

consistent in showing that cyclic (D-Phe-Pro-Gly-D-Ala-Pro) exists in the same single conformation in solution and in the solid state but that cyclic (D-Phe-Gly-Ala-Gly-Pro) appears to crystallize in two different forms under some conditions that may be in dynamic equilibrium in solution. The phenyl rings of crystalline cyclic (D-Phe-Gly-Ala-Gly-Pro) and cyclic (D-Phe-Gly-Val-Gly-Pro) undergo relatively slow ( $10\text{--}10^2$  Hz) reorientation about the  $C_\beta\text{--}C_\gamma$  bond axis, although the ring of (D-Phe-Pro-Gly-D-Ala-Pro) is static on this time scale. The N-H bond lengths for the two

different groups involved in intramolecular hydrogen bonds in cyclic (Gly-Pro-Gly-D-Ala-Pro) appear to be quite similar.

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**Registry No.** Cyclic (D-Phe-Pro-Gly-D-Ala-Pro), 75929-66-7; cyclic (D-Phe-Gly-Ala-Gly-Pro), 75929-67-8.

## Conformations, Possible H Bonding, and Microwave Spectrum of 3-Buten-2-ol

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**Abstract:** The microwave spectra of 3-buten-2-ol,  $\text{CH}_2=\text{CHCH}(\text{OH})\text{CH}_3$ , and  $\text{CH}_2=\text{CHCH}(\text{OD})\text{CH}_3$  have been investigated in the 18.0–40 GHz region. More than two conformations are believed to be present; however, the spectra of only two have been assigned. In conformer I the methyl carbon atom and the oxygen atom are in *skew* positions relative to the double bond. The methyl carbon is about  $118^\circ$  from the *syn* position while the oxygen is about  $-122^\circ$  from the *syn* position. The OH hydrogen is roughly *anti* to the methyl group. In conformer II the oxygen atom is about  $+4^\circ$  from the *syn* position with respect to the double bond and the methyl group is about  $+124^\circ$  from the *syn* position. The hydroxylic hydrogen is approximately *anti* to the hydrogen on carbon two. In both conformers the hydroxylic hydrogen is close to the double bond, so that it is possible that there is a hydrogen bond between the  $\pi$  electrons and the OH group. The dipole moment components of I have been determined from Stark-effect measurements: they are  $|\mu_a| = 1.30$  (1) D,  $|\mu_b| = 0.3$  (1) D,  $|\mu_c| = 0.47$  (7) D, and  $|\mu_{\text{tot}}| = 1.41$  (2) D. Rotational constants of three vibrationally excited states of I and the differences in the rotational constants  $A\text{--}C$  and  $\kappa$  of two vibrationally excited states of II are reported, which presumably all belong to the excited C–C torsion. Relative intensity measurements gave the energy difference between the lowest levels of I and II to be 520 (140) cal/mol with I below II. The lowest vibrational frequencies were 91 (19)  $\text{cm}^{-1}$  (I) and 138 (53)  $\text{cm}^{-1}$  (II). A vapor-phase infrared spectrum shows two peaks, one at 3645  $\text{cm}^{-1}$  and the other at 3657  $\text{cm}^{-1}$ , assigned to two OH stretching frequencies.

It has been suggested<sup>2</sup> that molecules containing the chain  $\text{C}=\text{C}\text{--}\text{C}\text{--}\text{O}\text{--}\text{H}$  may be able to form an internal hydrogen bond between the hydroxylic hydrogen and some part of the  $\text{C}=\text{C}$  double bond. Information about such bonding has been sought from electron-diffraction, infrared, and Raman spectra and other techniques. The most certain quantitative method is microwave spectroscopy which, however, has been applied to only a few such molecules.<sup>3–6</sup> The species 3-buten-2-ol has been studied in order to extend this list.

A considerable number of molecules with the  $\text{C}=\text{C}\text{--}\text{C}\text{--}\text{X}$  group occur with the skew or *syn* configuration<sup>7</sup> (see Figure 1, a–c). The anti planar structure is rare (Figure 1, d–f). Table I lists some molecules containing this chain whose conformation has been determined by microwave spectroscopy. It has been pointed out<sup>9a</sup> that the skew form is favored by more bulky groups X. Table I also suggests that a hydrogen bond may make the skew form more stable.

The above results for single substitutions indicate that when the chain is of the form  $\text{C}=\text{C}\text{--}\text{CH}(\text{OH})\text{CH}_3$  steric effects might lead to the energy order H *syn* lowest, OH *syn* second lowest, and  $\text{CH}_3$  *syn* third lowest (see Figure 1, b, c, a). However, the relative energies of OH and  $\text{CH}_3$  in the *syn* position are not certain because of the possible effect of hydrogen bonding.

The orientation of the hydroxyl hydrogen with respect to the C–C bond (rotation around the C–O bond) is less firmly predicted. In the absence of H bonding one normally expects the H in OH

**Table I.** Conformations of Related Molecules Determined by MW Spectroscopy

	% skew	% <i>syn</i>	ref
1-butene	83	17	8
$\text{CH}_2=\text{CHCH}_2\text{F}$	60	40	9
$\text{CH}_2=\text{CHCH}_2\text{Cl}$	84 <sup>a</sup>	16 <sup>a</sup>	10
$\text{CH}_2=\text{CHCH}_2\text{Br}$	100		11
$\text{CH}_2=\text{CHCH}_2\text{I}$	100		12
$\text{CH}_2=\text{CHCH}_2\text{OH}$	<100		3
$\text{CH}_3\text{CH}_2=\text{CHCH}_2\text{OH}$	100 <sup>b?</sup>		4
$\text{CH}_2=\text{C}=\text{CHCH}_2\text{OH}$	~100		6

<sup>a</sup> The population was determined with infrared spectroscopy<sup>10b</sup> and NMR<sup>10c</sup> spectroscopy. <sup>b</sup> From low-resolution MW which might not show other conformers.

to be staggered ( $\pm$  *gauche* or *anti*) with respect to the three bonds at the other end of the O–C axis, but if a hydrogen bond is indeed

