Microwave Spectrum, Conformational Equilibrium, Intramolecular Hydrogen Bonding, Dipole Moments and Centrifugal Distortion Constants of 3-Butyn-2-ol

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The microwave spectra of $CH_3CH(OH)C \equiv CH$ and one deuterated species, $CH_3CH(OD)-$ $-C \equiv CH$, have been studied in the 20.6−38.1 GHz spectral region at about −25 °C. Two $H-O-C-C \equiv C$ *gauche* conformations, each possessing an intramolecular hydrogen bond formed between the hydroxyl group hydrogen atom and the π-electrons of the triple bond were assigned. The energy difference between these two conformers is 0.4(4) kJ/mol, with the one denoted II being more stable than I. The third possible *anti* conformation denoted III is, if it exists, estimated to be at least 4 kJ/mol less stable than the two identified forms I and II.

The dipole moments are $\mu_a=0.944(17)$ D, $\mu_b \sim 0$ D, $\mu_c=0.777(17)$ D, and $\mu_{tot.}=1.233(20)$ D for I, and $\mu_a=0.629(14)$ D, $\mu_b=1.039(21)$ D, $\mu_c=0.594(9)$ D, and $\mu_{tot.}=1.352(21)$ D for II, respectively.

Three different vibrationally excited states were assigned for I, while two such states were identified for II. Extensive centrifugal distortion analyses were carried out for both rotamers.

In a penetrating study of the microwave spectrum of propargyl alcohol, $HOCH_2C \equiv CH$, Hirota[1] showed that this molecule exists *only* in the $H-O-C-C$ *gauche* conformation. The potential function he derived for the $C-O$ torsion has maxima in the *syn* and *anti* positions. Moreover, IR-studies[2] revealed that an intramolecular hydrogen bond is formed between the hydroxyl group hydrogen atom and the π-electrons of the triple bond in this molecule. A theoretical study[3] also indicates that internal hydrogen bonding is of importance in $HOCH_2C \equiv CH$.

As an extension of these studies, 3-butyn-2-ol, $CH_3CH(OH)C \equiv CH$, was selected for investigation. Three rotameric forms are possible for this molecule as shown in Fig. 1. Conformations I and II of this figure may possess intramolecular hydrogen bonds, while this interaction is not possible for III. The main object of this study has thus been to investigate the conformational behaviour of $CH_3CH(OH)C \equiv CH$ and the role played by internal hydrogen bonding for its conformational preferences. It is found that conformations I and II are preferred with II being more stable by 0.4(4) kJ/mol. Conformation III, if it exists, is at least 4 kJ/mol less stable than the two assigned rotamers I and II.

EXPERIMENTAL

A commercial sample of 3-butyn-2-ol was purified by gas chromatography before use. The spectrum was investigated in the 20.6−38.1 GHz spectral range with the cell cooled to about

Table 1. Selected transitions for the ground vibrational state of conformation I of $CH_3CH(OH)C \equiv CH$.

