

# Microwave Spectrum, Conformational Equilibrium, Intramolecular Hydrogen Bonding, Tunneling, and Quantum Chemical Calculations for 1-Ethenylcyclopropan-1-ol

Andrei Leonov,<sup>†</sup> Karl-Magnus Marstokk,<sup>‡</sup> Armin de Meijere,<sup>†,§</sup> and Harald Møllendal<sup>\*,†,⊥</sup>

Department of Chemistry, The University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway, and Institut für Organische Chemie der Georg-August-Universität, Tammannstrasse 2, D-37077 Göttingen, Germany

Received: November 16, 1999; In Final Form: February 17, 2000

The microwave spectra of 1-ethenylcyclopropan-1-ol,  $(\text{CH}_2)_2\text{C}(\text{OH})\text{C}=\text{CH}_2$ , and one deuterated species,  $(\text{CH}_2)_2\text{C}(\text{OD})\text{C}=\text{CH}_2$ , have been investigated in the 11.0–60.0 GHz region. The (*ac,ap*)- and (*ac,sc1*)-conformers denoted Syn 1 and Skew 1 were assigned. Each of these two forms is stabilized with an intramolecular hydrogen bond formed between the hydrogen atom of the hydroxyl group and the  $\pi$  electrons of the double bond. In the Syn 1 rotamer the  $\text{C}=\text{C}-\text{C}-\text{O}$  chain of atoms takes a syn conformation (dihedral angle =  $-2.6^\circ$ ) and the  $\text{H}-\text{O}-\text{C}-\text{C}=\text{C}$  link of atoms is gauche (dihedral angle =  $-67.2^\circ$  from syn). The  $\text{C}=\text{C}-\text{C}-\text{O}$  link of atoms takes a skew conformation (dihedral angle =  $132.1^\circ$  from syn) in the Skew 1 rotamer, while the  $\text{H}-\text{O}-\text{C}-\text{C}=\text{C}$  dihedral angle is  $-67.1^\circ$ . Syn 1 is preferred by  $4.9(6)$  kJ mol<sup>-1</sup> relative to Skew 1. Syn 1 is virtually a hybrid of the most stable conformer of unsubstituted ethenylcyclopropane, and unsubstituted cyclopropanol, Skew 1, is the corresponding hybrid of the second rotamer of ethenylcyclopropane and the most stable one of cyclopropanol. The spectrum of Syn 1 is perturbed by tunneling of the hydroxyl group. An analysis yielded 2280.184(60) MHz for the tunneling frequency and 39.82(19) MHz for the Coriolis coupling term  $\mu_{ca}$  for the normal species. The corresponding values were 72.401(27) and 5.2(10) MHz, respectively, for the deuterated species. A potential function for the tunneling motion consisting of three cosine terms was found to have the following potential constants:  $V_1 = -918.2$ ,  $V_2 = -900.0$ , and  $V_3 = 418.0$  cm<sup>-1</sup>. This double-minimum function yields a barrier of 16.6(50) kJ mol<sup>-1</sup> at the anti position and 10.6(30) kJ mol<sup>-1</sup> at syn. The microwave work has been assisted by ab initio computations at the MP2/cc-pVTZ level of theory as well as density functional theory calculations at the B3LYP/6-31G\* level. These calculations indicate that there are only three stable rotameric forms of the molecule. The gas-phase IR spectrum in the O–H stretching region revealed a broad and complex band red-shifted by roughly 50 cm<sup>-1</sup> presumably as a result of internal hydrogen bonding.

## Introduction

Several allylic alcohols that contain the  $\text{C}=\text{C}-\text{C}-\text{O}-\text{H}$  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 quantum chemical computations.<sup>1–7</sup> The molecules studied so far include the prototype compound 2-propen-1-ol ( $\text{H}_2\text{C}=\text{CHCH}_2\text{OH}$ , allyl alcohol)<sup>1</sup> and derivatives such as 3-buten-2-ol ( $\text{H}_2\text{C}=\text{CHCH}(\text{OH})\text{CH}_3$ ),<sup>2</sup> 2-methyl-2-propen-1-ol ( $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$ ),<sup>3</sup> *trans*-<sup>4a,b</sup> and *cis*-2-buten-1-ol<sup>4c</sup> ( $\text{H}_3\text{CCH}=\text{CHCH}_2\text{OH}$ ), 2,3-butadien-1-ol ( $\text{H}_2\text{C}=\text{C}=\text{CHCH}_2\text{OH}$ ),<sup>5</sup> 1,4-pentadien-3-ol ( $\text{H}_2\text{C}=\text{CHCH}(\text{OH})\text{CH}=\text{CH}_2$ ),<sup>6</sup> and 2-cyclopropylideneethanol ( $(\text{CH}_2)_2\text{C}=\text{CHCH}_2\text{OH}$ ).<sup>7</sup> Two aromatic compounds, viz. 2-<sup>8</sup> and 3-furanmethanol,<sup>9</sup> have also been studied. They are in a sense allylic alcohols because they carry the  $\text{C}=\text{C}-\text{C}-\text{O}-\text{H}$  link of atoms.

In all these compounds<sup>1–9</sup> the preferred rotamer has a heavy-atom skew conformation with a  $\text{C}=\text{C}-\text{C}-\text{O}$  dihedral angle roughly  $120^\circ$  from syn ( $0^\circ$ ). The  $\text{C}-\text{C}-\text{O}-\text{H}$  dihedral angle is gauche (approximately  $60^\circ$  from syn) in all molecules but

2-furanmethanol<sup>8</sup> (where hydrogen (H) bonding with the oxygen atom of the ring predominates), allowing a H bond to be formed with the  $\pi$  electrons of the double bond. A second  $\text{C}=\text{C}-\text{C}-\text{O}$  syn rotamer has been found in some of these cases.<sup>1j,2a,3b</sup> The conformation of  $\text{C}-\text{C}-\text{O}-\text{H}$  is gauche in the syn rotamers too,<sup>1c,j,2a,3b</sup> allowing a H bond to be formed with the  $\pi$  electrons. The syn forms are slightly less stable ( $1-3$  kJ mol<sup>-1</sup>) than their skew counterparts.<sup>1c,j,2a,3b</sup> In cases where there are two mirror-image forms of syn, tunneling of the hydroxyl group is a prominent feature of the MW spectrum.<sup>1j,3a</sup>