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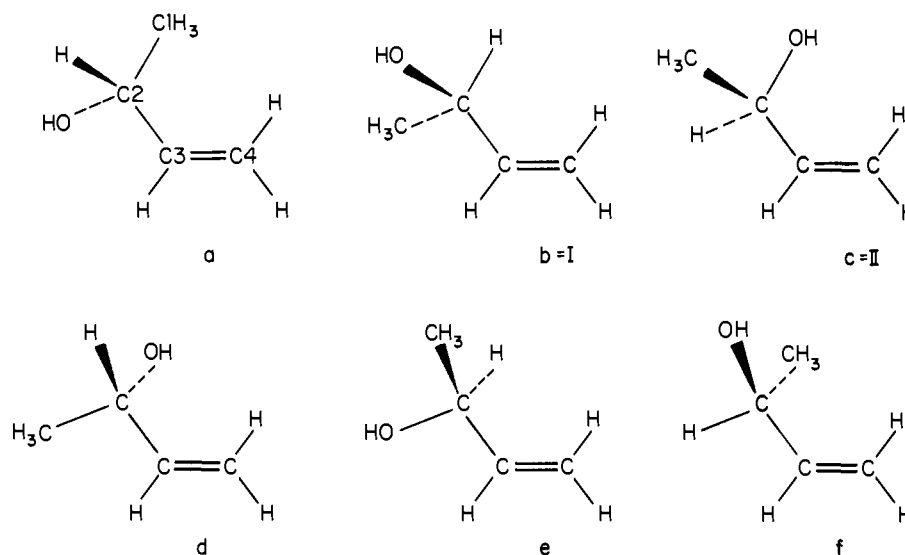


Figure 1. Possible conformers of 3-buten-2-ol. The identified conformers are I and II.

Table II. The Calculated Rotational Constants and Dipole Moment Components for the Most Probable Conformers of 3-Buten-2-ol<sup>a,b</sup>

conf	OH	CH <sub>3</sub>	H	A	B	C	$\mu_a$	$\mu_b$	$\mu_c$	H bond
I	SK	SK	+G	8240	3625	2825	1.5	0.3	0.5	yes
	SK	SK	-G	8455	3565	2842	0.4	1.0	1.3	no
	SK	SK	A	8570	3528	2807	0.7	1.0	1.1	no
	SK	SY	-G	8048	4068	3071	1.2	0.7	0.8	yes
	SK	SY	+G	7953	4097	3017	0.8	0.9	1.1	no
	SK	SY	A	8297	3992	3006	0.6	1.2	0.9	no
	SY	SK	+G	8063	4054	3043	1.1	0.4	1.1	yes
II	SY	SK	-G	8164	4026	3071	0.4	1.2	1.1	yes
	SY	SK	A	8168	3988	3016	1.4	0.7	0.7	no

<sup>a</sup>The geometrical parameters (except for C—C=C and C—C—O—H dihedral angles) are taken to be the same for all conformations. H bond refers to a suitability to form a hydrogen bond. <sup>b</sup>SK refers to skew, and SY to syn with respect to the double bond. +G means OH anti to the methyl group and -G means OH anti to the hydrogen on carbon two. A means OH anti to the C<sub>2</sub>-C<sub>3</sub> bond.

formed it is likely to change the angle about C—O so that H approaches more closely to some part of C=C.

It would therefore not be surprising if 3-buten-2-ol had several conformations, perhaps four, in which in turn the syn position is occupied by H, OH, or CH<sub>3</sub>, and when OH is syn, there are two favorable OH orientations, both of which could be H bonded.

In some infrared studies of alcohols in dilute solutions,<sup>13</sup> the authors observed that when two conformations were possible with different nearest neighbors of the OH group, the OH stretching vibration absorption band had an asymmetric shape. The OH stretching vibration at 3620 cm<sup>-1</sup> observed in 3-buten-2-ol was asymmetric,<sup>13b,c</sup> which suggested that there are at least two conformations present with different OH neighbors.

## Experimental Section

3-Buten-2-ol used at Harvard University was purchased from the Aldrich Chemical Co. (the Oslo sample came from the EGA Company).

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Both were used without further purification. The spectrum in the 18-34 GHz region was recorded at Oslo University at about -35 °C on a conventional spectrometer equipped with a free-running klystron (with a sample pressure of about 20 μm). At Harvard the spectrum in the 18-40 GHz region was recorded at room temperature with sample pressures between 15 and 35 μm on a Hewlett-Packard (HP) 8460A Stark modulated microwave spectrometer. The deuterated species was formed by direct exchange of the hydroxylic hydrogen with heavy water vapor in the waveguide. For amplitude-modulated radio frequency-microwave double resonance (RFMWDR),<sup>14</sup> an HP 606A or 608E signal generator was used together with three wideband amplifiers in series. Radio frequencies from 0.5 MHz up to about 90 MHz were used.

While searching for other conformers it became vital to determine if any of the MW lines belonged to impurities. A high-resolution NMR spectrum of the neat liquid was therefore recorded on a AM300 NMR spectrometer, from which it was concluded that the Aldrich Chemical Co. sample contained less than 0.05% impurities. In the EGA sample in Oslo methyl vinyl ketone<sup>15</sup> was identified as an impurity.

The vapor-phase infrared spectrum in the 900-4000 cm<sup>-1</sup> region was recorded on the Nicolet 7000 Fourier transform infrared spectrometer at Harvard with a 15-cm gas cell with CaF<sub>2</sub> windows.

The OH stretching frequency of 3-buten-2-ol was split by 12 cm<sup>-1</sup> (see Figure 2), the bands being at 3645 and 3657 cm<sup>-1</sup>. This is too small to be P-R splitting, and also a similar splitting persists in solution. Furthermore, some of the absorption bands in the 900-1500 cm<sup>-1</sup> region also seem to be split which might indicate the presence of another rotamer in which shifts of atoms heavier than H occur, most likely involving a change in the dihedral angle about C<sub>2</sub>-C<sub>3</sub>.

## Assignment

For any reasonable set of assumed structural parameters, 3-buten-2-ol is a near prolate asymmetric rotor ( $\kappa$  between -0.55 and -0.80). Preliminary rotational constants were calculated for several conformers from assumed structures primarily based on

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Table III. Observed  $R_a$  Transition Frequencies (MHz) of the Ground State, Three Vibrationally Excited States, and the OD Species of 3-Buten-2-ol, Conformer I

