Microwave Spectrum, Conformation, Intramolecular Hydrogen Bond and Dipole Moment of 2,3-Butadien-1-ol

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The microwave spectra of 2,3-butadien-1-ol, $CH_2OHCH=C=CH_2$ and one deuterated species, $CH_2ODCH=C=CH_2$, have been investigated in the 18.0−33.5 GHz region at −10 °C. Only one conformation, the *skew* form, with an intramolecular hydrogen bond formed between the hydroxyl hydrogen atom and the π electrons of the allene group was assigned. The dihedral O−C−C=C angle of the *skew* rotamer is 122(3)° from *syn* (58(3)° from *anti*). (See Fig. 1). Further conformations, if they exist, are at least 4 kJ/mol less stable than *skew*.

The dipole moment is $\mu_a=1.488(28)$ D, $\mu_b=0.8(2)$ D, $\mu_c=0.4(2)$ D, and $\mu_{tot.}=1.72(12)$ D. Six vibrationally excited states belonging to two different normal modes were also assigned.

Several conformations are possible for 2,3-buta-dien-1-ol because the compound has two internal axes of rotation, namely the C−O and C1−C2 axes. Four selected rotamers are shown in Fig. 1. The *anti* form in which the heavy atoms and the hydroxyl group hydrogen atom are coplanar, should be ideal for steric reasons as there are no close contacts between non-bonded atoms in this
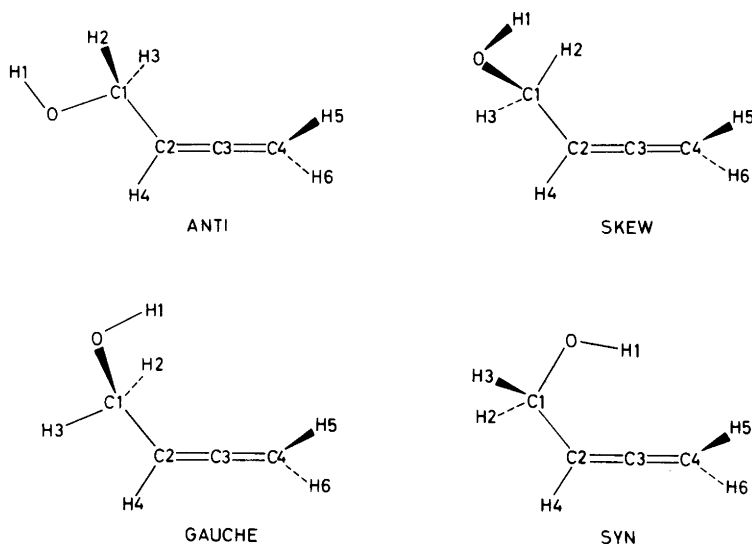
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Fig. 1. Four selected conformations of 2,3-butadien-1-ol. In the *skew* form, a 60° rotation, and in the *gauche* form a 120° rotation from *anti* about the C1−C2 bond has been made. Only *skew* was assigned and found to be at least 4 kJ/mol more stable than any other form of the molecule.

conformation.

The *skew* rotamer has the OCCC dihedral angle twisted 60° from *anti*. The hydroxyl hydrogen atom has been rotated (as compared to *anti*) so that a weak internal hydrogen bond might be formed between this atom and the π electrons of the allene group. In this conformation, the distance between H1 and C2 should be somewhat shorter than the sum of van der Waals radii of carbon and hydrogen. Moreover, the H2 and C3 atoms are brought into close proximity. It is unclear whether this contact would be repulsive or attractive in nature.

In the *gauche* conformation, a further 60° rotation about the C1−C2 bond has been made. The distances between H1 and C2, and between H1 and C3 should both be quite similar and roughly the same as the H1···C2 distance in the *skew* conformation. The O···C3 distance should be about the same as the van der Waals distance. H3 and H4, on the other hand, eclipse each other, and this might perhaps destabilize the *gauche* conformation.

