Microwave Spectrum of Oxiranemethanol (Glycidol), the Assignment of a Second Hydrogen-Bonded Conformer and Conformational Composition in the Gas Phase and in Solution

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The microwave spectrum of oxiranemethanol (glycidol) has been reinvestigated,and improved spectroscopic constants for the ground vibrational state have been obtained for the *H bond inner* conformer, which is stabilized by an internal hydrogen bond formed between the oxirane ring oxygen atom and the hydroxyl group hydrogen atom. Several vibrationally excited states not previously assigned are also reported. A 'new' conformer, denoted *H bond outer 1*, has been assigned. This rotamer is stabilized by an internal hydrogen bond formed essentially between the hydroxyl-group hydrogen atom and the pseudo-π-electrons of the oxirane ring. This conformer is 3.6(4) kJ mol^{-1} less stable than *H bond inner*. The dipole moment of *H bond outer 1* was determined to be (in units of 10^{-30} C m): μ_a = 4.17(20), μ_b = 5.505(43), μ_c = 0.515(98), and $\mu_{tot.}$ = 6.93(16). Two vibrationally excited states were also assigned for this conformer. Gas-phase infrared spectra have been recorded. *Ab initio* computations have been made for three selected conformations employing the 6–31G* basis set. The results from the gas phase are compared with a detailed conformational analysis in dilute $CDCl_3$ solution using both the ^1H and ^{13}C NMR spectra. It is found that the conformational compositions in solution and in the gas are remarkably similar.

At the outset many conformations are theoretically possible for oxiranemethanol (glycidol). In Figs. 1 and 2 three likely low-energy candidates are depicted. In the *H bond inner* conformer an intramolecular hydrogen (H) bond is formed between the hydroxyl-group H atom and the oxygen (O) atom of the oxirane ring. In *H bond outer 1* and *H bond outer 2*, hydrogen bonds of a different kind are presumed to be present. In *H bond outer 1* pseudo-π-electrons[1] of the C–O bond are proton acceptors rather than the oxirane O atom, whereas the pseudo-π-electrons of the C–C bond are acceptors in *H bond outer 2*.

In 1973 Oki and Murayama,[2] using infrared spectroscopy, claimed that oxirane derivatives similar to oxiranemethanol prefer conformers with intramolecular hydrogen bonds in carbon tetrachloride solutions. They also concluded that *H bond inner* and *H bond outer 1* coexist, while *H bond outer 2* was not detected. Two years later Brooks and Sastry[3] investigated the microwave (MW) spectrum of oxiranemethanol. They assigned the ground vibrational state of the *H bond inner* conformer. The possible existence of further conformers was left open.[3] Very recently, the *erythro*[4] and *threo*[5] stereoisomers of 1-oxiraneethanol were investigated in this laboratory. Only one conformer similar to *H bond inner* was assigned for *erythro*,[4] whereas two conformers similar to *H bond inner* and *H bond outer 1*, respectively, were assigned for *threo*.[5] The conformer similar to *H bond outer 1* of *threo* was found to be 2.8(4) kJ mol^{-1} less stable than the *H bond inner* conformer.[5]

The present search for conformers other than *H bond inner* of oxiranemethanol was undertaken because the IR work[2] indicates that more than one conformer is present, at least in carbon tetrachloride solution. In addition, two rotamers exist for *threo*-1-oxiraneethanol,[5] a molecule that is conformationally very similar to the title compound. A profound knowledge of the conformational properties of oxiranemethanol is considered to be essential, because this prototype compound is an important synthon, as discussed in two recent reviews.[6,7] In the present analysis assistance from gas-phase IR spectroscopy and *ab initio* computations was helpful in detecting the *H bond outer 1* conformer.

The conformational composition in solution is of interest, and we have therefore supplemented the IR work of Oki and Murayama[2] with an NMR study. It has very recently been shown[5] that the coupling patterns obtained from the ^1H NMR spectra can be used to obtain the conformational composition for two similar compounds, viz. *threo*-1-oxiranylethanol and *cis*-3-methyloxiran-2-ylmetha-

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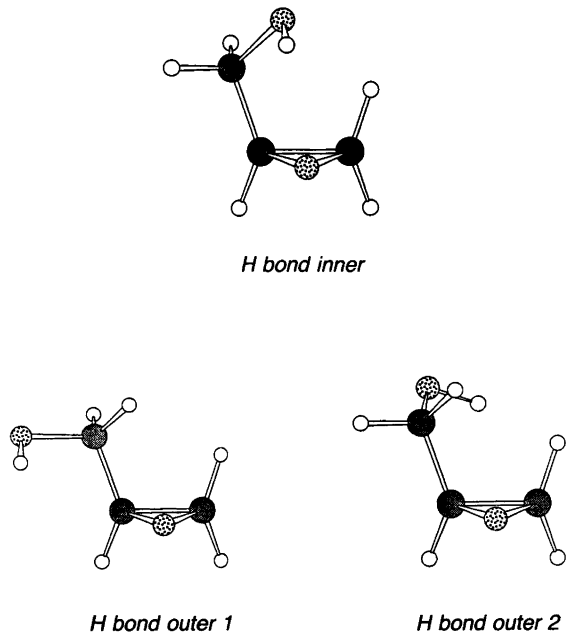

Fig. 1. The three conformations of oxiranemethanol that possess intramolecular hydrogen bonds. The *H bond inner* and *H bond outer 1* conformers were assigned in this work. *H bond inner* is the more stable by 3.6(4) kJ mol^{-1}. No indication of the stable coexistence of *H bond outer 2* was seen in its MW spectrum. In dilute $CDCl_3$ solution the population fraction for *H bond inner* is 0.75 and for *H bond outer 1* it is 0.25. *H bond outer 2* was not found in solution.

nol. It was also found[5] that the γ-effect obtained from ^{13}C NMR could not be used in the conformational analysis without due precautions. The γ-effect has previously been used to analyse the conformational composition of the title compound,[8] with results that are in disagreement with those presented below.