Transition	Observed frequency[a] (MHz)	Obs.-calc. frequency (MHz)	Centrifugal distortion	
			Total (MHz)	Sextic (MHz)
a-type				
$3_{1,2} \leftarrow 2_{1,1}$	21723.09	−0.03	−0.21	
$3_{2,1} \leftarrow 2_{2,0}$	20860.16	−0.10	−0.45	
$4_{0,4} \leftarrow 3_{0,3}$	25961.33	−0.07	−0.10	
$4_{1,3} \leftarrow 3_{1,2}$	28785.38	0.03	−0.35	
$4_{1,4} \leftarrow 3_{1,3}$	24970.85	0.00	−0.15	
$4_{2,2} \leftarrow 3_{2,1}$	28217.63	0.01	−0.69	
$4_{2,3} \leftarrow 3_{2,2}$	27039.02	0.05	−0.57	
$4_{3,1} \leftarrow 3_{3,0}$	27435.09	−0.01	−1.22	
$4_{3,2} \leftarrow 3_{3,1}$	27370.02	0.08	−1.20	
$5_{0,5} \leftarrow 4_{0,4}$	31824.66	−0.15	−0.23	
$5_{1,4} \leftarrow 4_{1,3}$	35662.44	−0.03	−0.55	
$5_{1,5} \leftarrow 4_{1,4}$	31035.20	−0.03	−0.26	
$5_{2,4} \leftarrow 4_{2,3}$	33637.25	−0.01	−0.77	
$5_{3,2} \leftarrow 4_{3,1}$	34490.06	0.01	−1.64	
$5_{3,3} \leftarrow 4_{3,2}$	34267.80	−0.04	−1.58	
$6_{1,6} \leftarrow 5_{1,5}$	37024.19	0.03	−0.43	
$14_{3,11} \leftarrow 14_{3,12}$	36633.62	−0.02	−9.42	
$16_{4,12} \leftarrow 16_{4,13}$	29598.56	0.03	−8.45	−0.01
$19_{5,14} \leftarrow 19_{5,15}$	28498.13	−0.03	−8.25	−0.03
$23_{6,17} \leftarrow 23_{6,18}$	34864.88	−0.01	−9.91	−0.09
$32_{9,23} \leftarrow 32_{9,24}$	25267.81	−0.13	23.94	−0.63
$36_{10,26} \leftarrow 36_{10,27}$	30097.28	−0.09	47.84	−1.26
$40_{11,29} \leftarrow 40_{11,30}$	35306.71	0.17	84.02	−2.36
$43_{12,31} \leftarrow 43_{12,32}$	30289.90	0.16	120.23	−3.32
c-type				
$2_{2,1} \leftarrow 1_{1,1}$	30251.24	−0.06	−0.27	
$3_{1,2} \leftarrow 2_{0,2}$	28706.53	−0.02	−0.35	
$4_{1,3} \leftarrow 3_{0,3}$	37641.00	−0.10	−0.67	
$6_{1,5} \leftarrow 5_{2,3}$	28769.14	0.14	0.33	
$7_{1,6} \leftarrow 6_{2,4}$	34090.07	0.02	0.47	
$10_{2,9} \leftarrow 9_{3,7}$	29844.38	−0.03	3.84	0.01
$13_{5,9} \leftarrow 12_{6,7}$	32454.01	0.16	8.07	0.04
$4_{3,2} \leftarrow 4_{2,2}$	25586.89	0.08	−1.00	
$7_{3,4} \leftarrow 7_{2,6}$	32583.49	0.04	−4.57	
$11_{4,8} \leftarrow 11_{3,8}$	24369.01	0.01	−10.09	0.01
$15_{5,11} \leftarrow 15_{4,11}$	28528.82	0.01	−24.41	0.02
$23_{7,17} \leftarrow 23_{6,17}$	34934.49	−0.03	−85.32	0.20
$32_{9,24} \leftarrow 32_{8,24}$	31147.67	−0.11	−199.21	0.91
$41_{11,31} \leftarrow 41_{10,31}$	24466.57	−0.07	−343.42	2.67
$52_{14,39} \leftarrow 52_{13,39}$	32785.69	0.10	−819.52	10.77
$61_{16,46} \leftarrow 61_{15,46}$	22971.71	−0.05	−1010.40	18.57
$68_{18,51} \leftarrow 68_{17,51}$	30087.63	−0.01	−1675.70	39.26
Coalescing *c*-type	K_{-1}-lines[b]			
$24_{12} \leftarrow 23_{13}$	32742.66	0.02	34.52	0.48
$26_{13} \leftarrow 25_{14}$	35950.77	0.09	44.58	0.73
$32_{17} \leftarrow 31_{18}$	34063.08	0.04	66.06	1.46

[a] 0.10 MHz. [b] The K_{-1}-energy doublets coalesce for high values of K_{-1}. Subscripts of J-quantum number refer to K_{-1} and not to K_{+1}.

