

Microwave, Electron Diffraction, *Ab Initio* and IR Study of 2-Cyclopropylethanol

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The structure and conformation of 2-cyclopropylethanol have been studied by microwave spectroscopy, gas electron diffraction, gas-phase infrared spectroscopy and by theoretical *ab initio* calculations at the 6-31G** level of theory. The microwave spectra of the parent and one deuterated species (hydroxyl group) have been investigated in the 26.5–39.5 GHz spectral region at –15°C. One conformer was assigned. This rotamer is stabilized by an intramolecular hydrogen bond formed between the hydrogen atom of the hydroxyl group and the pseudo- π electrons on the outside of the nearest C–C edge of the cyclopropyl ring. The identified conformer is shown to be present in a concentration of 10–30% of the total. The electron diffraction data are in accordance with the presence of three 2-cyclopropylethanol conformers, each being characterized by the dihedral angles associated with the C2–C3, C1–C2 and C1–O1 bonds, as follows: G+/G+/G– (48.6%); G+/G–/A (19.7%); G+/A/A (31.7%). The most abundant conformer is the one that was identified from the microwave spectrum. The observed conformational composition is in satisfactory agreement with that deduced from the energies of the conformers studied by the *ab initio* calculations.

It is now well established by means of microwave (MW) spectroscopy that the most stable conformations of α -hydroxy,^{1–3} α -amino⁴ and α -mercapto⁵ cyclopropanes are stabilized by intramolecular hydrogen (H) bonds formed between one H atom of the said groups and the pseudo- π electrons of the cyclopropane ring.⁶

When any of these groups are in the β -position, little is known about the conformational preferences. The simplest of such compounds, 2-cyclopropylethanol, has been studied previously in solution by two research groups^{7–9} using IR^{7–9} and NMR⁹ spectroscopy. Joris *et al.*⁷ found no evidence for intramolecular H bonding in the title molecule, while Oki *et al.*^{8,9} found that the conformer capable of exhibiting this interaction indeed exists in a mixture with other rotamers. The present work was undertaken in order to extend these studies to the gas phase, using the powerful methods of gas electron diffrac-

tion (GED) and MW spectroscopy supported by *ab initio* computations at a high level of theory, with the aim of definitely establishing whether a H-bonded conformer exists for this molecule and what other conformations might be present. The gas-phase IR spectrum was also recorded in order to correlate the IR shifts of the O–H stretching fundamental vibration with the conformational composition.

Experimental

Microwave experiment. Two samples were used in the MW work. The first was prepared employing the method of Ref. 10 with 3-buten-1-ol as the alkene. The second sample was obtained by hydroboration–oxidation¹¹ of vinylcyclopropane.¹² Both these samples were purified by preparative gas chromatography. The MW spectrum was studied using the Oslo spectrometer, which is described in Ref. 13. The 26.5–39.5 GHz spectral region was investigated with the microwave absorption cell cooled to about –15°C. Lower temperatures, which would have increased the MW spectral intensities, could not be employed owing to insufficient vapour pressure of the

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compound. The pressure was about 2–4 Pa, and the accuracy of the spectral measurements is presumed to be better than ± 0.10 MHz. The deuteration of the hydroxyl group was achieved by conditioning the MW cell with heavy water and then introducing the normal species.

Electron diffraction experiment. The sample used in the GED study was synthesized using the method of Hart and Wyman.¹⁴ Electron diffraction diagrams of 2-cyclopropylethanol were recorded with the Balzers Eldigraph KD-G2 unit.^{15,16} Two nozzle-to-plate distances were used. The 50 cm (four plates) and 25 cm (five plates) data gave intensity values in the s -regions 1.50–15.00 and 3.00–30.25 \AA^{-1} , respectively. For both sets of data a scattering increment of 0.25 \AA^{-1} was employed. The nozzle temperature was 23°C during the exposures.

The calculation of the scattering amplitudes and phases, the data reduction and the correction to the $s/|f'_c|^2$ modified molecular intensities were carried out as described elsewhere.^{17,18} A diagonal weighting scheme was applied, and the standard deviations in the structural parameters (σ_{LS}) should be augmented by a factor of two to account for data correlation. The experimental

molecular intensity curves and the corresponding radial distribution (RD) curve are shown in Figs. 2 and 3 below.

IR experiment. The gas-phase infrared spectrum in the 500–4000 cm^{-1} region was recorded at room temperature employing a Bruker IFS 88 spectrometer equipped with a multiple-reflection cell. The pressure was roughly 150 Pa, the path length was approximately 5.4 m, and the resolution 2 cm^{-1} .

Structural studies and results

Ab initio calculations. The computations were made using the Gaussian 90 program package¹⁹ running on the Cray-X-MP/216 computer in Trondheim. The 6-31G** basis set was chosen. There are three internal axes of rotation in 2-cyclopropylethanol namely C2–C3, C1–C2, and C1–O1 (Fig. 1). Consequently, a large number of conformations is possible. A complete mapping of the potential surface of these is beyond our present possibilities. Computations were restricted to the four conformations shown in Fig. 1, which are believed to be the four rotamers with the lowest energies. In all these four con-

Table 1. Structure of conformer I of 2-cyclopropylethanol as calculated by *ab initio* using the 6-31G** basis set.