Instrumentation, experimental conditions and computational procedure

Microwave experiment. The spectra were studied using the Oslo spectrometer, which is described in Ref. 9. The 15.0–39.5 GHz spectral region was investigated with the microwave absorption cell cooled to about −10 °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 1 Pa during the spectral measurements. The accuracy of the spectral measurements is presumed to be better than ±0.05 MHz. The deuteration of the hydroxyl group was achieved by conditioning the MW cell with heavy water and then introducing the normal species.

IR experiment. The gas-phase IR spectrum in the 500–4000 cm^{-1} region was taken at room temperature using a Bruker model IFS 88 spectrometer equipped with a multiple-reflection cell. The path length was about 7.2 m, the vapour pressure ca. 150 Pa and the resolution 1 cm^{-1}.

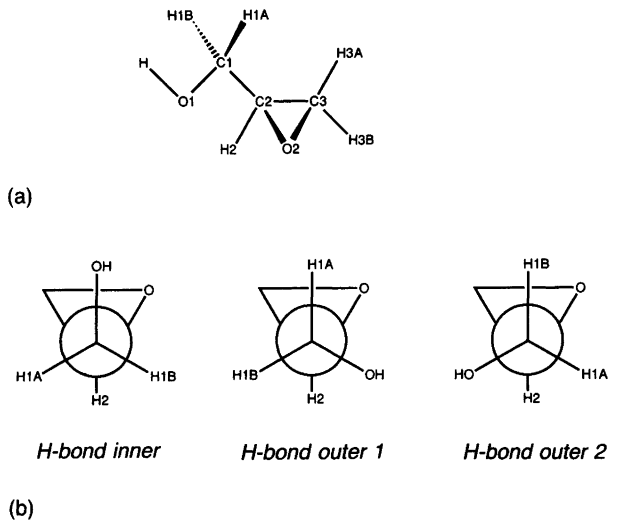

Fig. 2. Atom numbering (a) and Newman projections of the three rotamers viewed along the C1–C2 bond (b).

NMR experiments. These were performed using a JEOL JNM-GX270 instrument at 270 and 67.5 MHz for ^1H and ^{13}C NMR, respectively. The spectra were recorded for 1 M, 0.073 M and 3 mM solutions. Standard irradiation procedures were used to reveal shift values as well as the coupling pattern and the exact coupling constants.

Ab initio *calculations.* The computations were made using the Gaussian 88 program package.[10] The 6-31G* basis set[11–13] was chosen. The geometries of the three rotamers of Fig. 1 were completely optimized. No imaginary vibrational frequencies were calculated. The theoretical calculations thus indicate that the three forms of Fig. 1 are stable. A selection of the results obtained are given herein either in tables or in the text. Atom numbering is given in Fig. 2. In Table 1 structural parameters of particular interest to the conformational problem are collected; further results are in Tables 12 and 13 below. The parameters of Table 2 will be compared below with the corresponding observables obtained in this study and in the previous one by Brooks and Sastry.[3]

Microwave and infrared spectra

Strategy and assignment of the H bond inner *conformer.* The IR spectrum taken by Oki and Murayama[2] in the O–H stretching region of oxiranemethanol dissolved in carbon tetrachloride showed a well resolved splitting that was presumed to be caused by the presence of two different rotamers, viz. the *H bond inner* and the *H bond outer 1* conformers. In the case of *threo*-1-oxiraneethanol[5] the same kind of splitting of the O–H stretching vibration was seen in its gas-phase IR spectrum and ascribed to the presence of two conformers which are similar to *H bond inner* and *H bond outer 1*, respectively.[5]

The IR spectrum of gaseous oxiranemethanol in the

Table 1. Selected structural parameters[a,b] from *ab initio* calculations using the 6–31*G** basis set.

Conformation:	*H bond inner*	*H bond outer 1*	*H bond outer 2*
Dihedral angle/°			
O1–C1–C2–C3[c]	28.2	141.7	−98.2
H–O1–C1–C2[c]	53.9	−59.8	68.2
Non-bonded distance/pm			
H···O2[d]	237	272	
O1···O2	276	303	
H···C2[d]		256	264
H···C3[d]			324
O1···C3			339

[a]See text. [b]Atom numbering given in Fig. 2. [c]Dihedral angle measured from *syn*. [d]Hydroxyl-group hydrogen atom.

Table 2. Selected parameters obtained in the *ab initio* calculations with the 6–31G* basis set.

Conformation:		*H bond outer 1*	*H bond outer 2*
Energy relative to *H bond inner*[a]/kJ mol^{-1}		4.5	10.3
Conformation:	*H bond inner*	*H bond outer 1*	*H bond outer 2*
Rotational constants/MHz			
A	10 703.8	14 374.2	14 672.1
B	4 159.7	3 462.8	3 243.2
C	3 829.5	3 114.0	2 956.4
Dipole moments[b]/10^{-30} C m			
μ_a	2.37	5.07	0.28
μ_b	4.64	5.80	7.75
μ_c	3.07	0.42	1.68

[a]The total energy of the *H-bond inner* conformation was calculated to be −700 337 884.29 kJ mol^{-1}. [b]Components of the total dipole moment along the principal inertial axes. 1 D = 3.335 64×10^{-30} C m.

O–H stretching region is shown in Fig. 3. It is slightly different from its solution spectrum as well as the spectrum of gaseous *threo*-1-oxiraneethanol in that there is no clear-cut splitting indicating the presence of two rotamers. However, the spectrum of Fig. 3 has a rather complex structure that might indicate that more than one conformer is present in the gas phase.

