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Microwave Spectrum, Conformation, Intramolecular Hydrogen Bonding and *Ab Initio* Calculations for Ethylene Glycol Vinyl Ether

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The microwave spectra of ethylene glycol vinyl ether and one deuterated species (hydroxyl group) have been investigated in the 26.0–39.0 GHz spectral region at −15°C. One rotamer, denoted *Conformer I*, was assigned. This rotamer is stabilized by an intramolecular O–H ··· O hydrogen bond formed between the hydrogen atom of the hydroxyl group and the oxygen atom of the ether group. The C–C–O–C = C chain of atoms is practically planar, with the double bond and the O–CH_2 bonds in a *syn* conformation. The O–CH_2–CH_2–O link is in a *gauche* conformation, allowing the hydrogen bond to be formed. Absolute intensity measurements indicate that this rotamer is at least 3 kJ mol^{-1} more stable than any other rotameric form of the molecule. The microwave work has been assisted by infrared spectra of the gas as well as *ab initio* computations made at the MP2/6-31G** level of theory.

This laboratory has taken an interest in molecules which have intramolecular hydrogen (H) bonds. Ethylene glycol vinyl ether was chosen for study because this compound has two possible acceptor sites for internal H bonding, viz. the oxygen atom of the ether moiety and the double bond of the vinyl group. Rotational isomerism is possible around the C1–O1, C1–C2, C2–O2 and O2–C3 bonds (Fig. 1). Several different conformers may then possess hydrogen bonds of the O–H ··· O type if the oxygen of the ether group is acceptor, or of the O–H ··· π-electron type if the π-electrons of the double bond are an acceptor.

Shostakovskii *et al.*[1] studied the IR spectrum of ethylene glycol vinyl ether in dilute solutions of carbon tetrachloride and found that the hydroxyl stretching frequency is red-shifted in a way which is typical for a compound which is stabilized with an intramolecular hydrogen (H) bond. A complex structure of this fundamental frequency was noted. This may reflect that several rotamers are present in solution. Some of these rotamers may not be stabilized by internal H bonds at all.[1]

The solution study[1] was unable to answer which conformation predominates in solution. No gas-phase studies appear to have been made of the structural and conformational properties of ethylene glycol vinyl ether. The interesting problems that are associated with the conformational and structural properties of this compound prompted the present research.

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Experimental

The sample utilized in this work was purchased from Aldrich. It was checked by gas-phase chromatography and found to be more than 99.5% pure. Attempts to purify it completely by preparative gas-phase chromatography yielded no improved purity. The sample was therefore used as received. No impurities were detected in the microwave (MW) spectra.

The MW spectrum was studied using the Oslo spectrometer which is described in Ref. 2. The 26–39 GHz spectral region was investigated with the microwave absorption cell cooled to about −15°C. Lower temperatures, which would have increased the MW spectral intensities, could not be employed owing to insufficient vapour pressure of the compound. The pressure was about 3–8 Pa when the spectra were recorded and stored electronically using the computer programs written by Waal.[3] The accuracy of the spectral measurements is presumed to be better than ±0.10 MHz.

The gas-phase IR spectrum in the 500–4000 cm^{-1} spectral region was recorded at room temperature employing a Bruker IFS-88B spectrometer equipped with a cell having a path length of about 120 m. The pressure was a few Pa and the resolution was 2 cm^{-1}.

Results

Ab initio *calculations*. It has not been possible to make high-level *ab initio* computations for the many possible

stable conformers of ethylene glycol vinyl ether for economic reasons. A selection had to be made. The conformational preferences of ethylene glycol methyl ether[4] and methyl vinyl ether[5] were used as a starting point for selecting the three conformers sketched in Fig. 1. The rotamers drawn in this figure were assumed to be the predominating low-energy forms of the title compound for the following reasons: It is known that ethylene glycol methyl ether prefers a conformation that has the methyl group *anti* to the C–C bond. This rotamer, which is denoted *tGg'*, is stabilized with an intramolecular H bond formed between the hydroxyl group and the oxygen atom of the ether moiety.[4] The IR findings for the title compound[1] indicate that a similar H bond stabilizes at least one of its conformers in solution. Computations were therefore only made for conformers with internal H bonds because one, or perhaps several of these, were expected to have the lowest energies and hence be observable by microwave (MW) spectroscopy.