In the *syn* form, the heavy atoms and the hydroxyl group hydrogen atom are again coplanar. The H1···C2 and H1···C3 distances would both be much shorter than the sum of the van der Waals radii of hydrogen and carbon, and the

H1···C4 distance somewhat shorter than this sum. The O···C3 distance would also be a bit shorter than the sum of the van der Waals radii.

Some conformational problems related to that of $CH_2OHCH=C=CH_2$ have already been studied. Allyl alcohol, $CH_2OHCH=CH_2$, has a conformation similar to *skew* as its preferred form.[1] CH_2OHCHO,[2] $CH_2OHCOCH_3$,[3] and $CH_2OHCOOH$[4] all have conformations similar to *syn* as their most stable forms. In all these four last-mentioned compounds, intramolecular hydrogen bonding is important for their conformational preferences.

This work was undertaken in order to investigate the conformational preferences of 2,3-butadien-1-ol and the role played by intramolecular hydrogen bonding. It was found that the *skew* form is preferred by the molecule. This conformation is more stable than any other rotamer by at least 4 kJ/mol.

EXPERIMENTAL

$CH_2OHCH=C=CH_2$ was synthesized as described in Ref. 5 and purified by gas chromatography (Carbowax; 140 °C). The microwave spectrum was studied in the 18.0–38.5 GHz spectral region at a pressure of 1–3 Pa and a

Table 1. Microwave spectrum[a] of the ground vibrational state of $CH_2OHCH=C=CH_2$.

Transition	Observed frequency[a] (MHz)	Obs.-calc. frequency (MHz)	Centrifugal distortion (MHz)
$3_{0,3} \rightarrow 4_{0,4}$	18457.90	0.01	−0.26
$3_{1,2} \rightarrow 4_{1,3}$	18547.95	0.05	−0.06
$3_{1,3} \rightarrow 4_{1,4}$	18369.92	−0.01	−0.06
$4_{0,4} \rightarrow 5_{0,4}$	23071.39	−0.02	−0.51
$4_{1,3} \rightarrow 5_{1,4}$	23184.39	−0.11	−0.26
$4_{1,4} \rightarrow 5_{1,5}$	22962.04	0.00	−0.26
$5_{0,5} \rightarrow 6_{0,6}$	27684.31	0.03	−0.89
$5_{1,4} \rightarrow 6_{1,5}$	27820.88	0.04	−0.59
$5_{1,5} \rightarrow 6_{1,6}$	27553.87	−0.02	−0.59
$5_{2,3} \rightarrow 6_{2,4}$	27692.20	−0.05	0.32
$6_{0,6} \rightarrow 7_{0,7}$	32296.42	0.03	−1.41
$6_{1,5} \rightarrow 7_{1,6}$	32456.90	0.02	−1.06
$6_{1,6} \rightarrow 7_{1,7}$	32145.45	0.00	−1.06
$6_{2,4} \rightarrow 7_{2,5}$	32308.67	0.12	0.00
$7_{0,7} \rightarrow 8_{0,8}$	36907.56	−0.04	−2.11
$7_{1,7} \rightarrow 8_{1,8}$	36736.67	0.02	−1.71
$7_{2,5} \rightarrow 8_{2,6}$	36925.22	−0.06	−0.50

[a] ±0.10 MHz.

temperature of about −10 °C. Lower temperatures could not be utilized due to insufficient vapour pressure of the compound. A conventional spectrometer equipped with free-running klystrons was employed.

RESULTS

Microwave spectrum and assignment of the ground vibrational state. The microwave spectrum of 2,3-butadien-1-ol is quite simple and its assignment was readily made. The spectrum consists of lumps of lines of intermediate intensities with nearly constant spacings due to $J\rightarrow J+1$ *a*-type transitions. In the spectral region between the K_{-1}-pile-ups, only very weak lines were seen.