Formally, 1-ethenylcyclopropan-1-ol (ECP) can be regarded as an allylic alcohol with the two methylene groups of the cyclopropyl ring seen as substituents. However, the presence of this ring is a complicating factor that is likely to have interesting conformational consequences. In cyclopropane derivatives with unsaturated substituents such as CHO,<sup>10</sup> CFO,<sup>11</sup> CClO,<sup>12</sup> CO<sub>2</sub>H,<sup>13</sup> vinyl,<sup>14</sup> or nitro,<sup>15</sup> the most stable conformations are those with the plane of the substituent in the symmetry plane of the molecule.  $\text{C}=\text{C}-\text{C}-\text{O}$  syn form(s) are thus expected for ECP when this compound is regarded as a cyclopropyl derivative with an unsaturated substituent.

Several interesting questions then arise for ECP: e.g., will the tendency of allyl alcohols to prefer a skew form or the propensity of cyclopropane derivatives to prefer a syn form predominate? Are there several rotamers within a narrow energy

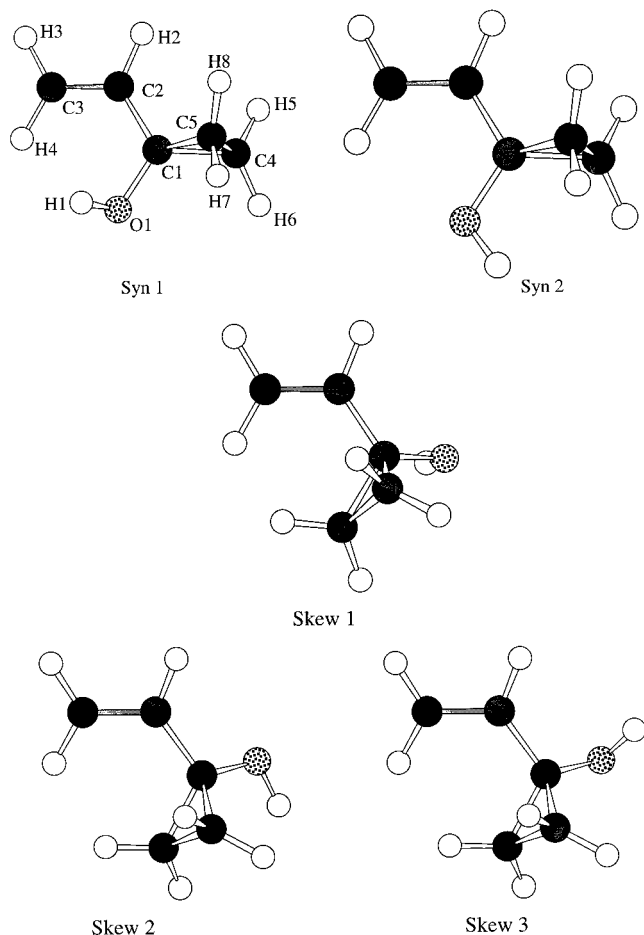
\* To whom correspondence should be addressed.

<sup>†</sup> Institut für Organische Chemie der Georg-August-Universität.

<sup>‡</sup> Department of Chemistry, The University of Oslo.

<sup>§</sup> E-mail: amejjere1@uni-goettingen.de.

<sup>⊥</sup> E-mail: harald.mollendal@kjemi.uio.no.



**Figure 1.** Five possible conformations of 1-ethenylcyclopropan-1-ol. Only three of these, viz., Syn 1 (*ac,ap*), Skew 1 (*ac,sc1*), and Skew 3 (*ac,sc2*) were found to be “stable” (i.e., minima on the potential energy hypersurface). Syn 1 and Skew 1 were assigned in this work. Syn 1 is 4.9(6) kJ mol<sup>-1</sup> more stable than Skew 1. In the IUPAC nomenclature, the first denominator stands for the conformation of the cyclopropanol subunit with respect to the O–H bond and the plane bisecting the cyclopropane ring, the second for that of the ethenylcyclopropane subunit.

range? In case this is so, what do they look like? Will any of them display unusual dynamics, i.e., tunneling? What is the role of internal H bonding? These are some of the questions we attempt to answer in this work. It should be added that the present work is a continuation of the studies of intramolecular H bonding made in Oslo.<sup>16</sup>

The conformational properties of ECP are dictated by the rotation around the O1–C1 and C1–C2 bonds (see Figure 1). A total of nine all-staggered conformations can thus be envisaged. Symmetry reduces this number to five that in principle can be distinguished by spectroscopy provided they are “stable”, i.e., minima on the potential energy hypersurface. Representatives of these five forms are shown in Figure 1. The O1–C1–C2=C3 chain of atoms form a dihedral angle  $\varphi$  of about +120° measured from syn  $\varphi = 0^\circ$  in the three skew conformations shown in Figure 1. The H1–O1–C1–C2 dihedral angle is near -60° (Skew 1), 180° (Skew 2), and +60° (Skew 3). In the two syn forms, the O1–C1–C2=C3 dihedral angle is approximately 0°, while the H1–O1–C1–C2 dihedral angle is about -60° (Syn 1) and 180° (Syn 2). Skew 1 and Syn 1 are both stabilized by a weak intramolecular H bond formed between the hydroxyl group H atom and the  $\pi$ -electrons of the C2=C3 double bond. This possibility is absent in the three other forms.

No investigations of the conformational properties of ECP have been reported. It was therefore decided to carry out a MW study assisted by quantum chemical calculations and infrared spectroscopy. MW spectroscopy is ideal for investigating conformational properties in cases where polar forms are present because of its high specificity. All conceivable rotamers of the ECP would each possess a sizable dipole moment that is a prerequisite for a MW spectrum. Advanced quantum chemical computations are often found to be useful in predicting rotational constants, dipole moments, and energy differences for the various conformers that are sufficiently close to the experimental ones to be really helpful starting points in the spectral analysis. In addition, they may give important information about molecular parameters that are not readily accessible experimentally. Such calculations are therefore of interest in their own right.