The orientation of the vinyl and the $-OCH_2CH_2OH$ parts of the molecule relative to one another is another important factor for the conformation(s) that ethylene glycol vinyl ether might prefer. It is well established that methyl vinyl ether prefers a C–O–C = C *syn* conformation[5] (dihedral angle = 0°), but has a high-energy *skew* conformer with a dihedral angle of about 138° (Ref. 5*a*). The *skew* conformer is 7.11(38) kJ mol^{-1} (enthalpy difference) less stable than *syn*.[5a] These observations led us to perform computations for the three selected rotamers sketched in Fig. 1 because they encompass the conformational preferences of ethylene glycol methyl ether and methyl vinyl ether.

In *Conformer I* and *Conformer II* the C2–O2–C3 = C4 chain of atoms has a *syn* conformation, just as the most stable rotamer of methyl vinyl ether has.[5] *Conformer I* has an intramolecular O–H ··· O hydrogen bond. *Conformer II* differs from *Conformer I* in that a rotation has been performed around the C2–O2 bond to bring the H atom of the hydroxyl group into a position where it can form an internal H bond with *both* the O2 atom and the π-electrons of the double bond at the same time.

In *Conformer III* the C2–O2–C3 = C4 chain of atoms takes a *skew* conformation (ca. 150° from *syn*). This corresponds to the atomic arrangement found in the less stable rotamer of methyl vinyl ether.[5a] The O1–H1 ··· O2 intramolecular H bond is retained in this conformer. A H bond interaction with the π-electrons of the double bond is of course not possible in this rotamer.

The computations of geometries, energies and vibrational frequencies were made at the MP2/6-31G** (frozen core) level. The Gaussian 92 program package[6] running on the Cray Y-MP computer in Trondheim and IBM RS6000 cluster in Oslo was employed. The three rotameric forms depicted in Fig. 1, which all have C_1 symmetries, were fully optimized. They were all found to be stable (energy minima). The optimized geometries are given in Table 1 together with other parameters of interest.

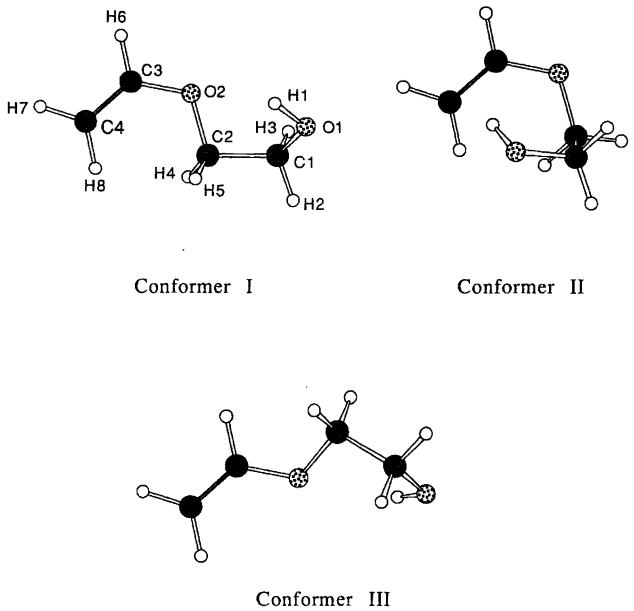

Fig. 1. Three of the many possible rotameric forms of ethylene glycol vinyl ether. These three rotamers all possess intramolecular hydrogen bonds. *Conformer I* was assigned in this work and shown to be at least 3 kJ mol^{-1} more stable than any other conformation.

A *skew* rotamer similar to *Conformer III* stabilized with an internal H bond and where the orientation of the O1–C1–C2–O2 chain is about −60° instead of +60.6° as in *Conformer III*, was also searched for. However, this rotamer was not found to be an energy minimum in the MP2/6-31G** computations.

Table 1 reveals some interesting findings: *Conformer I* is predicted to be the most stable rotameric form of ethylene glycol vinyl ether. The four dihedral angles that determine the conformation are quite 'normal': The H1–O1–C1–C2 dihedral angle is 53.7°, the O1–C1–C2–O2 dihedral angle is 61.2°, the C1–C2–O2–C3 dihedral angle is 183.5°, and the C2–O2–C3 = C4 dihedral angle is −1.5°. An intramolecular H bond of the O–H ··· O type definitely stabilizes this rotamer, as indicated by the relatively short H1 ··· O2 distance of 237 pm as compared with the sum of the van der Waals radii[7] of H and O (260 pm).