The spectrum * is shown in Table 1. Only low-K_{-1} transitions are included in this table; the high-K_{-1} lines were not sufficiently resolved from each other to allow accurate measurements to be made. This is due to the fact that the assigned *skew* conformation has Ray's asymmetry parameter $\kappa= -0.9938$.[6] *b*- and *c*-type *Q*-branch transitions which might be relatively strong, were searched for but not identified, presumably because of insufficient intensities produced by small dipole moment components along the *b*- and *c*-principal inertial axes. As will be shown below, it was only possible to make rather inaccurate determination of $\mu_b=0.8(2)$ *D* and

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* The microwave spectra of the vibrationally excited states of $CH_2OHCH=C=CH_2$ as well as of the ground vibrational state of $CH_2ODCH=C=CH_2$ are available from the authors upon request or from Molecular Spectra Data Center, Bldg. 221, Room B 265, National Bureau of Standards, Washington D.C. 20234, U.S.A., where they have been deposited.

$\mu_c=0.4(2)$ *D*.

Unfortunately, the assigned *a*-type *R*-branch lines do not produce an accurate value for the *A* rotational constant as seen in Table 2. Moreover, it should be pointed out that a large negative correlation of −0.953 exists between *A* and Δ_{JK}. Similar values were found for the vibrationally excited states.

Vibrationally excited states. The ground state lines were accompanied by a rich sattelite spectrum presumably belonging to vibrationally excited states of the molecule. Six vibrationally excited states belonging to two different normal modes were assigned as shown in Table 3.

The most prominent of these excited states has about 60 % of the intensity of the ground state at −10 °C. Relative intensity measurements yielded $90(30)$ cm^{-1} for this mode which is presumed to be the first excited state of the C1−C2 torsion.

There is an almost constant increase in each of the *B* and *C* rotational constants upon successive excitation of this mode, as can be seen in Table 3. This is typical for a harmonic mode. The increase of *B* is 9.71 MHz, and *C* increases by 4.17 MHz from the ground to the first excited C1−C2 torsional state (Tables 2 and 3). As will be shown below, the OCCC dihedral angle is 58(3)° from *anti*. Increase of this angle in model calculations by 1.5° results in increases of the *B* rotational by 11.70 MHz and of *C* by 5.88 MHz. This is quite similar to the observed values and indicates that the C1−C2 torsion is uncoupled to other vibrational modes.

Furthermore, increase of both *B* and *C* upon excitation presumably means that the conformation approaches the *gauche* and/or *syn* forms. It is

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Table 2. Spectroscopic constants[a] for the ground vibrational state of $CH_2OHCH=C=CH_2$ and $CH_2ODCH=C=CH_2$.

Species		$CH_2OHCH=C=CH_2$	$CH_2ODCH=C=CH_2$
Number of transitions		17	13
Root-mean-square dev. (MHz)		0.059	0.091
A_0	(MHz)	16688(192)	15824(190)
B_0	(MHz)	2329.6451(53)	2293.9667(92)
C_0	(MHz)	2285.1519(55)	2237.8011(91)
Δ_J	(kHz)[b]	1.030(47)	1.217(79)
Δ_{JK}	(kHz)	−25.2(27)	24.6(44)
κ[c]		−0.9938	−0.9917

[a] Uncertainties represent one standard deviation. [b] Further quartic centrifugal distortion constants preset at zero. [c] Ray's asymmetry parameter.[6]

Table 3. Spectroscopic constants[a] for vibrationally excited states of $CH_2OHCH=C=CH_2$.

Vib. state	First ex. C–C torsion	Second ex. C–C torsion	Third ex. C–C torsion	Fourth ex. C–C torsion	Fifth ex. C–C torsion	First ex. bending
No. of lines	15	12	15	9	10	15
R.m.s. (MHz)[d]	0.103	0.081	0.123	0.263	0.256	0.103
A_v (MHz)	18941(307)	17419(309)	16048(250)	16641(140)	19348(1562)	20408(1011)
B_v (MHz)	2339.3639(65)	2349.1666(76)	2359.132(12)	2369.299(29)	2379.618(52)	2326.6963(97)
C_v (MHz)	2289.3236(65)	2293.4351(94)	2297.559(11)	2301.587(35)	2305.651(51)	2285.5097(96)
Δ_J (kHz)[b]	1.441(62)	1.204(99)	1.60(11)	1.99(23)	1.96(43)	1.41(11)
Δ_{JK} (kHz)	-52.2(43)	-19.9(72)	6.5(77)	—[e]	-123(59)	-82.3(89)
κ^c	-0.9939	-0.9926	-0.9910	-0.9905	-0.9913	-0.9955

