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The Molecular Structure and Conformational Composition of 3-Buten-1-ol as Studied by Gas Electron Diffraction

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3-Buten-1-ol was found to exist in two conformations. The major conformer was present in 68.6(80) % and the following dihedral angles were determined: $\omega(C_2-C_3)$: 118.4(43)°; $\omega(C_1-C_2)$: −70.7-(25)°; $\omega(C-O)$: 26.0°. For the minor conformer the same angles were found to be: $\omega(C_2-C_3)$: 85.4(87)°; $\omega(C_1-C_2)$: 51.0°; $\omega(C-O)$: −38.0°. The numbers in parentheses are standard deviations from the least squares analyses. The parameters without standard deviations were indirectly determined.

The major conformer is stabilized by internal hydrogen bonding. The present results indicate that there might also be some internal hydrogen bonding in the minor conformer.

Several infrared spectroscopic studies of 3-buten-1-ol and similar saturated and unsaturated alcohols have been carried out.[1-4] The O−H stretching vibrations were shown to give rise to two distinct bands at 3635.2 cm^{-1} and 3596.1 cm^{-1}, the former frequency corresponding to the normal vibration of aliphatic primary alcohols, while the latter frequency was interpreted as due to interaction between the hydroxyl group and the π-electrons of the double bond.[1]

In a later study[4] the O−H stretching vibrations of 3-buten-1-ol were observed as two bands at 3575 and 3596 cm^{-1}. They were interpreted as due to the two rotational conformers shown in Fig. 1. The splitting of the bond was interpreted as due to a stronger hydrogen bond in the conformer that is assigned the smallest vibrational frequency.

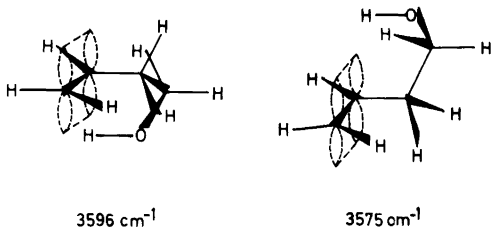

Fig. 1. The two rotational conformers.

A conformational analysis based on molecular mechanic calculations (MM) was carried out by Ivanova *et al.*[5] for the aliphatic alcohols $CH_2=CH-(CH_2)_nOH$, where $n=2-5$ and the analogous ethers $CH_2=CH(CH_2)_nOCH_3$. They calculated the conformational energies for unfolded and for coiled forms, with and without taking intramolecular interactions of the functional groups (U_{ir}) into account. They considered two types of possible intramolecular interactions, (a) hydrogen bond formation between the double bond and the hydroxyl group and (b) interactions between the unshared electron pairs of oxygen and the π-electrons. Both kinds of interactions are in principle possible for the unsaturated alcohols, while only the latter kind may be realized in the ethers. They found that the most favourable conditions for formation of an intramolecular hydrogen bonds is realized when $n=2$. For 3-buten-1-ol they found that when U_{ir} is neglected the conformational energy is 0.6 kcal/mol larger for the coiled than for the unfolded form. When U_{ir} is included the energy is 0.4 kcal/mol (a) or 0.8 kcal/mol (b) smaller than for the unfolded form.

Ditter and Luck[6,7] have studied the fine structure of the IR spectra of several alcohols and reported enthalpy for internal hydrogen bonding of about 1 kcal/mol for 3-buten-1-ol, as compared to about 0.5 kcal/mol for allyl and benzyl alcohols. Their results indicate that there might exist a strong conformational preference due to intramolecular hydrogen bonding in 3-buten-1-ol.

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EXPERIMENTAL

The sample of 3-buten-1-ol was synthesized by Professor Stanley C. Bunce at Rensselaer Polytechnic Institute, Troy, New York.

Electron diffraction photographs were obtained by the Balzer's Eldigraph KDG-2 unit.[8,9] The experimental conditions were as summarized: Nozzle-to-plate distances 500.12 mm (6 plates) and 250.12 mm (5 plates), electron wavelength as determined by calibration to benzene 0.05864 Å and the nozzle temperature 40 °C. Ranges of data were 1.250–15.625 and 2.500–31.000 ($Å^{-1}$) with increments Δs of 0.125 and 0.250 ($Å^{-1}$), respectively. The optical densities were measured by a Joyce-Loebl MK 111 C densitometer.[10] The experimental data were corrected in the usual way,[11] and the modification function used was $s|f'_C|^{-2}$. The scattering amplitudes and phases[11] were calculated using the partial-wave method[12] based upon the analytical HF potentials for the C- and O-atoms[13] and the best electron density of bonded hydrogen for the H-atom.[14] The inelastic scattering factors used were those of Tavard *et al.*[15]

STRUCTURE ANALYSIS

From the individual experimental modified molecular intensity curves a composite intensity curve was computed by scaling and averaging intensity values in the overlap region. The final molecular intensity curve is shown in Fig. 2. In Fig. 3 the radial distribution curve calculated from this connected curve is presented together with a molecular model showing the numbering of the atoms. The line diagram under the curve gives the positions and the relative weights of the most important interatomic distances according to the final models.