Table 2. Spectroscopic constants of the ground vibrational states of conformation I of $CH_3CH(OH)C \equiv CH$ and $CH_3CH(OD)C \equiv CH.^a$

Species		$CH_3CH(OH)C \equiv CH$	$CH_3CH(OD)C \equiv CH$
N.o.t.[b]		97	51
R.m.s.[c] (MHz)		0.072	0.090
A_0	(MHz)	8791.3172(47)	8281.9423(94)
B_0	(MHz)	3877.6161(21)	3867.1336(45)
C_0	(MHz)	2907.6441(20)	2843.9353(53)
Δ_J	(kHz)	0.892(11)	1.134(69)
Δ_{JK}	(kHz)	12.530(23)	12.72(18)
Δ_K	(kHz)	−3.152(74)	−4.25(72)
δ_J	(kHz)	0.2063(17)	0.176(10)
δ_K	(kHz)	7.445(35)	8.95(31)
Φ_J	(Hz)	0.025(13)	−[e]
Φ_{JK}	(Hz)	0.0096(92)	0.0276(22)
Φ_{KJ}	(Hz)	0.15(11)	−[e]
Φ_K	(Hz)[d]	0.14(27)	−[e]

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

−25 °C. Lower temperatures could not be used due to insufficient vapour pressure of the compound. The sample pressure was 1−3 Pa during the spectral measurements. The deuterated species was produced by direct exchange with D_2O in the wave guide.

RESULTS

Spectrum and assignment of the ground vibrational state of conformation I. The microwave spectrum of $CH_3CH(OH)C \equiv CH$ is fairly dense. The strongest lines observed have peak absorption coefficients of roughly 4×10^{-7} cm^{-1} at about −25 °C.

Preliminary sets of rotational constants were computed for the three rotameric forms shown in Fig. 1. The low-*J*, *a*-type *R*-branch lines of conformation I were identified after
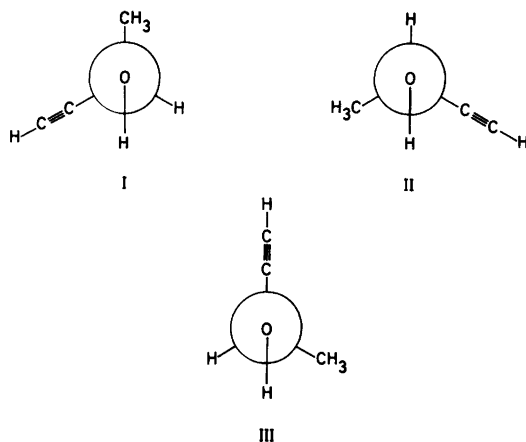

Fig. 1. The three all-staggered conformations of 3-butyn-2-ol viewed along the C−O bond. Conformations I and II were assigned with II as the more stable by 0.4(4) kJ/mol. III is, if it exists at all, at least 4 kJ/mol less stable than each of I and II.

Table 3. Spectroscopic constants of vibrationally excited states of conformation I of $CH_3CH(OH)C \equiv CH$.[a]

Vibrational state		Bend. I[d]	Bend. II[f]	Bend. III[f]
N.o.t.[b]		37	11	12
R.m.s.[c]		0.086	0.050	0.055
A_v	(MHz)	8744.7176(62)	8765.27(24)	8784.88(17)
B_v	(MHz)	3890.5729(28)	3886.7064(82)	3884.2433(54)
C_v	(MHz)	2908.4378(27)	2912.2183(62)	2911.7864(49)
Δ_J	(kHz)	$-^e$	$-^e$	$-^e$
Δ_{JK}	(kHz)	11.457(35)	$-^e$	$-^e$
Δ_K	(kHz)	$-^e$	$-^e$	$-^e$
δ_J	(kHz)	0.2015(25)	$-^e$	$-^e$
δ_K	(kHz)	7.42(13)	$-^e$	$-^e$

[a,b,c] Comments as for Table 2. [d] Sextic constants preset at ground-state values shown in Table 2. [e] Preset at ground-state values shown in Table 2. [f] Sextic constants preset at zero.