## Experimental Section

The sample of 1-ethenylcyclopropan-1-ol utilized in this work was synthesized according to the published procedure.<sup>17</sup> The compound was purified by low temperature crystallization from *n*-pentane, subsequent low temperature zone melting, and finally distillation. Purity was assessed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

The deuterated species was produced by seasoning the waveguide with D<sub>2</sub>O and then introducing the parent species. Roughly 50% deuteration was achieved in this manner. The MW spectrum was studied using the Oslo Stark spectrometer described in ref 18. The 11–40 GHz spectral region was investigated extensively. Selected measurements were also made in the 40–60 GHz interval. Radio frequency microwave frequency double resonance (RFMWDR) experiments were made as described in ref 19 using the equipment mentioned in ref 20. The microwave absorption cell was cooled to about -25 °C during the experiments. Lower temperatures, which would have increased the MW spectral intensities, could not be employed owing to insufficient vapor pressure of the compound. The pressure was 4–10 Pa when the spectra were recorded and stored electronically using the computer programs written by Waal.<sup>21</sup> The accuracy of the spectral measurements is presumed to be better than ±0.10 MHz. The resolution is approximately 0.4 MHz. The IR spectrum was taken at room temperature using a Bruker IFS 88 spectrometer with MCT detection and a long path minicell from Infrared Analysis. The path length was about 3 m and the pressure was approximately 200 Pa.

## Results and Discussion

**Quantum Chemical Calculations.** The Gaussian 94 program package<sup>22</sup> running on the IBM RS6000 cluster in Oslo was employed in all the quantum chemical calculations. The 6-31G\* basis set<sup>22</sup> and the correlation-consistent polarized triple- $\zeta$  basis set,<sup>23</sup> cc-pVTZ, provided with the program were used. Two different computational schemes, the elaborate MP2/cc-pVTZ procedure and the much less demanding B3LYP/6-31G\* method, were employed in the computations. In the first of these procedures, electron correlation was included using the second-order Møller–Plesset (MP2) perturbation theory.<sup>24</sup> In the second procedure, density functional theory (DFT) calculations were carried out employing the B3LYP procedure.<sup>25</sup> Full geometry optimization was made in both the MP2 and in the B3LYP computations.

The reason for selecting these two computational schemes is that the MP2/cc-pVTZ procedure is assumed to produce accurate structures<sup>26</sup> for the conformations in question. Good estimates

of the rotational constants are therefore expected from such calculations. This of course facilitates the spectral assignments.

It is assumed that the B3LYP/6-31G\* structures, dipole moments, and vibrational frequencies<sup>25</sup> are also quite accurate. Calculations of the structures and vibrational frequencies were first made with the B3LYP procedure allowing for full geometry optimization. The B3LYP structures thus obtained were then used as input in the MP2 computations. MP2 vibrational frequencies were not computed owing to lack of resources.

Of the five possible conformations in Figure 1, only three, viz. Syn 1 as well as Skew 1 and Skew 3 were found to be stable in the B3LYP calculations, because no negative vibrational frequencies<sup>27</sup> were computed for any of them. No stable Syn 2 or Skew 2 forms were identified in these calculations. The B3LYP computations in fact refined to one of the three stable forms mentioned above in each case when conformations corresponding to Syn 2 or Skew 2 were used as starting point in the computations. Because the MP2/cc-pVTZ calculations are so comprehensive, no calculations for an assumed starting geometry of the hypothetical Syn 2 or Skew 2 forms were carried out using this computational scheme. It is believed on the basis of the B3LYP calculations that Syn 2 and Skew 2 indeed do not exist as stable forms of ECP, and that the other three conformers (Syn 1, Skew 1, and Skew 2) are the only stable forms of this compound. The hypothetical Syn 2 and Skew 2 conformations have an anti conformation for the H1–O1–C1=C2 chain of atoms. It is interesting to note that only the gauche form has been found for the related compound cyclopropanol in a MW study.<sup>28</sup> It thus appears that the H1–O1–C1=C2 anti conformation is generally not stable in cyclopropanols.

The MP2 geometries of the three stable conformers are given in Table 1 together with some other parameters of interest. The corresponding parameters obtained in the B3LYP calculations are rather similar to these. They are given in Table 1S in the Supporting Information.

There is nothing unusual about the bond lengths, bond angles, and dihedral angles of the three stable rotamers (Table 1). Interestingly, Syn 1 is predicted to be stabilized by more than 7 kJ mol<sup>-1</sup> relative to the other two stable forms (Skew 1 and Skew 3). The tendency to prefer syn forms with respect to the ethenyl moiety for cyclopropyl derivatives with unsaturated groups thus seems to be of overriding importance (see above).

The internal H bond interaction is optimal in both Syn 1 and Skew 1. It is assumed that this interaction is the reason Skew 1 is preferred to Skew 3, which cannot have a H bond. The MP2 distances between the H1 and C2 and C3 atoms calculated from the structure in Table 1 are 266 and 286 pm, respectively, in Syn 1 and 263 and 356 pm in Skew 1. The sum of the van der Waals distances for hydrogen (120 pm<sup>29</sup>) and aromatic carbon (170 pm<sup>29</sup>) is 290 pm and thus slightly longer than the distances between H1 atom and C2 atom in these two cases. This indicates a modest H bond strength.

Another indication that the H bond interaction must be rather weak, but definitely not absent, comes from the IR spectrum of the O–H stretching frequency of the gas. It is seen in Figure 2 that this rather broad band has peaks at 3631 and 3625 cm<sup>-1</sup> and a shoulder at 3620 cm<sup>-1</sup>. The O–H stretching frequency of methanol<sup>30</sup> falls at 3682 cm<sup>-1</sup>. The O–H stretching frequency of the title compound is thus red-shifted by roughly 50 cm<sup>-1</sup> as compared to methanol.