The molecular structure and conformational composition of 3-buten-1-ol was studied by least squares refinements on the molecular intensity data, in combination with information obtained from radial distribution curves.

In principle there are twenty-seven possible conformers of 3-buten-1-ol if triple potentials of the C–C and C–O single bonds are assumed. The position of the hydroxyl hydrogen atom of each of the actual existing conformers cannot be expected to be accurately determined. In the preliminary studies the C–O dihedral angle was therefore not included as a parameter, reducing the number of possible conformers to nine. Among these were, however, four pairs of enantiomers. As the electron diffraction method does not distinguish between molecules with mirror image conformations the

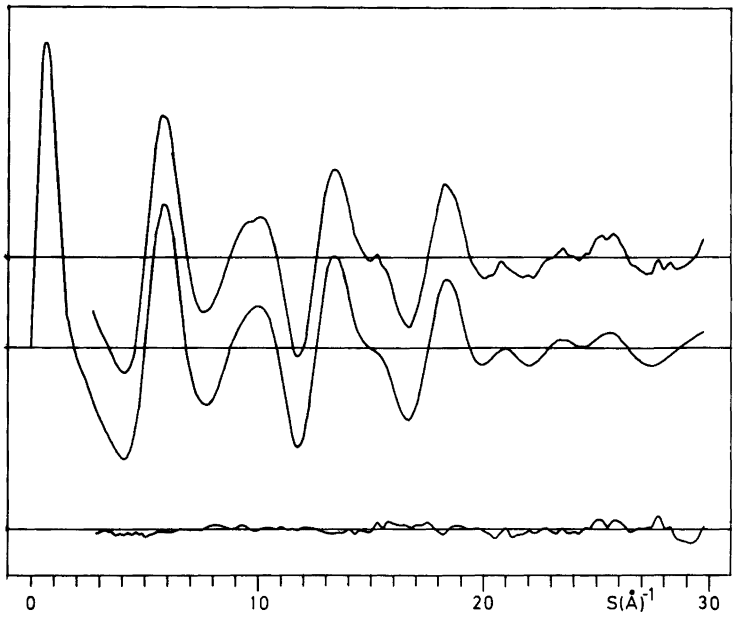

Fig. 2. Experimental (upper) and theoretical (lower) molecular intensity functions for 3-buten-1-ol and the differences between the two.

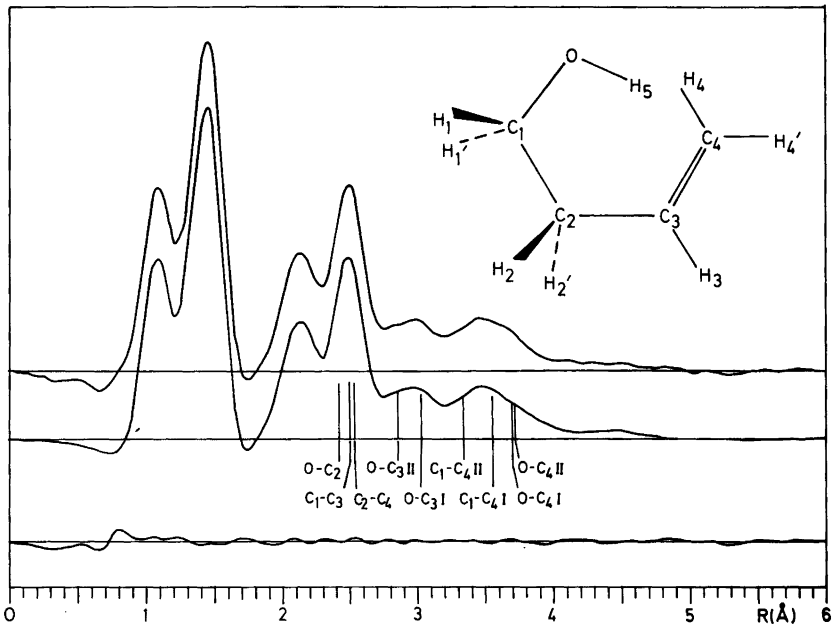

Fig. 3. Experimental (upper) and theoretical (lower) radial distribution functions of 3-buten-1-ol and the differences between the two. Artificial damping constant $k=0.002$. A schematic molecular model is shown to give the numbering of the atoms and the vertical lines indicate the positions of the most important interatomic distances.

number of preliminary models was reduced to five.

