Acta Chemica Scandinavica, 1998: 52: 1122 1136
Printed in UK all rights reserved

ACTA
CHEMICA SCANDINAVICA
ISSN 0904 213X

Conformational Properties of 2-Cyclopropylideneethanol as Studied by Microwave, Infrared and Raman Spectroscopy and by *Ab Initio* Computations

Stefan Bräse,[a] Peter Klæboe,[b] K.-M. Marstokk,[b] Armin de Meijere,[a] Harald Møllendal,[b,*] and Claus J. Nielsen[b]

[a]Georg-August-Universität, Tammannstrasse 2, D-37077 Göttingen, Germany and [b]Department of Chemistry, The University of Oslo, PO Box 1033 Blindern, N-0315 Oslo, Norway

Bräse, S., Klæboe, P., Marstokk, K.-M., de Meijere, A., Møllendal, H. and Nielsen, C. J., 1998. Conformational Properties of 2-Cyclopropylideneethanol as Studied by Microwave, Infrared and Raman Spectroscopy and by *Ab Initio* Computations. Acta Chem. Scand. 52: 1122 1136. © Acta Chemica Scandinavica 1998.

The microwave spectra of 2-cyclopropylideneethanol, $(CH_2)_2C{=}CH\ CH_2OH$, and one deuterated species (hydroxyl group) have been investigated in the 23.0–39.0 GHz spectral region at 263 K. One conformer, denoted *Skew 1*, was assigned. In this rotamer the C=C–C–O dihedral angle is 122° from *syn* (0°) and the C–C–O–H dihedral angle is 66° from *syn*. The hydrogen atom of the hydroxyl group forms a weak intramolecular hydrogen bond with the π electrons of the C=C double bond. The gas-phase IR spectrum in the OH stretching region revealed a broad and complex band at a rather high wavenumber. This absorption split into three bands, presumed to belong to two conformers with an internal hydrogen bond and one without, when the compound was isolated in argon matrices at 5 K. Large shifts were observed between the IR spectra of the amorphous and crystalline solids at liquid nitrogen temperature due to hydrogen bonding. Certain weak IR and Raman bands present in the amorphous or liquid phases vanished in the crystal and are attributed to one or more additional conformers in the liquid. Some IR bands in the range 3670–3630 cm^{-1}, present in the argon matrix spectra at 5 K of a ca. 550 K vapour deposit, vanished after annealing and were tentatively attributed to high energy conformers. From temperature variations in the Raman spectra of the liquid *Skew 1* was estimated to be 2.5 ± 0.6 kJ mol^{-1} lower in enthalpy than other conformations. The experimental work has been assisted by *ab initio* computations at the MP2/6-31G** level of theory.

Several allylic alcohols that contain the C=C–C–O–H chain of atoms have been investigated in recent years by microwave (MW), infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy as well as by electron diffraction (ED) and *ab initio* computations.[1–8] The molecules studied so far include 2-propen-1-ol ($H_2C{=}CHCH_2OH$, allyl alcohol),[1] 3-buten-2-ol [$H_2C{=}CHCH(OH)CH_3$],[2] 2-methyl-2-propen-1-ol [$H_2C{=}CH(CH_3)CH_2OH$, 2-methylallyl alcohol],[3] *trans*-[4a,b] and *cis*-[4c] 2-buten-1-ol ($H_3CCH{=}CHCH_2OH$, *trans*- and *cis*-crotyl alcohol), 2,3-butadien-1-ol ($H_2C{=}C{=}CHCH_2OH$)[5] and 1,4-pentadien-3-ol [$H_2C{=}CHCH(OH)CH{=}CH_2$].[6] In addition, two aromatic compounds with such a link of atoms, *viz.* 2-[7] and 3-furanmethanol,[8] have recently been investigated in this laboratory.

In all these compounds other than 2-furanmethanol[7] (where the oxygen atom of the ring is involved in intramolecular hydrogen (H) bonding in its most stable conformer), the preferred rotamer has been found to take a heavy-atom *skew* conformation with a C=C–C–O dihedral angle about 120° from *syn* (0°). The C–C–O–H dihedral angle was found to be *gauche* (approximately 60° from *syn*). This dihedral angle allows for close proximity between the H atom of the hydroxyl group and the π electrons of the double bond. This interaction is by most workers[1–8] assumed to be a weak intramolecular H bond, although objections to this view have been heard.[1g,2b,c]

In addition to the H-bonded heavy-atom *skew* conformer, a second heavy-atom C=C–C–O *syn* rotamer

* To whom correspondence should be addressed.

has been found experimentally in some of these cases.[1–3] The C–C–O–H conformation is *gauche* in these heavy-atom *syn* rotamers.[1–3] This again allows the hydroxylic H atom to come close to the π electrons of the double bond, a prerequisite for the formation of an internal H bond. Generally, this second heavy-atom *syn* form is slightly less stable (1–3 kJ mol^{-1}) than the *skew* conformer in the cases where it has been found.[1–3]

Based on the findings made for the other allylic compounds,[1–8] the five conformations shown in Fig. 1 are considered to be all the possible *stable* conformers of 2-cyclopropylideneethanol (CPE). In the three *skew* conformations, the C3=C2–C1–O1 chain of atoms is about −120° from *syn*, whereas the C2–C1–O1–H1 dihedral angle is ca. 60° (*Skew 1*), +60° (*Skew 2*) and 180° (*Skew 3*). In the two *syn* rotamers, the C3=C2–C1–O1 dihedral angle is 0°, while the C2–C1–O1–H1 dihedral angle is −60° (*Syn 1*) and 180° (*Syn 2*).

The *Skew 1* conformer of CPE corresponds to the more stable *skew* rotamers mentioned above, and *Syn 1* to the less stable *syn* forms. *Skew 1* and *Syn 1* both have the possibility of being stabilised by a weak intramolecular H bond formed between the hydroxyl group H atom and the π-electrons of the C2=C3 double bond. This possibility is of course absent in the three other forms shown in Fig. 1.

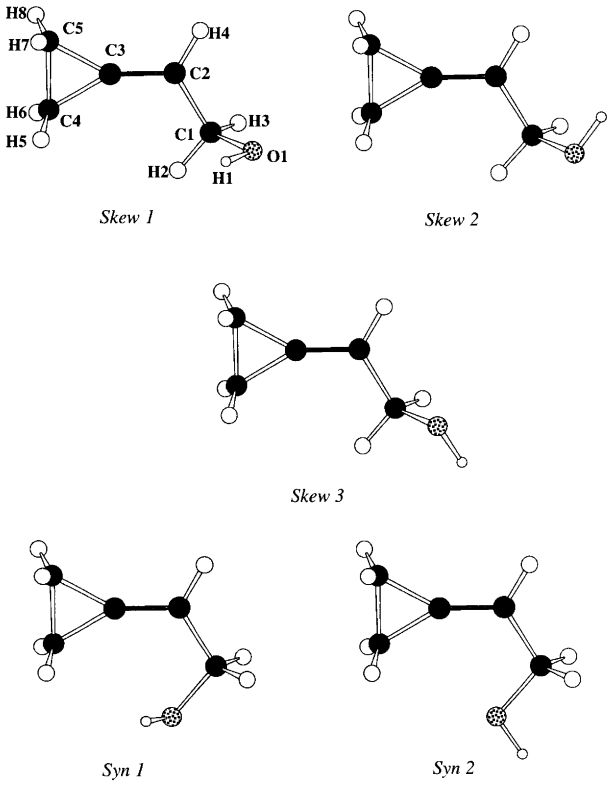

Fig. 1. The five conformations presumed to be stable forms of 2-cyclopropylideneethanol. Atom numbering is given on the sketch of *Skew 1*. This conformer was found in the MW spectrum. There is considerable evidence in the IR spectrum for the presence of *Syn 1* as well as of one additional conformer without an internal H bond.

Syn 1 has an additional interesting feature: In this conformation the non-bonded distances between H1 and C3, and between H1 and C4, are rather short (ca. 260 pm and 270 pm, respectively) compared to the sum of the van der Waals radii of hydrogen and aromatic carbon (290 pm[9]). An interaction of the H1 atom with the pseudo-π electrons of the cyclopropyl ring,[10] which have their maximum electron density in the plane of the ring on the outside, is then possible. These electrons can undoubtedly take part in weak intramolecular H bonding, as has been shown in many cases.[11]

One important reason to study CPE was to see if this extra 'help' from the pseudo-π electrons would lead to a stabilisation of the *Syn 1* relative to *Skew 1*. It is shown in this work that this kind of extra stabilisation is not very important in CPE, since *Skew 1* is undoubtedly the most stable conformer in this case too.