transition	ground state		$\nu = 1$		$\nu = 2$		$\nu = 3$		OD	
	$\nu$	$\Delta\nu^a$	$\nu$	$\Delta\nu$	$\nu$	$\Delta\nu$	$\nu$	$\Delta\nu$	$\nu$	$\Delta\nu$
3(1,2) ← 2(1,1)	20452.02	-0.03	20524.05	-0.12						
4(0,4) ← 3(0,3)	24916.02	0.06	24953.82	0.11	24989.74	-0.09				
4(1,3) ← 3(1,2)	27144.31	-0.05	27235.17	0.01	27324.37	-0.02	27411.74	0.00	26913.85	0.01
4(1,4) ← 3(1,3)	24030.40	-0.11	24063.65	-0.09						
4(2,2) ← 3(2,1)	26559.39	-0.10	26657.93	-0.02	26755.51	-0.06	26851.95	0.05		
4(2,3) ← 3(2,2)	25701.58	0.10			25833.81	0.27				
5(0,5) ← 4(0,4)	30656.99	-0.03	30690.98	-0.03	30273.03	-0.03	30753.02	-0.07	30022.98	0.02
5(1,5) ← 4(1,4)	29905.84	-0.05	29942.96	0.01	29978.51	-0.02	30012.34	0.01	29355.32	-0.03
5(1,4) ← 4(1,3)	33709.15	-0.03	33812.86	-0.01	33914.26	-0.02	34013.12	-0.08	33358.98	-0.03
5(2,4) ← 4(2,3)	32011.50	-0.02	32090.33	0.03	32167.37	0.00	32242.35	0.00	31611.99	-0.01
5(2,3) ← 4(2,2)	33568.95	-0.05	33700.54	0.04	33830.70	0.00			33450.75	-0.03
5(3,3) ← 4(3,2)	32468.82	0.02	32567.74	0.07	32659.19	0.10	32751.93	0.28	32167.12	0.07
5(3,2) ← 4(3,1)	32608.65	-0.03	32713.08	0.04	32816.20	-0.07	32917.79	-0.22	32366.85	-0.12
5(4,2) ← 4(4,1)	32419.90	0.02	32515.13	-0.01	32608.80	-0.14	32701.05	0.05	32118.40	0.00
5(4,1) ← 4(4,0)	32423.04	-0.18	32518.74	-0.02	32612.83	-0.03	32705.16	-0.09	32123.93	-0.08
6(0,6) ← 5(0,5)	36272.99	0.02	36304.44	-0.01	36333.84	0.01	36361.14	-0.05	35487.63	0.05
6(1,6) ← 5(1,5)	35721.66	0.01	35761.11	0.01	35798.70	0.01	35834.24	0.01	35035.54	0.03
6(2,5) ← 5(2,4)	38247.62	0.06	38335.63	-0.01	38421.53	0.02	38504.90	0.10	37730.03	0.01
6(3,4) ← 5(3,3)	38999.65	0.08	39114.64	0.04	39227.76	0.05	39338.90	0.31	38632.17	0.06
6(3,3) ← 5(3,2)	39358.99	0.00	39495.12	-0.03	39630.15	-0.05	39763.71	0.31	39138.46	0.00
6(4,3) ← 5(4,2)	38967.39	0.04	39084.12	0.04	39199.08	0.08	39311.95	-0.07	38619.02	0.02
6(4,2) ← 5(4,1)	38982.21	-0.02	39100.12	-0.09	39216.54	0.05	39330.72	-0.16	38643.87	-0.03
6(5,2) ← 5(5,1)	38887.53	0.11	39001.45	0.13	39113.50	0.15	39223.47	0.07	38523.27	0.22
6(5,1) ← 5(5,0) <sup>b</sup>		-0.12		-0.12		-0.14				-0.23

<sup>a</sup> Observed - calculated. <sup>b</sup> Not resolved.

Table IV. Other Observed Transition Frequencies (MHz) of 3-Buten-2-ol, Conformer I

transition	$\nu$	$\Delta\nu^a$	transition	$\nu$	$\Delta\nu$
2(2,1) ← 1(1,1)	28318.40	-0.06	14(3,11) ← 14(3,12)	28011.28	-0.11
3(1,2) ← 2(0,2)	26739.85	-0.04	14(5,10) ← 14(4,10)	34577.70	-0.06
3(2,2) ← 2(1,2)	35550.31	0.04	15(3,12) ← 15(3,13)	34165.06	-0.06
3(2,1) ← 2(1,1)	33639.34	0.08	15(5,11) ← 15(4,11)	30828.16	-0.03
4(4,1) ← 4(3,1)	34889.78	0.11	16(5,12) ← 16(4,12)	26648.24	-0.01
4(1,3) ← 3(0,3)	34915.78	0.04	17(4,13) ← 17(4,14)	26826.63	-0.11
4(2,2) ← 3(1,2)	39746.75	0.04	18(4,14) ← 18(4,15)	33458.97	-0.10
6(3,3) ← 6(2,5)	27110.50	0.09	18(4,14) ← 18(3,15)	37222.74	-0.05
6(4,2) ← 6(3,4)	34874.79	0.01	18(5,13) ← 18(4,14)	30799.69	-0.07
7(3,4) ← 7(2,6)	28980.49	0.07	19(5,14) ← 19(4,15)	31998.15	-0.13
7(4,3) ← 7(3,5)	34954.90	0.17	19(6,14) ← 19(5,14)	36212.98	-0.12
7(4,4) ← 7(3,4)	33581.90	-0.20	20(5,15) ← 20(4,16)	34565.54	-0.07
8(3,5) ← 8(2,7)	31868.83	0.03	20(6,14) ← 20(5,15)	38029.78	-0.15
8(4,4) ← 8(3,6)	35245.04	0.10	20(6,15) ← 20(5,15)	31267.77	-0.08
8(4,5) ← 8(3,5)	32372.52	0.16	21(5,16) ← 21(5,17)	31366.04	-0.10
9(2,8) ← 9(0,9)	33601.21	0.15	21(5,16) ← 21(4,17)	38451.04	-0.05
9(1,8) ← 9(1,9)	30622.72	-0.09	21(6,15) ← 21(5,16)	36595.43	-0.10
9(3,7) ← 9(1,8)	33974.09	0.07	22(5,17) ← 22(5,18)	38685.20	-0.09
9(3,6) ← 9(2,8)	35987.20	0.03	22(6,16) ← 22(5,17)	36353.87	-0.09
9(4,5) ← 9(3,7)	35910.17	0.03	23(6,17) ← 23(5,18)	37520.00	-0.04
9(4,6) ← 9(3,6)	30570.40	0.02	24(6,18) ← 24(6,19)	28189.94	-0.03
10(2,9) ← 10(0,10)	37272.57	0.25	24(7,18) ← 24(6,18)	35725.57	-0.14
10(1,9) ← 10(1,10)	35397.42	-0.04	25(6,19) ← 25(6,20)	35764.31	-0.05
10(3,8) ← 10(1,9)	35324.11	0.06	25(7,19) ← 25(6,19)	29843.73	-0.01
10(4,6) ← 10(3,8)	37169.54	0.12	28(7,21) ← 28(7,22)	31825.79	0.14
10(4,7) ← 10(3,7)	28153.63	0.03	29(8,22) ← 29(7,22)	33465.87	0.28
11(3,9) ← 11(1,10)	37408.67	0.07	31(8,23) ← 31(8,24)	27247.59	0.09
11(2,9) ← 11(2,10)	27720.03	-0.05	32(8,24) ← 32(8,25)	35401.93	0.20
11(4,7) ← 11(3,9)	39284.88	-0.03	34(9,26) ← 34(8,26)	29878.09	0.07
12(2,10) ← 12(2,11)	33262.58	-0.02	35(9,26) ← 35(9,27)	30171.68	0.07
13(2,11) ← 13(2,12)	38684.22	0.02	36(9,27) ← 36(9,28)	38938.12	0.16
13(5,9) ← 13(4,9)	37728.27	-0.09	39(10,29) ← 39(10,30)	33085.20	-0.22

<sup>a</sup> Observed - calculated.

the structure of 3-buten-1-ol.<sup>5,16</sup> The calculated rotational constants and dipole moment components for the most probable conformers are shown in Table II.