Distances/pm		Angles/°		Dihedral angles/°	
O1–H1	94.3	H1–O1–C1	109.3	H1–O1–C1–H3	177.8
C1–O1	140.1	O1–C1–H2	106.1	H1–O1–C1–H2	61.8
C1–H2	108.4	O1–C1–H3	110.7	H1–O1–C1–C2	–61.8
C1–H3	109.1	O1–C1–C2	113.1	O1–C1–C2–H4	–173.7
C1–C2	152.5	C1–C2–H4	108.5	O1–C1–C2–H5	–57.6
C2–H4	108.9	C1–C2–H5	108.7	O1–C1–C2–C3	64.8
C2–H5	108.7	C1–C2–C3	113.5	C1–C2–C3–H6	58.4
C2–C3	151.6	C2–C3–H6	114.1	C1–C2–C3–C4	–157.7
C3–H6	108.0	C2–C3–C4	120.5	C1–C2–C3–C5	–86.7
C3–C4	149.6	C2–C3–C5	121.0	C2–C3–C4–H7	2.6
C4–H7	107.7	C3–C4–H7	117.8	C2–C3–C4–H8	–141.5
C4–H8	107.6	C3–C4–H8	118.4	C2–C3–C5–H9	–2.1
C5–H9	107.6	C3–C5–H9	118.4	C2–C3–C5–H10	142.8
C5–H10	107.7	C3–C5–H10	118.6		
C4–C5	149.8				

Substitution coordinates of hydroxyl group hydrogen atom/pm

	a	b	c
Calcd. from rotational constants ^a	115.5(1)	134.26(9)	Imaginary
From <i>ab initio</i> ^b	131.5	143.2	28.4

Hydrogen bond parameters^b

Distances/pm		Angles/°	
H1 ... C3	271.5	O1–H1 ... C3	101.0
H1 ... C5	274.1	O1–H1 ... C5	120.6
O1 ... C3	304.0	O1–H1, C3–C5 ^c	54.3
O1 ... C5	332.2		

Sum of van der Waals radii^{d,e}/pm

H ... C _{ring}	290
C _{ring} ... O	310

^a Calculated using the rotational constants of Table 4 in Kraitchman's equations.²⁷ ^b Calculated from the structure above. ^c Angle between O1–H1 and C3–C5 bonds. ^d Taken from Ref. 25. ^e The van der Waals radius of carbon was taken to be 170 pm as given in Ref. 25 for the half-thickness of an aromatic molecule.

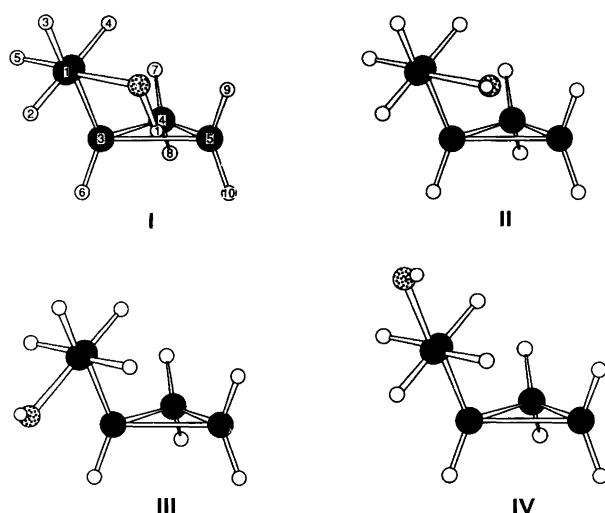


Fig. 1. The four 2-cyclopropylethanol conformers, presumed to be the ones with the lowest energies. Atom numbering given on sketch of conformer I. Conformer I, whose MW spectrum was assigned, has an intramolecular H bond formed between the hydroxyl group H atom and the pseudo- π electrons on the outside of the C3–C5 edge.

formers the C1–C2–C3–H6 chain of atoms are *gauche* (60° from *syn*), because this conformation is generally preferred for large substituents, such as for example cyclopropanemethane chloride and -bromide.^{20–23} In rotamer I (G+/G+/G–) the H1–O1–C1–C2 chain is *gauche* to allow an intramolecular H bond to be formed, while this angle is *anti* in II (G+/G+/A), III (G+/G–/A), and IV

Table 2. Selected parameters obtained for conformations I–IV of 2-cyclopropylethanol in the *ab initio* calculations with the 6-31G** basis set.