Experimental

Sample. The sample utilised in this work was synthesised as previously described by us in a different context.[12] A slow decomposition was seen during the MW experiments, and the sample was therefore kept at dry-ice temperature (−78 °C) or in a refrigerator (233 K) when not in use. One impurity/decomposition product, namely ethanol, was identified by its MW spectrum. The deuterated species (hydroxyl group) was produced by seasoning the wave guide with D_2O and then introducing the parent species. In this manner 30–40% deuteration was achieved.

Microwave experiment. The MW spectrum was studied using the Oslo spectrometer which is described in Ref. 13. The 23–39 GHz spectral region was investigated with the microwave absorption cell cooled to about 263 K. Lower temperatures, which would have increased the MW spectral intensities, could not be employed owing to insufficient vapour pressure of the compound. The pressure was about 3–8 Pa when the spectra were recorded and stored electronically using the computer programs written by Waal.[14] The accuracy of the spectral measurements is presumed to be better than ±0.10 MHz.

Infrared experiment. The vapour-phase IR spectrum in the 3700–3600 cm^{-1} region was recorded at room temperature with a Bruker IFS 88 spectrometer equipped with a multiple reflection cell. The path length was about 3 m, the vapour pressure ca. 90 Pa and the resolution 2 cm^{-1}.

The sample was evaporated on a CsI window at 80 K and shock frozen in a conventional cryostat with windows of CsI. Two different sample thicknesses were recorded at ca. 80 K. Each sample was subsequently annealed to temperatures approaching the melting point (around 215 K), and the sample changed appearance

from a glassy to an apparent crystalline deposit. The sample was again cooled to 80 K and the spectra recorded with a resolution of 1 cm^{-1} on a Perkin–Elmer model 2000 FTIR spectrometer in the range 4000–400 cm^{-1}. Subsequent annealing above ca. 195 K did not change the spectra significantly, suggesting that a completely crystalline solid was obtained.

A closed-cycle helium cooled Displex unit from APD (model HS-4) with windows of CsI was employed for the matrix experiments. The compound was mixed with argon in the ratio 1:500, and the gas mixtures were deposited on the cold window at ca. 14 K for several hours. The cryostat was equipped with a nozzle of quartz which could be heated electrically to temperatures between ambient and 900 K. No decomposition products formed during the hot nozzle deposition were detected. After the unannealed samples had been recorded at 5 K, the samples were first annealed at 35 K and later at 39 K for 25 min, before the spectra of the annealed samples were recorded.

Raman experiments. Raman spectra were recorded on a triple monochromator spectrometer (model RT 30) from Dilor, using the 514.5 nm line from a Spectra-Physics model 2000 argon ion laser for excitation. Spectra of the liquid, including semiquantitative polarisation measurements, were recorded at ambient temperature. Additional spectra were recorded at various temperatures between 295 and 215 K in a capillary cooled by cold nitrogen gas.[15] Below the melting point the sample crystallised readily and the Raman spectrum of the crystal was recorded.

Results

Ab initio *calculations.* All computations were made at the MP2/6-31G** (frozen core) level of theory. This level is expected to predict geometries quite well, while vibrational frequencies are generally found to be a few per cent too high.[16] The H bond interaction and the energy differences are also well accounted for in this computation scheme.[16,17] The calculations were carried out employing the Gaussian 92 program package.[18] The five conformations depicted in Fig. 1 were fully optimised. They were all found to be stable, as no imaginary vibrational frequencies[16] were computed for any of them. The optimised geometries are given in Table 1 together with other parameters of interest.

In order to investigate whether the five conformations sketched in Fig. 1 are indeed the stable forms of CPE, searches for further stable rotamers were made starting with the C3=C2–C1–O1 dihedral angle in the *anti* (180°) and *gauche* (−60°) positions. However, no stable forms with such dihedral angles were found. In fact, the Gaussian program refined to one of the five conformations shown in Fig. 1 in all cases. It is therefore assumed that these five forms represent all the possible stable conformers of CPE.

It is of interest to compare important bond lengths of the calculated structures among the five conformers of CPE in Table 1 to those of methylene cyclopropane[19] and allyl alcohol,[1b] since accurate structures are available for both these last-mentioned compounds. The bond length corresponding to the C4–C5 bond (Fig. 1) is 154.15(20) pm in methylene cyclopropane,[19] and that corresponding to the C3–C4 and C3–C5 bond lengths in CPE is 145.70(20) pm in methylene cyclopropane. The bond lengths listed in Table 1 are thus slightly longer, and slightly shorter, respectively, than the corresponding ones in methylene cyclopropane.[19] The bond length corresponding to the C2=C3 double bond is 133.17(20) pm in methylene cyclopropane,[19] nearly the same as the computed values (Table 1). The H1–O1, O1–C1, C1–C2 and C2=C3 bond lengths calculated for the various conformers of CPE (Table 1) are also close to their counterparts in allyl alcohol.[1b] The close agreement between the MP2/6-31G** structures of the various conformers of CPE and its congeners for which accurate experimental structures are available was expected, since the MP2/6-31G** structures of molecules containing the same elements as CPE are generally rather realistic.[16]

MW spectrum and assignment of Skew 1. The *ab initio* results in Table 1 predict that *Skew 1* is the most stable conformer. The *ab initio* calculated rotational constants indicate that this form is a prolate symmetrical top with an asymmetry parameter $\kappa \approx -0.9805$ and its largest dipole moment component along the *a*-axis.

The survey spectra taken at low voltage (ca. 80 V cm^{-1}) revealed characteristic pile-ups close to the predicted frequencies. This led to a quick assignment of the ^aR-branch transitions. Attempts were made to find the strongest *b*- and *c*-type transitions of the spectrum, but none was found, presumably because the corresponding components of the dipole moment along the corresponding principal axes are too small, as indicated in the *ab initio* computations (Table 1). The measured transitions are listed in Table 2 and the spectroscopic constants (*A*-reduction I^r-representation[20]) are listed in Table 3. Only Δ_J and Δ_{JK} were fitted, with the rest of the centrifugal distortion constants constrained at zero because the molecule is so close to a prolate symmetrical top. The lines with the highest K_{-1} pseudo-quantum numbers coalesced into the pile-up peak. Only well separated lines with low K_{-1} pseudo-quantum numbers (Table 2) have therefore been used to determine the spectroscopic constants in Table 3.

Attempts to determine the dipole moment by Stark effect measurements failed because the transitions were so weak that quantitative measurements could not be made.

The ground-state spectrum was accompanied by several vibrationally excited states. The first three excited states of what is presumed to be the torsional vibration around the C1–C5 bond, were assigned; their spectro-

Table 1. Structure, rotational constants, principal-axes coordinates of the hydroxyl-group H atom, dipole moments and energy differences of the five stable rotamers of 2-cyclopropylideneethanol as calculated by *ab initio* methods at the MP2/6-31G** (frozen core) level.