**Conformer I.** The first transitions assigned at Harvard were K doublets of  $J = 6 \leftarrow 5$  and  $5 \leftarrow 4$  a-type R-branch transitions which were seen at low Stark voltages and then confirmed by RFMWR. The  $J = 3 \leftarrow 2$  and  $J = 4 \leftarrow 3$  a-type R-branch

transitions were first assigned by the Stark effect and rigid rotor fit in Oslo. R-type lines (a and c, up to  $J = 6$ ) determined B, C,  $\Delta J_K$ , and A, the latter only moderately well. Subsequently Q-branch transitions (a-, b-, and c-type) were assigned up to  $J = 40$ , the difficulty being that Q-branch transitions for lower  $J$ 's were very weak. The same strategy was also used for the deuterated species. The measured frequencies are listed in Tables III, IV, and V and the rotational constants and the centrifugal distortion constants are shown in Table VI, all for the conformer labeled I (see Figure 1).

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Table V. Other Observed Transition Frequencies (MHz) of CH<sub>2</sub>=CHCH(OD)CH<sub>3</sub>, Conformer I

transition	$\nu$	$\Delta\nu^a$	transition	$\nu$	$\Delta\nu$
2(2,1) ← 1(1,1)	26936.08	0.01	18(6,13) ← 18(5,13)	31235.66	-0.01
3(2,2) ← 2(1,2)	34150.01	0.13	20(5,15) ← 20(5,16)	32561.38	-0.17
3(2,1) ← 2(1,1)	32188.11	0.08	21(5,16) ← 21(5,17)	39912.90	-0.04
4(1,3) ← 3(0,3)	34508.52	-0.04	21(7,15) ← 21(6,15)	39559.09	-0.03
4(2,2) ← 3(1,2)	38325.38	-0.03	22(7,16) ← 22(6,16)	34083.19	-0.12
8(3,5) ← 8(2,7)	31483.30	0.04	23(6,17) ← 23(6,18)	31364.23	-0.11
8(4,4) ← 8(3,6)	32569.16	-0.04	23(7,17) ← 23(6,17)	28304.11	-0.14
8(4,5) ← 8(3,5)	28609.88	0.04	24(6,18) ← 24(6,19)	39206.24	-0.04
9(3,6) ← 9(2,8)	36469.15	-0.08	26(7,19) ← 26(7,20)	29393.83	-0.05
9(4,5) ← 9(3,7)	33600.01	0.01	26(8,19) ← 26(7,19)	36366.00	-0.17
11(3,9) ← 11(1,10)	36469.16	0.08	27(7,20) ← 27(7,21)	37562.63	0.04
11(4,7) ← 11(3,9)	38477.12	-0.17	27(8,20) ← 27(7,20)	29879.44	-0.09
11(5,7) ← 11(4,7)	36989.12	0.08	29(8,21) ← 29(8,22)	26839.37	-0.06
12(3,10) ← 12(1,11)	39608.83	0.14	30(8,22) ← 30(8,23)	35138.51	0.19
12(2,10) ← 12(2,11)	35344.98	0.00	30(9,22) ← 30(8,22)	38125.06	0.05
12(5,8) ← 12(4,8)	34617.13	0.10	31(9,23) ← 31(8,23)	30996.86	0.21
13(5,9) ← 13(4,9)	31508.02	0.11	36(10,26) ← 36(10,27)	28694.56	0.10
14(5,10) ← 14(4,10)	27768.51	0.10	37(10,27) ← 37(10,28)	37794.36	0.23
15(3,12) ← 15(3,13)	38052.95	-0.01	40(11,29) ← 40(11,30)	33911.97	-0.24
17(6,12) ← 17(5,12)	35864.02	0.01			

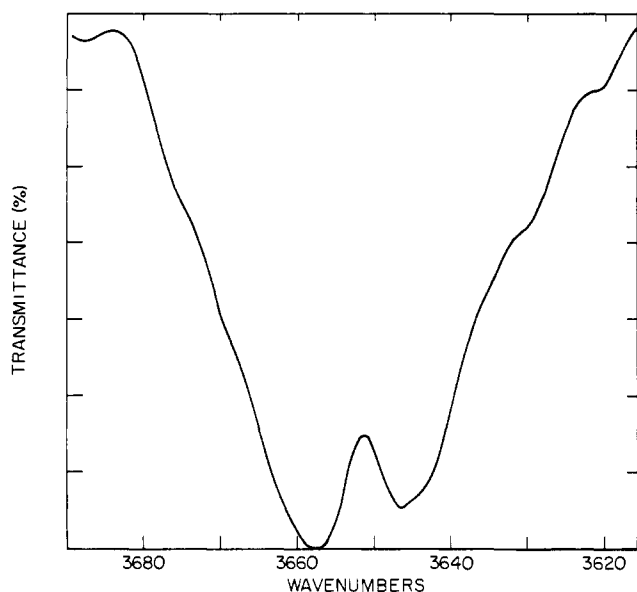
<sup>a</sup> Observed - calculated.

Figure 2. OH stretching absorption band (3-buten-2-ol) in vapor.

**Vibrationally Excited States of I.** The ground-state vibrational lines of I were accompanied by relatively intense satellites toward higher frequencies. With the aid of RFMWDR, three vibrationally excited states were identified and R-type transitions were measured. The measured frequencies are listed in Table III, and the rotational constants and  $\Delta_{JK}$ 's are shown in Table VI. This vibrational mode must be quite harmonic, because the changes in the rotational constants are very constant. The values in Table VI for the rotational constants corrected for this vibrational mode were obtained from formulas of the type  $A_v = A_0 - \alpha^A(v + 1/2) + \beta^A(v + 1/2)^2$ .