Conformation	I	II	III	IV
Energy relative to I ^a /kJ mol ⁻¹	0.0	4.4	0.6	1.1
Rotational constants/MHz				
A	7 484.8	7 562.4	8 548.1	11 206.0
B	2 218.7	2 205.2	1 893.1	1 638.9
C	1 878.7	1 878.5	1 884.5	1 559.6
Dihedral angle/°				
\angle C1–C2–C3–H6	58.4	59.8	59.0	61.0
\angle O1–C1–C2–C3	64.8	67.4	-63.4	-179.3
\angle H1–O1–C1–C2	-61.8	-177.2	175.5	-179.7
Dipole moments ^b /10 ⁻³⁰ Cm				
μ_a	4.61	4.24	2.50	0.31
μ_b	2.36	1.94	0.30	4.79
μ_c	3.60	2.94	5.37	2.73

^aThe total energy of conformer I was calculated to be $-708\,832.27$ kJ mol⁻¹. ^bComponents of the total dipole moment along the principal inertial axes. 1 debye = $3.335\,64 \times 10^{-30}$ C m.

(G/A/A), because ethanol derivatives without internal H bonds generally prefer this conformation by roughly 3 kJ mol⁻¹ over the H1–O1–C1–C2 *gauche* rotamer.²⁴ Conformers I–IV are presumed to be those one could hope to assign by MW spectroscopy, and they are thought to make up most of the ED scattering intensities.

Complete geometry optimization was carried out for each of the four conformations shown in Fig. 1. They were all found to be stable, as no imaginary vibrational frequencies were computed. The fully optimized geometry of I is given in Table 1, while selected conformational parameters of conformers I–IV are shown in Table 2. The dihedral angles of II–IV were calculated to take their normal values close to 60° and 180° (Table 2), as expected. No unusual features concerning the other structural parameters of rotamers II–IV were found in the computa-

Table 3. MW spectrum of the ground vibrational state of conformer I of 2-cyclopropylethanol.

Transition	Observed frequency ^a /MHz	Obs. – calc. frequency/MHz
7 _{0,7} ← 6 _{0,6}	27 990.54	-0.06
7 _{1,6} ← 6 _{1,5}	29 820.11	0.08
7 _{1,7} ← 6 _{1,6}	27 427.05	-0.04
7 _{2,5} ← 6 _{2,4}	29 581.90	0.04
7 _{2,6} ← 6 _{2,5}	28 719.29	-0.04
7 _{3,4} ← 6 _{3,3}	29 035.70	0.00
7 _{3,5} ← 6 _{3,4}	28 968.34	-0.01
7 _{4,3} ← 6 _{4,2}	28 943.47	-0.09
7 _{4,4} ← 6 _{4,3}	28 941.97	0.09
7 _{6,1} ← 6 _{6,0}	28 905.11	0.02
7 _{6,2} ← 6 _{6,1}	28 905.11	0.02
8 _{0,8} ← 7 _{0,7}	31 770.34	-0.06
8 _{1,7} ← 7 _{1,6}	33 962.73	0.06
8 _{1,8} ← 7 _{1,7}	31 283.43	-0.05
8 _{2,6} ← 7 _{2,5}	33 965.97	0.02
8 _{2,7} ← 7 _{2,6}	32 764.44	0.03
8 _{3,5} ← 7 _{3,4}	33 256.39	0.03
8 _{3,6} ← 7 _{3,5}	33 123.80	-0.04
8 _{4,4} ← 7 _{4,3}	33 102.87	0.02
8 _{4,5} ← 7 _{4,4}	33 098.27	0.00
8 _{5,3} ← 7 _{5,2}	33 063.27	-0.01
8 _{5,4} ← 7 _{5,3}	33 063.27	0.06
8 _{6,2} ← 7 _{6,1}	33 044.00	-0.03
8 _{6,3} ← 7 _{6,2}	33 044.00	-0.03
8 _{7,1} ← 7 _{7,0}	33 032.94	0.05
8 _{7,2} ← 7 _{7,1}	33 032.94	0.05
9 _{0,9} ← 8 _{0,8}	35 520.30	0.09
9 _{1,8} ← 8 _{1,7}	38 049.06	-0.07
9 _{1,9} ← 8 _{1,8}	35 123.29	0.10
9 _{2,7} ← 8 _{2,6}	38 354.31	-0.03
9 _{2,8} ← 8 _{2,7}	36 787.45	0.04
9 _{3,6} ← 8 _{3,5}	37 278.07	-0.12
9 _{4,5} ← 8 _{4,4}	37 273.36	-0.04
9 _{4,6} ← 8 _{4,5}	37 262.43	0.03
9 _{6,3} ← 8 _{6,2}	37 186.84	0.01
9 _{6,4} ← 8 _{6,3}	37 186.84	0.01
9 _{7,2} ← 8 _{7,1}	37 170.87	-0.01
9 _{7,3} ← 8 _{7,2}	37 170.87	-0.01
9 _{8,1} ← 8 _{8,0}	37 160.95	0.01
9 _{8,2} ← 8 _{8,1}	37 160.95	0.01

^a ± 0.10 MHz.

Table 4. Ground-state spectroscopic constants^{a,b} of conformer I of 2-cyclopropylethanol.

