

The Molecular Structure and Conformation of Gaseous Benzyl Alcohol by Electron Diffraction

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The molecular structure and conformation of benzyl alcohol have been studied by the gas electron diffraction method. The oxygen atom was found to be twisted out of the plane of the phenyl ring by ca. 54° rotation of the C_{Ar}–C bond. Conformers with the hydroxyl hydrogen *anti* to one of the methylene hydrogens (*endo*) were found to be most stable, but it was not possible to distinguish between the two possible *endo* conformers.

The conformational properties of benzyl alcohol and the possibilities for intramolecular hydrogen bonding in this molecule have been the subject of several spectroscopic studies.^{1–5}

The O–H stretching vibrations give rise to an asymmetric IR absorption band with maxima at about 3635 and 3615 cm⁻¹. In an IR study of competitive intramolecular hydrogen bonding in a series of benzyl alcohols, Campbell *et al.*¹ interpreted the data for the mother compound as resulting from a conformational mixture consisting of 35% of a conformer with a free hydroxyl group and 65% of an intramolecular hydrogen-bonded (OH⋯π) conformer.

In a later IR study Lutsikii *et al.*² support the conclusion that an OH⋯π internally hydrogen-bonded conformer is predominating in benzyl alcohol, and they suggest a stabilization energy of 2.0 ± 0.8 kJ mol⁻¹ due to intramolecular hydrogen bonding.

Granzhan *et al.*³ have also studied unsaturated alcohols by IR-spectroscopy. They ascribe the benzyl alcohol low-frequency band at 3615 cm⁻¹ as due to a conformer in which the O–H bond eclipses the C_{Ar}–C bond.

Oki *et al.*⁴ have pointed out that the O–H

frequencies in benzyl alcohol are so similar to those of ethanol (3637 and 3623 cm⁻¹) that they might merely be those characteristic of a primary alcohol.

The conformations of benzyl alcohol and derivatives have also been studied by NMR spectroscopy by Abraham and Bakke.⁵ They found that an *endo* conformation of the OH proton (anti to a CH proton) is favoured over the *exo* conformation (H *anti* to phenyl) by ca. 4 kJ mol⁻¹. Their results are consistent with either a conformer with a C_{Ar}–C torsional angle of 60° or with a model with free rotation around the C_{Ar}–C bond. In conclusion they state that their results provide no support for the existence of an intramolecular hydrogen bond in benzyl alcohol.

EXPERIMENTAL

Electron diffraction photographs of a commercial sample of benzyl alcohol were obtained by the Balzers Eldigraph KDG-2 unit.^{6,7} The experimental conditions were as summarized: Nozzle-to-plate distances 498.66 mm (3 plates) and 248.52 mm (3 plates), electron wavelength as determined by calibration to benzene 0.05864 Å and the nozzle temperature 105–115 °C. Ranges of data were 1.250–15.750 and 2.250–31.250 (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.⁸ The experimental data were corrected in the usual way⁹ and the modification function used was $s|r_C|^{-2}$. The scattering amplitudes and phases⁹ were calculated using the partial-wave method¹⁰ based upon analytical HF potentials for the C and O atoms¹¹ and the best electron density of bonded hydrogen for the H atoms.¹² The inelastic scattering factors used were those of Tavard *et al.*¹³