Relative intensity measurements of the most intense satellite were made by employing the method of Esbitt and Wilson.<sup>17</sup> These led to the value of  $91 \pm 19 \text{ cm}^{-1}$  for the vibrational frequency, determined from nine different transitions. A similar frequency has been found in 1-butene,<sup>8</sup> 3-buten-1-ol,<sup>5</sup> and 2,3-butadien-1-ol,<sup>6</sup> namely, 93 (4), 84 (20), and 90 (30)  $\text{cm}^{-1}$ , respectively. In all three molecules it was assigned to the C<sub>2</sub>-C<sub>3</sub> torsional mode which also seems a reasonable choice for 3-buten-2-ol, form I.

**Conformer II.** From the estimated rotational constants, the microwave spectra of other conformers with reasonably strong a-type dipole moments were predicted to have distinct K doublets

Table VI. Rotational and Centrifugal Distortion Constants of 3-Buten-2-ol, Conformer I

	ground state	$v = 1$	$v = 2$	$v = 3$	OD
A	8234.201 (7)	8234.1 (2)	8233.0 (3)	8231.7 (5)	7776.389 (10)
B	3616.184 (7)	3632.383 (7)	3648.40 (1)	3664.18 (1)	3607.173 (9)
C	2827.474 (6)	2828.655 (6)	2829.734 (9)	2830.67 (1)	2766.377 (9)
$\Delta_J$	0.91 (11)	<i>b</i>	<i>b</i>	<i>b</i>	0.80 (14)
$\Delta_{JK}$	21.33 (5)	21.1 (2)	21.5 (2)	21.5 (1)	21.48 (7)
$\Delta_K$	-15.2 (3)	<i>b</i>	<i>b</i>	<i>b</i>	-16.3 (4)
$\delta_J$	0.155 (2)	<i>b</i>	<i>b</i>	<i>b</i>	0.166 (3)
$\delta_{JK}$	9.32 (5)	<i>b</i>	<i>b</i>	<i>b</i>	9.58 (7)
$A_0$	8234.15 (31)	$\alpha^A = -0.3$ (4)	$\beta^A = -0.30$ (9)		
$B_0$	3608.00 (2)	$\alpha^B = -16.42$ (3)	$\beta^B = -0.105$ (6)		
$C_0$	2826.81 (1)	$\alpha^C = -1.33$ (1)	$\beta^C = -0.064$ (3)		

<sup>a</sup> Rotational constants A, B, and C are in MHz. Centrifugal distortion constants are in kHz. Standard deviations are given in parentheses. <sup>b</sup> The value of the ground state was assumed.

of  $J = 5 \leftarrow 4$  and  $6 \leftarrow 5$  similar to those of the identified conformer I. Unfortunately, the stronger  $J = 6 \leftarrow 5$  doublets were predicted to be at higher frequencies than 40 GHz (the limit of the R band). Extensive searches for the other R transitions were performed with low Stark voltage and RFMWDR techniques. However, the lines which might have belonged to another conformer were very weak.

On the other hand, there were many strong unidentified lines in the spectrum for which it was not possible to resolve the Stark pattern. They were judged to be high- $J$  Q-branch lines of a second conformer (II) with a small value of  $\mu_a$ .

The only other rotamer in Table II predicted to have a small value of  $\mu_a$  and to be somewhat stabilized by weak H bonding would have OH in the syn position and the hydroxylic H in the gauche position (anti to H on C<sub>2</sub>).

The predicted rotational constants and dipole moment components (from additivity rules) were used as the start of a standard graphical fitting procedure in which plots of  $\log \Delta E_{J,K,\tau}(\kappa)$  vs. the asymmetry parameter  $\kappa$  were made for a number of b-type Q branches of high calculated intensities ( $J$  between 15 and 22). Then the log of the frequency of each of the strong unidentified transitions was marked on a scale, which was moved up and down and also sideways until the marks for the observed lines fitted the plotted curves for some particular value of  $\kappa$  and of the vertical position (which gives  $\log [(A - C)/2]$ ). By trial and error and considerable patience a good fit was ultimately found which was improved by introducing a set of centrifugal distortion coefficients as a correction on the observed frequencies.

(17) Esbitt, A. S.; Wilson, E. B. *Rev. Sci. Instrum.* **1963**, *34*, 901-907.

Table VII. Observed b-Type Transition Frequencies (MHz) of 3-Buten-2-ol, Conformer II

transition	$\nu$	$\Delta\nu^a$	transition	$\nu$	$\Delta\nu$
2(2,1) ← 1(1,0)	27177.20	-0.07	12(4,9) ← 12(3,10)	39662.57	-0.07
4(1,4) ← 3(0,3)	27776.32	-0.04	12(5,7) ← 12(4,8)	32520.22	0.01
5(0,5) ← 4(1,4)	30926.04	0.14	13(3,10) ← 13(4,9)	24849.63	0.04
6(0,6) ← 5(1,5)	37386.16	-0.08	13(5,8) ← 13(4,9)	30103.16	0.00
6(1,6) ← 5(0,5)	38553.36	0.01	14(4,10) ← 14(3,11)	28281.14	-0.05
6(4,2) ← 6(3,3)	30585.74	-0.02	14(5,9) ← 14(4,10)	28401.26	-0.01
6(4,3) ← 6(3,4)	31843.25	0.01	15(5,10) ← 15(4,11)	27951.23	0.00
7(2,6) ← 7(3,5)	27291.84	0.02	15(6,9) ← 15(5,10)	39775.27	0.06
8(2,7) ← 8(3,6)	29657.43	-0.27	16(4,12) ← 16(3,13)	39046.34	-0.03
8(4,4) ← 8(3,5)	27475.19	0.03	16(5,11) ← 16(4,12)	29111.94	-0.02
8(4,5) ← 8(3,6)	32587.55	-0.05	16(6,10) ← 16(5,11)	36785.01	-0.01
9(1,8) ← 9(2,7)	25222.49	-0.17	17(5,12) ← 17(4,13)	32031.01	-0.08
9(4,6) ← 9(3,7)	33536.00	-0.04	17(6,11) ← 17(5,12)	34353.12	-0.01
10(2,8) ← 10(3,7)	20595.15	-0.12	18(5,13) ← 18(4,14)	36613.89	-0.01
10(4,6) ← 10(3,7)	23664.12	0.00	18(6,12) ← 18(5,13)	33101.86	-0.01
10(4,7) ← 10(3,8)	35002.49	-0.04	19(6,13) ← 19(5,14)	33494.93	0.00
10(5,5) ← 10(4,6)	37217.91	0.01	20(6,14) ← 20(5,15)	35770.64	0.00
11(4,7) ← 11(3,8)	22712.11	0.00	21(6,15) ← 21(5,16)	39915.47	0.06
11(4,8) ← 11(3,9)	37042.01	-0.05	21(7,14) ← 21(6,15)	38535.21	0.00
11(5,6) ← 11(4,7)	35051.95	-0.01	22(7,15) ← 22(6,16)	38087.74	0.00
12(2,10) ← 12(3,9)	29401.58	0.08	23(7,16) ← 23(6,17)	39604.19	0.04
12(4,8) ← 12(3,9)	23018.26	-0.07			