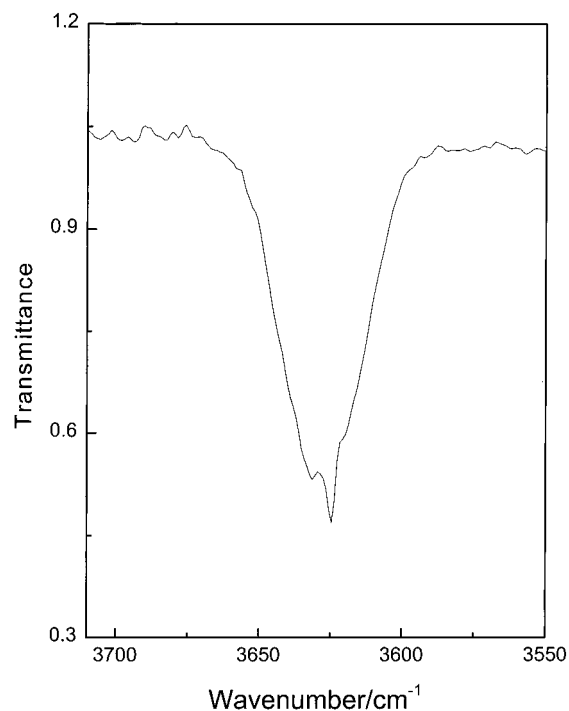
Syn 1 has a mirror-image form (not distinguishable by MW spectroscopy) that can be produced by rotating the H1–O1–C1=C2 dihedral angle until it becomes +67.2° instead of

**TABLE 1: Structure,<sup>a</sup> Rotational Constants, Dipole Moments, and Energy Differences of Syn 1, Skew 1, and Skew 3 of 1-Ethenylcyclopropan-1-ol As Calculated at the MP2/cc-pVTZ Level of Theory**

	conformer		
	Syn 1	Skew 1	Skew 3
Bond Length/pm			
O1–H1	96.4	96.4	96.3
C1–O1	140.0	140.9	140.9
C1–C2	147.3	148.0	148.1
C2–C3	133.6	133.5	133.5
C2–H2	108.4	108.5	108.6
C3–H3	107.9	108.0	108.0
C3–H4	108.0	108.1	108.0
C1–H4	149.9	149.6	151.0
C1–C5	151.1	150.1	148.9
C4–H5	107.9	107.9	107.9
C4–H6	107.9	107.9	108.0
C5–H7	107.9	107.9	107.8
C5–H8	108.0	107.9	107.8
Angle/deg			
H1–O1–C1	106.6	106.5	107.1
O1–C1–C2	116.5	114.0	114.6
C1–C2–C3	124.2	125.6	126.3
C1–C2–H2	115.8	114.6	114.8
C2–C3–H3	120.9	120.9	120.8
C2–C3–H4	120.8	121.5	121.7
O1–C1–C4	113.9	112.9	116.4
O1–C1–C5	117.1	117.0	113.7
C1–C4–H5	117.9	117.6	117.6
C1–C4–H6	115.2	115.8	116.5
C1–C5–H7	115.7	115.8	115.2
C1–C5–H8	118.2	119.3	119.0
Dihedral Angle <sup>b</sup> /deg			
H1–O1–C1–C2	-67.2	-67.1	72.9
O1–C1–C2–C3	-2.6	132.1	135.3
O1–C1–C2–H2	176.9	-47.6	-45.7
C1–C2–C3–H3	179.4	179.0	178.0
C1–C2–C3–H4	-1.8	-0.8	-2.2
H1–O1–C1–C4	148.5	151.6	-72.7
H1–O1–C1–C5	81.1	83.9	-140.4
O1–C1–C4–H5	142.5	143.2	148.9
O1–C1–C4–H6	-0.7	-1.3	3.3
O1–C1–C5–H7	-3.9	-4.7	0.2
O1–C1–C5–H8	-148.4	-150.6	-144.2
Rotational Constants/MHz			
A	6431.8	5505.7	5507.0
B	2964.4	3180.7	3192.7
C	2435.2	2517.8	2506.3
Dipole Moment <sup>c</sup> /10 <sup>-30</sup> C m			
$\mu_a$	0.13	3.34	0.97
$\mu_b$	2.80	1.83	0.97
$\mu_c$	4.07	2.94	5.13
$\mu_{tot}$	4.94	4.80	5.30
Energy Difference <sup>d</sup> /kJ mol <sup>-1</sup>			
	0.0 <sup>e</sup>	6.97	12.35

<sup>a</sup> Atom numbering is given in Figure 1. <sup>b</sup> Measured from syn = 0°. <sup>c</sup> 1 debye = 3.335 64 × 10<sup>-30</sup> C m. <sup>d</sup> Relative to Syn 1. <sup>e</sup> Total energy obtained in the MP2/cc-pVTZ computations: -708 784.40 kJ mol<sup>-1</sup>.

-67.2° as for the conformer shown in Figure 1. A double-minimum potential will be associated with this rotation around the O1–C1 bond. The presence of this double-minimum potential manifests itself in the MW spectrum (see below). B3LYP calculations were made at intervals of 30° of the said dihedral angle allowing all other structural parameters to vary freely. The resulting potential function was predicted to have a maximum of 14.4 at the syn (0°) and 15.2 kJ mol<sup>-1</sup> at the anti (180°) position of the H1–O1–C1=C2 dihedral angle. The existence of no further conformations was indicated in these computations.



**Figure 2.** Gas-phase infrared spectrum of 1-ethenylcyclopropan-1-ol in the O–H stretching region. This band has maxima at 3631 and 3625  $\text{cm}^{-1}$  and a shoulder at 3620  $\text{cm}^{-1}$ .