Conformer II has two abnormal dihedral angles (Table 1): The O1–C1–C2–O2 dihedral angle is calculated to be 71.7°, about 12° larger than in the preferred *tGg'* form of ethylene glycol methyl ether.[4] Table 1 reveals that the C1–C2–O2–C3 dihedral angle is −93.7°. *Ab initio* calculations at the 4-21 G level of theory for the *gGg'* conformer of ethylene glycol methyl ether,[4f] which is similar to *Conformer II*, yielded −88.4° for the C–C–O–C dihedral angle in this molecule. The deviation (by about 28.4°) from −60° has been explained by steric repulsion.[4g]

The unusual values for these two dihedral angles in *Conformer II* are clearly a compromise of several effects:

Table 1. Structure,[a] rotational constants, principal-axes coordinates of the H atom of the hydroxyl group, dipole moments and energy differences of three selected rotamers of ethylene glycol vinyl ether obtained in the *ab initio* computations at the MP2/6-31G** (frozen core) level.

Rotamer:	*Conformer I*	*Conformer II*	*Conformer III*
Distances/pm			
H1–O1	96.6	96.6	96.7
C1–O1	141.8	142.1	141.4
C1–H2	109.0	109.1	109.0
C1–H3	109.5	109.5	109.5
C1–C2	151.1	151.5	151.2
C2–H4	109.4	109.1	109.4
C2–H5	109.3	109.1	109.4
C2–O2	143.1	143.6	143.3
C3–O2	136.6	136.7	137.3
C3–H6	108.2	108.2	108.6
C3–C4	133.9	134.1	133.4
C4–H7	107.8	107.8	107.8
C4–H8	107.7	107.7	107.9
Angles/°			
H1–O1–C1	105.3	107.0	105.1
O1–C1–H2	106.9	106.1	107.1
O1–C1–H3	111.7	111.6	111.7
O1–C1–C2	111.0	113.6	110.7
C1–C2–H4	111.8	109.4	111.6
C1–C2–H5	110.5	111.2	109.9
C1–C2–O2	105.5	111.6	105.7
C2–O2–C3	116.0	118.3	114.6
O2–C3–H6	109.9	109.1	115.3
O2–C3–C4	127.8	129.4	121.7
C3–C4–H7	118.4	117.8	119.7
C3–C4–H8	123.7	123.9	121.1
Dihedral angles[b]/°			
H1–O1–C1–H2	186.6	179.1	187.0
H1–O1–C1–H3	68.3	61.7	68.6
H1–O1–C1–C2	−53.7	−61.3	−53.1
O1–C1–C2–H4	181.0	187.6	180.8
O1–C1–C2–H5	−57.3	−52.0	−57.9
O1–C1–C2–O2	61.2	71.7	60.6
C1–C2–O2–C3	183.5	−93.7	−166.1
C2–O2–C3–H6	178.8	189.5	25.0
C2–O2–C3–C4	−1.5	9.4	−157.2
O2–C3–C4–H7	180.1	181.5	183.7
O2–C3–C4–H8	0.1	2.3	2.7
Non-bonded distances[c]/pm			
H1 ··· O2	230.7	270.9	229.1
O1 ··· O2	276.9	303.6	276.3
H1 ··· C3	350.1	270.5	340.1
H1 ··· C4	451.2	259.3	428.0
O1 ··· C3	402.1	328.7	393.6
O1 ··· C4	485.6	311.0	497.0
Rotational constants[d]/MHz			
A	10384.3	5463.9	10576.8
B	1814.9	2859.3	1697.1
C	1682.2	2133.0	1576.8
Principal-axis coordinates[d] of the H atom of the hydroxyl group/pm			
|*a*|	168.4	59.7	133.3
|*b*|	130.1	131.2	145.8
|*c*|	36.4	81.2	18.3
Dipole moment[e]/10^{-30} C m			
μ_a	5.50	1.45	3.97
μ_b	2.91	3.15	6.28
μ_c	2.50	0.51	0.23
Energy difference[g]/*kJ mol*$^{-1}$			
	0.0	9.2	9.5

[a] See Fig. 1 for definition. [b] Measured from *syn*=0°. [c] Sum of van der Waals radii:[7] O ··· O 280 pm; O ··· C (half-thickness of aromatic molecule) 310 pm; O ··· H 260 pm; H ··· C (half-thickness of aromatic molecule) 290 pm. [d] Calculated from the structures given above in this table. [e] 1 D=3.33564×10^{-30} C m. [f] The total energy of *Conformer I* was calculated to be −805344.56 kJ mol^{-1} (−306.7395317 a.u.). [g] Energy difference between *Conformer I* and each of the two other conformations.