[a,b,c] Comments as for Table 2. [d] R.m.s. is the root-mean-square deviation. [e] Present at zero.

thus likely that the lowest barrier is found between the observed *skew* and/or the hypothetical *gauche* or *syn* forms. The barrier towards the hypothetical *anti* form is likely to be higher.

The first excited state of what is believed to be the lowest bending mode was also assigned as shown in Table 3. This excited state is roughly 1/3 as intense as the ground vibrational state. Relative intensity measurements yielded 200(30) cm^{-1}.

In addition to these assignments, two or three much weaker satellites were noted, but no definite assignments could be reached.

The assignments made as described above include all the strongest and all lines of intermediate intensities. Presumably, conformations other than *skew* should possess sizable dipole moments. This would lead to easily detectable spectra provided that at least 10 % or so of the total gaseous composition belonged to another form. It is therefore concluded that the identified *skew* conformation make up at least about 90 % of the gas and is at least 4 kJ/mol more stable than any other conformation of the molecule. This estimate is considered to be conservative.

Dipole moment. Stark coefficients of the four transitions shown in Table 4 were used to determine the dipole moment employing the standard procedure.[7] Small formal standard deviations of 0.06 D were found for μ_b and 0.07 D for μ_c, respectively. However, such small standard deviations for these two dipole moment components are unrealistic in this case, because the A rotation constant is poorly determined. The second-order perturbation sums[8] depend strongly on A in the case of μ_b and μ_c, and the uncertainties of these two dipole moment components were therefore judiciously increased to 0.2 D. It is also presumed that μ_b is in fact less than 0.8 D, since no b-type lines were found.

The total dipole moment of 1.72(12) D is similar to that of allyl alcohol[1] (1.55(4) D) as expected.

Deuterated species. The deuterated species, $CH_2ODCH=C=CH_2$, was studied mainly to determine the position of the hydroxyl hydrogen atom. The assignment was straight forward. The spectroscopic constants are shown in Table 2. The correlation coefficient between A and Δ_{JK} is -0.858 in this case. Kraitchman's coordinates[9] for the hydroxyl hydrogen atom are found in

Table 4. Stark coefficients[a] and dipole moment[b] of $CH_2OHCH=C=CH_2$.

Transition		$\Delta v/E^2$ (MHzV^{-2} cm^{-2})$\times 10^6$	
		Obs.	Calc.
$4_{1,4} \rightarrow 5_{1,5}$	$|M|=1$	2.51(6)	2.31
	$|M|=2$	10.1(5)	9.24
$4_{1,3} \rightarrow 5_{1,4}$	$M=0$	−0.392(9)	−0.373
	$|M|=1$	−2.70(5)	−2.56
	$|M|=2$	−9.7(5)	−9.1
$5_{1,4} \rightarrow 6_{1,5}$	$|M|=1$	−0.865(9)	−0.926
	$|M|=3$	−5.74(6)	−5.66
	$|M|=4$	−10.1(2)	−9.81
$4_{0,4} \rightarrow 5_{0,5}$	$M=0$	−2.72(5)	−2.65

Dipole moment
$\mu_a=1.488(28)$ D, $\mu_b=0.8(2)$ D^b
$\mu_c=0.4(2)$ D^b $\mu_{tot}=1.72(12)$ D

[a] Uncertainties represent one standard deviation. [b] See text.

Table 5. Plausible structural parameters[a] (bond lengths in *pm*, angles in *degrees*) of $CH_2OHCH=C=CH_2$.