The MW spectrum of oxiranemethanol is dense, with absorptions occurring every few MHz throughout the entire MW region, a fact noted by Brooks and Sastry.[3] In order to facilitate the assignment of possible rotamers other than *H bond inner*, it was decided to remeasure the ground vibrational state of this conformer. The next step would be to assign several of its intense vibrationally excited states,

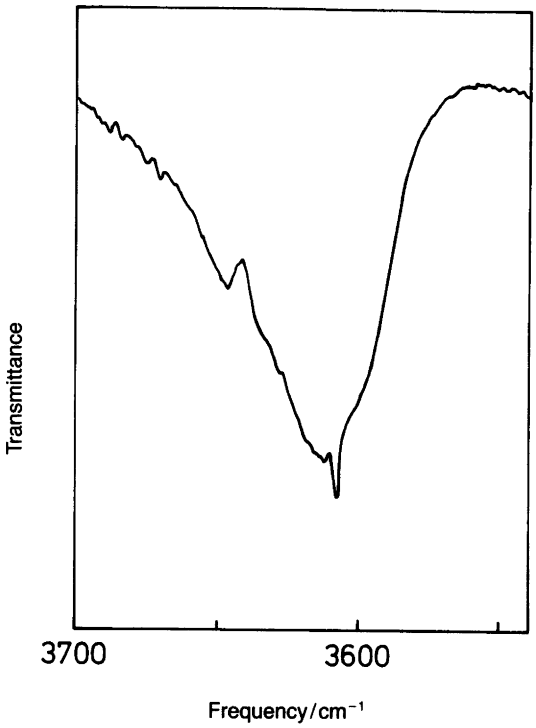

Fig. 3. Gas-phase infrared spectrum in the O–H stretching region of oxiranemethanol. The most prominent absorption maxima are at 3608, 3612 and 3647 cm^{-1}.

which was not done by Books and Sastry.[3] If prominent transitions then remained unassigned, a search amongst them for further conformers would be made.

Starting with the rotational constants given in Ref. 3, the ground vibrational states of the parent and hydroxyl-group deuterated species were readily remeasured. A portion of the spectrum* of the parent species is listed in Table 3. The spectroscopic constants (A-reduction I^r-representation)[14] obtained using 249 selected transitions for the parent species and 111 transitions for the deuterated species are shown in Table 4. These constants are more accurate than those already in the literature.[3]

According to the *ab initio* computations described above, the lowest vibrational mode which is the torsional vibration around the C1–C2 bond, was calculated to occur at 175 cm^{-1}. (This value is not given in Table 1 or 2.) The intensity of the first excited state of this vibration is thus predicted to have roughly 38% of the intensity of the ground vibrational state at −10 °C. A spectral pattern compatible with this was found after some searching. 147 transitions were ultimately used to derive the spectroscopic constants listed in Table 5.

The second and third excited states of this torsion were then found with ease; their spectroscopic constants are included in the same table.

*The complete spectra of both rotamers are available from the authors upon request, or from the National Institute of Standards and Technology, Molecular Physics Division, Bldg. 221, Rm. B265, Gaithersburg, MD 20899, USA.

Table 3. Selected transitions of the ground-state MW spectrum of the *H bond inner* conformer of oxiranemethanol.

Transition	Observed frequency[a]/Hz	Obs.−calc. frequency/MHz
$2_{1,2} \leftarrow 1_{1,1}$	15 448.08	−0.02
$2_{2,1} \leftarrow 1_{1,1}$	35 145.81	−0.02
$3_{1,3} \leftarrow 2_{1,2}$	23 164.62	−0.03
$4_{2,3} \leftarrow 3_{2,2}$	31 527.27	−0.02
$5_{2,4} \leftarrow 5_{1,4}$	16 866.17	−0.02
$6_{2,4} \leftarrow 6_{1,5}$	16 772.66	0.02
$7_{2,5} \leftarrow 7_{1,6}$	16 357.03	0.00
$8_{2,6} \leftarrow 8_{1,8}$	27 501.29	−0.05
$9_{3,6} \leftarrow 9_{2,7}$	29 762.20	0.01
$10_{2,9} \leftarrow 10_{1,10}$	28 364.70	−0.01
$11_{2,9} \leftarrow 11_{1,10}$	16 781.72	−0.01
$12_{3,10} \leftarrow 12_{2,10}$	25 735.48	0.03
$14_{2,12} \leftarrow 14_{1,13}$	20 467.40	0.00
$15_{3,13} \leftarrow 15_{2,13}$	20 454.74	0.02
$16_{3,14} \leftarrow 16_{2,14}$	18 492.62	−0.03
$17_{3,15} \leftarrow 17_{2,15}$	16 489.59	0.01
$18_{3,15} \leftarrow 18_{2,16}$	24 770.40	0.00
$20_{3,17} \leftarrow 20_{2,18}$	26 737.06	−0.01
$21_{3,18} \leftarrow 21_{2,19}$	33 582.89	0.01
$22_{4,19} \leftarrow 22_{3,19}$	26 782.66	0.03
$24_{4,20} \leftarrow 24_{3,21}$	32 190.09	0.00
$25_{4,22} \leftarrow 25_{3,22}$	18 976.07	−0.01
$26_{4,23} \leftarrow 26_{3,23}$	16 455.69	0.00
$30_{5,26} \leftarrow 30_{4,26}$	29 754.24	0.02
$34_{5,30} \leftarrow 34_{4,30}$	17 490.01	−0.03
$39_{6,34} \leftarrow 39_{5,34}$	27 906.26	0.03
$42_{6,37} \leftarrow 42_{5,37}$	17 852.97	−0.03
$47_{7,41} \leftarrow 47_{6,41}$	28 446.22	−0.02
$50_{7,44} \leftarrow 50_{6,44}$	17 750.80	−0.04
$55_{8,48} \leftarrow 55_{7,48}$	28 402.23	−0.01
$58_{8,51} \leftarrow 58_{7,51}$	17 347.72	0.02
$63_{9,55} \leftarrow 63_{8,55}$	27 957.27	0.02
$64_{9,56} \leftarrow 64_{8,56}$	23 845.30	0.02
$71_{10,62} \leftarrow 71_{9,62}$	27 266.27	−0.05
$72_{10,63} \leftarrow 72_{9,63}$	23 126.20	0.02
Coalescing *P*- and *R*-branch transitions[b]		
$10_{10} \leftarrow 11_{9}$	34 876.73	0.03
$13_{11} \leftarrow 14_{10}$	23 998.10	0.01
$18_{14} \leftarrow 19_{13}$	22 961.95	0.03
$21_{11} \leftarrow 20_{12}$	18 520.16	−0.02
$22_{16} \leftarrow 23_{15}$	17 015.26	0.01
$24_{12} \leftarrow 23_{13}$	29 408.57	0.01
$26_{19} \leftarrow 27_{18}$	23 895.73	0.03
$28_{15} \leftarrow 27_{16}$	22 477.51	0.01
$31_{22} \leftarrow 32_{21}$	22 903.51	0.01
$33_{18} \leftarrow 32_{19}$	23 435.71	0.01
$35_{23} \leftarrow 36_{24}$	29 804.75	0.00
$36_{20} \leftarrow 35_{21}$	21 429.56	−0.01
$37_{26} \leftarrow 38_{25}$	26 864.51	0.02
$40_{22} \leftarrow 39_{23}$	27 286.83	0.00
$40_{28} \leftarrow 41_{27}$	28 857.84	−0.01
$41_{28} \leftarrow 42_{27}$	21 003.50	−0.01
$44_{25} \leftarrow 43_{26}$	20 299.34	0.00
$45_{31} \leftarrow 46_{30}$	27 945.57	0.03
$49_{28} \leftarrow 48_{29}$	21 142.11	0.00
$54_{30} \leftarrow 53_{31}$	34 724.94	−0.01