Conformer:[a]	*Skew 1*	*Skew 2*	*Skew 3*	*Syn 1*	*Syn 2*
Distance/pm					
O1–H1	96.5	96.4	96.5	96.5	96.4
O1–C1	143.0	143.1	143.0	141.9	142.1
C1–H2	109.5	108.9	109.5	109.2	109.9
C1–H3	109.1	109.7	109.8	109.9	109.9
C1–C2	149.8	149.9	149.4	150.3	149.8
C2–H4	108.5	108.7	108.5	108.6	108.6
C2–C3	132.9	132.8	132.8	132.8	132.6
C3–C4	146.8	146.7	146.7	146.8	146.1
C3–C5	146.4	146.4	146.4	146.6	146.9
C4–C5	153.7	153.7	153.7	153.5	153.5
C4–H5	108.3	108.3	108.3	108.2	108.2
C4–H6	108.3	108.3	108.3	108.4	108.2
C5–H7	108.3	108.3	108.3	108.3	108.3
C5–H8	108.3	108.3	108.3	108.3	108.3
Angle/°					
H1–O1–C1	106.1	106.9	107.3	106.4	107.0
O1–C1–H2	111.6	105.8	111.7	105.8	111.2
O1–C1–H3	105.0	110.5	110.5	111.3	111.2
O1–C1–C2	111.8	112.6	107.6	114.1	109.8
C1–C2–H4	117.0	117.4	116.7	116.4	115.7
C1–C2–C3	122.9	123.1	122.9	124.2	124.7
C2–C3–C4	147.6	147.5	147.8	148.9	149.2
C2–C3–C5	149.1	149.2	148.9	147.9	147.6
C3–C4–H5	118.9	119.0	119.1	118.5	118.5
C3–C4–H6	119.0	118.7	118.7	119.5	118.4
C3–C5–H7	118.8	118.9	118.9	118.7	118.8
C3–C5–H8	118.8	118.7	118.7	119.0	118.8
Dihedral angle[b]/°					
H1–O1–C1–H2	−65.9	176.5	67.2	189.7	59.3
H1–O1–C1–H3	177.5	60.1	−52.7	74.3	−59.3
H1–O1–C1–C2	57.2	−63.7	187.4	−49.5	180.0
O1–C1–C2–H4	56.5	61.8	54.3	179.0	180.0
O1–C1–C2–C3	−122.1	−118.4	−126.2	−0.3	−0.0
C1–C2–C3–C4	−1.9	0.7	1.5	−3.0	0.0
C1–C2–C3–C5	180.4	179.7	180.5	181.9	180.0
C2–C3–C4–H5	−72.4	−74.5	−74.5	−70.0	−72.9
C2–C3–C4–H6	75.3	73.1	73.2	77.6	73.0
C2–C3–C5–H7	72.2	74.4	74.3	70.7	73.6
C2–C3–C5–H8	−75.2	−73.1	−73.2	−76.8	−73.7
Non-bonded distances[c,d]/pm					
H1···C2	254.6	262.2	319.0	253.0	321.2
H1···C3	335.7	383.1	425.5	258.8	370.2
H1···C4	420.4	497.2	512.4	269.9	399.9
Rotational constants/MHz					
A	10860.8	10873.8	11289.4	8019.2	8113.5
B	1727.1	1724.1	1716.7	2355.0	2360.0
C	1640.0	1628.9	1620.2	1894.0	1895.4
Principal-axis coordinates of the H1 atom[d]/pm					
|*a*|	217.7	289.4	331.9	121.9	261.5
|*b*|	16.7	76.2	45.4	125.4	125.6
|*c*|	133.8	47.7	32.8	66.5	0.0
Principal-axis dipole moment component[e]/10^{-30} C m					
μ_a	7.81	3.60	0.57	4.34	4.36
μ_b	1.60	3.86	4.26	3.14	1.93
μ_c	1.17	4.37	4.30	3.40	0.00
Energy difference[f]/kJ mol^{-1}	0.0	6.17	6.56	2.29	10.72

[a] See Fig. 1 for definition. [b] Measured from *syn* = 0°. [c] Calculated from the structures given above in this table. [d] Sum of van der Waals radii[9] of hydrogen and carbon (half-thickness of aromatic molecule) is 290 pm. [e] 1 D = 3.335 64 × 10^{-30} C m. [e] The total energy of conformer *Skew 1* was calculated to be −707 986.00 kJ mol^{-1}. [f] Energy difference between *Skew 1* and each of the other four conformations.

Table 2. MW spectrum of the ground vibrational state of *Skew 1* of 2-cyclopropylideneethanol.

Transition $J'K'_{-1}, K'_{+1} \leftarrow J''K''_{-1}, K''_{+1}$	Observed frequency/MHz[a]	Obs. − calc. freq/MHz
$7_{1,6} \leftarrow 6_{1,5}$	23 944.14	−0.02
$7_{2,5} \leftarrow 6_{2,4}$	23 675.80	−0.07
$7_{2,6} \leftarrow 6_{2,5}$	23 639.83	−0.03
$8_{0,8} \leftarrow 7_{0,7}$	26 967.90	−0.02
$8_{1,7} \leftarrow 7_{1,6}$	27 360.99	−0.08
$8_{1,8} \leftarrow 7_{1,7}$	26 657.07	0.03
$8_{2,6} \leftarrow 7_{2,5}$	27 068.28	−0.14
$8_{2,7} \leftarrow 7_{2,6}$	27 014.55	0.00
$9_{0,9} \leftarrow 8_{0,8}$	30 322.45	0.03
$9_{1,8} \leftarrow 8_{1,7}$	30 776.44	0.00
$9_{1,9} \leftarrow 8_{1,8}$	29 984.93	−0.01
$9_{2,7} \leftarrow 8_{2,6}$	30 465.00	0.05
$10_{0,10} \leftarrow 9_{0,9}$	33 671.41	0.09
$10_{1,9} \leftarrow 9_{1,8}$	34 190.06	0.01
$10_{1,10} \leftarrow 9_{1,9}$	33 311.52	0.11
$10_{2,8} \leftarrow 9_{2,7}$	33 865.96	0.12
$10_{3,8} \leftarrow 9_{3,7}$	33 791.47	0.01
$10_{4,6} \leftarrow 9_{4,5}$	33 787.80	0.08
$10_{4,7} \leftarrow 9_{4,6}$	33 787.80	0.10
$11_{0,11} \leftarrow 10_{0,10}$	37 014.07	−0.11
$11_{1,10} \leftarrow 10_{1,9}$	37 601.77	0.12
$11_{1,11} \leftarrow 10_{1,10}$	36 636.31	−0.06
$11_{2,10} \leftarrow 10_{2,9}$	37 132.06	−0.15
$11_{3,8} \leftarrow 10_{3,7}$	37 176.25	−0.07
$11_{3,9} \leftarrow 10_{3,8}$	37 172.52	−0.01
$11_{4,7} \leftarrow 10_{4,6}$	37 167.52	−0.06
$11_{4,8} \leftarrow 10_{4,7}$	37 167.52	−0.02

Table 3. Ground-state spectroscopic constants[a,b] of *Skew 1* of 2-cyclopropylideneethanol.

Species:	Parent	Deuterated
No. of transitions:	27	18
R.m.s. dev.[c]/MHz:	0.082	0.117
A_0/MHz	10 713.6(39)	10 344.9(86)
B_0/MHz	1 732.990 7(45)	1 700.958 4(87)
C_0/MHz	1 644.893 8(49)	1 624.795 4(89)
Δ_J/kHz	0.625(20)	0.611(38)
Δ_{JK}[d]/kHz	−9.77(18)	−8.03(50)

[a] *A*-reduction, I^r-representation.[20] [b] Uncertainties represent one standard deviation. [c] Root-mean-square deviation. [d] Further quartic constants preset at zero.

scopic constants are found in Table 4.* Relative intensity measurements using selected transitions performed largely as described in Ref. 21 yielded 70(20) cm^{-1} for this vibration, compared to 74 cm^{-1} as predicted by the *ab initio* calculations (see later).

The MW spectrum of the deuterated species (hydroxyl group) was studied to locate the position of the H1 atom. The assignment of this spectrum was straightforward. The spectroscopic constants are found in Table 3.

The substitution coordinates[22] of H1 were calculated as $|a| = 195.00(58)$ and $|c| = 131.15(95)$ pm, while $|b|$ was computed to have an imaginary value. These values are not widely different from those predicted for *Skew 1* (Table 1) and represent conclusive evidence that *Skew 1* has indeed been assigned and not confused with *Skew 2* or *Skew 3*, which would have rotational constants close to those of *Skew 1*, but rather different coordinates for the H1 atom, as seen in Table 1.

MW search for further conformations. The above assignments include all the strongest transitions seen in the MW spectrum. However, numerous rather weak lines remain unassigned in the spectrum, as well as a few strong signals from ethanol. As already mentioned, the compound decomposed slowly in the brass cell used. It is possible that some of these transitions belong to unidentified decomposition products. It is also possible that some belong to one or more high-energy forms of CPE. The existence of at least one such form seems quite likely on the basis of the IR results discussed below. The *ab initio* computations predict (see above) that the *Syn 1* conformer should be the second most stable conformation with a 2.3 kJ mol^{-1} higher energy than *Skew 1*. Unfortunately, this hypothetical high-energy rotamer is computed to have much smaller components of the dipole moment along the principal inertial axes (Table 1) than *Skew 1*. A detection of this rotamer would therefore be considerably more demanding than that of *Skew 1*, because the intensity of the spectrum is proportional to the square of the dipole moment component along a principal inertial axis. Another factor which might complicate the assignment of the hypothetical *Syn 1* form is the fact that the hydroxyl group may tunnel because there will be two mirror-image forms of this rotamer. A splitting of the rotational lines into two and a non-rigid-rotor fit would result. This has already been reported for the *syn* form of allyl alcohol.[1j]

Structure. It is seen from Table 3 that the experimental rotational constants of *Skew 1* are very close to those calculated from the MP2/6-31G** structure (Table 1). In fact, the agreement is better than about 1% for all three constants. Moreover, the structural parameters of the ring, and the allylic part of the molecule are very similar to their experimental counterparts in cyclopropane[20] and allyl alcohol,[1b] as discussed above. Also, the substitution coordinates of the hydroxyl group H atom are fairly close to their theoretical counterparts, as remarked in the previous section. No experimental data are at hand that could really improve the MP2/6-31G** structure of the *Skew 1* conformer. The *ab initio* structure shown in Table 1 is therefore adopted as a plausible structure for the *Skew 1* conformer of CPE, as it is expected to be very close to the experimental structure.