Species:	Parent	Deuterated ^c
No. of transitions:	40	26
R.m.s. deviation ^d /MHz:	0.052	0.079
A_0 /MHz	7 347.03(21)	7 168.56(44)
B_0 /MHz	2 236.8729(37)	2 224.2773(74)
C_0 /MHz	1 885.4009(37)	1 863.7296(87)
Δ_J /kHz	0.800(21)	0.809(47)
Δ_{JK} /kHz	-2.343(28)	-2.106(55)

^aA-reduction, I' -representation.²⁶ ^bUncertainties represent one standard deviation. ^cDeuteration has taken place in the hydroxyl group. ^dRoot-mean-square deviation. ^eFurther quartic constants preset at zero.

tions, and therefore their full theoretical structures are not listed in Table 2.

It is seen in Table 2 that conformer I was calculated to be slightly more stable than the other three rotamers. The internal H bond of I must be very weak, as the H1...C3 and H1...C5 distances are computed to be only slightly shorter than the sum of the van der Waals radii²⁵ of hydrogen and the half-thickness of aromatic carbon (Table 1).

MW spectrum and assignments. The predicted dipole moments shown in Table 2 are substantial for all the four conformations, yet the MW spectrum of this molecule is strikingly weak. The absence of strong lines is in itself taken as an indication that not one or two, but several conformers with rather similar energies are present.

A rather large a -axis dipole moment component (Table 2) was predicted for I. The strongest transitions expected for this conformer were thus expected to be the a - R -lines. These transitions, which turned out to be remarkably weak, were readily assigned* and are listed in Table 3. Searches for b - and c -type transitions were then made, but none could be assigned with certainty. The spectroscopic constants (A -reduction, I' -representation²⁶) are collected in Table 4.

The ground-state transitions were accompanied by satellite lines presumably originating from vibrationally excited states of this conformer, but they were very weak, and none of them was assigned.

The deuterated species (hydroxyl group) was studied in order to locate exactly the position of the H1 atom using Kraichman's equations.²⁷ The assignments were made in a straightforward manner for this isotopomer. The spectroscopic constants are collected in Table 4, whereas Kraichman's substitution coordinates²⁷ for H1 are reported in Table 1. There is satisfactory agreement

* The complete spectra of the parent and deuterated species are available from the authors upon request, or from The National Institute of Standards and Technology, Microwave Data Center, Molecular Physics Division, Bldg. 221, Rm. B265, Gaithersburg, MD 20899, USA, where they have been deposited.

between these coordinates (Table 1) and those obtained in the theoretical computations for conformer I. Large discrepancies (not given in Tables 1 or 2) were calculated for rotamers I-IV for the same atom. This shows beyond doubt that I has indeed been assigned, and not confused with any other rotameric form or an impurity.

After the above assignments had been made, there remained only very weak unassigned transitions which may belong to vibrationally excited states of I, to further conformers, or perhaps to impurities.

Absolute intensity and conformational composition. The MW spectrum of I is much weaker than expected if this conformer were the only one present. Absolute intensities of MW transitions may in principle allow the determination of the fraction of molecules belonging to a particular rotamer.²⁸ In the present case the following procedure was used to derive a crude, yet quantitative, estimate of the fraction of molecules belonging to the assigned conformer I.

The peak absorption coefficient α (in cm^{-1}) of any asymmetric-top transition is given by eqn. (1).²⁹ The symbols and units employed in this formula are those of

$$\alpha = 3.85 \times 10^{-14} \frac{\nu_0^2 \mu_a^2 \lambda_g \sigma}{T^{5/2} (\Delta\nu)_1} F_{\nu}(ABC)^{1/2} g_1 \exp(-E_{J\nu}/kT) \quad (1)$$

Refs. 29 and 30. In order to calculate α for the $8_{3,5} \leftarrow 7_{3,4}$ transition using this formula for later comparison with experiment, the following approximations were made: For this a -type R -branch transition $\exp(-E_{J\nu}/kT) = 1$ at 258 K to a good approximation. In our case σ and $g_1 = 1$. The rotational constants were taken from Table 4 and with them, λ_a was calculated to be 6.9 for this transition. μ_a was taken to be 1.4 Debye, as found by the *ab initio* computations shown in Table 2. The vibrational frequencies calculated by *ab initio* (not shown in Table 2) were reduced³¹ by 10% and used to calculate F_0 by assuming that $F_0 = \Pi(1 - \exp(-h\nu_i/kT))$ for the ground vibrational state. F_0 was calculated to be 0.072 at 258 K in this manner. $(\Delta\nu)_1$ was estimated to be roughly 40 MHz Torr^{-1} , with a large uncertainty. With these values, α was calculated to be $1.7 \times 10^{-7} \text{ cm}^{-1}$ for the said transition. There is a large uncertainty attached to this number. We estimate this uncertainty to be at least 50%.