Intramolecular H bonding with the O2 atom is favoured by a small O1–C1–C2–O2 dihedral angle. H bonding with the π-electrons of the double bond is favoured by a large value for C1–C2–O2–C3 dihedral angle. The interactions between the lone-pair electrons on the O2 atom and the electrons of the bonds attached to the C2 atom favours a large C1–C2–O2–C3 dihedral angle (preferably 120°), whereas non-bonded repulsion essentially between the O1 atom and the C4 atom (see sum of van der Waals radii in the legend of Table 1) dictates a small value for this angle. The sum of all these effects is thought to be the main reason why *Conformer II* is computed to be 9.2 kJ mol^{-1} less stable than *Conformer I* (Table 1) and possess 'unusual' O1–C1–C2–O2 and C1–C2–O2–C3 dihedral angles.

The C2–O2–C3 = C4 dihedral angle of −157.2° which determines the *skew* atomic arrangement in the hypothetical *Conformer III* is much larger than the corresponding dihedral angle in methyl vinyl ether [−138° (Fig. 5*a*)]. *Conformer III* is predicted to be less stable than *Conformer I* by 9.5 kJ mol^{-1} (Table 1), rather similar to 7.11(38) kJ mol^{-1} seen for the corresponding energy difference in methyl vinyl ether.[5a] *Conformer III* is not sterically crowded; see the non-bonded atomic distances in Table 1. The H bond in it is actually very similar to that in *Conformer I*. The high energy with respect to *Conformer I* can presumably be ascribed to the fact that the *skew* conformation of the C2–O2–C3 = C4 link of atoms is not preferred, as already observed for methyl vinyl ether[5] and ethyl vinyl ether.[8]

MW spectrum and assignment of the ground vibrational state of Conformer I. The *ab initio* computations predict that *Conformer I* is the most stable conformer of the molecule. The theoretical rotational constants of this table indicate that it is a prolate asymmetrical top with the asymmetry parameter $\kappa \approx -0.97$ and its largest dipole moment component along the *a*-inertial axis.

The survey spectra taken at low voltage (ca. 100 V cm^{-1}) revealed characteristic pile-ups close to the predicted frequencies. This lead to an immediate assignment of the "*R*-branch lines. The comparatively strong *b*- and *c*-type *Q*-branch transitions were searched for next and found with ease. Finally, the high-*J P*- and *R*- branch lines were found by gradually extending the assignments to higher and higher values of *J*. Ultimately, 249 transitions with a maximum *J* of 90 were assigned. Three sextic centrifugal distortion constants had to be varied in the least-squares fit in order to produce a fit with a root-mean-square deviation comparable to the experimental uncertainty of ±0.10 MHz. Transitions involving even higher values of *J* than 90 were searched for, but they were presumably so weak owing to their unfavourable Boltzmann factors, that no definite assignments could be made. A portion of the spectrum is listed in Table 2 and the spectroscopic constants (*A*-reduction I^r-representation)[9] are given in Table 3.

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

The deuterated species (hydroxyl group) was studied to locate the position of the H atom of the hydroxyl group. The assignment of this spectrum was straightforward. The spectroscopic constants are found in Table 2. The substitution coordinates[10] were calculated as $|a| = 170.56(16)$, $|b| = 130.41\ (19)$ and $|c| = 31.90(90)$ pm. These values are in good agreement with those predicted for *Conformer I* ($|a| = 168.4$, $|b| = 130.1$ and $|c| = 36.4$ pm; Table 1) and represent additional conclusive evidence that *Conformer I* has indeed been assigned and not confused with any other rotameric from of the molecule.

Vibrationally excited states of Conformer I. The ground-state spectrum was accompanied by several vibrationally excited states. A total of five such states were assigned. The most prominent of these states was the first excited state of what is presumed to be the lowest torsional vibration. The first four excited states of this mode were ultimately assigned; their spectroscopic constants are

Table 2. MW spectrum of the ground vibrational state of *Conformer I* of ethylene glycol vinyl ether.