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

Table 4. Spectroscopic constants[a,b] of *Skew 1* of 2-cyclopropylideneethanol in vibrationally excited states of the C1–C2 torsional vibration.

Vibrational state:	1st ex.	2nd ex.	3rd ex.
No. of transitons:	29	23	20
R.m.s. dev.[c]/MHz:	0.105	0.103	0.083
A_v/MHz	10 684.6(51)	10 663.7(46)	10 615.7(49)
B_v/MHz	1 737.912 8(56)	1 742.819 5(65)	1 747.658 6(55)
C_v/MHz	1 649.653 4(68)	1 654.361 1(64)	1 658.868 8(79)
Δ_J/kHz	0.563(27)	0.682(27)	0.788(29)
Δ_{JK}[d]/kHz	−9.37(24)	−8.88(48)	−5.26(44)

[a–d]Comments as for Table 3.

Infrared vapour phase spectra. The infrared spectrum of gaseous CPE in the O–H stretching region is seen in Fig. 2. This absorption band is characterised by being rather broad and with a complicated structure which might reflect the existence of more than one conformer and/or a rotational fine structure. The absorption maximum falls at 3654 cm^{-1}, with a shoulder at 3643 cm^{-1}. As a comparison the vapour spectrum of 2-fluoroethanol was observed[23] as a band centre at 3653 cm^{-1} in the IR and at 3654 cm^{-1} in the Raman spectra common to both conformers of this molecule. The shape of this absorption band is not very unlike that reported for gaseous allyl alcohol[1k] which has two absorption maxima at 3670 and 3650 cm^{-1}, respectively.[1k]

The band at 3654 cm^{-1} is rather high for a compound that is alleged to have an intramolecular H bond. In molecules such as oxiranemethanol (glycidol)[24] and *threo-* and *erythro*-1-oxiranylethanol,[25] which have weak O–H···O internal H bonds, the absorption maxima are typically found 50–60 cm^{-1} lower than observed for CPE. An alcohol without internal H bond, e.g. methanol, has an O–H stretching vibration of 3682 cm^{-1} in the gas phase.[26] Ethanol which has two conformers (the O–H bond is *anti* and *gauche* to the C–C bond), have absorption maxima at 3676 and 3660 cm^{-1}, respectively, [26] for the two conformers. Alcohols not possessing internal H bonds thus have their O–H stretching vibration at slightly higher wavenumbers than CPE. This is an indication for a weak interaction between H1 and the π electrons of the C2=C3 double bond.

A number of partly overlapping peaks are attributed to the C–H stretching modes ν_2–ν_8, of which the only band with characteristic contour has a sharp Q-branch and C-type contours at 3068 cm^{-1}, assigned as ν_2. The most intense IR band with *P-* and *R*-branches at 1026 and 1016 cm^{-1}, is assigned as the C–O stretch, ν_{23}, in agreement with the IR intensity predictions.

Infrared matrix isolation spectra. As is apparent from Fig. 3 the IR spectrum of CPE matrix isolated in argon is very rich and the fundamentals as well as various combination bands and overtones give rise to sharp peaks. After annealing to 35 K for 15 min certain changes occurred in the spectrum. These changes may be due to bands from high energy conformers passing the barrier and converting to the most stable conformer. Alternatively, the changes can be caused by site effects in the matrix.

All together four IR peaks were observed in the argon spectra of a 550 K vapour deposit in the O–H stretching

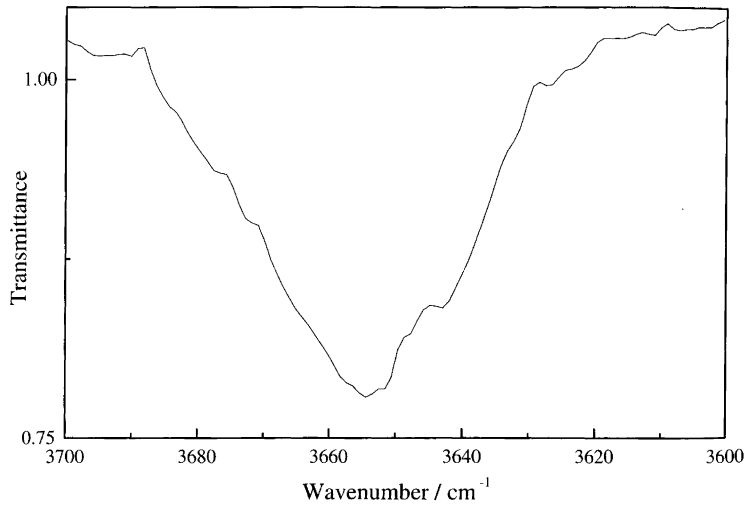

Fig. 2. Vapour-phase infrared spectrum in the O–H stretching region of 2-cyclopropylideneethanol. The maximum is found at 3654 cm^{-1} and a shoulder at 3643 cm^{-1}.

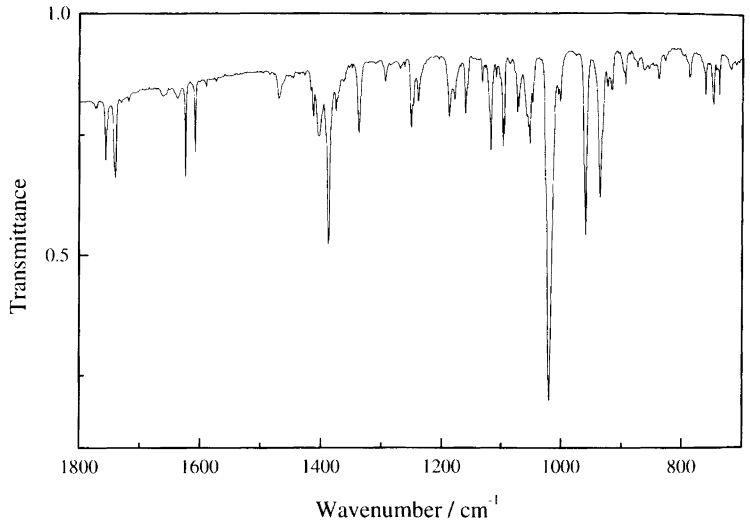

Fig. 3. IR spectrum of matrix isolated of 2-cyclopropylideneethanol in the region 1800–700 cm^{-1}.

region at 3670, 3650, 3642 and 3631 cm^{-1} (Fig. 4), whereas in the spectra of a 300 K deposit the 3670 cm^{-1} band was missing. These bands are probably caused by conformers with intramolecular H-bonding like in the vapour spectra since no intermolecular H-bonding is expected at the 1:1000 solute/matrix ratio. After annealing to 35 K the 3670 and 3650 cm^{-1} band vanished while the 3642 and 3631 cm^{-1} band remained. After further annealing to 39 K the 3642 cm^{-1} band disappeared as well, leaving the lowest peak alone, now appearing at 3630 cm^{-1}. The bands vanishing after annealing were probably caused by the disappearance of some conformers.

The lowest O–H band at 3631 cm^{-1} present alone after annealing to 39 K belongs undoubtedly to the *Skew 1* conformer with the lowest conformational energy and the strongest H-bond. The next band at 3642 cm^{-1} which is due to a weakly H-bonded conformer, probably belongs to the second lowest conformer *Syn 1*, calculated to have 2.3 kJ mol^{-1} higher energy than *Skew 1*. After annealing to 39 K this conformer converts to *Skew 1*. with rotations around both the C–C and the C–O bonds requiring a barrier height of ca. 14 kJ mol^{-1} from the Barnes plot.[27] The band at 3650 cm^{-1} apparently belongs to a conformer with no H-bond which converts to *Skew 1* and/or *Syn 1* at 35 K and may belong to *Skew 2* or *Skew 3*. Finally the band at 3670 cm^{-1} has negligible intensity in the spectra of a 300 K deposit, but appears with appreciable intensity in the spectra of a 500 K deposit (Fig. 4) indicating a higher conformational energy, possibly *Syn 2*.

