0.01
$4_{1,4} \rightarrow 4_{2,3}$	21458.40	-0.02	-0.11	
$10_{1,9} \rightarrow 10_{2,8}$	19551.55	-0.03	-14.47	-0.01
$13_{1,12} \rightarrow 13_{2,11}$	29740.58	-0.05	-65.43	-0.01
$5_{2,3} \rightarrow 5_{3,2}$	29757.37	0.02	0.81	
$14_{2,12} \rightarrow 14_{3,11}$	24916.00	-0.03	-19.40	-0.09
$5_{2,4} \rightarrow 5_{3,3}$	31103.06	-0.08	-0.48	
$7_{2,6} \rightarrow 7_{3,5}$	32041.76	-0.10	1.71	-0.01
$16_{3,13} \rightarrow 16_{4,12}$	31433.78	-0.01	66.36	-0.43
$19_{3,16} \rightarrow 19_{4,15}$	31976.96	0.12	-41.14	-0.40
$1_{1,0} \rightarrow 2_{2,1}$	30298.88	-0.06	-0.55	
$4_{1,4} \rightarrow 5_{0,5}$	25852.40	0.03	-2.83	
Coalescing $K_{-1}$ -lines				
$24_{11} \rightarrow 25_{10}$	24929.25	-0.03	-281.10	0.62
$31_{14} \rightarrow 32_{13}$	30895.41	-0.06	-577.60	2.04
$36_{17} \rightarrow 37_{16}$	24314.20	0.04	-682.60	1.77
$42_{20} \rightarrow 43_{19}$	23957.77	0.11	-959.97	1.98
$45_{21} \rightarrow 46_{20}$	29923.67	-0.07	-1311.74	5.24

<sup>a</sup>  $\pm 0.10$  MHz.

readily extended to *b*-type *Q*- and *R*-branch lines. No *c*-type transitions were definitely identified owing to the small dipole moment along this axis (see below). A portion of the ground state spectrum is shown in Table 1.\* In the least-squares fitting of the spectral data, only two sextic centrifugal distur-

tion constants were included with the result shown in Table 2. The rotational constants of this table can undoubtedly be ascribed to the conformation depicted in Fig. 1. This rotamer possesses an intramolecular hydrogen bond formed between the hydroxyl hydrogen atom and the double bond. The carbon-atom skeleton conformation of this molecule is similar to that of the *skew* form of 1-butene.<sup>4</sup>

*Vibrationally excited states.* The ground state lines were accompanied by several excited state transitions. Three of these were ultimately assigned as shown in Table 3. The strongest of these absorp-

\* The complete microwave spectra of  $\text{CH}_2\text{OHCH}_2\text{CH}=\text{CH}_2$  and  $\text{CH}_2\text{ODCH}_2\text{CH}=\text{CH}_2$  are available from the authors upon request, or from Molecular Spectra Data Center, Bldg. 221, Rm. B 265, National Bureau of Standards, Washington D.C. 20234, U.S.A., where they have been deposited.

Table 2. Spectroscopic constants of the ground vibrational state of  $\text{CH}_2\text{OHCH}_2\text{CH}=\text{CH}_2$  and  $\text{CH}_2\text{ODCH}_2\text{CH}=\text{CH}_2$ .<sup>a</sup>

Species		$\text{CH}_2\text{OHCH}_2\text{CH}=\text{CH}_2$	$\text{CH}_2\text{ODCH}_2\text{CH}=\text{CH}_2$
Number of transitions		76	27
rms (MHz)		0.091	0.088
$A_0$	(MHz)	9185.7124(74)	8852.609(33)
$B_0$	(MHz)	3330.0652(26)	3324.908(14)
$C_0$		2742.3434(24)	2710.228(14)
$\Delta_J$	(kHz)	5.3802(58)	4.75(30)
$\Delta_{JK}$	(kHz)	-31.77(11)	-29.41(22)
$\Delta_K$	(kHz)	73.35(11)	67.1(29)
$\delta_J$	(kHz)	1.7362(63)	1.771(11)
$\delta_{JK}$	(kHz)	8.23(21)	7.96(30)
$H_J$	(Hz)	-0.0137(15)	<sup>b</sup>
$H_{JK}$	(Hz)	-0.918(82)	<sup>b</sup>

<sup>a</sup>Uncertainties represent one standard deviation. rms is the root-mean-square deviation of the fit. <sup>b</sup>Not varied in least-squares fit.

tion lines were about 60% as strong as the corresponding ground state transitions. Relative intensity measurements made largely as prescribed by Esbitt and Wilson<sup>5</sup> yielded  $84(20)\text{ cm}^{-1}$  for what is believed to be the C2-C3 torsional mode. This is close to  $93(4)\text{ cm}^{-1}$  determined for the corresponding frequency of 1-butene.<sup>4</sup>