The *observed* value for α was $2.5(7) \times 10^{-8} \text{ cm}^{-1}$, which is approximately seven times lower. This value was obtained by calibrating the cell with OCS transitions whose absolute peak intensities are reported in Ref. 32. It is then concluded that between 10 and 30% of the gas is conformer I. The remaining portion of the gas is presumed to consist of several further conformers left unassigned. It is impossible from the MW data alone to say how many or what other rotamers are present. It is also impossible to say if I is the most stable conformer, i.e. the global minimum, although this is considered to be most likely, and in agreement with the theoretical computations (Table 2) and ED findings (see below).

Electron diffraction study. The molecular structure and conformational composition of 2-cyclopropylethanol were determined from least-squares refinements of the molecular intensity data, in combination with information obtained from radial distribution (RD) curves. Vibrational amplitudes (u) and perpendicular correction coefficients (K) for all interatomic distances of three conformers (see below) were calculated,³³ based on a valence force field transferred from other similar molecules.^{34,35} The geometries of the conformers were based on r_a molecular models, which include corrections for shrinkage effects.³⁶

When three-fold rotation barriers at the C2–C3, C1–C2 and C1–O1 bonds are assumed, the molecule may in principle exist in 27 different conformations. Among these there are 13 pairs of mirror images. The species within a mirror image pair are, however, indistinguishable by the GED method, and the number of possible unique contributing conformers that might be observed is therefore reduced to 14. Because of the low scattering power of the H atom, the GED method cannot normally distinguish with certainty between conformers differing only in the position of one H atom, especially when several conformers are present simultaneously. It will accordingly be difficult to distinguish between conformers with different H1–O1–C1–C2 dihedral angles, but where the other geometric parameters are nearly identical, such as for example in the case of conformers I and II.

As pointed out above, an *anti* H1–O1–C1–C2 dihedral angle is generally preferred over *gauche* by about 3 kJ mol⁻¹.²⁴ Exceptions to this rule are expected to occur when conformers with a H1–O1–C1–C2 *gauche* dihedral angle are specially stabilized, for example by internal H bonding, or when *anti* conformers are destabilized, for example by steric interactions. In the present case it thus seems reasonable to assume that conformers other than the one that might be internally H-bonded, have *anti* H1–O1–C1–C2 dihedral angles.

In order to elucidate the validity of this assumption, and to establish whether it is justified to omit other conformers than conformations I–IV studied above by *ab initio* computations, molecular mechanics (MM3) calculations³⁷ with complete geometry optimization were carried out for all the 14 unique conformations. The MM3 calculations indicate that conformers with *anti* H1–O1–C1–C2 dihedral angles are about 2 kJ mol⁻¹ more stable than their analogous *gauche* conformers. Conformers with *anti* C1–C2–C3–H6 dihedral angles were calculated to be of 8.5 (A/A/A) and 12.5 (A/G/A) kJ mol⁻¹ higher energy than the minimum-energy conformer (G/A/A), indicating that they may be safely omitted in a conformational model. Furthermore, the energy differences between conformers with C1–C2–C3–H6/O1–C1–C2–C3 dihedral angles corresponding to G+/G+, G+/G– or G+/A were calculated to be less than 1 kJ mol⁻¹, indicating that these conformers should all be present in measurable amounts in the conformational mixture. A theoretical three-conformer model was

therefore adopted for the GED study, and the molar fractions of the conformers were included as adjustable parameters in the least-squares study, with the restriction that the sum of the molar fractions is equal to 1.0.

The theoretical radial distribution (RD) curves calculated for the three conformers included in the GED conformational model are shown in Fig. 3, together with the experimental RD curve. None of the single conformer RD curves are compatible with the experimental one. The theoretical RD curve for conformer I (Fig. 1) gives, for example, too much contribution around $r \approx 300$ pm, while the RD curves for the other two conformers give too little contribution in this region. The experimental RD curve also indicates that there is a substantial contribution from IV, because of the relatively large area for distances outside $r \approx 450$ pm. The RD curves do therefore indicate that all three conformers are present in the conformation mixture.

The geometry of each conformer may be described by 17 independent parameters: seven bond distances, seven valence angles and three dihedral angles. For the G+/G+/G– conformer (which is the same as conformer I) the following geometrical parameters were chosen: $r(\text{C2–C3})$, $r(\text{C1–C2})$, $r(\text{C–C})_{\text{cpr}}$, $r(\text{C1–O1})$, $r(\text{O1–H1})$, $r(\text{C}_{\text{sp}^2\text{–H}})$, $r(\text{C}_{\text{sp}^3\text{–H}})$, $\angle \text{C1–C2–C3}$, $\angle \text{C2–C3–M}$ (M bisects the C4–C5 cyclopropyl bond), $\angle \text{C2–C1–O1}$, $\angle \text{C2–C3–H}$, $\angle \text{H–C1(2)–H}$, $\angle \text{H–C4(5)–H}$ and $\angle \text{C1–O1–H1}$, and the dihedral angles C1–C2–C3–H6, O1–C1–C2–C3 and C2–C1–O1–H1. Inherent in this model are several assumptions, the most important ones being those of equilateral cyclopropyl ring and of local C_{2v} symmetry of the methylene groups. The latter assumption is supported by the results from the *ab initio* calculations, which show only minor deviations from the assumed local symmetry.