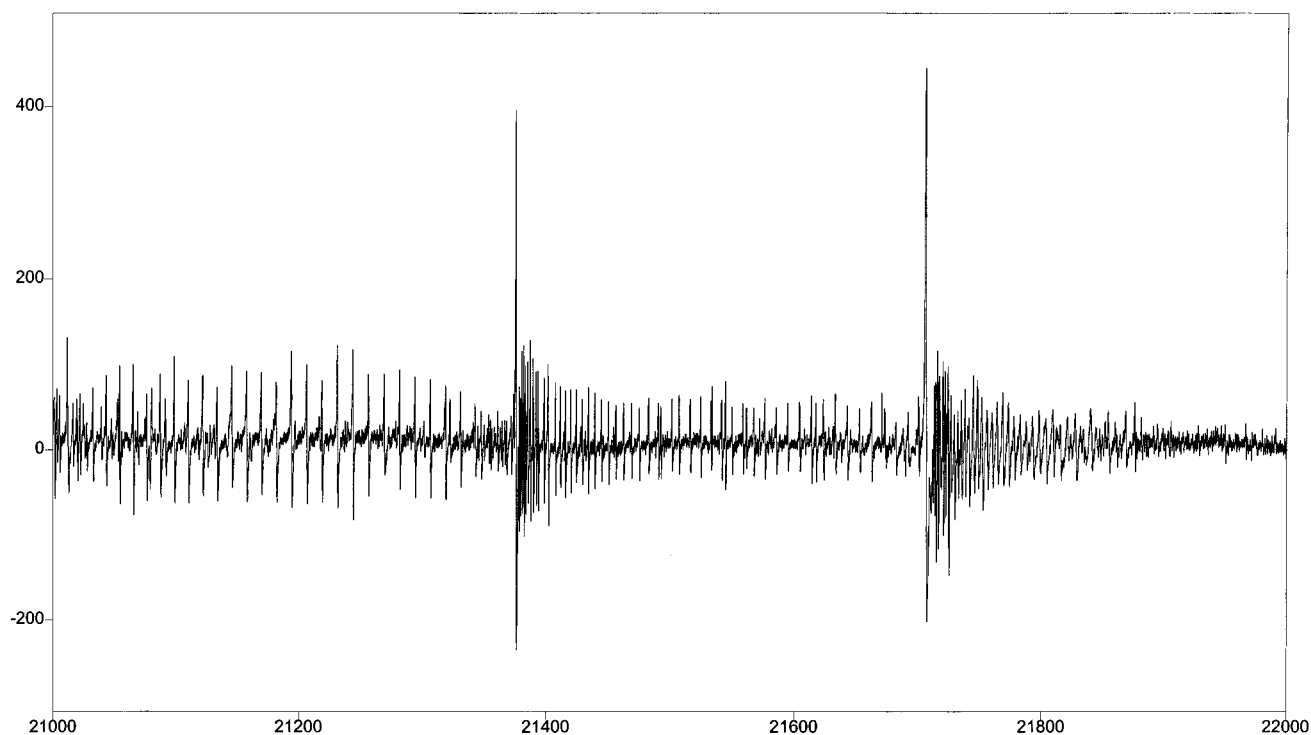
**MW Spectrum and Assignment of Syn 1.** The survey spectra taken at field strengths of about 100 and 1000  $\text{V cm}^{-1}$  revealed a very dense, medium intense spectrum with absorption lines occurring every few megahertz throughout the entire spectral range. Some unusual features were immediately seen in the 20–22 and 15–16 GHz regions where numerous comparatively strong transitions with rapid Stark effects coalesce in band heads at 21 375 and 21 706 MHz. Similar, but less intense spectral lines coalesce at 15 334, 15 618, and 15 736

MHz. The first mentioned band heads are shown in Figure 3. It is assumed that all five band heads somehow are associated with the tunneling of the hydroxyl group, but we were unable to give definite assignments.

The ab initio results in Table 1 predict that Syn 1 is the most stable conformer. Its largest dipole moment components (Table 1) are predicted to lie along the *b*- and *c*-inertial axes. As tunneling was suspected for this rotamer, searches were first made for *b*-type transitions since they were assumed to deviate less from “normal” behavior than the *c*-type transitions do. Searches for the strong medium-*J* *b*-type Q-branch transitions of Syn 1 were first made. These lines, which are among the strongest ones in the spectrum, were soon identified. They always appeared as doublets of equal intensity. The separation between the doublets varied from not being resolved (less than about 0.4 MHz) up to about 60 MHz at most.

The strongest low-*J* *b*R-branch lines were searched for next, and again found as doublets. These *b*-type transitions were first fitted to Watson’s Hamiltonian<sup>31</sup> including quartic centrifugal distortion constants. The root-mean-square (rms) deviations of these fits were roughly 1 MHz, 10 times the experimental uncertainty. The frequencies of strong *c*-type transitions were now predicted using this Hamiltonian. No candidates for these *c*-type lines could be found in the vicinity of the predicted frequencies. It was then clear that a more sophisticated approach had to be followed in order to assign the *c*-type lines.

The unusual spectrum of Syn 1 is explained as follows: The H atom of the hydroxyl group performs a large-amplitude motion governed by a double-minimum potential associated with the torsion around the C1–O1 bond. The spatial direction of the *c*-component of the dipole moment is inverted when one conformation is transformed into its mirror image. The ground state is a symmetrical or (+) state denoted  $0^+$ . The first excited state is an antisymmetrical or (–) state denoted  $0^-$ . The energy separation between these two states is denoted  $\Delta$ , often called the tunneling frequency. The selection rules for the *a*- and *b*-type



**Figure 3.** MW spectrum in the 21–22 GHz spectral region showing the pileups at 21 375 and 21 706 MHz. The intensity scale is arbitrary. The spectrum was taken at a field strength of about 100  $\text{V cm}^{-1}$ .