Table 4. Stark coefficients and dipole moment of conformation I of $CH_3CH(OH)C \equiv CH$.[a]

Transition		$\Delta v/E^2$ (MHz $V^{-2}cm^2$)$\times 10^6$	
		Obs	Calc.
$3_{1,2} \leftarrow 2_{0,2}$	M $=0$	$-0.884(10)$	-0.918
	$|M|=1$	3.05(3)	3.27
	$|M|=2$	15.6(2)	15.8
$3_{1,2} \leftarrow 2_{1,1}$	$|M|=1$	$-1.36(2)$	-1.40
	$|M|=2$	$-5.70(6)$	-5.29
$4_{1,4} \leftarrow 3_{1,3}$	$|M|=1$	$-0.675(8)$	-0.591
	$|M|=3$	2.83(4)	2.86

Dipole moment (D)[b]

$\mu_a = 0.944(17)$ $\mu_c = 0.777(17)$ $\mu_{tot.} = 1.223(20)^c$

[a] Uncertainties represent one standard deviation. [b] 1 D$=3.33564\times10^{-30}$ C m. [c] μ_b preset at zero. See text.

some searching by their rigid-rotor fit and typical Stark effects. Q-branch lines of the c-type variety were then readily assigned and extended to high values of J, with the $68_{18,51} \leftarrow 68_{17,51}$ transition representing the maximum value of J. The weaker R-branch c-type lines with maximum J found for the coalescing $32_{17} \leftarrow 31_{18}$ pair of transitions, and the a-type Q-branch lines with maximum J found for the $43_{12,31} \leftarrow 43_{12,32}$ transition, were now easily assigned. No b-type lines were found presumably because $\mu_b \sim 0$ D (see dipole moment section below). A total of slightly more than 100 transitions were ultimately assigned; a portion of which is shown in Table 1.* The spectroscopic constants (I^r−representation, A-reduction) are displayed in Table 2. They were determined using 97 transitions.

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* The complete spectra of the two conformations are available from the authors upon request, of from the Molecular Spectra Data Center, National Bureau of Standards, Bld. 221 Rno. B 265, Washington, D.C., 20234, U.S.A., where they have been deposited.

Table 5. Selected transitions for the ground vibrational state of conformation II of $CH_3CH(OH)C \equiv CH$.

Transition	Observed frequency [a] (MHz)	Obs.-calc. frequency (MHz)	Centrifugal distortion	
			Total (MHz)	Sextic (MHz)
a-type				
$3_{1,2} \leftarrow 2_{1,1}$	21832.75	−0.02	−0.21	
$4_{0,4} \leftarrow 3_{0,3}$	26034.15	0.03	−0.10	
$4_{1,3} \leftarrow 3_{1,2}$	28919.11	0.00	−0.35	
$4_{1,4} \leftarrow 3_{1,3}$	25071.88	−0.06	−0.15	
$4_{2,2} \leftarrow 3_{2,1}$	28406.05	−0.01	−0.68	
$4_{2,3} \leftarrow 3_{2,2}$	27166.63	0.13	−0.56	
$5_{0,5} \leftarrow 4_{0,4}$	31901.60	0.11	−0.23	
$5_{1,4} \leftarrow 4_{1,3}$	35806.40	0.02	−0.54	
$5_{1,5} \leftarrow 4_{1,4}$	31153.70	0.02	−0.26	
$5_{2,3} \leftarrow 4_{2,2}$	35971.25	−0.09	−0.97	
$5_{3,3} \leftarrow 4_{3,2}$	34451.15	−0.01	−1.56	
$6_{0,6} \leftarrow 5_{0,5}$	37656.54	−0.02	−0.43	
$6_{1,6} \leftarrow 5_{1,5}$	37158.68	0.01	−0.43	
b-type				
$3_{3,1} \leftarrow 3_{2,2}$	26032.22	−0.07	−0.49	
$4_{2,3} \leftarrow 4_{1,4}$	20686.08	0.04	−0.93	
$5_{2,4} \leftarrow 5_{1,5}$	23319.23	−0.05	−1.43	
$7_{3,5} \leftarrow 7_{2,6}$	29688.07	−0.02	−3.99	
$12_{4,8} \leftarrow 12_{3,9}$	25759.89	−0.07	−12.23	
$16_{5,11} \leftarrow 16_{4,12}$	31695.68	−0.12	−26.31	0.01
$20_{6,14} \leftarrow 20_{5,15}$	37519.57	0.06	−47.31	0.03
$2_{2,0} \leftarrow 1_{1,1}$	29836.23	0.08	−0.27	
$4_{1,4} \leftarrow 3_{0,3}$	27913.56	0.03	−0.22	
$6_{0,6} \leftarrow 5_{1,5}$	36524.95	−0.01	−0.28	
$11_{4,8} \leftarrow 10_{5,5}$	30541.40	−0.05	4.86	−0.01
$19_{9,11} \leftarrow 18_{10,8}$	35412.25	0.14	15.43	−0.05
c-type				
$9_{4,6} \leftarrow 9_{3,6}$	29458.03	−0.02	−7.08	
$14_{5,10} \leftarrow 14_{4,10}$	30439.57	0.02	−21.57	0.01
$19_{6,14} \leftarrow 19_{5,14}$	28043.02	0.00	−45.77	0.05
$28_{8,21} \leftarrow 28_{7,21}$	23947.06	−0.02	−120.19	0.41
$36_{10,27} \leftarrow 36_{9,27}$	24000.45	−0.06	−243.01	1.51
$47_{13,35} \leftarrow 47_{12,35}$	30245.38	0.04	−601.85	6.66
$59_{16,44} \leftarrow 59_{15,44}$	26436.23	−0.07	−1055.09	19.70
Coalescing K_{-1}-lines [b]				
$21_{11} \leftarrow 20_{12}$	27910.42	0.12	11.62	
$25_{13} \leftarrow 24_{14}$	35324.07	0.01	22.63	−0.02
$31_{17} \leftarrow 30_{18}$	35393.78	0.04	25.24	0.24
$37_{21} \leftarrow 36_{22}$	35518.11	−0.04	19.81	1.02
$40_{23} \leftarrow 39_{24}$	35588.89	0.02	13.00	1.74