[a] ±0.05 MHz. [b] The K_{-1} doublets coalesce for high values of J and K_{-1}. Subscripts of J quantum number refer to K_{-1}.

Table 4. Spectroscopic constants[a,b] of the *H bond inner* conformer of oxiranemethanol in the ground vibrational state.

Species:	Parent	Deuterated[c]
No. of transitions:	249	111
R.m.s. dev.[d]/MHz:	0.022	0.037
A_0/MHz	10 347.857 5(11)	10 010.297 7(33)
B_0/MHz	4 102.357 28(45)	4 056.730 8(31)
C_0/MHz	3 781.948 26(42)	3 717.017 3(31)
Δ_J/kHz	2.382 57(54)	2.457 (66)
Δ_{JK}/kHz	−1.426 9(32)	−1.513 (14)
Δ_K/kHz	5.181 2(11)	5.39 (24)
δ_J/kHz	0.315 582(86)	0.354 08(26)
δ_K/kHz	−9.782 (10)	−7.223 (17)
Φ_J/Hz	−0.004 03(19)	−[e]
Φ_{JK}/Hz	0.016 60(21)	0.034 98(70)
Φ_{KJ}/Hz	−0.104 4(38)	−[e]
Φ_K[f]/Hz	0.077 2(24)	−[e]

[a] *A*-reduction *I*[r]-representation.[14] [b] Uncertainties represent one standard deviation. [c] Deuteration has taken place at the hydroxyl group. [d] Root-mean-square deviation. [e] Fixed at zero. [f] Further sextic centrifugal distortion constants fixed at zero.

Relative intensity measurements made largely as described in Ref. 15 yielded 145(15) cm^{-1} for this torsional vibration. It is seen in Tables 4 and 5 that the rotational constants vary linearly upon excitation of the torsional mode; behaviour typical for a harmonic vibration.[16]

The second lowest normal mode of the *H bond inner* conformer was calculated by *ab initio* methods to have a frequency of 273 cm^{-1}. This is presumably the lowest heavy-atom bending vibration. As shown in Table 6, it is assumed that the first excited state of this mode has been assigned. The intensities of its MW transitions were about 25 % of those of the ground-state counterparts. Relative intensity measurements yielded 253(25) cm^{-1} for this vibration.

The third lowest vibrational mode was computed by *ab initio* methods to have a frequency of 378 cm^{-1} . The intensities of its transitions should thus be approximately 12 % of the intensities of the corresponding ground-state transitions. However, the first excited state of this mode was not found, presumably because it was too weak.

Assignment of the H bond outer 1 *conformer.* After the assignment of the spectrum of the *H bond inner* rotamer was completed, there remained a spectrum which was so intense that it could hardly be ascribed to unassigned vibrationally excited states of the *H bond inner* conformer. The *ab initio* computations (Table 2) predict *H bond outer 1* to have the second lowest energy. Rather large *a*- and *b*-axis dipole moment components are predicted for this conformer (Table 2), and the assignment of its spectrum was made next. The *b*-type *Q*-branch lines, which are the stron-

Table 5. Spectroscopic constants[a,b] of the *H bond inner* conformer of oxiranemethanol in vibrationally excited states of the torsion around the C1–C2 bond.

Vibrational state:	1st excited	2nd excited	3rd excited
No. of transitions:	147	75	55
R.m.s. dev.[c]/MHz:	0.022	0.029	0.040
A_v/MHz	10 369.667 7(13)	10 391.567 3(48)	10 413.539 7(58)
B_v/MHz	4 079.227 93(48)	4 057.396 7(43)	4 036.604 0(35)
C_v/MHz	3 769.120 26(45)	3 756.265 2(43)	3 743.359 2(35)
Δ_J/kHz	2.343 34(61)	2.495 (97)	2.305 (57)
Δ_{JK}/kHz	−0.933 1(27)	−0.412 3(97)	0.200 (21)
Δ_K/kHz	4.946 2(32)	5.03(30)	4.05(60)
δ_J/kHz	0.301 950(94)	0.288 40(21)	0.275 57(31)
δ_K/kHz	−11.332 8(84)	−12.967 (15)	−14.764 (23)
Φ_J/Hz	0.002 476(70)	−[d]	−[d]
Φ_{JK}[e]/Hz	0.016 08(49)	0.032 9(47)	−[d]

[a,b]Comments as for Table 4. [c]Root mean-square deviation. [d]Preset at zero. [e]Further sextic constants preset at zero.

Table 6. Spectroscopic constants[a,b] of the *H bond inner* conformer of the parent species of oxiranemethanol in the first excited state of the lowest bending vibration.

No. of transitions:	108
R.m.s. dev.[c]/MHz:	0.031
A_v/MHz	10 380.806 8(20)
B_v/MHz	4 086.475 44(78)
C_v/MHz	3 765.557 12(75)
Δ_J/kHz	2.340 2(26)
Δ_{JK}/kHz	−1.801 9(65)
Δ_K/kHz	5.820 (17)
δ_J/kHz	0.317 96(18)
δ_K/kHz	−9.097 (20)
Φ_J/Hz	0.001 30(57)
Φ_{JK}[d]/Hz	0.034 6(91)

[a–c]Comments as for Table 5. [d]Further sextic centrifugal distortion constants preset at zero.

gest ones of this rotamer, were assigned first. The ^aR- and ^bR-transitions were found after some searching. No *c*-type lines were identified with certainty, presumably owing to the small *c*-axis dipole moment component (see section on dipole moment determination below). Ultimately, the *b*-type transitions could be identified up to $J = 73$. Selected transitions are collected in Table 7 and the spectroscopic constants are given in Table 8.