TABLE 2: Spectroscopic Constants<sup>a,b</sup> of the 0<sup>+</sup> and 0<sup>-</sup> States of the Syn 1 Conformer of 1-Ethenylcyclopropan-1-ol

	normal species		deuterated species	
	0 <sup>+</sup>	0 <sup>-</sup>	0 <sup>+</sup>	0 <sup>-</sup>
<i>A</i> /MHz	6385.4056(84)	6385.3017(96)	6104.3616(50)	6104.3449(54)
<i>B</i> /MHz	2937.5418(61)	2937.5384(62)	2926.0885(27)	2926.0655(27)
<i>C</i> /MHz	2415.0811(69)	2415.0792(72)	2378.9124(40)	2378.9104(40)
$\Delta^c$ /MHz	2280.184(60)		72.401(27)	
$\mu_{ca}$ /MHz	39.82(19)		5.2(10)	
$\Delta_j$ /kHz	0.286(30)	0.254(30)	0.385(13)	0.355(12)
$\Delta_{JK}$ /kHz	1.561(31)	2.624(43)	2.004(32)	2.319(29)
$\Delta_K$ /kHz	5.13(24)	-3.17(35)	1.08(13)	-0.11(12)
$\delta_j$ /kHz	0.0494(10)	0.0643(13)	0.0470(18)	0.0616(17)
$\delta_K$ /kHz	-0.135(25)	-0.383(33)	0.144(50)	-0.247(47)
no. of transitions in fit	324		160	
rms <sup>d</sup> deviation/MHz	0.244		0.096	
maximum value of <i>J</i>	66		70	

<sup>a</sup> As defined by Nielsen.<sup>32</sup> <sup>b</sup> Uncertainties represent one standard deviation. <sup>c</sup>  $\Delta = W_{01}$  (energy separation between 0<sup>-</sup> and 0<sup>+</sup> states<sup>32</sup>). <sup>d</sup> Root-mean-square.

transitions of the 0<sup>+</sup> and 0<sup>-</sup> states follow rigid-rotor selection rules. The selection rules for the *c*-type transitions are those of a rigid rotor plus (-)  $\leftarrow$  (+), or (-)  $\leftarrow$  (+). In this case large deviation from rigid-rotor behavior is expected. A splitting of approximately 2 $\Delta$  is thus expected for each *c*-type rotational transition.

Fortunately, a computer program has been written by Nielsen<sup>32</sup> to deal with spectra of this type. This program is based on the reduced Hamiltonian defined as follows:<sup>32</sup>

$$H_{\text{red}} = |0\rangle \{H_r^{(0)} + H_d^{(0)}\} \langle 0| + |1\rangle \{H_r^{(1)} + H_d^{(1)} + W_{01}\} \langle 1| + |0\rangle H_c \langle 1| + |1\rangle H_c \langle 0|$$

where the label 0 corresponds to the (+) state and the label 1 corresponds to the (-) state.

Using *I'* representation,<sup>31</sup> one has

$$H_r(\nu) = B^{(\nu)} J_b^2 + C^{(\nu)} J_c^2 + A^{(\nu)} J_a^2$$

where  $\nu$  refers to the (+) or the (-) state, respectively.

$$H_d = \{ \text{Watson}^{31} \text{ quartic and sextic centrifugal distortion constants} \}^{(\nu)}$$

$$W_{01} = \langle 1|H_{\text{vib}}^0|1\rangle - \langle 0|H_{\text{vib}}^0|0\rangle$$

$W_{01}$  corresponds to  $\Delta$  above.

$H_c$  is the Coriolis term of the form

$$H_c = \mu_{ij} \langle J_j J_i + J_i J_j \rangle$$

where *i* and *j* refer to the principal inertial axis.  $\mu_{ij}$  is the reduced moment of inertia.

In the first attempts to find the *c*-type transitions  $\Delta$  was assumed to be about 21 375 MHz, which is the most intense of the band heads. The coalescing lines were assumed to be high-*J* *c*-type Q-branch transitions. However, no successful assignments could be made in this manner. The alternative band head frequencies of 21 706, 15 334, 15 618, and 15 736 MHz were then used with the same negative result.

It was then decided to see if we could be more successful with the spectrum of the deuterated species, (CH<sub>2</sub>)<sub>2</sub>C(OD)C=CH<sub>2</sub>. Tunneling should be reduced by at least 1 order of magnitude in this isotopomer as compared to the normal species, making assignments easier. The assignment of the *b*-type transitions was straightforward. Nearly all of these doublet lines had now coalesced into a single line. Only a few of them were split by

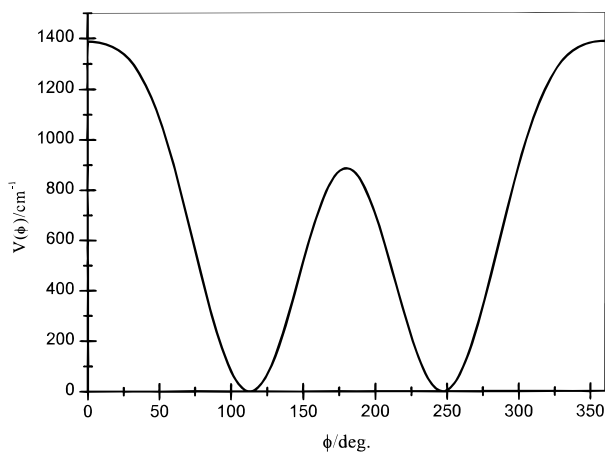
up to about 0.7 MHz. The frequencies of the *c*-type transitions were then predicted from these *b*-type lines. Pairs of lines split by roughly 100–150 MHz were now readily assigned. Their average frequencies agreed well with the frequencies predicted from the *b*-type transitions.

Nielsen's program was now employed. Only quartic centrifugal distortion constants were included because centrifugal distortion is not very prominent in this compound. Various Coriolis coupling schemes were tested. It turned out that fits using  $\mu_{ca}$  was the most efficient ones. In fact,  $\mu_{ca}$  was the only coupling constant for which a significant value could be obtained. A total of 160 transitions with a maximum value of *J* = 70 were used to derive the spectroscopic constants listed in Table 2. Only the resolved *b*-type doublets were used in this fit. It is seen from this table that  $\Delta = 72.400(27)$  and  $\mu_{ca} = 5.2(10)$  MHz, and the fit itself is as good as the experimental uncertainty with a rms deviation = 0.096 MHz. A full listing of the observed transitions and the least-squares fit residuals is given in Table 3S in the Supporting Information.

We now turned to the normal species again. From a similar compound, cyclopropanol,<sup>28</sup> it is known that the tunneling frequency  $\Delta$  of the normal species is about 25 times as large as the corresponding  $\Delta$  of the deuterated species. A value of about 2000 MHz was thus guessed for the normal species of ECP. With this in mind, a few trial fits resulted in the assignment of the *c*-type lines. The fitting procedure was then carried out in the same manner as for the deuterated species. The final results using 324 *b*- and *c*-type transitions (given in Table 2S in the Supporting Information) are presented in Table 2. No *a*-type lines were identified presumably because they are too weak owing to a small  $\mu_a$  (Table 1).