Assumed bond lengths and angles

C=C	130.9	∠C=C=C	180.0
C−O	141.5	∠C−C−O	112.0
C−C	151.4	∠C−C=C	122.0
O−H	95.0	∠C−O−H	104.0
H_2C−H	109.3	∠H−C=C	121.0
=C−H	108.5	∠C−C−H	109.5

Fitted dihedral angle of *skew* conformation
∠O−C−C=C 122(3) from *syn* (58(3) from *anti*)

Kraitchman's coordinate[b] for hydroxyl hydrogen atom

	|a|	|b|	|c|
Calculated from rotational constants	178.8(75)	120.6(66)	49.1(38)
Calculated from structure	175.2	115.8	58.7

Hydrogen bond parameters

H1···C2	253	O···C3	346
H1···C3	332		
∠OH1···C2	73	∠OH1···C3	91
∠OH1···C2C3C4[c]	52		

Sum of van der Waals Radii[d]

H···C[e]	290	O···C[e]	310

Rotational constants (MHz)

		$CH_2OHCH=C=CH_2$			$CH_2ODCH=C=CH_2$		
		Obs.	Calc.	Diff. (%)	Obs.	Calc.	Diff. (%)
A_0	(MHz)[f]	16688	19623	17.6	15824	18445	16.6
B_0	(MHz)	2329.65	2330.08	0.02	2293.97	2295.00	0.04
C_0	(MHz)	2285.15	2289.57	0.19	2237.80	2244.14	0.28

[a] See text. [b] Ref. 9. [c] Angle between O−H bond and C=C=C group. [d] Taken from Ref. 10. [e] van der Waals radius of carbon assumed to be 170 *pm* as in aromatic compounds.[10] [f] Too uncertain to be used for fitting of structure.

Table 5. Rather large uncertainties were obtained for these coordinates. This is caused by the inaccurate *A* rotational constants.

Structure. Only two isotopic species were studied for 2,3-butadien-1-ol and reliable values were only found for the *B* and *C* rotational constants in each case. A complete geometrical structure cannot, therefore, be determined for the *skew* conformation. A selection of structural parameters to be fitted must be made.

The Kraitchman coordinates (Table 5) of the hydroxyl hydrogen atom are so inaccurate that it was not considered worthwhile to fit any of the geometrical parameters of this hydrogen atom. However, these coordinates suffice to show that the *skew* form undoubtedly possesses an intramolecular hydrogen bond.

The rotational constants strongly depend on the OCCC dihedral angle. This angle was fitted in steps of 1° until a satisfactory agreement was found between the observed and calculated *B* and *C* rotational constants. This occurred with a dihedral angle of 122(3)° from *syn* (58(3)° from *anti*). The error limit has been derived taking into account the inherent uncertainties of the assumed structural parameters.

DISCUSSION

The intramolecular hydrogen bond of 2,3-butadien-1-ol is strained and rather weak and similar to that of allyl alcohol.[1] The hydrogen bond is characterized by having a H1···C2 (Fig. 1) non-bonded distance of 253 *pm* which is approximately 40 *pm* shorter than the sum of the van der Waals radii of hydrogen and aromatic carbon as shown in Table 5. The OH1···C2 angle is 73° and the angle between the O−H1 and allene group is 52°. In addition, the non-bonded distance between H2 and C3 is rather short, *viz.* 257 *pm*. It is not obvious if this contact is attractive.

The reasons why 2,3-butadien-1-ol prefers the *skew* conformation can only be hinted at. Hydrogen bonding can perhaps explain why *skew* is more stable than the sterically ideal hypothetical *anti* conformation. Moreover, steric overcrowding might perhaps explain why the *syn* form is not as stable as *skew*. It is more difficult to explain why the *skew* is more stable than the *gauche* form. The hydrogen bonding situation should be

fairly similar in these two conformations. *Skew* has the close H2···C3 contact, while H3 and H4 eclipse each other in *gauche*. H2 and C3 might attract each other in *skew*, wheras H3 and H4 might repel each other in *gauche*. This would then result in that the *skew* form is also more stable than the *gauche* conformation by more than 4 kJ/mol.

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