The main reason for studying the hydroxyl-group deuterated species was to determine beyond doubt the location of the hydroxyl-group H atom in the *H bond outer 1* conformer. The assignment of this species was readily made; its spectroscopic constants are shown in Table 8.

The changes of the rotational constants upon deuteration strongly depend upon the conformation. The changes seen in Table 8 are very close to those predicted for the *H bond outer 1* conformer. There is thus no doubt that the hydroxyl group points towards the edge of the oxirane ring, where the pseudo-π-electron density is at a maximum.[1]

Vibrationally excited states of H bond outer 1. As in the case of the *H bond inner* conformer, the torsion around the C1–C2 bond (Fig. 2) was expected to be the lowest vibrational mode. As shown in Table 9, two successively excited states of this mode were assigned. Relative intensity measurements yielded 127(15) cm^{-1} for this vibration, a value that is a little lower than that of the *H bond inner* conformer [145(15) cm^{-1}; see above]. The *ab initio* value for this frequency was calculated as 109 cm^{-1}. It is seen in Tables 8 and 9 that the rotational constants vary linearly upon excitation of this mode. This indicates that the torsional vibration is rather harmonic[16] for this rotamer also.

Ab initio calculations predict the lowest bending vibration to have a frequency of 267 cm^{-1}. The first excited state of this mode should thus be approximately 25 % as intense as the ground vibrational state. However, the first excited state of this vibration was not found, presumably because of insufficient intensities and the crowded nature of the spectrum.

Dipole moment. The dipole moment was determined following a standard procedure.[17] The results are given in Table 10. The experimental dipole moments both for *H bond inner* given in Ref. 3 and *H bond outer 1* of Table 10 are in reasonably good agreement with the *ab initio* values shown in Table 2 above.

The dipole moment and its principal inertial axes components strongly depend upon the conformation of the molecule. The findings of Table 10 thus present additional evidence that *H bond outer 1* has indeed been assigned.

Energy difference. The energy difference between the the *H bond inner* and *H bond outer 1* conformers was determined from relative intensity measurements. Strong lines, presumed to be free from overlapping transitions, were used. The energy difference was found to be 3.6(4) kJ mol^{-1}, with *H bond inner* as the more stable. This value is close to the *ab initio* value of 4.5 kJ mol^{-1} (Table 2).

Table 7. Selected transitions of the ground-state MW spectrum of the *H bond outer 1* conformer of oxiranemethanol.

Transition	Observed frequency[a]/Hz	Obs.−calc. frequency/MHz
$2_{2,0} \leftarrow 2_{1,1}$	31 318.18	0.09
$4_{0,4} \leftarrow 3_{0,3}$	25 856.43	−0.02
$4_{2,3} \leftarrow 3_{2,2}$	25 938.61	0.10
$5_{1,4} \leftarrow 4_{1,3}$	33 276.89	−0.01
$5_{2,4} \leftarrow 4_{2,3}$	32 411.69	0.07
$6_{0,6} \leftarrow 5_{1,5}$	30 407.92	0.01
$7_{2,6} \leftarrow 7_{1,7}$	36 906.74	0.09
$9_{1,8} \leftarrow 9_{0,9}$	20 610.45	0.02
$11_{1,10} \leftarrow 11_{0,11}$	26 262.08	0.00
$12_{2,10} \leftarrow 11_{3,9}$	30 373.20	−0.07
$13_{2,12} \leftarrow 12_{3,9}$	27 822.89	−0.06
$15_{2,13} \leftarrow 15_{1,14}$	29 571.82	0.00
$17_{2,15} \leftarrow 17_{1,16}$	33 387.84	−0.04
$19_{2,17} \leftarrow 19_{1,18}$	38 920.12	0.02
$20_{4,17} \leftarrow 19_{5,14}$	35 728.92	−0.02
$23_{5,18} \leftarrow 22_{6,17}$	34 501.50	−0.05
$25_{6,19} \leftarrow 24_{7,18}$	25 777.85	0.06
$26_{6,21} \leftarrow 25_{7,18}$	32 466.63	−0.09
$29_{7,23} \leftarrow 28_{8,20}$	30 650.50	−0.08
Coalescing *P*- and *R*-branch transitions[b]		
$18_8 \leftarrow 19_7$	35 516.93	0.01
$19_8 \leftarrow 20_7$	28 961.32	0.00
$22_9 \leftarrow 23_8$	30 656.12	0.04
$23_9 \leftarrow 24_8$	24 094.05	0.04
$25_{10} \leftarrow 26_9$	32 358.98	0.02
$28_{11} \leftarrow 29_{10}$	34 071.55	0.01
$31_{12} \leftarrow 32_{11}$	35 795.34	0.01
$36_{13} \leftarrow 37_{12}$	24 457.56	−0.01
$39_{14} \leftarrow 40_{13}$	26 227.55	−0.05
$38_{10} \leftarrow 37_{11}$	25 185.44	0.05
$41_{11} \leftarrow 40_{12}$	23 347.52	0.08
$43_{11} \leftarrow 42_{12}$	36 586.05	0.05
$44_{16} \leftarrow 45_{15}$	36 326.88	−0.09
$49_{17} \leftarrow 50_{16}$	25 149.20	−0.02
$51_{14} \leftarrow 50_{15}$	24 291.52	0.04
$52_{18} \leftarrow 53_{17}$	27 009.50	0.00
$56_{15} \leftarrow 55_{16}$	35 450.89	−0.01
$58_{20} \leftarrow 59_{19}$	30 799.97	0.04
$61_{21} \leftarrow 62_{20}$	32 732.51	0.07
$64_{18} \leftarrow 63_{19}$	22 907.95	−0.06
$67_{23} \leftarrow 68_{22}$	36 677.83	0.04
$68_{23} \leftarrow 69_{22}$	30 277.38	−0.11
$73_{20} \leftarrow 72_{21}$	38 102.14	0.09

[a,b]Comments as for Table 3.