The other two conformers, G+/G–/A (which is the same as III) and G/A/A (which is the same as IV), were

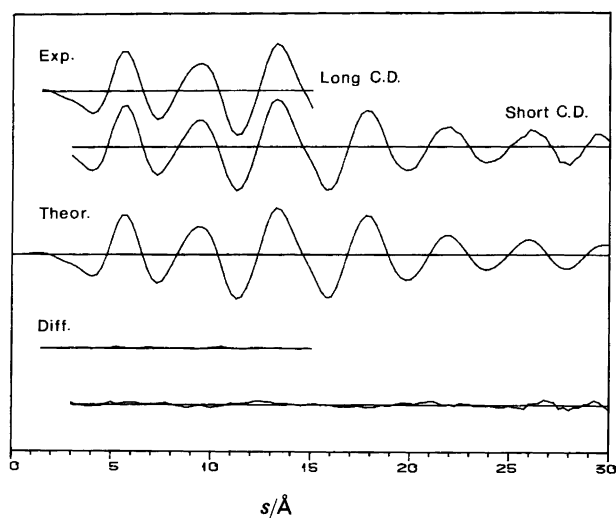


Fig. 2. Experimental and theoretical GED molecular intensities and their differences. The theoretical curves are calculated from the parameters in Table 5.

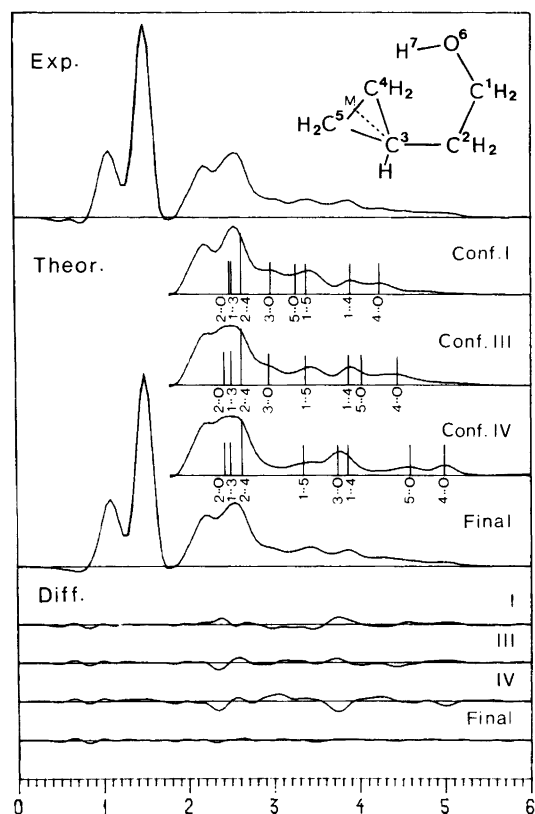


Fig. 3. Experimental and theoretical RD curves and their differences. The theoretical RD curves are shown separately for each of the conformers I, III and IV, as well as for the determined conformational composition (Table 5). The positions of the bond distances and the CC and CO non-bonded distances are indicated.

described by the same parameters as used for the G+/G+/G- conformer, with the following modifications: The deviations in the C1-C2-C3, C2-C3-M and C2-C1-O1 valence angles, relative to the same angles in the G+/G+/G- conformer, were fixed at the angle differences deduced from the *ab initio* calculations. The *anti* C2-C1-O1-H1 dihedral angles were fixed at the *ab initio* values. For the G+/G-/A conformer the C1-C2-C3-H6 and O1-C1-C2-C3 dihedral angles were introduced as independent parameters. A total of 21 independent parameters were therefore used to describe the geometries and the conformational composition of 2-cyclopropylethanol.

Because of the very large number of independent parameters it is difficult to determine all of them simultaneously with high precision in the least-squares analysis. The final results, which are presented in Table 5, are based on simultaneous refinements of all parameters defining the heavy-atom skeleton of conformer G+/G+/G-, as well as the parameters defining the composition of the conformational mixture. In addition, the vibrational amplitudes for the CC and CH bond distances and the shortest CH non-bonded distances (over one valence angle) were refined, linked together in groups. The other vibrational amplitudes were kept constant at the values calculated in the normal coordinate analyses. The table shows which of the geometrical parameters that have been kept constant during the refinement. For most of these the assumed parameter values are transferred from the *ab initio* calculations.

As it is possible to include rotational constants from microwave spectroscopy in GED least-squares intensity

Table 5. Structure parameters for 2-cyclopropylethanol, as determined by gas-phase electron diffraction. Standard deviations are in parentheses.