The molecular models are based on the following assumptions:

1. Bond distances and valence angles are the same in all conformers.

2. $r(=\overset{|}{C}-H)$ is 0.007 Å smaller than $r(-\overset{|}{C}-H)$.

3. Equal HCH angles and local C_{2v} symmetry at the saturated CH_2 groups.

4. Equal $H-C=C$ angles at C_4.

5. Coplanarity of the bonds connected to the CC double bond.

The five different molecular models were tested individually and in combination. From these preliminary studies it became clear that the C_1-C_2 bond could not be eclipsed with the double bond and that no detectable contribution from a conformer with the C–O bond *anti* relative to C_3-C_2 was present. (Models with the C_2-C_3 dihedral angle equal to 180° was also tested and rejected.)

Only two models, differing mainly in the direction of the *gauche* C_1-C_2 dihedral angle (g^+ and g^-) therefore remained to be studied. Twenty parameters were then necessary to determine the geometry and the conformational composition of 3-buten-1-ol. These parameters which consist of six bond distances, seven valence angles, three torsion angles for each conformer and one parameter for the mol fractions may be identified from Table 3.

In order to calculate a theoretical molecular intensity function for use in the least squares refinements it is necessary to assign values for the vibrational amplitudes (u-values) for all internuclear distances. These vibrational parameters are in principle obtainable from electron diffraction data, but in a rather complicated case like the present one only few of the vibrational amplitudes may be expected to be determined experimentally. A normal coordinate analysis based on an assumed force field was therefore carried out.[16,17] The force field was varied until reasonable agreement with observed vibrational frequencies was obtained.[2,4] The established force field is presented in Table 1 and is fairly reasonable compared to other published data;[18,19] k(C=C) is, however, somewhat small compared to what is normally published (*ca.* 9.6 mdyn/Å). The calculated vibrational amplitudes

Table 1. Force constants applied in the normal coordinate analysis of 3-buten-1-ol.

Stretching (mdyn Å^{-1})	
C=C	7.04
C–C	4.50
C–O	5.00
O–H	7.39
=C–H	5.08
–C–H	4.62
In-plane bending (mdyn Å rad^{-2})	
C=C–C	1.10
C–C–C	0.90
C–C–O	0.90
C=C–H	0.675
C–C–H	0.650
H–C–O	0.700
H–C–H	0.500
Out-of-plane bending (mdyn Å rad^{-2})	
H | =C–	0.20
Torsion (mdyn Å rad^{-2})	
–C=C–	0.20
$-C_2-C_3-$	0.09
$-C_1-C_2-$	0.09
$-C_1-O-$	0.09

(*u*-values) and perpendicular amplitude correction coefficients (*K*-values) are given in Table 2.

The final molecular models from the least squares refinements are presented in Table 3, which also includes the standard deviations (1σ) as obtained using diagonal elements in the applied weight matrix. Molecular models of the two conformers are shown in Fig. 4.

It was not possible to refine all geometrical parameters simultaneously in the least squares analysis. Some of the parameters ($\angle$C–O–H, ω(C–O) of conformer I and $\omega(C_1-C_2)$ and ω(C–O) of conformer II) were therefore determined by a combined trial-and error/least squares procedure. The actual parameter was varied systematically over the expected range of values, and for each parameter value a least squares analysis was carried out, refining the parameters that it was possible to refine. The parameter value corresponding to the lowest squared error sum was then chosen for further work. The process was repeated until selfconsistency was obtained. It is difficult to assign reliable error limits to a parameter obtained by this method. Generally the uncertainty of a parameter determined in this way will depend on the curvature of the squared error sum as a function of the actual parameter. In the present case the C–O dihedral angles of both conformers are very uncertain, while an error limit of about 10° may be estimated for $\angle$C–O–H and $\omega(C_1-C_2)$ for conformer II.

DISCUSSION

The present study shows that the 3-buten-1-ol molecules exist in two conformers in the vapour phase. Models of the geometry of the two conformers are shown in Fig. 4. If other conformers exist, they must be present in small amounts (less than 10 %).