Searches for H bond outer 2. The assignments reported above include all the strongest lines of the spectrum, as well as a large majority of the transitions of intermediate intensity. Many weak lines have also been assigned. Searches for *H bond outer 2* were now made among the strongest ones of the remaining lines. The rotational constants and dipole moments computed by the *ab initio* method reported in Table 2 were used as the starting point. However, these searches were unsuccessful. It is believed that most, if not all, of the unassigned comparatively weak transitions belong to vibrationally excited states either of *H bond inner* or *H bond outer 1*. If the computed energy difference of

Table 8. Spectroscopic constants[a,b] of the *H bond outer 1* conformer of oxiranemethanol in the ground vibrational state.

Species:	Parent	Deuterated[c]
No. of transitions:	164	52
R.m.s. dev.[d]/MHz:	0.050	0.044
A_0/MHz	13 857.077 9(38)	13 343.965 (12)
B_0/MHz	3 420.503 99(89)	3 361.235 7(34)
C_0/MHz	3 065.878 1(11)	2 996.076 0(32)
Δ_J/kHz	2.341 2(35)	2.441 (50)
Δ_{JK}/kHz	−15.156 (35)	−16.067 (75)
Δ_K/kHz	54.852 (21)	47.6(27)
δ_J/kHz	0.402 40(86)	0.439 9(11)
δ_K/kHz	3.184 (80)	3.31(10)
Φ_J/Hz	0.010 532(26)	−[e]
Φ_{KJ}[f]/Hz	0.237 4(16)	−[e]

[a–f]Comments as for Table 4.

Table 9. Spectroscopic constants[a,b] of the *H bond outer 1* conformer of oxiranemethanol in the first and second excited states of the torsion around the C1–C2 bond.

Vibrational state:	1st excited	2nd excited
No. of transitions:	133	23
R.m.s. dev.[d]/MHz:	0.038	0.024
A_v/MHz	13 840.543 2(29)	13 818.643 (25)
B_v/MHz	3 418.692 64(72)	3 417.552 6(60)
C_v/MHz	3 066.645 12(82)	3 067.956 2(57)
Δ_J/kHz	2.223 3(31)	2.61 (10)
Δ_{JK}/kHz	−14.124 (32)	−13.861 (89)
Δ_K/kHz	52.411 (19)	33.8(57)
δ_J/kHz	0.377 62(69)	0.367 55(62)
δ_K/kHz	3.268 (62)	3.527(95)
Φ_J/Hz	0.008 308(26)	−[e]
Φ_{KJ}[f]/Hz	0.190 0(19)	−[e]

[a–f]Comments as for Table 4.

Table 10. Stark coefficients[a] and dipole moments[a] of the *H bond outer 1* conformer of oxiranemethanol.

Transition	$\|M\|$	$\Delta\nu E^{-2}/10^{-6}$ MHz V^{-2} cm^2	
		Obs.	Calc.
$7_{1,6} \leftarrow 7_{0,7}$	5	12.4(2)	12.0
	6	17.5(3)	17.1
	7	23.3(3)	23.2
$8_{1,7} \leftarrow 8_{0,8}$	6	9.90(10)	10.0
	7	13.2(2)	13.6
	8	17.4(2)	17.7
$9_{1,8} \leftarrow 9_{0,9}$	7	7.76(10)	7.77
	8	10.2(1)	10.1
	9	12.8(1)	12.8
$5_{1,5} \leftarrow 4_{1,4}$	2	−3.85(5)	−3.85

Dipole moment/10^{-30} C m

$\mu_a = 4.17(20)$ $\mu_b = 5.505(43)$ $\mu_c = 0.515(98)$ $\mu_{tot.} = 6.93(16)$

[a]Uncertainties represent one standard deviation.
1 D = 3.335 64 × 10^{-30} C m.

Table 11. Plausible molecular structure[a] of the *H bond inner* and *H bond outer 1* conformers of oxiranemethanol.

Structural parameters kept fixed:

Bond distances/pm		Angles/°		Dihedral angle[b]/°	
$C–O_{ring}$	142.0	C1–C2–C3	121.2	$HC3H_{ring}$	90.0[b]
C2–C3	146.6	H–C3–C2	116.6	$HC2C1_{ring}$	90.0[b]
C1–C2	151.7	C3–C2–H	116.6		
C1–O1	142.0	C2–C1–H[c]	109.47		
$C_{ring}–H$	108.5	C2–C1–O1	110.5		
O–H	96.0	C1–O1–H	106.0		

Fitted dihedral angles/°

H bond inner[d]		*H bond outer 1*[d]	
O1–C1–C2–C3	27(3) (from *syn*)	O1–C1–C2–C3	141(3) (from *syn*)
H–O1–C1–C2	47(5) (from *syn*)	H–O1–C1–C2	−55(5) (from *syn*)
O1–C1–C2–O2	41.5 (from *syn*)[e]	O1–C1–C2–O2	−72.5 (from *syn*)[e]

[a]See text. [b]Angle between the plane of the epoxy ring and the adjacent atoms. [c]Atoms assumed to be arranged tetrahedrally around C1. [d]Uncertainties are estimated to represent three standard deviations. [e]This dependent parameter has been calculated from the fitted structure.

10.3 kJ mol^{-1} (Table 2) between *H bond inner* and *H bond outer 2* were correct, the concentration in the gas phase of the latter would be about 100 times larger than that of the former, making an eventual assignment practically impossible by the present methods. Intensity considerations lead us to conclude that *H bond outer 2* is at least 5 kJ mol^{-1} less stable than *H bond inner*. This estimate is considered to be conservative.

Structure. The six rotational constants determined for each of the *H bond inner* and *H bond outer 1* conformers furnish insufficient information for a full structure determination. Assumptions have to be made. In our case only the O1–C1–C2–C3 and the C2–C1–O1–H dihedral angles were fitted in steps of 1°, keeping the rest of the structural parameters fixed at the values shown in Table 11. The structural parameters kept fixed were taken from related

Table 12. Rotational constants, substitution coordinates for the hydroxyl-group H atom and hydrogen-bond parameters for the *H bond inner* conformer of oxiranemethanol.