Some additional IR bands were observed in the argon matrices at 3579, 3576, 3531, 3524 and 3514 cm^{-1}, which were very weak in the unannealed spectrum but were enhanced after annealing. These bands have no counterparts in the IR vapour spectrum. The positions of these

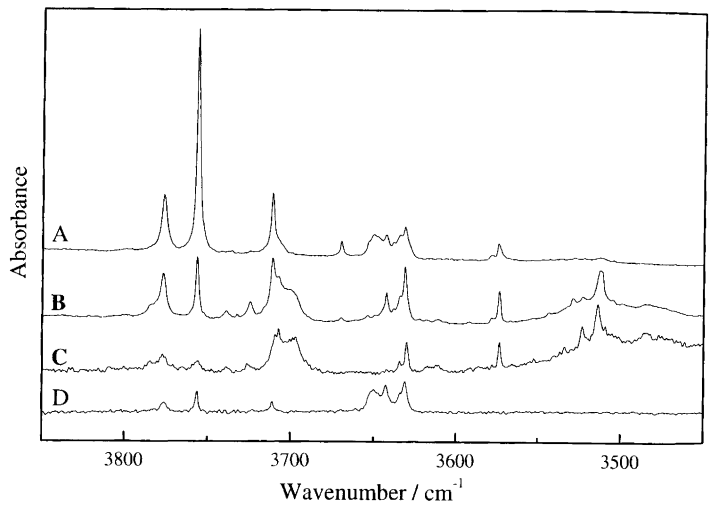

Fig. 4. IR matrix isolation spectra (3850–3450 cm^{-1}) obtained at 5 K of 2-cyclopropylideneethanol: (A) spectrum of a 550 K vapour deposit; (B) after annealing to 35 K; (C) after annealing to 39 K; (D) spectrum of a room temperature vapour deposit.

bands suggest that they are caused by more strongly H-bonded OH stretches than the intramolecular OH stretches discussed above. They are either OH bands of dimers or complexes with small amounts of water in the matrix.

Only quite small spectral changes were observed in the range below 1500 cm^{-1} after annealing, suggesting that they may partly be caused by site effects rather than conformational changes. Thus, the peak at 1187 is shifted to 1189 cm^{-1}, the bands at 1097 and 1095 cm^{-1} vanish and those at 1070 and 1073 cm^{-1} are shifted to 1072 and 1064 cm^{-1} with enhanced intensities.

Infrared crystal spectra. The sample which was first formed by condensing the vapour on a CsI window at 80 K, was apparently an amorphous solid with broad bands. After the sample had been annealed close to the melting point the bands became much sharper. When additional annealing produced no further changes, the sample was considered truly crystalline. The IR spectra of the amorphous and crystalline solids are given in Figs. 5–7. Many broad bands from the amorphous spectrum appeared as multiple sharp peaks in the crystal. Generally, the spectral changes were much more prominent in the infrared than in the corresponding Raman spectra (see below). This is undoubtedly a consequence of intermolecular H-bonding, formed during the crystallisation, which is known to influence the IR spectra. The very broad and intense H-bonded OH stretching band at 3230 cm^{-1} is split into two bands at 3334 and 3235 cm^{-1} in the crystal. Two intense IR bands were observed at 642 and 668 cm^{-1} in the crystal, absent in the amorphous spectra, which are well known bands belonging to out-of-plane bonded OH stretching modes.

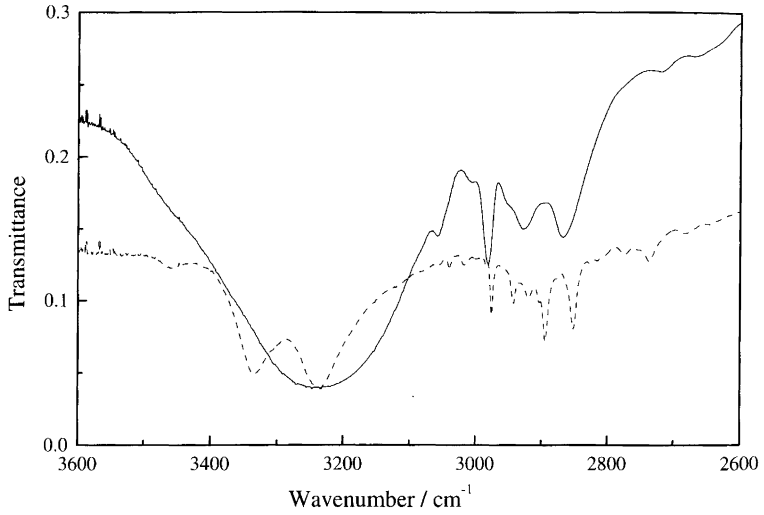

Fig. 5. IR spectrum (3600–2600 cm^{-1}) of 2-cyclopropylideneethanol as an amorphous (solid curve) and crystalline solid (dashed curve) at 80 K.

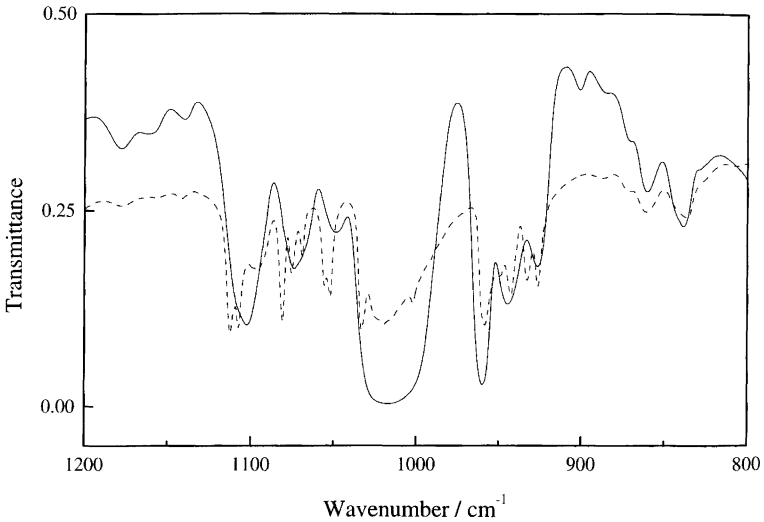

Fig. 6. IR spectrum (1200–800 cm^{-1}) of 2-cyclopropylideneethanol as an amorphous (solid curve) and crystalline solid (dashed curve) at 80 K.

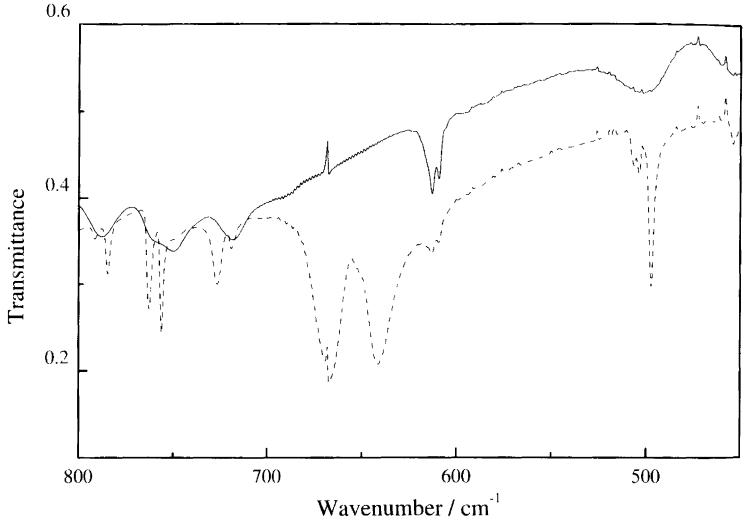

Fig. 7. IR spectrum (800–450 cm^{-1}) of 2-cyclopropylideneethanol as an amorphous (solid curve) and crystalline solid (dashed curve) at 80 K.

In addition, various sharp peaks were observed around 2900 cm^{-1}, in the 1120–925 cm^{-1} and 800–700 cm^{-1} ranges. The additional bands are partly caused by fundamentals and combination bands which were overlapping in the amorphous state and partly by crystal splitting.

Of special interest are bands which are present in the vapour, liquid and amorphous spectra vanishing in the crystal spectra, which are generally interpreted as bands of one or more conformer(s) which disappear in the crystal. Only a few such cases were observed and some of these are uncertain due to the low intensities. Among the observed vanishing IR bands: 1179, 1159, 1004, 901 and 826 cm^{-1}, those at 1004, 901 and 826 cm^{-1} were reliable since they were also observed in the corresponding Raman spectra (see below).

Raman liquid spectra. The complete Raman spectra of the liquid including semiquantitative polarisation measurements were recorded. The spectrum is shown in Figs. 8 and 9. The wavenumbers are collected in Table 5. Characteristic differences between the IR and Raman spectra are observed, in particular the modes connected with O–H stretching and bending are very weak in Raman but strong in infrared.