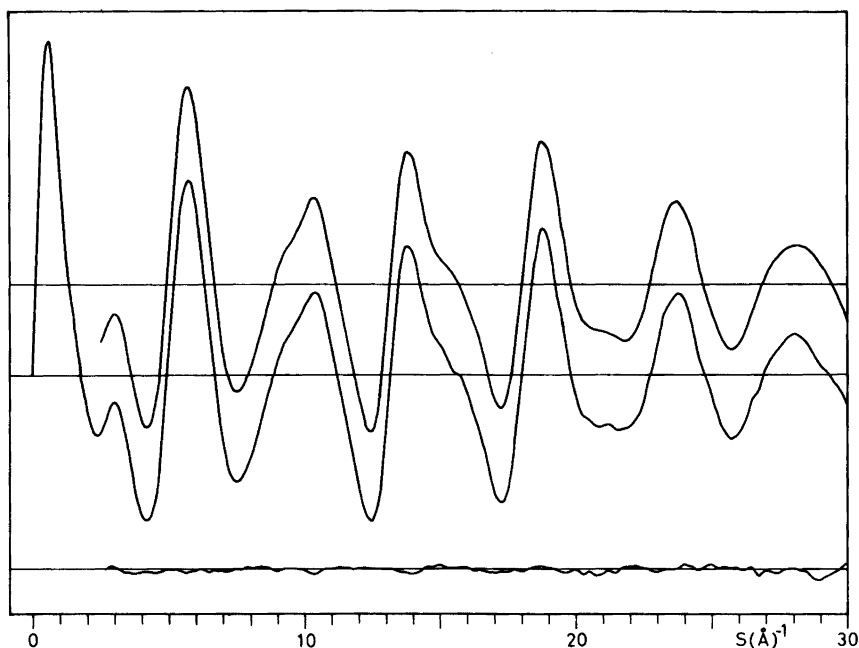


Fig. 1. Benzyl alcohol. Experimental (upper) and theoretical (lower) molecular intensity functions and the difference curve.

STRUCTURE ANALYSIS

From the individual modified experimental molecular intensity curves a composite intensity curve was computed by scaling the curves and averaging the intensities in the overlap region. The final experimental molecular intensity curve is shown in Fig. 1. The experimental RD curve for benzyl alcohol is shown in Fig. 3.

The vibrational amplitudes necessary for calculating theoretical molecular intensity and radial distribution (RD) functions were obtained from a normal coordinate analysis based on an assumed force field.^{14,15} The applied force constants are shown in Table 1. The vibrational frequencies calculated from these force constants gave a satisfactory correspondence with the observed frequencies.¹⁻³ The calculated vibrational amplitudes (u -values) and perpendicular amplitude correction coefficients (K -values) for model A (see Table 3) are presented in Table 2.

In order to gain information about the conformational problem several theoretical RD curves were calculated. These were based on preliminary values for the geometrical parameters, the calculated vibrational amplitudes, and were differing only in

Table 1. Force constants applied in the normal coordinate analysis of benzyl alcohol.

Stretching (mdyn Å ⁻¹)	
C—C	4.20
C—O	5.00
O—H	7.40
C=C=C _{Ar}	7.30
=C—H	5.08
—C—H	4.62
In-plane bending (mdyn Å rad ⁻²)	
H—C—O	0.700
C—C—H	0.650
C—C—O	0.660
H—C—H	0.500
C=C—C	1.100
C=C=C=C	1.500
C=C—H	0.420
Out-of-plane bending (mdyn Å rad ⁻²)	
—C=C—	0.30
Torsion	
—O—C—	0.09
—C ₁ —C ₆ —	0.09
—C=C—	0.30

Table 2. Benzyl alcohol. Calculated vibrational amplitudes (u) and perpendicular amplitude correction (k) coefficients. Non-bonded distances including hydrogen omitted.

Dist.	($r, \text{\AA}$)	$u, \text{\AA}$	$k, \text{\AA}$
C=C _{Ar}	(1.394)	0.043	0.0047
C _{Ar} -C	(1.514)	0.049	0.0045
C-O	(1.415)	0.046	0.0300
C _{Ar} -H	(1.072)	0.077	0.0146
C-H	(1.101)	0.079	0.0372
O-H	(1.036)	0.070	0.1049
O...C ₁	(2.45)	0.079	0.0144
O...C ₂	(2.96)	0.138	0.0093
O...C ₆	(3.56)	0.171	0.0052
O...C ₃	(4.29)	0.126	0.0043
O...C ₅	(4.72)	0.153	0.0022
O...C ₄	(5.01)	0.114	0.0022
C ₁ ...C ₅	(2.41)	0.060	0.0051
C ₆ ...C ₇	(2.54)	0.077	0.0045
C ₂ ...C ₇	(2.49)	0.077	0.0028
C ₁ ...C ₄	(2.78)	0.058	0.0040
C ₅ ...C ₇	(3.81)	0.076	0.0041
C ₃ ...C ₇	(3.78)	0.077	0.0021
C ₄ ...C ₇	(4.29)	0.077	0.0028