Distances/pm		Amplitudes/pm All conformers	Angles/° Conformer I	
O1-H1	94.3 (ass.)	7.60	C2-C3-M	126.2(13)
C _{cpr} -H ^a	111.0(2)	8.34	C1-C2-C3	111.3(15)
C1(2)-H	112.0(2)	8.50	C2-C1-O1	116.2(12)
C1-O1	141.5(2)	5.13	C1-O1-H1	109.3 ^b
C1-C2	153.4(21)	5.47	C2-C3-H6	114.1 ^b
C2-C3	151.6(20)	5.39	H-C1(2)-H	107.2 ^b
(C-C) _{cpr} ^a	151.9(8)	5.48	H-C4(5)-H	114.0 ^b
Dihedral angles/°	I (G+/G+/G-)	III (G+/G-/A)	IV (G/A/A)	
C1-C2-C3-H6	59.2(3.7)	59.0 ^b	61.0 ^b	
O1-C1-C2-C3	55.7(5.3)	-63.45 ^b	-179.3 ^b	
H1-O1-C1-C2	-61.8 ^b	175.5 ^b	-179.7 ^b	
Contribution (%)	48.6(127)	19.7(148)	31.7(69)	
Hydrogen bond parameters				
Distances/pm		Angles/°		
H1...C3	265.1	O1-H1...C3	100.5	
H1...C5	270.5	O1-H1...C5	115.8	
O1...C3	297.1	O1-H1, C3-C5	62.4	
O1...C5	322.8			

^aThe subscript cpr denotes cyclopropyl. ^bKept constant, equal to the value obtained from *ab initio* calculations.

Table 6. Correlation matrix for GED study of 2-cyclopropylethanol

	r_1	r_2	r_3	r_4	r_5	\angle_6	\angle_7	\angle_8	f_9	f_{10}	u_{11}	u_{12}	u_{13}	α_{14}	α_{15}
1. $r(\text{C2-C3})$	100														
2. $r(\text{C1-C2})$	-20	100													
3. $r(\text{C3-C4})$	-65	-60	100												
4. $r(\text{C1-O1})$	12	-28	13	100											
5. $r(\text{C-H})$	-8	-11	15	2	100										
6. $\angle \text{C2-C3-M}$	-85	61	22	-22	7	100									
7. $\angle \text{C1-C2-C3}$	-45	-69	90	15	17	2	100								
8. $\angle \text{C2-C1-O1}$	1	-80	60	11	17	-34	57	100							
9. $f(-\text{C2-C3-})$	-60	23	31	-12	7	60	31	-13	100						
10. $f(-\text{C1-C2-})$	8	63	-55	-11	-13	29	-61	-60	6	100					
11. $u(\text{C-C})$	32	-89	43	44	9	-64	54	65	-27	-53	100				
12. $u(\text{C-H})$	-5	2	4	10	-14	4	1	-3	5	-1	7	100			
13. $u(\text{C-H})$	43	55	-77	-7	-7	-1	-63	-60	-10	46	-37	3	100		
14. $\alpha(\text{G+}/\text{G+})$	30	-18	-11	6	1	-28	-9	-28	-25	3	21	0	14	100	
15. $\alpha(\text{G+}/\text{G-})$	-5	19	-10	-5	-4	10	-12	24	15	11	-17	-2	-3	-89	100

refinements,³⁸ it might be appropriate to comment on why this has not been done in the present study, which is based on experimental data from both these methods. Experimental rotational constants have, however, been measured for only one conformer, while the GED study includes contributions from three conformers. It is therefore not feasible properly to combine the two types of experimental data in a unique way. The rotational constants (in MHz) that might be calculated from the GED results in Table 5 are, however, in fairly good agreement with those determined experimentally in the MW study in the case of rotamer I ($A = 7264.63$, $B = 2266.23$, $C = 1895.16$).

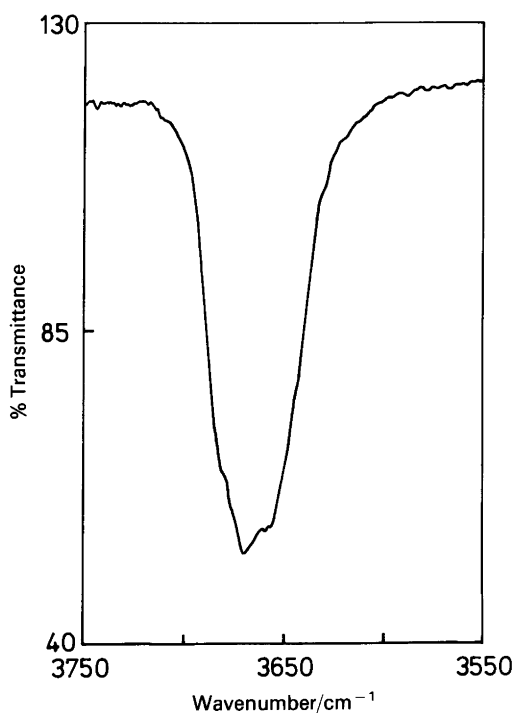


Fig. 4. Gas-phase infrared spectrum in the O-H stretching vibration region. Absorption maxima at 3670, 3659 and 3655 cm^{-1} . Shoulders at 3680 and 3644 cm^{-1} .