Raman crystal spectra. Raman spectra of the solid were obtained in two ways, by cooling the liquid in a capillary until crystallisation or by condensing the vapour on a copper finger at 80 K and subsequent annealing below the melting point temperature. Both procedures gave similar spectra which are given in Figs. 8 and 9. Although

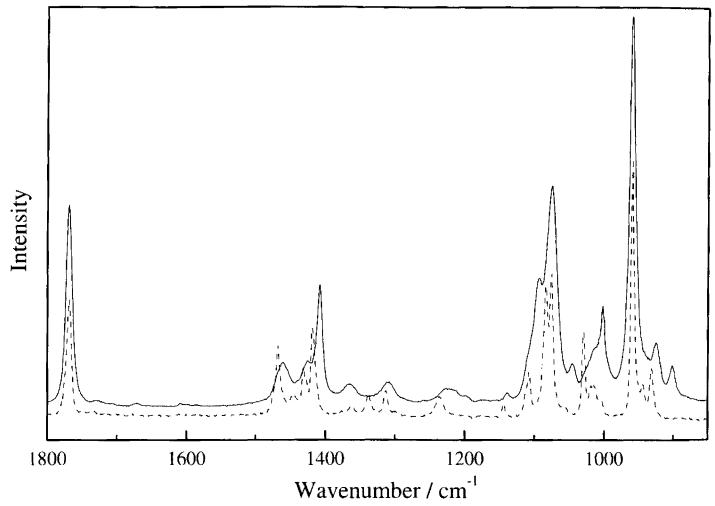

Fig. 8. Raman spectrum of 2-cyclopropylideneethanol as a liquid at 273 K (solid curve) and crystalline solid at 190 K (dashed curve) in the range 1800–850 cm^{-1}.

Table 5. Infrared and Raman spectral data for 2-cyclopropylideneethanol.[a]

IR				Raman		Interpretation	
Vapour	Ar matrix	Amorphous (85 K)	Crystal (85 K)	Liquid	Crystal	*Skew 1*	*Syn 1*
	3776 w[b]						
	3756 m	3470 w sh	3462 w	3470 vw			
	3711 w			3400 vw			
	3670 w *						
3654 m, 3643 m sh	3650 m *	3230 vs br	3334 vs	3330 vw	3350 vw	ν_1	
	3642 m		3235 vs	3258 vw	3257 vw		
	3631 m						ν_1
	3579 vw						
	3574 w						
	3528 vw						
	3522 vw						
	3513 w						
				3180 vw			
3068 m	3066 w	3059 w	3040 w	3057 m D	3055 m	ν_2	
				3049 m sh D	3040 m	ν_3	
		3007 w	3017 w		3015 w		
			2989 vw		2986 w		
			2984 vw				
3000 s, 2994 s	2998 m, 2986 w	2980 s	2976 m	2985 vs P	2978 vs	ν_4	
2965 m	2965 w	2955 w	2942 m	2943 m P	2944 m	ν_5	
2942 m, 2932 m	2941 w, 2935 w	2927 m	2920 m		2925 vw	ν_6, ν_7	
			2904 w				
	2892 m		2894 m				
	2886 m		2874 w	2897 w sh P	2901 m		
2881 s	2877 m	2867 s br	2851 m	2876 m P	2850 m	ν_8	
	2866 m						
				2812 w sh P			
	1773 vw, 1770 vw						
1769 w sh, 1754 m, 1747 w sh	1756 m	1770 w	1780 w	1770 s P	1760 s	ν_9	
	1740 m	1718 m	1722 w				
	1730 vw			1730 vw P	*		
	1711 vw						
	1661 vw br, 1655 vw sh			1673 vw P	*		
	1637 w						
	1624 m						
	1608 m			1610 vw D	*		
				1601 vw D ?	*?		
	1589 vw			1588 vw D			
				1585 vw sh D			
1468 w	1469 w, 1460 w sh		1469 m	1463 w D	1467 m	ν_{10}	
	1445 vw	1455 m br	1447 m		1445 w	ν_{11}	
	1427 vw			1427 m D	1429 w, 1426 vw	ν_{12}	
	1416 vw, 1413 w, 1403 m		*	1416 w sh D?	*		ν_{12}
			1412 w				
1389 s, 1386 s	1388 s	1408 m br	1409 w	1411 m P	1420 m	ν_{13}	
	1375 w	1368 m	1365 s	1365 w P	1361 vw		
	1350 vw	1347 m	1347 w				

Table 5. (Continued.)

IR				Raman		Interpretation	
Vapour	Ar matrix	Amorphous (85 K)	Crystal (85 K)	Liquid	Crystal	*Skew 1*	*Syn 1*
1341 w	1337 m	1336 w	1337 w		1338 w	ν_{14}	
	1293 w	1299 m br	1308 m, 1296 w	1312 w D	1313 w	ν_{15}	
	1268 vw		1270 w				
	1261 vw	1257 vw					
1247 m, 1242 m	1251 m, 1248 w, 1239 w	1246 w	1243 w		1246 w		
		1224 m br	1235 vw, 1224 w	1223 w D			
				1215 w sh D	*		
	1187 w	1205 vw	*	1201 w sh P	*		
1182 w sh, 1168 w	1178 w	1179 w	*	1175 vw	*	ν_{16}	
	1160 w, 1157 w	1159 vw	*(?)				
	1132 w	1137 vw	1142 vw	1140 w D	1144 vw	ν_{17}	
1143 m, 1129 m	1118 m	~1115 m sh	1112 m	1115 w sh	1115 vw		
	1109 vw			1110 w sh			
1093 vw	1097 m, 1095 m	1101 s br	1107 m	1096 m br	1110 w	ν_{18}	
			1095 w br				
	1085 vw		1081 m		1084 s		
	1073 w	1074 m	1075 w	1075 s P	1075 s	ν_{19}	
1065 vw	1070 w		1069 w			ν_{20}	
	1057 w, 1054 w, 1051 m, 1048 w	1048 m	1055 m, 1052 m	1046 w P	1058 vw	ν_{21}	
	1033 vw		1033 m		1028 m	ν_{22}	
1026 vs, 1016 vs	1021 vs, 1020 vs, 1018 vs	1017 vs br	1018 vs br	1014 w sh D?	1018 vw, 1013 vw	ν_{23}	
	1005 vw, 1001 w		*	1003 m P	1003 vw		ν_{23}
959 m, 952 m, 937 m	959 s	960 s	958 s	960 s P	958 vs	ν_{24}	
	935 m	945 m br	948 w, 943 m	943 vw	942 vw	ν_{25}	
	923 w	927 m	932 m, 926 m	925 w P	930 w	ν_{26}	
	917 w						
	897 vw, 894 w	901 w	*	902 w P	*		ν_{26}
	874 vw	871 vw	871 vw				
863 vw	862 vw	861 w	860 w				
844 vw	855 w	845 w					
	838 w	838 w	835 w				
	828 vw	826 vw	*	818 vw	*		ν_{27}
775 w sh	788 w	788 m	794 vw, 785 w	785 w D	789 m	ν_{27}	
	761 w	761 m	763 m				
749 w, 739 w	747 w	750 m	756 m	753 w D	761 m, 756 w	ν_{28}	
	738 w						
	718 vw	718 m	727 w, 719 vw	720 m D	727 m, 721 w sh	ν_{29}	

Table 5. (Continued.)

IR				Raman		Interpretation	
Vapour	Ar matrix	Amorphous (85 K)	Crystal (85 K)	Liquid	Crystal	*Skew 1*	*Syn 1*
	710 vvw						
	668 w		668 s br	657 vw br			
	663 vw *		642 s br				
	662 w						
		613 m	613 w	609 m P	607 w		
		609 m	609 w	581 vw P	*		ν_{30}
			508 w		502 vw		
496 w	501 w	502 m br	504 w	491 m P	497 w	ν_{30}	
			497 s				
425 vw		455 w	454 m	450 m P	450 m	ν_{31}	
				334 w sh D	333 w	ν_{32}	
				299 m D	301 s	ν_{33}	
					274 vw		
				214 m P?	226 w	ν_{34}	
				171 w br P	189 m	ν_{35}	
				119 w sh	121 m	ν_{36}	
					91 s		
					75 w		
					53 m		
					40 w		

[a]Weak bands in the region 2800–1800 cm^{-1} have been omitted. [b]Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad. P and D denote respectively polarised and depolarised bands in the Raman effect. Asterisks denote bands disappearing upon annealing.