the C_{Ar}-C dihedral angle. Three of these theoretical RD curves, corresponding to $\omega(\text{C}_{\text{Ar}}-\text{C})$ equal to 0, 60 and 90° are shown in Fig. 2, where also the difference between experimental and theoretical curves are illustrated. From Fig. 2 it will clearly be seen that a 90° conformer is incompatible with the experimental data. A planar conformer cannot be excluded at this stage, but the 60° conformer obviously fits the experimental data best.

The further refinements of the molecular structure of benzyl alcohol were based on least squares refinements of the molecular intensity data. In calculating molecular models hexagonal symmetry of the aromatic ring and local C_{2v} symmetry of the methylene group were assumed. Twelve parameters were then necessary to describe the geometry of benzyl alcohol. These include six bond lengths (C=C_{Ar}, C_{Ar}-C, C-O, O-H, C-H(CH₂), C_{Ar}-H) four valence angles ($\angle \text{CCO}$, $\angle \text{COH}$, $\angle \text{HCH}$, $\angle \text{C}_7\text{C}_1\text{C}_2$) and two dihedral angles [$\omega(\text{C}_{\text{Ar}}-\text{C})$, $\omega(\text{C}-\text{O})$].

Some of the vibrational amplitudes for the non-bonded distances were refined in groups with the restriction that the amplitudes within one group

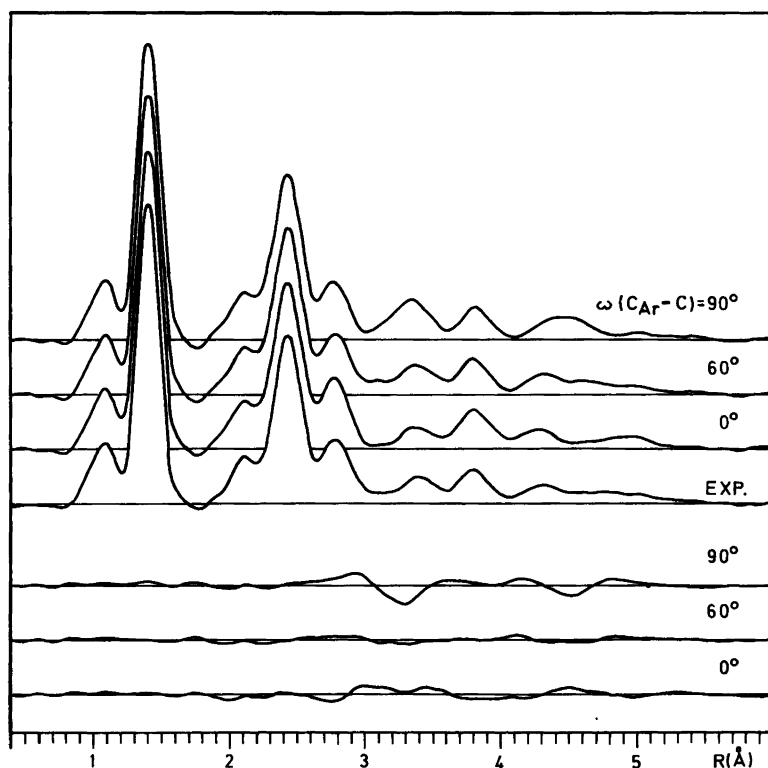


Fig. 2. Benzyl alcohol. Experimental and theoretical radial distribution curves. $\omega(\text{C}_{\text{Ar}}-\text{C})$: 0, 60, 90°.