The tunneling frequency  $\Delta = 2280.184(60)$  MHz is about 30 times larger than the corresponding value of the deuterated species, whereas  $\mu_{ca} = 39.82(19)$  MHz is approximately 8 times larger than its counterpart in the deuterated compound. The rms deviation of the fit is 0.244 MHz, which is quite satisfactory. Inclusion of the Coriolis coupling constants  $\mu_{ab}$  and  $\mu_{bc}$  in the least-squares fit yielded no improvement. The standard deviations of these two parameters were found to be about as large as the constants themselves.  $\mu_{ca}$  was therefore the only coupling constant retained in the final fit.

It should be mentioned that some of the *b*-type Q-branch transitions deviate from this fit by up to approximately 3 MHz. The lines in question are some of those that fall at the lowest frequencies of the different<sup>b</sup> Q-branch series (where the series "turns around" and moves toward higher frequencies with higher values of the *J* quantum number). This deviation is assumed to



**Figure 4.** Potential function  $V(\phi) = (1/2)V_1(1 - \cos \phi) + (1/2)V_2(1 - \cos 2\phi) + (1/2)V_3(1 - \cos 3\phi)$  with  $V_1 = -918.2$ ,  $V_2 = -900.0$ , and  $V_3 = 418.0 \text{ cm}^{-1}$  for the internal rotation of the hydroxyl group of the Syn 1 (*ac,ap*)-rotamer of 1-ethenylcyclopropan-1-ol.

arise from higher order effects not accounted for in the Hamiltonian employed here. These transitions (less than 10) were omitted in the final fit.

The tunneling frequency of gauche cyclopropanol is 4115.26(42) MHz,<sup>28</sup> similar to the value in Table 2 (2280.184(60) MHz). It is interesting that H bonding with the  $\pi$  electrons does not seem to influence the tunneling frequency to any great extent.

The  $\Delta = 2280.184(60)$  MHz frequency is much less than the five pileup frequencies (15 334, 15 618, 15 736, 21 375, and 21 706 MHz) mentioned above. It is suggested that these five frequencies have something to do with the tunneling motion of the hydroxyl group, presumably excited states, but no detailed explanation can be offered. Similar pileups have been observed before, e.g., in the tunneling spectrum of ethylene glycol (at about 17.1 GHz), and remain unassigned to this date.<sup>33</sup>

**Potential Function of the Hydroxyl Group Rotation.** Some information that can be used to calculate a potential function for the torsional vibration of the hydroxyl group is available: The tunneling frequencies ( $\Delta$ ) for the normal and the deuterated species are known experimentally (Table 2). The H1–O1–C1=C2 dihedral angle (henceforth called  $\phi$ ) was assumed to have the MP2 value shown in Table 1 ( $67^\circ$  from syn,  $113^\circ$  from anti). The syn and anti positions were assumed to be maxima in agreement with the B3LYP calculations (see above).

A simplified Hamiltonian is assumed for the internal rotation:

$$H = Fp^2 + V(\phi)$$

where the potential function  $V(\phi)$  consists of three cosine terms:

$$V(\phi) = (1/2)V_1(1 - \cos \phi) + (1/2)V_2(1 - \cos 2\phi) + (1/2)V_3(1 - \cos 3\phi)$$

The  $F$  value was calculated to be  $19.706 \text{ cm}^{-1}$  for the normal species and  $9.903 \text{ cm}^{-1}$  for the deuterated species using the method of Pitzer and Gwinn.<sup>34</sup> The eigenvalues of the Hamiltonian were calculated as described by Lewis et al.<sup>35</sup>  $\phi$  was assigned a value of  $0^\circ$  at the anti position, as is often done.  $V(\phi)$  was assumed to have its minimum at  $113^\circ$  from anti ( $67^\circ$  from syn). The potential constants  $V_1$ ,  $V_2$ , and  $V_3$  were then adjusted to give the best fit to the data. This was obtained with  $V_1 = -918.2$ ,  $V_2 = -900.0$ , and  $V_3 = 418.0 \text{ cm}^{-1}$ . The resulting double-minimum-potential function is drawn in Figure 4. The maximum at anti position ( $\phi = 0^\circ$ ) is calculated to be  $1387.2$

**TABLE 3: Spectroscopic Constants<sup>a,b</sup> of the Ground Vibrational State of the Skew 1 Conformer of 1-Ethenylcyclopropan-1-ol**

$A/\text{MHz}$	5506.94(24)
$B/\text{MHz}$	3161.668(19)
$C/\text{MHz}$	2494.889(21)
$\Delta_J/\text{kHz}$	0.823(61)
$\Delta_{JK}/\text{kHz}$	7.179(99)
no. of transitions in fit	21
rms deviation/MHz	0.147

<sup>a</sup> A reduction,  $I'$  representation.<sup>31</sup> <sup>b</sup> Uncertainties represent one standard deviation. <sup>c</sup> Further quartic constants preset at zero.

$\text{cm}^{-1}$  ( $16.59 \text{ kJ mol}^{-1}$ ). The maximum at syn ( $\phi = 180^\circ$ ) is  $887.0 \text{ cm}^{-1}$  ( $10.61 \text{ kJ mol}^{-1}$ ). The potential function depends very critically on the assumptions made, and it is difficult to make estimates of the uncertainties. The best values we can come up with are  $16.6(50)$  for the anti and  $10.6(30) \text{ kJ mol}^{-1}$  for the syn barrier, respectively. These values are rather close to those found in the B3LYP calculations above ( $15.2$  and  $14.4 \text{ kJ mol}^{-1}$ , respectively) and similar to those found for cyclopropanol.<sup>28</sup>