The observed changes of the rotational constants upon excitation are  $\Delta A = 89.29\text{ MHz}$ ,  $\Delta B = -16.96\text{ MHz}$ , and  $\Delta C = -10.43\text{ MHz}$ , respectively. If the C2C3 dihedral angle ( $\alpha$  of Fig. 2) is opened up  $2^\circ$  in the molecular model discussed below, the changes of the rotational constants were calculated as  $\Delta A = 74\text{ MHz}$ ,  $\Delta B = -31\text{ MHz}$ , and  $\Delta C = -10\text{ MHz}$ , respectively. There is thus rough agreement between the observed and calculated changes of the rotational constants upon excitation of this mode.

The second excited state of this mode was also assigned. As can be seen from Table 3, the progressive changes of each of the rotational constants upon excitation are quite constant indicating that this mode is fairly harmonic.

The first excited state of what is assumed to be the C3-C4 torsional mode ( $\beta$  of Fig. 2) was also identified as shown in Table 3. A frequency of  $172(15)\text{ cm}^{-1}$  was determined by relative intensity measurements for this vibration. This is close to what has been found for other hydrogen-bonded ethanol derivatives such as *e.g.*  $\text{CH}_2\text{OHCH}_2\text{F}$  ( $152(10)\text{ cm}^{-1}$ ),<sup>5</sup>  $\text{CH}_2\text{OHCH}_2\text{Cl}$  ( $155(10)\text{ cm}^{-1}$ ),<sup>7</sup> and  $\text{CH}_2\text{OHCH}_2\text{NH}_2$  ( $140 \pm 30\text{ cm}^{-1}$ ).<sup>8</sup> An increase of C3-C4 dihedral angle of  $2^\circ$  yielded changes of the rotational constants in rough agreement with the observed ones.

Table 3. Spectroscopic constants<sup>a</sup> of vibrationally excited states of  $\text{CH}_2\text{OHCH}_2\text{CH}=\text{CH}_2$ .

Vib. state		First ex. C2C3 tors.	Second ex. C2C3 tors.	First ex. C3C4 tors.
Number of transitions		39	26	26
rms (MHz)		0.087	0.080	0.067
$A_v$	(MHz)	9275.001(20)	9362.265(27)	9217.074(24)
$B_v$	(MHz)	3313.1092(98)	3295.982(12)	3318.202(14)
$C_v$	(MHz)	2731.9126(95)	2721.573(11)	2734.290(14)
$\Delta_J$	(MHz)	4.70(20)	4.75(23)	5.36(31)
$\Delta_{JK}$	(kHz)	-29.73(17)	-27.53(33)	-31.60(24)
$\Delta_K$	(kHz)	80.4(21)	69.0(43)	76.0(28)
$\delta_J$	(kHz)	1.5547(76)	1.440(10)	1.7498(92)
$\delta_{JK}$	(kHz)	8.32(26)	7.68(32)	7.80(28)

<sup>a</sup>Comments as for Table 2.

*Searches for further conformations.* The above assignments include all the strongest lines of the spectrum as well as the majority of the intermediate intensity transitions and several weak ones. Very many weak lines remain unassigned. It is very probable that a considerable fraction of these belong to further unassigned vibrationally excited states of the identified conformation. They may also belong to one or more additional conformations left unassigned. However, it is estimated from the intensities of the spectral lines that at least about 80 % of the gas belong to the identified conformation at  $-20^\circ\text{C}$ . Assuming zero entropy difference, the hydrogen-bonded form is thus more stable by at least 3 kJ/mol. With the same assumption about the entropy difference, it is calculated from the composition obtained in the electron-diffraction work (68.6 % hydrogen-bonded conformation at  $40^\circ\text{C}$ ) that this rotamer is more stable by 2.0(5) kJ/mol. Both these numbers are close to the solution ( $\text{CCl}_4$ ) value<sup>3</sup> of about 4 kJ/mol.

*Dipole moment.* Stark coefficients of three *a*-type  $J=4\rightarrow 5$  transitions were used to determine the dipole moment. A d.c. voltage was applied between the Stark septum and the cell with modulating square wave voltage superimposed. The field strength was calibrated using the OCS  $J=1\rightarrow 2$  transition with  $\mu_{\text{OCS}}=0.71521$  D.<sup>9</sup> The second order Stark

coefficients and their estimated standard deviations are shown in Table 4. A least-squares fit using a diagonal weight matrix was performed. The weights were chosen as the inverse squares of the standard deviations of the Stark coefficients appearing in Table 4. The dipole moment determined in this manner was:  $\mu_a=1.23(2)$  D,  $\mu_b=1.02(2)$  D, and  $\mu_c=$

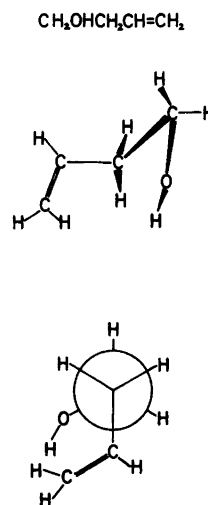


Fig. 1. Models of the assigned hydrogen-bonded conformation of 3-buten-1-ol.