The correlation matrix from the GED study is presented in Table 6. Not surprisingly, many of the geometrical parameters are relatively strongly correlated. It is, however, gratifying to note that the molar fractions (α_{14} and α_{15} of this table) are only weakly correlated with the other parameters. The strong negative correlation between α_{14} ($\text{G+}/\text{G+}/\text{G-}$) and α_{15} ($\text{G+}/\text{G-}/\text{A}$) may be interpreted in the following way: If we force the concentration of rotamer I (α_{14}) to increase, this will be accompanied by a roughly similar decrease in the concentration of conformer III (α_{15}), while the molar fraction of rotamer IV ($\alpha = 1.0 - \alpha_{14} - \alpha_{15}$) will be only modestly influenced. This interpretation supports the observation that the molar fraction of IV has the lowest standard deviation of the three (see Table 5).

IR study. The gas-phase O-H stretching fundamental band which is shown in Fig. 4 is relatively broad and has a quite complex fine structure with absorption maxima at 3670, 3659 and 3655 cm^{-1} . Shoulders are seen at 3680 and 3644 cm^{-1} . The interpretation of this complex band is not obvious. Some of the splitting may be ascribed to rotational fine structure, because other absorption bands were also seen to possess fine structures consisting of two or three absorption peaks. Typically, P - R splittings of about 13 cm^{-1} were observed. The broadness of the O-H stretching band may be interpreted as an indication that several conformers are present and that one of them is presumably involved in intramolecular H bonding. This interpretation is of course in agreement with the results obtained by the other methods described above.

Discussion

The results from all four methods of investigation (MW, GED, IR and *ab initio* calculations) consistently show that several conformers are present simultaneously in gaseous 2-cyclopropylethanol. Only one of the various conformers is capable of forming an intramolecular H bond. The H-bonded conformer identified from the MW

spectra and from the GED study is observed to be the most abundant one. The results from the *ab initio* calculations support these observations, as the H-bonded conformer is calculated to have the lowest energy among the four conformations that were considered.

The GED study indicates that a minimum of three conformers are present in the gas phase, corresponding to the following C1–C2–C3–H6 and O1–C1–C2–C3 dihedral angle combinations: G+/G+, G+/G– and G/A. Conformers with *anti* C1–C2–C3–H6 dihedral angles have not been included in the conformational model, because MM3 calculations indicate that the energies of such conformers are substantially higher than for those included, and also because the experimental RD curve shows that there is no noticeable contribution in the *r*-range outside 600 pm.

As it is difficult to determine the exact position of the H atom of the hydroxyl group in a conformational mixture by GED, the H1–O1–C1–C2 dihedral angle has been assumed to be *gauche* in the G+/G+ conformer (I) and *anti* in the other two conformers. The reasoning behind these choices is outlined above.

The energy differences between analogous conformers with *anti* and *gauche* H1–O1–C1–C2 dihedral angles are generally 2–3 kJ mol⁻¹ in favour of the *anti* conformer.²⁴ Thus, there will almost certainly be minor contributions present also from G+/G– and G/A conformers with *gauche* H1–O1–C1–C2 dihedral angles, as well as from a G+/G+ conformer with *anti* H1–O1–C1–C2 dihedral angle (conformer II). The observed molar fraction of each of the three model conformers represent the total contribution from conformers with the stated C1–C2–C3–H6 and O1–C1–C2–C3 dihedral angles, regardless of the orientation of the H1–O1–C1–C2 dihedral angles.

The preference of rotamer I is ascribed to stabilization by an intramolecular H bond formed between the H atom of the hydroxyl group and the pseudo- π electrons on the outside of the nearest C–C edge of the cyclopropyl ring. The H bond is probably relatively weak since the H1...C3 and H1...C5 non-bonded distances are only slightly shorter than the sum of the van der Waals radii²⁵ of the atoms involved (Tables 1 and 5). The intramolecular H bond in 2-cyclopropylethanol may be compared to those deduced for the C4...H–O and C5...H–O distances in the H-bonded conformers observed to be present in gases of 4-penten-1-ol¹⁸ and 4-pentyn-1-ol.³⁹ In 4-penten-1-ol these distances are reported to be 225 and 265 pm, respectively, and in 4-pentyn-1-ol 227 and 256 pm, respectively. These data indicate that the internal H bonds are of approximately the same strength in the enol and ynol, while the H bond is considerably weaker in 2-cyclopropylethanol.

A rough estimate of the energy associated with intramolecular H bonding in 2-cyclopropylethanol may be proposed by adding the calculated energy difference between conformers II and I (4.4 kJ mol⁻¹) to the generally observed energy difference between *gauche* and *anti* H–O–C–C fragments (2–3 kJ mol⁻¹).²⁴ This gives

and estimate of ca. 7 kJ mol⁻¹ for the energy associated with internal H bonding in 2-cyclopropylethanol.

The geometry of the complex between cyclopropane and water has very recently been reported.⁴⁰ Interestingly, it was found that the water is H-bonded to the edge of the cyclopropane ring in a way that is rather similar to that observed for conformer I.

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