Transition $J''_{K''-1,K''+1} \leftarrow J'_{K-1,K'+1}$	Observed frequency[a]/MHz	Obs. − calc. freq./MHz
$6_{1,6} \leftarrow 5_{0,5}$	28 184.62	−0.03
$8_{1,8} \leftarrow 7_{0,7}$	34 221.01	0.09
$8_{5,3} \leftarrow 7_{5,2}$	27 545.80	−0.17
$8_{5,4} \leftarrow 7_{5,3}$	27 545.80	−0.07
$9_{3,6} \leftarrow 8_{3,5}$	31 004.13	0.00
$10_{0,10} \leftarrow 9_{0,9}$	34 213.70	−0.14
$10_{2,9} \leftarrow 9_{2,8}$	34 389.32	−0.13
$11_{1,11} \leftarrow 10_{1,10}$	38 466.23	0.10
$11_{5,6} \leftarrow 10_{5,5}$	37 880.24	0.02
$11_{5,7} \leftarrow 10_{5,6}$	37 880.24	0.02
$13_{2,12} \leftarrow 13_{1,13}$	32 126.37	0.07
$15_{1,15} \leftarrow 14_{2,13}$	32 154.83	−0.07
$16_{2,15} \leftarrow 16_{1,16}$	35 013.02	0.07
$19_{2,17} \leftarrow 18_{3,16}$	26 190.02	−0.06
$21_{2,19} \leftarrow 21_{2,19}$	37 516.75	−0.01
$22_{3,19} \leftarrow 22_{2,20}$	37 908.01	0.07
$24_{1,23} \leftarrow 24_{0,24}$	35 641.82	0.13
$26_{3,23} \leftarrow 25_{4,22}$	31 596.97	0.00
$28_{2,26} \leftarrow 28_{1,27}$	29 764.44	−0.04
$31_{2,29} \leftarrow 31_{1,30}$	34 863.40	0.03
$33_{4,30} \leftarrow 32_{5,27}$	35 646.44	−0.09
$36_{5,32} \leftarrow 35_{6,29}$	28 521.69	−0.09
$39_{3,36} \leftarrow 39_{2,27}$	37 744.10	0.03
$43_{4,40} \leftarrow 43_{3,40}$	34 808.57	0.01
$47_{4,44} \leftarrow 47_{3,44}$	27 218.96	0.05
$52_{8,45} \leftarrow 51_{9,42}$	30 963.80	−0.04
$59_{5,55} \leftarrow 59_{4,55}$	36 384.84	0.00
$63_{5,59} \leftarrow 63_{4,59}$	27 426.04	0.00
$75_{6,70} \leftarrow 75_{5,70}$	35 956.75	0.08
$90_{7,84} \leftarrow 90_{6,84}$	36 941.18	−0.06
Coalescing *P*- and *R*-branch transitions[b]		
$27_8 \leftarrow 28_7$	35 296.63	−0.04
$33_9 \leftarrow 34_8$	32 134.63	0.01
$39_{10} \leftarrow 40_9$	28 971.16	0.04
$50_{12} \leftarrow 51_{11}$	26 130.48	0.01
$62_{15} \leftarrow 63_{14}$	37 501.22	0.02
$72_{12} \leftarrow 71_{13}$	29 312.25	0.08
$78_{13} \leftarrow 77_{14}$	32 376.45	−0.03
$85_{14} \leftarrow 84_{15}$	38 906.37	0.11

[a] ±0.10 MHz. [b] The K_{-1} energy levels coalesce for high values of *J* and K_{-1}.

Table 3. Ground-state spectroscopic constants[a,b] of *Conformer I* of ethylene glycol vinyl ether.

Species	Parent	Deuterated
No. of transitions:	249	33
R.m.s. dev.[c]/MHz:	0.074	0.098
A_0/MHz	10519.2845(28)	1145.2(22)
B_0/MHz	1782.78038(48)	1764.0574(73)
C_0/MHz	1659.57043(45)	1634.902 1(75)
Δ_J/kHz	0.463 53(25)	0.438(25)
Δ_{JK}[d]/kHz	−4.4824(41)	4.00(89)
Δ_J/kHz	62.403(12)	[d]
δ_J/kHz	0.0174 60(45)	[d]
δ_K/kHz	5.065(15)	[d]
Φ_J/Hz	0.000 396(37)	[e]
Φ_{KJ}/Hz	−0.131(20)	
Φ_K/Hz	−1.15(18)	
ϕ_J[f]/Hz	−0.000 114 2(17)	

[a] *A*-reduction, I^r-representation.[9] [b] Uncertainties represent one standard deviation. [c] Root-mean-square deviation. [d] Pre-set at the value of the parent species (previous column). [e] Pre-set at zero. [f] Further sextic constants pre-set at zero.