The most abundant conformer (I) is undoubtedly internally hydrogen bonded, and should accordingly be associated with the smallest vibrational O–H stretching frequency observed at 3575 cm^{-1}.[4]

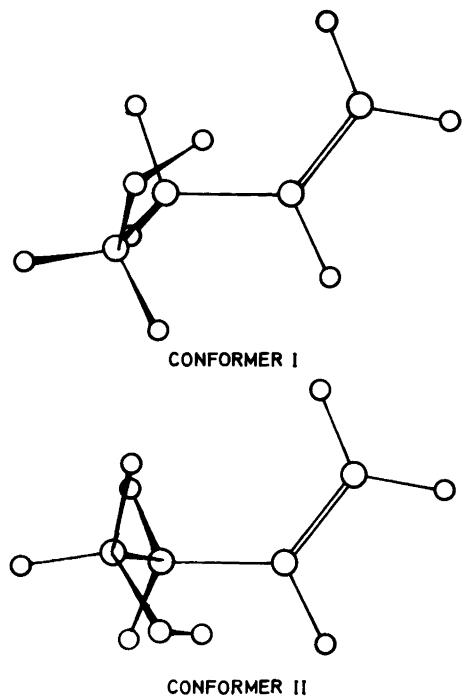

Fig. 4. Molecular models for the two conformers of 3-buten-1-ol.

Table 2. Calculated values for the vibrational amplitudes (u, Å), and perpendicular amplitude correction coefficients (K, Å) for the two conformers of 3-buten-1-ol found to exist in the vapour phase.

Distance type	(R, Å)	u	K	u_{exp}	(R, Å)	u	K
Conformation-independent distances							
C=C	(1.331)	.044	.0172				
C_2-C_3	(1.496)	.049	.0065				
C_1-C_2	(1.528)	.049	.0073				
C–O	(1.415)	.047	.0145				
O–H	(1.014)	.070	.0487	.066			
C_1–H	(1.100)	.079	.0222	.075			
O···C_2	(2.43)	.075	.0070				
C_4···C_2	(2.53)	.064	.0084				
C_1···C_3	(2.50)	.076	.0050				
O···H_1	(2.04)	.107	.0310	.125(8)[a]			
C_1···H_5	(1.91)	.100	.0394	.118(8)[a]			
C_4···H_3	(2.07)	.098	.0443	.116(8)[a]			
C_3···H_4'	(2.09)	.098	.0237	.116(8)[a]			
C_1···H_2	(2.14)	.100	.0154	.090(4)[b]			
C_2···H_1	(2.15)	.096	.0189	.086(4)[b]			
C_3···H_2	(2.12)	.090	.0168	.080(4)[b]			
C_2···H_3	(2.21)	.077	.0285				
C_2···H_4	(2.80)	.136	.0313				
C_2···H_4'	(3.49)	.099	.0165				
Conformation-dependent distances							
	Conformer I				Conformer II		
O···C_3	(3.02)	.164[c]	.0029		(2.84)	.166[c]	.0065
O···C_4	(3.69)	.246	.0017		(3.70)	.245	.0005
O···H_2	(3.33)	.115	.0103		(2.75)	.178	.0131
O···H_3	(3.48)	.275	.0100		(3.03)	.262	.0207
O···H_2'	(2.60)	.178	.0128		(3.33)	.110	.0100
O···H_4	(3.80)	.364	.0131		(4.06)	.319	.0100
O···H_4'	(4.49)	.288	.0067		(4.38)	.291	.0060
C_1···C_4	(3.56)	.151[d]	.0021		(3.30)	.166[d]	.0044
C_2···H_5	(2.31)	.170	.0194		(2.38)	.170	.0225
C_3···H_5	(2.50)	.255	.0171		(2.25)	.250	.0239
C_4···H_2	(2.67)	.137	.0157		(2.74)	.140	.0130
C_3···H_1'	(3.42)	.109	.0135		(2.80)	.175	.0106
C_1···H_3	(2.84)	.167	.0220		(3.10)	.163	.0140
C_4···H_2'	(3.21)	.126	.0116		(3.34)	.111	.0134
C_4···H_1'	(4.49)	.134	.0068		(3.19)	.250	.0144
C_3···H_1	(2.65)	.172	.0154		(3.42)	.108	.0114
C_4···H_5	(2.89)	.334	.0150		(3.03)	.351	.0126
C_1···H_4	(3.87)	.213	.0142		(3.40)	.250	.0216
C_4···H_1	(3.83)	.211	.0064		(4.29)	.155	.0080
C_1···H_4'	(4.41)	.151	.0087		(4.23)	.161	.0097

[a] Refined in a group with the same difference between the u-values as calculated. [b] Refined together with same restriction as in *a*. [c] Experimentally determined to 0.109(19) (Conformer I) and 0.107(19) (Conformer II). [d] Experimentally determined to 0.155(45) (Conformer I) and 0.171 (Conformer II).