[a,b] Comments as for Table 1.

Vibrationally excited states of I. The ground state lines were accompanied by a rich satellite spectrum presumably belonging to vibrationally excited states. Three such states were assigned as shown in Table 3. They are presumed to be heavy-atom bending vibrations, because relatively large changes of the rotational constants are observed upon excitation, although it is possible that the excited state denoted *Bend. III* in Table 3, is a low-frequency torsional vibration.

Only low-J a-type R-branch lines were identified for *Bend. II* and *Bend. III*, while c-type Q-branch lines up to the $48_{13,36} \leftarrow 48_{12,36}$ transition were also assigned for *Bend. I*. Relative intensity measurements made largely as prescribed in Ref. 4 yielded frequencies of 171(40) cm^{-1} for *Bend. I*, 215(40) cm^{-1} for *Bend. II*, and 242(50) cm^{-1} for *Bend. III*, respectively. In the related molecule propargyl alcohol, the lowest bending vibrations occur at 235 cm^{-1} and 312 cm^{-1}, respectively.[2b]

Dipole moment of I. Standard procedure[5] was used to determine the dipole moment reported in Table 4. Initially, all three dipole moment components were fitted, however, μ_b was found to be small and imaginary. In the final fit, μ_b was preset at zero. Bond moment calculations[6] yielded μ_a=1.2 D, μ_b=0.3 D, and μ_c=1.1 D, respectively. This is reasonably close to the experimental values of Table 4. If a modified bond moment of 0.8 D is used for the sp^3-sp carbon-carbon bond with the sp-end assumed to be negative as explained in Ref. 7, μ_a=0.5 D, μ_b=0.3 D, and μ_c=1.3 D were obtained. The ordinary bond-moment method is thus slightly better than the modified procedure in this case (*cf.* Table 4 and above).

Assignment of the ground vibrational state of conformation II. The b-type lines were first assigned for this conformation. a- and c-type lines which are much weaker than those of the b-type variety, were then readily assigned. Extension to high values of J was now made. The highest values of J assigned for the various series are shown in Table 5, which includes a selection from the about 150 transitions which were measured for this conformation. The spectroscopic constants displayed in Table 6 were determined from 147 selected transitions.