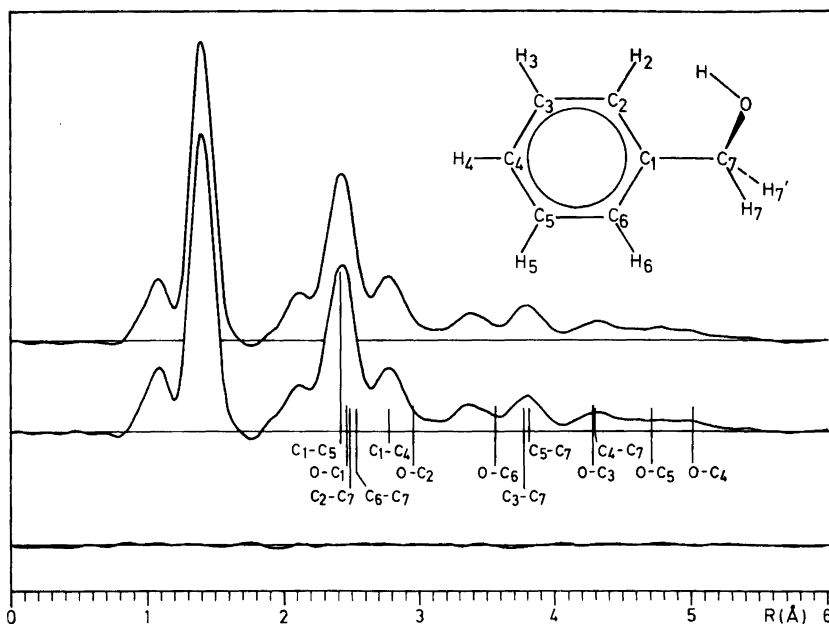


Fig. 3. Benzyl alcohol. Experimental (upper) and theoretical (lower) radial distribution functions and the difference curve. Artificial damping constant $k=0.002$. The theoretical RD curve is calculated for model A, in Table 3.

should differ by the same amounts as did the calculated u -values.

u -Values for the shortest CC and CO non-bonded distances over one valence angle were refined in one group [$u(\text{OC}_1)$, $u(\text{C}_1\text{C}_3)$, $u(\text{C}_2\text{C}_7)$, $u(\text{C}_6\text{C}_7)$]. Other groups were $u(\text{OC}_2)$ and $u(\text{OC}_6)$; $u(\text{OC}_3)$ and $u(\text{OC}_5)$; $u(\text{C}_3\text{C}_7)$ and $u(\text{C}_5\text{C}_7)$; $u(\text{C}_1\text{C}_4)$ and $u(\text{C}_4\text{C}_7)$. The resulting u -values were very similar to the calculated ones, the deviations being between 0.0008 and 0.0085 Å. These findings support a model where the oxygen atom is fixed relative to the phenyl ring.

The two parameters defining the position of the OH hydrogen atom ($\angle \text{COH}$ and $\omega(\text{C}-\text{O})$) did not refine well in the least squares process. They were therefore studied by varying each of them in small steps over the expected parameter range, carrying out least squares analyses for each fixed parameter value. The value that gave the smallest squared error sum for each of these parameters was in principle chosen for further work.

The study of the C—O dihedral angle did not give unambiguous results. Fig. 4 shows the squared error sum as a function of the C—O dihedral angle, when most of the geometrical parameters were

varied in least squares refinements. The function shows two approximately equal minima corresponding to the two *endo* conformers, and a maximum corresponding to the *exo* conformer.

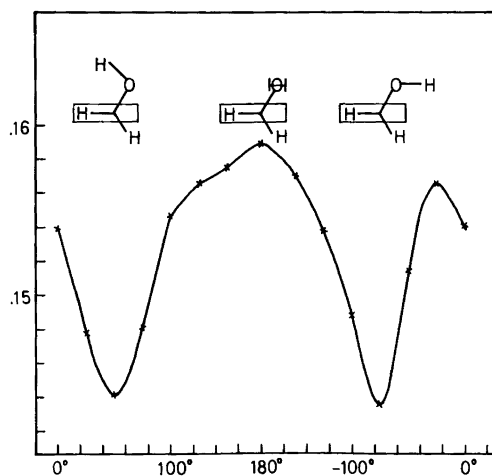


Fig. 4. Benzyl alcohol. The squared error sum for similar least squares runs as a function of the C—O dihedral angle.