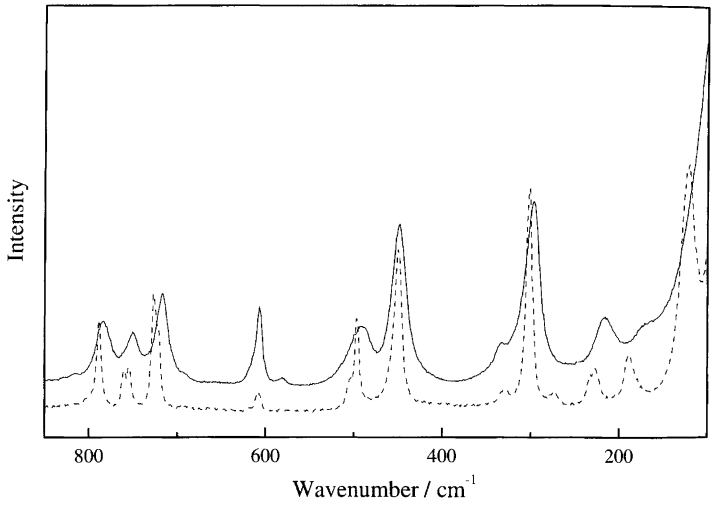

Fig. 9. Raman spectrum of 2-cyclopropylideneethanol as a liquid at 273 K (solid curve) and crystalline solid at 190 K (dashed curve) in the range 850–100 cm^{-1}.

the Raman spectrum did not change nearly as much as the IR spectrum upon crystallisation, it was observed that certain bands vanished after crystallisation, interpreted as due to one or more conformers present in the liquid vanishing in the crystal. However, apart from the band around 902 cm^{-1}, which is medium intense in the Raman spectrum, most of the vanishing bands were weak. The low intensities of the vanishing bands suggest that that the additional conformer(s) is (are) present in lower concentration than the major conformer in the liquid. The number of sharp bands observed below 150 cm^{-1}, ascribed to lattice modes, clearly reveal that the sample was truly crystalline. Sharper bands and additional peaks were observed in the Raman spectra of the crystal compared to those of the liquid or amorphous phases, but the changes were not as profound as observed in the IR spectra.

More important are the Raman bands due to additional conformers, present in the liquid but vanishing in the crystal spectra as a consequence of there being only one conformer present in the crystal lattice. Such bands were observed at 1730, 1673, 1610, 1601, 1416, 1215,

Table 6. Calculated and observed vibrational fundamentals for the *Skew 1* and *Syn 1* conformations of 2-cyclopropylideneethanol.[a]

	Skew 1				*Syn 1*			
No.	*Ab initio*	Scaled	Obs.	Interpretation	*Ab initio*	Scaled	Obs.	$\Delta\nu_{skew-syn}$
ν_1	3880 m[b]	3686	3650 m	OH stretch	3892 m	3697	3631 m	−11
ν_2	3309 w	3143	3066 w	Antisym. CH_2 stretch in ▷=	3307 m	3142		1
ν_3	3298 vw	3133	3049[c]	Antisym. CH_2 stretch in ▷=	3296 vw	3131		0
ν_4	3241 m	3079	2998 m	=C–H stretch	3227 m	3066		13
ν_5	3211 w	3050	2965 w	Sym. CH_2 stretch in ▷=	3210 m	3050		0
ν_6	3209 w	3049	2941 w	Sym. CH_2 stretch in ▷=	3205 w	3045		4
ν_7	3181 m	3022	2935 w	Antisym. CH_2 stretch in $-CH_2OH$	3160 m	3002		20
ν_8	3099 m	2944	2881 s	Sym. CH_2 stretch in $-CH_2OH$	3063 m	2910		34
ν_9	1880 vw	1786	1756 m	C=C stretch	1886 w	1792	1740 m	−6
ν_{10}	1560 vw	1482	1469 w	Sym. CH_2 deformation in $-CH_2OH$	1562 vw	1484		−2
ν_{11}	1535 vw	1458	1445 vw	Sym. CH_2 rock in ▷=	1537 vw	1460		−2
ν_{12}	1508 vw	1432	1427 vw	Antisym. CH_2 rock in ▷=	1510 vw	1435	1416[c]	−3
ν_{13}	1448 m	1375	1388 s	Antisym. CH_2 deformation in $-CH_2OH$	1453 m	1380		−5
ν_{14}	1406 m	1335	1337 m	C–O–H bend	1407 w	1337		−2
ν_{15}	1350 vw	1282	1293 w	C–C–H bend	1362 vw	1294		−12
ν_{16}	1231 w	1169	1178 w	CH_2 twist in CH_2OH	1236 w	1174		−5
ν_{17}	1207 vw	1146	1132 w	Antisym CH_2 twist in ▷=	1208 vw	1148		−2
ν_{18}	1154 w	1096	1096 m	Sym CH_2 twist in ▷=	1166 m	1108		−12
ν_{19}	1134 w	1077	1073 w	C–C stretch	1130 m	1073		4
ν_{20}	1130 w	1073	1070 w	Antisym CH_2 wag in ▷=	1129 m	1073		0
ν_{21}	1107 w	1052	1051 m	C–O stretch	1109 m	1054		−2
ν_{22}	1087 w	1033	1033 vw	Ring breathing	1090 w	1036		−3
ν_{23}	1076 s	1022	1020 vs	Sym CH_2 wag in ▷=	1035 m	983		39
ν_{24}	1016 m	965	959 s	=C–H out-of-plane bend	1025 m	974		−9
ν_{25}	980 m	931	935 m	Ring deformation	979 w	930		1
ν_{26}	963 m	914	923 w	CH_2 rock in $-CH_2OH$	944 m	897	894	17
ν_{27}	820 w	778	788 w	Antisym CH_2 rock in ▷=	798 w	758	818[c]	20
ν_{28}	780 vw	741	747 w	Sym CH_2 rock in ▷=	785 w	746		−5
ν_{29}	754 w	716	718 vw	Ring deformation	759 w	721		−5
ν_{30}	508 w	483	501 w	C–C–O bend	631 w	599	581[c]	−116
ν_{31}	458 w	435	450[c]	C–C=C bend in ▷=	368 m	350		85
ν_{32}	376 vs	357	334[c]	OH torsion	333 m	316		41
ν_{33}	273 w	259	299[c]	▷= out of plane bend	294 vs	279		−20
ν_{34}	210 w	199	214[c]	C=C–C bend in $C=C-CH_2OH$	202 w	191		7
ν_{35}	162 vw	154	171[c]	C=C torsion	163 vw	155		−1
ν_{36}	74 w	70	119[c]	—CH_2OH torsion	87 w	83		−13

[a]Data from Ar matrix except when otherwise noted. [b]Infrared intensities given relative to the strongest band: vs, very strong (more than 99%); s, strong (99–81%); m, medium (80–11%); w, weak (10–1%); vw, very weak (less than 1%). [c]Raman liquid phase data.

1201, 1175, 1003, 902, 818 and 581 cm^{-1}, and listed with asterisks in Table 5, but many of these are very weak and uncertain. Among them the peaks at 1201, 1003, 902 and 818 cm^{-1} vanished also in the IR spectra (see above), strongly suggesting conformational origin.

Raman variable temperature spectra. Additional spectra of the liquid were recorded below ambient temperature at 233, 243, 253, 263 and 273 K, resulting in somewhat sharper bands. From intensity changes of bands which are attributed to specific conformers the enthalpy difference ($\Delta_{conf}H$) between the conformers can be evaluated with standard van't Hoff plots. Among the IR and Raman bands vanishing on crystallisation and assigned to the *Syn 1* conformer, the only peak useful for quantitative calculations was the medium intense Raman band at 902 cm^{-1} which was compared quantitatively to the neighbour peak at 925 cm^{-1} assigned to *Skew 1*. All the other presumed *Syn 1* peaks were too weak. Since the 901 and 925 cm^{-1} bands were situated close to the strong Raman band at 960 cm^{-1}, the spectra had a tilted background. For this reason it was not possible to make a direct quantitative calculation from the Raman curves.

The Raman spectrum was treated with a curve separation program in the 1000–850 cm^{-1} range involving four peaks. For each temperature the ratio between the 902 and the 925 cm^{-1} bands were plotted against $1/T$ in the conventional van't Hoff plots. Separate calculations were carried out for band areas and peak heights. Both sets of data revealed that the 902 cm^{-1} band, which disappears in the crystal, belongs to the high energy conformer assumed to be *Syn 1* from the microwave results. The plots based upon band areas and those on peak heights gave ΔH° values equal to 2.5 ± 0.6 and 1.2 ± 0.6 kJ mol^{-1}, respectively. The results reflect that the bandwidths changed with temperature, and the former values were

considered the more reliable. Compared with the *ab* initio value of ΔH equal to 2.29 kJ mol^{-1} (MP2/6-31G** level), the variable temperature value from the liquid lies within the experimental uncertainty, which is undoubtedly fortuitous.