Vibrationally excited states of II. Two such states were definitely assigned and their spectroscopic constants are listed in Table 7. *Bend. III* of this table corresponds to *Bend. III*

Table 6. Spectroscopic constants of the ground vibrational states of conformation II of $CH_3CH(OH)C \equiv CH$ and $CH_3CH(OD)C \equiv CH^a$.

Species N.o.t.[b] R.m.s.[c] (MHz)		$CH_3CH(OH)C \equiv CH$ 147 0.059	$CH_3CH(OD)C \equiv CH$ 74 0.073
A_0	(MHz)	8599.7376(26)	8209.9865(68)
B_0	(MHz)	3899.3493(13)	3855.6814(33)
C_0	(MHz)	2919.3530(12)	2880.5794(29)
Δ_J	(kHz)	0.8999(55)	0.992(38)
Δ_{JK}	(kHz)	12.223(22)	12.596(80)
Δ_K	(kHz)	−4.063(25)	−5.82(35)
δ_J	(kHz)	0.2028(17)	0.2331(51)
δ_K	(kHz)	7.400(39)	7.432(85)
Φ_J	(Hz)	−0.0178(55)	−[e]
Φ_{JK}	(Hz)	0.064(11)	0.28(17)
Φ_{KJ}	(Hz)	−0.35(12)	−[e]
Φ_K	(Hz)[d]	0.21(10)	−[e]

[a,b,c,d,e] Comments as for Table 2.

Table 7. Spectroscopic constants of vibrationally excited states of conformation II of $CH_3CH(OH)C\equiv CH$.[a]

Vibrational state		Bend. III	Methyl torsion[e]
N.o.t.[b]		46	33
R.m.s.[c]		0.075	0.090
A_v	(MHz)	8676.6825(64)	8597.263(15)
B_v	(MHz)	3902.6584(29)	3899.5558(73)
C_v	(MHz)	2923.7315(24)	2920.2457(72)
Δ_J	(kHz)	$-^d$	$-^d$
Δ_{JK}	(kHz)	13.174(81)	12.68(19)
Δ_K	(kHz)	$-^d$	$-11.21(99)$
δ_J	(kHz)	0.2202(71)	0.226(10)
δ_K	(kHz)	7.44(13)	6.54(19)

[a,b,c] Comments as for Table 2. [d] Preset at ground state value shown in Table 6. [e] Could also be the first excited state of the C−O torsion.

of Table 3, because the changes of the rotational constants upon excitation are quite similar in these cases as one would expect them to be for two so geometrically similar conformations as I and II. Relative intensity measurements[4] yielded 225(40) cm^{-1} for this vibration. This is similar to 242(50) cm^{-1} obtained for *Bend. III* of conformation I, as expected.

The second excited state of Table 7 is believed to be the methyl group torsional vibration, but it could be the C−O torsion just as well. It is presumed to be a torsional vibration because the rotational constants shown in Table 7 are so similar to the ground state values shown in Table 6. This is expected for a vibration involving little reduced mass, as do indeed the methyl and C−O torsions. Relative intensity measurements yielded 315(60) cm^{-1} for this vibration.

Excited states corresponding to *Bend. I* and *Bend. II* are believed to have been observed. However, no satisfactory fit to a centrifugally distorted asymmetric rotor could be obtained. Root-mean-square deviations of a few MHz were obtained for the strong Q-branch series.

Table 8. Stark coefficients and dipole moment of conformation II of $CH_3CH(OH)C\equiv CH$.[a]

		$\Delta v/E^2$ (MHz V^{-2}cm^2)×10^6	
Transition		Obs.	Calc.
$2_{2,1}\leftarrow 1_{1,0}$	M =0	1.14	1.09
	$\|M\|=1$	−114.	−115.
$7_{3,5}\leftarrow 7_{2,6}$	$\|M\|=5$	−5.09	−5.10
	$\|M\|=6$	−7.41	−7.36
	$\|M\|=7$	−9.90	−10.1
$5_{0,5}\leftarrow 4_{1,4}$	M =0	−0.445	−0.502
	$\|M\|=1$	−3.99	−3.91
	$\|M\|=2$	−14.7	−14.2

Dipole moment (D)[b]

μ_a=0.629(14) μ_b=1.039(21) μ_c=0.594(9) $\mu_{tot.}$=1.352(21)

[a,b] Comments as for Table 4.