Table 4. Spectroscopic constants[a,b] vibrationally excited states of ethylene glycol vinyl ether.

Vibrational state[c]:	$v_T=1$	$v_T=2$	$v_T=3$	$v_T=4$	$v_{TB}=1$
No. of transitions:	62	60	45	23	84
R.m.s. dev.[d]/MHz:	0.072	0.091	0.083	0.096	0.074
A_v/MHz	10431.853(18)	10350.583(47)	10276.728(34)	10246.0(92)	10593.432(13)
B_v/MHz	1783.6189(27)	1784.5905(38)	1785.6663(46)	1786.7245(82)	1778.4799(28)
C_v/MHz	1663.2388(27)	1666.9758(38)	1670.7478(46)	1674.3590(80)	1656.6416(27)
Δ_J/kHz	0.460(14)	0.474(20)	0.472(24)	0.501(31)	0.430(13)
Δ_{JK}/kHz	−4.376(33)	−4.416(45)	−4.048(53)	−4.03(15)	−4.844(24)
Δ_K/kHz	50.0(22)	47.1(52)	62.403[e]	62.403[e]	72.2(22)
δ_J/kHz	0.01624(30)	0.01394(28)	0.01365(26)	0.017469[e]	0.01439(16)
δ_K/kHz	4.910(71)	5.5174(54)	4.583(71)	5.065[e]	5.513(31)
ϕ_J[f]/Hz	−0.000 101(22)	[g]	[g]	[g]	−0.000 129(14)

[a–c] Comments as for Table 3. [d] v_T denotes the different vibrationally excited states of the lowest torsional vibration. v_{TB} denotes the first excited state of the second lowest torsional vibration, or the lowest bending vibration; see text. [e] Fixed. [f] Further sextic constants pre-set at zero. [g] All sextic constants pre-set at zero

found in Table 4.[†] The changes of the rotational constants upon successive excitation of this vibration are quite constant, as seen in Table 4. This is typical for a harmonic mode.[11] Relative intensity measurements using selected transitions of the ground and the first excited state of this mode were performed largely as described in Ref. 12 and yielded 95(20) cm^{-1} for this vibration, compared to 79 cm^{-1} calculated by *ab initio* above (not given in Table 1).

The first excited state of another fundamental mode, presumably the second lowest torsional fundamental (or perhaps a bending vibration), was also assigned, as indicated in Table 4. Its frequency was determined to be 147 cm^{-1} by relative intensity measurements. The second lowest fundamental was calculated to be 141 cm^{-1} in the MP2/6-31G** computation above.

MW search for further conformations. The above assignments include all the strongest transitions as well as the large majority of transitions of intermediate intensity seen in the MW spectrum. Many weak lines were also assigned. Rotamers other than *Conformer I* were searched for, but none was found. This is one indication that *Conformer I* is considerably more stable than any other rotameric form. Another such indication is that the *absolute* intensity of the spectrum of *Conformer I* is comparatively large. (The strongest "*R*-transitions in the *R*-band have peak-absorption intensities of roughly 2×10^{-7} cm^{-1}). Moreover, the MP2/6-31G** computations (Table 1) indicate that *Conformer I* is clearly preferred. Our final conclusion is that *Conformer I* is at least 3 kJ mol^{-1} more stable than any other rotameric form of ethylene glycol vinyl ether. This estimate is considered to be conservative and is in agreement with the theoretical predictions.

[†] The complete spectra 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.

IR spectrum in the O–H stretching region. The gas-phase spectrum in this region is seen in Fig. 2. The hydroxyl stretching vibration is split into two peaks at 3639 and 3649 cm^{-1}. This splitting is thought to be rotational fine structure of just one conformer, and *not* arising from rotational isomerism. A *PR*-splitting of about 10 cm^{-1} was calculated using Seth-Paul's formulation.[13] This in excellent agreement with observation and independent evidence that *Conformer I* indeed the predominating one.

The IR spectrum also presents evidence for weak intramolecular H bonding because the O–H stretching vibration is centered around 3654 cm^{-1}, a red-shift of about 30 cm^{-1} as compared to gas-phase O–H stretching fundamental in methanol (3682 cm),[14] which of course has no intramolecular H bond.