Table 3. Geometrical parameters and conformational composition of 3-buten-1-ol. The numbers in brackets are standard deviations from the least squares analyses.

Distances	r_a (Å)	Angles	Degrees
C=C	1.331(2)	∠C=C−C	127.8(6)
C_2-C_3	1.496(5)	$\angle C_1C_2C_3$	111.6(6)
C_1-C_2	1.528(6)	∠C−C−O	112.3(5)
C−O	1.415(2)	∠C−O−H	103.4[b]
O−H	1.014(8)[a]	$\angle C_3=C_4-H$	120.5(25)
C_1-H	1.100(2)[a]	$\angle C_4=C_3-H$	116.1(23)
		∠H−C−H	109.4(28)
	Conformer I	$\omega(C_2-C_3)$	118.4(43)
	68.6(80)%	$\omega(C_1-C_2)$	−70.7(25)
		ω(C−O)	26.0[b]
	Conformer II	$\omega(C_2-C_3)$	85.4(87)
	31.4(80)%	$\omega(C_1-C_2)$	51.0[b]
		ω(C−O)	−38.0[b]

[a] Could not be refined simultaneously. [b] Determined by combined trial-and-error and least squares refinements.

It is also possible that conformer II is stabilized by internal hydrogen bonding, although to a smaller extent. This suggestion is primarily based on the result obtained for the C_2-C_3 dihedral angle of conformer II. If solely a three-dimensional torsional potential should determine $\omega(C_2-C_3)$, it would be expected to be equal to 120° (or 0°). In conformer I $\omega(C_2-C_3)$ does not deviate significantly from 120° and the geometry is favorable for OH···π interaction. In conformer II the hydroxyl group is too far away from the π bond for an effective OH···π interaction to occur when $\omega(C_2-C_3)$ is 120°. The small C_2-C_3 dihedral angle of conformer II might therefore be a result of the inherent more favourable geometry for intramolecular hydrogen bonding when this angle is reduced.

In Table 4 the conformers observed in the present study are compared to the minimum energy conformations calculated by molecular mechanics methods.[5] The results obtained for the major conformer agree fairly well with the calculated data for the model where hydrogen bonding is allowed for (Column two from right). The calculated conformational energies apparently indicate that interactions between the unshared electron pairs of oxygen and the π electrons might be energetically more favourable than internal hydrogen bonding. The authors of the MM paper do not however promote arguments in that direction.

In the proposed stereochemical 3-buten-1-ol models of Ananthasubramanian *et al.*[4] no dihedral angles are given. Fig. 2 in their paper does, however, show a model responsible for the observed frequency at 3575 cm^{-1} that seems to be very close to conformer I of the present study. The other proposed model (3596 cm^{-1}) does however, seem to be one where C_1-C_2 is eclipsed with the CC double bond and does not therefore correspond to the observed minor conformer (II).

The bond distances and valence angles observed for 3-buten-1-ol are in agreement with what is observed for structurally related molecules[20-25] and therefore will not be commented further.

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Table 4. The observed dihedral angles (°) of 3-buten-1-ol compared to results from molecular mechanics calculations.[5]

	Conf. I[a]	Conf. II[a]	Unfolded model	Coiled without U_{ir} *c*	Coiled without U_{ir} *d*	Coiled, U_{ir} included *c*	Coiled, U_{ir} included *d*
$\omega(C_2-C_3)$	118.4(43)	85.4(87)	119	118	118	117	117
$\omega(C_1-C_2)$	−70.7(25)	51.0[b]	180	−64	−64	−60	−56
ω(C−O)	26.0[b]	−38.0[b]	180	82	178	67	−179
Conformational energy (kcal/mol):			57.2	57.8	57.2	56.8	56.4

[a] Present study. [b] See Table 3[b]. [c] Allowing for interaction between hydroxyl group and π electrons as hydrogen bonding. [d] Allowing for interaction between the unshared electron pairs of oxygen and the π electrons.

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