Assignment of vibrational spectra. We do not claim to have made an unambiguous assignment of the vibrational spectra. We have relied heavily upon the results from *ab initio* calculations, that is, the predicted wavenumbers of the fundamental modes of vibration and their infrared absorption cross-section. Table 6 collects these data, calculated in the MP2/6-31G** level of approximation, for the *Skew 1* and *Syn 1* conformers together with our observations and the interpretation according to the largest terms in the potential energy distribution. The *ab initio* calculated wavenumbers are invariably too high. However, as can be seen, a reasonable agreement is obtained by simply scaling the calculated values by 0.95.

Discussion

The fact that CPE prefers the C3=C2–C1–O1 chain of atoms in a *skew* conformation for its most stable rotamer (*Skew 1*) parallels the findings made for all other allylic alcohols,[1–8] both aliphatic[1–6] and aromatic.[7,8] The presence of the pseudo-π electrons of the cyclopropyl ring which might interact with the hydroxylic H1 atom in the *Syn 1* (but not in the *Skew 1*) thus does not influence the general tendency to prefer a C=C–C–O *skew* arrangement[1–8] to any great extent.

The interaction between the hydroxyl group H1 atom and the π electrons of the double bond is weak. Evidence for this comes from the geometry of the alleged H bonds in *Skew 1* and *Syn 1* as well as from the fact that the maximum of the O–H stretching frequency falls at such a high frequency as 3654 cm^{-1}. Other factors than the H bond are likely to stabilise the *Skew 1* and *Syn 1* forms. It has been pointed out[2c] that in the *skew* conformations favourable mixing of the σ*-orbital of the C–O bond and the π-orbital of the C=C double bond exists. In the *syn* forms, co-planarity of the C=C and C–O bonds allows favourable effective mixing of the π- and π*-orbitals of the C=C bond and π-lone pair orbital on the oxygen atom. This electronic effect comes in addition to a very weak H-bond interaction, and makes the *Skew 1* and *Syn 1* conformers the preferred forms of CPE.

Acknowledgement. Mrs. Anne Horn is thanked for drawing the figures and for experimental assistance. This work has received support from the Research Council of Norway (Programme for Supercomputing) through a grant of computing time.

References

1. (a) Murty, A. N. and Curl, R. F. *J. Chem. Phys. 46* (1967) 4176; (b) Badawi, H., Lorencak, P., Hillig, K. W., Imachi, M. and Kuczkowski, R. L. *J. Mol. Struct. 162* (1987) 247; (c) Vanhouteghem, F., Pyckhout, W., van Alsenoy, C., van den Enden, L. and Giese, H. J. *J. Mol. Struct. 140* (1986) 33; (d) Aspiala, A., Lotta, T., Murto, J. and Räsänen, M. *J. Chem. Phys. 79* (1983) 4183; (e) Schleyer, P. v. R., Trifani, D. S. and Bacskai, R. L., *J. Am. Chem. Soc. 80* (1958) 6691; (f) Oki, M. and Iwamura, H. *Bull. Chem. Soc. Jpn. 32* (1959) 567; (g) Bakke, J. M., Schie, A. M. and Skjetne, T. *Acta Chem. Scand., Ser. B 40* (1986) 703; (h) Brouwer, H. and Stothers, J. B. *Can. J. Chem. 50* (1972) 1361; (i) Pierre, J.-L., *Bull. Soc. Chim. Fr.* (1970) 3116; (j) Melandri, S., Favero, P. and Caminati, W. *Chem. Phys. Lett. 223* (1994) 541; (k) Silvi, B. and Perchard, J. P. *Spectrochim. Acta, Part A 32* (1976) 11.
2. (a) Smith, Z., Carballo, N., Wilson, E. B., Marstokk, K.-M. and Møllendal, H. *J. Am. Chem. Soc. 107* (1985) 1951; (b) Kahn, S. D. and Hehre, W. J. *Tetrahedron Lett. 26* (1985) 3647; (c) Kahn, S. D. and Hehre, W. J. *J. Am. Chem. Soc. 109* (1987) 666.
3. (a) Caminati, W. and Fantoni, A. C. *Chem. Phys. 105* (1986) 59; (b) Caminati, W., Fantoni, A. C., Velino, B., Siam, K., Schäfer, L., Ewbank, J. D. and van Alsenoy, C. *J. Mol. Spectrosc. 124* (1987) 72.
4. (a) Lum, D. K., Baumann, L. E., Malloy, T. B., Jr. and Cook, R. L. *J. Mol. Struct. 50* (1987) 1; (b) Caminati, W., Velino, B. and Fantoni, A. C. *Mol. Phys. 61* (1987) 1269; (c) Caminati, W., Paolucci, C., Velino, B. *J. Mol. Spectrosc. 137* (1989) 362.
5. Horn, A., Marstokk, K.-M., Møllendal, H. and Priebe, H. *Acta Chem. Scand., Ser. A 37* (1983) 679.
6. Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand. 44* (1990) 18.
7. Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand. 48* (1994) 25.
8. Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand. 47* (1993) 849.
9. Pauling, L. *The Nature of the Chemical Bond*, 3rd Edn., Cornell University Press, New York 1960, p. 260.
10. Walsh, A. D. *Trans Faraday Soc. 45* (1949) 179.
11. (a) Wilson, E. B. and Smith, Z. *Acc. Chem. Res. 20* (1987) 257; (b) Møllendal, H., *J. Mol. Struct. 97* (1983) 303; (c) Møllendal, H.,In: Laane, J., Dakkouri, M., van der Veken, B. and Oberhammer, H., Eds., *Structures and Conformations of Non-Rigid Molecules*, Kluwer Academic Publishers, Dordrecht, Netherlands 1993, p. 277; (d) K.-H. Hellwege, Ed., *Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, New Series, Vol. II/7 (1976), Vol II/15 (1987) and Vol. II/21 (1992),* Springer-Verlag, Berlin; (e) Harmony, M. D., Laurie, V. W., Kuczkowski, R. L., Schwendeman, R. H., Ramsay, D. A., Lovas, F. J., Lafferty, W. J. and Maki, A. G. *J. Phys. Chem. Ref. Data 8* (1979) 619.
12. Stolle, A., Ollivier, J. Piras, P. P., Salaün, J. and de Meijere, A. *J. Am. Chem. Soc. 114* (1992) 4051.
13. Guirgis, G. A., Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand. 45* (1991) 482.
14. Ø. Waal, 1994. *Personal communication.*
15. Miller, F. A. and Harney, B. M. *Appl. Spectrosc. 24* (1970) 291.
16. Hehre, W. J., Radom, L., Schleyer, P. v. R. and Pople, J. A. *Ab Initio Molecular Orbital Theory*, Wiley, New York 1985.
17. Frisch, M. J., Pople, J. A. and Del Bene, J. E. *J. Phys. Chem. 89* (1985) 3664.
18. Frisch, I. M., Trucks, G. W, Head-Gordon, M., Gill, P. M. W., Wong, M. W., Foresman, J. B., Johnson, B. G., Schlegel, H. B., Robb, M. A., Replogle, E. S., Gomperts, R., Andres, J. L., Raghavachari, K., Binkley, J. S., Gonzalez, C., Martin, R. L., Fox, D. J., Defrees, D. J.,

Baker, J., Stewart, J. J. P. and Pople, J. A. *Gaussian 92*, Revision C, Gaussian, Inc., Pittsburgh, PA 1992.
19. Laurie, V. W. and Stigliani, W. M. *J. Am Chem. Soc. 92* (1970) 1485.
20. Watson, J. K. G. In: Durig, J. R., Ed. *Vibrational Spectra and Structure,* Elsevier, Amsterdam 1977, Vol. 6.
21. Esbitt, A. S. and Wilson, E. B. *Rev. Sci. Instrum. 34* (1963) 901.
22. Kraitchman J. *Am. J. Phys. 21* (1953) 17.
23. Durig, J.R., Klacboe, P., Gurgis, G.A., Wang, L. and Liu, J. *Z. Phys. Chem. 191* (1995) 23.
24. Marstokk, K.-M., Møllendal, H. and Stenstrøm, Y. H. *Acta Chem. Scand. 46* (1992) 432.
25. Marstokk, K.-M., Møllendal, H., Samdal, S. and Stenstrøm, Y. H. *Acta Chem. Scand. 46* (1992) 325.
26. Richter, W. and Schiel, D. *Ber. Bunsenges. Phys. Chem. 85* (1981) 548.
27. Barnes, A. J. *J. Mol. Struct., 113* (1984) 161.

Received March 20, 1998.