The reason for this deviation is presumed to be a slight coriolis interaction between *Bend. I* and *Bend. II*. Attempts to fit these candidates using Nielsen's program,[8] yielded coupling constants with very large standard deviation, a large r.m.s.-deviation and high correlations. No definite assignments of these two excited states could thus be reached this way. The best parameter values we got for *Bend. I* of conformation II were $A-C=5662.1$ MHz and $\kappa=-0.650629$, respectively.

Dipole moment of II. The dipole moment of II was determined in the same manner as described for I with the results shown in Table 8. These values should be compared with $\mu_a=1.1$ D, μ_b 0.8 D, and $\mu_c=1.0$ D, obtained using the bond-moment method,[6] and $\mu_a=0.3$ D, $\mu_b=0.8$ D, and $\mu_c=0.8$ D, using its modifications[7] which is seen to be slightly better than the bond-moment method in this case.

Energy difference between I and II. Intensity comparisons were made for several selected, well-isolated, strong low-*J* lines belonging to the two identified conformations in

Table 9. Plausible molecular structure[a] (bond lengths in *pm*, angles in *degrees*) of conformations *I* and *II* of $CH_3CH(OH)C\equiv CH$.

Structural parameters kept fixed for both I and II

$C\equiv C$	120.6	$\angle H-C\equiv C$	180.00
$C-CC$	146.0	$\angle C\equiv C-C$	180.00
$C-C$	153.5	$\angle C-C-O$	112.5
$C-O$	141.5	$\angle C-C-H$	109.47
$H-C\equiv$	106.0	$\angle H-C-H$	109.47
$H-C$	109.3		
$H-O$	95.0		

Fitted structural parameters

	Conformation I	Conformation II
$\angle C-C-CH_3$	112.0(15)	110.5(15)
$\angle O-C-CH_3$	108.1(15)	112.8(15)
$\angle C-C-O-H^b$	56(5) from *syn*	45(5) from *syn*

Rotational constants (MHz) for conformation I

	$CH_3CH(OH)C\equiv CH$			$CH_3CH(OD)C\equiv CH$		
	Obs.	Obs.-calc.	Diff. (%)	Obs.	Obs.-calc.	Diff. (%)
A_0	8791.3172(47)	8.08	0.09	8281.9423(94)	6.25	0.08
B_0	3877.6161(21)	−11.18	0.29	3867.1336(45)	−10.23	0.26
C_0	2907.6441(20)	3.44	0.12	2843.9353(53)	2.74	0.10

Rotational constants (MHz) for conformation II

	$CH_3CH(OH)C\equiv CH$			$CH_3CH(OD)C\equiv CH$		
	Obs.	Obs.-calc.	Diff. (%)	Obs.	Obs.-calc.	Diff. (%)
A_0	8599.7376(26)	9.26	0.11	8209.9865(68)	−13.80	0.16
B_0	3899.3493(13)	−28.58	0.73	3855.6814(33)	−29.33	0.76
C_0	2919.3530(12)	−2.30	0.08	2880.5794(29)	−3.99	0.14

Kraitchman's coordinates[c] for the hydroxyl group hydrogen atom

	Conformation I			Conformation II		
	|a|	|b|	|c|	|a|	|b|	|c|
From rotational constants	0.58403(16)	1.89315(6)	imaginary	0.70063(8)	1.34639(4)	1.00834(6)
From plausible structure	0.585	1.883	0.171	0.706	1.305	0.979

Hydrogen bond parameters

	Conformation I	Conformation II
$H \cdots C \equiv CH$	248	240
$H \cdots C \equiv C-C$	339	329
$O \cdots C \equiv CH$	239	239
$O \cdots C \equiv C-C$	346	346
$\angle O-H \cdots C^d$	74	78
$\angle H \cdots C \equiv CH$	131	128
$\angle O-H, C \equiv C^e$	66	57

Sum of van der Waals radii[f]

$H \cdots C^g$	290

[a] See text. [b] Dihedral angle. [c] Ref. 10. [d] Nearest carbon atom of the acetylene group. [e] Angle between O–H and $C \equiv C$ bonds. [f] Ref. 13. [g] van der Waals radius of carbon taken to be 170 pm as for aromatic carbon.[13]

the limit of completely unsaturated transitions.[9] The internal energy difference was found to be: $\Delta E^\circ = E^\circ_{0,II} - E^\circ_{0,I} = -0.4$ kJ/mol, with one standard deviation of 0.4 kJ/mol. Conformation II thus tends to be slightly more stable than I.