<sup>a</sup> Observed - calculated.Table VIII. Rotational Constants and Centrifugal Distortion Constants of 3-Buten-2-ol, Conformer II<sup>a</sup>

	ground state		O-H $\nu = 1$	O-H $\nu = 2$
	O-H	O-D		
<i>A</i>	8068.20 (1)	7731.95 (3)	<i>A</i> - <i>C</i> 5069.76 (1)	5046.10 (1)
<i>B</i>	3989.58 (1)	3959.30 (2)	$\kappa$ -0.601	-0.601
<i>C</i>	2972.85 (1)	2937.64 (2)		
$\Delta_J$	0.42 (20)	0.17 (36)		
$\Delta_{JK}$	1.11 (13)	2.02 (16)		
$\Delta_K$	10.08 (52)	7.30 (62)	13.8 (6)	12.1 (4)
$\delta_J$	0.17 (1)	0.15 (1)	0.13 (1)	0.177 (3)
$\delta_K$	3.00 (12)	3.25 (17)	3.6 (1)	2.80 (1)

<sup>a</sup> Rotational constants are in MHz and centrifugal distortion constants in kHz. Standard deviations are given in parentheses.

Table VII shows the final agreement between the observed and calculated b-type transitions. The remaining rotational constant *A* was obtained from the observed *R<sub>b</sub>* transitions, and the rotational constants and CD coefficients are tabulated in Table VIII. Neither a-type nor c-type lines were identified. The deuterated species was also analyzed, and the measured transitions are listed in Table IX.

**Vibrationally Excited States of II.** The ground-state vibrational lines of II were accompanied by relatively intense satellites toward lower frequencies. Two vibrationally excited states were identified, and *Q<sub>b</sub>*-type transitions were measured. The measured transitions are listed in Table X, and the differences *A*-*C* and asymmetry parameters  $\kappa$  are shown in Table VIII.

From the relative intensity measurements<sup>17</sup> of six different transitions, the lowest vibrational frequency (probably the *C*<sub>2</sub>-*C*<sub>3</sub> torsional mode) was determined to be 138 (53) cm<sup>-1</sup>.

### Dipole Moment

**Conformer I.** The absorption cell spacing was calibrated by using the OCS transitions  $J = 2 \leftarrow 1$  and  $J = 3 \leftarrow 2$  with  $\mu(\text{OCS}) = 0.71521$  D.<sup>18</sup> The dipole moment components along the principal axes of inertia were determined from a measurement of the Stark components of the a-type  $3 \leftarrow 2$ ,  $4 \leftarrow 3$ ,  $5 \leftarrow 4$ , and  $6 \leftarrow 5$  transitions. Each component was studied for about four different voltages in the range 200-1700 V; the graphs obtained for  $(\Delta\nu/E^2)$  vs.  $E^2$  were fairly linear, and their intercepts were used. The second-order Stark coefficients and the dipole moment are shown in Table XI. Bond-moment calculations<sup>19</sup> yielded  $\mu_a = 1.5$  D,

$\mu_b = 0.2$  D, and  $\mu_c = 0.6$  D, in fair agreement with the experimental results.

**Conformer II.** From the predicted structure, bond-moment calculations<sup>19</sup> yielded  $\mu_a = 0.4$  D,  $\mu_b = 1.2$  D, and  $\mu_c = 1.13$  D. From the final structure of conformer II (see below), the calculated dipole moment components were 0.2, 1.1, and 1.1 D, respectively. However, in spite of the large predicted  $\mu_c$  dipole moment, no experimental c-type transitions were found. Also due to the weakness of the transitions and the fact that the stronger observed transitions have high *J* values, no transitions were found which would be suitable for measurement of the individual Stark components.

### Energy Difference between Conformers I and II

The energy difference was estimated from the ratio of the intensities of transitions of the two conformers. Harrington's saturation method<sup>20</sup> for intensities and also the usual method which employs unsaturated lines<sup>17</sup> were used. The need to use a calculated value for  $\mu_b$  (1.1 D) will introduce error (a 10% error in  $\mu_b$  would mean an error of  $\sim 80$  cal/mol in  $\Delta E$ ). This source of error could be eliminated by measuring at two temperatures, but for the small achievable range of temperatures, the two-temperature method introduces a worse error of its own. The results of the two methods used agreed within their standard deviations, and the average value was 520 (140) cal/mol, the conformer I being the more stable.

### Structure

Six moments of inertia were determined for each conformer of the 3-buten-2-ol molecule; therefore only limited information about its structure could be inferred. The initial structural parameters were transferred electron-diffraction values from 3-buten-1-ol<sup>16</sup> (see Table XII). The neutron diffraction OH distance<sup>21</sup> 0.969 Å was used. It is an average over a number of molecules. It was also assumed that the dihedral angle differences (*C*=*C*-*C*-*O*) - (*C*=*C*-*C*-*C*) = (*C*=*C*-*C*-*C*) - (*C*=*C*-*C*-*H*) were 120°.

**Conformer I.** It was quickly established that the dihedral angles of the oxygen and of the methyl carbon are about 120° and -120° from syn, respectively (see Figure 1). Several parameters were then adjusted in order to fit the six rotational constants and the Kraitchman's coordinates of the hydroxylic hydrogen. The OH hydrogen is oriented roughly anti to *C*<sub>1</sub>-*C*<sub>2</sub>. The assumed and the final adjusted parameters are listed in Table XII, and the comparison between the observed and model values of the rota-

(18) Muentzer, J. S. *J. Chem. Phys.* **1968**, *48*, 4544-4547.

(19) Smyth, C. P. "Dielectric Behavior and Structure"; McGraw-Hill: New York, 1955; p 244.

(20) Harrington, H. W. *J. Chem. Phys.* **1967**, *46*, 3698-3707.(21) Ceccarelli, C.; Jeffrey, G. A.; Taylor, R. *J. Mol. Struct.* **1981**, *70*, 255-271.