Table 3. Benzyl alcohol. Structural results from least squares refinements for three conformers (see Fig. 4). Distances in Å (r_a), angles in degrees.

$\omega(\text{C}-\text{O})$	A(<i>endo</i>) 50°	B(<i>exo</i>) 180°	C(<i>endo</i>) -75°
$r(\text{C}_{\text{Ar}}-\text{C})$	1.514(2)	1.515(2)	1.515(2)
$r(\text{O}-\text{C})$	1.415(3)	1.415(3)	1.415(3)
$r(\text{O}-\text{H})$	1.034(11)	1.032(11)	1.032(11)
$r(\text{C}_{\text{Ar}}-\text{H})$	1.072(2)	1.073(2)	1.073(2)
$r(\text{C}=\text{C})$	1.394(1)	1.394(1)	1.394(1)
$\angle \text{C}-\text{C}-\text{O}$	114.5(5)	114.7(5)	114.3(5)
$\angle \text{C}-\text{O}-\text{H}$	(105.3) ^a	(105.3)	(105.3)
$\angle \text{C}-\text{C}-\text{H}$	109.4(15)	109.6(16)	109.3(16)
$\angle \text{C}_7\text{C}_1\text{C}_2$	118.0(8)	117.8(8)	118.3(9)
$\omega(\text{C}_{\text{Ar}}-\text{C})$	53.8(20)	53.2(21)	53.7(21)

^a Determined by combined trial-and-error/least squares calculations.

The other structural parameters were practically independent of $\omega(\text{C}-\text{O})$. The geometrical parameters corresponding to the *exo* and the two *endo* conformers, are presented in Table 3.

In the present case it was not possible to determine the conformational composition. Obviously any combination of the two *endo* conformers will fit the experimental data, while an eventual contribution from an *exo* conformer is too small to be detected with certainty.

DISCUSSION

The present study shows that benzyl alcohol exists in conformers where the oxygen atom is twisted out of the plane defined by the aromatic ring. The distortion is characterized by a $\text{C}_{\text{Ar}}-\text{C}$ dihedral angle of about 54°.

The position of the OH hydrogen cannot be determined with certainty, as this atom gives only minor contributions to the scattered intensities. The present results strongly indicate that the *endo* conformers are the most stable ones, but it is not possible to distinguish between the two different *endo* conformers (A and C). This is a regrettable situation, as one might expect internal OH $\cdots\pi$ hydrogen bonding to occur in conformer A, but not in conformer B.

According to the present ED results it is therefore possible, but not proved certain, that the major

conformer of benzyl alcohol is stabilized by internal OH $\cdots\pi$ hydrogen bonding. The distances between the OH group in conformer A and the C_1 and C_2 atoms are small enough to allow for some interaction ($\text{C}_1\cdots\text{O}:2.45$ Å, $\text{C}_1\cdots(\text{O})\text{H}:2.53$ Å, $\text{C}_2\cdots\text{O}:2.96$ Å, $\text{C}_2\cdots(\text{O})\text{H}:3.01$ Å). The $\text{C}_2\text{C}_1\text{C}_7$ valence angle of 118° does also act toward improving the conditions for eventual internal hydrogen bonding. This angle is, however, determined with a standard deviation of 0.8° and is therefore hardly significantly smaller than 120°.

The result for the CCO valence angle (114.5°) does, however, not point in the same direction. A reduction of this angle should be expected to improve the conditions for internal hydrogen bonding. In ethylene chlorohydrine, for example, which is strongly stabilized by internal hydrogen bonding, the CCO valence angle is 111.5°.¹⁶ The ED results do not therefore give the final answer to the question of whether benzyl alcohol is stabilized by internal hydrogen bonding or not.

The other geometrical parameters for benzyl alcohol are in agreement with what is observed for structurally related molecules and will therefore not be commented further.

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