	Parent species			Deuterated species		
	Obs.	Calc.	Diff.(%)	Obs.	Calc.	Diff.(%)
Rotational constants/MHz:						
A	10 347.9	10 359.4	0.11	10 010.3	10 026.5	0.16
B	4 102.4	4 136.6	0.83	4 056.7	4 089.5	0.81
C	3 781.9	3 791.8	0.26	3 717.0	3 728.7	0.31

Substitution coordinates of hydroxyl group hydrogen atom/pm:

	|*a*|	|*b*|	|*c*|
Calc. from rotational constants[a]	101.073(4)	113.188(4)	63.259(7)
Calc. from plausible structure[b]	100.4	110.3	66.1
From *ab initio*	113.0	112.8	69.4

Hydrogen-bond parameters:

Distances/pm		Angles/°	
H···O2	232	O1–H···O2	111
O1···O2	281	O1–H, C2–O2[c]	13

Sum of van der Waals radii[d]/pm:

H···O	260
O···O	280
C_{ring}···H[e]	290

[a]Calculated using Kraitchman's equations.[19] [b]Table 10. [c]Angle between the O1–H and C2–O2 bonds. [d]Taken from Ref. 23. [e]van der Waals radius of carbon taken to be 170 pm as in aromatic molecules.[23]

molecules for which accurate structures have been determined.[18] This choice of parameters is considered to be slightly more accurate than the alternative choice of the *ab initio* structures, which give rotational constants which differ from the experimental one by more than 3 % in the cases of the *A* rotational constants, a fact that can be seen from Tables 2, 4 and 8. A difference this large is unsatisfactory.

The O1–C1–C2–C3 dihedral angle was found as 27(3)° from *syn* in the *H bond inner* conformer, and 141(3)° from *syn* in *H bond outer* (Table 11). The C2–C1–O1–H dihedral angle is 47(5)° from *syn* and −55(5)° from *syn*, respectively, in the two cases. Important non-bonded parameters calculated from the plausible structures of the two conformers are found in Tables 12 and 13. In these two tables it is seen that the rotational constants and Kraitchman's substitution coordinates[19] of the hydroxyl-group H atom are well reproduced using the structure of Table 11. The substitution coordinates[19] of the hydroxyl-group H atom are also reasonably well reproduced in both cases in the *ab initio* computations, as shown in Tables 12 and 13.

The uncertainty limit (approximately three standard deviations) is estimated to be 3 and 5° in the case of the O1–C1–C2–C3 and C2–C1–O1–H dihedral angles, respectively. These uncertainty limits are considered to take into account uncertainties arising from the choice of the plausible structure of Table 11.

It is noted that the *H bond inner* conformer is transformed into the *H bond outer 1* conformer by swinging the molecule 114° around the C1–C2 bond and rotating the hydroxyl group by 102°. The 13° deviation in the case of *H bond inner*, and the 5° deviation of *H bond outer 1* in the C2–C1–O1–H dihedral angle from the ordinary *gauche* angle (± 60°) bring the hydroxyl group hydrogen atom into closer proximity with the O2 atom, thereby strengthening the two internal hydrogen bonds.

The geometry determined for the *H bond inner* rotamer is essentially the same as that of Brooks and Sastry.[3] However, some difference is seen, particularly for the geometry of the hydroxyl-group H atom.

The full *ab initio* structures, which are not published in detail in this work, are also close to the plausible structures of Tables 11–13. In particular it is noted that the dihedral angles that determine the conformations (Table 1) are essentially the same as the plausible structure values (Tables 11–13).

A comparison with the conformational results obtained for *erythro*-[4] and *threo*-1-oxiraneethanol[5] is in order. The O1–C1–C2–C3 dihedral angle and the corresponding dihedral angles in the two stereoisomers of 1-oxiraneethanol[4,5] are convenient conformational parameters to compare. The O1–C1–C2–C3 dihedral angle is 27(3)° from *syn* for the *H bond inner 1* in the present case, whereas its counterpart is 30(3)° in *erythro*-1-oxiraneethanol[4] and 27(3)° in *threo*-1-oxiraneethanol.[5] There is thus no appreciable difference in this particular angle in these three closely related cases. However, in the cases of *H bond outer 1* and its counterpart in *threo*-1-oxiraneethanol[5] the values are 141(3)° and 135(3)° (from *syn*), respectively, for this same dihedral angle. No value is available for it in the case of *erythro*-1-oxiraneethanol, since the corresponding conformation was not assigned, presumably because it has

Table 13. Rotational constants, substitution coordinates for the hydroxyl-group H atom and hydrogen-bond parameters for the *H bond outer 1* conformer of oxiranemethanol.

	Parent species			Deuterated species		
	Obs.	Calc.	Diff.(%)	Obs.	Calc.	Diff.(%)
Rotational constants/MHz						
A	13 857.1	13 782.0	0.54	13 344.0	13 286.6	0.43
B	3 420.5	3 420.3	0.01	3 361.2	3 361.0	0.01
C	3 065.9	3 056.0	0.32	2 996.1	2 987.1	0.30

Substitution coordinates of hydroxyl group hydrogen atom/pm:	|*a*|	|*b*|	|*c*|
Calc. from rotational constants[a]	158.374(5)	116.268(7)	30.416(27)
Calc. from plausible structure[b]	158.6	114.7	30.2
From *ab initio*	168.4	112.9	34.9

Hydrogen-bond parameters			
Distances/pm		Angles/°	
H···O2	268	O1–H···O2	105
O1···O2	307	O1–H···C2	73
H···C2	250	H···O2–C2	81
		O1–H, C2–O2[c]	11

[a–c]Comments as for Table 12.

a relatively high energy.[4,5] The 6° difference seen in the case of the title compound and *threo*-1-oxiraneethanol[5] may reflect different steric conditions in the two molecules.