Table 4. Stark coefficient<sup>a</sup> and dipole moment of the hydrogen-bonded conformation of  $\text{CH}_2\text{OHCH}_2\text{CH}=\text{CH}_2$ .

Transition		$\Delta\nu/E^2$ (MHz V <sup>-2</sup> cm <sup>2</sup> ) × 10 <sup>6</sup>	
		Obs.	Calc.
$4_{0,4}\rightarrow 5_{0,5}$	$ M =0$	-0.141(3)	-0.175
	$ M =1$	0.231(3)	0.220
	$ M =2$	1.45(2)	1.41
	$ M =3$	3.46(4)	3.38
	$ M =4$	6.17(9)	6.15
$4_{1,3}\rightarrow 5_{1,4}$	$ M =1$	-0.663(7)	-0.648
	$ M =2$	-1.37(2)	-1.39
	$ M =3$	-2.54(3)	-2.62
$4_{2,3}\rightarrow 5_{2,4}$	$ M =1$	-1.89(3)	-1.87
	$ M =2$	13.8(2)	13.5
	$ M =3$	39.9(5)	39.6
$\mu_a=1.23(2)$ D		$\mu_b=1.02(2)$ D	
$\mu_c=0.44(7)$ D		$\mu_{\text{tot}}=1.65(5)$ D	

<sup>a</sup>Uncertainties represent one standard deviation.

Table 5. Plausible structural parameters<sup>a</sup> and observed and calculated rotational constants of  $\text{CH}_2\text{OHCH}_2\text{CH}=\text{CH}_2$ . Distances in pm and angles in degrees.

Assumed structural parameters					
C=C	131.1	$\angle \text{C}=\text{C}-\text{C}$	127.8		
C2-C3	149.6	$\angle \text{C}2\text{C}3\text{C}4$	111.6		
C3-C4	152.8	$\angle \text{CCO}$	112.3		
C-O	141.5	$\angle \text{COH}$	105.0		
O-H	115.0	$\angle \text{C}=\text{C}-\text{H}$	121.5		
C1-H	109.0	$\angle \text{HC}3\text{H}$	109.48		
C2-H	109.0	$\angle \text{HC}4\text{H}$	109.48		
C3-H	109.3				
C4-H	109.3				
Fitted structural parameters					
$\angle \text{C}1\text{C}2\text{C}3\text{C}4$	$\alpha = 75(3)$				
$\angle \text{C}2\text{C}3\text{C}4\text{O}$	$\beta = 116(3)$ (64(3) from <i>syn</i> )				
$\angle \text{C}3\text{C}4\text{OH}$	$\gamma = 225(10)$				
Rotational constants (MHz)					
$\text{CH}_2\text{OHCH}_2\text{CH}=\text{CH}_2$			$\text{CH}_2\text{ODCH}_2\text{CH}=\text{CH}_2$		
Obs.	Calc.	Diff. %	Obs.	Calc.	Diff. %
9185.713	9208.604	0.25	8852.609	8876.371	0.27
3330.065	3336.367	0.19	3324.908	3329.818	0.15
2742.342	2733.517	0.32	2710.228	2700.692	0.35
Kraitchman's coordinates for hydroxyl hydrogen atom					
a	41.48(7) <sup>b</sup>	49.2 <sup>c</sup>			
b	142.28(2) <sup>b</sup>	142.1 <sup>c</sup>			
c	25.55(13) <sup>b</sup>	23.7 <sup>c</sup>			
Hydrogen bond parameters					
H...C2	242	H...C1	263		
O...C2	298	O...C1	350		
Angle between O-H and C=C bonds (°) 42					
Angle between C-O and C=C bonds (°) 48					
$\angle \text{O}-\text{H}\cdots\text{C}1$	132	$\angle \text{O}-\text{H}\cdots\text{C}2$	108		
$\angle \text{H}\cdots\text{C}2=\text{C}1$	84	$\angle \text{H}\cdots\text{C}1=\text{C}2$	66		
Sum of van der Waals radii <sup>a</sup>					
C-H	290	C-O	310		

<sup>a</sup>See text. <sup>b</sup>Calculated from rotational constants. <sup>c</sup>Obtained from molecular model.