Table IX. Observed b-Type Transition Frequencies of CH<sub>2</sub>=CHCH(OD)CH<sub>3</sub>, Conformer II

transition	$\nu$	$\Delta\nu^a$	transition	$\nu$	$\Delta\nu$
4(1,4) ← 3(0,3)	27219.48	0.04	12(3,9) ← 12(2,10)	29841.45	0.10
5(1,5) ← 4(0,4)	32498.12	0.08	13(3,10) ← 13(2,11)	35620.50	-0.16
5(0,5) ← 4(1,4)	30691.12	-0.14	13(5,8) ← 13(4,9)	27167.97	0.04
6(1,6) ← 5(0,5)	37955.08	0.09	14(4,10) ← 14(3,11)	28622.95	0.00
6(0,6) ← 5(1,5)	37013.14	-0.07	15(4,11) ← 15(3,12)	33948.93	-0.11
6(4,2) ← 6(3,3)	28305.15	0.04	16(5,11) ← 16(4,12)	28566.77	0.12
8(3,6) ← 8(2,7)	28482.32	0.09	16(6,10) ← 16(5,11)	32833.35	-0.24
8(5,3) ← 8(4,4)	36904.97	-0.06	17(5,12) ← 17(4,13)	32418.15	0.08
9(3,7) ← 9(2,8)	31482.03	-0.17	17(6,11) ← 17(5,12)	31115.75	0.02
9(4,6) ← 9(3,7)	31698.87	-0.13	18(5,13) ← 18(4,14)	37739.54	0.16
9(5,4) ← 9(4,5)	35758.82	0.01	18(6,12) ← 18(5,13)	30903.26	0.02
10(3,8) ← 10(2,9)	34951.64	-0.01	19(6,13) ← 19(5,14)	32529.36	0.01
10(5,5) ← 10(4,6)	34016.37	0.09	20(6,14) ← 20(5,15)	36065.17	-0.16
11(2,9) ← 11(1,10)	36206.65	0.12	20(7,13) ← 20(6,14)	36280.90	0.10
11(4,8) ← 11(3,9)	35528.08	0.22	22(7,15) ← 22(6,16)	36499.78	-0.03
11(5,6) ← 11(4,7)	31733.92	0.09			

<sup>a</sup> Observed - calculated.Table X. Observed Q<sub>b</sub> Transitions (MHz) of 3-Buten-2-ol, Conformer II, Excited States

transition	$v = 1$		$v = 2$	
	$\nu$	$\Delta\nu^a$	$\nu$	$\Delta\nu$
8(4,4) ← 8(3,5)	27333.16	-0.10		
9(4,6) ← 9(3,7)	33368.23	0.03		
10(4,6) ← 10(3,7)	23541.77	-0.12	23432.92	-0.04
10(4,7) ← 10(3,8)	34828.50	-0.05		
10(5,5) ← 10(4,6)			36854.73	0.07
11(4,7) ← 11(4,8)	22596.44	-0.06	22491.69	-0.05
11(4,8) ← 11(3,9)	36859.21	-0.13	36687.17	0.00
11(5,6) ← 11(4,7)	34869.98	0.07	34708.94	0.04
12(4,8) ← 12(3,9)	22904.04	-0.01	22797.33	-0.05
12(4,9) ← 12(3,10)	39468.60	0.16		
12(5,7) ← 12(4,8)	32350.38	0.00		
13(5,8) ← 13(4,9)	29946.12	-0.02	29808.38	0.00
14(4,10) ← 14(3,11)	28148.32	0.03	28015.60	0.08
14(5,9) ← 14(4,10)	28254.95	0.00	28124.80	0.03
15(5,10) ← 15(4,11)	27810.78	0.01	27682.03	0.07
16(5,11) ← 16(4,12)	28970.41	0.03	28835.02	-0.04
17(5,12) ← 17(4,13)	31880.14	-0.03	31729.88	-0.01
17(6,11) ← 17(5,12)	34174.24	0.16	34017.93	0.01
18(5,13) ← 18(4,14)	36445.13	-0.06	36272.00	-0.05
18(6,12) ← 18(5,13)	32933.44	0.17	32781.97	0.01
19(6,13) ← 19(5,14)	33330.14	0.09	33175.40	0.08
20(6,14) ← 20(5,15)			35433.65	0.11
21(6,15) ← 21(5,16)			39542.50	-0.05
21(7,14) ← 21(6,15)	38336.00	-0.21	38162.00	0.02
22(7,15) ← 22(6,16)			37723.40	0.18

<sup>a</sup> Observed - calculated.

tional constants and the  $r_s$  coordinates is shown in Table XIII. It was possible to fit the experimental parameters reasonably well with very few small changes in the structural parameters, but these are not unique. The calculation of dipole moment components from bond moments also supports the conformational assignment, see Tables II and XI.

**Conformer II.** The assignment of the structure of II was not as obvious, mainly due to the fact that no c-type lines were found. Also, the values of the experimental rotational constants were close to the predicted rotational constants of several possible conformers. With the aid of the rotational constants of the OD species and the Kraitchman coordinates of the hydroxylic hydrogen it was possible to confirm the structure which had been used to predict and analyze the spectrum (see Figure 1). This structure has OH in the syn position, CH<sub>3</sub> skew, and the hydroxylic hydrogen fairly near the double bond (anti to the hydrogen on carbon two). Very few small changes in the structural parameters were necessary in order to fit the six rotational constants and the Kraitchman coordinates (see Tables XII and XIII), but again, these parameters are not uniquely determined by the available data.

### Discussion

**Other Conformers.** There still remain a good many unidentified and moderately strong lines. Some of these are probably vibra-

Table XI. Stark Coefficients and Dipole Moment of 3-Buten-2-ol, Conformer I<sup>a</sup>

transition	M	$\Delta\nu/E^2$ (MHz V <sup>-2</sup> cm <sup>2</sup> ) × 10 <sup>6</sup>	
		obsd	calcd
3(1,2) ← 2(1,1)	1	-4.30	-4.05
	2	-15.60	-15.27
4(0,4) ← 3(0,3)	2	1.05	1.06
	3	2.60	2.83
4(1,4) ← 3(1,3)	0	-0.57	-0.64
	2	2.45	2.20
	3	6.27	5.74
4(2,2) ← 3(2,1)	1	-22.60	-21.70
	2	-87.60	-88.91
5(1,5) ← 4(1,4)	0	-0.27	-0.27
	2	0.86	0.85
	3	2.28	2.24
	4	4.20	4.20
5(2,4) ← 4(2,3)	0	-0.66	-0.86
	1	2.15	1.71
6(0,6) ← 5(0,5)	0	-0.18	-0.18
	1	-0.38	-0.38
	2	-1.10	-0.96
	3	-1.95	-1.94
6(1,6) ← 5(1,5)	4	-3.20	-3.31
	0	-0.13	-0.16
	1	0.08	0.14
	2	1.05	1.04
6(3,3) ← 5(3,2)	3	2.69	2.54
	4	4.86	4.64
	0	0.32	0.47
	1	-20.32	-18.01
6(3,4) ← 5(3,3)	0	0.30	0.46
	1	21.30	-18.92

<sup>a</sup>  $\mu_a = 1.30$  (1);  $\mu_b = 0.31$  (1);  $\mu_c = 0.47$  (7);  $\mu_{TOT} = 1.41$  (2).

tional satellites for low frequencies of both forms I and II, but it seems very likely that some of them arise from at least one additional conformation. One might expect that the unidentified conformer (or conformers) also contains a weak hydrogen bond, and that would mean the conformer on either line 4 or 7 in Table II (namely CH<sub>3</sub> syn with the hydroxylic H anti to the H on C<sub>2</sub> and OH syn with the hydroxylic H anti to the methyl group).