**Assignment of Skew 1.** This conformer is predicted to be less stable than Syn 1 by as much as  $7.0 \text{ kJ mol}^{-1}$  (Table 1). The best way to assign such high-energy rotamers with relatively weak spectra “drowned” in the dense and strong spectrum of another conformer is to use the RFMWDR technique<sup>19</sup> because it is so specific, provided that the prolate conformer in question has a sizable dipole moment component along the  $a$ -inertial axis. This was fortunately predicted to be the case for Syn 1 ( $\mu_a \approx 3.3 \times 10^{-30} \text{ C m}$ ; Table 1). Model calculations using the rotational constants in Table 1 indicate a frequency difference of about 4.5 MHz between the  $9_{6,3}$  and  $9_{6,4}$  energy levels. The RF pump was set at this frequency. The  $10_{6,4} \leftarrow 9_{6,3}$  and  $10_{6,5} \leftarrow 9_{6,4}$  pair of transitions was searched for around 57.3 GHz, while the  $9_{6,3} \leftarrow 8_{6,2}$  and the  $9_{6,4} \leftarrow 8_{6,3}$  pair was looked for in the vicinity of 51.5 GHz. These double resonance searches met with immediate success. The assignments were then extended to further  $^aR$  transitions using RFMWDR spectroscopy where possible. Additional assignments of high- $K_{-1}$  lines of the same kind could be made at low (about  $50 \text{ V cm}^{-1}$ ) field strengths. Low- $K_{-1}$  lines could not be assigned with certainty because they are slowly modulated and often overlapped by the much stronger transitions of the Syn 1 rotamer present nearly everywhere in the spectrum. A total of 21  $a$ -type transitions shown in Table 4S in Supporting Information were assigned. No  $b$ - or  $c$ -type lines could be found. The spectroscopic constants (A reduction  $I'$  representation<sup>31</sup>) are shown in Table 3. Only two of the quartic centrifugal constants could be determined from the collection of transitions available. Assignment of the deuterated species was not attempted owing to the low intensity of the spectrum of this high-energy conformer.

It is seen in Table 1 that Skew 1 and Skew 3 should have very similar rotational constants. However, the dipole moments have radically different orientations within the molecule. Skew 1 has its largest component along the  $a$ -inertial axis, whereas Skew 3 has its largest component along the  $c$ -axis. The fact that  $^aR$  transitions are the only ones assigned is taken as evidence that Skew 1 has not been confused with Skew 3.

The energy difference between Skew 1 and Syn 1 was determined by relative intensity measurements made as in the manner described in ref 37. The energy difference depends on the ratio of the dipole moments squared.<sup>38</sup> This ratio was calculated from the values of the dipole moments listed in Table 1. The energy difference was found to be  $4.9 \text{ kJ mol}^{-1}$ . One standard deviation was estimated to be  $\pm 0.6 \text{ kJ mol}^{-1}$ . The

energy difference of 4.9(6) kJ mol<sup>-1</sup> is in fair agreement with the MP2 result (7.0 kJ mol<sup>-1</sup>).

Skew 3 is predicted to be about 12 kJ mol<sup>-1</sup> less stable than Syn 1 (Table 1). This rotamer is computed to have its major dipole moment component along the *c*-inertial axis. Finding such a high-energy form in this dense spectrum would undoubtedly be very difficult. Our attempts to do so were futile.

The strongest transitions present in this spectrum have been assigned to Syn 1. Yet, the above assignments of the spectra of Syn 1 and Skew 1 represent only a fraction of the very large number of transitions present. The B3LYP calculations indicate that there are several low-lying vibrational modes that are well populated at -25 °C. Each of these states is expected to have a tunneling spectrum of its own. No assignments of vibrationally excited states were made.

**Structure.** The substitution coordinates<sup>39</sup> of H1 of Syn 1 were calculated as  $|a| = 31.966(61)$ ,  $|b| = 174.633(13)$ , and  $|c| = 78.662(28)$  pm, respectively, from the rotational constants and their standard deviations of the 0<sup>+</sup> states of the normal and deuterated species. The actual uncertainties are much larger than these formal standard deviations (in parentheses) owing to the large-amplitude motions that the H1 atom performs. The values calculated from the structure in Table 1 are  $|a| = 31.37$ ,  $|b| = 176.52$ , and  $|c| = 76.38$  pm, respectively, and are in good agreement with the substitution values. This is one indication that the structure in Table 1 is close to the “real” structure of this rotamer. Another indication is the fact that the rotational constants in Tables 1 and 2 deviate by less than 1% in each case. The same is seen for Skew 1. This agreement is not believed to be fortuitous, but in fact reflects that MP2/cc-pVTZ structures are close to the “correct” structures, as has already been pointed out.<sup>26</sup> The structures of Syn 1 and Skew 1 shown in Table 1 are therefore adopted as *plausible* structures. It is expected that any experimental structures that might be determined in the future will be very close to those shown in Table 1.

## Conclusions

Two conformers of ECP denoted Syn 1 and Skew 1 have been assigned using MW spectroscopy. The two forms are interconverted by rotating approximately 120° around the C1–C2 bond. Syn 1 is the most stable form of the molecule, being 4.9(6) kJ mol<sup>-1</sup> more stable than Skew 1. The prevalence of these two conformers is a consequence of several factors: Both rotamers are stabilized by a weak internal H bond formed between the H atom of the hydroxyl group and the  $\pi$  electrons of the ethenyl group. Tunneling of the hydroxyl group is a prominent feature of the spectrum of Syn 1. A double-minimum potential could be determined for this species. Interaction between the lone pairs on oxygen and the electrons of the cyclopropyl group and the conjugative interaction between the ethenyl and the cyclopropyl group are likely to also contribute to the stabilities of these two conformers. Essentially, the preferred (*ac,ap*)-rotamer Syn 1 is the hybrid of the most stable conformations of the ethenylcyclopropane<sup>14</sup> and the cyclopropanol<sup>28</sup> subunits, while the (*ac,sc1*)-rotamer Skew 1 is the hybrid of the second stable rotamer of unsubstituted ethenylcyclopropane<sup>14</sup> and the most stable one of unsubstituted cyclopropanol.<sup>28</sup> Ab initio calculations at the MP2/cc-pVTZ level provide reliable structures and energy differences for the two rotamers.

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

**Supporting Information Available:** Table 1S contains the B3LYP structures. Tables 2S–4S contain the MW transitions used to determine the spectroscopic constants shown in Tables 2 and 3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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