Structure. It is seen from Table 3 that the experimental rotational constants of *Conformer I* in the ground vibrational state are close to those calculated from the MP2/6-31G** structure (Table 1). In fact, the agreement is better than about 2% for all three constants. Differences of this order of magnitude are to be expected because the

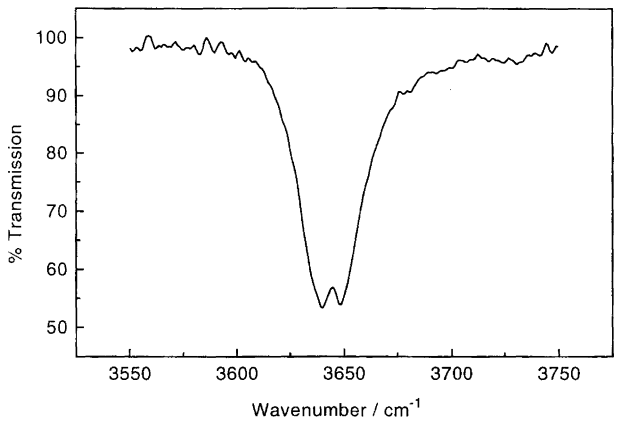

Fig. 2. Gas-phase IR spectrum of ethylene glycol vinyl ether in the O–H stretching region. The fine structure is thought to be rotational.

rotational constants are 'contaminated' with zero-point vibrational interaction, while the *ab initio* rotational constants are calculated from an approximation of the equilibrium structure. Moreover, the structural parameters in Table 1 are very similar to their experimental counterparts in ethylene glycol methyl ether[4] and methyl vinyl ether.[5] Moreover, the substitution coordinates of the H1 atom are close to their theoretical counterparts (Table 1), as remarked in the previous section. No experimental data are at hand that could really improve the MP2/6-31G** structure of *Conformer I*. The *ab initio* structure shown in Table 1 is therefore adopted as a *plausible* structure for *Conformer I* of ethylene glycol vinyl ether. It is expected that this structure will be very close to any experimental structure of ethylene glycol vinyl ether that might be determined in the future.

Discussion

The comparatively strong MW spectrum of *Conformer I* of ethylene glycol vinyl ether suggests that this rotamer is the preferred one (by at least 3 kJ mol^{-1}). The clear preference of *Conformer I* is undoubtedly a result of several effects. Intramolecular hydrogen bonding is stabilizing *Conformer I*. Other rotamers having the same heavy-atom arrangement as *Conformer I* but with the H atom of the hydroxyl group not involved in internal H bonding must have considerably higher energies. Such forms are therefore not observed in the MW spectrum, and there is no indication in the IR spectrum in the O–H stretching region (Fig. 2) for their presence. However, small fractions (a few percent) cannot of course be ruled out.

Intramolecular H bonding is *not* the only effect that favours *Conformer I*. The orientations around the C2–O2 and O2–C3 bonds are, in addition to the H bond, the most favourable ones in this rotamer.

The real significant difference between *Conformer I* and *Conformer III* is the orientation around the O2–C3 bond (-1.5 and $-157.2°$, respectively; Table 1). The considerable energy difference calculated to be 9.5 kJ mol^{-1} presumably comes from the preference of the *syn* to the *skew* arrangement for the C2–O2–C3 = C4 chain of atoms. Our finding that *syn* is clearly favoured parallels the observations made for methyl vinyl ether[5] and ethyl vinyl ether.[8] This conformational destabilization of the *skew* form as compared to the *syn* has been explained by Bond and Schleyer[15] largely a as a result of electrostatic interaction between the electrons of the ether oxygen atom and the electrons of the double bond.

The major structural difference between *Conformer I* and *Conformer II* is the orientation around the C2–O2 bond (183.5 and $-93.7°$, respectively; Table 1). Bonding requirements would have preferred $-60°$ for the C1–C2–O2–C3 dihedral angle in *Conformer II*, but this would have led to a collision between the hydroxyl and vinyl groups. The dihedral angle of $-93.7°$ is clearly a compromise between bonding requirements and steric repulsion, making *Conformer II* less stable than *Conformer I* by about 9.2 kJ mol^{-1}. A similar explanation has also been offered[4g] to explain the conformational preference of the *tGg'* relative to the *gGg'* form in ethylene glycol methyl ether.

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