**Problems with Structural Determination in Hydrogen-Bonded Systems.** It has been observed that in hydrogen-bonded O···H—O, O—H···N, and O···H—N systems, the O···O (or O···N) effective distance changes upon deuteration (the Ubbelohde effect, e.g., ref 22–25). It was established that either contraction or elongation occurs depending on the molecule. In the 2-aminoethanol<sup>22</sup> and

Table XII. Plausible Structural Parameters of 3-Buten-2-ol

Assumed Parameters <sup>a</sup>					
C=C	1.331	C <sub>1</sub> -H	1.093	C-C-O	112.3
C <sub>2</sub> -C <sub>3</sub>	1.496	C <sub>2</sub> -H	1.093	C-O-H	105.0
C <sub>1</sub> -C <sub>2</sub>	1.528	C <sub>3</sub> -H	1.090	C=C-H	121.5
C-O	1.415	C <sub>4</sub> -H	1.090	H-C-H	109.5
O-H	0.969				
Adjusted Parameters					
		conformer I		conformer II	
C=C-C		126.8		126.8	
C-C-C		110.3		112.3	
$\alpha^b$		122.0		4.0	
$\beta^c$		53.0 <sup>d</sup>		70.0 <sup>e</sup>	

<sup>a</sup> Parameters taken from ref 16, O-H distance from ref 21. Bond distances are given in angstroms and angles in degrees. <sup>b</sup> Dihedral angle O-C-C=C. <sup>c</sup> Dihedral angle H-O-C<sub>2</sub>-C<sub>3</sub>. <sup>d</sup> Roughly anti to the methyl group. <sup>e</sup> Roughly anti to the hydrogen on carbon two.

Table XIII. Comparison of Observed and Model Values of the Rotational Constants and the  $r_s$  Coordinates of 3-Buten-1-ol

	OH species		OD species		change upon deuteration	
	calcd	obsd - calcd	calcd	obsd - calcd	calcd	obsd - calcd
Conformer I						
A	8240.3	-6.1	7787.5	-11.1	452.8	5.0
B	3625.0	-8.8	3615.1	-7.9	9.9	-0.9
C	2824.5	3.0	2763.8	2.6	60.7	0.4
Conformer II						
A	8068.2	5.1	7732.0	-1.9	336.2	7.0
B	3989.6	0.4	3959.3	1.5	30.3	-1.1
C	2972.9	-22.9	2937.6	-23.7	35.3	0.8
Kraitchman's Coordinates for Hydroxylic Hydrogen						
		from rotational constants	from molecular model	diff		
Conformer I						
a		0.573	0.598	0.025		
b		1.910	1.898	0.012		
c		0.091	0.091 <sup>b</sup>	0.000		
Conformer II						
a		0.370	0.381	0.011		
b		1.371	1.340 <sup>b</sup>	0.031		
c		0.934	0.949 <sup>b</sup>	0.015		

<sup>a</sup> Rotational constants are in MHz and coordinates in Å. <sup>b</sup> This coordinate calculated from the model is negative.

malonaldehyde<sup>23</sup> molecules, this effect was measured by double substitution of the two heavy atoms, and it was found to be -0.006 Å (shrinkage of the OH...N to OD...N distance) and 0.021 Å (elongation of the O...O distance), respectively. In (2-methoxyethyl amine,<sup>24</sup> which exists in a gauche form with an intramo-

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lecular hydrogen bond of the N-H...O type, the four isotopes NH<sub>2</sub>, NHD, NDH, and D<sub>2</sub> were assigned; the four possible sets of the amino hydrogen  $r_s$  coordinates gave different H...H distances. In other molecules, shorter or longer O-H or N-H distances than usual were found, which could be corrected to normal values by adjusting the O...O or O...N distance.<sup>25</sup> Thus an unusual apparent OH bond length value can be a symptom of elongation (or shrinkage) of the appropriate non-bonded distance on deuteration and consequently this may suggest the presence of H bonding.

**OH Distance in Unsaturated Alcohols.** In allyl alcohol Murty and Curf<sup>2</sup> determined the O-H distance by the usual substitution method, obtaining 0.97 Å, which agrees very well with the neutron diffraction value averaged over many molecules of 0.969 Å.<sup>21</sup> In 2,3-butadiene-1-ol an assumed OH distance (0.95 Å) was used to fit rotational constants of the parent and OD species. It seems that in these unsaturated alcohols as well as in the title compound there is no shift of heavy atoms upon deuteration, which may indicate that the hydrogen bond in these systems is very weak. In 3-buten-1-ol, however, a 1.15 Å O-H distance was used<sup>5</sup> in order to reproduce Kraitchman's coordinates *a* and *b* reasonably well. Unfortunately, there have not been enough isotopic species studied in order to verify this rather large value.

**Evidence for Hydrogen Bonding.** There are three observations which support the view that both conformations I and II should be considered to be weakly hydrogen bonded. First, the plausible structures (Table XII) give distances between the hydroxylic hydrogen and C<sub>3</sub> and C<sub>4</sub> of 2.49 and 3.34 Å, respectively, for form I and 2.63 and 2.81 Å for form II. The sum of the van der Waals radii of H and of the aromatic carbon is 2.90 Å.<sup>26</sup> The distance to C<sub>3</sub> has therefore shrunk in both forms. This sort of contraction is often used as evidence for H bonding.

Second, the two conformations of presumably highest abundance (I and II) both have the OH group oriented about C-O in the direction which brings H nearer to C<sub>3</sub> than either of the other staggered configurations of the OH.

Third, there seems to be an anomaly in the  $\mu_c$  dipole component. Unfortunately, complete dipole data were not obtained experimentally, but the absence of c-type transitions in II despite the rather large  $\mu_c$  predicted from bond dipole additivity suggests that there may be an effect of H bonding on  $\mu_c$ . The above are in addition to the OH frequency shift indication.

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**Registry No.** CH<sub>2</sub>=CHCH(OH)CH<sub>3</sub>, 598-32-3; CH<sub>2</sub>=CHCH(O-D)CH<sub>3</sub>, 91461-77-7.

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