NMR spectra

The numbering used is according to Fig. 2. Values are relative to TMS both for ^1H and ^{13}C NMR spectra. ^1H NMR (3 mM, 270 MHz, $CDCl_3$): δ 1.59 (dd, $J_{1B,OH}$ 5.4 Hz, $J_{1A,OH}$ 7.4 Hz, OH), 2.78 (dd, $J_{2,3A}$ 3.0 Hz, $J_{3A,3B}$ 4.9 Hz, H3A), 2.82 (dd, $J_{2,3B}$ 4.4 Hz, $J_{3A,3B}$ 4.9 Hz, H3B), 3.18 (dddd, $J_{1B,2}$ 2.5 Hz, $J_{2,3A}$ 2.9 Hz, $J_{1A,2} = J_{2,3B}$ 4.4 Hz, H2), 3.63 (ddd, $J_{1A,2}$ 4.4 Hz, $J_{1A,OH}$ 7.4 Hz, $J_{1A,1B}$ 12.8 Hz, H1A), 3.98 (ddd, $J_{1B,2}$ 2.5 Hz, $J_{1B,OH}$ 5.4 Hz, $J_{1A,1B}$ 12.8 Hz, H1B) ppm. ^{13}C NMR (3 mM, 67.5 MHz, $CDCl_3$): δ 44.22 (C3), 52.07 (C2), 61.74 (C1) ppm.

Assignments of shifts. A comparison of the shift values of *threo*-1-oxiraneethanol and *cis*-3-methyloxiran-2-ylmethanol[5] with those found for oxiranemethanol gave the correct assignments. A further confirmation for the H3A and H3B shift values was found from the coupling constants $J_{2,3A}$ and $J_{2,3B}$. They were found to be nearly identical to those reported for the $^3J_{trans}$ and $^3J_{cis}$, respectively, of ethylene oxide.[20]

According to the gas-phase results above and the IR work[2] *H bond inner* and *H bond outer 1* were expected to be the two dominating conformers in solution. With this assumption, H1A would experience one 180° and one 60° coupling with H2, while H1B would experience two 60° couplings. From the Karplus equation it is well known that $J_{180} > J_{60}$.[21] Since the observed coupling constants are simply a weighted sum of each of these, it follows that $J_{1A,2} > J_{1B,2}$ and hence we have the above assignments. Another point is that if the coupling constants are interchanged, *H bond outer 2* appears as more stable than *H bond outer 1*, a highly unlikely result.

Conformational analysis in solution. In concentrated solutions of oxiranemethanol, dimers as well as other species containing *intermolecular* hydrogen bonds are likely to exist in addition to monomers. In order to ensure that only monomers are present, the coupling constants and ^{13}C shift values were taken using a 3 mM concentration. At such a low concentration it has already been shown[2] that only monomers are present. Interestingly, while the shift values of the ^1H and ^{13}C NMR spectra changed only slightly upon going from a 1 M to a 3 mM solution, the resolution in the ^1H NMR spectrum decreased with increasing concentration. This is probably due to a more dynamic situation with more *intermolecular* hydrogen bonding between the hydroxyl group and the oxirane ring in the more concentrated solutions.

In some previous publications there has been a dispute as to whether the ^1H NMR analysis with respect to the interpretation of the coupling constants[22] or the well known γ-effect obtained from shifts in the ^{13}C NMR spectra[8] is the best basis for a conformational analysis for α-substituted epoxides. In a recent publication[5] we used both procedures and pointed out that the former is more trustworthy for α-hydroxyepoxides and that the reason for this was the electronic changes in the hydroxyl group that take place when hydrogen bonds are formed. Here we wish to see if the same is true for oxiranemethanol.

The ^1H NMR data were analysed as described in Ref. 5. For the coupling between H1 and H2 we used J_{60} = 2.5 Hz and J_{180} = 10 Hz for the dihedral angles of 60° and 180°, respectively, and $J_{1A,2}$ = 4.4 Hz and $J_{1B,2}$ = 2.5 Hz (Fig. 2b). This yielded a population fraction for *H bond inner* of 0.75 and for *H bond outer 1* of 0.25, while *H bond outer 2* according to this analysis is absent. This is in agreement both with the MW results above and IR data[2] obtained in carbon tetrachloride solution.

However, use of the γ-effect yields a different result: epoxypropane is the only *reference* substance which can be chosen for oxiranemethanol. This choice yields a γ-effect of −3.9 ppm in 3 mM solution, as obtained from the the ^{13}C NMR shift values (previously reported to be −3.7 ppm in a 10 % w/v solution[8]). This γ-effect will yield *H bond outer 1* as a *more* stable conformer than *H bond inner*,[5,8] contradicting our other results. Our conclusion is therefore that the γ-effect cannot be used to obtain the correct conformational composition of oxiranemethanol in solution.

Discussion

The hydrogen bond in *H bond inner* is quite different from that in *H bond outer 1*. In *H bond inner* the O1–H···O2 distance is about 30 pm shorter than the sum of the van der Waals radii[23] of H and O (Table 12), whereas this distance is approximately equal to the sum of the van der Waals radii in *H bond outer 1* (Table 13). There is thus clearly hydrogen bond interaction between H and O2 in the *H bond inner* conformer, while the existence of a O1–H···O2 H bond in the *H bond outer 1* is doubtful. Moreover, the geometry of the *H bond outer 1* conformer is very similar to the geometries found for (hydroxymethyl)cyclopropane derivatives,[24,25] which are known to possess intramolecular hydrogen bonds[24–26] formed between the hydroxyl-group H atom and the pseudo-π-electrons of the cyclopropyl ring.[1] We agree with Oki and Murayama[2] that this kind of interaction is a major one for the stabilization of the *H bond outer 1* conformer as well.

Another factor that might help stabilize both *H bond inner* and *H bond outer 1* is the fact that the O1–H and C2–O2 bond dipoles are 13° from being antiparallel in the former conformer (Table 12) and 11° in the latter (Table 13). This is ideal for a dipole–dipole stabilization.

Pseudo-π-electrons are also predicted to be present along the edge of the C2–C3 bond.[1] However, the hypothetical *H bond outer 2* conformer, which could benefit from these electrons, is calculated (Table 2) to be considerably less stable than *H bond outer 1*. In no previous

studies of epoxides,[2-5] nor in this one, have conformers that have internal hydrogen bonds formed with the pseudo-π-electrons belonging to the C–C edge been observed.

It is interesting to note that the conformational equilibrium in $CDCl_3$ solution is so similar to that in the gas phase. This indicates that the solvation free energies of *H bond inner* and *H bond outer 1* are rather similar.

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