Searches for conformation III. The definite assignments made as described above include about 400 transitions. Moreover, some 20 additional lines were presumed to belong to the slightly perturbed *Bend. I* and *Bend. II* excited states of conformation II. This includes all strong lines of the spectrum as well as the great majority of the lines of medium intensities and many weak transitions. There were thus only a few lines left of appreciable intensities to search among for the hypothetical conformation III.

This rotamer was predicted to have all three dipole moment components close to 1 D using the bond-moment method.[6] However, no lines with suitable Stark effects could be found at their predicted frequencies. It is therefore concluded that conformation III is at least 4 kJ/mol less stable than I or II if it exists at all as a stable conformation of the molecule.

Deuterated species. The deuterated species, $CH_3CH(OD)C \equiv CH$, was studied in order to confirm the assingments of the two conformers beyond doubt. Many transitions were measured for both I and II; the resulting spectroscopic constants are shown in Tables 2 and 6. Kraitchman's coordinates[10] for the exchanged hydroxyl hydrogen atom of the two rotamers are shown in Table 9.

Structure of the two conformations. Only two isotopic species were studied for the two conformers investigated in this work. A complete geometrical structure cannot, therefore, be determined for each of the two assigned forms I and II. Assumptions have to be made. The structural parameters kept fixed are shown in Table 9. They were taken from recent, accurate studies of related compounds. Moreover, the acetylene group was assumed to be linear. Three parameters, *viz.* the $C-C-CH_3$ and $O-C-CH_3$ angles, and the $C-C-O-H$ dihedral angle were fitted to the rotational constants and Kraitchman's coordinates of the hydroxyl group hydrogen atom with the results shown in Table 9. The uncertainties (approximately three standard deviations) were estimated to be ±1.5 for each of the two heavy-atom angles. Due to the large-amplitude $C-O$ torsional vibration an uncertainty of $\pm5°$ is estimated[11] for each of the two $C-C-O-H$ dihedral angles. It is seen from Table 9 that both the rotational constants and Kraitchman's coordinates for the hydroxyl group hydrogen atom are reasonably well reproduced.

DISCUSSION

The fact that I and II are the stable forms of 3-butyn-2-ol is perhaps caused by two major effects, internal hydrogen bonding between the hydroxyl group hydrogen atom and the π-electrons of the triple bond as well as repulsion between these electrons and the lone-pair electrons of the oxygen atom. In the observed conformations I and II, repulsion between the π-electrons and the lone-pair electrons is presumed to be much less than it would have been in the hypothetical rotamer III. In addition, internal hydrogen bonding would have been absent in III.

There are some notable differences between I and II. The fact that II tends to be slightly more stable than I by 0.4(4) kJ/mol is paralleled by a smaller $C-C-O-H$ dihedral angle for II $(45(5)°)$ from *syn*; (Table 9) than for I $(56(5)°)$. This brings the hydroxyl group hydrogen atom into closer proximity with the π-electrons in II than in I which may result in a bit stronger hydrogen bond in II than in I.

The difference found for the $C-C-O$ angles of I $(108.1(15)°)$ and II $(112.8(15)°)$ has a parallel in ethanol. In the *anti* conformation of ethanol which corresponds to rotamer I of 3-butyn-2-ol, the $C-C-O$ angle is $107.8°$. No accurate experimental value is available for this angle in the case of the *gauche* rotamer of ethanol which corresponds to II. However, a recent *ab initio* calculation[12] yielded $113.42°$ for the $C-C-O$ angle in *gauche* ethanol, very close to $112.8(15)°$ found for this angle in 3-butyn-2-ol (Table 9).

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