0.44(7) D, yielding a total dipole moment of 1.65(5) D.

*Deuterated species.* The deuterated species,  $\text{CH}_2\text{ODCH}_2\text{CH}=\text{CH}_2$  was studied in order to obtain conclusive evidence for the existence of a hydrogen bond in this molecule. Using Kraitchman's equations<sup>10</sup> with the rotational constants of

$\text{CH}_2\text{OHCH}_2\text{CH}=\text{CH}_2$  and  $\text{CH}_2\text{ODCH}_2\text{CH}=\text{CH}_2$  with the former as the parent molecule, it is thus possible to determine the geometrical coordinates of the hydroxyl group hydrogen atom with high precision. 27 transitions were measured for this isotopic species and the spectroscopic constants shown in Table 2 were determined. Kraitchman's

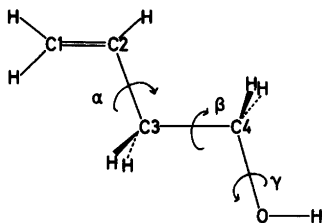


Fig. 2. Definition of atom numbering and dihedral angles. This conformation has  $\alpha = \beta = \gamma = 0^\circ$ .

coordinates for the hydroxyl hydrogen atom are shown in Table 5.

**Structure.** Only six moments of inertia were determined for the conformation shown in Fig. 1. Consequently, a full molecular structure cannot be determined. Instead we restricted ourselves to fitting the  $\alpha$ ,  $\beta$ , and  $\gamma$  dihedral angles of Fig. 2, because they are sensitive to the rotational constants and because they were not determined with as high accuracy in the electron-diffraction investigation as were the remaining structural parameters.

The structural parameters of the C-H bonds were assumed as shown in Table 5. The remaining bond lengths and angles were taken from the electron-diffraction work as indicated in this table.

The  $\alpha$  and  $\beta$  dihedral angles were first fitted until satisfactory agreement between the observed and calculated rotational constants were found. This occurred with  $\alpha = 75(3)^\circ$  and  $\beta = 116(3)^\circ$  ( $64(3)^\circ$  from *syn*). These error limits are assumed to encompass both systematic and random errors. The corresponding angles were determined as  $\alpha = 61.6(43)^\circ$  and  $\beta = 109.3(25)^\circ$  in the electron-diffraction investigation. These error limits are one standard deviation. There is thus agreement between the two determinations within the error limits.

Determination of the  $\gamma$  dihedral angle proved to be much more uncertain than in the case of  $\alpha$  and  $\beta$  angles and was made in the following manner: The COH angle was assigned a value of  $105^\circ$ . The O-H bond length and  $\gamma$  were varied in an attempt to reproduce Kraitchman's coordinates for the hydroxyl group hydrogen atom. A very large value of 115 pm for the O-H and  $225^\circ$  for  $\gamma$  had to be assumed in order to reproduce reasonably well the *b*- and *c*-axis coordinates. An even longer O-H bond length would have to be assumed in order to reproduce the *a*-axis coordinate of this atom. The unrealistically large O-H bond length is believed to be caused by bond shortening effects due to substitu-

tion and/or the low-lying vibrations of this molecule. Similar observations have been made before.<sup>11</sup> However, it is felt that the  $\gamma$  dihedral angle can be estimated as  $225(10)^\circ$  from the present microwave data.

## DISCUSSION

The hydrogen bond of 3-buten-1-ol is rather weak. The H $\cdots$ C2 and H $\cdots$ Cl distances are roughly 50 and 30 pm, respectively, shorter than the sum of the van der Waals radii of hydrogen<sup>12</sup> (120 pm) and aromatic carbon<sup>12</sup> (170 pm). The O-H $\cdots$ Cl angle of about  $132^\circ$  and the O-H $\cdots$ C2 angle of approximately  $108^\circ$  are presumably not favourable for covalent bond formation. Dipole-dipole interaction between the C1=C2 and O-H bonds are not ideal as the angle between them is approximately  $42^\circ$ .

Yet, the rather strained hydrogen bond apparently has some marked structural and thermodynamic influence on 3-buten-1-ol. The  $\alpha$  dihedral angle is, for example, about  $15^\circ$  larger than the corresponding angle in 1-butene.<sup>4</sup> This brings the double bond closer to the hydroxyl hydrogen atom than what would have been the case if  $\alpha$  had taken the "normal" value of about  $60^\circ$  as found in 1-butene.

Not only the geometry but the thermodynamic properties of the conformational equilibrium also seem to be influenced by the hydrogen bond. In 1-butene both the *skew* and *cis* forms are similar in energy, while in 3-buten-1-ol the hydrogen-bonded form which is similar to the *skew* form of 1-butene is the predominating species.

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